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Supplementary Material

Degradation of antibiotic fosfomycin by peroxymonosulfate/ferrate and simultaneous phosphate removal with in situ formed ferric nanoparticles

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Experimental Procedures

Text S1. Quantification of FOS via Liquid Chromatography-Triple Quadrupole Mass Spectrometry.

Fosfomycin (FOS) was quantified using a liquid chromatography-triple quadrupole mass spectrometer (LC-MS/MS; TSQ Quantiva, Thermo Scientific) fitted with a heated electrospray ionization (H-ESI) source. Data collection and analysis were conducted using Thermo Scientific Xcalibur software (version 4.1). Chromatographic separation was achieved on a Thermo Hypersil GOLD C18 column (10 × 2.1 mm, 1.9 μm). The mobile phase consisted of two components: deionized (DI) water containing 0.1% formic acid and methanol. A gradient elution program (detailed in **Table S2**) was employed, with a constant flow rate of 0.2 mL min^{-1}. The injection volume of each sample was 2 μL, and the column temperature was kept constant at 35 °C. For mass spectrometric detection, the instrument was operated in negative ionization mode. The target ion for FOS was monitored at a mass-to-charge ratio (m/z) of 137. Instrument parameters were set as follows: spray voltage = 2.5 kV; capillary temperature = 320 °C; and vaporizer temperature = 350 °C.

Text S2. Identification of degradation products of FOS.

Following 20 minutes of Fe(VI)/PMS treatment, reaction solutions were collected to maximize the variety of transformation products for identifying FOS degradation products. These products were analyzed using ultra-high-performance liquid chromatography coupled with hybrid quadrupole-orbitrap mass spectrometry (UPLC-Q-Exactive Orbitrap-MS, Thermo, Bremen, Germany). The mass spectrometer, equipped with an electrospray ionization (ESI) source, was operated in both positive and negative ionization modes across a mass-to-charge (m/z) range of 70–1000. Instrument parameters were set as follows: capillary temperature = 320 °C; auxiliary gas heater temperature = 350 °C; spray voltage = 4.0 kV (positive mode) and 3.0 kV (negative mode). Nitrogen gas (99.999% purity) was used as the collision and dissociation gas at a flow rate of 10 L min^{-1}. Chromatographic separation was achieved on a Hypersil GOLD C18 column (100 × 2.1 mm, 1.9 μm). The mobile phase comprised deionized (DI) water with 0.1% formic acid and methanol, delivered at a flow rate of 0.25 mL min^{-1}. Samples were injected with a volume of 10 μL, and the column temperature was maintained at 35 °C.

Text S3. Toxicity assessment of FOS and its degradation products.

The toxicity of FOS and its degradation products was evaluated by using *Escherichia coli* (*E. coli*) ATCC25922, a representative Gram-negative bacterium, obtained from the Beijing Microbiological Culture Collection Center (Beijing, China). Prior to the toxicity test, *E. coli* was cultured in a 200 mL conical flask containing 100 mL of Luria-Bertani (LB) medium. The flask was incubated in a thermostatic water bath shaker (SHA-B, Bo Yuan Instrument Manufacture, China) at 37 °C for 18–20 hours. Following incubation, the bacterial cells were harvested by centrifugation at 8, 000 rpm for 10 minutes, washed twice with fresh LB medium, and resuspended in the same medium to prepare a uniform bacterial suspension for subsequent experiments.

For assessing FOS and its degradation products' toxicity, *E. coli* cells were exposed to varying concentrations of FOS over an 8-hour period. At regular intervals, samples were collected, and the absorbance of the bacterial suspension was measured at 600 nm to monitor cell growth, thereby evaluating the toxic effects of FOS on *E. coli*.[1] Additionally, the toxicity of transformation products generated during the degradation process was investigated using the same bacterial strain. The survival rate of E. coli was calculated using Equation S1,

$$\text{Survival}\ (\%) = \frac{\mathrm{OD}_{600,\mathrm{t}}}{\mathrm{OD}_{600,0}} \times 100\% \qquad (\mathrm{S1})$$

