Electronic Supplementary Information

Facile *in situ* hydrothermal synthesis of Fe_3O_4@MIL-101 composites for removing textile dyes†

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Chemicals

Ferric chloride ($FeCl_3 \cdot 6H_2O$), sodium acetate (CH_3COONa), ethylene glycol (EG), diethylene glycol (DEG), chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, 99%), absolute ethanol and N,N-dimethyl formamide solution (DMF) were obtained from Guangfu Fine Chemical Research Institute (Tianjin, China). Terephthalic acid (99%) was purchased from Aladdin. Direct violet, direct dark green, acid orange, acid chrome black T, reactive brilliant blue, reactive yellow, vat pink, alkali blue, congo red, and methylene blue were kind gifts from Xiao-Hong Dai (Tianjin Polytechnic University, Tianjin, China)

Characterisation

The high resolution powder X-ray diffraction (PXRD) experiment was carried out on a Miniflex 600 diffractometer (Rigaku, Japan) with $Cu_{K\alpha}$ radiation source (λ=1.5418 Å). The magnetic properties were studied using a LDJ 9600-1 vibrating sample magnetometer (LDJ Electronics Inc., USA) at room temperature by cycling the field from –6 to 6 kOe. The scanning electron microscopy (SEM) images were recorded on a Hitachi S4800 SEM at 3.0 kV. The Hitachi S4800 SEM is also equipped with an energy dispersive X-ray spectrometer (EDX) system and allows the elemental analysis of samples. The transmission electron microscope (TEM) micrograph was recorded on a JEM-2100F TEM (JEOL, Japan) operating at a 200 kV accelerating voltage. The surface area, pore volume, and pore size distributions of samples were measured on a TriStar 3000 sorptometer (Micromeritics, Norcross, GA) using nitrogen adsorption at 77 K in the range $0.02 \leq P/P_0 \leq 0.20$, respectively. Zeta potential of Fe_3O_4@MIL-101 composites (0.01% w/w) in the lake water sample (pH 8.8) was measured on a zetasizer nano ZS 90 (Malvern Instruments Ltd, England).

Synthesis of Fe_3O_4 nanospheres

Fe_3O_4 nanospheres were synthesized by solvothermal reduction method. Briefly, 0.54 g of $FeCl_3 \cdot 6H_2O$ and 1.5 g of anhydrous sodium acetate were dissolved in a mixture of EG and DEG (V_{EG}/V_{DEG}, 1/19, total volume is 20 mL) and stirred vigorously, the obtained homogeneous solution was transferred into a Teflon-lined autoclave and reacted at 200 °C for 12 h to give Fe_3O_4 nanospheres. When the autoclave was cooled to room temperature, the black Fe_3O_4 nanospheres were recovered by a magnet and washed with ultrapure water and ethanol, the product was dried under vacuum at 60 °C for 12 h.

Synthesis of Fe_3O_4@MIL-101 composites

$Cr(NO_3)_3 \cdot 9H_2O$ (2.0 g, 5 mmol), terephthalic acid (0.83 g, 5 mmol), and deionized water (15 mL) were mixed and homogenized for 30 min under sonication, resulting in a dark blue-colored suspension. To the above mixture, the aqueous suspension of Fe_3O_4 nanospheres (100 mg) in deionized water (5 mL) obtained under ultrasonication for 10 min was added with stirring. The reactant mixture was placed in a Teflon-lined autoclave bomb and kept in an oven at 218 °C for 18 h. After the synthesis and equilibration at room temperature, the product Fe_3O_4@MIL-101 composites were separated from the reaction media by an external magnetic field. In order to remove the residual terephthalic acid species in the pores, Fe_3O_4@MIL-101 composites were washed with deionized water at 70 °C for 5 h and sequentially with ethanol at 60 °C for 3 h until no colored impurities were detected in the mother liquor solution. Then, the solid was finally dried by heating at 120 °C for 12 h under vacuum. During purification of Fe_3O_4@MIL-101 composites, the as-synthesized product was recovered simply by using an external magnetic field without the need for centrifugation or filtration.

