One-pot and sustainable synthesis of magnetic MIL-100(Fe) with novel Fe_3O_4 morphology and its application in heterogeneous degradation

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Preparation of materials

All chemicals were purchased from commercial sources and used without further treatments.

1. Preparation of conventional MIL-100(Fe)

MIL-100(Fe) was prepared according to the previous reported [1]. Typically, a mixture of $FeCl_2·4H_2O$, H_3BTC, HF, HNO_3 and H_2O with a molar ratio of 1:0.67:2:0.6:277 was transferred into a Teflon liner. After stirred at 500 rpm for 30 min, the Teflon liner was sealed in a stainless-steel bomb and heated at 150 ◦C for 24 h. After Saffron yellow MIL-100(Fe) powder was collected, treatment in hot water (60 ◦C) for 3 h to remove the residual H_3BTC. Then, the obtained saffron yellow powder was centrifuged at 8000 rpm for 10 min and dried under vacuum at 100 ◦C for 12 h.

2. Preparation of Fe_3O_4

Fe_3O_4 was prepared for comparison purposes. Synthesis procedure was the same with MIL-100(Fe)-M (H_3BTC/4 NaOH) in this study, with one difference: without the H_3BTC. Two different aqueous solutions were prepared firstly. Solution 1 contained 10.0 mmol NaOH. Solution 2 was prepared by dissolving 3.75 mmol of $FeCl_2·4H_2O$ in deionized water. After becoming completely clear solutions in both cases, Solution 1 was added dropwise over Solution 2 under stirring. The stirring continued at room temperature for a certain time. The solid was recovered by an external magnet, and then three times with water and one more time with ethanol. The sample was dried at room temperature.

Catalysis mechanism in SPEF oxidation process

With the proceeding of heterogeneous solar photo-electro-Fenton (SPEF) reaction, most of sodium sulfadiazine (SD) pollutant was removed and/or decomposed into intermediates, reducing the conversion rate of H_2O_2 to •OH through Fenton oxidation reaction. The amount of •OH, formed by the catalytic decomposition of H_2O_2 with active sites on cathode, is strongly depending on the nature of Fenton catalysts, to some extent, can reflect the Fenton catalytic activity.[2]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$$
$$\bullet OH + SD \rightarrow CO_2 + H_2O + \cdots$$
$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + \bullet OH$$
$$H_2O_2 + h\nu \rightarrow 2\bullet OH$$
$$RH + \bullet OH \rightarrow R\cdot + H_2O$$
$$R\cdot + O_2 \rightarrow ROO\bullet$$
$$ROO\cdot + \bullet OH + O_2 \rightarrow \ldots\ldots \rightarrow CO_2 + H_2O$$
$$RH + h\nu \rightarrow \text{Degradation products}$$

Figure

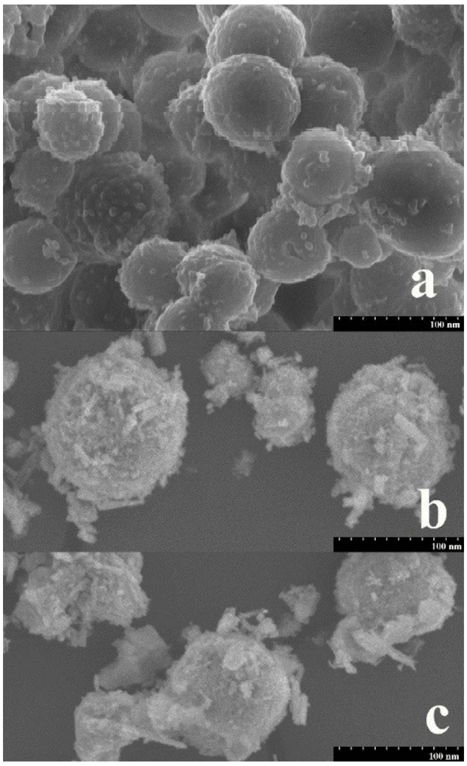


Fig. S1 SEM of the MIL-100(Fe)-M (H_3BTC/3.5 NaOH) (a) MIL-100(Fe)-M (H_3BTC/4.5 NaOH) (b), MIL-100(Fe)-M (H_3BTC/5.0 NaOH) (c)

