

## **Supporting Information**

### **Effect of Metal Ions on Oxidation of Micropollutants by Ferrate(VI):**

#### **Enhancing Role of Fe<sup>IV</sup> Species**

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**Text S1. Chemicals and Reagents**

Potassium ferrate ( $\text{K}_2\text{FeO}_4$ , > 90% purity) was synthesized by the oxidation of ferric ion by alkaline hypochlorite. Iron(III) nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 99.99%), hydroxylamine hydrochloride ( $\text{HONH}_2 \cdot \text{HCl}$ , 99%), sodium borate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , > 99%), calcium chloride ( $\text{CaCl}_2$ , 97%), aluminum chloride ( $\text{AlCl}_3$ , 99%), cobalt chloride ( $\text{CoCl}_2$ , 98%), nickel chloride ( $\text{NiCl}_2$ , 98%), and scandium chloride ( $\text{ScCl}_3$ , 99.9%) were purchased from Alfa Aesar (Wordhill, MA). Sodium bicarbonate ( $\text{NaHCO}_3$ , 99.7-100.3%), sodium phosphate dibasic ( $\text{Na}_2\text{HPO}_4$ , > 99.0%), sodium hydroxide ( $\text{NaOH}$ , 99%), and hydrochloride ( $\text{HCl}$ , 99%) were supplied from Sigma-Aldrich (St. Louis, MO). Target micropollutants were flumequine (FLU, > 98%, Alfa Aesar, Wordhill, MA), atenolol (ATL, MP Biomedicals, LLC, Illkirch, France), aspartame (APT, > 98%, spectrum chemical MFG. CORP, New Brunswick, New Jersey), and diatrizoate (DTA, 98%, Alfa Aesar, Wordhill, MA). Suwannee River Humic Acid (SRHA) and Suwannee River Natural Organic Matter (SRNOM) were obtained from International Humic Substances Society (St. Paul, MN).  $\text{Fe}^{\text{III}}$ -TAML was purchased from GreenOx Catalysts, Inc. (Pittsburgh, PA). Methanol of high performance liquid chromatography (HPLC) grade was acquired from Merck (Darmstadt, Germany). Solutions were prepared using the ultrapure water (resistivity >  $18 \text{ M}\Omega \text{ cm}^{-1}$ , a Milli-Q water purification system, Millipore, Waters Alliance, Milford, MA, USA).

Solution of  $\text{Fe}^{\text{VI}}$  was prepared prior to each experiment by dissolving solid particles of  $\text{K}_2\text{FeO}_4$  into 2.0 mM borate buffer (pH 9.0). When the experiments were carried out without buffer,  $\text{K}_2\text{FeO}_4$  salt was dissolved in ultrapure water. A molar absorption coefficient  $\varepsilon_{510\text{nm}} = 1150 \text{ M}^{-1} \text{ cm}^{-1}$  was used for calculation of concentrations of  $\text{Fe}^{\text{VI}}$ .

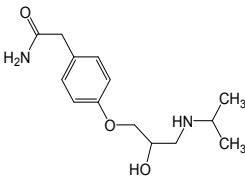
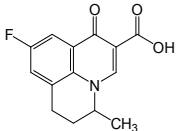
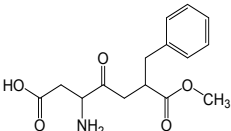
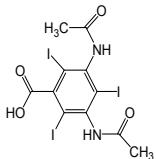
Absorbance measurements were made on an UV-visible spectrometer (DR-5000, Hach Co., USA). Stock solutions of micropollutants (i.e., FLU, APT, ATL, and DTA) at 20.0  $\mu$ M were prepared by dissolving specific amounts of FLU, APT, ATL, and DTA into 2.0 mM borate buffer. Stock solution of Fe(III) (0.1 M) was freshly prepared by dissolving 0.4040 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 10.0 mL ultrapure water before each batch of experiments and used quickly to avoid hydrolysis. Solutions of NaOH and HCl solutions were used to adjust the pH of solution mixtures. Stock solutions of Ca(II), Al(III), Sc(III), Ni(II), Co(II), and  $\text{Fe}^{\text{III}}$ -TAML were prepared using the similar methods like that of Fe(III).

Additionally, the removal of DTA (5.0  $\mu$ M) by  $\text{Fe}^{\text{VI}}$ -Fe(III) system (i.e.,  $[\text{Fe}^{\text{VI}}]:[\text{Fe}(\text{III})] = 0.5$ ) in surface water samples was evaluated at pH 8.0. The samples of river and lake waters were obtained from Brazos River (N 30°42'33", E 96°28'5", College Station, Texas) and Lake Bryan (N 30°33'30", E 96°25'25", Bryan, Texas), respectively. No target pollutant was detected in these natural waters. The characteristics of river water are pH, 8.36,  $\text{UV}_{254}$ , 0.071,  $\text{UV}_{400}$ , 0.006 and dissolved organic matters (DOC),  $12.95 \pm 0.16$  mg/L. The parameters for lake water are pH, 9.43,  $\text{UV}_{254}$ , 0.202,  $\text{UV}_{400}$ , 0.017 and DOC,  $15.64 \pm 0.27$  mg/L. Both water samples were filtered through 0.45  $\mu$ m hydrophilic PVDF membrane (Millipore Millex-HV) prior to adding 2.0 mM borate and pH was adjusted to 8.0. A stock solution of DTA (40.0  $\mu$ M) was added into each of the surface water sample (200.0 mL), followed by additions of solid  $\text{K}_2\text{FeO}_4$  and ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) to obtain the final molar ratio of 0.5. The samples were quenched after 10 min of reaction using 200.0  $\mu$ L of 1.0 M hydroxylamine solution, and subsequently, 1.0 mL sample was filtered and transferred to the HPLC vial prior to analysis.

