Supplementary Material

Post-modification of magnetic metal-organic frameworks with β-cyclodextrin for efficient removal of fungicides from environmental water

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Text S1. Preparation of Fe_3O_4@β-CD

Fe_3O_4@β-CD was first mixed with a solution tetrahydrofuran (50.0 mL) and DMF (6.0 mL) containing 1.23 g β-CD, 0.60 g of TFT, and sodium carbonate under nitrogen protection. Next, the above mixture was stirred homogeneously and refluxed under nitrogen protection at 85 ºC for 24 h. After cooling down to room temperature, the resulting suspension was separated by external magnetic field, then the resulting product was washed to completely exclude residual catalyst K_2CO_3 with a hydrochloric acid solution (0.01 M) till no more bubbles cleared. After magnetic separation of the resulting product, Fe_3O_4@ β-CD was washed by suitable volume of distilled water, tetrahydrofuran, and dichloromethane, respectively. The final precipitate was vacuum dried at 45 ºC and then Fe_3O_4@ β-CD was obtained.

Text S2. Preparation of TFT cross-linked β-CD (TFN-CD)

1.23 g β-CD, 0.60 g of TFT, and sodium carbonate were mixed with a solution tetrahydrofuran (50.0 mL) and DMF (6.0 mL) under nitrogen protection. Next, the above mixture was stirred homogeneously and refluxed under nitrogen protection at 85 ºC for 24 h. After cooling down to room temperature, the resulting suspension was separated by centrifuge, then the resulting product was washed to completely exclude residual catalyst K_2CO_3 with a hydrochloric acid solution (0.01 M). TFN-CD was washed by suitable volume of distilled water, tetrahydrofuran, and dichloromethane, respectively. The final precipitate was vacuum dried at 45 ºC.