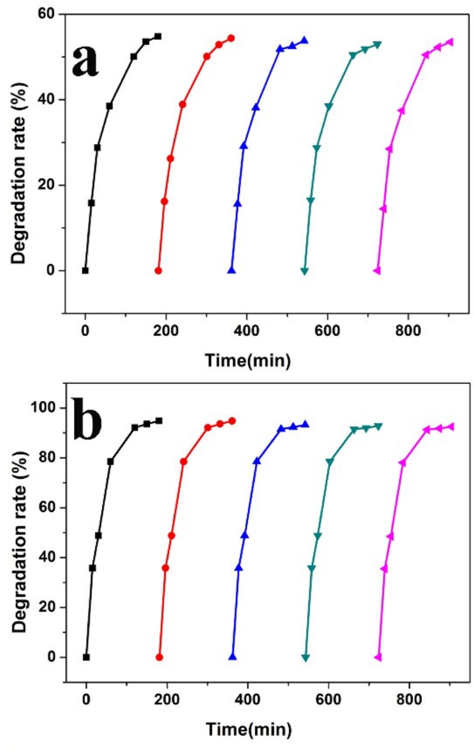
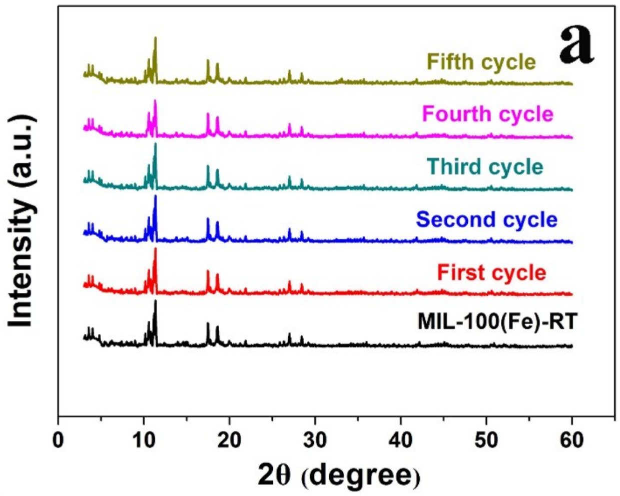


Fig. S2 Catalytic activity of reused MIL-100(Fe)-RT(a)and MIL-100(Fe)-M (H_3BTC/4 NaOH) (b)



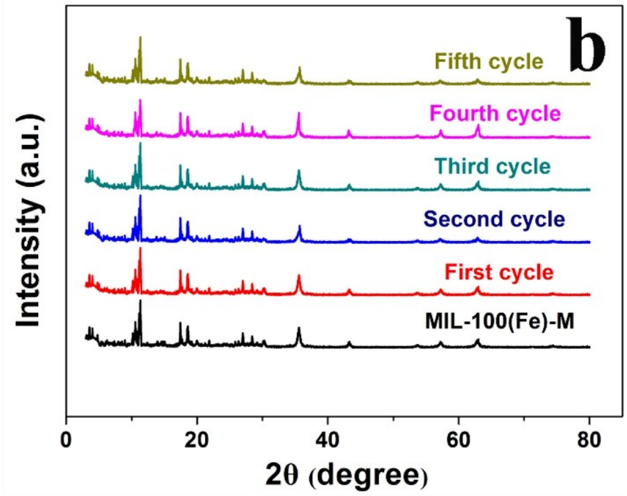


Fig. S3 XRD spectrum of MIL-100(Fe)-RT(a) and MIL-100(Fe)-M (H_3BTC/4 NaOH) (b) after five cycles for photodegradation of SD

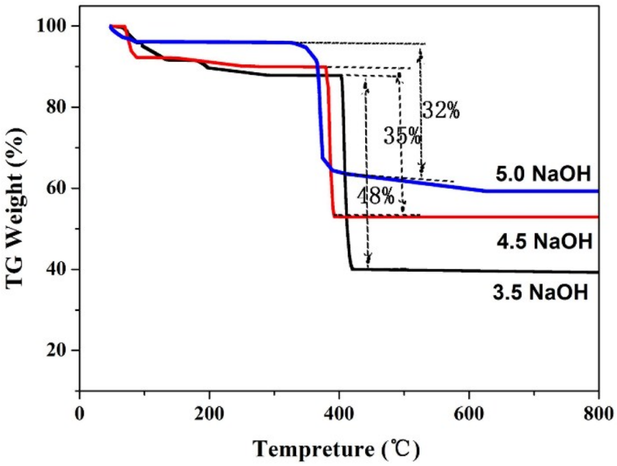


Fig. S4 TGA plots of MIL-100(Fe)-M (H_3BTC/3.5 NaOH), MIL-100(Fe)-M (H_3BTC/4.5 NaOH), and MIL-100(Fe)-M (H_3BTC/5.0 NaOH)

