

Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.  
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## Supplementary Information

for

### **Treatment of 2,4,6-tribromophenol-contaminated water using iron ion/calcium sulfite: The dual role of oxidation and coagulation**

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**Text S1.** Identification of active substances and their contribution to pollutant degradation

5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was employed as a spin trap to capture free radicals potentially generated in the system,<sup>1</sup> and the types of free radicals in the Fe(III)/CaSO<sub>3</sub> system were detected by an electron paramagnetic resonance spectrometer (EPR). The results are shown in Fig. S2a.

At 1, 3, and 8 minutes, corresponding signals of DMPO-SO<sub>3</sub><sup>•-</sup> were observed in the solution. Along with the progress of the reaction, the spectral intensity of DMPO-SO<sub>3</sub><sup>•-</sup> initially increased and then decreased, indicating the generation of SO<sub>3</sub><sup>•-</sup> in the solution. Given that SO<sub>3</sub><sup>•-</sup> has been confirmed to generate highly oxidative free radicals such as SO<sub>4</sub><sup>•-</sup>, HO<sup>•</sup>, and SO<sub>5</sub><sup>•-</sup> through a series of reactions in the presence of oxygen,<sup>2-4</sup> it is speculated that the degradation of TBP in the Fe(III)/CaSO<sub>3</sub> system is primarily accomplished through the action of strong oxidative free radicals within the system.

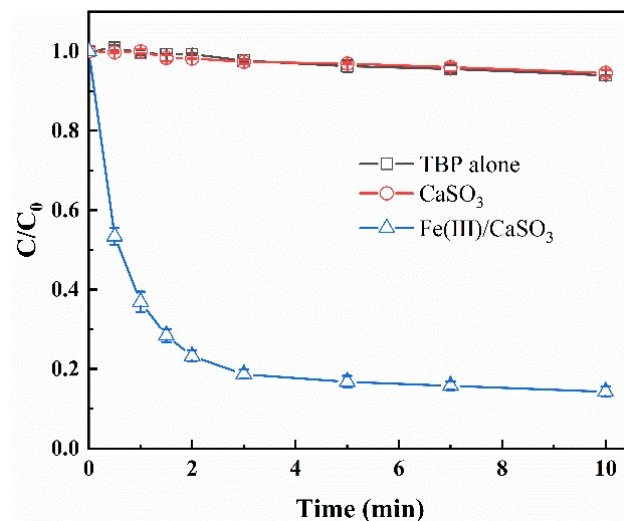
To further elucidate the contributions of each radical to TBP degradation, the effects of ethanol (EtOH) and tert-butanol (TBA) on the efficiency of TBP degradation in the Fe(III)/CaSO<sub>3</sub> system were investigated. By comparing the reaction rates of TBP and radical scavengers with HO<sup>•</sup>, SO<sub>4</sub><sup>•-</sup>, and SO<sub>5</sub><sup>•-</sup>, it was found that 10 mM TBA (1000 times the concentration of TBP) was sufficient to scavenge most of the HO<sup>•</sup> while consuming only a small amount of SO<sub>4</sub><sup>•-</sup> and SO<sub>5</sub><sup>•-</sup>.<sup>5</sup> On the other hand, 10 mM EtOH can scavenge most of the HO<sup>•</sup> and SO<sub>4</sub><sup>•-</sup>, while consuming only a small amount of SO<sub>5</sub><sup>•-</sup>.<sup>6</sup> As shown in Fig. S2b, when no scavenger was added to the system, the degradation rate of TBP was 86.1%; when 10 mM TBA and EtOH were added, the degradation rate of TBP decreased to 73.9% and 36.9%, respectively. These results indicated that both EtOH and TBA could inhibit TBP degradation to a certain extent. In the Fe(III)/CaSO<sub>3</sub> system, SO<sub>4</sub><sup>•-</sup>, SO<sub>5</sub><sup>•-</sup> and HO<sup>•</sup> might all participate in the oxidative degradation of TBP, while SO<sub>4</sub><sup>•-</sup> and SO<sub>5</sub><sup>•-</sup> played the dominant role in TBP degradation in this system.