***Text S2. Stopped-flow measurements***

Kinetics of the reaction between  $\text{Fe}^{\text{VI}}$  and four selected micropollutants were conducted under pseudo first-order conditions, in which the concentrations of FLU, ATL, APT, and DTA were in excess. Solutions of both reactants were prepared in 2.0 mM borate buffer. The pH of each solution was adjusted to the desired value by adding either hydrochloric acid or sodium hydroxide. The instrument used was a stopped-flow spectrophotometer (SX.18MV, Applied Photophysics, UK), equipped with a photomultiplier detector. The kinetic traces were analyzed by the non-linear least-squares algorithm within the SX 18MV software. The pseudo-first-order rate constants,  $k_1$ , were calculated from the best fit to the decay of  $\text{Fe}^{\text{VI}}$  with time. The rate constants obtained represent the average value of four kinetics runs. The obtained  $k_1$  values were corrected by subtracting the values from the rate constants without micropollutants (i.e., only 2.0 mM borate buffer) for the self-decomposition of  $\text{Fe}^{\text{VI}}$ .

84 **Table S1.** Chemical structures and HPLC conditions of the organic contaminants in this study.

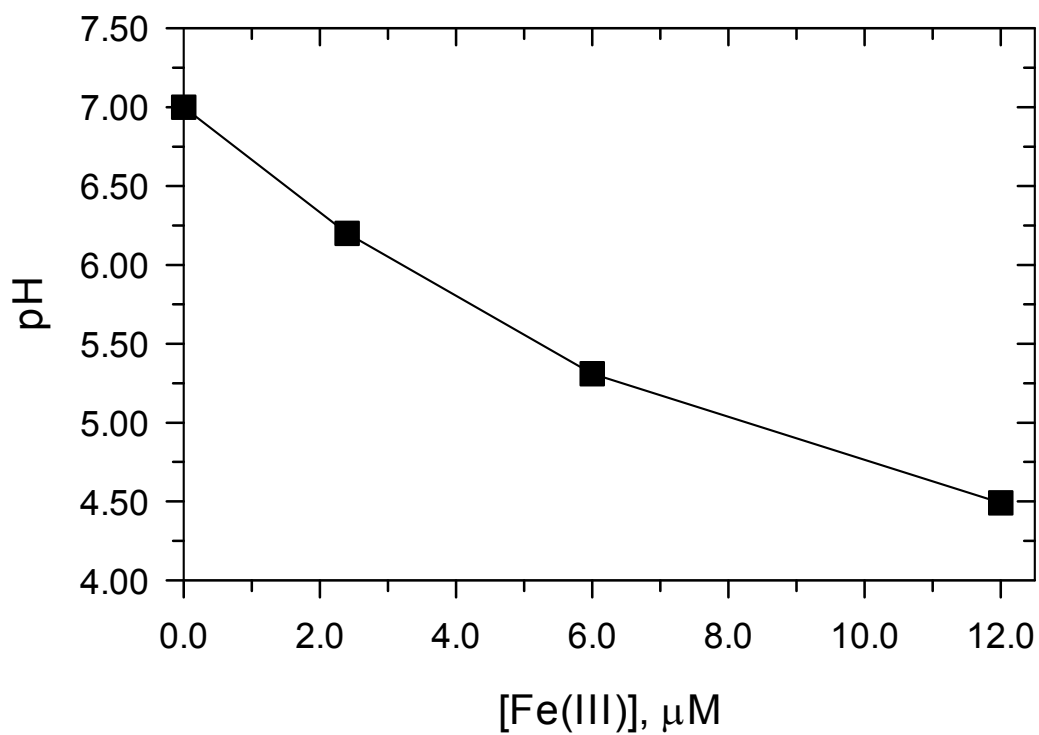
Chemicals	Abbr.	Category	Molecular structure	pK <sub>a</sub>	Mobile phase Methanol/water	Flow rate (mL/min)	UV <sub>max</sub> (nm)	Retention time (min)
Atenolol	ATL	Beta-blocker		9.6	20:80	0.8	224	5.830
Flumequine	FLU	Fluoroquinolone antibiotic		6.5	70:30	1.0	324	4.730
Aspartame	APT	Artificial sweetener		3.2 7.9	50:50	0.8	215	4.693
Diatrizoic acid	DTA	X-ray contrast medium		3.4	35:65	0.8	238	4.393

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86 **Table S2.** Accurate mass measurements of ATL and its OPs by Fe<sup>VI</sup>-Fe(III) system.

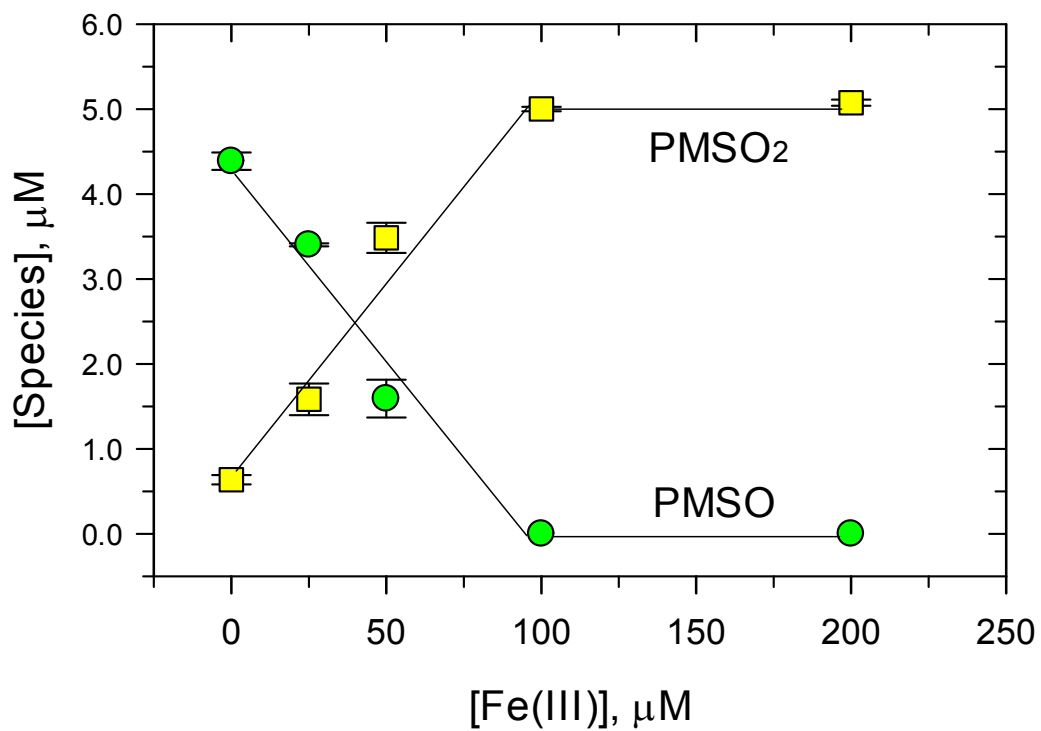
Comp.	$R_t$ (min)	Molecular weight (MW)	Experimental MW	Calculated MW	Error (ppm)
ATL	3.217	C <sub>14</sub> H <sub>22</sub> N <sub>2</sub> O <sub>3</sub>	266.16300	266.16304	-0.15
OP-282	2.844	C <sub>14</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub>	282.15796	282.15796	0.00
OP-240	2.296	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>	240.11088	240.11101	-0.54
OP-238	4.645	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub>	238.09523	238.09539	-0.67
OP-224	3.215	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	224.11642	224.11609	1.47
OP-222	4.995	C <sub>11</sub> H <sub>14</sub> N <sub>2</sub> O <sub>3</sub>	222.10038	222.10044	-0.27
OP-209	4.829	C <sub>10</sub> H <sub>11</sub> NO <sub>4</sub>	209.06864	209.06881	-0.81
OP-193	4.894	C <sub>10</sub> H <sub>11</sub> NO <sub>3</sub>	193.07397	193.07389	0.41
OP-167	5.629	C <sub>8</sub> H <sub>9</sub> NO <sub>3</sub>	167.05847	167.05824	1.38
OP-151	2.684	C <sub>8</sub> H <sub>9</sub> NO <sub>2</sub>	151.06339	151.06333	0.40