Scheme S1. Radical interconversion reactions.[2–5]

$$HCO_3^- + HO^{\cdot} \rightarrow CO_3^{\cdot -} + H_2O \quad (1)$$

$$HCO_3^- + SO_4^{\cdot -} \rightarrow CO_3^{\cdot -} + SO_4^{2-} + H^+ \quad (2)$$

$$CO_3^{2-} + HO^{\cdot} \rightarrow CO_3^{\cdot -} + OH^- \quad (3)$$

$$CO_3^{2-} + SO_4^{\cdot -} \rightarrow CO_3^{\cdot -} + SO_4^{2-} \quad (4)$$

$$Cl^- + HO^{\cdot} \rightarrow ClOH^{\cdot -} \quad (5)$$

$$Cl^- + SO_4^{\cdot -} \rightarrow SO_4^{2-} + Cl^{\cdot} \quad (6)$$

$$NO_3^- + HO\cdot \rightarrow NO_3\cdot + OH^- \quad (7)$$

$$NO_3^- + SO_4^{\cdot -} \rightarrow NO_3\cdot + SO_4^{2-} \quad (8)$$

Supplementary Figures

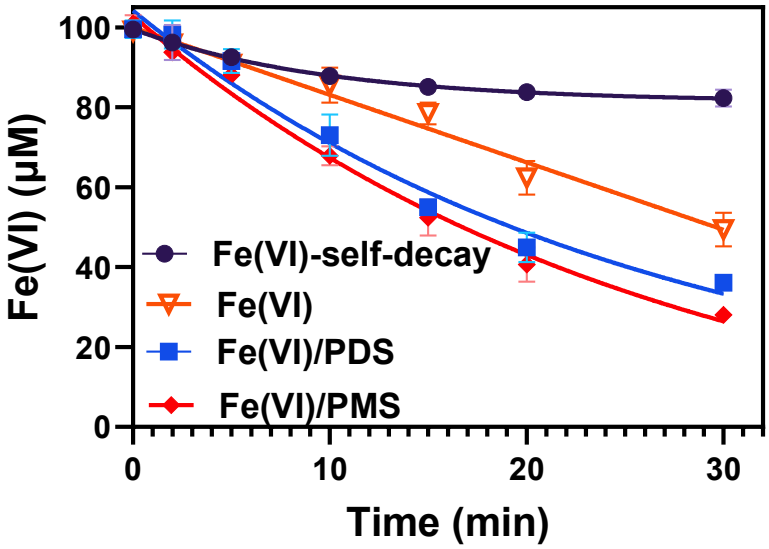


Figure S1. Fe(VI) concentration change during FOS degradation in Fe(VI), Fe(VI)/PDS, and Fe(VI)/PMS systems. Experimental conditions: $[FOS]_0$ = 10 μM, Fe(VI) = 200 μM, $[PDS]_0$ = $[PMS]_0$ = 100 μM, initial pH = 7.0, and temperature = 25 ℃.

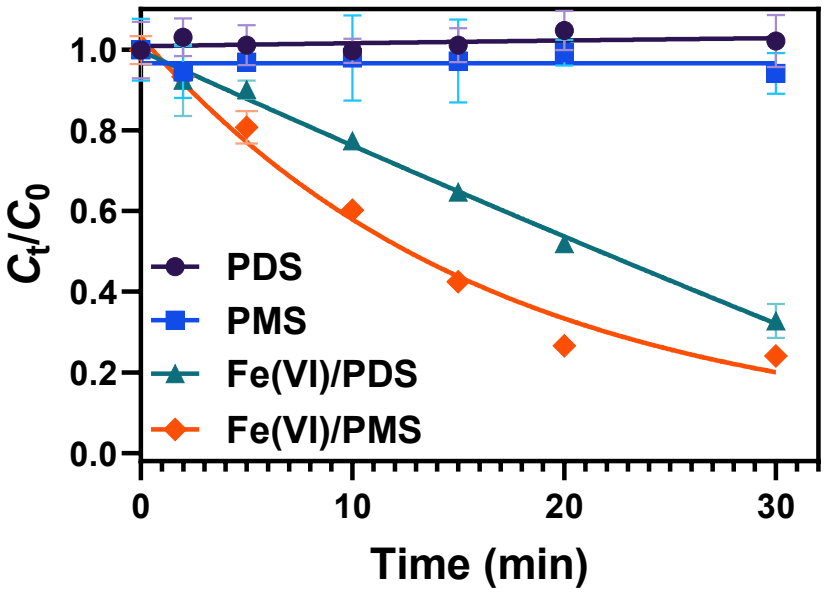


Figure S2. Residual persulfate concentration during FOS degradation in PDS, PMS, Fe(VI)/PDS, and Fe(VI)/PMS systems. Experimental conditions: $[FOS]_0$ = 10 μM, Fe(VI) = 200 μM, $[PDS]_0$ = $[PMS]_0$ = 100 μM, initial pH = 7.0, and temperature = 25 °C.