**Table S1.** Water quality parameters

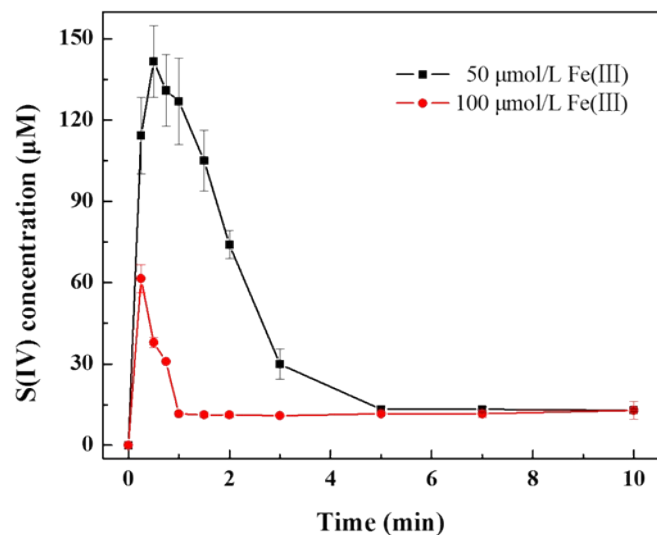
Parameter	Unit	Lake water	Secondary sedimentation tank effluent
Turbidity	NTU	44.2	1.36
pH	–	8.03	7.73
UV <sub>254</sub>	cm <sup>-1</sup>	0.072	0.085
DOC	mg/L	5.78	6.24

**Table S2.** The ratios of different elements based on the XPS results

Type	Characteristic peaks	LW (%)		SSTE (%)	
		Fe(III)/CaSO <sub>3</sub>	Fe(III)	Fe(III)/CaSO <sub>3</sub>	Fe(III)
Fe 2p	Fe(II)	27.4	17.6	28.1	19.5
		11.8	7.8	12.4	8.5
	Fe(III)	42.2	51.8	41.3	50.0
		18.6	22.8	18.2	22.0
O 1s	Fe-O	7.2	9.7	10.0	7.8
	Fe-OH	36.0	21.0	15.3	40.8
	C=O	28.1	27.3	58.8	36.7
	C-O	28.8	42.0	15.9	14.7

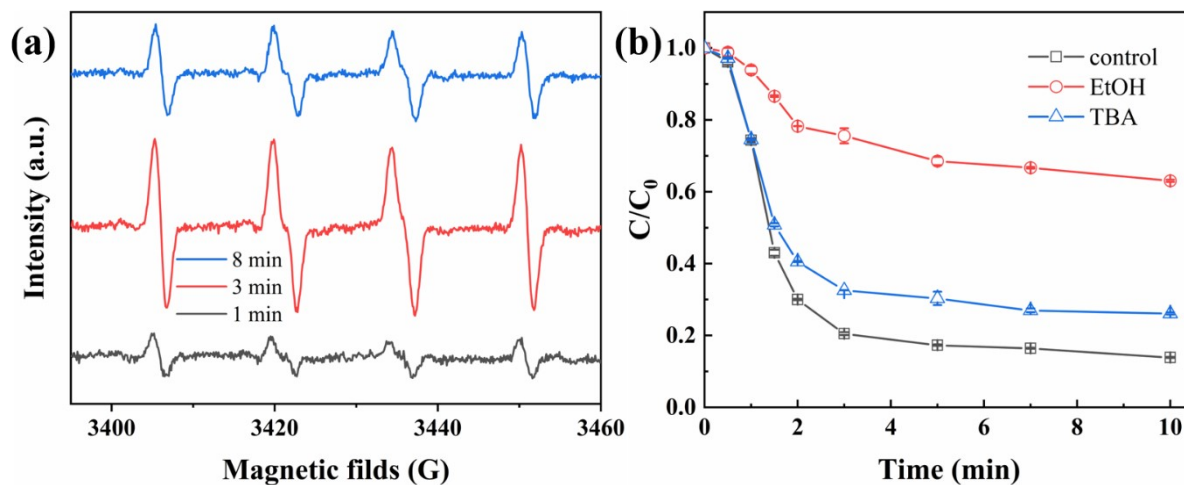


**Fig. S1** Removal of TBP in the Fe(III)/CaSO<sub>3</sub> system under pure water background. Conditions: [TBP] = 10 μM, [Fe(III)] = 50 μM, [CaSO<sub>3</sub>] = 400 μM, initial pH 3.5, temperature 25 °C.

