

Supplementary Information

One-step synthesized Zn-doped UiO-66 for effective removal of tetracycline hydrochloride from wastewater

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1. Experimental section

1.1 Adsorbent characterization

The morphology and elemental distribution of the samples were characterized by field emission scanning electron microscopy (FE-SEM, GeminiSEM 300) operated at EHT = 3.00 kV, Signal A = SE2, WD = 5.9 mm, Mag = 20.00 k \times . Crystalline phase identification was performed by X-ray diffraction (XRD, Rigaku SmartLab) using Cu K_{α} radiation with 2θ ranging from 5° to 80°. Surface chemical composition and valence states were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). Nitrogen adsorption-desorption measurements were conducted at 77 K using a BSD-660S A6 analyzer (BeiShiDe Instrument) to determine the specific surface area and pore size distribution. Prior to measurements, samples were degassed at 200 °C for 2 h under vacuum. Surface charge properties were characterized by zeta potential measurements (Zetasizer Nano ZS90, Malvern Panalytical). Functional groups were identified using Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet 6700) with a spectral range of 4000-400 cm^{-1} .

2. Results

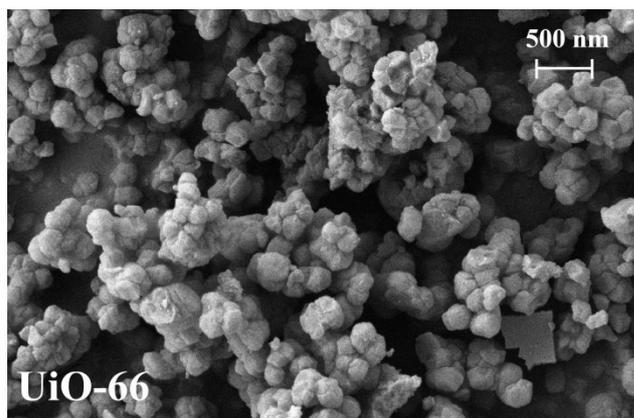


Fig. S1 SEM images of UiO-66

Table S1 The ICP-OES characterization data of the pristine Zn-UiO-66 material

Sample Name	Element	wt%
Zn-UiO-66	Zr	21.053
	Zn	2.776
Zn-UiO-66-TCH	Zr	25.358
	Zn	2.226

Table S2 The post-adsorption solution was analyzed by ICP-MS.

Element	Elemental Content C_x (ug/L)
Zr	40.458
Zn	2.635

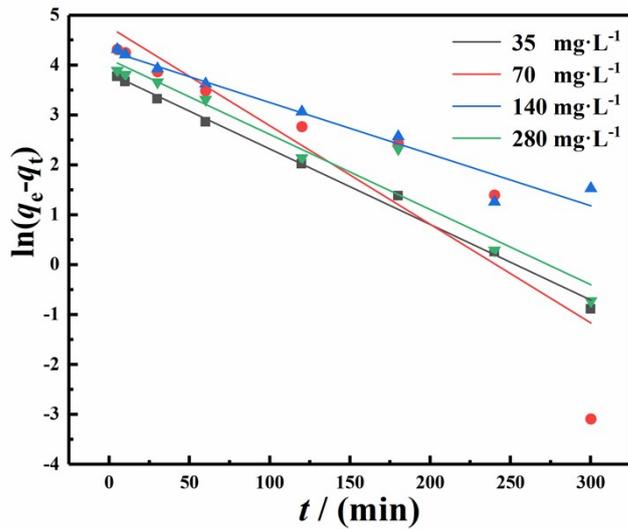


Fig. S2 Adsorption kinetics of Zn-UiO-66 at different initial TCH concentrations follows first-order kinetics

Table S3 Adsorption kinetics model parameters for pseudo-first-order and pseudo-second-order kinetics

C_0 (mg·L ⁻¹)	Pseudo-first-order kinetics			Pseudo-second-order kinetics		
	K_1 (min ⁻¹)	q_e (mg·g ⁻¹)	R^2	K_2 (g·mg ⁻¹ ·min ⁻¹)	q_e (mg·g ⁻¹)	R^2
35	0.0151	46.3323	0.9942	1.16×10^{-3}	85.1064	0.9984
70	0.0198	117.0932	0.8185	0.53×10^{-3}	124.2236	0.9962
140	0.0104	72.7312	0.9542	0.52×10^{-3}	132.9787	0.9954
280	0.0151	61.4547	0.9486	0.63×10^{-3}	79.2393	0.9912

The Langmuir (Equation S1) and Freundlich (Equation S2) models.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (\text{S1})$$

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (\text{S2})$$

q_e stands for the equilibrium adsorption capacity, C_e is the residual concentration of

TCH at equilibrium, q_{\max} is the maximum adsorption capacity, K_L and K_F are the constants of the Langmuir and Freundlich adsorption models, respectively, and $1/n$ is the heterogeneity factor.