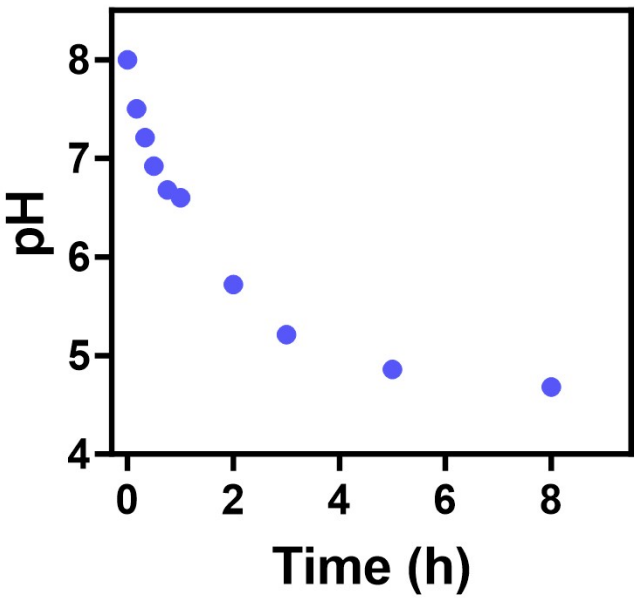


Figure S3. Changes in the pH of the reaction system during the reaction process.

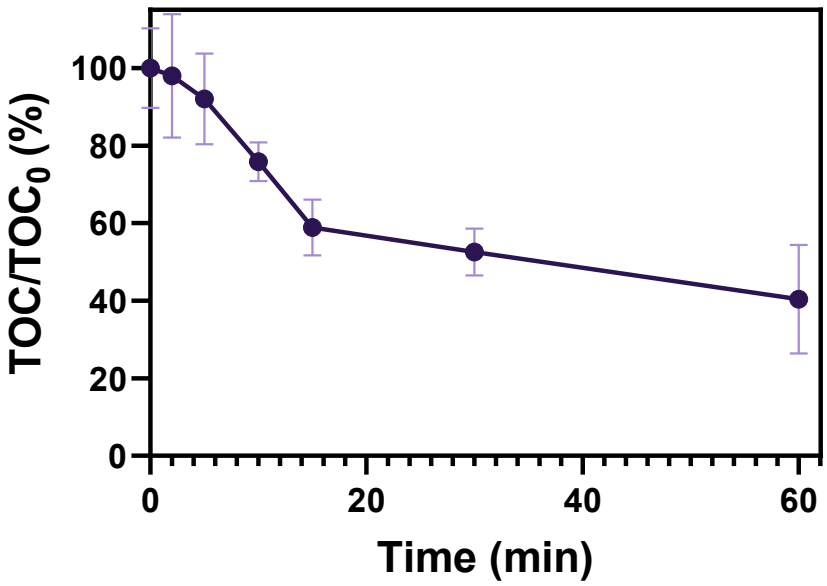


Figure S4. Changes of total organic carbon (TOC) content during FOS degradation. Experimental conditions: $[FOS]_0$ = 10 μM, Fe(VI) = 200 μM, $[PMS]_0$ = 100 μM, initial pH = 7.0, and temperature = 25 ℃.