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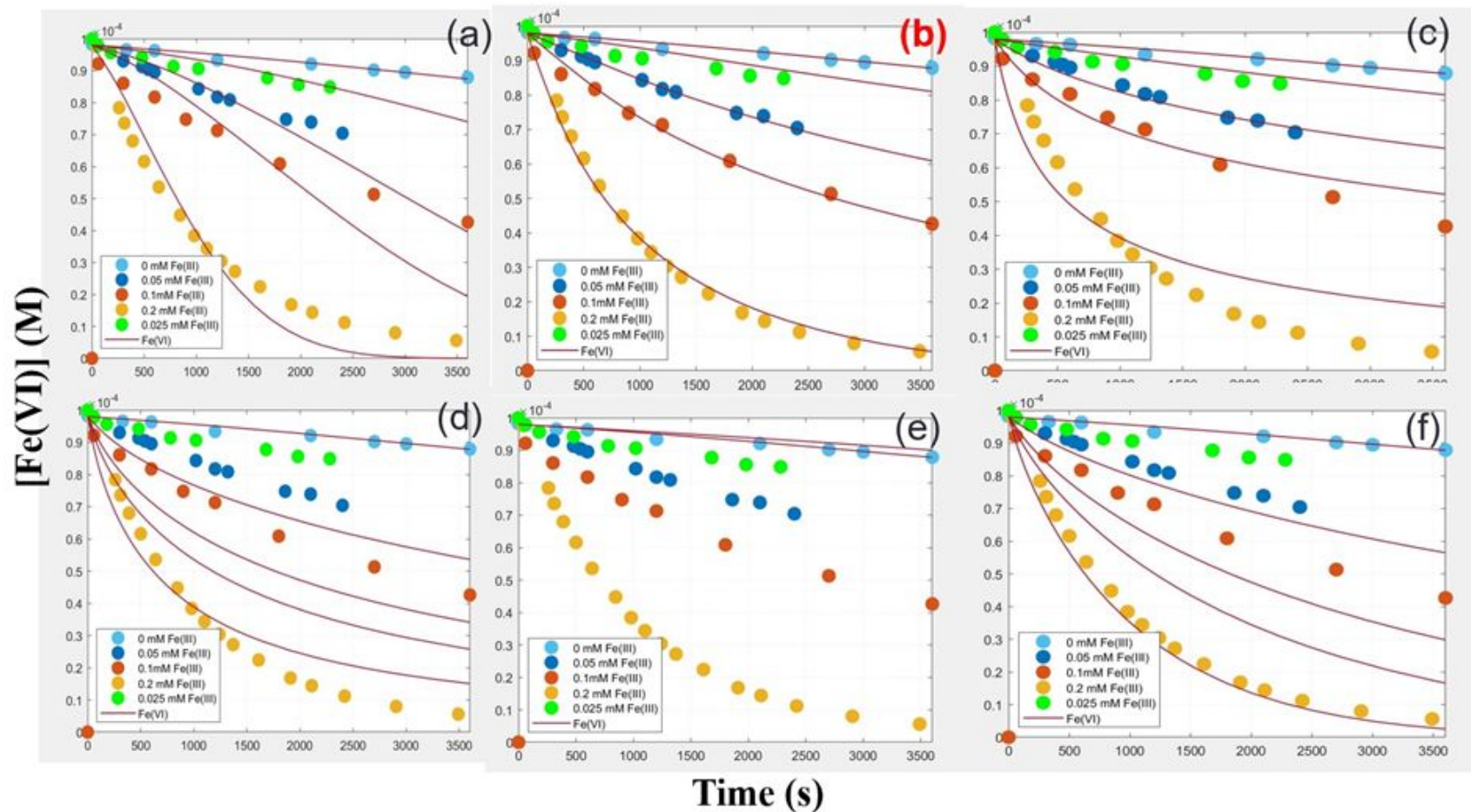
89 **Figure S1.** Decrease in pH after the addition of different amount of Fe(III) into deionized  
90 water. The pH of the deionized water was first adjusted to pH 7.0 by adding drops of  
91 diluted NaOH before adding desired amount of Fe(III) using the concentrated solution of  
92 ferric nitrate (0.02 M).  
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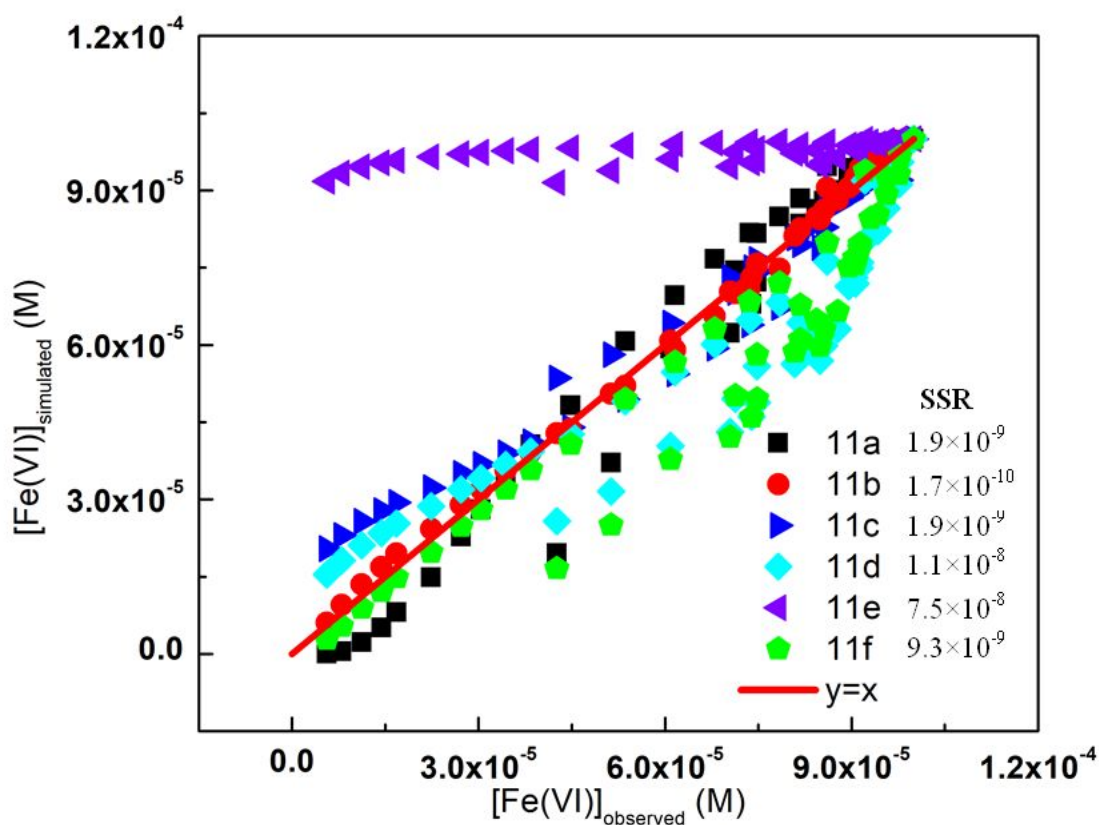
95 **Figure S2.** Oxidation of PMSO and formation of PMSO<sub>2</sub> in Fe<sup>VI</sup>-Fe(III) system.  
 96 (Experimental conditions: [PMSO] = 5.0  $\mu\text{M}$ , [Fe<sup>VI</sup>] = 100.0  $\mu\text{M}$ , pH 9.0 (2.0 mM borate  
 97 buffer), and reaction time = 10 min).



