Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Fe_3O_4-MWCNT magnetic nanocomposites as efficient peroxidase mimic catalysts in a Fenton-like reaction for water purification without pH limitation

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Supplemental Experimental

1. Electron spin resonance

220 μL samples were prepared at room temperature by adding 50 μL of 3% H_2O_2, 20 μL of 0.2 M 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) and 150 μL of water into a 1 mL plastic tube in the presence of 40 mg Fe_3O_4-MWCNTs or Fe_3O_4 MNPs, respectively. The prepared sample solution was transferred to a quartz capillary tube and placed in the ESR cavity. DMPO was used to trap the ·OH radicals to form the DMPO/·OH spin adduct. The ESR spectra were obtained on a Bruker ESR E500 with microwave bridge (receiver gain, 60dB; modulation amplitude, 3 Gauss; microwave power, 10 mW; microwave frequency, 9.85 GHZ; Sweep time, 40.96 s).

As can be seen from Figure S3, similar to ESR spin-trapping spectra of the Fe_3O_4 MNPs, the ESR spectra in the presence of Fe_3O_4-MWCNTs displayed a 4-fold characteristic peak of the DMPO-•OH adduct with an intensity ratio of 1:2:2:1. The produced radicals attack MB molecules, resulting in decoloration.

2. Hydroxyl radical formation with terephthalic acid as a fluorescence probe

0.4 M H_2O_2, 0.6 mM terephthalic acid and different loadings of the Fe_3O_4-MWCNTs were first incubated at 25 °C for 12 h. The Fe_3O_4-MWCNTs were then removed from the reaction solution by an external magnetic field. The resulting solutions were used for fluorometric measurement.

Hydroxyl radical can react readily with terephthalic acid, forming highly fluorescent 2-hydroxy terephthalic acid[1] that can be identified from fluorescence spectrometer. As shown in new Figure S4, the fluorescence intensity was weak when there was no Fe_3O_4-MWCNTs. And the gradual increase of the fluorescence intensity was observed as the loading of the Fe_3O_4-MWCNTs increased, suggesting that the amount of the generated ·OH increased by the catalysis of

Fe_3O_4-MWCNTs.

References

1. K. Ishibashi, A. Fujishima, T. Watanabe and K. Hashimoto, *J. Photoch. Photobio. A,* 2000, **134**, 139–142.

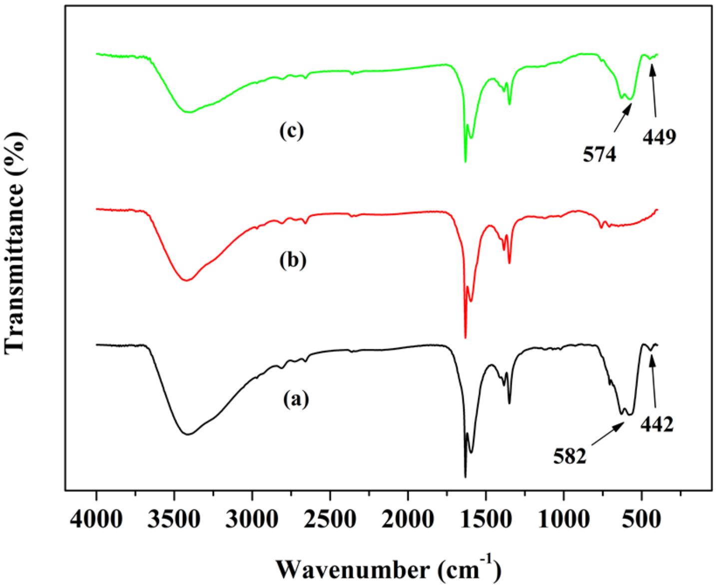

Figure S1. FT-IR spectra of Fe_3O_4 (a), MWCNTs (b) and Fe_3O_4-MWCNTs.