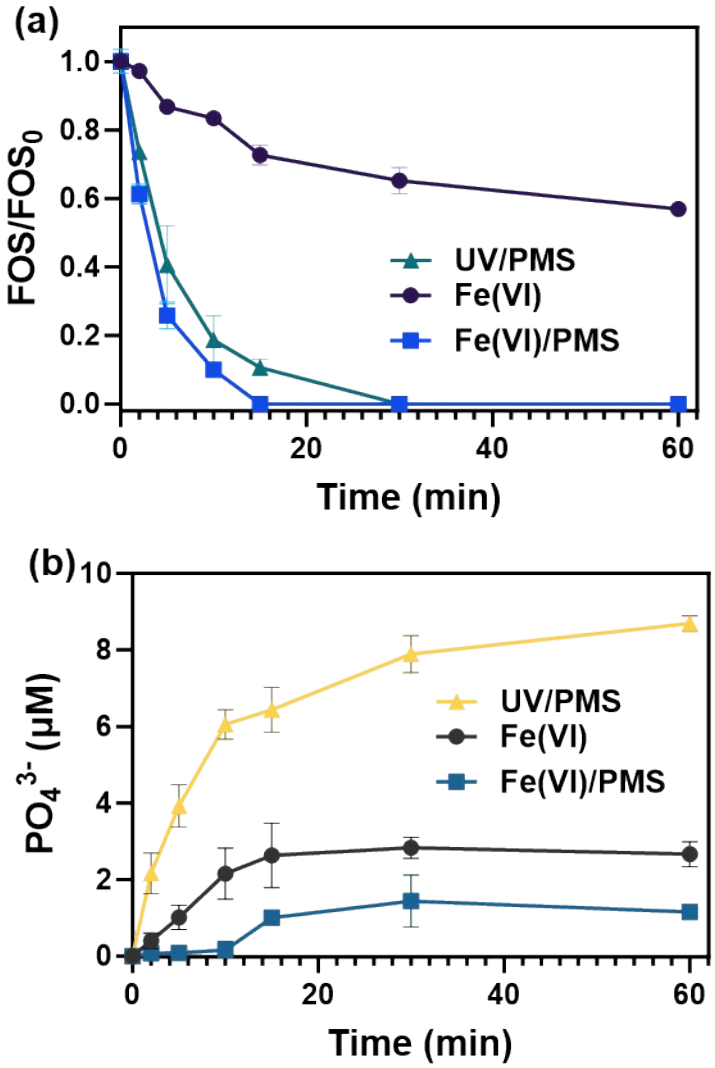


Figure S5. (a) FOS degradation and (b) release and precipitation of phosphate from FOS degradation by UV/PMS, Fe(VI), and Fe(VI)/PMS systems. Experimental conditions: $[FOS]_0$ = 10 μM, Fe(VI) = 200 μM, $[PMS]_0$ = 100 μM, initial pH = 7.0, and temperature = 25 ℃. UV irradiation experiments were performed on a photocatalytic reactor (XPA-7, Nanjing Xujiang Motor Factory, China) with a 500 W high-pressure ultraviolet mercury lamp (emission at 365nm, Nanjing Xujiang Motor Factory, China) as the UV irradiation source.

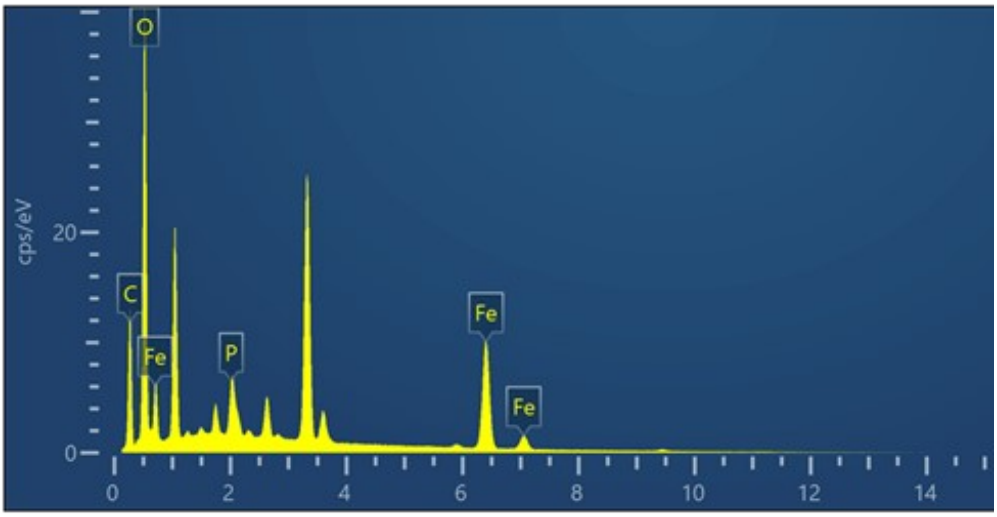


Figure S6. SEM-EDS image of the formed floc particles.

