

Room temperature synthesis of flower-like hollow covalent organic framework for efficient enrichment of microcystins

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1.1. Chemicals and reagents

1,3,5-tris(4-aminophenyl) benzene (TPB, 99%), 2,5-divinylterephthalaldehyde (DVA, 98%) were obtained from Jilin Chinese Academy of Sciences-Yanshen Technology Co. Ltd. Anhydrous tetrahydrofuran (THF, 97%) and acetonitrile (ACN, 97%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) was obtained by Milli-Q water purification system (Millipore, USA). Formic acid (FA, 99%), methanol (MeOH), and ethanol were purchased from J&K Scientific Co. Ltd. (Beijing, China). Crucian, prawns and pond snails were purchased from the local market (Fuzhou, China).

Microcystin-RR (MC-RR) ($\geq 95\%$), Microcystin-YR (MC-YR) ($\geq 95\%$), and Microcystin-LR (MC-LR) ($\geq 95\%$) were gained from Enzo Life Biochem Inc. (New York, USA). Stock standard solutions ($100 \mu\text{g mL}^{-1}$) were made by dissolving MC-RR, MC-YR and MC-LR in pure methanol, respectively, and then stored at $-18 \text{ }^\circ\text{C}$. The mixed standard solutions of the three MCs were made by stepwise dilution with water before use and stored at $4 \text{ }^\circ\text{C}$ for 24 hours.

1.2. Instruments

Transmission electron microscopy (TEM) images were performed on FEI Tecnai G₂ F₂₀ instruments (FEI, USA). Scanning electron microscopy (SEM) images were obtained with a JSM-6300F SEM instrument (JEOL, Japan). Fourier-transform infrared (FT-IR) spectrograms were taken using a Nicolet iS50 spectrometer (Thermo Fisher,

USA). The powder X-ray diffraction (PXRD) was carried out on a CEM DY5261/Xpert3 X-ray diffractometer, and the corresponding data were collected in the range of 1.5-30° with a scan rate of 5° min⁻¹. N₂ adsorption-desorption isotherms were measured with ASAP 2020 instrument (Micromeritics, USA), and the sample was analyzed after degasification at 150 °C for 8 h under vacuum. The surface areas were calculated from Brunauer-Emmett-Teller (BET) method. Nonlocalized density functional theory (NLDFT) was used to evaluate the pore size distribution.

MCs were quantified by a scientific Accela HPLC system connected with a TSQ Quantum Access MaxTM triple quadrupole mass spectrometer (Thermo Fisher, USA). And three MCs were separated with a Hypersil GOLD aQ column (5 μm, 150 × 2.1 mm, Thermo Fisher, USA) at room temperature. The mobile phases were composed of 60% of H₂O and 40% of ACN both containing 0.1% of FA. The flow rate was 200 μL min⁻¹. The injection volume of sample was set at 10 μL. The electrospray ionization (ESI) in positive mode was chosen as ion source for MS/MS analysis. The source-dependent parameters were set as follows: ESI spray voltage, +3000V; vaporizer temperature, 300 °C; capillary temperature, 270 °C; sheath gas (nitrogen), 35 psi; auxiliary gas (nitrogen, 99.999%), 10 psi; and collision gas (helium, 99.999%). Qualitative and quantitative analyses were achieved with the selected reaction monitoring (SRM) mode. Detailed mass spectrometry conditions, including collision energy (CE), tube lens voltage and SRM transitions can be found in Table S1.