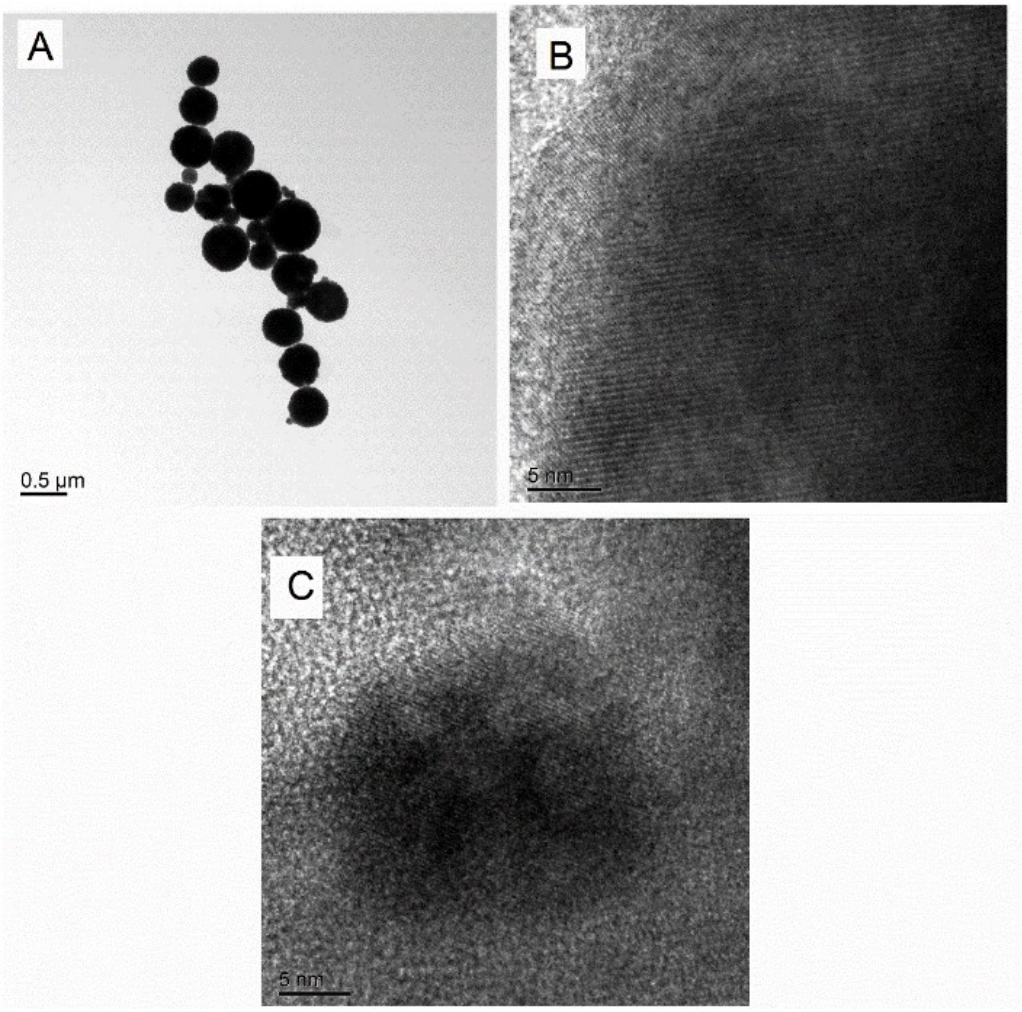


Fig. S1. TEM image of Fe_3O_4 (A) and HR-TEM of Fe_3O_4@MIL-100 (Fe) (B) and HR-TEM of Fe_3O_4@MIL-100 (Fe)/ β-CD(C).

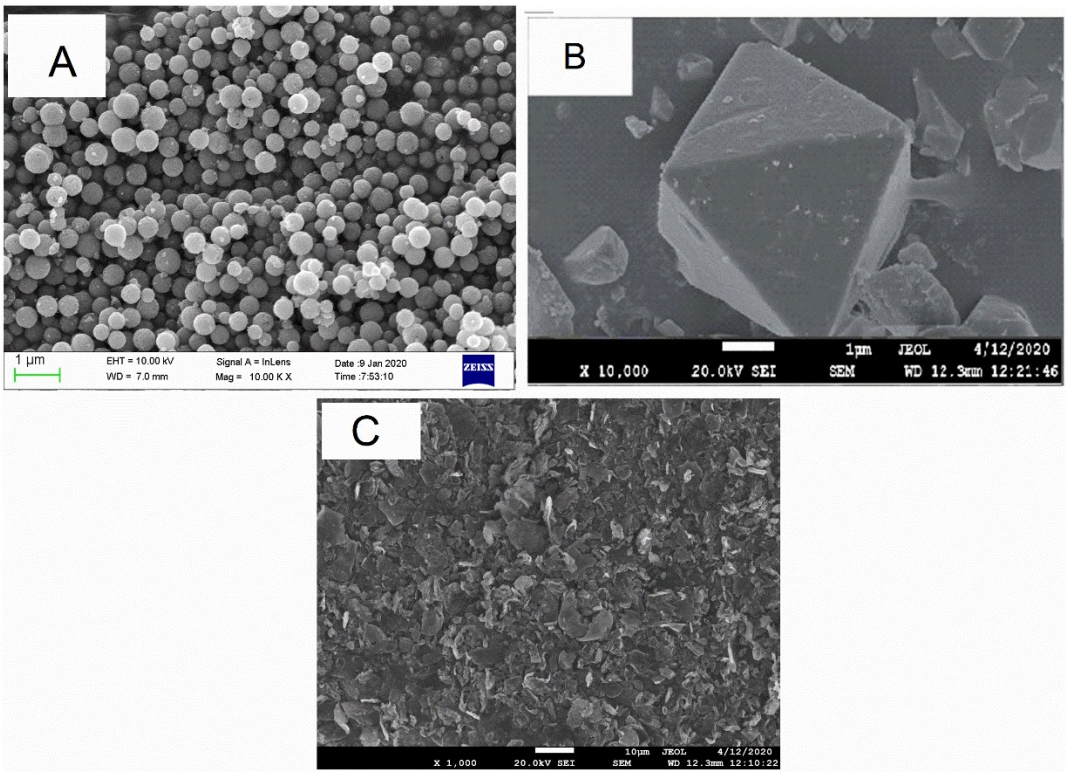


Fig. S2. SEM image of Fe_3O_4 (A), MIL-100 (Fe) (B), and Fe_3O_4@β-CD(C).