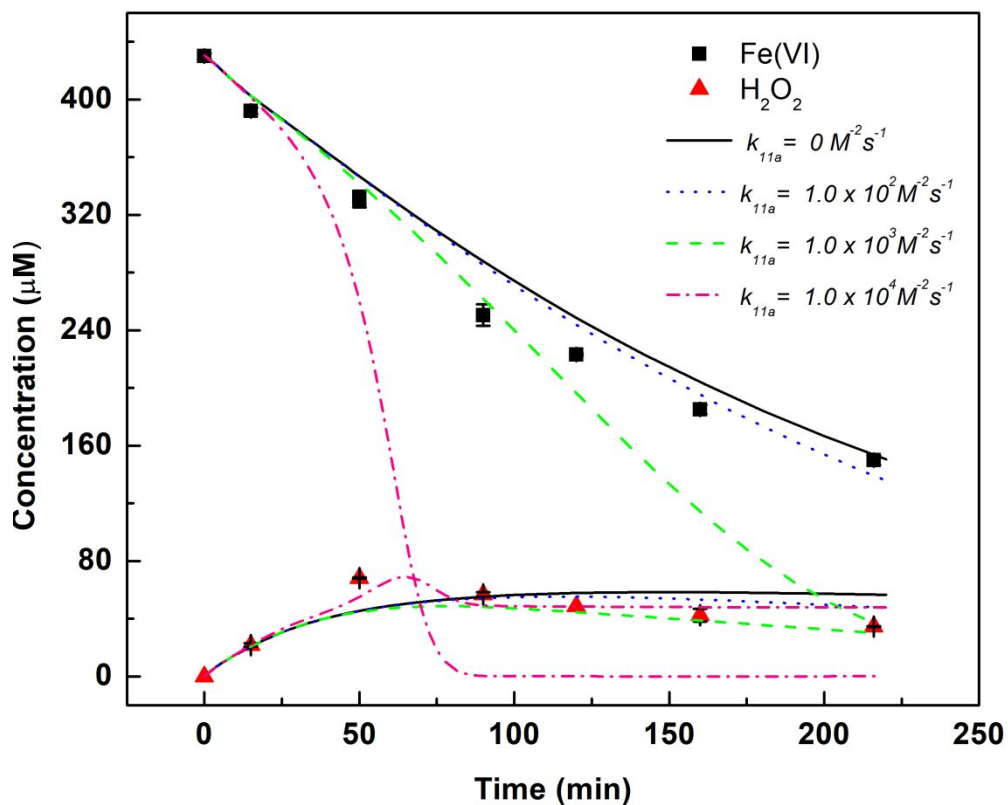


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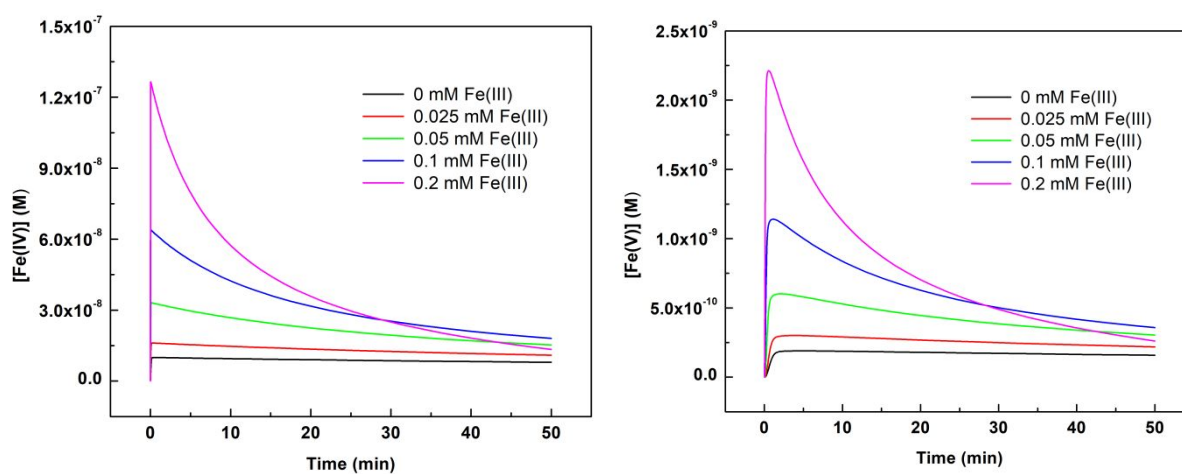
99 **Figure S3.** Kinetic simulation of  $\text{Fe}^{\text{VI}}$  decay at different levels of  $\text{Fe}^{\text{III}}$  based on Eq. 11a (A), Eq. 11b (B), Eq. 11c (C), Eq.  
 100 11d (D), Eq. 11e (E) and Eq. 11f (F). (Experimental conditions:  $[\text{Fe}^{\text{VI}}] = 100.0 \mu\text{M}$ ,  $[\text{Fe}^{\text{III}}] = 0\text{--}200.0 \mu\text{M}$ ,  $[\text{borate buffer}] =$   
 101  $2.0 \text{ mM}$ , and reaction time = 140 min). Note: the simulated  $k$  values for Figure S3 A-F were  $1.1 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ ,  $2.67 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ ,  