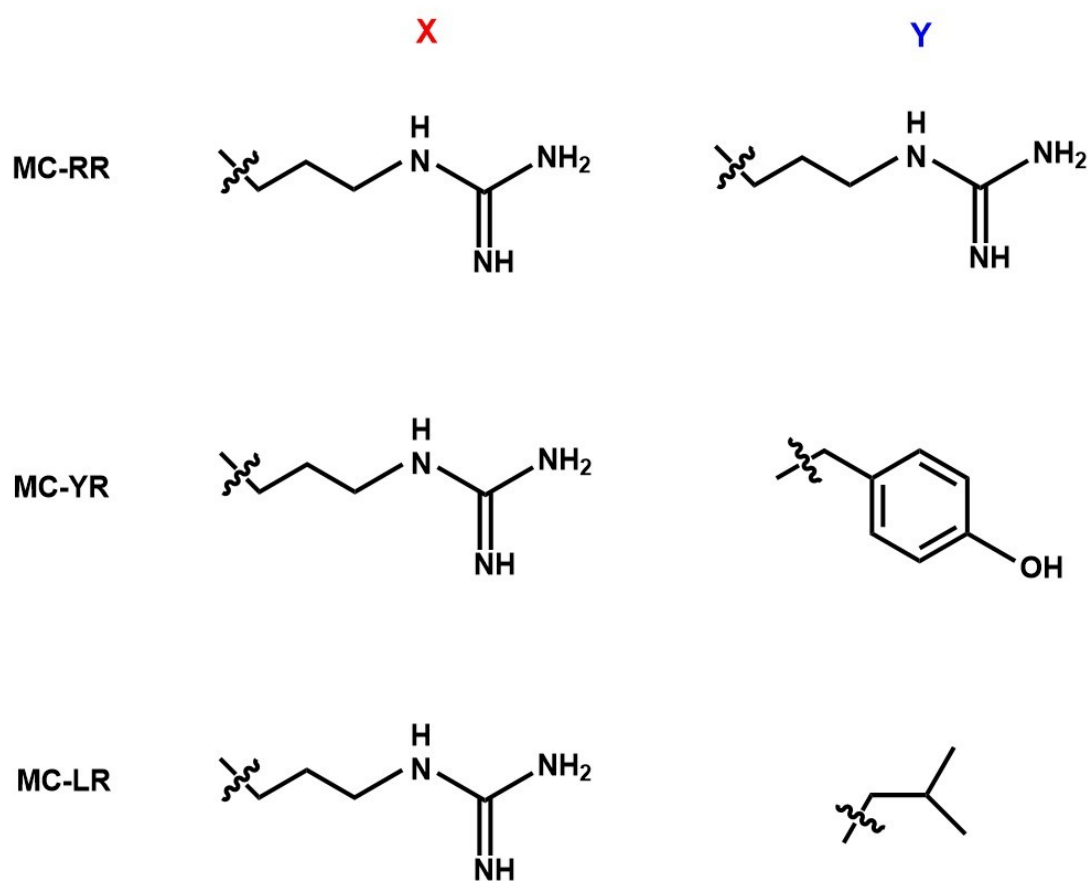
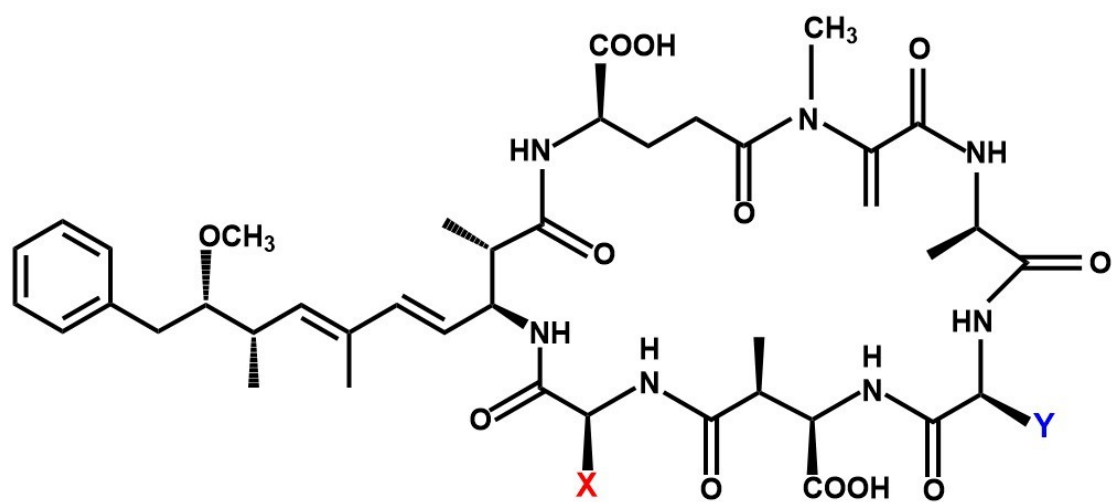


Fig. S1 General chemical structure of MCs.