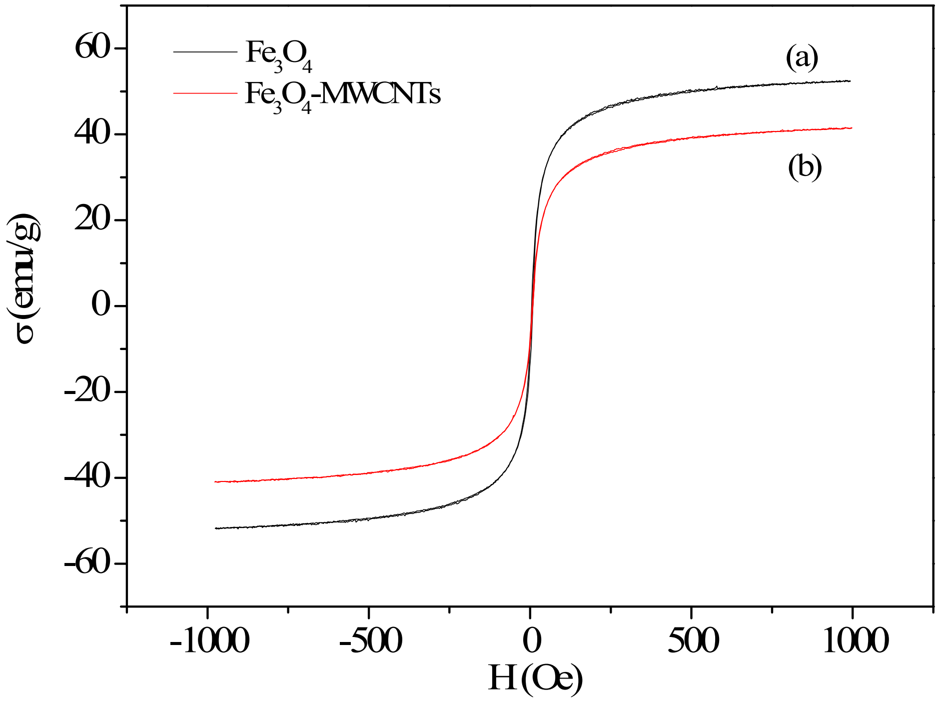

Figure S2. VSM magnetization curves of Fe_3O_4 and Fe_3O_4-MWCNTs.

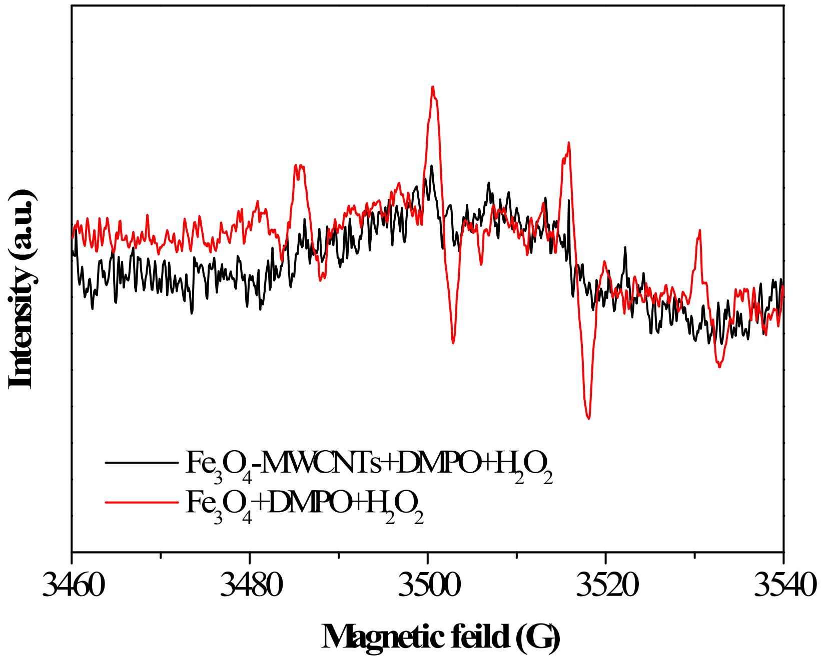

Figure S3. ESR spin-trapping spectra of Fe_3O_4-MWCNTs at 0.4 mg mL^{-1} (black) and Fe_3O_4 at 0.4 mg mL^{-1} (red) in presence of H_2O_2.