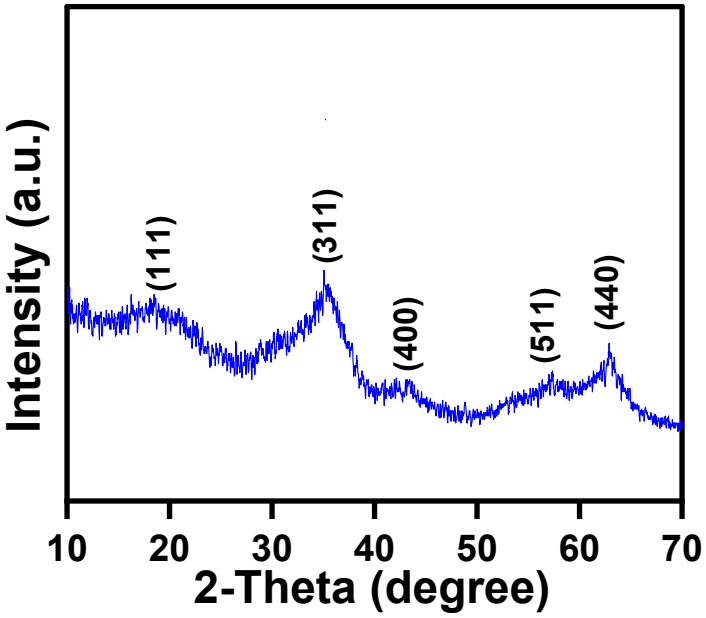


Figure S7. XRD pattern of the formed floc particles.

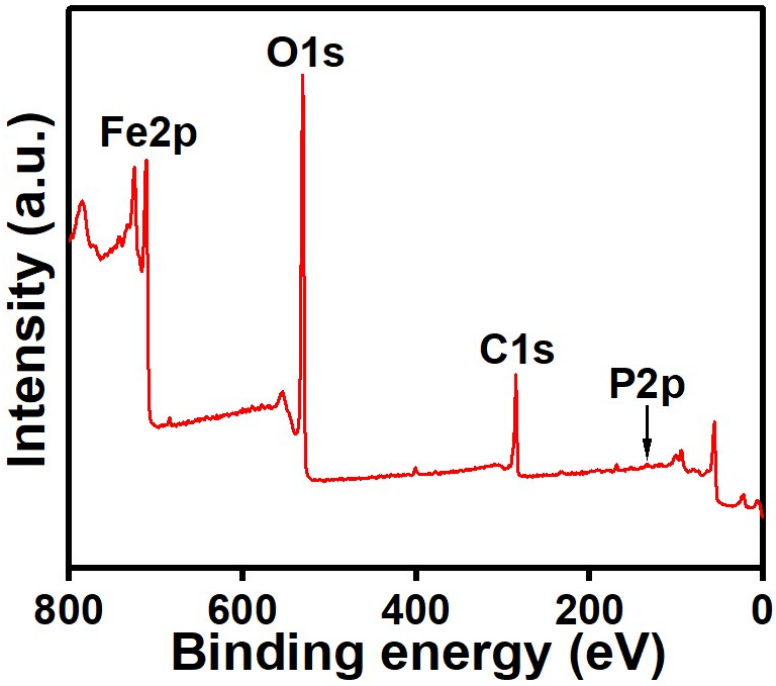


Figure S8. XPS full patterns of the formed floc particles.

