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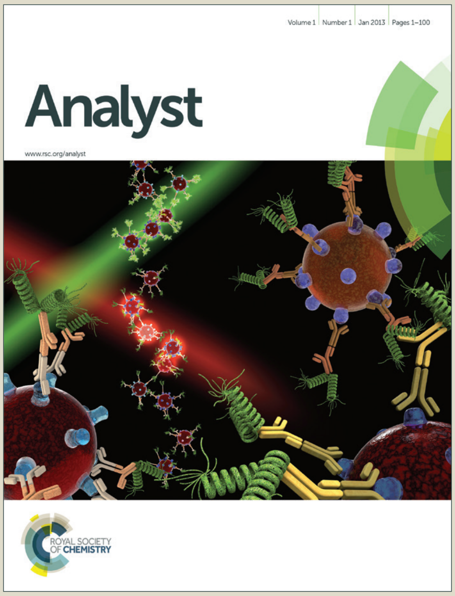

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Two novel zeolitic imidazolate frameworks (ZIFs) as sorbents for solid-phase extraction (SPE) of polycyclic aromatic hydrocarbons (PAHs) in environmental water samples

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Abstract

In this work, two novel zeolitic imidazolate framework (ZIF) materials, ZIF-7 and ZIF-11 were firstly introduced as solid-phase extraction (SPE) sorbents for PAHs efficient extraction and highly sensitive analysis in environmental water samples with high performance liquid chromatography (HPLC) coupled with fluorescence detection. ZIF-7 and ZIF-11 were successfully synthesized and characterized with SEM, FTIR, XRD and water contact angels, exhibiting unique and excellent stability, spatial structure and chemical composition promising for environmental PAHs efficient enrichment through hydrophobic, π–π and π–complexation interactions. Topology effect on PAHs extraction was compared between ZIF-7 and ZIF-11, considering they have the same composition in metal ion (Zn^{2+}) and organic linker, but differing in spatial structure with ZIF-7 in cube, while ZIF-11 in rhombic dodecahedron. At last, ZIF-11 with markedly better extraction efficiencies was selected for subsequent analysis. Under optimum extraction conditions such as sample volume, extraction time, desorption conditions, volume of organic modifier and salt concentration, a robust and high efficient method based on ZIF-11 as novel SPE sorbent has been successfully developed for environmental PAHs analysis. Satisfactory precision and accuracy ranging from 1-2.4×10^3 ng L^{-1} as well as ultrasensitive detection limits of 0.08-1.6 ng L^{-1} have been successfully achieved. Moreover, ZIF-11 extraction also exhibited high recoveries of 82.4% to 112.7% with relative standard deviations (RSDs)

being less than 9% for PAHs in environmental water samples. Thereby, our novel, convenient and efficient extraction method based on ZIF-11 as sorbent is promising for a good application in future trace-level environmental PAHs analysis.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds composed of two or more fused aromatic rings.[1] They mainly arise from incomplete combustion or pyrolysis of organic matters such as oil, coal, petrol, wood, garbage, tobacco, meats or other organic materials.[2] Thereby, PAHs exist widely in our surrounding environment nowadays, with long-term persistence due to stable molecular structures.[3, 4] Importantly, they are bio-accumulative in organisms and can be metabolically activated to generate reactive oxygen species (ROS), leading to DNA damage and consequent carcinogenic, mutagenic, and teratogenic effects on living beings.[5, 6] Therefore, PAHs have gained wide attentions and been recognized as one of the most important persistent organic pollutants (POPs).[7] Moreover, 16 PAHs with high toxicity have been listed by American Environmental Protection Agency (EPA) as priority pollutants.[8]

Notably, PAHs analysis of environmental waters is important due to their serious contamination and drinking water is frequently used in everyday life of human being.[9] However, high hydrophobic PAHs are at trace amount in environmental waters due to their little solubility. Moreover, environmental water samples are containing multiple interferent substances. Therefore, PAHs direct analysis is very difficult and pre-concentration of real water samples becomes rather necessary. Nowadays, various pre-concentration techniques have been developed, such as solvent extraction,[10] solid phase extraction (SPE),[11] solid-phase microextraction (SPME),[12-14] pressurized liquid extraction,[15] and supercritical fluid extraction.[16] In particular, SPE has generated wide applications considering its high recovery, low consumption of organic solvents as well as convenience for operation. Apparently, adsorbent plays a key role for highly efficient sample enrichment and subsequent ultrasensitive analysis. Thereby, multiple materials have been synthesized for PAHs analysis, with C18-functionalized materials being most commonly utilized nowadays.[17, 18] However, they suffered from poor selectivity for PAHs due to non-specific hydrophobic interaction with other substances. Recently, molecular imprinted polymers (MIP)[19] and magnetic nanoparticles[3, 20] have also been explored as novel sorbents and exhibited high efficiency for PAHs enrichment. However, their synthesis processes were fussy and solvent-consuming. Therefore, novel materials with excellent properties of powerful extraction ability, ease for synthesis and usage with sufficient stability are still highly desired.

Metal-organic frameworks (MOFs) are a fascinating class of zeolite-like materials constructed by metal ions or clusters chelating with organic ligands.[21, 22] Based on availability of diverse metal ion, organic ligands as well as chelating ratio difference, MOFs have shown excellent properties of numerous structures, tunable pore sizes as well as high surface areas; thereby, MOFs have already been widely applied in various fields, such as gas adsorption, gas separation, catalysis as well as sensors.[23-28] Recently, MOFs have also exhibited unique and excellent performance in sample pre-concentration techniques for gaseous and solution samples analysis, through their unique structures as well as proper composition of metal or organic ligands.[11, 29-35] For example, most utilized organic ligands in MOFs such as carboxylic acids or imidazoles, could efficiently absorb analytes with aromatic rings group through strong hydrophobic and π–π interaction.[11, 35] Relative reports for environmental PAHs extraction with MOFs are also gradually increasing.[11, 31, 33, 35, 36] For example, with high hydrophobicc opper (II) isonicotinate (Cu (4-C_5H_4N-COO)$_2$ (H_2O)$_4$) coordination polymer, up to 200 to 2337 fold enrichment was achieved for PAHs in environmental water.[31] Thereafter, MOF-5 with great porosity structure was utilized for PAHs pre-concentration by taking advantage of both hydrophobic and π–π interaction.[11] However, MOF-5 instability in water greatly limited its application. Recently, Ge et al. utilized zeolitic imidazolate frameworks-8 (ZIF-8) for PAHs extraction, considering its better stability in water and organic solvent.[35, 36] ZIF-8 exhibited more efficient extraction performance for PAHs than commercial sorbents C8 and C18, due to strong π–π interaction and π–complexation from numerous Zn^{2+}

sites and organic linkers with PAHs. However, small sample volume available for pre-concentration greatly hampered its application.

