

Supporting Information

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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2. Experimental

2.5 HPLC analysis

Table S1 Time program of emission and excitation wavelengths of FLD in the analysis of PAHs.

Time (min)	Emission (nm)	Excitation (nm)	PAHs
0	340	260	Flu
13.2	370	250	Ant
15.5	462	289	FlA
17.5	380	320	Pyr
21	403	266	BaA
25	430	294	BbF, BkF

3. Results and discussion

3.1. Characterization of ZIFs

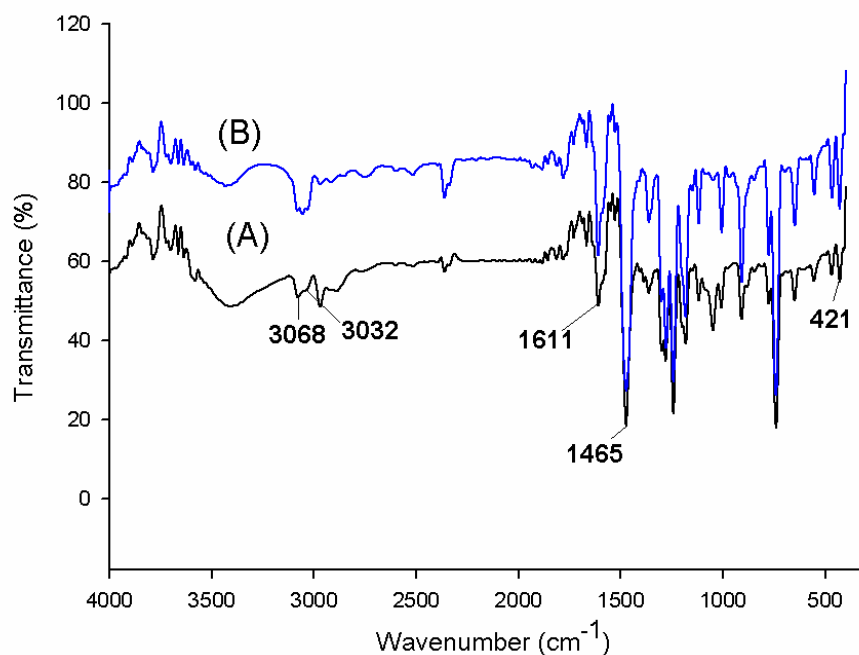


Figure S1 FT-IR spectra of (A) ZIF-7 and (B) ZIF-11 crystals.

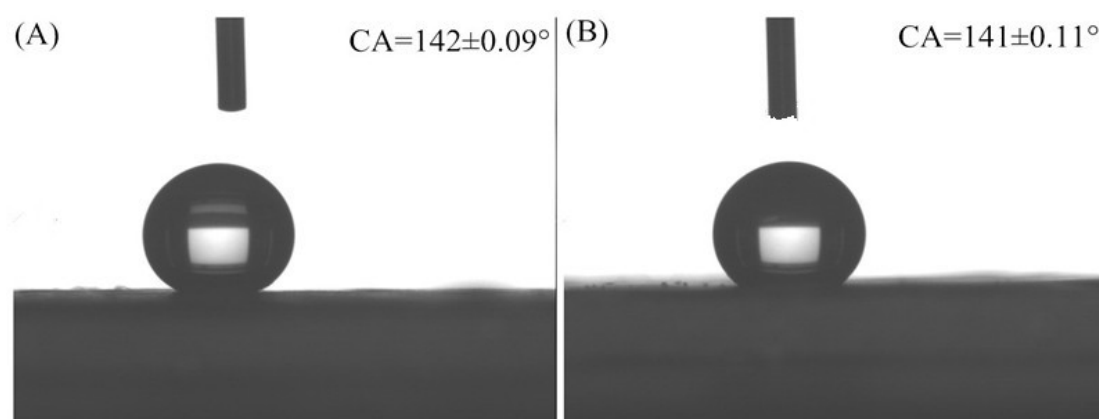


Figure S2 Water contact angle images for (A) ZIF-7, (B) ZIF-11.