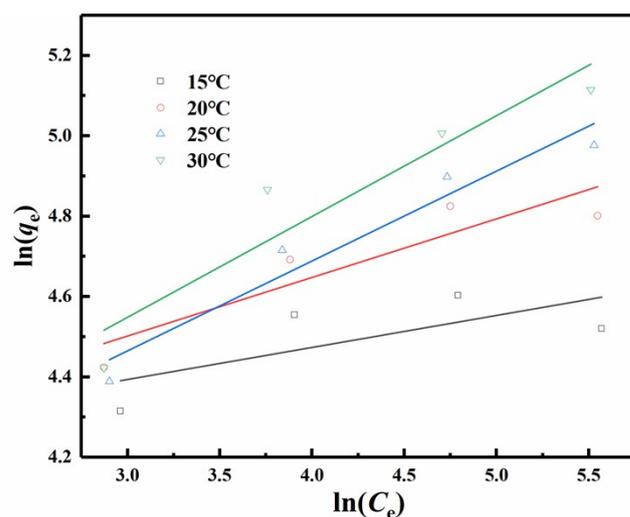


Fig. S3 Freundlich Adsorption Isotherm of TCH on Zn-UiO-66

The thermodynamic parameters of TCH adsorption on Zn-UiO-66 were analyzed using Equations S3 and S4

$$\ln K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (\text{S3})$$

$$\Delta G = \Delta H - T\Delta S \quad (\text{S4})$$

ΔG is the adsorption free energy, ΔH is the adsorption enthalpy, ΔS is the adsorption entropy, R is the gas constant, T is the absolute temperature of adsorption ($T(\text{K}) = t + 273$), K_0 is the thermodynamic equilibrium constant and calculated by plotting $\ln K_d$ ($K_d = q_e/C_e$) versus C_e and extrapolating C_e to zero.

Table S4 Thermodynamic parameters for TCH adsorption on Zn-UiO-66

T (K)	$\ln K_0$	ΔG (kJ·mol ⁻¹)	ΔH (kJ·mol ⁻¹)	ΔS (J·mol ⁻¹ ·K ⁻¹)
288	0.65	-1.6		
293	0.81	-2.0		
298	0.88	-2.2	20.89	77.86
303	1.11	-2.8		

Table S5 Comparison of the Zn-UiO-66 adsorbent with other materials on TC adsorption at room temperature.

Adsorbent	T (K)	Isotherm model	q_{\max} (mg·g ⁻¹)	Reference
SiO ₂ @UiO-66-400	278	Langmuir	36.3	1
CoUiO-1	318	Langmuir	226.2	2
UiO-66-COOH/GO	303	Langmuir	164.9	3
NH ₂ -MIL-101(Cr)	318	Langmuir	50.8	4
UiO-66	318	Langmuir	7.2	5
UiO-66	303	Langmuir	61.5	This work
Zn-UiO-66	303	Langmuir	178.9	This work

Table S6 The recovery rate of Zn-UiO-66 and the recovery rate of TCH from Zn-UiO-66.

Sample	recovery rate	Sample	recovery rate
Zn-UiO-66	99.8%	TCH	81.2%
	99.5%		78.9%
	99.5%		77.6%
	99.6%		76.7%

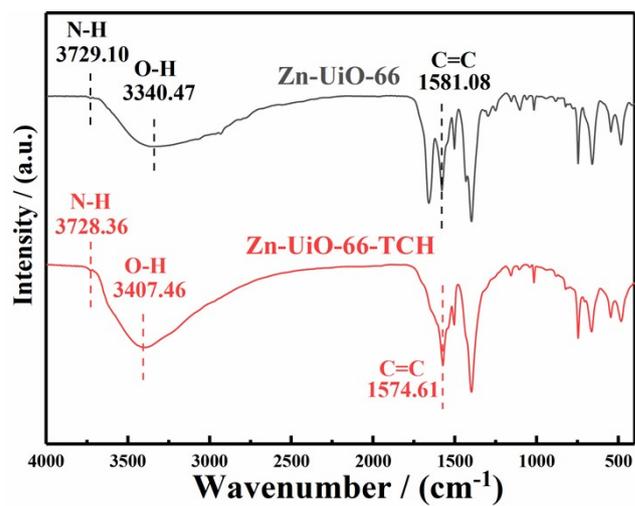


Fig. S4 FTIR spectra of Zn-UiO-66 and Zn-UiO-66-TCH

3. References

- 1 M. Wu, X. Li, Y. He, K. Li, S. Yang, M. Zhu, N. Sun, *Inorg. Chem. Commun.*, 2025, **173**, 113899.
- 2 J. Cao, Z. Yang, W. Xiong, Y. Zhou, Y. Peng, X. Li, C. Zhou, R. Xu, Y. Zhang, *Chem. Eng. J.*, 2018, **353**, 126-137.
- 3 K. Wang, J. Wu, M. Zhu, Y. Zheng, X. Tao, *J. Solid State Chem.*, 2020, **284**, 121200.
- 4 N. Tian, Q. Jia, H. Su, Y. Zhi, A. Ma, J. Wu, S. Shan, *J. Porous Mater.*, 2016, **23**, 1269-1278.
- 5 J. Fu, X. Liu, G. Huang, Z. Wang, *Chem. Eng. J.*, 2025, **505**, 159260.