To overcome above disadvantages, herein, we selected ZIF-7 and ZIF-11 as sorbent for SPE disk extraction of PAHs in aid of filter membrane, with 7 kinds of representative PAHs as model compounds, including fluorene (Flu), anthracene (Ant), fluoranthene (FlA), pyrene (Pyr), 1,2-benzanthracene (BaA), benzo(b)fluoranthene (BbF) and benzo(k)fluoranthene (BkF) considering their similar structures and characteristics. Topology effect on PAHs adsorption was firstly investigated with ZIF-7 and ZIF-11 considering their same metal ion (Zn^{2+}) and organic ligand (benzimidazole) but differing in spatial structure with ZIF-7 in cube, while ZIF-11 in rhombic dodecahedron.[37, 38] At last, ZIF-11 was selected for subsequent extraction due to its larger cages and better thermal and chemical stability. Under optimum extraction conditions, including sample volume, extraction time, desorption conditions, volume of organic modifier and salt concentration, an efficient and convenient SPE method for PAHs pretreatment based on ZIF-11 as sorbent have been successfully developed with ultrahigh-sensitivity, high recoveries and precision.

2. Experimental section

2.1. Reagents and materials

Ammonium hydroxide (25-28%), toluene, methanol and ethanol were purchased from Sinopharm Chemical (Tianjin, China). Zinc acetate dihydrate (99%), benzimidazole (bIm, 98%) and acetonitrile (HPLC grade) were obtained from J&K Chemical (Beijing, China). All other solvents and reagents of analytical grade were from Kermel (Tianjin, China). Ultrapure water purified from a Milli-Q system (Millipore, USA) was utilized throughout our experiments. PAH reference standards of Flu, Ant, FlA, Pyr, BaA, BbF and BkF were purchased from Acros Organics (NJ, USA). Stock solution of PAHs at 100 or 50 μg mL^{-1} each was prepared with MeOH dissolution. Working solution mixture composed of Flu (750μg L^{-1}), Ant (2000 μg L^{-1}), FlA (4000 μg L^{-1}), Pyr (2000 μg L^{-1}), BaA(750 μg L^{-1}), BbF (750μg L^{-1}) and BkF

(200 μg L^{-1}) was freshly prepared with methanol dilution, too. All solutions were stored in the dark at 4 ℃.

Environmental water samples were collected from spring water in Yuelu Mountain (Changsha, China), tap water in our laboratory and Xiangjiang River (Changsha, China), correspondingly. Thereafter, water samples were filtered through 0.22 μm cellulose acetate membrane and stored at 4 ℃ before use.

2.2. Instrumentations

The size and morphology of ZIF crystals as-synthesized were observed with scanning electron microscopy (SEM) (JSM-6360LV, JEOL, Japan). Fourier transform infrared spectra (FTIR) were recorded on a WQF-410 FTIR spectrometer (Braic Corp., China). The X-ray diffraction (XRD) spectra were acquired on D8-advance X-ray diffract meter (Bruker, Germany). Nitrogen adsorption/desorption isotherms were estimated with N_2 adsorption at 77 K using Autosorb-1C/TCD automatic chemisorption & physisorption analyzer (Quantachrome, USA). The static water contact angles were measured at 25 ℃ on a DSA100 contact angle measurement instrument (KRUSS, Germany).

The liquid chromatographic (LC) analysis was carried out on a Shimadzu LC system equipped with two LC-20AT pumps, a CTO-10AS VP column oven and a RF-10A XL FLD detector and controlled by a Shimadzu LC solution workstation (Shimadzu, Kyoto, Japan).

2.3. Preparation of ZIF-7 and ZIF-11 crystals

ZIF-7 and ZIF-11 crystals with different topologies as illustrated in Scheme.1, were synthesized by zinc acetate dihydrate reacting with benzimidazole but in different solvents. The synthesis processes of ZIF-7 and ZIF-11 were according to procedures previously reported.[37, 39] In brief, benzimidazole dissolved in ethanol or methanol/toluene mixture, was mixed with ammonium hydroxide at room temperature. Then zinc acetate was added and stirred for 3 h, a milk-like suspension was gradually formed. After filtration collection and washing with ethanol for three times, the ZIF white crystals as-synthesized were dried at 60 ℃ in oven overnight.

2.4. Extraction procedure

The whole extraction procedure with ZIF materials is illustrated in Scheme 2. Briefly, ZIF-7 or ZIF-11 crystals at 100 mg were ultrasonically dispersed in 3 mL methanol (as organic modifier). Then the prepared ZIF suspension was added into 200 mL of sample solution spiked with 50 μL PAHs working solution for extraction . After sonic extraction for 3 minutes, the aqueous solution was filtered through cellulose acetate membrane with a filtration device, leaving ZIF crystals on the membrane. Subsequently, the crystals were eluted with acetonitrile. Thereby, PAHs could be efficiently desorbed from ZIF materials. The collected eluent passed through a 0.22 μm filter, then was subjected to nitrogen gas drying to about 300 μL under a gentle nitrogen flow at 30 ℃. Finally, the solution was filled with acetonitrile to 400 μL, with 20 μL injected for HPLC-FLD analysis.

