Electronic Supplementary Information (ESI)

Effect of particle size distribution of UiO-67 nano/microcrystals on the

adsorption of organic dyes from aqueous solution

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Experimental

Sample preparation

Materials and chemicals: Zirconium chloride (ZrCl₄, 98%) was purchased from Nanjing Chemical Reagent Co., Ltd. Polyvinylpyrrolidone (PVP, 30 K), acetic acid (HAc, 99.5%), and *N*,*N*-dimethylformamide (DMF, 99.5%) were obtained from Tianjin Chemical Reagent Co., Ltd. 4,4'-Biphenyldicarboxylic acid (H₂BPDC, 99%) was purchased from Sinapharm Chemical Reagent Co., Ltd. All chemicals were analytically pure and used as received without further purification.

Synthesis of UiO-67: In a typical procedure, $ZrCl_4$ (45 mg, 0.13 mmol), H₂BPDC (43.7 mg, 0.13 mmol), and HAc (0.5 mL) were dissolved in 15 mL DMF at room temperature. The mixture was transferred into a 25 mL Teflon-lined autoclave, which was sealed and maintained at 120 °C for 24 h. The reaction vessel was then removed from the oven and allowed to cool to room temperature. The particles were isolated by centrifugation, washed three times with DMF, and the obtained particles were designated as UiO-67-1. The

coordination polymer particles designated as UiO-67-2 and UiO-67-3 were synthesized by the same procedure used for the preparation of UiO-67-1, except that 1.5 or 2.0 mL of HAc, respectively, was used. Before measurements, the as-obtained CPPs were immersed in methanol for 3 days. The methanol was replenished daily. Then the UiO-67 particles were dried under vacuum at 100 °C for 5 h.

2.2 Characterization

Powder X-ray diffraction (PXRD) data were obtained on a Bruker D8 Advance X-ray diffractometer with CuK α radiation ($\lambda = 1.5418$ Å) at room temperature. Scanning electron microscopy (SEM) images were measured on a scanning electron micro-analyzer (Hitachi S-3400), employing an accelerating voltage of 15 kV. UV-Vis spectra were collected on a UV-3600 UV-vis spectrophotometer (Shimadzu). Fourier-transform infrared (FT-IR) spectra were recorded in the 400–4000 cm⁻¹ range on a Bruker Vector 22 FT-IR spectrophotometer using KBr pellets. Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo (TGA/DSC1) thermal analyzer under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹. The zeta potential and particle size distribution were measured with a Zetasizer Nano Z (Malvern Instruments) at 25 °C. Nitrogen sorption experiments were performed at 77 K on a Micromeritics ASAP2460 volumetric gas sorption instrument. Surface areas were determined by the Brunauer–Emmett–Teller (BET) equation. Ultra-high purity N₂ was used in the adsorption study.

2.3 Effect of initial solution pH

The effect of initial solution pH on CR and MB adsorption was investigated at 25 °C. The pH of the initial dye solution was adjusted in the range of 4–12 using dilute aqueous HCl or NaOH. UiO-67-2 (5 mg) were dispersed in CR or MB solution (50 mL, 20 mg L^{-1}) at the desired pH, and the suspension was continuously stirred for 24 h to achieve adsorption equilibrium. Concentrations of CR/MB were monitored at wavelength of 662/463 nm using a UV-vis spectrophotometer, and the amounts of adsorbed dye (q_e , mg g⁻¹) were calculated in terms of residual dye concentration after adsorption:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where C_0 and C_e (mg L⁻¹) are the initial and equilibrium dye concentrations, respectively, V (L) is the volume of the dye solution, and m (g) is the mass of the UiO-67-2.

2.4 Adsorption kinetics study

Adsorption kinetics were studied at 25 °C under neutral conditions.UiO-67-2 (5 mg) was dispersed in CR solution (50 mL, 20 mg L⁻¹), and the obtained suspension was stirred at 25 °C. At regular time intervals, ~4-mL aliquots were removed and centrifuged, and the CR concentrations in the supernatant were determined using a UV-vis spectrophotometer.

2.5 Adsorption equilibrium study

To study the adsorption isotherms, UiO-67-2 (5 mg) was dispersed in CR solutions (50 mL) of different initial concentrations (20–500 mg L^{-1}) under neutral conditions. The obtained mixtures were stirred at 25 °C for 24 h and centrifuged, with the CR concentrations of the obtained supernatants determined using UV-vis spectroscopy.