 102  $5.6 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ ,  $1.5 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ ,  $5.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and  $2.5 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. The solid lines show the best possible model fits  
 103 to the experimental data for (a)-(f).



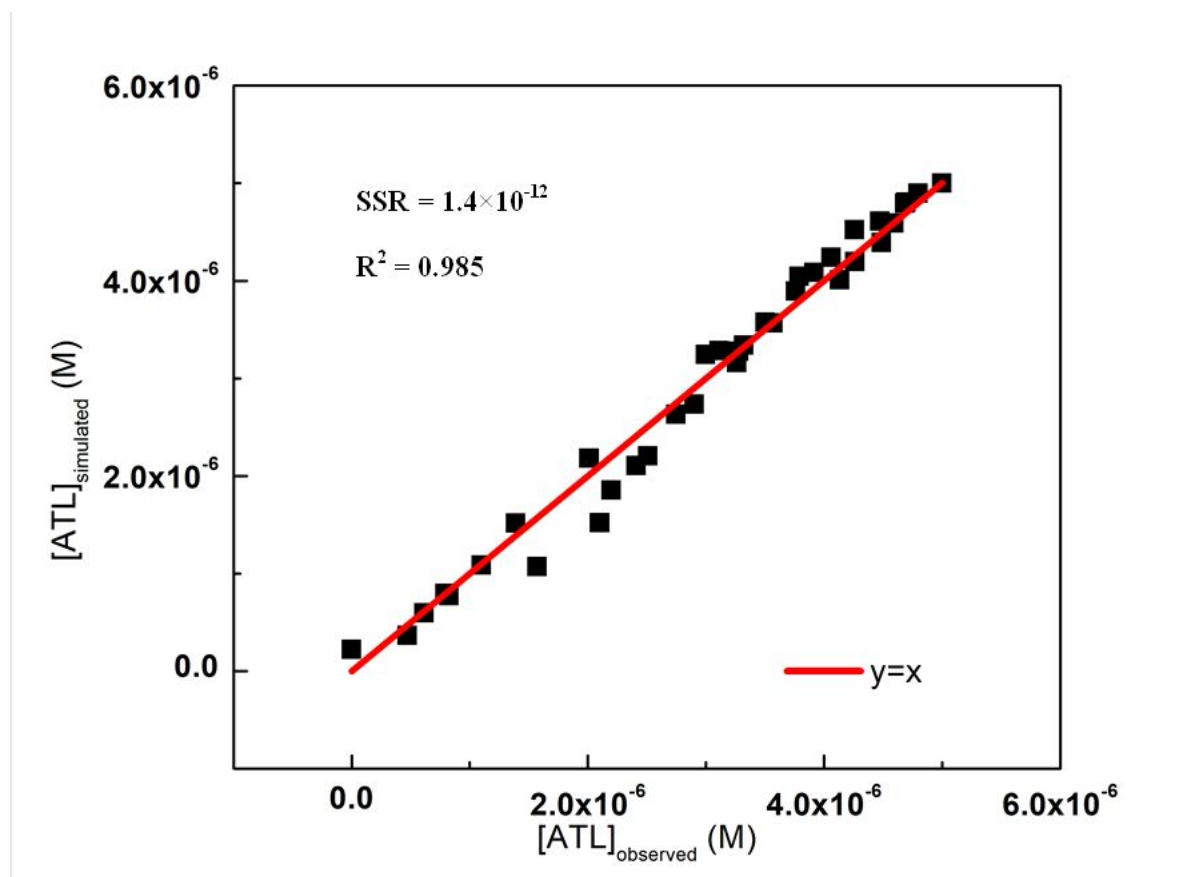
**Figure S4.** Statistical analysis between observed  $\text{Fe}^{\text{VI}}$  decay and simulated  $\text{Fe}^{\text{VI}}$  decay by modeling (Eqs. 1-10 and 11a-11f, Table 1) based on Figure S3. SSR stands for the sum of squared residuals, which is the sum of the squares of discrepancy between predicted and observed data. A lower SSR indicated a better fitting.