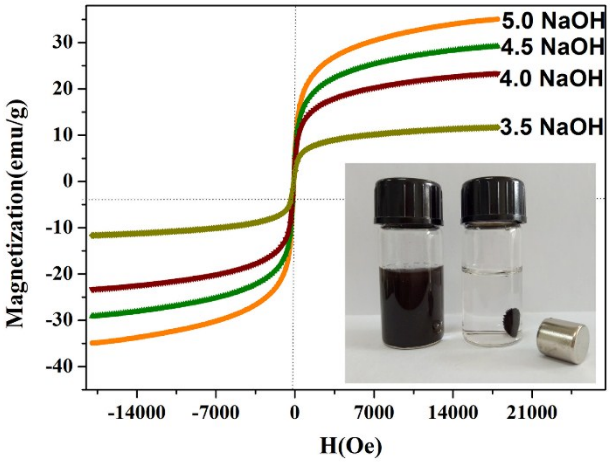


Fig. S5 Magnetization curve of MIL-100(Fe)-M (H_3BTC/3.5-5.0 NaOH) and inset showed the photographs before and after magnetic separation.

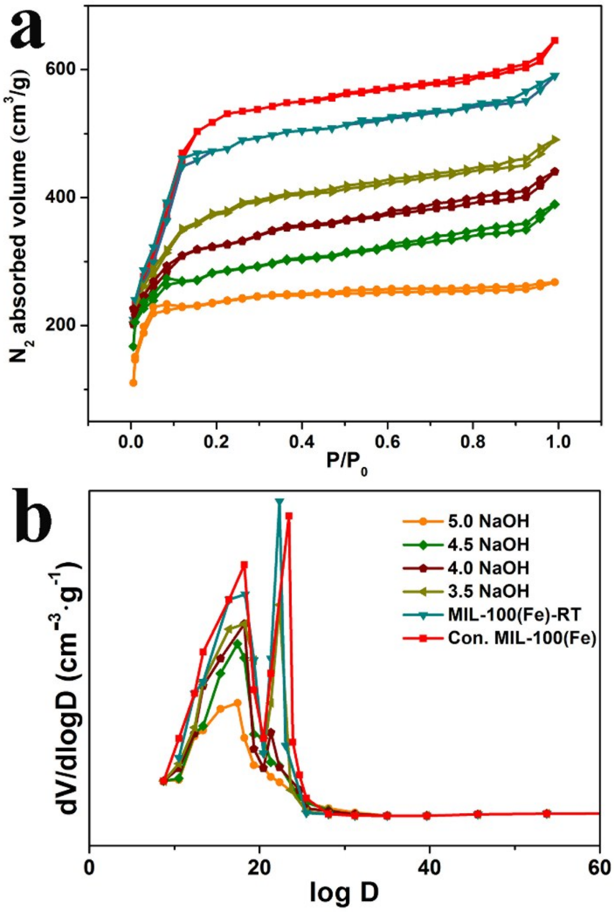


Fig. S6 N_2 adsorption/desorption isotherms (a) and pore size distribution curves (b) of samples: conventional MIL-100(Fe), MIL-100(Fe)-RT (black) and MIL-100(Fe)-M (H_3BTC/3.5-5.0 NaOH), Full and empty symbols represent adsorption and desorption experimental points, respectively.

Tab. S1 Textural properties of the samples

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	ext. S_{BET} ($m^2 \cdot g^{-1}$) [a]	V_p ($cm^3 \cdot g^{-1}$) [b]	PSD peaks (nm)[c]
MIL-100(Fe)	2214	216	0.86	1.82, 2.34
MIL-100(Fe)-RT	2097	187	0.81	1.83. 2.23
MIL-100(Fe)-M (H_3BTC/3.5NaOH	1676	134	0.72	1.82, 2.23
MIL-100(Fe)-M (H_3BTC/4NaOH)	1433	112	0.68	1.81
MIL-100(Fe)-M (H_3BTC/4.5NaOH	1121	86	0.55	1.74
MIL-100(Fe)-M (H_3BTC/5NaOH)	663	73	0.34	1.76

a Data from t-plot. External S_{BET} is the difference between the total SBET and the microporous S_{BET}. **b** Pore volume measured at p/p_0 = 0.98. **c** Maxima of the peaks found in pore size distribution by the applying BJH method to the adsorption branches

Reference

1. R. Liang, S. Luo, F. Jing, L. Shen, N. Qin and L. Wu, *Applied Catalysis B: Environmental*, 2015, **176–177**, 240-248.
2. M. Li, Z. Qiang, C. Pulgarin and J. Kiwi, Applied Catalysis B: Environmental, 2016, **187**, 83-89.