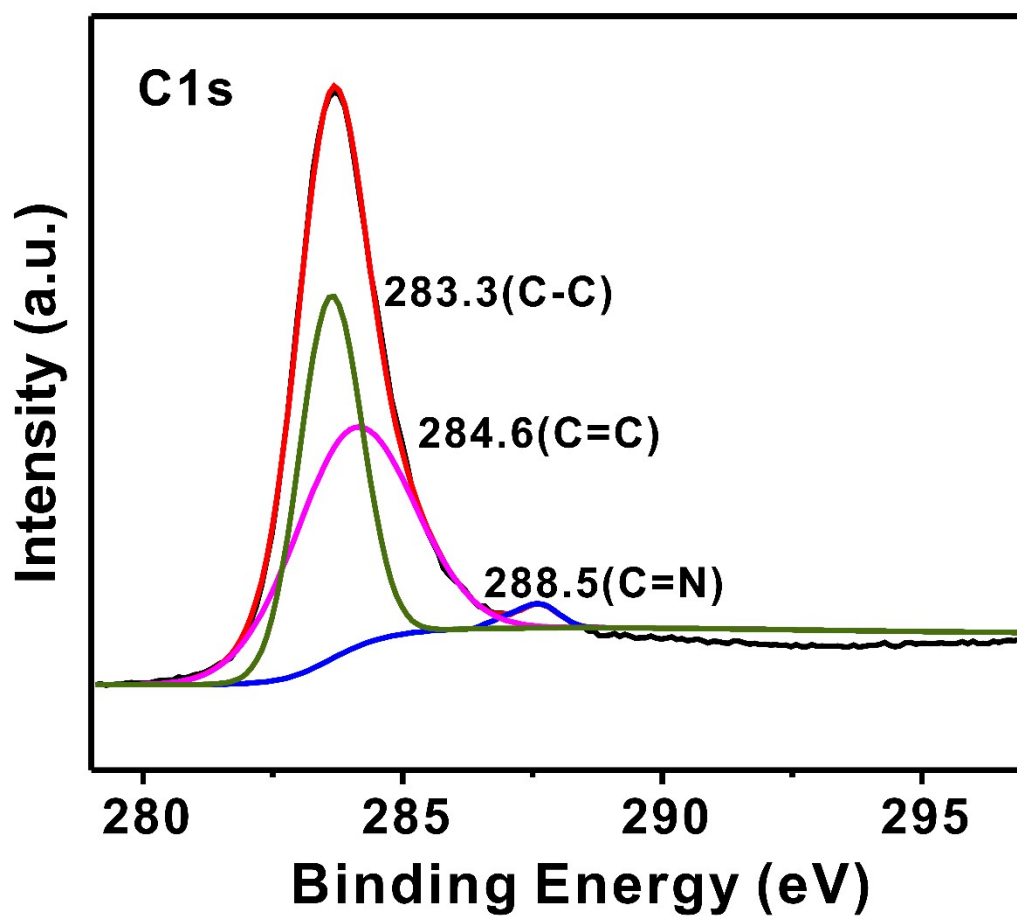


Fig. S2 XPS C1s spectra of HFH-COF

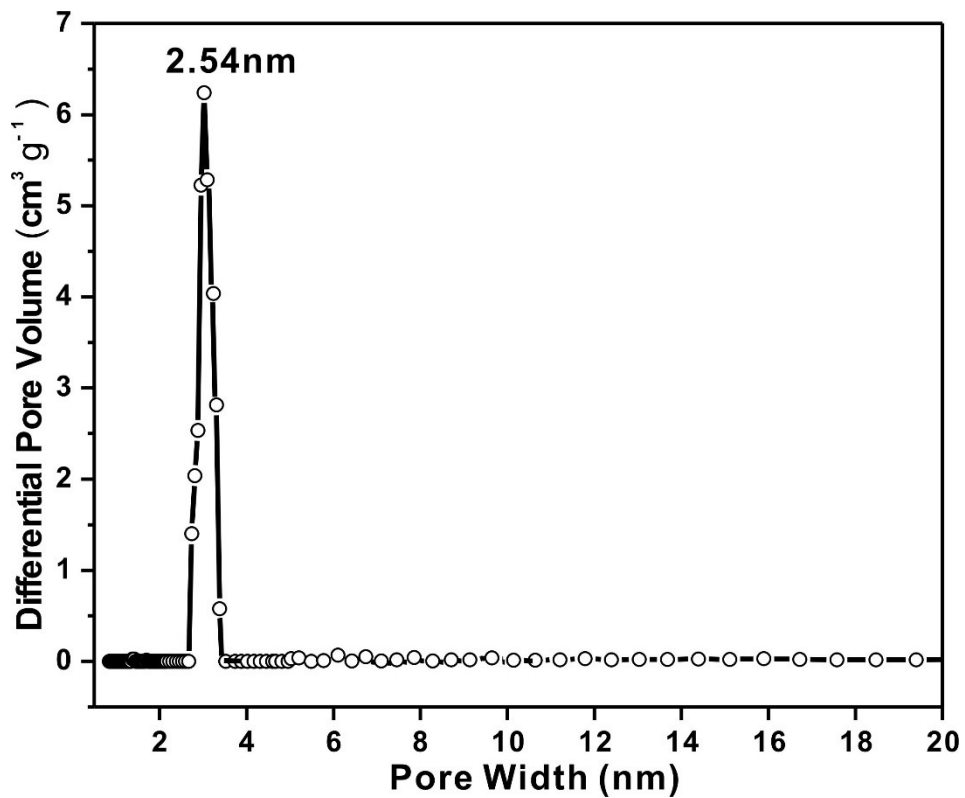


Fig. S3 Pore size distribution of S-COF was