2.5. HPLC analysis

The chromatographic separation and analysis of PAHs was conducted on a Diamonsil C18 column (250 mm× 4.6 mm, particle size 5 μm, Dikma Technologies, China). The mobile phase was consisted of water (solvent A) and acetonitrile (solvent B) with a flow rate set at 1 mL min^{-1}. The gradient elution program was as follows: 0-15 min, maintaining solvent B at 75 %; 15-18 min, increasing solvent B from 75 % to 90 %; 18-26 min, maintaining solvent B at 90 %; 26-27 min, decreasing solvent B to 75 %; 27-32 min, with solvent B constant at 75 % to equilibrate the column. The time program of fluorescence detection is given in Table S1.

3. Results and discussion

3.1. Characterization of ZIFs

ZIF-7 and ZIF-11 possess the same metal ion and organic linker but with different topologies as reported.[37, 38] Firstly, the size and shape of ZIF crystals before and after extraction were observed with scanning electron microscopy (SEM). Obviously, ZIF crystals at micrometer level have been successfully synthesized, with ZIF-7 crystals in cube while ZIF-11 crystals in rhombic dodecahedron structure clearly observed in SEM graphs, as shown in Fig. 1 A and C. Moreover, ZIF-7 and

ZIF-11 crystals after extraction showed the same shape and size, as shown in Fig. 1 B and D, indicating their excellent stability to water and organic solvents as reported,[37, 40] being suitable for environmental water sample analysis.

Subsequently, XRD spectra of ZIF-7 and ZIF-11 were collected from 5 to 40 degree and 2 to 40 degree, respectively. Obviously, characteristic peaks of ZIF-7 (7.12°, 7.60°, triangles) and ZIF-11 (4.31°, 6.03°, 7.52°, asterisks) matched well with those previously reported,[37, 39, 40] as shown in Fig. 2, indicating ZIF-7 and ZIF-11 crystals with ideal inner structures had been successfully constructed.

Thereafter, chemical compositions of ZIF-7 and ZIF-11 crystals as-synthesized were confirmed by FTIR analysis. Considering the same metal ion and organic ligands of the two crystals, their FTIR spectra were similar to each other, as Fig. S1 shows. The bands in the region of 600–1500 cm^{-1} were associated with the entire ring stretching or bending.[39] Peaks at 3068 and 3032 cm^{-1} were attributed to the =C–H stretching of aromatics, while peaks at 1611 and 1465 cm^{-1} were assigned to the C–C stretching of the aromatic ring.[37] Meanwhile, the band at 421 cm^{-1} corresponded to Zn-N stretching.[41] Thereby, the above results confirmed the successful chelation of Zn^{2+} and benzimidazole in ZIF-7 and ZIF-11 crystals. Therefore, ZIF-7 and ZIF-11 crystals with ideal size, shape, inner structure and chemical composition have been successfully synthesized.

Furthermore, surface hydrophobicity of ZIF-7 and ZIF-11 crystals were further investigated with the contact angle experiments, since higher hydrophobic material may induce greater contact angle.[31, 33, 42] As shown in Fig. S2, the contact angles of ZIF-7 and ZIF-11 were measured as 142 ± 0.09° and 141 ± 0.11°, respectively, indicating high and similar hydrophobicity of ZIF-7 and ZIF-11 as-synthesized. Therefore, environmental PAHs extraction could be effectively achieved.

3.2. Topology effect on PAHs extraction

Thereafter, ZIF-7 and ZIF-11 crystals were compared on solid phase extraction (SPE) efficiency for target PAHs from water samples. Obviously, ZIF-11 exhibited higher extraction efficiency for all analytes, especially for FlA and Pyr, comparing with ZIF-7, as shown in Fig. 3.

PAHs probably interacted with ZIF materials through both surface binding and entry into ZIF inner pores.[33, 43] However, PAHs with dimensions of width and length both above 4.99 Å[43] are much bigger than pore apertures of ZIF-7 and -11 (~3.0 Å) (section **3.1.1**, Supporting Information). Therefore, PAHs would prefer to interact with organic ligands and metal ions on the outside surface through π–π interaction and π-complexation interaction, respectively, similar to phenomenon as previously reported.[44, 45] Notably, ZIF-11 with RHO topology possesses larger cages than ZIF-7 with SOD topology.[37] Thereby, topologies of ZIF materials probably played key roles in PAHs extraction efficiency difference, considering that ZIF-7 and ZIF-11 have similar size exclusion effect and hydrophobic interaction as described above. The RHO topology is composed of truncated cuboctahedron cages with 8, 6, and 4 membered ring windows and 48 Zn (II) ions within a unit cell, however, there are only 24 Zn (II) ions and 6 and 4 membered ring windows in the cages of SOD topology, according to the previous reports.[37, 38] Therefore, greater interaction with PAHs due to more organic ligands and metal ions probably existed on the outside surface of the larger cages in ZIF-11, thereby, resulting in higher PAHs adsorption and extraction efficiency. Consequently, ZIF-11 was chosen as sorbent for the subsequent extraction and analysis for target PAHs.

3.3. Extraction optimization

Working aqueous solution composed of Flu (187.5 ng L^{-1}), Ant (500 ng L^{-1}), FlA (1000 ng L^{-1}), Pyr (500 ng L^{-1}), BaA (187.5 ng L^{-1}), BbF(187.5 ng L^{-1}) and BkF (50 ng L^{-1}) were prepared with PAHs stock solution dilution, and utilized for extraction optimization. To achieve maximum recoveries of target PAHs, main factors affecting extraction efficiency, including sample volume, extraction time, desorption conditions, volume of organic modifier and salt concentration have been taken into account.

3.3.1. Optimization of sample volume

In SPE, sample volume probably affects concentration factors and satisfactory recoveries for target analytes. Thereby, aqueous solutions ranging from 100 to 300 mL were investigated for PAHs extraction. As shown in Fig. 4, PAHs recoveries could reach up to above 75% and changed little with sample volume increasing from

100 to 200 mL. However, samples exceeding 200 mL severely undermined PAHs recoveries. Obviously, larger sample volume induces higher concentration factor and detection sensitivity for target analytes under similar recoveries.[3] Thereby, sample volume at 200 mL was utilized for subsequent extraction analysis.

