

Oxidative degradation of tetracycline by magnetite and persulfate: performance, water matrix effect, and reaction mechanism

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Table of contents

Text S1. HPLC-MS/MS operational parameters for identifying the transformation product of tetracycline removed by magnetite/PS

Table S1. Common parameters of municipal effluent wastewater

Table S2. Transformation products (TPs) of tetracycline removed by Fe₃O₄/PS

Figure S1. HPLC peak when TC was removed by only Fe₃O₄

Figure S2. HPLC peak when TC was removed by Fe₃O₄/PS

Figure S3. Reduction in TC concentration in (red) municipal effluent and (black) ultrapure water ([Fe₃O₄] = 1 g/L, [PS]₀ = 1 mM, [TC]₀ = 41.6 μM)

Figure S4. The total ion chromatogram (HPLC-MS/MS) of tetracycline removed by Fe₃O₄/PS and its transformation products in samples taken over the reaction time

Figure S5. Intensity of the fragment chart analysis relating to the transformation products of TC eluted at different retention times

Text S1. HPLC-MS/MS operational parameters for identifying the transformation product of tetracycline removed by Fe₃O₄/PS

The HPLC system was a Vanquish Flex, provided by Thermo Fisher Scientific, USA, and the column used for chromatographic separation was a C18 column (4.6 x 50 mm, 3.5 μm, Eclipse Agilent, USA). The temperature of the HPLC column oven was 35°C, and the pump flow rate was 0.3 mL/min. The sample injection volume was 10 μL, and the HPLC gradient was formed by changing the mix ratio of Milli-Q water, including 0.1% of formic acid (solvent A), and methanol, including 0.1% of formic acid (solvent B). The tandem mass spectrometer equipped with a triple quadrupole was a TSQ Quantis from Thermo Fisher Scientific, USA. For the full-scan mode, the gradient began with 5% B, followed by a linear increase of gradient B up to 100% within 15 mins, following which 100% B was kept running for another 5 mins. Initial gradient conditions were also re-established for 3 mins. A positive ESI ionization mode (ESI⁺) was applied, and the spray voltage was fixed to 4000 V. The scanning m/z range was from 60 Da to 600 Da

Table S1. Common parameters of municipal effluent wastewater.

	Concentrations
pH	6.89
TOC (mg/L)	12.25
Cl ⁻ (mg/L)	77.04
NO ₃ ⁻ (mg/L)	39.08
SO ₄ ²⁻ (mg/L)	50.88
Na ⁺ (mg/L)	52.55
K ⁺ (mg/L)	11.63
Mg ²⁺ (mg/L)	6.43
Ca ²⁺ (mg/L)	32.2
Mn ²⁺ (μg/L)	31.42
Co ²⁺ (μg/L)	0.17
Ni ²⁺ (μg/L)	8.01
Cu ²⁺ (μg/L)	0.83

Table S2. Transformation products (TPs) of tetracycline removed by Fe₃O₄/PS.

Products	m/z value	Retention time (min)	Formula	Structure
Tetracycline	445	5.09	C ₂₂ H ₂₄ N ₂ O ₈	
TP 1	344	10.69	C ₁₈ H ₁₆ O ₇	
TP 2	358	11.06	C ₁₉ H ₁₆ O ₇	
TP 3	274	11.77	C ₁₆ H ₁₇ O ₄	
			C ₁₆ H ₁₅ O ₄	
TP 4	290	12.02	C ₁₆ H ₁₈ O ₅	
TP 5	256	12.92	C ₁₄ H ₂₄ O ₄	
TP 6	284	13.82	C ₁₅ H ₂₄ O ₅	