calculated by using the NLDFT model

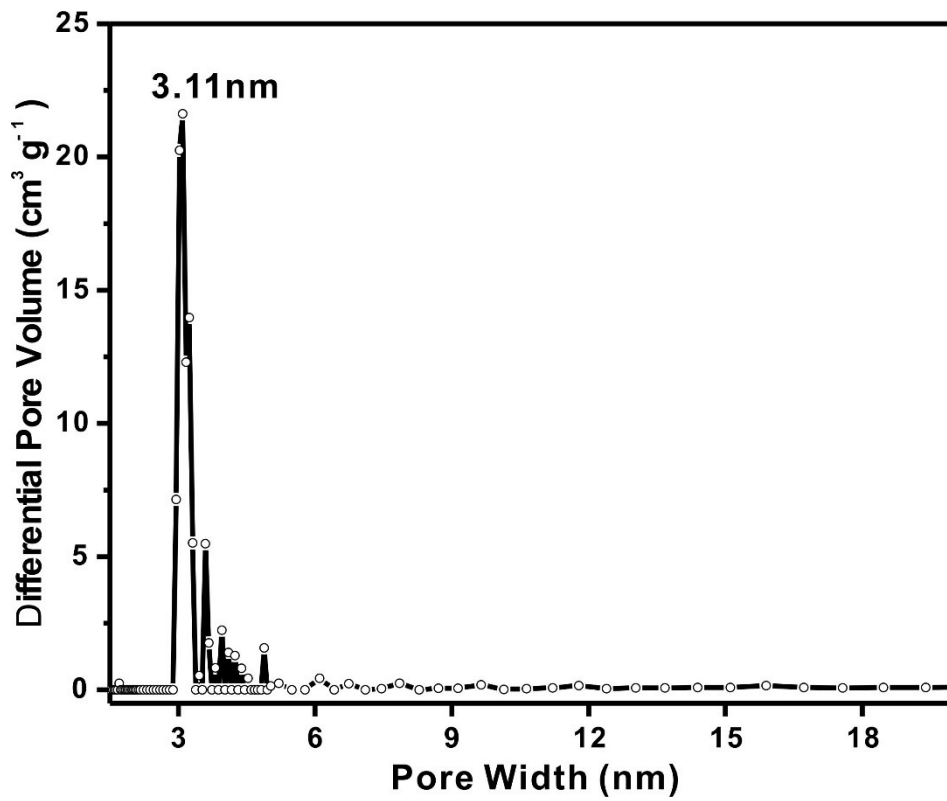


Fig. S4 Pore size distribution of HFH-COF was calculated by using the NLDFT model.