3.3.2. Optimization of extraction time

Extraction time plays a key role for highly efficient extraction and ultrasensitive analysis in SPE process. Thereby, PAHs spiked solution was ultrasonically extracted with ZIF-11 for 0-12 min. As shown in Fig. S3, recoveries of seven PAHs reached highest value after extraction for 3 min. However, prolonged extraction decreased PAHs recoveries, probably due to re-dissolution of PAHs absorbed on sorbents into sample solution. Hence, ultrasonic extraction with ZIF-11 was set at 3 min in subsequent experiments.

3.3.3. Optimization of desorption conditions

For PAHs complete desorption from ZIF-11 and subsequent sensitive analysis, proper desorption conditions have been investigated after ZIF-11 extraction. Thereby, six kinds of desorption solvent were compared for PAHs efficient desorption, including methanol, acetonitrile, ethyl acetate, acetone, dichloromethane and n-hexane. Obviously, acetonitrile was more preferable than other solvents, as shown in Fig. S4. Thereby, acetonitrile was selected for subsequent desorption.

Thereafter, solvent volume utilized in PAHs desorption was also taken into account ranging from 2 to 5×2 mL. As shown in Fig. S5, the recoveries improved rapidly with desorption solvent usage increasing from 2 to 5×2 mL. Thereby, for convenient analysis, acetonitrile at 10 mL (2 mL each time) was selected for subsequent elution.

3.3.4. Optimization of organic modifier volume

In extraction process, irreversible adsorption of PAHs onto glassware surface would probably happen due to their low solubility in water, resulted in low PAHs recoveries.[20] To effectively prevent above limitation, organic solvent was normally added into water samples. Moreover, organic solvent can also improve ZIF-11 hydrophilic surface, making it more liable for dispersion in water. In such case, methanol is generally utilized as organic modifier considering its good solubility in water.[2, 11] To achieve efficient extraction, sample solution added with methanol ranging from 3 to 30 mL was investigated in this work. As shown in Fig. 5A, methanol addition at 3 mL yielded the best recoveries, while exceeding 3mL obviously lowered PAHs recoveries, probably because excessive organic modifier may increase analyte solubility in water. Consequently, sample solution with 3 mL methanol addition was utilized for further extraction.

3.3.5. Optimization of salt concentration

The salt effect on extraction was also investigated in this work, with salt concentration ranging from 0 to 0.2 M. Apparently, the maximum recoveries for seven PAHs were achieved with 0.05 M NaCl addition in sample solution, as shown in Fig. 5B. The results were probably due to “salt out” effect, that is, salt ion driving PAHs molecules into the sorbent from aqueous solution. However, salt concentration over 0.05 M would decrease PAHs extraction efficiency, probably due to the metal cation in salt competing with PAHs in occupation with ZIF-11 organic linker through cation-π interaction. Meanwhile, exceeded salt addition might increase sample solution, causing viscosity as previously reported,[35] PAHs withdrawn into the solution. Therefore, 0.05 M NaCl was added in sample solution in following extraction process.

Thereby, the optimum conditions for PAHs extraction were achieved as follows: ZIF-11 crystals at 100 mg dissolved in 3mL methanol were firstly ultrasonically to dispersed. Thereafter, the ZIF-11 suspension was further ultrasonically dispersed for 3 min into 200 mL water sample with 0.05 M NaCl addition. The crystals were then separated from sample solution with suction filtration, followed by centrifugal elution with 2 mL acetonitrile for 5 times. At last, the acetonitrile eluent was collected and concentrated under nitrogen flow at 30 ºC for HPLC-FLD analysis.

3.4. Method validation

Under optimum extraction conditions, our proposed method based on ZIF-11 was validated through 200 mL ultrapure water samples spiked with PAHs standard at a series of concentrations. Our established method exhibited good linearity throughout the concentration range of 1 to 2.4×10^{3} ng L^{-1}, with excellent correlation coefficients

(R^2) ranging from 0.9994 to 0.9998, accompanying with high detection sensitivity with LODs (S/N=3) at 0.08 to 1.6 ng L^{-1}, as listed in Table 1. Moreover, good precisions have also been achieved for target PAHs with relative standard deviations (RSDs) for five replicate experiments ranging from 2.7 to 3.9%. According to the Drinking Water Direction of the European Union (98/83/EC) and the Standards for Drinking Water Quality of China (GB 5749—2006), the total contaminant levels of PAHs must be under 100 ng L^{-1}.[46] Therefore, the present method was sufficient for highly sensitive analysis of trace PAHs in environmental water samples.

3.5. Application in real water samples analysis

Thereafter, our SPE method based on ZIF-11 as sorbent was utilized for PAHs extraction and analysis in environmental water samples to test its practical applicability, including spring water from Yuelu Mountain, tap water and Xiangjiang river water. Only Flu, FlA, Pyr and BkF have been detected in Xiangjiang river water at 45.7 ng L^{-1}, 56.8 ng L^{-1}, 54.1 ng L^{-1}, and 5.3 ng L^{-1}, correspondingly, while no target PAHs were detectable in tap and spring water samples probably below LODs, as shown in Table S2 and Fig. S6.

The accuracy of our method was further evaluated with PAHs recoveries after standard spiked into above water samples for five replicate experiments. Although recoveries of Ant and BaA spiked in tap water were low, probably due to ClO_2 degradation as previously described,[3, 47, 48] other PAHs were not influenced and satisfactory recoveries for all target PAHs in spring water, and Xiangjiang river water have been achieved at 82.4% to 112.7% with RSDs below 9% for both intra-day and inter-day experiments, as shown in Table 2. Therefore, our SPE method based on ZIF-11 as sorbent for PAHs in environmental water samples was robust to resist interferent substances in complex in-field water samples, exhibiting excellent extraction and analytical performance.

