

Supplementary Information

Simultaneous extraction of permethrin diastereomers and deltamethrin in environmental water samples based on aperture regulated magnetic mesoporous silica

Meixing Zhang^a, Jie Mei^b, Siying Lv^a, Jiahao Lai^a, Xiaoni Zheng^a, Jing Yang^{a,*},
Shihai Cui^{a,**}

a. Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Jiangsu Key Laboratory of Biomedical Materials, College of Chemistry and Materials Science, Jiangsu Provincial Key Laboratory of Materials Cycling and Pollution Control, Nanjing Normal University, 1 Wenyuan Road, Nanjing, 210023, China.

b. Nanjing Normal University Taizhou College, Taizhou, 225300, China.

*Corresponding author.

Jing Yang Tel.: +86 25 85891705. E-mail address: chemyangjing@njnu.edu.cn.

**Corresponding author.

Shihai Cui Tel.: +86 25 85891705. E-mail address: cuishihai@njnu.edu.cn.

Table S1. The chemical structures of the analytes.

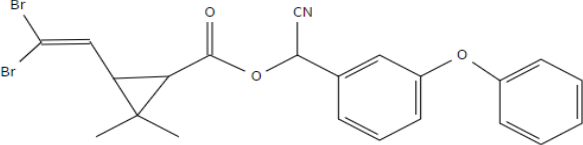
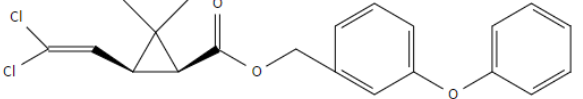
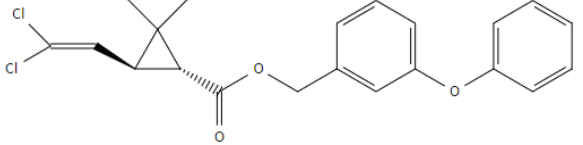
Analyte	CAS	Structure
Del	52918-63-5	
<i>cis</i> -Per	61949-76-6	
<i>trans</i> -Per	61949-77-7	

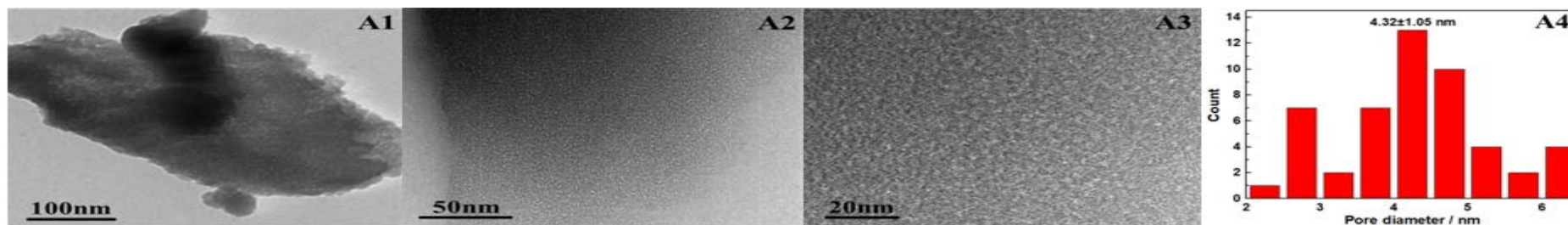
Table S2. Formulae of adsorption kinetic and isotherm experiments.

$Q_t = \frac{(C_0 - C_t)V}{m}$	Adsorption capacity	(1)
$\ln(Q_e - Q_t) = \ln Q_e - k_1 t$	Pseudo-first order	(2)
$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t$	Pseudo-second order	(3)
$Q_t = k_p t^{\frac{1}{2}} + C$	Intra-particle model	(4)
$\frac{1}{Q_e} = \frac{1}{Q_{max}} + \frac{1}{K_L Q_{max} C_e}$	Langmuir equation	(5)
$\log Q_e = \log K_F + \frac{1}{n} \log C_e$	Freundlich equation	(6)
$\ln K^\theta = -\frac{\Delta H^\theta}{RT} + \frac{\Delta S^\theta}{R}$	Van't Hoff equation	(7)
$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$	Gibbs function definition	(8)
$K^\theta = 10^6 K_L$		(9)