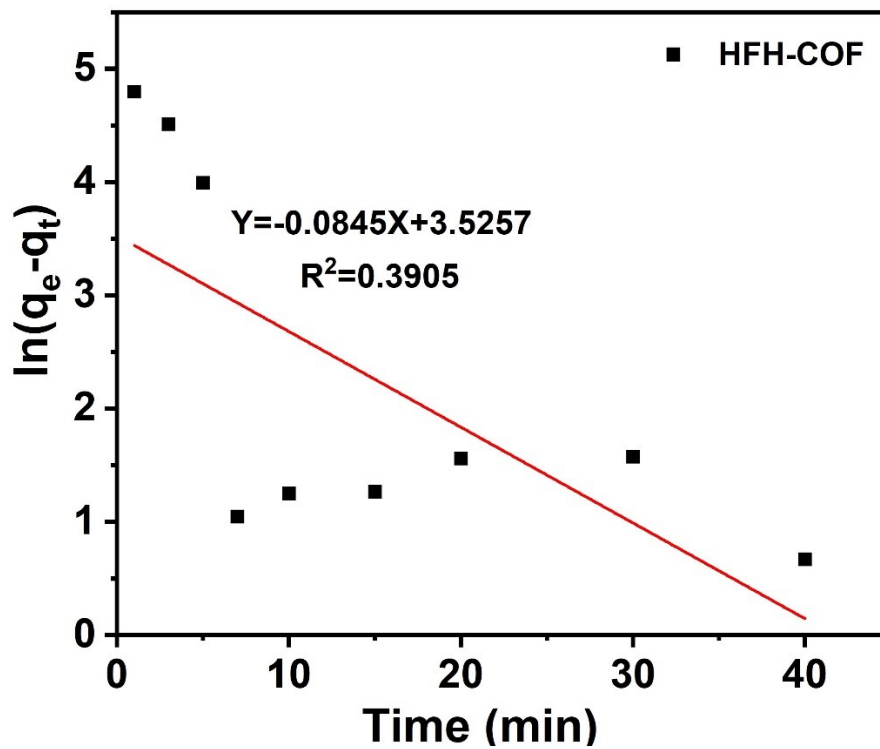


Fig. S5 Pseudo first-order kinetic model of HFH-COF on MC-RR

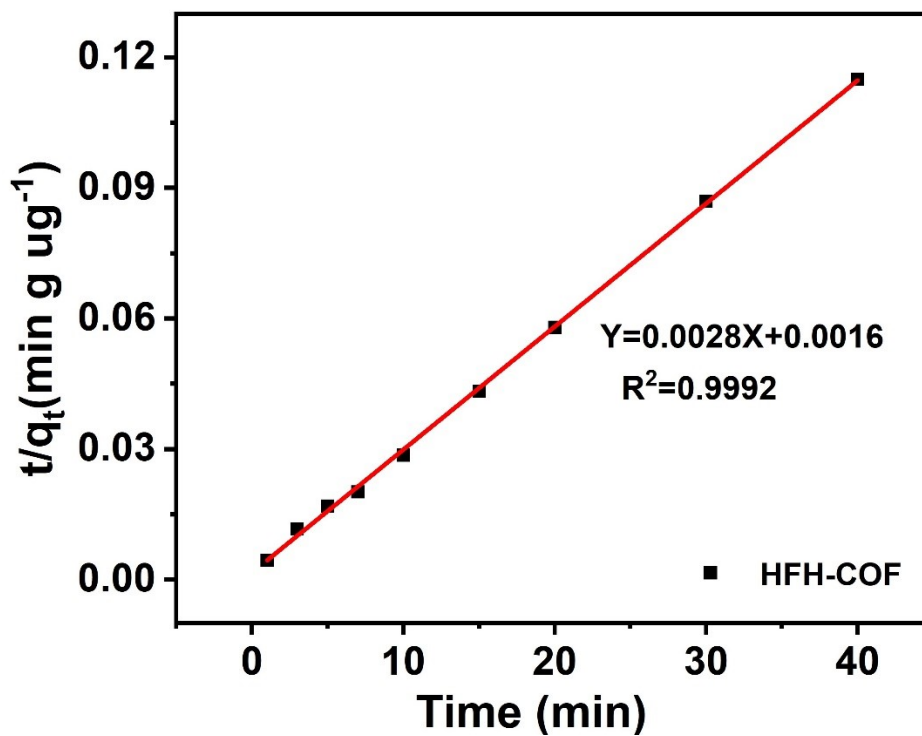


Fig. S6 Pseudo second order kinetic model of HFH-COF on MC-RR

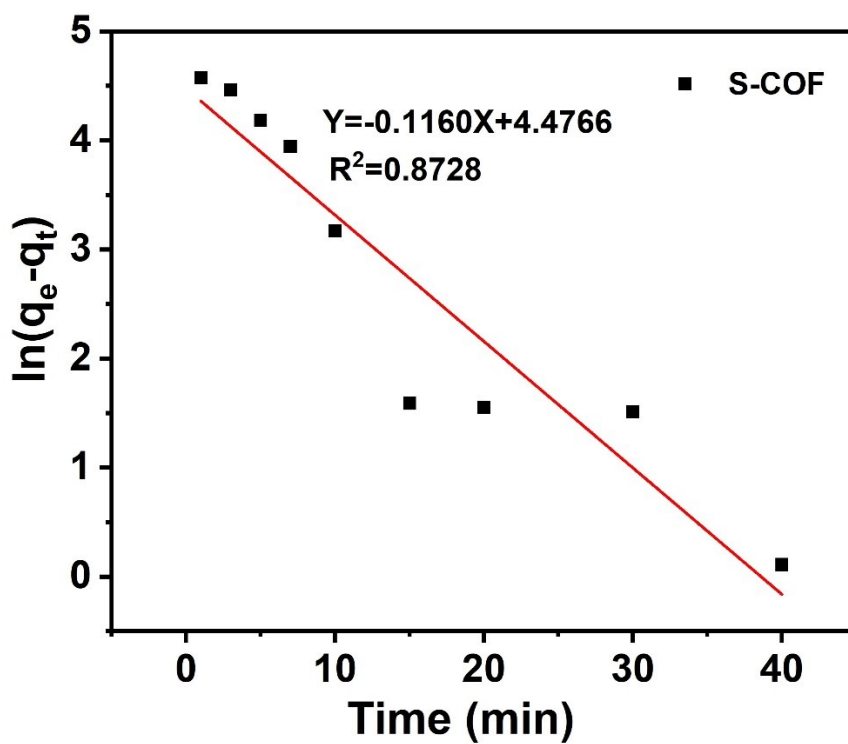


Fig. S7 Pseudo first-order kinetic model of S-COF on MC-RR

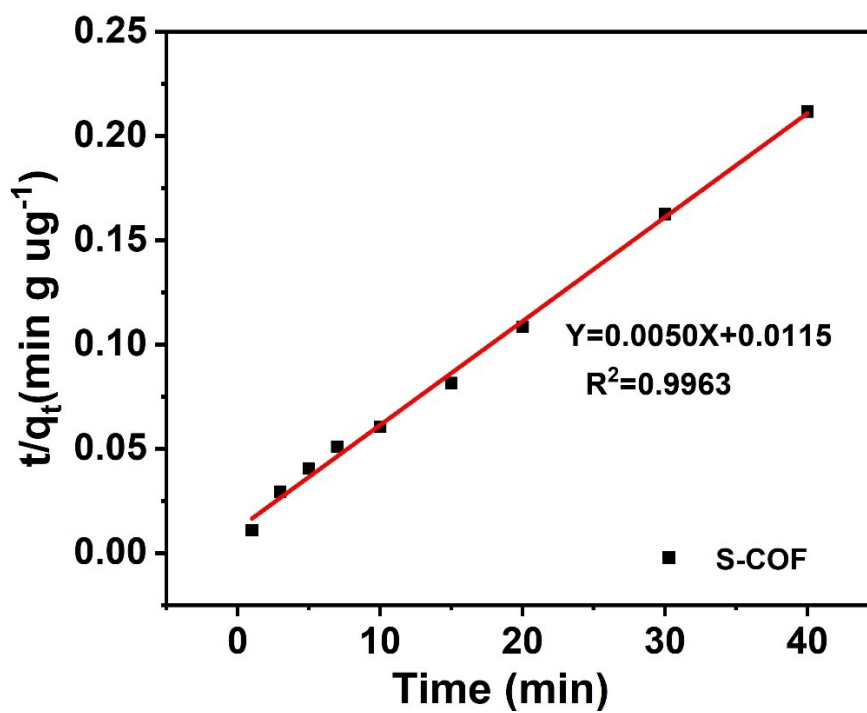


Fig. S8 Pseudo second order kinetic model of S-COF on MC-RR

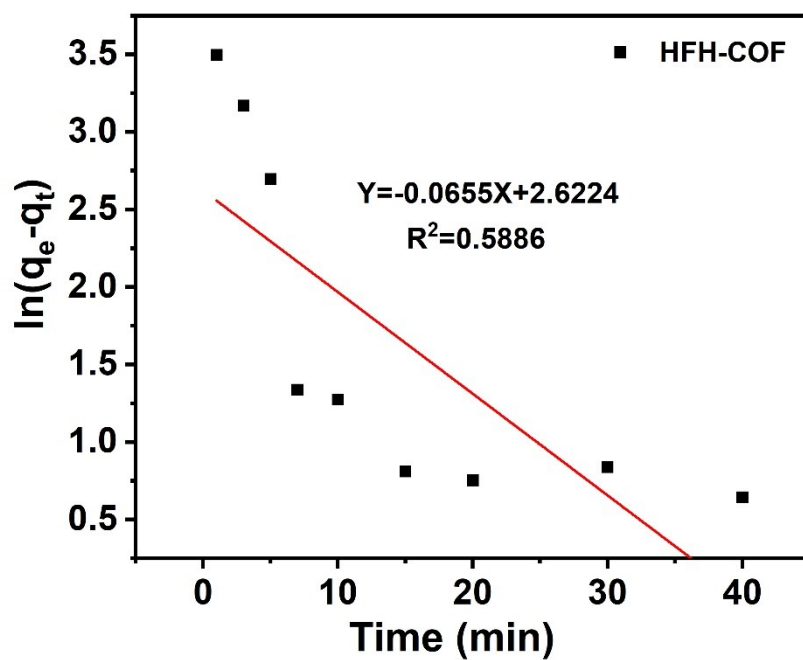


Fig. S9 Pseudo first-order kinetic model of HFH-COF on MC-YR

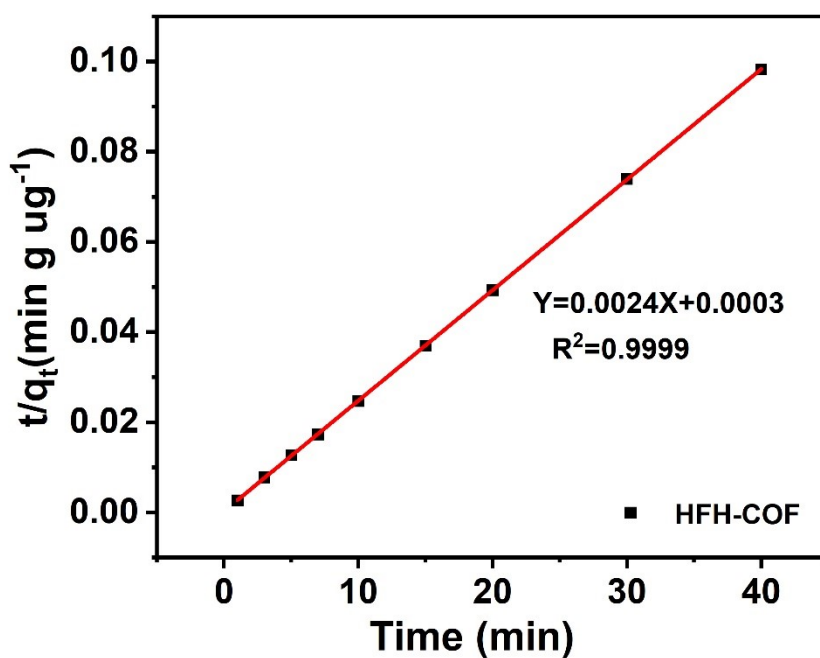


Fig. S10 Pseudo second order kinetic model of HFH-COF on MC-YR