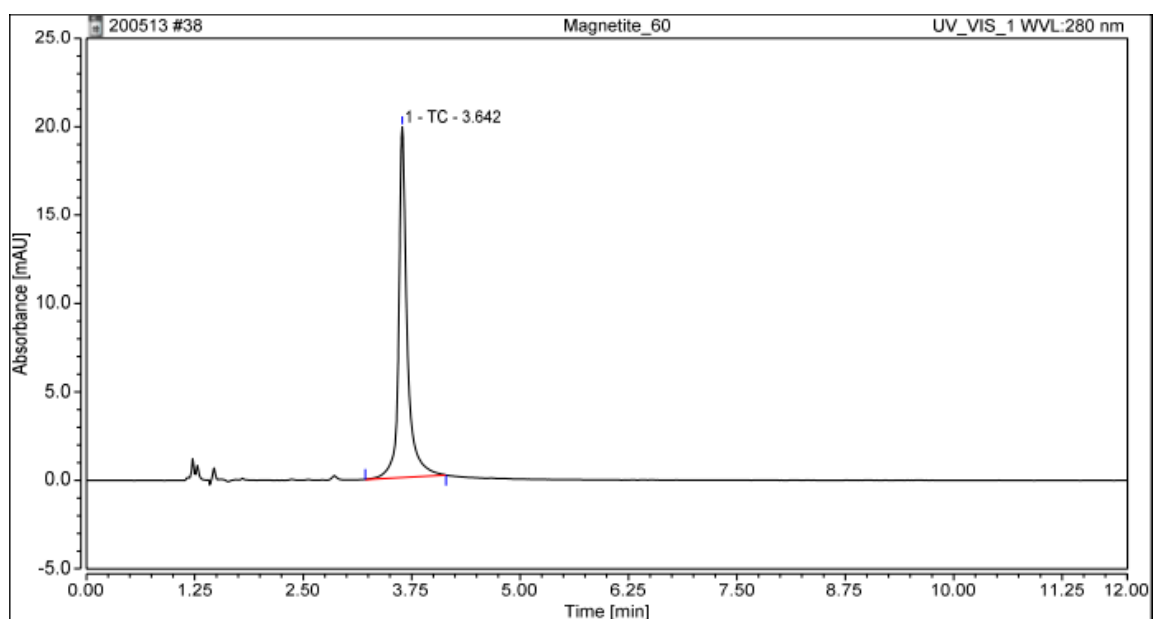


Figure S1. HPLC peak of TC treated by only Fe_3O_4 .

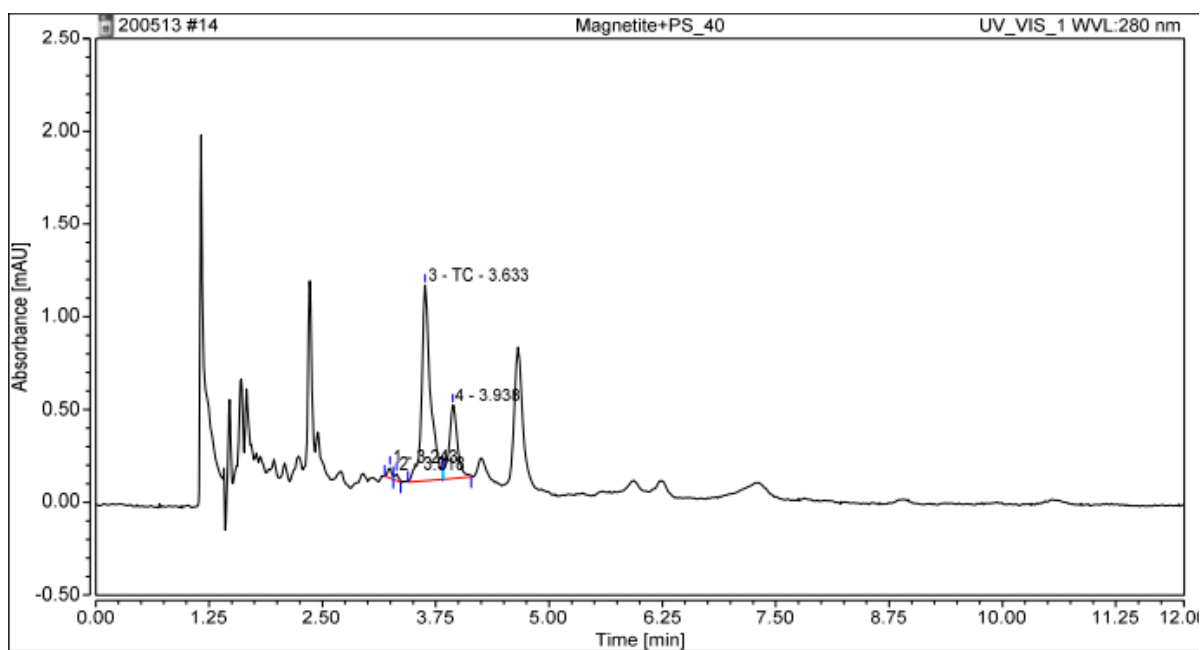


Figure S2. HPLC peak of TC treated by $\text{Fe}_3\text{O}_4/\text{PS}$.