3.1.1. Nitrogen adsorption/desorption isotherms

Nitrogen adsorption/desorption isotherms were also measured for ZIF-7 and ZIF-11. However, the results (not shown) indicated that the uptakes of N_2 at 77 K in ZIF-7 and ZIF-11 were both very low, which matched well with the previous reports.¹⁻⁴ According to the relevant literature,^{2,3} this is attributed to the small aperture of the channels in ZIF-7 and ZIF-11. The pore diameters of ZIF-7 and ZIF-11 are 4.3 and 14.6 Å, respectively, which are both larger than nitrogen molecule (3.6 Å).⁵ However,

their pore apertures are only 2.9 and 3.0 Å, which exclude N₂ to penetrate into the pores.

3.3. Extraction optimization

3.3.2. Optimization of extraction time

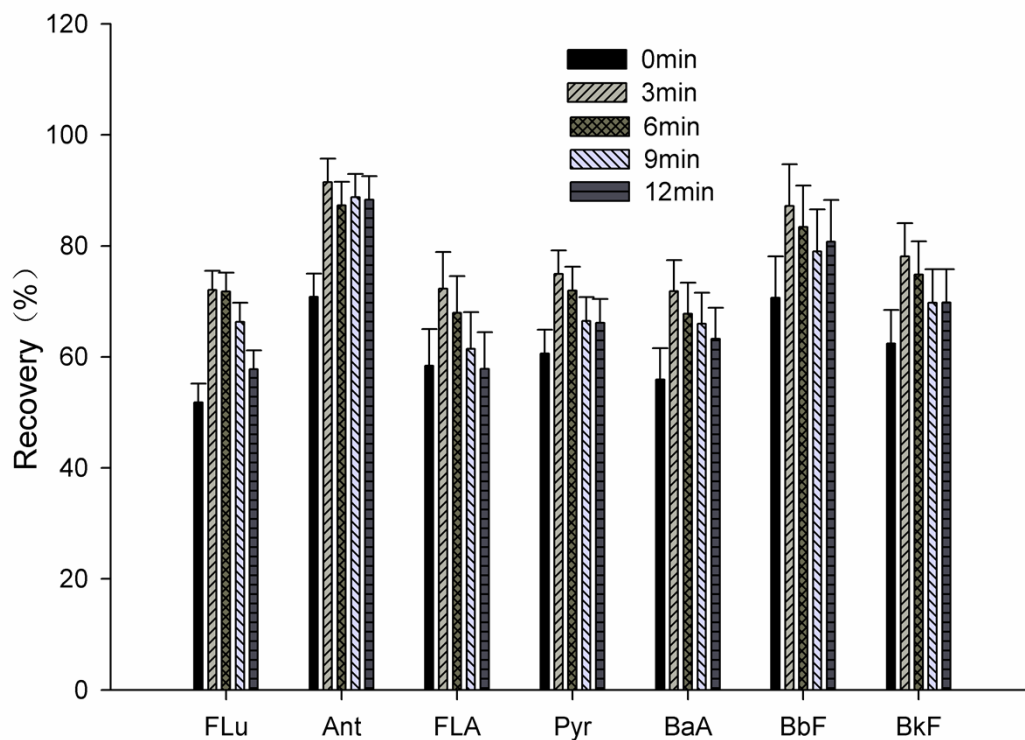


Figure S3 Effect of extraction time on the recoveries of PAHs. Extraction conditions: sorbent, 100 mg; sample volume, 200 mL; desorption conditions, 3×2 mL acetonitrile; organic modifier, 3 mL methanol; no salt addition.

