

Supporting Information

Optimization of the Electro-Peroxone Process for Micropollutant Abatement Using Chemical Kinetic Approaches

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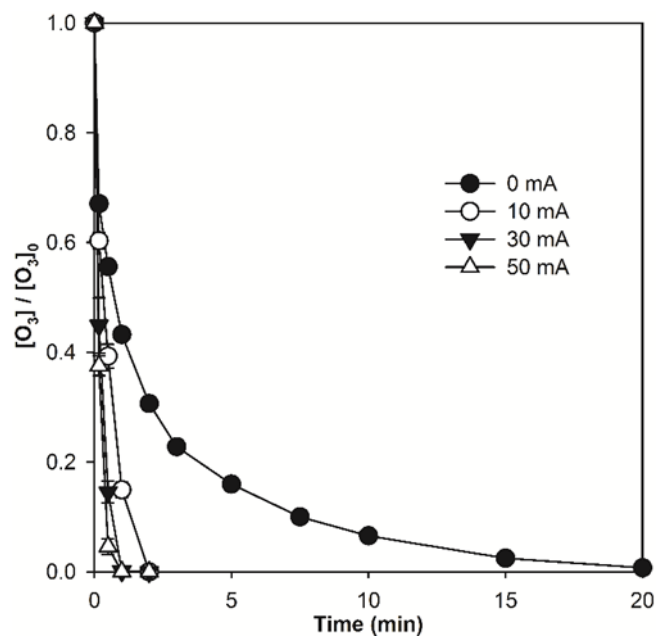


Figure S1. O_3 decay during E-peroxone treatment of surface water at different currents (0 mA (ozonation), 10 mA, 30 mA, and 50 mA). (Reaction conditions: each micropollutant concentration $\sim 150 \mu\text{g/L}$, and specific ozone dose = $1.5 \text{ mg } O_3/\text{mg}$ dissolved organic carbon (DOC)).

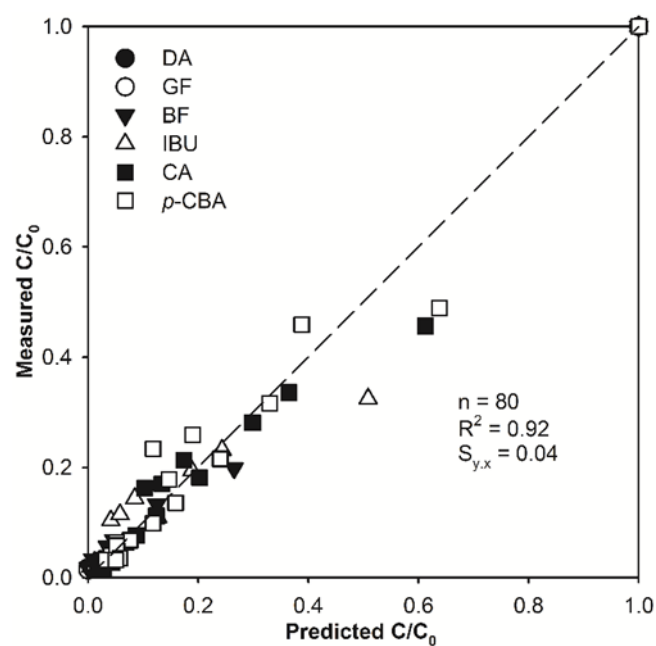


Figure S2. Correlation analysis between experimentally measured and model predicted micropollutant abatement by the E-peroxone process at different currents (0 mA (ozonation), 10 mA, 30 mA, and 50 mA). n is the number of data points, R^2 is the correlation coefficient, and $S_{y,x}$ is the standard deviation of the linear regression with an equation $y=x$. (Reaction conditions: each micropollutant concentration $\sim 150 \mu\text{g/L}$, and specific ozone dose = $1.5 \text{ mg } O_3/\text{mg}$ dissolved organic carbon (DOC)).