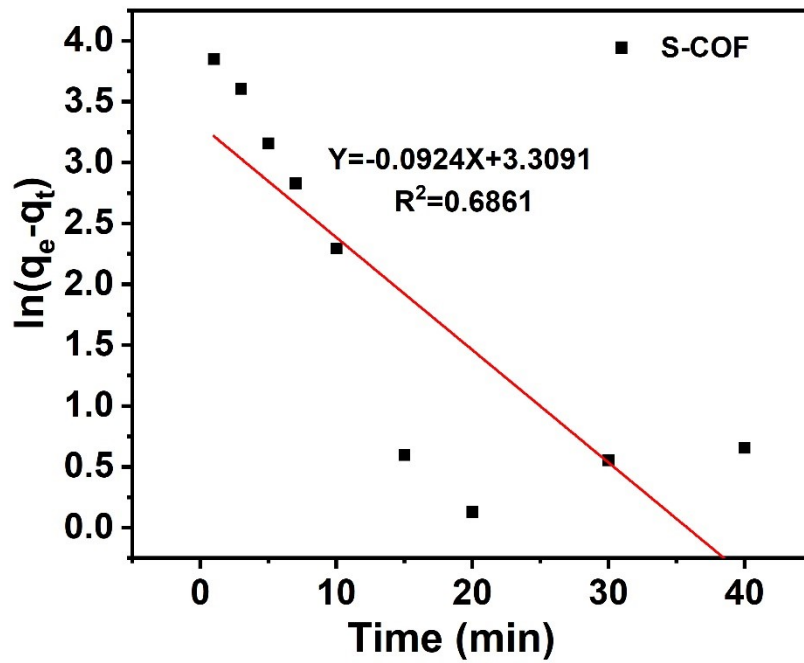


Fig. S11 Pseudo first-order kinetic model of S-COF on MC-YR

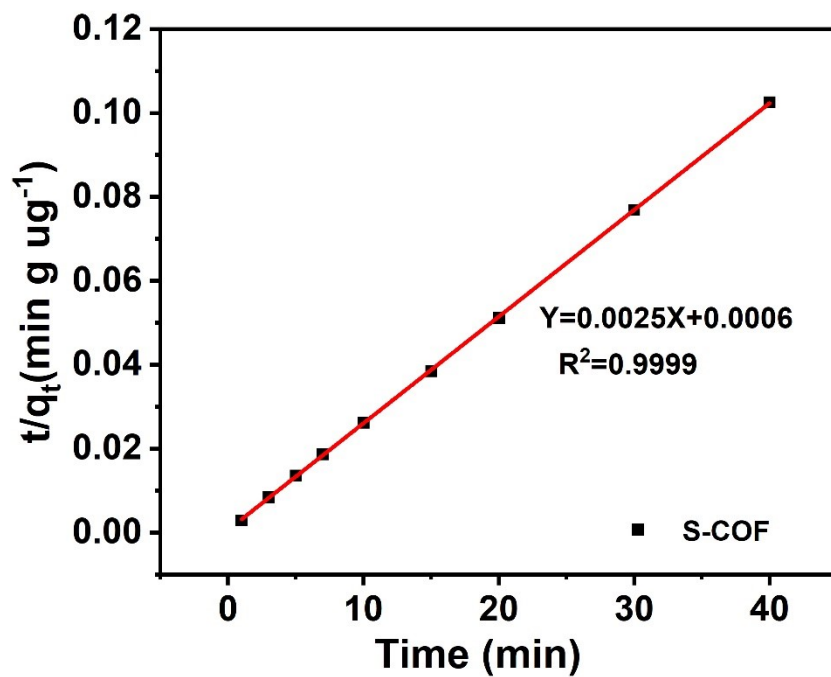


Fig. S12 Pseudo second order kinetic model of S-COF on MC-YR

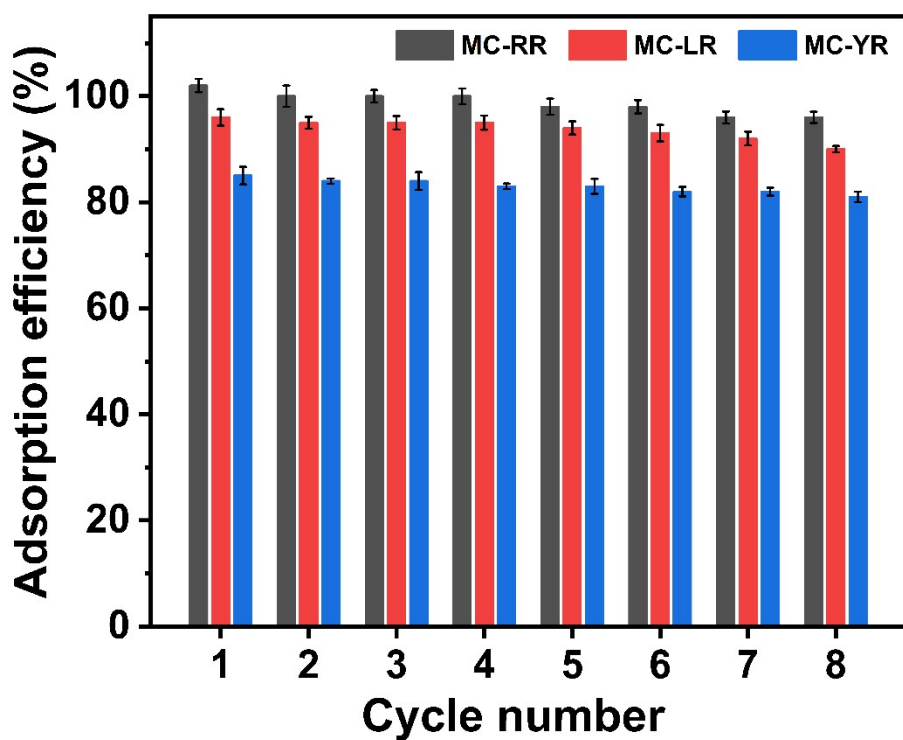


Fig. S13 Recyclability of HFH-COF for d-SPE of MCs.

Table S1. MS parameters by auto tuning for MC-LR, MC-RR, MC-YR.

Compounds	Assignment	Parent ion (Q1, m/z)	Quantification ion (Q3, m/z)	SRM Collision Energy (eV)	Tube Lens Voltage (V)
MC-LR	$[M+2H]^{2+}$	498.465	135.110	15	85
MC-RR	$[M+2H]^{2+}$	519.965	135.000	36	109
MC-YR	$[M+2H]^{2+}$	523.326	135.139	20	89

Table S2. BET comparison of some COFs.