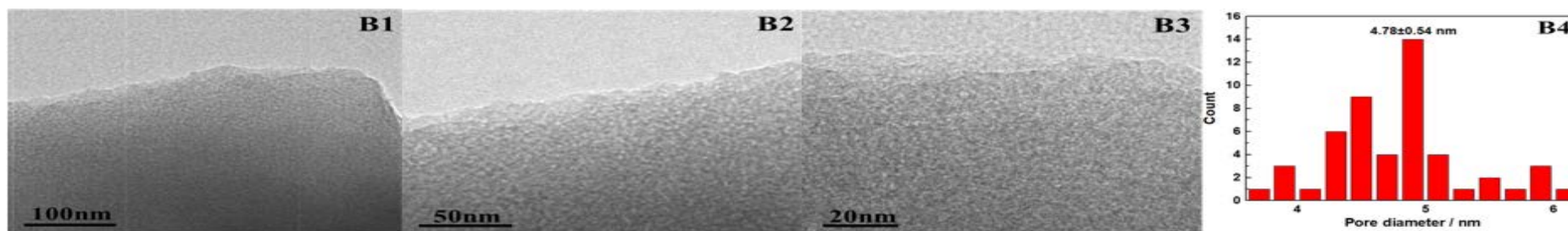
Q_t : the adsorbed amount in the time t ($\mu\text{g}\cdot\text{mg}^{-1}$); C_0 : the original insecticide

concentrations ($\mu\text{g}\cdot\text{mL}^{-1}$); C_t : the insecticide concentration in time t ($\mu\text{g}\cdot\text{mL}^{-1}$); V : the solution volume (mL); m : the mass of the adsorbent (mg); Q_e : the amounts of insecticide adsorbed at equilibrium ($\mu\text{g}\cdot\text{mg}^{-1}$); k_1 : the pseudo first-order rate constant (min^{-1}); k_2 : the pseudo-second order adsorption rate constant ($\text{mg}\cdot\mu\text{g}^{-1}\cdot\text{min}^{-1}$); k_p : the intra-particle diffusion rate constant ($\mu\text{g}\cdot\text{mL}^{-1}\cdot\text{min}^{-1/2}$); C : the intercept of intra-particle model; Q_{max} : the maximum monolayer capacity of the adsorbent ($\mu\text{g}\cdot\text{mg}^{-1}$); K_L : the Langmuir binding constant ($\text{mL}\cdot\mu\text{g}^{-1}$); C_e : the equilibrium concentration of analytes in solution ($\mu\text{g}\cdot\text{mL}^{-1}$); K_F : the Freundlich constant ($\text{mL}\cdot\mu\text{g}^{-1}$); n : the heterogeneity factor (dimensionless); ΔG^0 : the Gibbs free energy ($\text{kJ}\cdot\text{mol}^{-1}$); ΔH^0 : the enthalpy ($\text{kJ}\cdot\text{mol}^{-1}$); ΔS^0 : the entropy ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); R : the perfect gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); T : the reaction temperature (K); K^0 : the equilibrium constant (dimensionless).

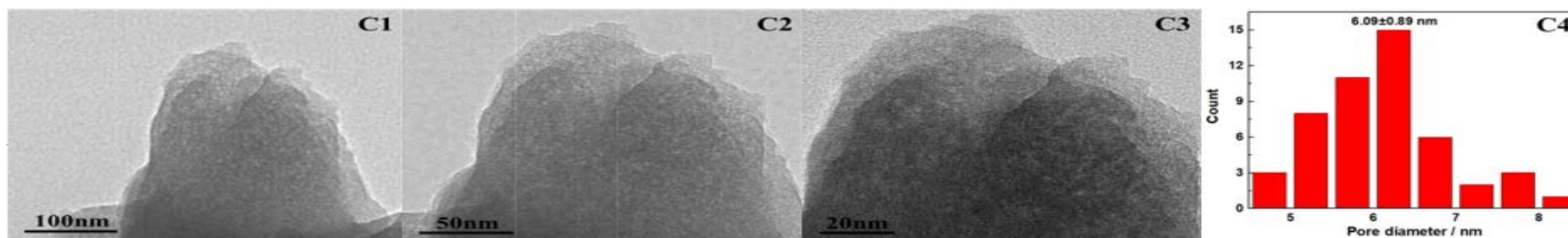
60 °C:



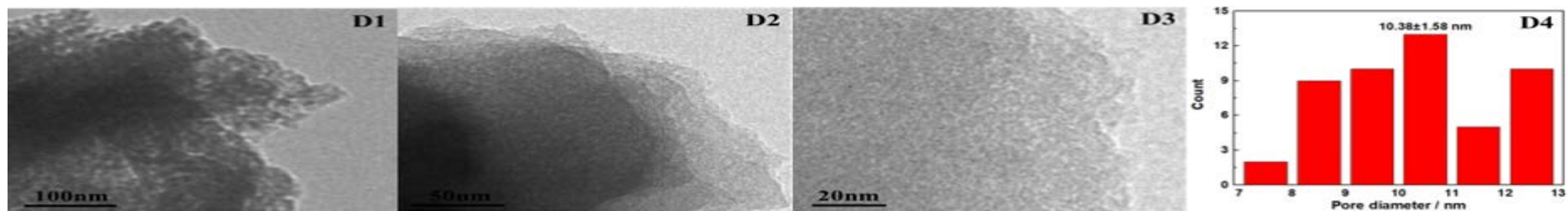
80 °C:



100 °C:



120 °C:



150 °C:

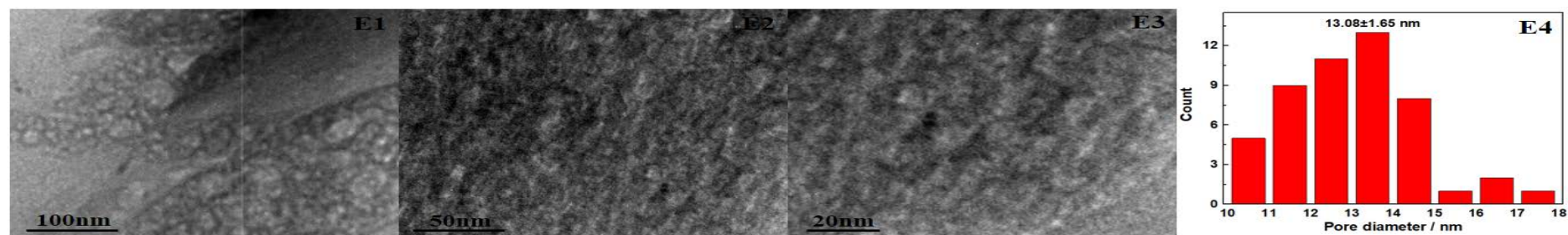


Fig. S1. TEM images of FK60 (A), FK80 (B), FK100 (C), FK120 (D) and FK150 (E).