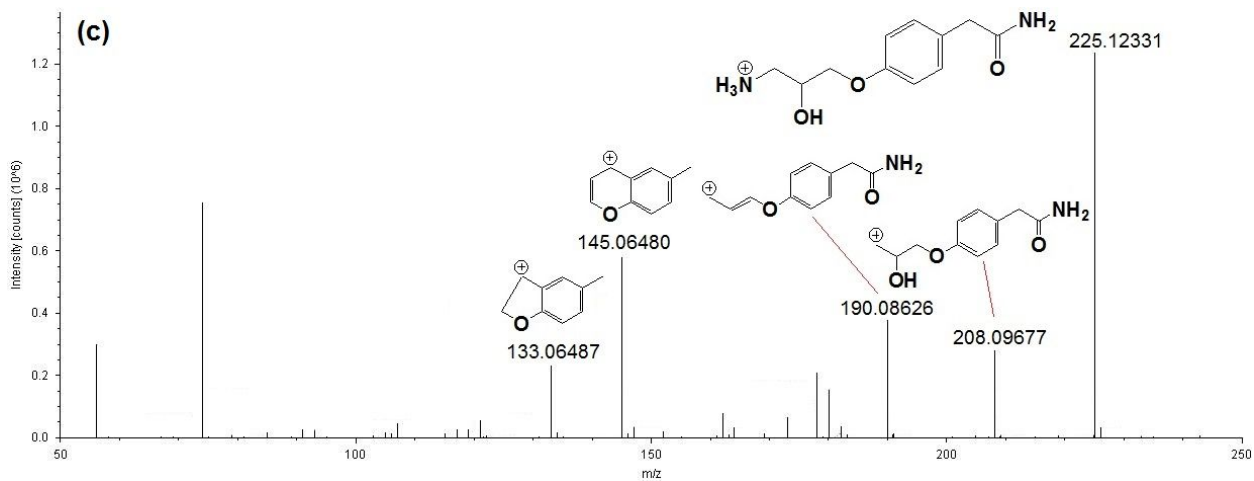
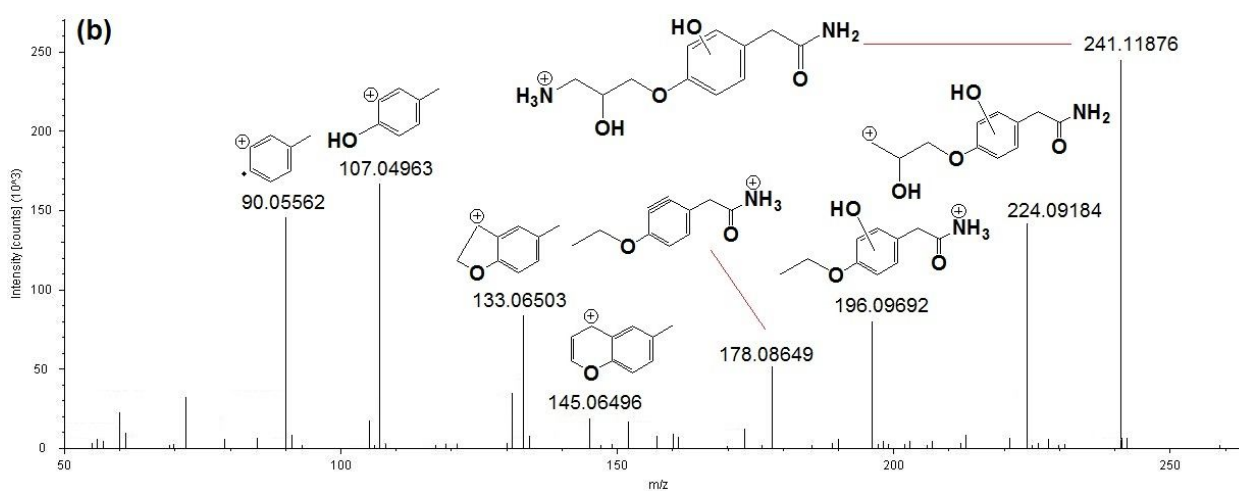
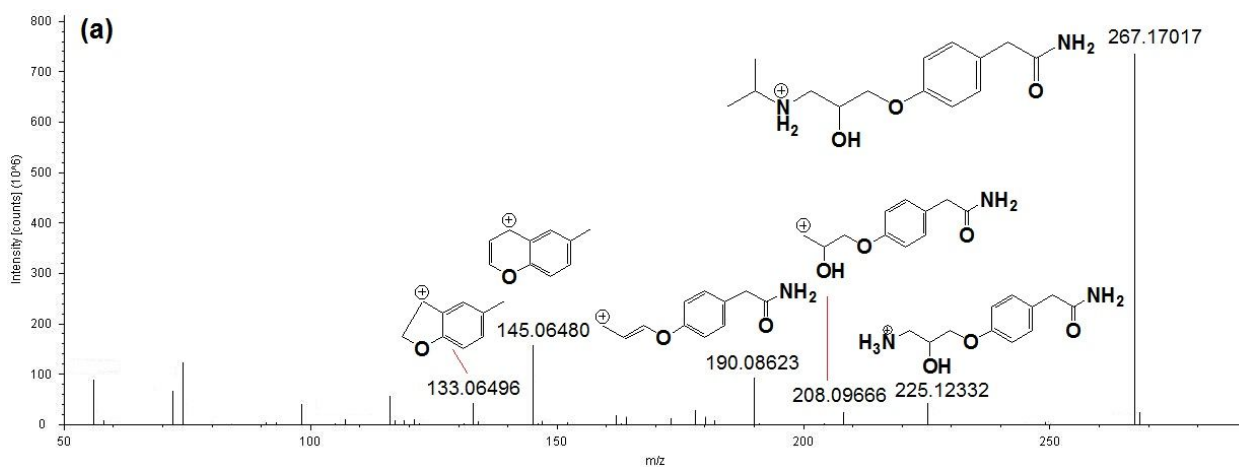
**Figure S5.** Sensitivity analysis of  $k_{11a}$  on Fe<sup>VI</sup> decay. (Experimental and kinetic modeling conditions: [Fe<sup>VI</sup>] = 430.0 μM, pH 9.0, reaction time = 227 min, and no Fe(III) addition). The data points were re-created according to a previous work.<sup>1</sup>