Adsorbent materials	BET(m ² g ⁻¹)	Reference
MCNTs@TpPa-1	218.05	1
TpBD-(CF ₃) ₂	987	2
TPBD-(NO ₂) ₂	439	2
TPBD-(NH ₂) ₂	391	2
Fe ₃ O ₄ @TabTfa-F ₄	442.3	3
TATB-DATP-COF	267	4
PDA-TAPB-COF	655	4
OMePDA-TAPB-COF	2226	4
COF-320	566	4
HFH-COF	2134.5	This work

Table S3. The pseudo-first-order and pseudo-second-order parameters of MC-RR and MC-YR on HFH-COF and S-COF.

analyt e	absorbent	Experi mental q _e (μg g ⁻¹)	Pseudo-first-order model			Pseudo-second-order model		
			q _{e,1} (μg g ⁻¹)	k ₁ (min ⁻¹)	R ₁	q _{e,2} (mg g ⁻¹)	k ₂ (g μg ⁻¹ min ⁻¹)	R ₂
MC- RR	HFH-COF S-COF	351 190	33.9775 87.9352	0.0845 0.1160	0.3905 0.8728	357.1429 200.0000	0.0049 0.0007	0.9992 0.9963
MC- YR	HFH-COF S-COF	408 392	13.7687 27.3605	0.0655 0.0924	0.5886 0.6861	416.6667 400.0000	0.0192 0.0104	0.9999 0.9999

Table S4. The interference of potential ions on the determination of MCs.

Ions	Tolerance limit (mmol L ⁻¹)
Na ⁺ , K ⁺ , Cl ⁻ , NO ₃ ⁻ , NH ₄ ⁺	80
Mg ²⁺ , Ca ²⁺	8
Fe ³⁺ , CO ₃ ²⁻ , SO ₄ ²⁻	0.02

Reference

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2. S. P. S. Fernandes, P. Kovář, M. Pšenička, A. M. S. Silva, L. M. Salonen and B. Espiña, *ACS Applied Materials & Interfaces*, 2021, **13**, 15053-15063.
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