Adsorption experiments

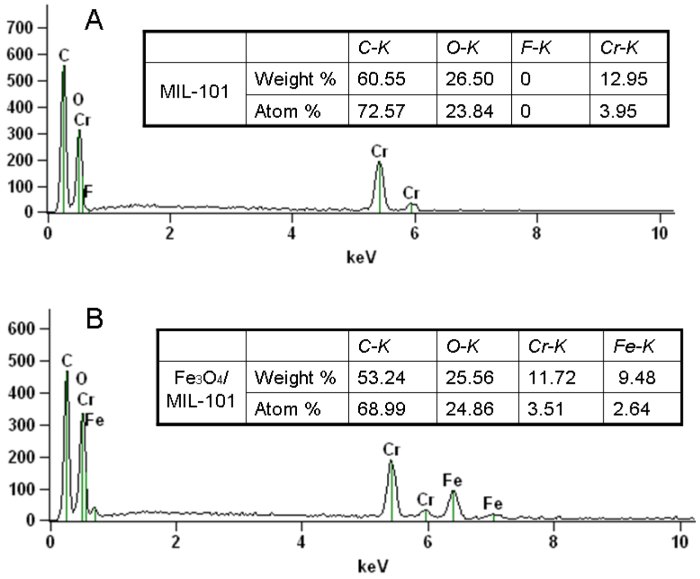
The adsorption of ten different textile dyes in aqueous solution on the as-synthesized Fe_3O_4@MIL-101 composites was performed in a batch experiment. The initial dye concentration in each sample was adjusted to 50 mg L^{-1}. A certain mount of Fe_3O_4@MIL-101 composites dispersed in the deionized water under ultrasonication was then added into the dye solutions, and the solution volume was fixed to 5 mL. The suspensions without adjusting pH were incubated on a rotary shaker at 250 rpm at 25 °C for a certain time, then the dye loaded Fe_3O_4@MIL-101 composites were separated magnetically and precipitated in several minutes in the presence of an external magnet. The concentrations of the remnant dye in the supernatant solution were determined with UV–vis spectrophotometry at their respective absorbance maxima.

For a kinetic study, the concentration of Fe_3O_4@MIL-101 composites was 0.1 mg mL^{-1}. Kinetic experiments were performed by withdrawing the samples at different time intervals and the supernatant was collected for the determination of the concentration of residual dyes.

Decontamination of dyes in lake water and adsorbent regeneration

Fe_3O_4@MIL-101 composites were applied to the removal of ten different textile dyes from spiked lake water sample. The lake water sample was first filtered and then the spiked dye concentration in each sample was adjusted to 50 mg L^{-1}. Fe_3O_4@MIL-101 composites were added to the lake water to make the final concentration of 0.6 mg mL^{-1}. The suspensions were incubated on a rotary shaker at 250 rpm at 25 °C for 20 min, the supernatant was then collected by using an external magnetic field.

For a desorption study, a mixture of 0.5 mL of 0.01 mol L^{-1} NaOH solution and 0.5 mL of N,N-dimethyl formamide as the eluent solution was added to the used Fe_3O_4@MIL-101 composites in a centrifuge tube. Fe_3O_4@MIL-101 composites were dispersed under ultrasonication and regenerated on a rotary shaker at 250rpm at 25 °C for 20 min, the collected magnetic adsorbent was then washed thoroughly with deionized water to a neutral pH. The regenerated Fe_3O_4@MIL-101 composites were reused for decontamination of dyes in lake water samples, and the procedure was repeated for 3 times.



		C-K	O-K	F-K	Cr-K
MIL-101	Weight %	60.55	26.50	0	12.95
	Atom %	72.57	23.84	0	3.95

		C-K	O-K	Cr-K	Fe-K
Fe_3O_4/ MIL-101	Weight %	53.24	25.56	11.72	9.48
	Atom %	68.99	24.86	3.51	2.64

Fig. S1. EDX spectra of MIL-101 (A) and Fe_3O_4@MIL-101 (B)