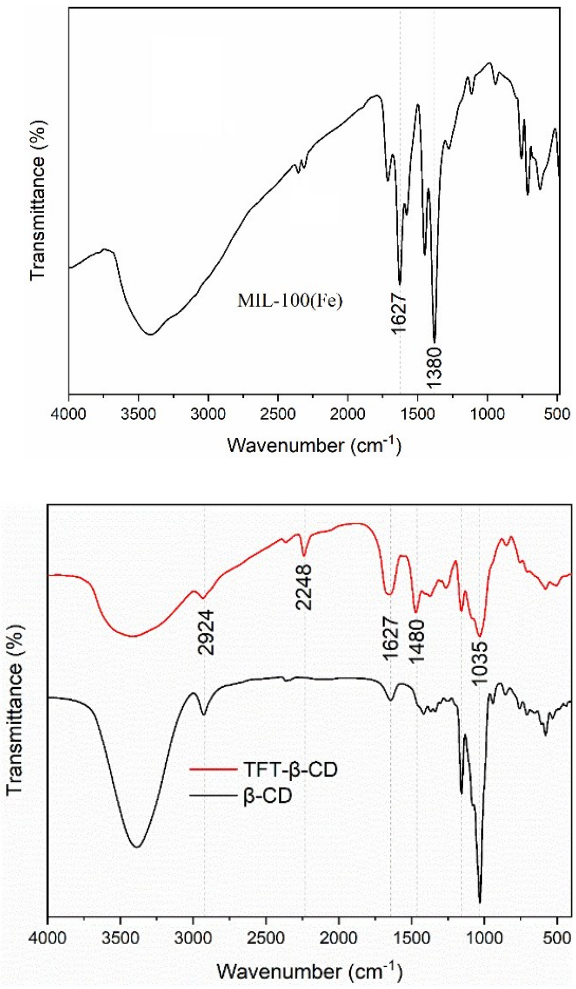


Fig. S3. The FT-IR spectra of MIL 100 (Fe), β-CD, and TFT cross-linked β-CD (TFT-β-CD).

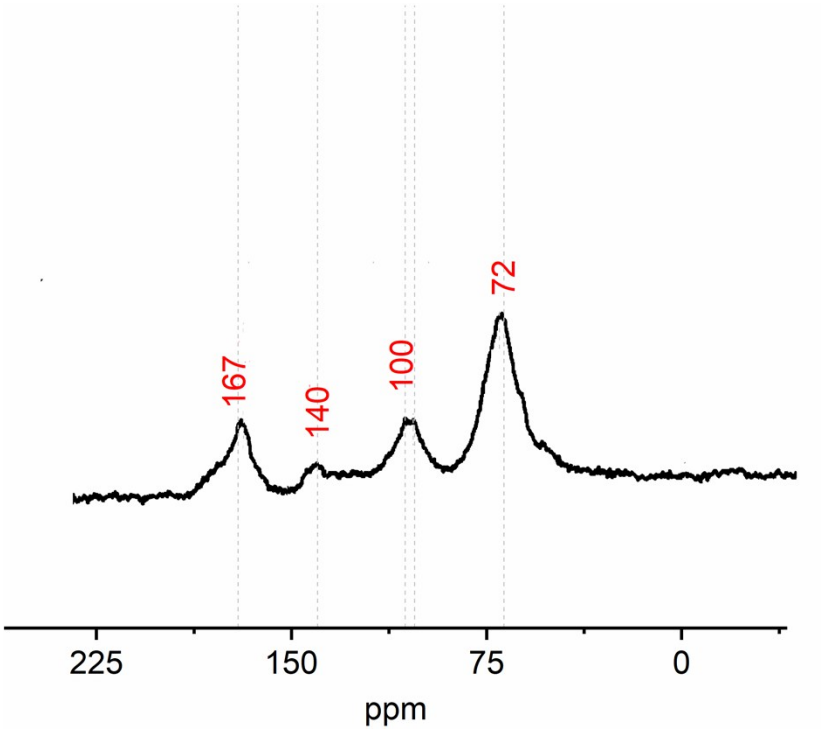
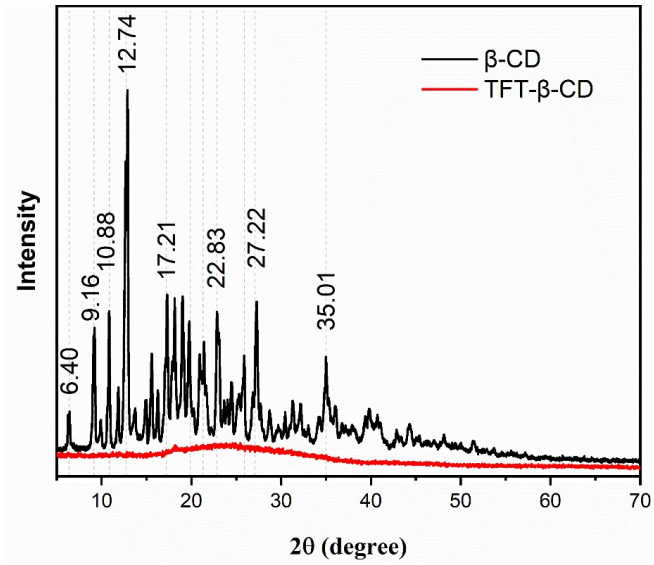