3.5. Comparison with other methods

In this work, a fast, efficient and sensitive method based on ZIF-11 materials for environmental PAHs extraction has been successfully developed, by taking advantage of ZIF-11 unique spatial structure with large cages as well as molecular composition composed of abundant benzyl groups and metal sites on the surface. Moreover, our ZIF-11 based method was compared with other MOF-based PAHs extraction techniques previously reported.[11, 31, 33, 35, 49] The comparison is summarized in Table 3. Obviously, ZIF-11 synthesized at room temperature for only 3 h was more simple and time-saving, comparing with other MOF materials synthesized with high temperatures (~ 140℃) for more than 10 h.[33, 35, 49] Moreover, ZIF-11 with good water stability was superior to MOF-5 for environmental PAHs extraction.[11] Furthermore, our ZIF-11 based method also exhibited excellent extraction efficiency and analytical performance comparing with other methods.[11, 31, 33, 35, 49] Specifically, ZIF-11 sorbent could treat exceeding 200 mL environmental water samples in no more than 3 min with satisfactory detection limits, while, other methods could treat no more than 50 mL samples but requiring 20 min extraction, as shown in Table 3. Thereby, our SPE method based on ZIF-11 as sorbent proved to be excellent with convenient operation, good stability, high extraction efficiency and low LODs for PAHs pre-concentration and analysis in environmental water samples.

4. Conclusions

In this study, ZIF-7 and ZIF-11 crystals were first and successfully utilized in SPE analysis of PAHs in environmental water samples. ZIF-7 and ZIF-11 possess the same metal ion and organic linker, but their topologies are different with ZIF-7 in cube while ZIF-11 in rhombic dodecahedron. Thereby, the two crystals were first compared for their PAHs extraction efficiency. ZIF-11 with its larger cages with more metal ions and organic linkers in topologies exhibited better extraction efficiency and was selected for subsequent analysis. Good analytical performances with higher extraction efficiency, satisfactory LODs and good RSD values have been successfully achieved, by which ultrasensitive and robust analysis of environmental water have been realized. Thereby, this work sheds a light on ZIF spatial structure effect on SPE extraction ability and future application of ZIF materials in chromatographic analysis.

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Tables:

Table 1 Analytical performance data of the proposed method for the determination of PAHs.

Table 2 Recoveries and RSDs of spiked real water samples (n=5)

Table 3 Comparison of the proposed method with reported literatures.

Figure Legends:

Scheme 1 Preparation scheme of ZIF-7 and ZIF-11 crystals.

Scheme 2 Scheme of the extraction process.

Figure 1 SEM images of ZIF-7 crystals before adsorption (A) and after adsorption (B), ZIF-11 crystals before adsorption (C) and after adsorption (D).

Figure 2 XRD patterns of (A) ZIF-7 crystals and (B) ZIF-11 crystals.

Figure 3 Comparison of ZIF-7 and ZIF-11 as sorbents for the SPE of PAHs. Extraction condition: sorbents, 100 mg; sample volume, 200 mL; extraction time, 3 min; desorption conditions, 3×2 mL acetonitrile; organic modifier, 3 mL methanol; no salt addition.

Figure 4 Effect of sample volume on recoveries of PAHs. Extraction conditions: sorbent, 100 mg; extraction time, 3 min; desorption conditions, 3×2 mL acetonitrile; organic modifier, 3 mL methanol; no salt addition.

Figure 5 Effect of (A) the volume of organic modifier and (B) the concentration of NaCl on the recoveries of PAHs. Extraction conditions: sorbent, 100 mg; sample volume, 200 mL; extraction time, 3 min; desorption conditions, 5×2 mL acetonitrile.

Table 1 Analytical performance data of the proposed method for the determination of PAHs.

PAHs	Linear range (ng L^{-1})	Calibration curve	R^2	LOD (ng L^{-1})	RSD (%) (n=5)
Flu	3.75-450	Y=8160.0X＋39013	0.9997	0.3	3.2
Ant	10-1200	Y=3054.6X＋30856	0.9994	0.8	3.0
FlA	20-2400	Y=2691.6X＋63103	0.9996	1.6	3.1
Pyr	10-1000	Y=6204.0X＋87749	0.9996	0.8	3.9
BaA	3.75-450	Y=9034.0X＋45618	0.9996	0.3	2.9
BbF	3.75-450	Y=9233.1X＋38918	0.9996	0.3	3.3
BkF	1-120	Y=72092X＋63612	0.9998	0.08	2.7

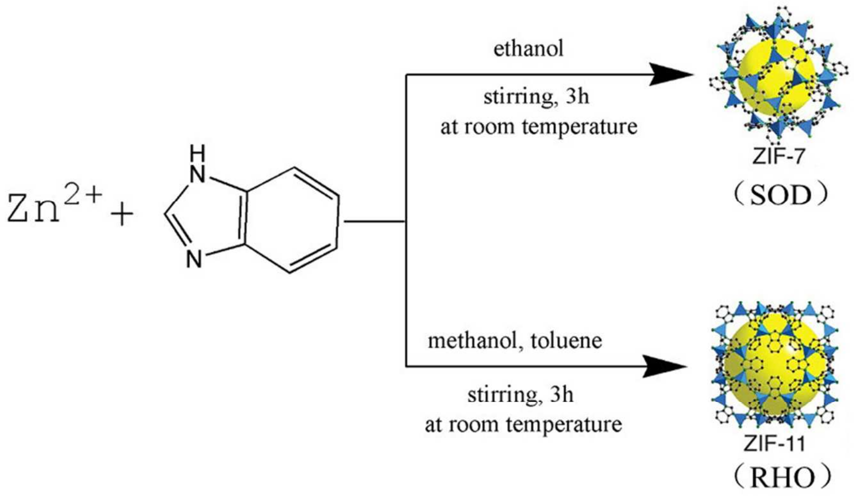
Table 2 Recoveries and RSDs of spiked real water samples (n=5)