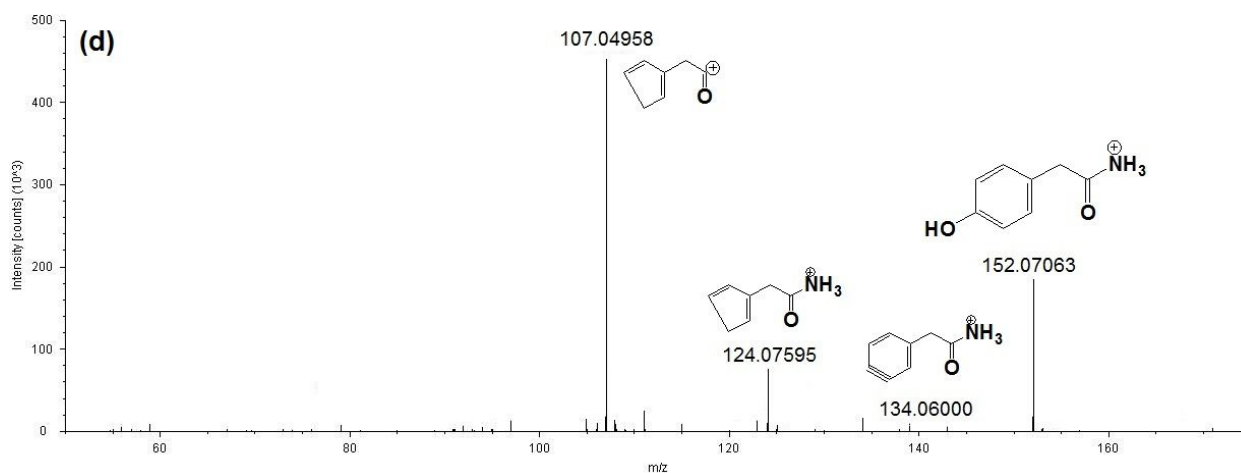


**Figure S6.**  $\text{Fe}^{\text{IV}}$  (left) and  $\text{Fe}^{\text{V}}$  (right) evolution profiles in  $\text{Fe}^{\text{VI}}$ - $\text{Fe(III)}$  system. (Simulation conditions:  $[\text{Fe}^{\text{VI}}] = 100.0 \mu\text{M}$ ,  $[\text{Fe(III)}] = 0\text{--}0.2 \text{ mM}$ ,  $[\text{borate buffer}] = 2.0 \text{ mM}$ , and reaction time =  $140 \text{ min}$ ).

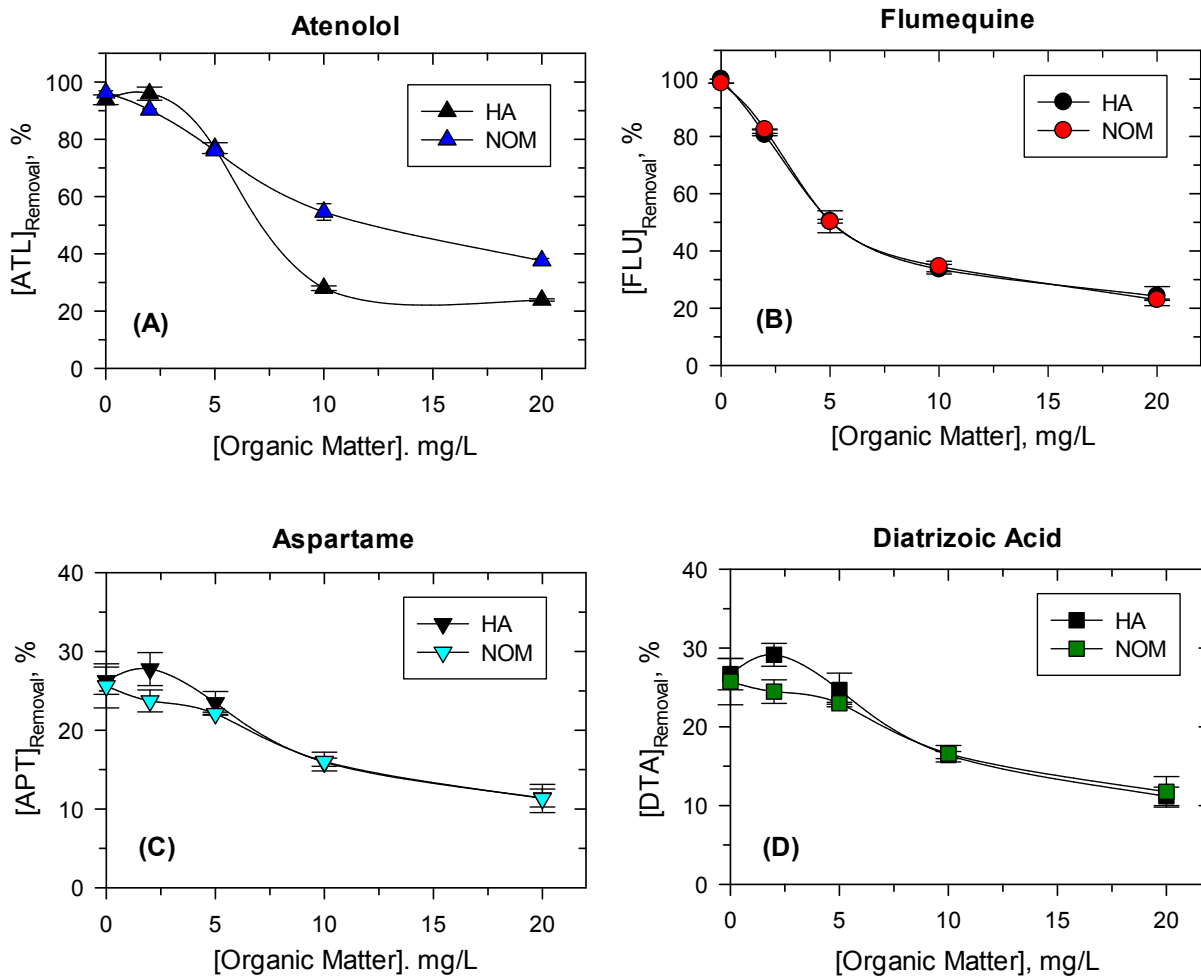


**Figure S7.** Statistical analysis between observed ATL degradation and simulated ATL degradation by modeling (Reactions 1-10, 11b, 12 and 13, Table 1) based on the data of Figure 3 in the manuscript. SSR stands for the sum of squared residuals, which is the sum of the squares of discrepancy between predicted and observed data. A lower SSR indicated a better fitting.