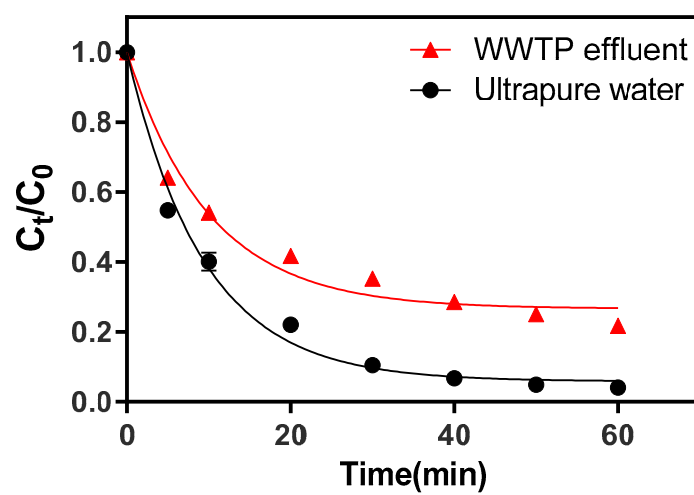


Figure S3. Reduction in TC concentration in (red) WWTP effluent and (black) ultrapure water

($[\text{Fe}_3\text{O}_4] = 1 \text{ g/L}$, $[\text{PS}]_0 = 1 \text{ mM}$, $[\text{TC}]_0 = 41.6 \text{ } \mu\text{M}$).

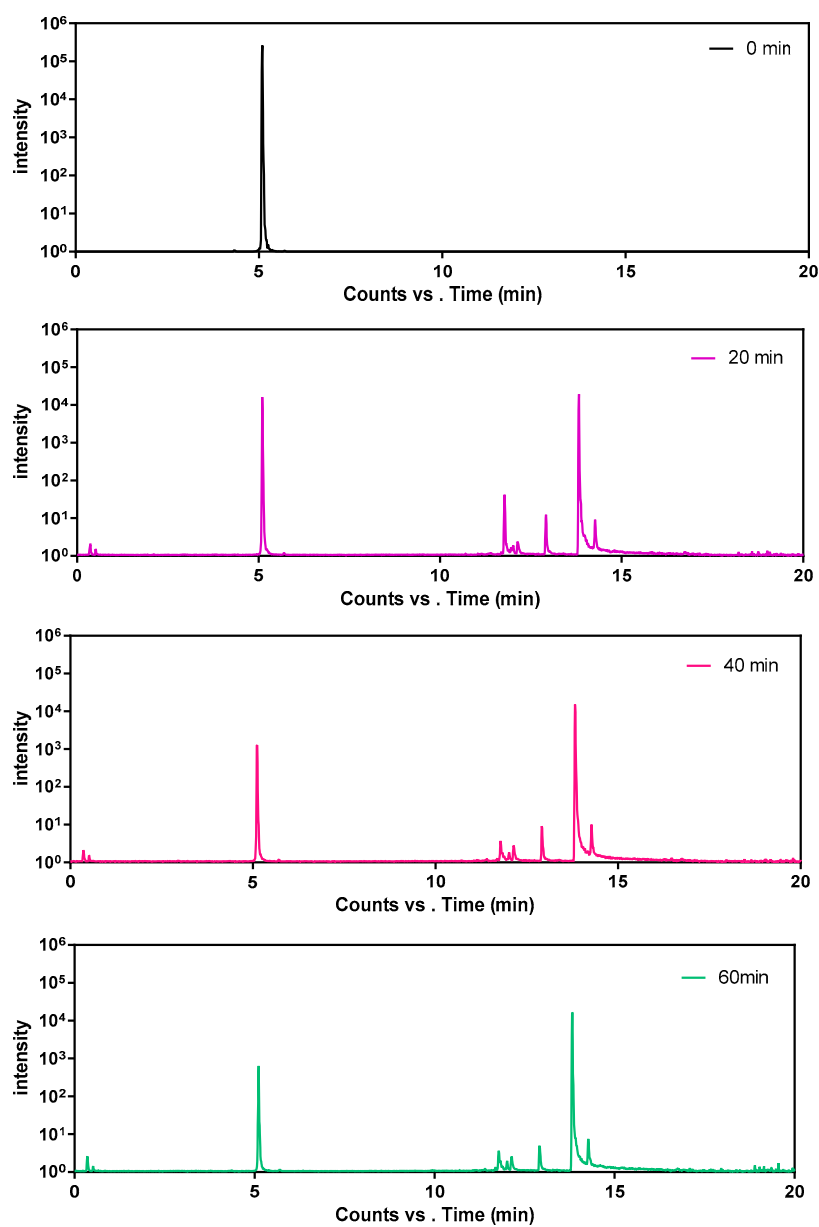


Figure S4. The total ion chromatogram (HPLC-MS/MS) of tetracycline removed by $\text{Fe}_3\text{O}_4/\text{PS}$ and its transformation products in samples taken over the reaction time