PAHs	Spiked (ng L^{-1})	Spring water				Tap water				River water			
		Intra-day		Inter-day		Intra-day		Inter-day		Intra-day		Inter-day	
		Re (%)	RSD (%)	Re (%)	RSD (%)	Re (%)	RSD (%)	Re (%)	RSD (%)	Re (%)	RSD (%)	Re (%)	RSD (%)
Flu	15	88.3	2.2	85.5	3.3	95.1	1.5	95.5	5.4	95.2	3.4	94.8	2.6
	187.5	89.9	2.0	84.3	3.2	104.1	1.2	103.7	4.2	98.6	3.2	97.4	1.4
	375	112.7	1.9	109.7	1.4	96.6	1.3	96.9	3.7	92.0	5.5	86.7	2.0
Ant	40	98.5	1.3	96.2	2.4	low	-	low	-	100.6	8.4	104.7	4.0
	500	93.9	4.6	91.9	3.4	low	-	low	-	111.2	1.8	109.8	1.2
	1000	96.2	1.6	94.6	2.6	low	-	low	-	99.0	1.9	97.6	1.9
FlA	80	91.4	8.8	91.6	1.3	85.5	3.9	86.6	1.1	82.5	1.8	82.4	4.4
	1000	85.6	1.2	84.9	1.2	85.8	5.8	86.5	1.0	83.5	6.9	83.1	5.7
	2000	86.9	1.2	87.2	3.7	98.7	1.7	88.7	2.3	85.1	2.6	84.6	7.1
Pyr	40	93.5	1.2	96.2	3.1	95.5	2.9	91.0	6.8	91.1	1.9	91.5	5.6
	500	90.1	1.3	97.0	4.9	93.1	4.9	92.7	1.7	94.5	1.0	95.3	2.2
	1000	92.9	1.0	91.9	1.5	90.9	1.7	91.2	4.5	92.9	1.1	92.6	5.5

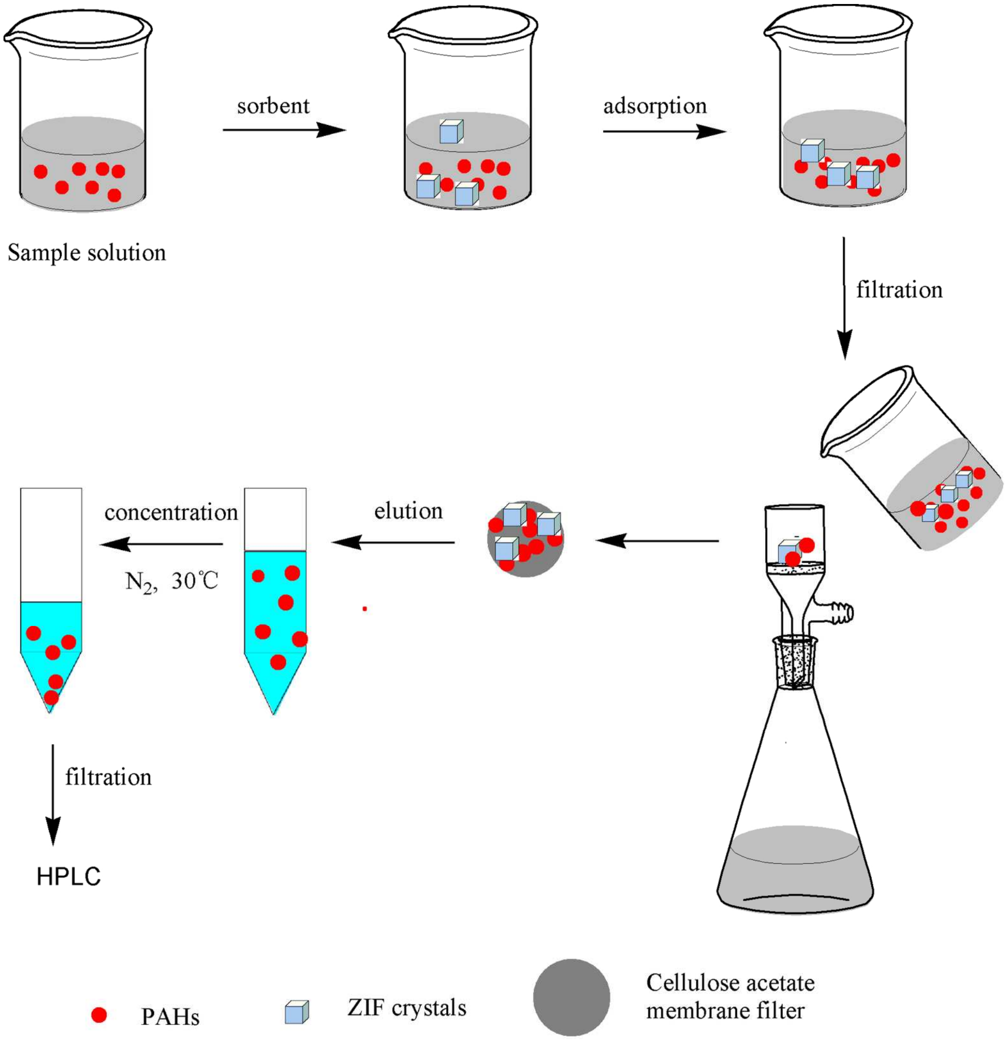
	15	87.7	5.5	83.9	4.3	low	-	low	-	85.5	6.8	86.1	4.8
BaA	187.5	88.3	3.0	87.4	1.5	low	-	low	-	86.2	7.1	85.2	4.2
	375	87.8	1.0	87.8	1.8	low	-	low	-	89.8	6.6	90.1	2.7
	15	95.0	2.8	98.4	8.4	92.9	3.2	91.5	1.8	96.7	4.3	95.4	6.5
BbF	187.5	93.7	1.5	95.6	6.6	92.9	1.4	93.2	5.3	98.1	3.6	97.6	4.3
	375	97.7	2.4	97.9	3.1	92.0	1.5	92.0	1.3	93.8	1.5	93.5	5.4
	4	99.8	3.6	98.0	2.1	97.1	2.8	96.9	2.3	95.4	4.9	95.2	2.0
BkF	50	93.0	2.4	96.0	4.8	98.0	1.5	97.9	1.7	93.8	3.4	93.2	1.2
	100	96.7	2.8	96.7	1.9	95.3	1.5	95.4	1.6	97.6	2.3	97.4	1.3

Table 3 The comparison of the proposed method with reported literatures.