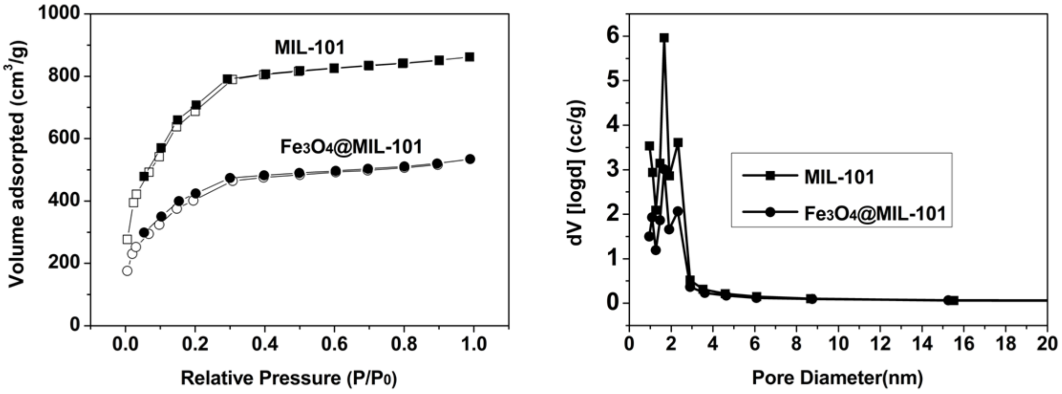


Fig. S2. (A) N_2 adsorption–desorption isotherms (hollow: adsorption, solid: desorption) and (B) the pore size distribution of the as-synthesized MIL-101and Fe_3O_4@MIL-101

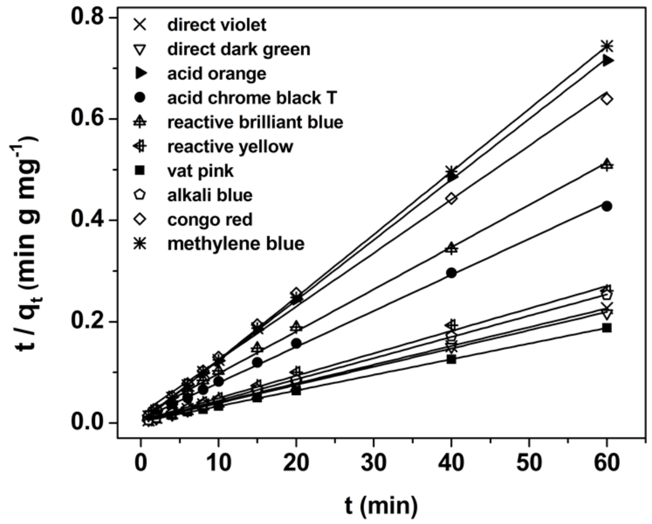


Fig. S3. Plots of pseudo-second-order kinetics for the adsorption of the dyes on Fe_3O_4@MIL-101

Table S1 Kinetic parameters for the adsorption of ten dyes on Fe_3O_4@MIL-101 at 25°C

		Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	$q_{e(exp)}$/ mg g^{-1}	$q_{e(cal)}$/ mg g^{-1}	K_1/ min^{-1}	R^2	$q_{e(cal)}$/ mg g^{-1}	K_2/ g mg^{-1} min^{-1}	R^2
direct violet	264.8	60.5	1.02×10^{-1}	0.718	270.3	3.30×10^{-3}	0.999
direct dark green	277.2	34.6	4.16×10^{-2}	0.485	277.8	3.82×10^{-3}	0.999
reactive brilliant blue	117.7	24.9	3.83×10^{-2}	0.736	120.1	4.92×10^{-3}	0.998
reactive yellow	230.0	11.2	2.95×10^{-2}	0.222	226.2	3.94×10^{-3}	0.995
vat pink	319.9	48.1	7.43×10^{-2}	0.634	323.6	3.91×10^{-3}	1.000
acid orange	83.9	3.78	3.74×10^{-2}	0.448	83.9	3.60×10^{-2}	1.000
acid chrome black T	140.1	18.5	3.92×10^{-2}	0.446	140.7	6.13×10^{-3}	0.999
congo red	93.8	13.6	2.08×10^{-2}	0.515	94.5	6.11×10^{-3}	0.995
alkali blue	237.2	24.8	5.96×10^{-2}	0.595	238.7	7.11×10^{-3}	1.000
methylene blue	80.7	0.46	5.80×10^{-2}	0.265	80.7	2.28×10^{-1}	1.000