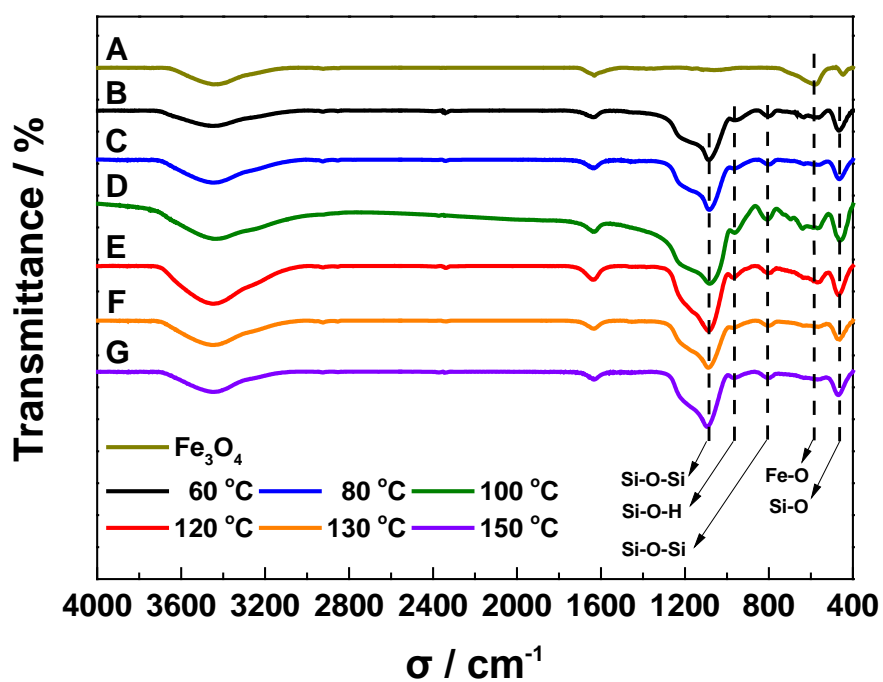


Fig. S2. FT-IR analysis of Fe_3O_4 (A), FK60 (B), FK80 (C), FK100 (D), FK120 (E), FK130 (F) and FK150 (G).

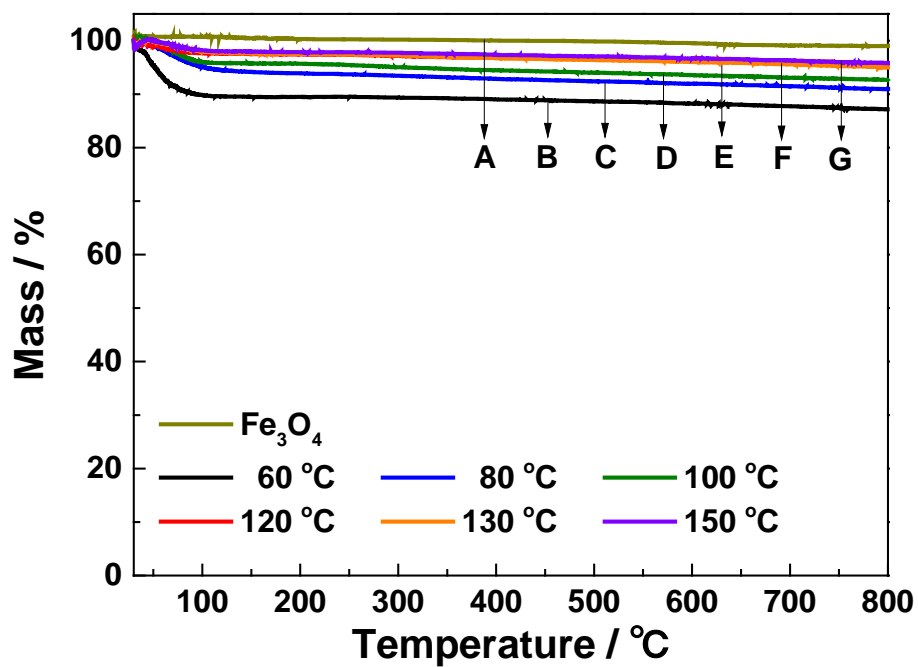


Fig. S3. TG curves of Fe_3O_4 (A), FK60 (B), FK80 (C), FK100 (D), FK120 (E), FK130 (F) and FK150 (G).