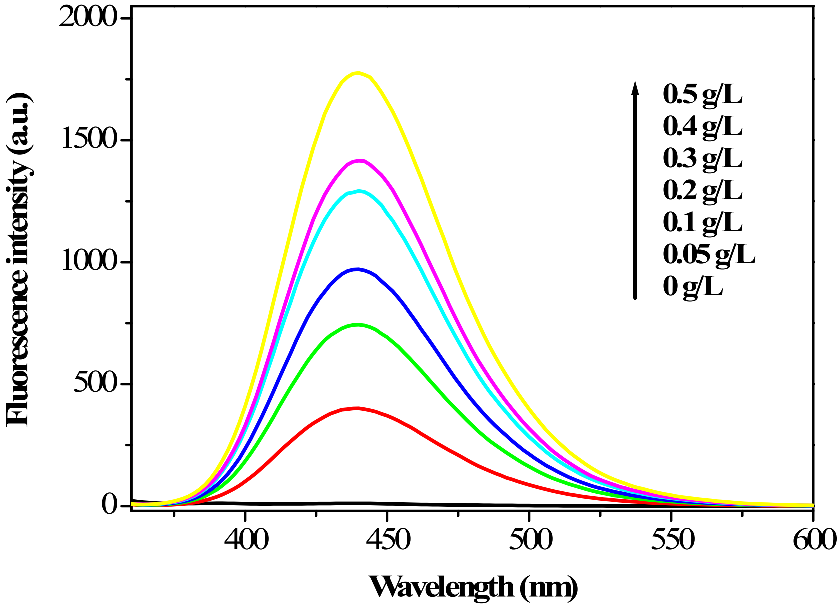

Figure S4. The effect of Fe_3O_4-MWCNTs loading (g/L) on the formation of hydroxyl radicals with terephthalic acid as a fluorescence probe. Reaction conditions: terephthalic acid concentration: 0.6 mM; H_2O_2 concentration: 0.4 M; reaction temperature: 25 °C; reaction time: 12 h

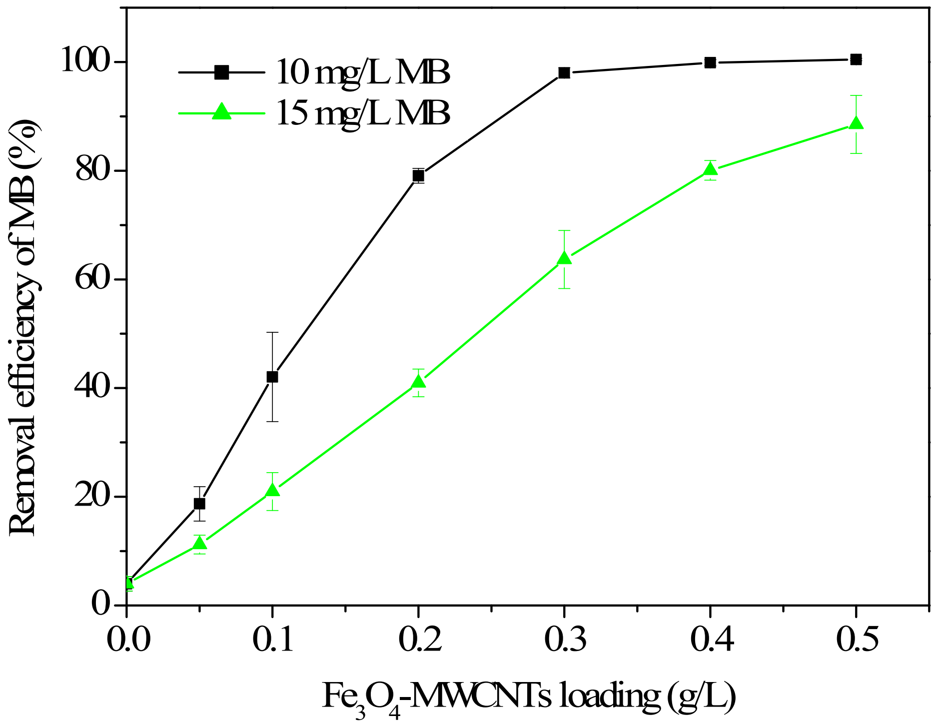

Figure S5. Effect of Fe3O4-MWCNTs loading on the removal of different concentrations of MB. Reaction conditions: pH 5.5, 0.4 M H_2O_2.

Table S1. Leaching of Fe after suspending 7.5 mg Fe_3O_4-MWCNTs in 25 mL water with different pH for 12 h. Numbers in parentheses represent relative standard deviation (n=2)

pH	1.0	2.0	3.0	4.0	5.0	6.0
The released Fe^{3+} (mg L^{-1})	4.78(0.10)	2.14(0.29)	1.66(0.01)	0.78(0.03)	0.25(0.02)	0.25(0.03)
The leaching rate of Fe^{3+} (%)	6.00 (0.13)	2.69(0.36)	2.08(0.01)	0.97(0.04)	0.31(0.02)	0.31(0.03)