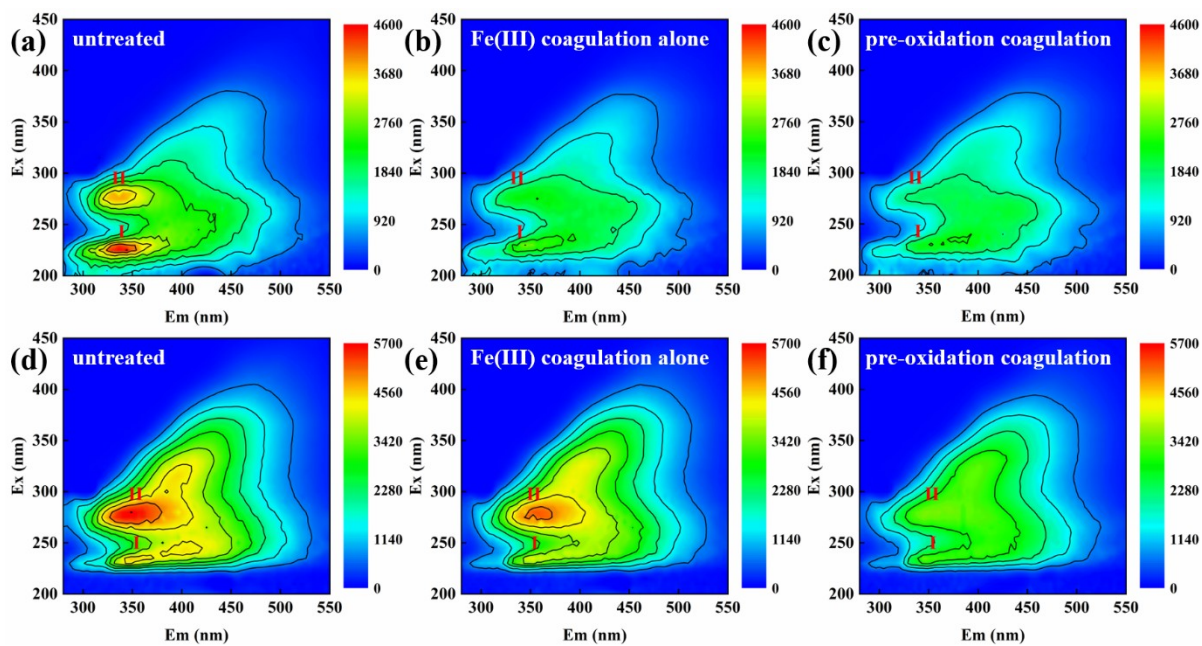


**Fig. S2** Variation of S(IV) concentration in the Fe(III)/CaSO<sub>3</sub> system. Conditions: [TBP] = 10 µM, [CaSO<sub>3</sub>] = 400 µM, initial pH 3.5, temperature 25 ± 1 °C.

