

Supporting Materials

Enhanced removal of doxycycline by simultaneous potassium ferrate(VI) and montmorillonite: Reaction mechanism and synergistic effect

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Text S1. The Fe(VI) determination by ABTS method

At predetermined time intervals, 2.0 mL of the sample was collected and mixed with 4.0 mL of ABTS solutions at excess concentration of 450 μM , prepared in 0.2 M phosphate/0.6 M acetate buffers at pH 4.2, to measure the absorbance at 415 nm for calculation of Fe(VI) residual concentration by followed equation:

$$[\text{Fe(VI)}] = \frac{\Delta A_l^{415} V_{\text{final}}}{34000 V_{\text{sample}}} \quad (\text{Equation S1})$$

Where ΔA_l^{415} is the absorbance at 415nm after correcting for blank in cell of path length l . l is the path length of optical cell. V_{final} is the final volume after addition of all reagents and buffer (6 mL), and V_{sample} is the volume of original sample (2 mL).

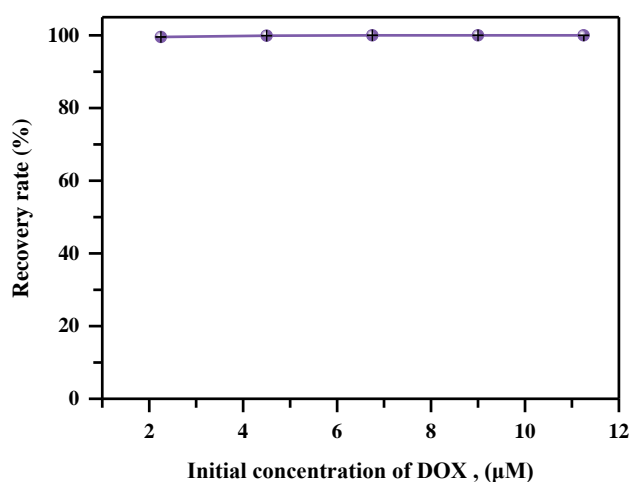


Figure S1. The recovery rate after filtering by 0.22 μm membrane

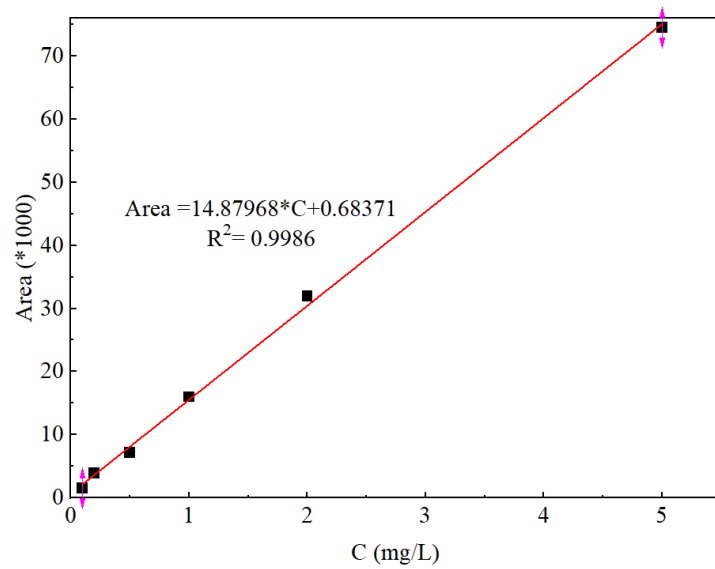


Figure S2. The standard curve of DOX

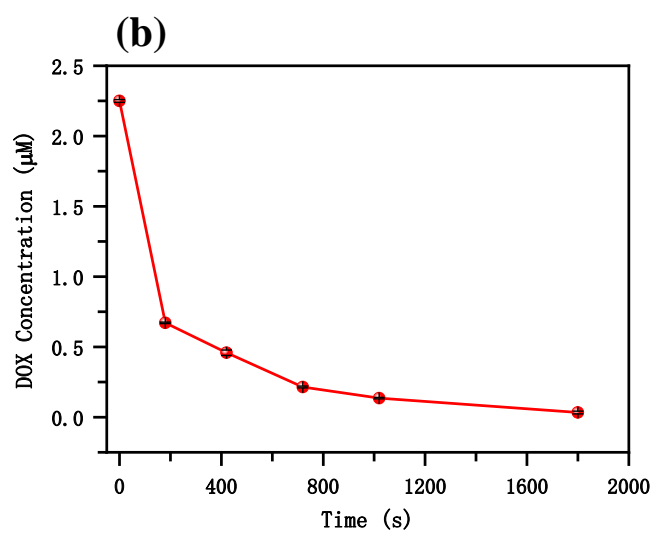
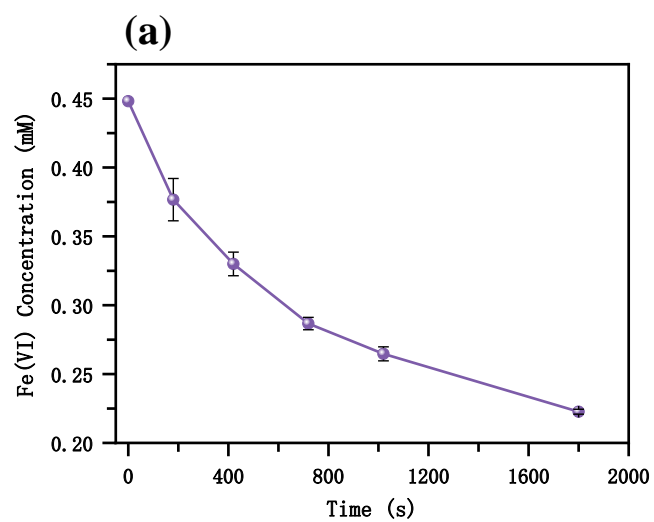


Figure S3. Concentration of Fe(VI) (a) and DOX (b) with the reaction time

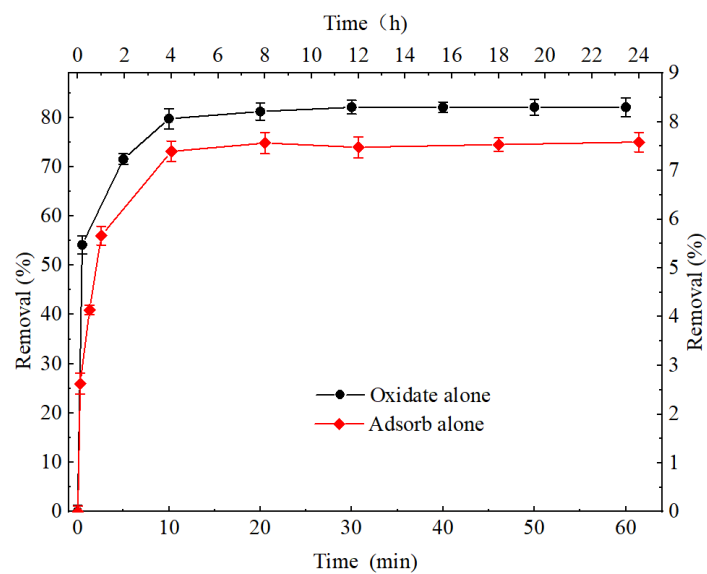


Figure S4. Comparison of oxidation alone (left axis) and adsorption alone (right axis) on DOX removal