Method	Material	Analytical method	Loading volume (mL)	Extraction time (min)	LOD (ng L^{-1})	References
On-line SPE	$Cu(4\text{-}C5H4N\text{-}COO)_2(H2O)_4$	HPLC-PAD	50	20	2-14	[31]
μ-SPE	ZIF-8	GC-MS	8	20	2-12	[35]
MSPE	$Fe_3O_4@SiO_2$/MIL-101	HPLC-PAD	20	20	2.8-27.2	[49]
SPE	MOF-5	LC-FLD	40	80	0.4-4	[11]
SPME	MOF-53(Al)	GC-MS/MS	10	30	0.1-0.73	[33]
SPE	ZIF-11	LC-FLD	200	3	0.08-1.6	Proposed method



Scheme 1 Preparation scheme of ZIF-7 and ZIF-11 crystals.
208x124mm (300 x 300 DPI)



Scheme 2 Scheme of the extraction process.
177x183mm (300 x 300 DPI)

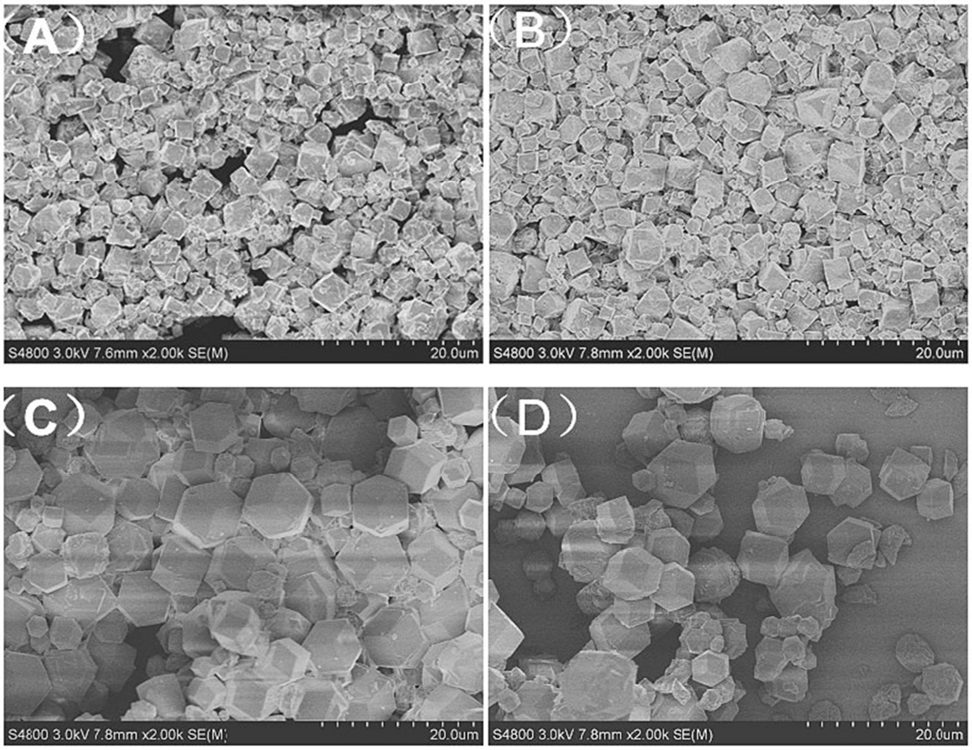


Figure 1 SEM images of ZIF-7 crystals before adsorption (A) and after adsorption (B), ZIF-11 crystals before adsorption (C) and after adsorption (D).
225x175mm (300 x 300 DPI)