2.6 Desorption and reusability experiments

After CR or MB adsorption, UiO-67-2 was thoroughly cleaned by repeated ultrasonication in ethanol and centrifugation, being subsequently activated by heating in vacuum at 100 °C for 10 h. The activated material was reused for the adsorption of CR or MB

from an aqueous solution (20 mg L^{-1}) over 24 h. After each run, the CR concentration of the filtrate was determined by UV-vis spectroscopy. Following the above procedure, the recyclable UiO-67-2 was reused for CR adsorption four times.

In addition, the adsorption kinetics of other dyes and the corresponding isotherms were investigated using the above-mentioned procedures, using MO or MB instead of CR.



Fig. S1 PXRD spectra of (a) simulated UiO-67 and (b) samples of UiO-67 synthesized without addition to HAc.



Fig. S2 SEM images of samples of UiO-67 synthesized without addition to HAc.



Fig. S3 Particle size distribution of UiO-67-1 directly dispersed in water.



Fig. S4 Particle size distribution of UiO-67-2 directly dispersed in water.



Fig. S5 Particle size distribution of UiO-67-3 directly dispersed in water.



Fig. S6 Molecular structures of the investigated dyes.



Fig. S7 Zeta potential of UiO-67-1 directly dispersed in water.



Fig. S8 Zeta potential of UiO-67-2 directly dispersed in water.



Fig. S9 Zeta potential of UiO-67-3 directly dispersed in water.



Fig. S10 Effect of pH on dye adsorption on the UiO-67 nanocrystals: (a) CR and (b) MB.

Type of adsorbent	$q (\text{mg g}^{-1})$	Reference
UiO-67-3	1144.9	This work
CPPSs-1	1033.2	9
$[Co(L_1)(tp)]_n$	928.4	10
Ce(III)-doped UiO-66	825.7	11
In-based ICP hierarchical architectures	577	12
Hierarchical hollow NiO	440	13

Table S1 Summary of CR maximum adsorption capacities (q) on various adsorbents.

Type of adsorbent	$q (\text{mg g}^{-1})$	Reference
UiO-67-3	576.5	This work
MOF-235	477	14
MIL-100(Cr)	211	15
NMC-3-600	170.1	16
AC/ferrospinel composite	95.8	17
Acrylic acid grafted Ficus carica fiber	51.55	18
Functionalized CNTs loaded TiO ₂	42.85	19

Table S2 Summary of MO maximum adsorption capacities (q) on various adsorbents.

Type of adsorbent	$q (mg g^{-1})$	Reference
UiO-67-2	314.3	This work
Ce(III)-doped UiO-66	145.1	11
UiO-66-P composite	91.1	8a
PZS nanotubes	69.2	20
FMAs	40	21
CS-MCM	31.8	22
HKUST-1	15.3	23

Table S3 Summary of MB maximum adsorption capacities (q) on various adsorbents.

		parameters	UiO-67-1	UiO-67-2	UiO-67-3
Adsorption kinetics	Pseudo- first-order	$q_{e,Exp} (\text{mg g}^-)$	153.2	462.6	480.8
		$q_{e,Cal} (\text{mg g}^-)$	105.6	354.8	386.5
		k_{l} (min ⁻¹)	0.0054	0.0086	0.01221
		R^2	0.9268	0.9873	0.9894
Pseudo-second-		$q_{e,Exp} (\text{mg g}^-)$	153.2	462.6	480.8
014		$q_{e,Cal} (\operatorname{mg} g^{-1})$	110.3	383.5	408.4
		$k_2 (g mg^{-1})$	1.5×10 ⁻³	2.2×10 ⁻⁴	1.8×10 ⁻⁴
		R^2	0.9982	0.9895	0.9917
Adsorption	Tempkin	<i>A</i> (L g ⁻¹)	4.78	1.07	2.20
isotherm		В	16.9	159.0	310.3
		R^2	0.9616	0.8930	0.9747
	Freundlich	n	9.07	2.64	4.06
		$k_F (\text{mg g}^{-1})$	95.2	80.1	314.9
		$(L \operatorname{Ing}^{2})^{*})$ R^{2}	0.9446	0.8368	0.8539
	Langmuir	$q_{m,Exp} (\text{mg g}^-)$	181.8	740.6	1144.9
		$q_{m,Cal} (\operatorname{mg} g^{-1})$	183.5	746.3	1285.9
		$b (L mg^{-1})$	0.1495	0.1804	0.1307
		R^2	0.9998	0.9998	0.9999
Thermodynan	nic constant	ΔG (kJ mol ⁻	-4.7	-4.2	-5.0
-		K_d	4665.9	4447.8	5524.1

Table S4 Characteristic parameters of the adsorption of CR on the UiO-67.