Fig. S4. The ^{1}C NMR of TFT cross-linked β-CD (TFT-β-CD).



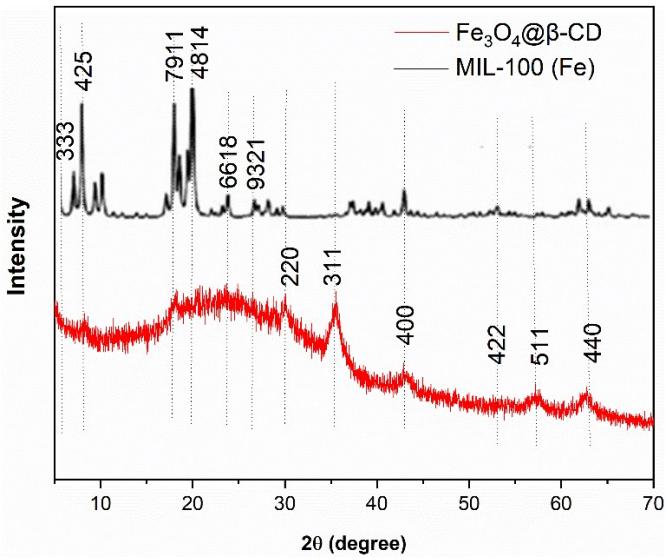


Fig. S5. The XRD pattern of β-CD, TFT cross-linked β-CD (TFT-β-CD), MIL-100(Fe) and Fe_3O_4@β-CD.