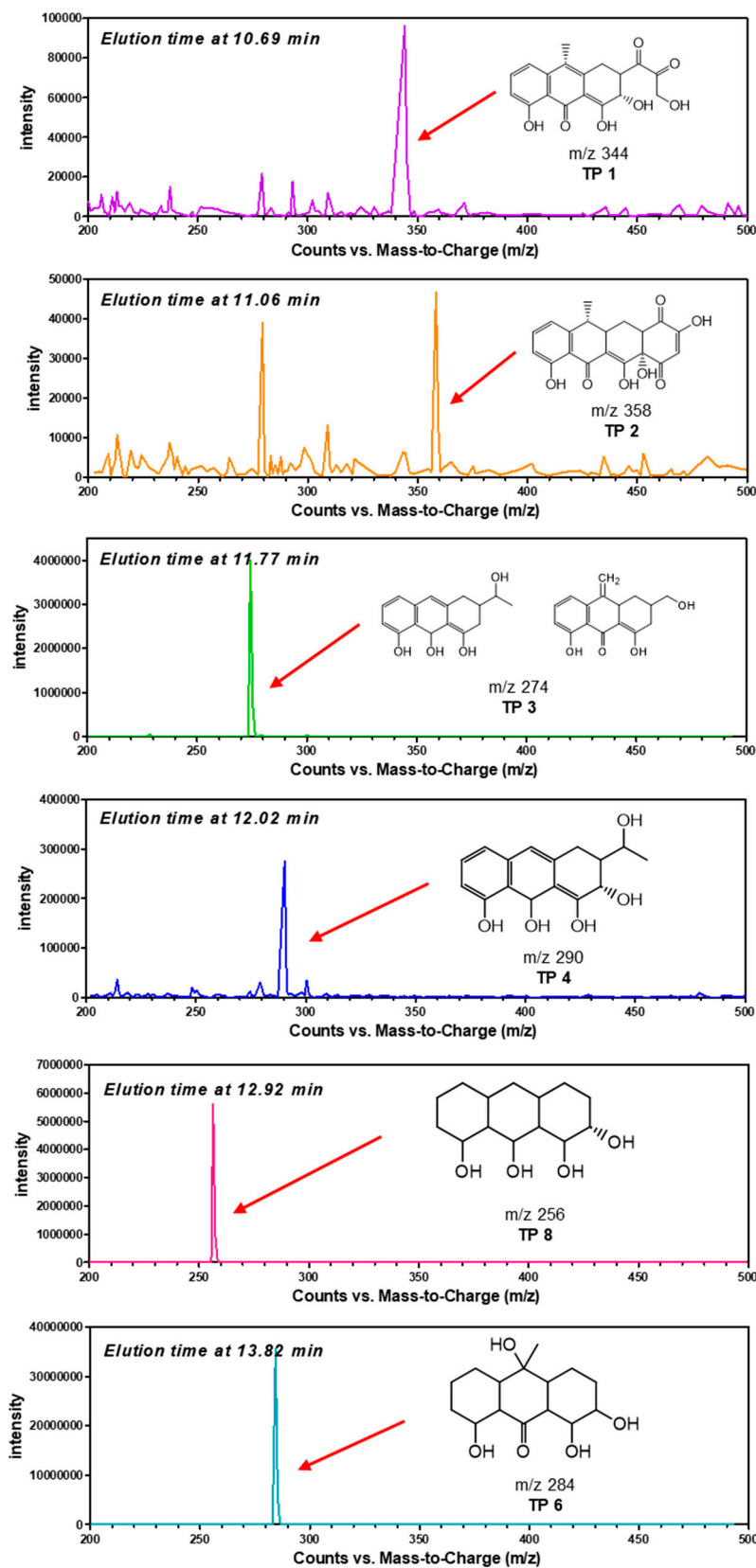


Figure S5. Intensity of the fragment chart analysis relating to the transformation products of TC eluted at different retention times.