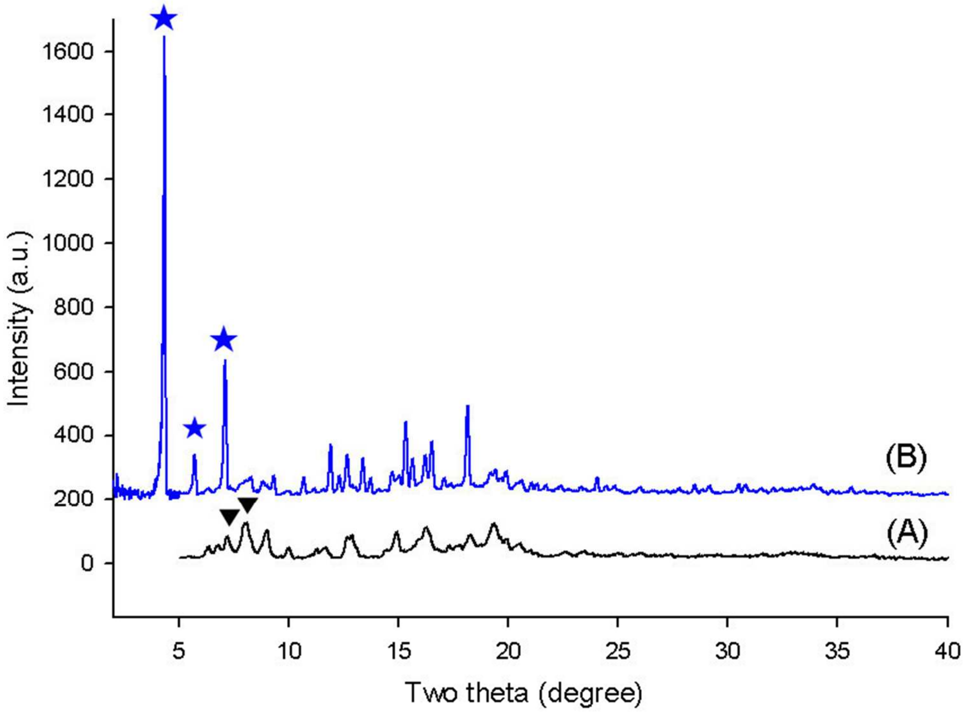


Figure 2 XRD patterns of (A) ZIF-7 crystals and (B) ZIF-11 crystals.
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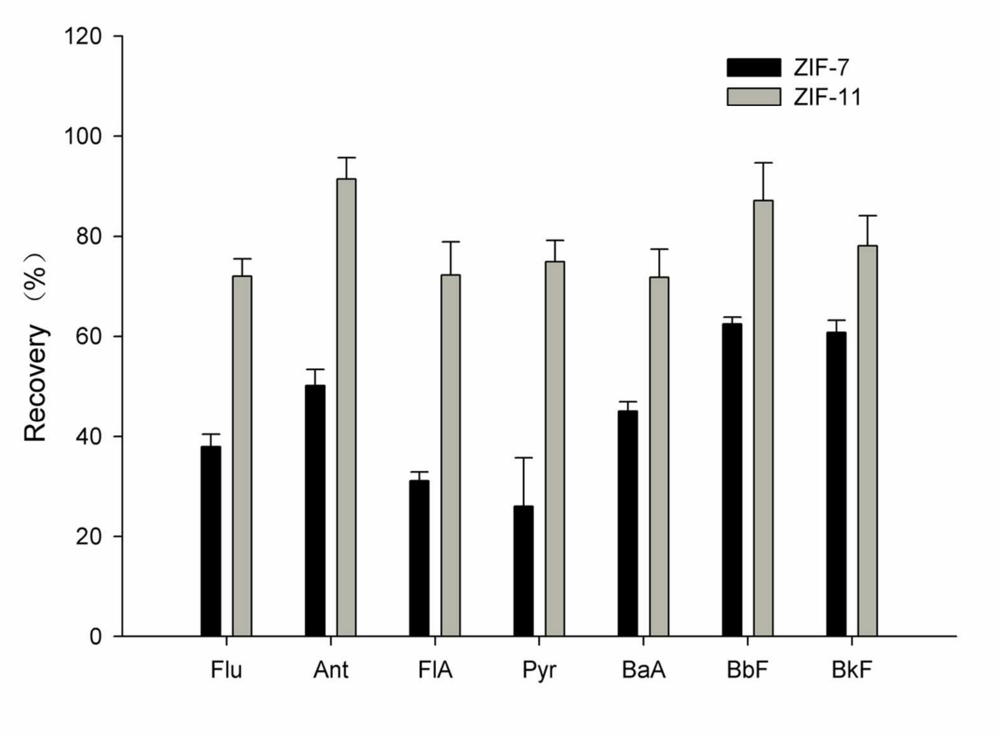

Figure 3 Comparison of ZIF-7 and ZIF-11 as sorbents for the SPE of PAHs. Extraction condition: sorbents, 100 mg; sample volume, 200 mL; extraction time, 3 min; desorption conditions, 3×2 mL acetonitrile; organic modifier, 3 mL methanol; no salt addition.
109x80mm (300 x 300 DPI)

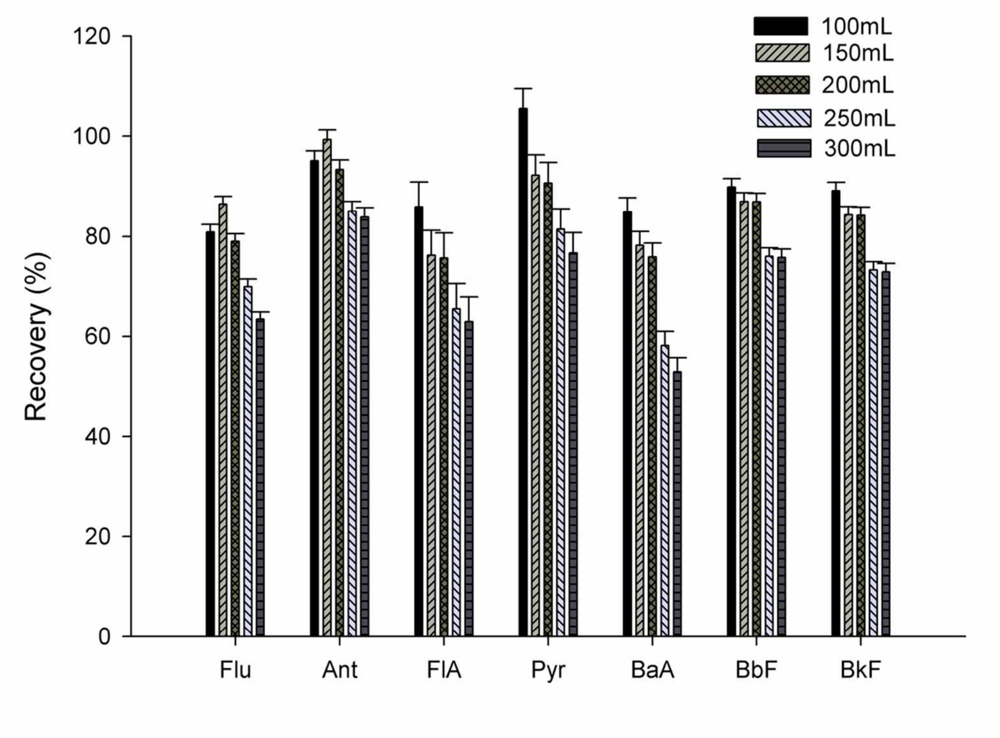

Figure 4 Effect of sample volume on recoveries of PAHs. Extraction conditions: sorbent, 100 mg; extraction time, 3 min; desorption conditions, 3×2 mL acetonitrile; organic modifier, 3 mL methanol; no salt addition.
109x80mm (300 x 300 DPI)

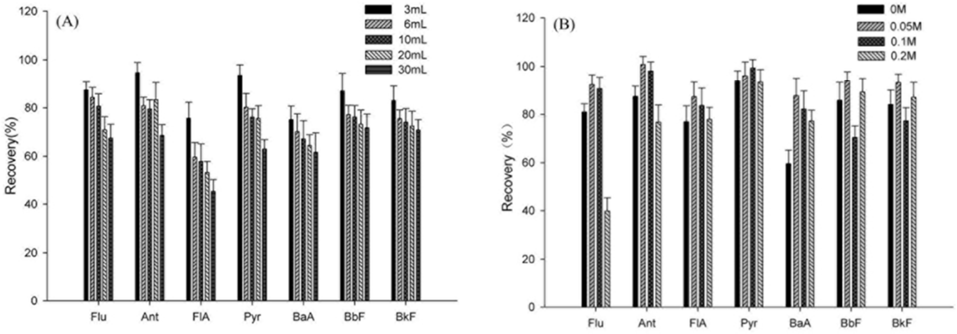

Figure 5 Effect of (A) the volume of organic modifier and (B) the concentration of NaCl on the recoveries of PAHs. Extraction conditions: sorbent, 100 mg; sample volume, 200 mL; extraction time, 3 min; desorption conditions, 5×2 mL acetonitrile.
91x33mm (300 x 300 DPI)