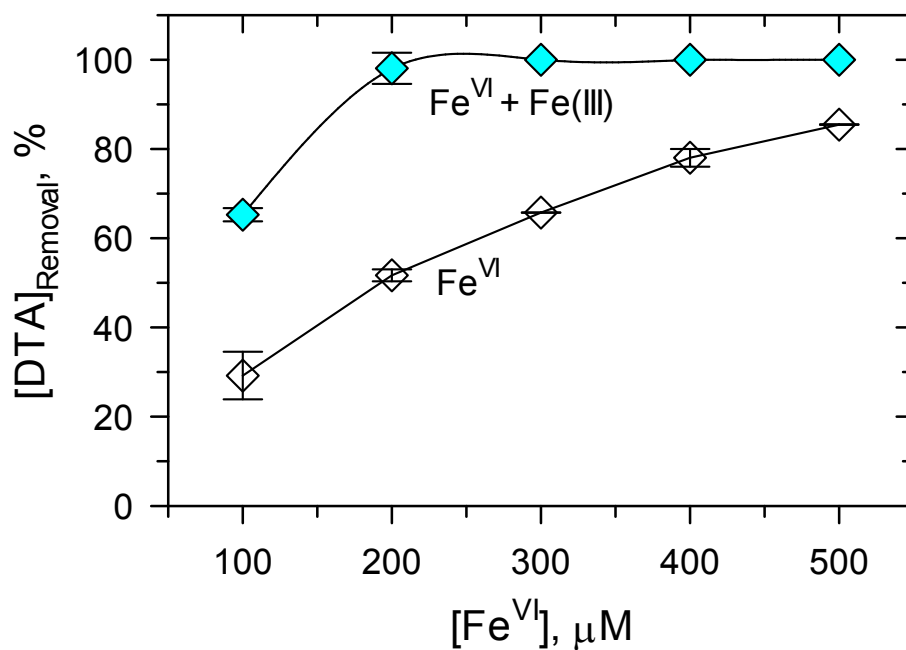


**Figure S8.** The LC/MS/MS spectra of ATL (a) and its OPs (b, OP-240; c, OP-225; d, OP-151), generated by Fe<sup>VI</sup>-Fe(III) system, with their proposed fragmentation structures.

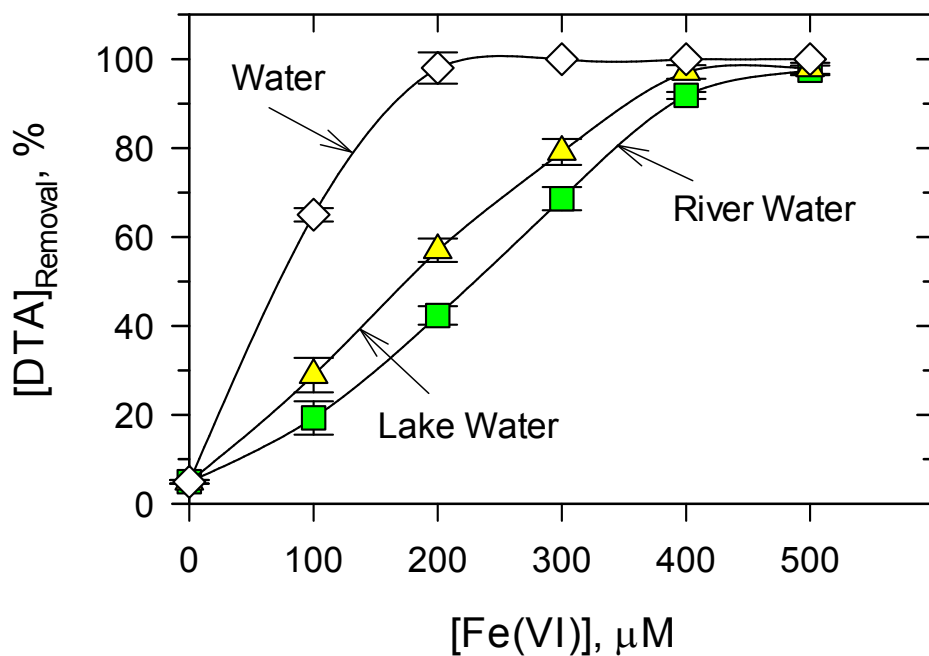


**Figure S9.** Effect of SRHA and SRNOM on the removal of micropollutants by  $\text{Fe}^{\text{VI}}$ - $\text{Fe}(\text{III})$  system. (a) ATL, (b) FLU, (c) APT, and (d) DTA. ( $[\text{Micropollutant}] = 5.0 \mu\text{M}$ ,  $[\text{Fe}^{\text{VI}}] = 100.0 \mu\text{M}$ ,  $[\text{Fe}(\text{III})] = 200.0 \mu\text{M}$ , pH 9.0 (2.0 mM borate buffer), and reaction time = 10 min).





**Figure S10.** Effect of concentration of Fe<sup>VI</sup> on the removal of DTA in Fe<sup>VI</sup>-Fe(III) system containing fixed molar ratio of Fe<sup>VI</sup> to Fe(III) as 0.5 (i.e., [Fe<sup>VI</sup>]/[Fe(III)] = 0.5). (Experimental conditions: [DTA] = 5.0 μM, pH 8.0 (2.0 mM borate buffer), and reaction time = 10 min).



**Figure S11.** Effect of concentration of  $\text{Fe}^{\text{VI}}$  on the removal of DTA in surface waters collected from Brazos River and Lake Bryan by  $\text{Fe}^{\text{VI}}$ - $\text{Fe}^{\text{III}}$  system at a fixed molar ratio of 0.5 ( $[\text{Fe}^{\text{VI}}]/[\text{Fe}^{\text{III}}]$ ) at pH 8.0. (Experimental conditions:  $[\text{DTA}] = 5.0 \mu\text{M}$ .  $[\text{borate buffer}] = 2.0 \text{ mM}$  and reaction time = 10 min).

156    **Supporting references**

- 157    (1) Luo, C.; Feng, M.; Sharma, V.K.; Huang, C.H. Revelation of ferrate(VI) unimolecular decay  
158    under alkaline conditions: Investigation of involvement of Fe(IV) and Fe(V) species. *Chem. Eng.*  
159    *J.* **2020**, 388, 124134.