Notes: initial concentration of dyes, 50 mg L^{-1}; $q_{e(cal)}$, calculated adsorption capacity; $q_{e(exp)}$, experimental adsorption capacity; k_2, pseudo-second-order kinetic constant

Table S2 Comparison of the dyes adsorption capacity over Fe_3O_4@MIL-101 and MIL-101

	Adsorption capacity/mg g^{-1}	
dye	Fe_3O_4@MIL-101	MIL-101
direct violet	264.8	405.1
direct dark green	277.2	456.8
reactive brilliant blue	117.7	331.3
reactive yellow	230.0	541.3
vat pink	319.9	335.6
acid orange	83.9	270.2
acid chrome black T	140.1	356.4
congo red	93.8	178.6
alkali blue	237.2	186.6
methylene blue	80.7	64.3

Notes: initial concentration of the dyes, 50 mg L^{-1}

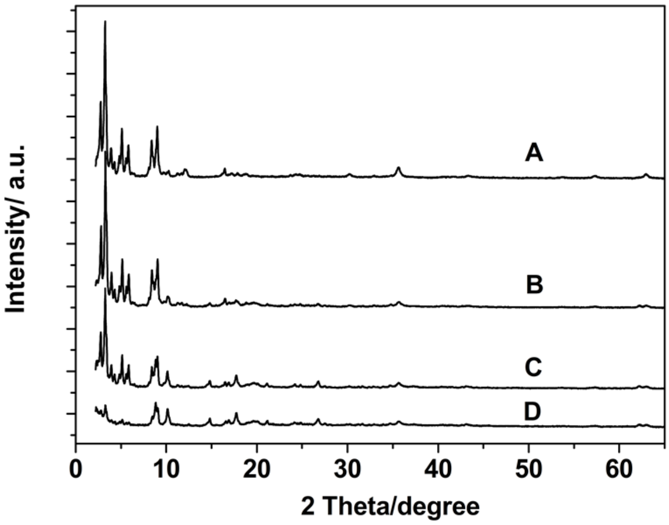


Fig. S4. Powder XRD patterns of Fe_3O_4@MIL-101: (A) fresh; (B) after 2 h incubated in deionized water on a rotary shaker at 250 rpm; (C) after 2 h incubated in lake water on a rotary shaker at 250 rpm; (D) after 2 h incubated in the eluent solution on a rotary shaker at 250 rpm

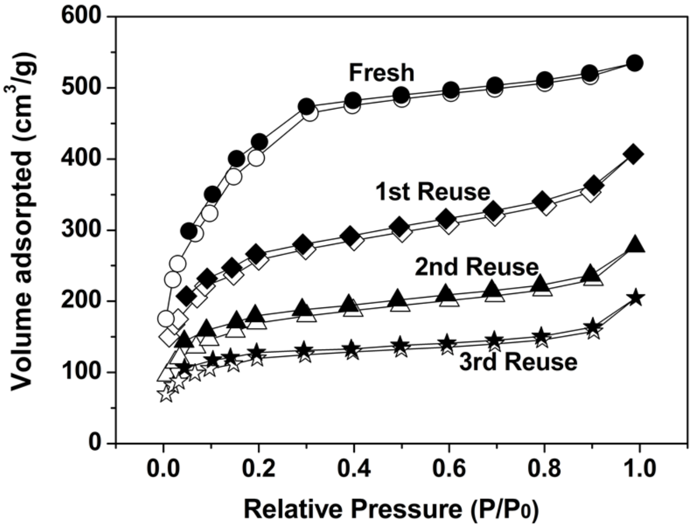


Fig. S5. N_2 adsorption–desorption isotherms of fresh Fe_3O_4@MIL-101, 1st reused Fe_3O_4@MIL-101, 2nd reused Fe_3O_4@MIL-101 and 3rd reused Fe_3O_4@MIL-101.

Table S3 The BET surface areas and pore volumes.

	Specific surface (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (nm)
Fresh Fe_3O_4@MIL-101	1482	0.822	2.302
1st Reuse	911.0	0.629	1.705
2nd Reuse	594.8	0.429	1.442
3rd Reuse	426.3	0.317	1.487