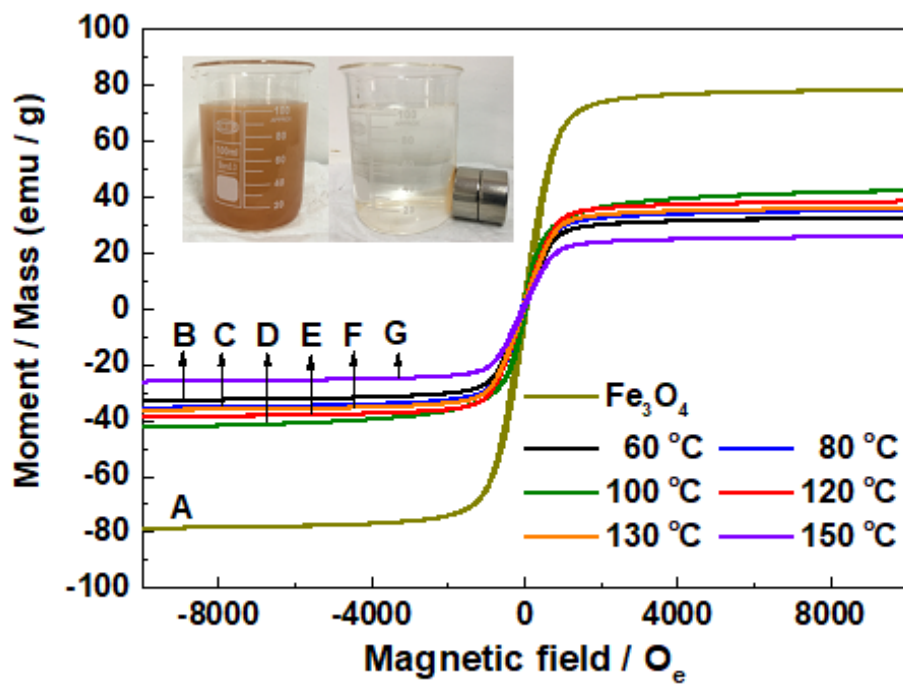


Fig. S4. Magnetic curves of Fe₃O₄ (A), FK60 (B), FK80 (C), FK100 (D), FK120 (E), FK130 (F) and FK150 (G).

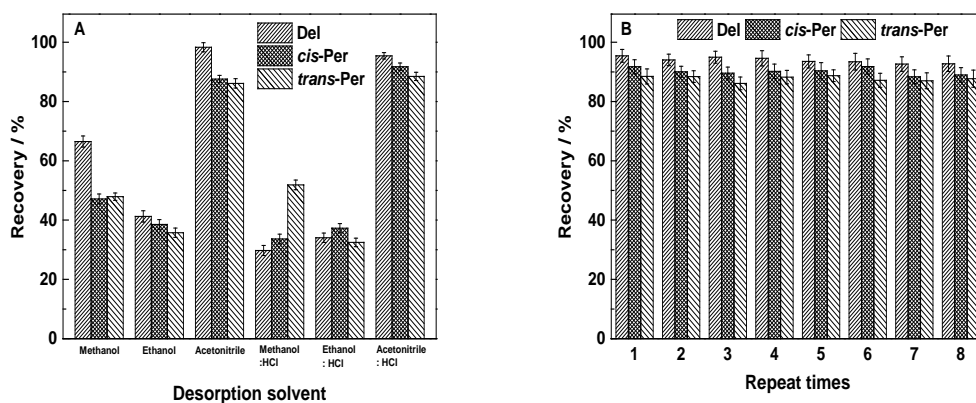


Fig. S5. Condition selection of the MSPE procedure including desorption solvent (A) and reusability (B).

Table S3. Validation of the established MSPE-HPLC method.

Analyte	Linear range ($\mu\text{g}\cdot\text{L}^{-1}$)	Calibration curves	SD (slope)	SD (intercept)	Correlation coefficient (r)	RSD (%) (n=6)	LOD ($\mu\text{g}\cdot\text{L}^{-1}$)	LOQ ($\mu\text{g}\cdot\text{L}^{-1}$)
Del	0.07-1200	$y=12.29x+121.78$	0.25	188.46	0.9991	2.34	0.02	0.07
<i>cis</i> -Per	0.02-1200	$y=8.40x+1233.88$	0.15	108.78	0.9994	1.27	0.01	0.02
<i>trans</i> -Per	0.33-1200	$y=7.82x-241.71$	0.28	205.39	0.9975	1.16	0.10	0.33