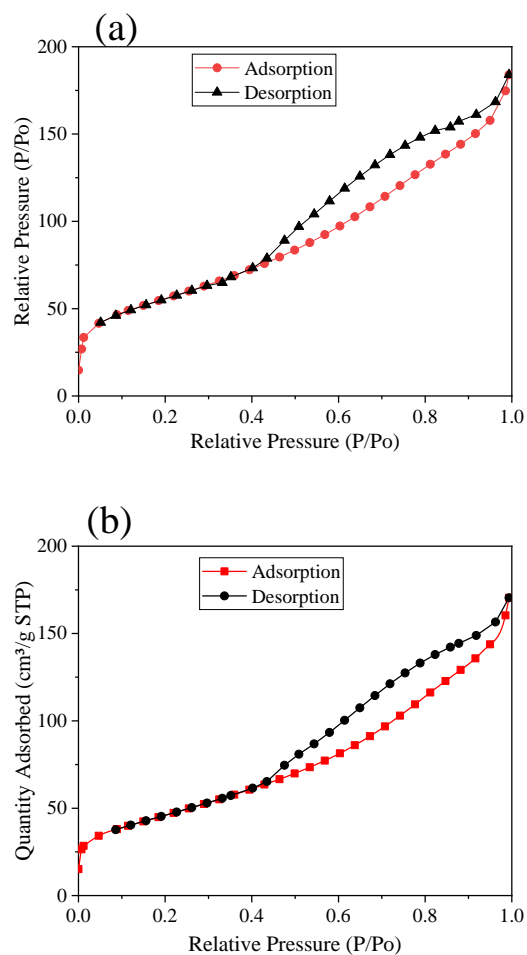


Figure S5. Isotherm Linear Plot: Montmorillonite (a), Fe(III)+montmorillonite (b)

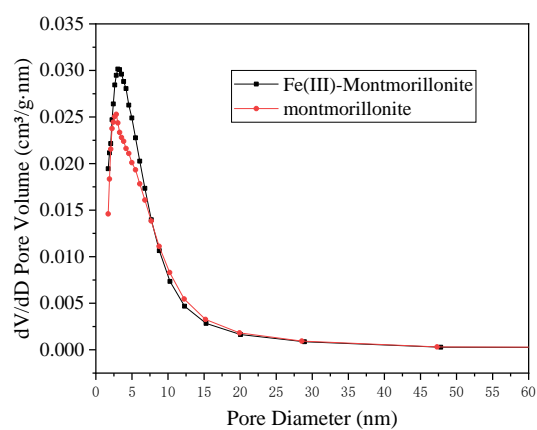
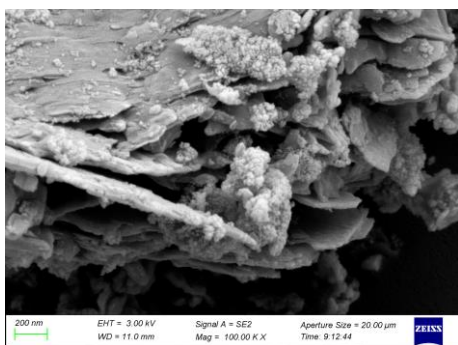
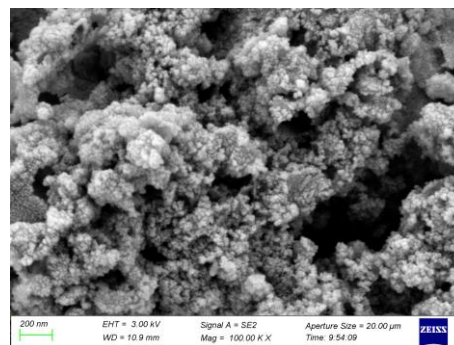


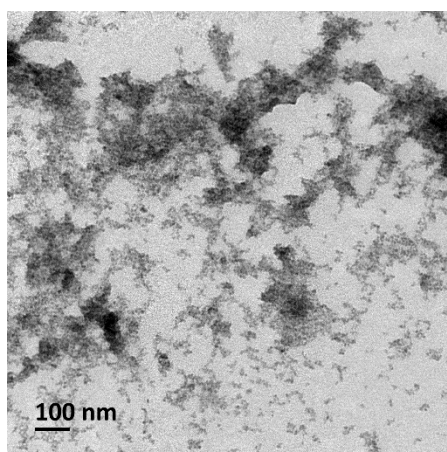
Figure S6. BJH Adsorption dV/dD Pore Volume



(a)



(b)



(c)