		parameters	UiO-67-1	UiO-67-2	UiO-67-3
Adsorption kinetics	Pseudo- first-order	$q_{e,Exp} (\text{mg g}^-)$	72.8	108.6	112.3
		$q_{e,Cal} (\operatorname{mg} g^{-1})$	45.6	75.8	83.2
		k_1 (min ⁻¹)	0.0063	0.0042	0.0051
		R^2	0.9497	0.9258	0.9219
Pseudo-second- order		$q_{e,Exp} (\text{mg g}^-)$	72.8	108.6	112.3
		$q_{e,Cal} (mg g^{-1})$	54.7	79.1	85.2
		$k_2 (g mg^{-1} min^{-1})$	3.9×10 ⁻³	2.4×10 ⁻³	1.5×10 ⁻³
		R^2	0.9985	0.9992	0.9993
Adsorption isotherm	Tempkin	A (L g ⁻¹)	0.02	1.52	1.49
isotherm		В	36.3	122.1	131.0
		R^2	0.9094	0.9902	0.9754
	Freundlich	п	3.64	2.29	2.54
		$k_F (mg g^{-1})$ (L mg^{-1}) ^{1/n})	45.0	46.1	48.3
		R^2	0.9144	0.9072	0.9095
	Langmuir	$q_{m,Exp} (\text{mg g}^{-1})$	206.3	530.3	569.8
		$q_{m,Cal} (\operatorname{mg} g^{-1})$	212.8	613.5	645.2
		$b (L mg^{-1})$	0.0476	0.0176	0.0192
		R^2	0.9995	0.9975	0.9990
Thermodynamic	nic constant	ΔG (kJ mol ⁻	-7.5	-10	-9.7
		, K _d	6638.1	7103.5	6912.6

 Table S5 Characteristic parameters of the adsorption of MO on the UiO-67.

		parameters	UiO-67-1	UiO-67-2	UiO-67-3
Adsorption kinetics f	Pseudo- irst-order	$q_{e,Exp} (\text{mg g}^-)$	99.5	190.5	135.1
Kilettes ilist-order		$q_{e,Cal} (\operatorname{mg} g^{-})$	74.9	46.4	71.7
		k_{l} (min ⁻¹)	0.0084	0.0138	0.0368
	R^2	0.9573	0.8834	0.9726	
Pseudo-second- order		$q_{e,Exp} (\operatorname{mg} g^{-1})$	99.5	190.5	135.1
		$q_{e,Cal} (\operatorname{mg} g^{-})$	63.3	173.9	139.1
	$k_2 (g mg^{-1})$	1.8×10 ⁻³	5.3×10 ⁻³	1.4×10 ⁻³	
		R^2	0.9974	0.9999	0.9994
Adsorption		$q_{m,Exp} (\operatorname{mg g}^{-1})$	173.2	314.3	215.6
Langmuir Low content	Langmuir	$q_{m,Cal} (\operatorname{mg} g^{-1})$	196.5	320.5	223.7
	Low	$b (L mg^{-1})$	0.09	1.07	0.304
	content	R^2	0.9998	0.9999	0.9996
Thermodynamic constant Langmuir High content	constant	ΔG (kJ mol ⁻	-5.7	-5.9	-2.9
	Langmuir	$q_{m,Exp} (\operatorname{mg} g^{-1})$	149.1	287.4	200.0
	igh content	$q_{m,Cal} (\operatorname{mg} g^{-1})$	71.9	200.1	131.6
		$b (L mg^{-1})$	0.0086	0.0113	0.0141
		R^2	0.9853	0.9895	0.9958
Thermodynamic cons	constant	ΔG (kJ mol ⁻	-11.7	-11.1	-10.5
		, K _d	7638.3	7303.4	7102.8

 Table S6 Characteristic parameters of the adsorption of MB on the UiO-67.



Fig. S11 (a, c and e) Pseudo-first-order and (b, d and f) pseudo-second-order fits of experimental adsorption kinetics data. Figs a and b, Figs c and d) and Figs. e and f are the adsorption kinetics data of CR, MO and MB, respectively.



Fig. S12 Plots of the experimental data fitted with (a, d) Temkin, (b, e) Freundlich, and (c, f) Langmuir isotherm models. Figs a-c and Figs. d-f are the adsorption isotherm of CR, and MO, respectively.



Fig. S13 Plots of the MB experimental data fitted with Langmuir isotherm models.



Fig. S14 Recycle of the removal efficiency of (a) UiO-67-3 for GR and (b) UiO-67-2 for MB.