3.3.3. Optimization of desorption conditions

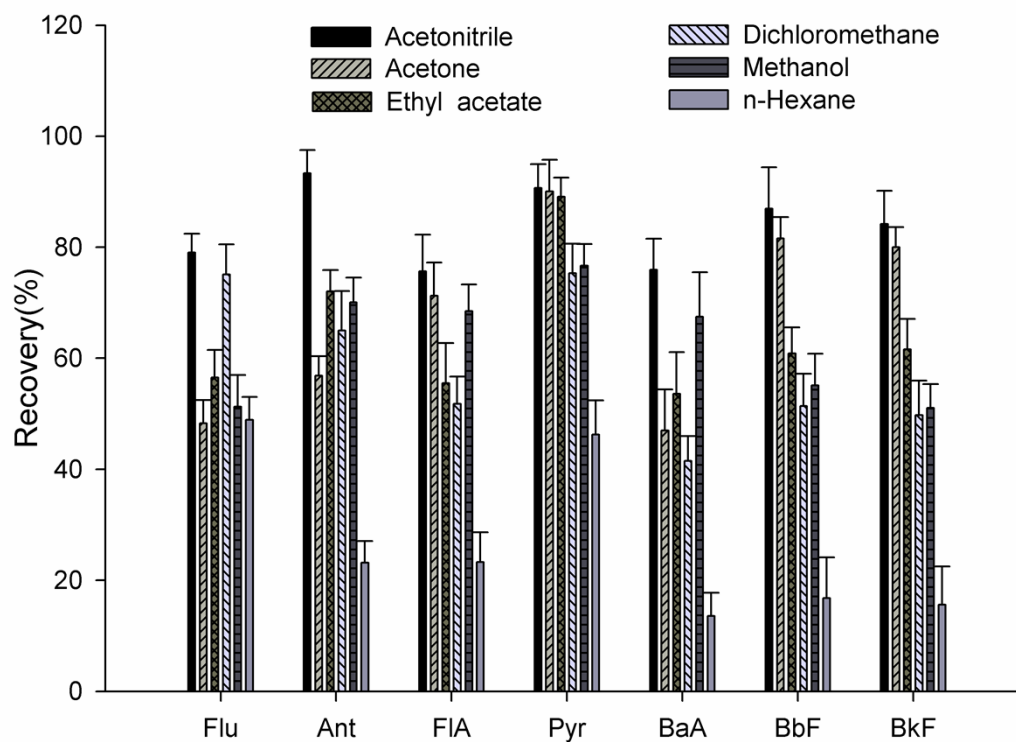


Figure S4 Effect of the type of elution solvent on the recoveries of PAHs. Extraction conditions: sorbent, 100 mg; sample volume, 200 mL; extraction time, 3 min; desorption solvent volume, 3×2 mL; organic modifier, 3 mL methanol; no salt addition.

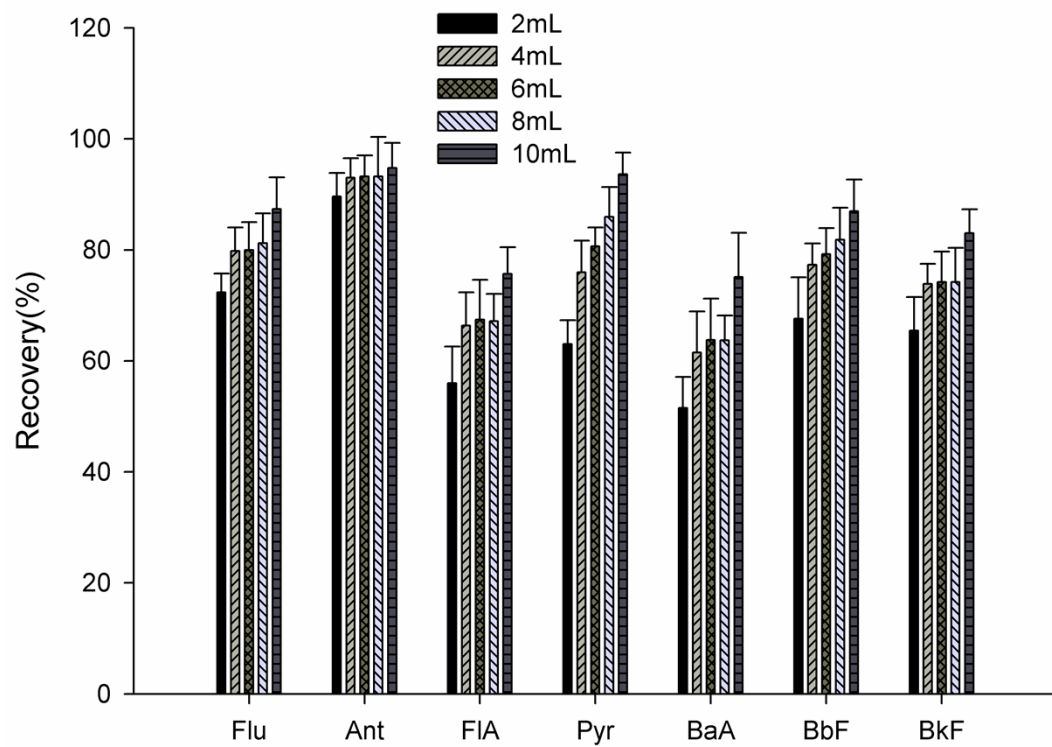


Figure S5 Effect of eluent volume on the recoveries of PAHs. Extraction conditions: sorbent, 100 mg; sample volume, 200 mL; extraction time, 3 min; desorption solvent, acetonitrile; organic modifier, 3 mL methanol; no salt addition.