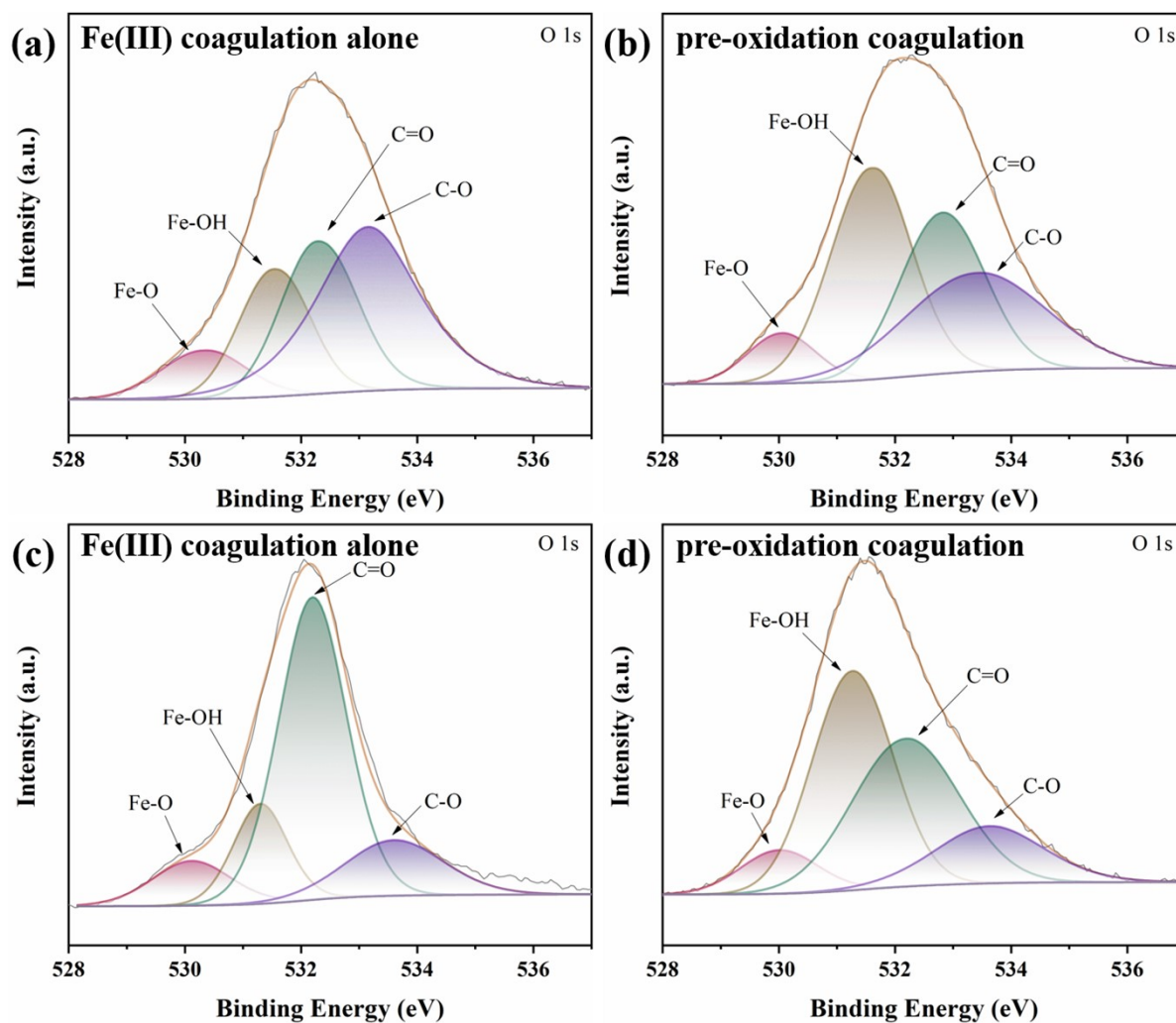




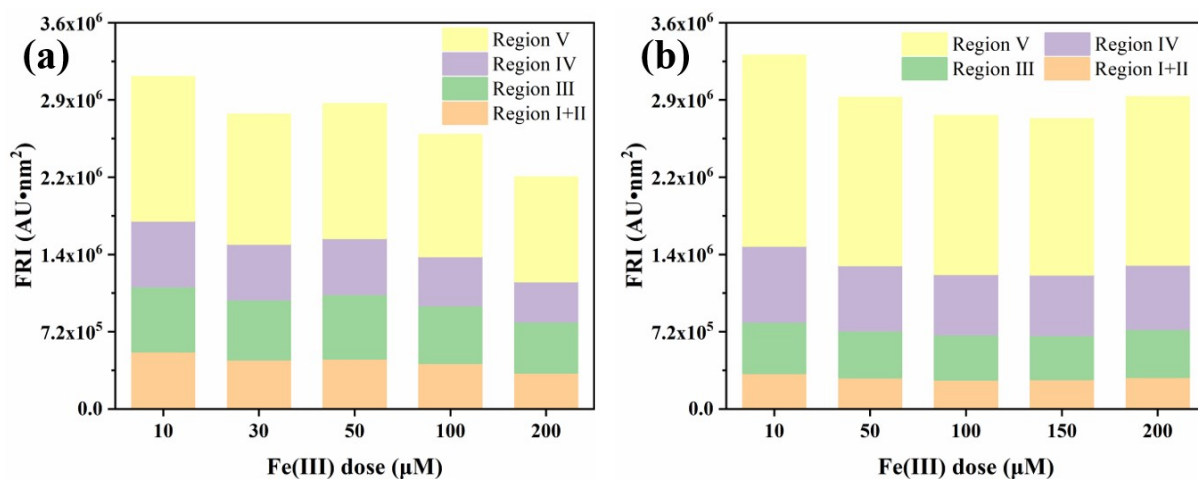
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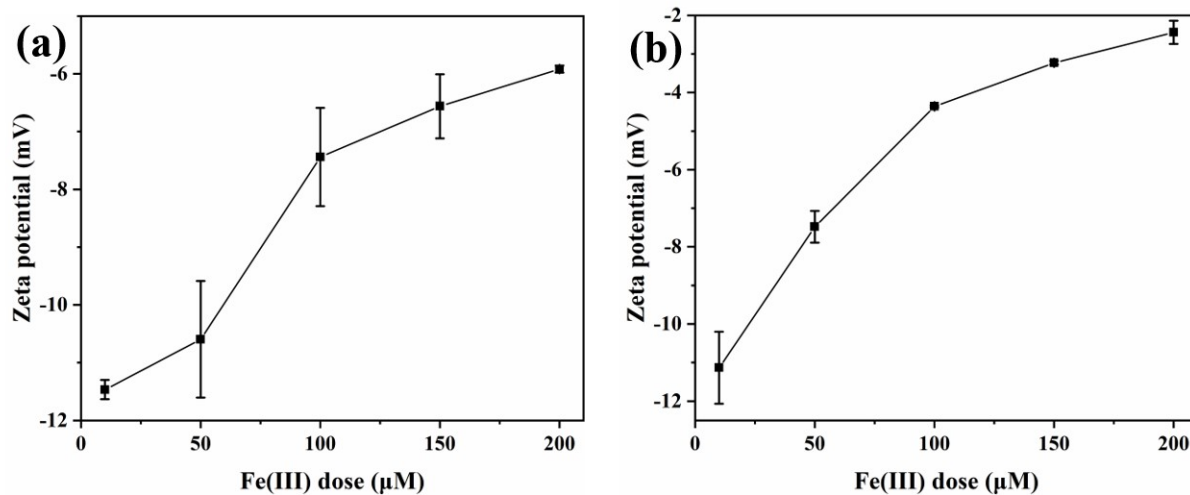
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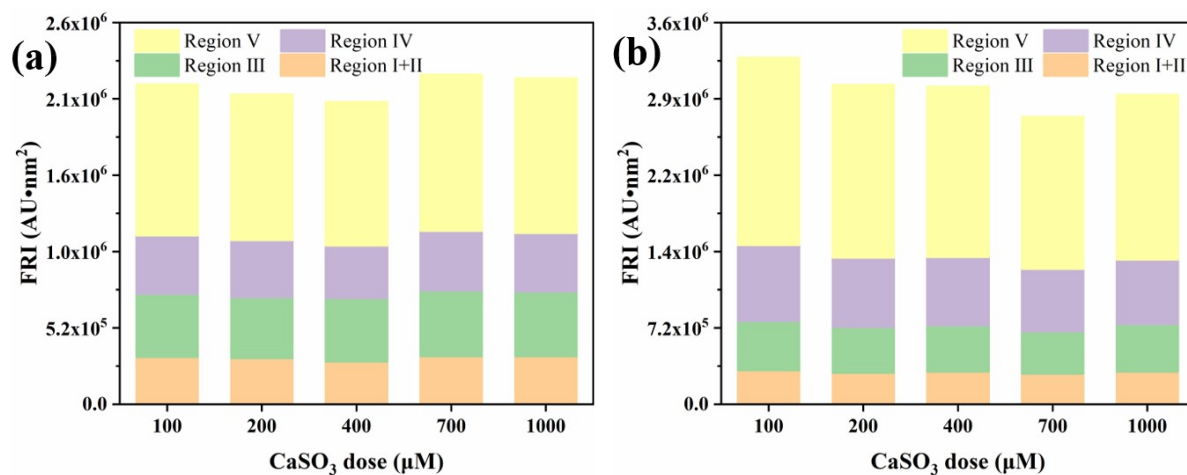
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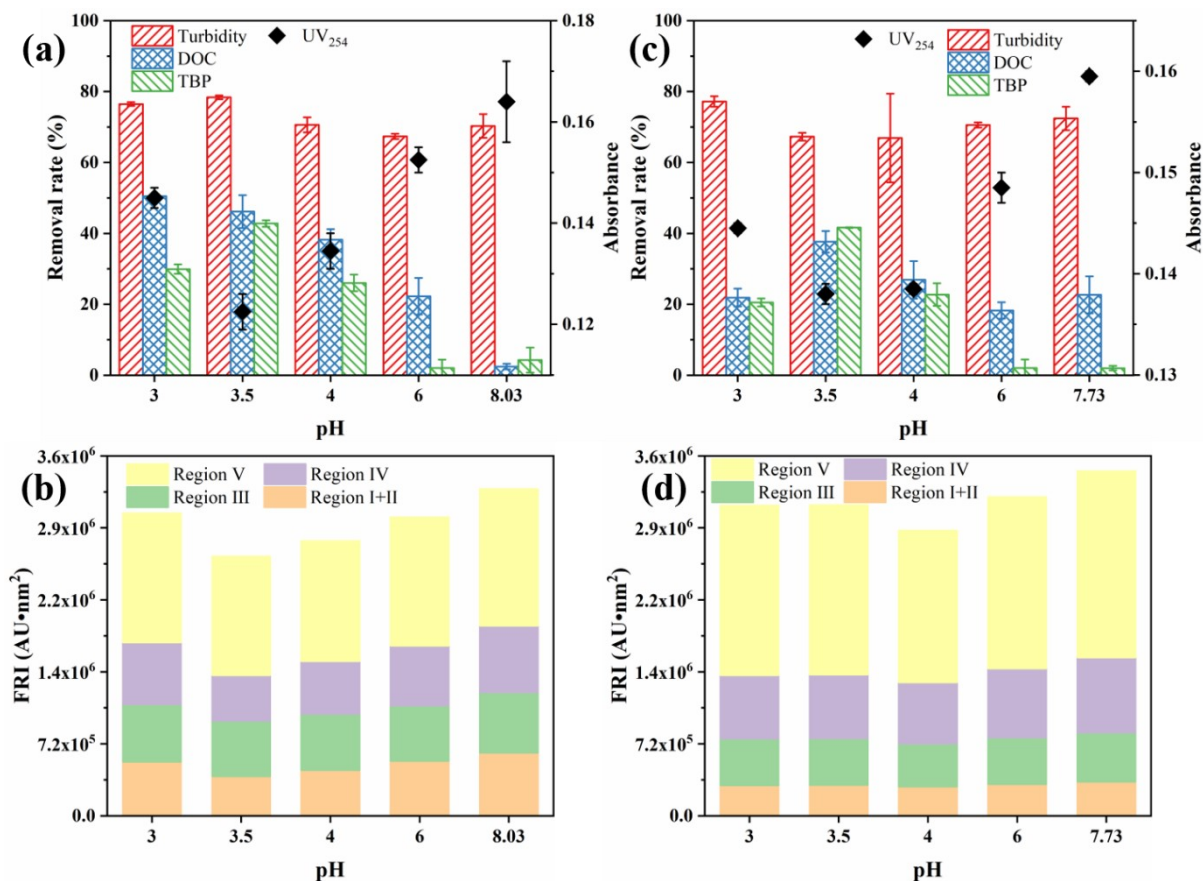
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**Fig. S7.** Effects of Fe(III) concentration on zeta potential values in the Fe(III)/CaSO<sub>3</sub> system: (a) lake water; (b) secondary sedimentation tank effluent. Conditions: [TBP] = 10  $\mu\text{M}$ , [CaSO<sub>3</sub>] = 400  $\mu\text{M}$ , initial pH 3.5, temperature 25 °C.



**Fig. S8.** Effects of CaSO<sub>3</sub> dosage on fluorescent organic matter removal in the Fe(III)/CaSO<sub>3</sub> system: (a) lake water; (b) secondary sedimentation tank effluent. Conditions: [TBP] = 10 μM, [CaSO<sub>3</sub>] = 400 μM, initial pH 3.5, temperature 25 °C.



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