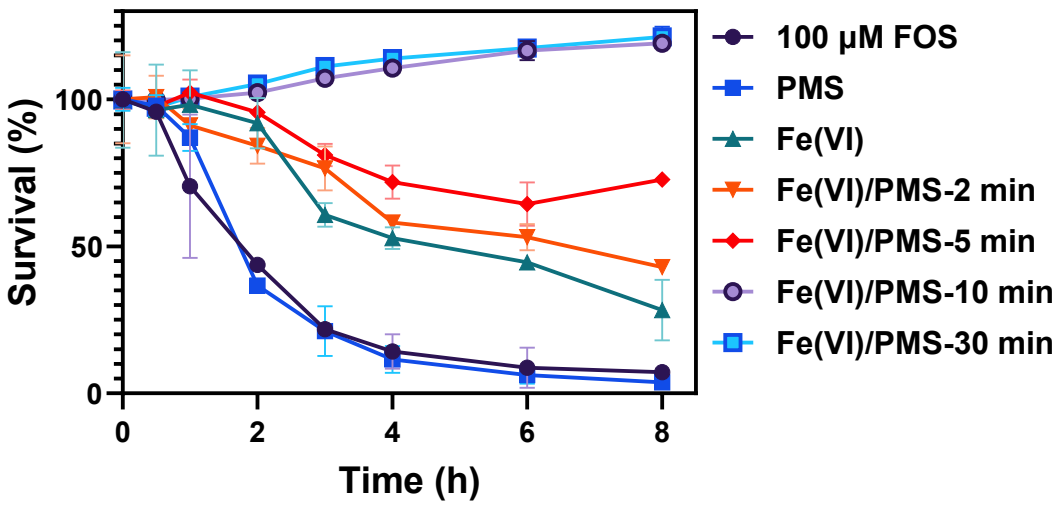


Figure S9. The survival of *E. coli* under the exposure of FOS before and after Fe(VI)/PMS oxidation.

Supplementary Tables

Table S1. Primary properties of various water samples.

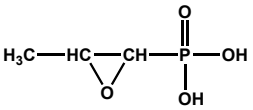
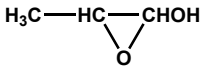
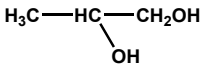
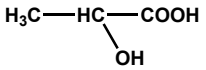
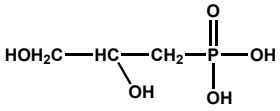
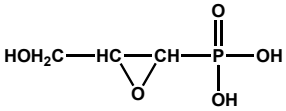
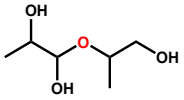
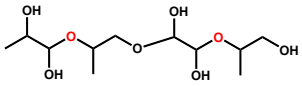
Parameter	Unit	Pearl River water	Tap water	WWTP effluent water	South China Sea water
pH	-	7.23	7.32	6.75	8.17
TOC	mg L^{-1}	4.032	0.889	6.768	1.369
Na^{+}	mg L^{-1}	15.77	13.08	41.17	12408
K^{+}	mg L^{-1}	5.33	2.98	17.68	421
Cu^{2+}	μg L^{-1}	0.98	0.17	0.28	61.23
Mg^{2+}	mg L^{-1}	4.69	2.78	9.37	1552
Cl^{-}	mg L^{-1}	13.96	10.23	54.86	18984.02
HCO_3^{-}	mg L^{-1}	5.33	4.21	4.12	6.01
SO_4^{2-}	mg L^{-1}	22.09	15.71	42.28	2706.02

Table S2. The mobile phase composition and gradient elution for measurement of FOS.

Time(min)	%A	%B
0	98	2
3.0	10	90
5.0	98	2

A: 0.1% formic acid B: methanol
Flow rate: 0.2 mL min^{-1} Temperature: 35 ℃ Injection volume: 2 μL

Table S3. Products of FOS identified by LC-MS and LC-MS/MS in the negative mode.

Compound	Formula	Retention time (min)	Observed m/z	Fragmentation ions (MS^2, m/z)	Structure
FOS	$C_3H_7O_4P$	3.38	137.0008	93.0458, 78.9590, 62.9641	
P1-74	$C_3H_6O_2$	3.02	72.9736	62.9854	
P2-76	$C_3H_8O_2$	8.45	74.9701	67.8836, 55.4528	
P3-90	$C_3H_6O_3$	5.34	88.9881	60.9931	
P4-156	$C_3H_9O_5P$	4.85	154.9774	59.0139	
P5-154	$C_3H_7O_5P$	1.08	152.8949	59.0139	
P6-150	$C_6H_{14}O_4$	11.02	149.0602	120.9545, 63.9926	
P7-298	$C_{12}H_{26}O_8$	15.58	294.1532	183.0120	

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