3.5 Application in real water samples analysis

Table S2 Analysis results for the determination of PAHs in unspiked real water samples (n=5).

a) not detected

PAHs	Spring water		Tap water		River water	
	Detected	RSD	Detected	RSD	Detected	RSD
	Concentrations (ng L ⁻¹)	(%)	Concentrations (ng L ⁻¹)	(%)	Concentrations (ng L ⁻¹)	(%)
Flu	n.d. ^{a)}	-	n.d.	-	45.7	8.5
Ant	n.d.	-	n.d.	-	n.d.	-
FlA	n.d.	-	n.d.	-	56.8	3.9
Pyr	n.d.	-	n.d.	-	54.1	2.7
BaA	n.d.	-	n.d.	-	n.d.	-
BbF	n.d.	-	n.d.	-	n.d.	-
BkF	n.d.	-	n.d.	-	5.3	1.9

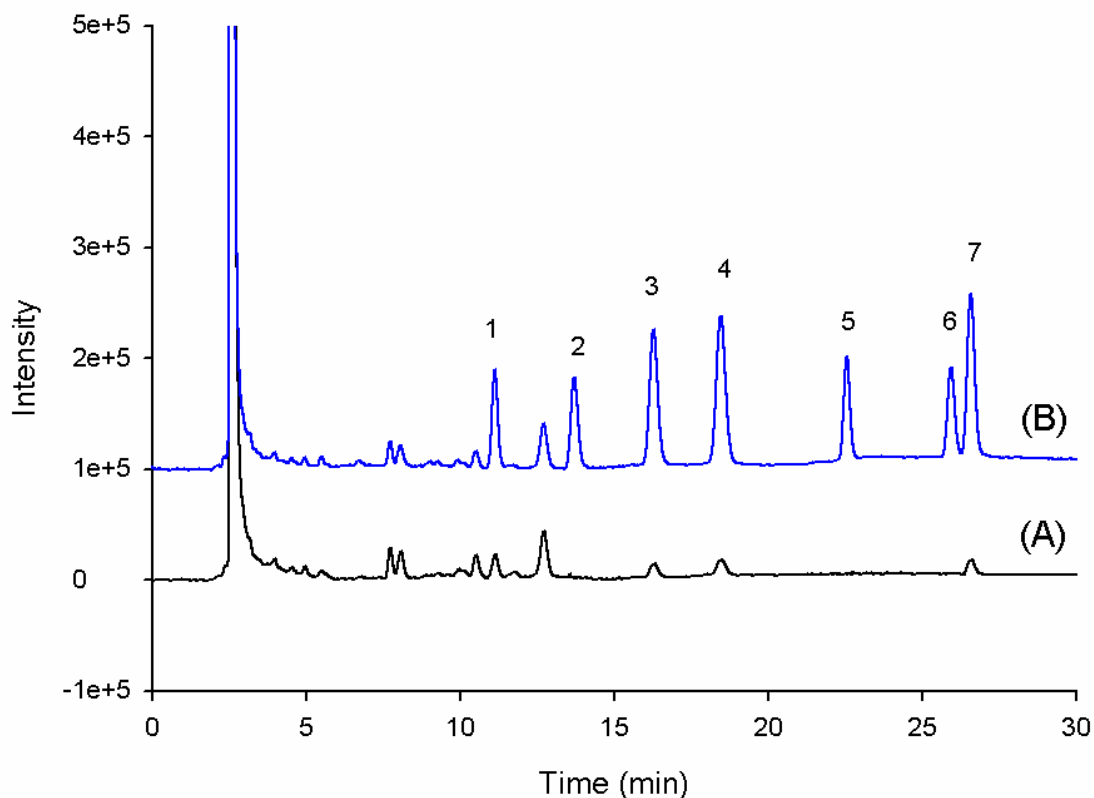


Figure S6 Chromatograms of PAHs in Xiangjiang river water: (A) unspiked; (B) spiked: 187.5 ng L⁻¹ Flu, 500 ng L⁻¹ Ant, 1000 ng L⁻¹ FIA, 500 ng L⁻¹ Pyr, 187.5 ng L⁻¹ BaA, 185.7 ng L⁻¹ BbF, 50 ng L⁻¹ BkF. Peaks: (1) Flu; (2) Ant; (3) FIA; (4) Pyr; (5) BaA; (6) BbF; (7) BkF.

References

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