Figure S7. (a) SEM-montmorillonite; (b) SEM-Fe(III) with montmorillonite; (c) TEM-Fe(III)-montmorillonite particles

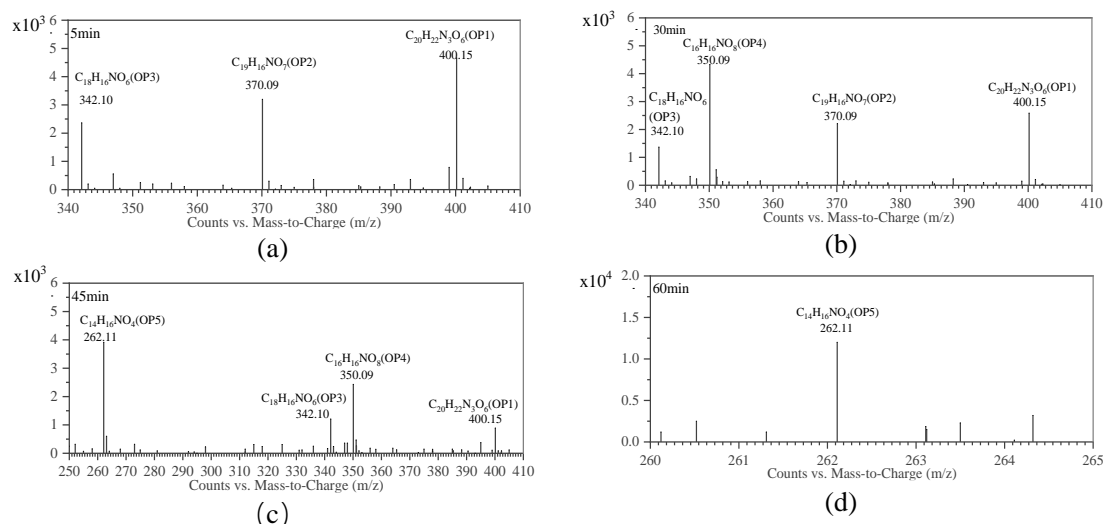


Figure S8. GC-MS spectra of DOX degraded (a) 5 min intermediates; (b) 30 min intermediates; (c) 45min intermediates; (d) 60 min intermediates.

Table S1. The UPLC and GC–MS conditions

High-performance liquid chromatography (HPLC)		Gas Chromatography-Mass Spectrometer (GC–MS)	
Mobile phase	A: 30% acetonitril B: 70% 0.01M formic acid	Chromatographic column	SE-54
Flow rate	0.8 ml/min	Carrier gas	He (>99.999%)
Injection volume	20 µL	Flow rate	0.7 mL/min
Column temperature	30 °C	Injection volume	1 µL
Detection wavelength	350 nm,	Injection temperature	280 °C
		Source	EI ion

Table S2 Dissociation constants (*pKa*) of doxycycline

<i>pK_a</i> [25]	pH	Doxycycline form[32]
3.02±0.3 7.97±0.15 9.15±0.30	< 3.4	DOX ⁺
	3.4-7.7	DOX
	7.7-9.5	DOX ⁻
	> 9.5	DOX ⁻²

Table S3. Detection products in DOX degradation by GC-MS

Molecular formula	Time (min)							Number
	0	1	5	10	30	45	60	
	✓	✓	✓	trace	trace	×	×	DOX
	×	✓	✓	✓	✓	trace	×	OP1
	×	×	✓	✓	✓	×	×	OP2
	×	×	✓	✓	✓	✓	×	OP3
	×	×	×	×	✓	✓	×	OP4
	×	×	×	×	×	✓	✓	OP-5

Table S4. Textural attributes of adsorbents

Samples	BET Surface Area (m ² /g)	Langmuir Surface Area (m ² /g)	BJH Pore Volume (cm ³ /g)	BJH Pore Size (nm)
Fe(III)-montmorillonite	195.37	724.73	0.27	5.98
Montmorillonite	159.33	652.85	0.26	6.42