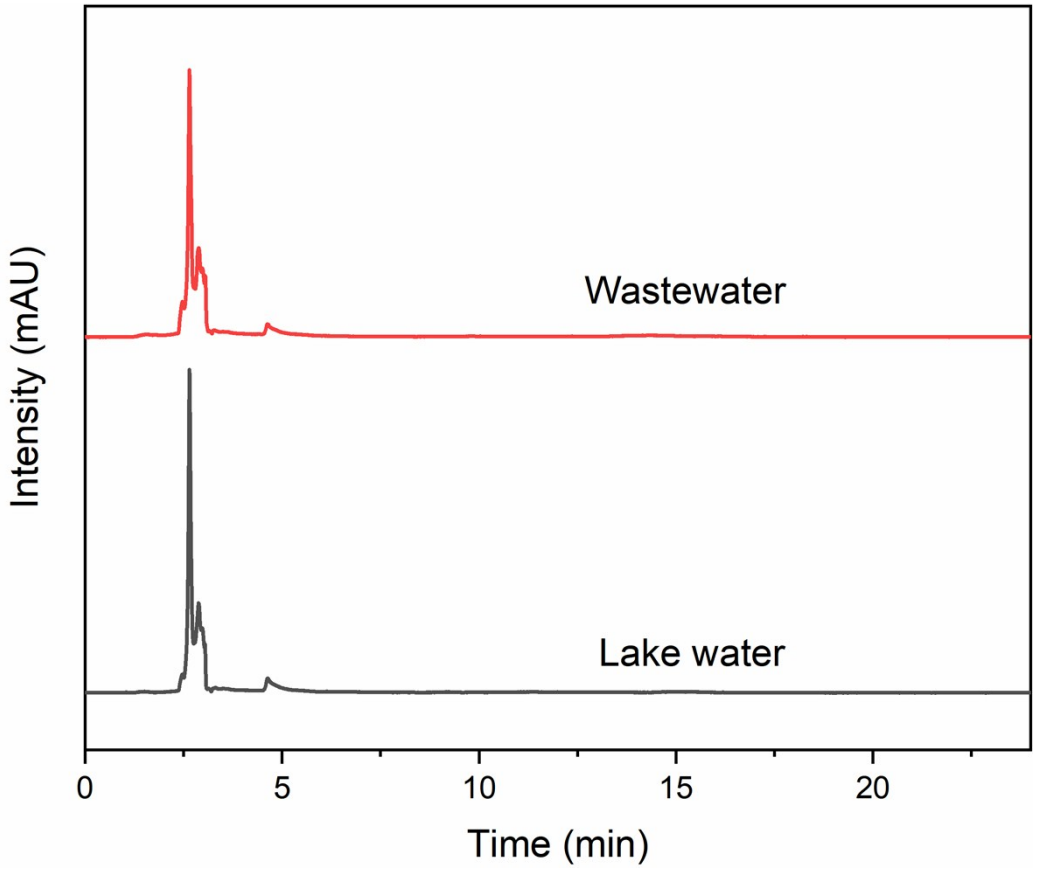
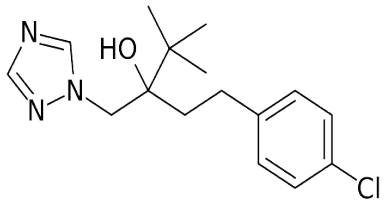
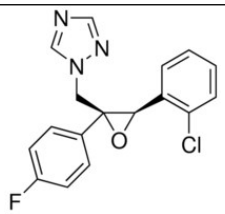
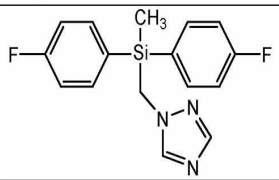
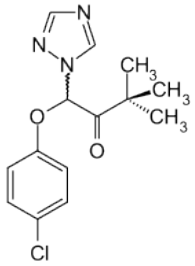


Fig. S6. The typical chromatograms of actual lake water and wastewater.

Table S1. The nitrogen adsorption-desorption isotherms of Fe_3O_4@MIL-100 (Fe), and Fe_3O_4@MIL-100 (Fe)/ β-CD.

Sample	SBET ($m^2 \cdot g^{-1}$)	BJH Pore size (nm)	BJH Volume size ($m^3 \cdot g^{-1}$)
Fe_3O_4@MIL-100 (Fe)	330.89	3.25	0.12
Fe_3O_4@MIL-100 (Fe)/β-CD	2.60	1.73	0.010

Table S2. The chemical structures, Log *P* and p*Ka* values of the four triazole fungicides.

Analytes	Structure	Log *P* [a]	p*Ka* [b]
Tebuconazole		3.77 ± 0.55	3.27 13.70
Epoxiconazole		3.30 ± 0.71	2.75 ± 0.10
Flusilazole		3.70	3.27
Triadimefon		2.77	2.70

[a,b] Values from Scifinder Scholar Database, calculated by Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2019 ACD/Labs).

Table S3. The Langmuir Freundlish, and Temkin model parameters by Fe_3O_4@MIL-100 (Fe)/β-CD.

Model	Parameters	Tebuconzole	Flusilazole
Langmuir	q_m (mg/g)	64.52	102.10
	b (L/mg)	0.332	0.0559
	R^2	0.9907	0.9955
Freundlish	K_F （L/mg）	21.18	18.62
	n	2.80	2.17
	R^2	0.9806	0.9712

Table S4. Kinetic parameters of pseudo-second order for adsorption by Fe_3O_4@MIL-100 (Fe)/β-CD.

Model	Parameters	Tebuconzole	Flusilazole
pseudo-first order	q_e (mg g^{-1})	0.96253	1.23898
	K_1 (min^{-1})	-0.030	-0.0322
	R^2	0.67554	0.56435
pseudo-second order	q_e (mg g^{-1})	55.74	58.00
	K_2 (g mg^{-1} min^{-1})	-0.02168	-0.4797
	h	-67.3	-1615
	R^2	0.99951	0.99996