To get further into the degradation pathway, the contribution of directly electrolysis (f_E), O_3 oxidation (f_{O_3}), and $\bullet OH$ oxidation ($f_{\bullet OH}$) to micropollutant abatement were calculated at 2 min of E-peroxone process when O_3 was completely depleted according to Equations (S1)–(S3) and presented in Figure. S3.

$$f_E = \frac{k_{Et}}{k_{\bullet OH} \int [\bullet OH] dt + k_{O_3} \int [O_3] dt + k_{Et}} \quad (S1)$$

$$f_{O_3} = \frac{k_{O_3} \int [O_3] dt}{k_{\bullet OH} \int [\bullet OH] dt + k_{O_3} \int [O_3] dt + k_{Et}} \quad (S2)$$

$$f_{\bullet OH} = \frac{k_{\bullet OH} \int [\bullet OH] dt}{k_{\bullet OH} \int [\bullet OH] dt + k_{O_3} \int [O_3] dt + k_{Et}} \quad (S3)$$

where k_E is the pseudo-first order rate constant during electrolysis, and k_{O_3} and $k_{\bullet OH}$ are the second order rate constants with O_3 and $\bullet OH$, respectively.

As shown in Figure. S3, direct electrolysis played negligible role on the removal of all tested micropollutants, with f_E less than 0.2%. This is mainly due to its rather slow abatement kinetics limited by mass transfer of pollutants to the electrode surface [1,2]. As a consequence, O_3 and $\bullet OH$ oxidation dominated micropollutant abatements during the E-peroxone process. For DA and GF with $k_{O_3} > 10^4 M^{-1} s^{-1}$, they were mainly abated via O_3 oxidation ($f_{O_3} > 93\%$). In comparison, BF, IBU, CA, and *p*-CBA have relatively low reactivity with O_3 ($k_{O_3} < 590 M^{-1} s^{-1}$), and thus $\bullet OH$ oxidation dominated their abatements during the E-peroxone process ($f_{\bullet OH} \geq 81\%$).

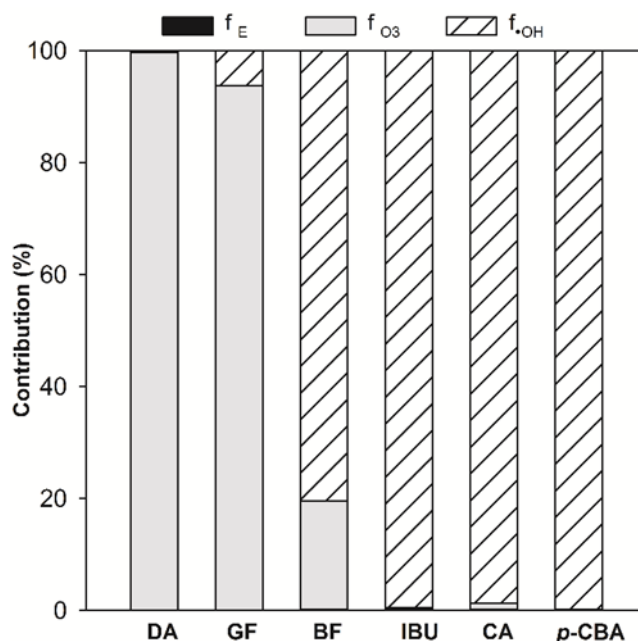


Figure S3. Contribution of electrolysis (f_E), O_3 oxidation (f_{O_3}), and $\bullet OH$ oxidation ($f_{\bullet OH}$) to micropollutant abatement during the E-peroxone treatment of surface water. (Reaction conditions: current = 30 mA, each micropollutant concentration $\sim 150 \mu g/L$, and specific ozone dose = 1.5 mg O_3/mg dissolved organic carbon (DOC)).

The current efficiency (CE) of H₂O₂ electro-generation was calculated according to Equation (S4), where *n* is the number of electrons consumed for converting O₂ to H₂O₂ (2 electrons), *F* is the Faraday constant (96,486 C/mol), *C*_{H₂O₂} is the concentration of H₂O₂ electro-generated (M), *V* is the solution volume (L), *I* is the current (A), and *t* is the reaction time (s).

$$CE(\%) = \frac{nFC_{H_2O_2}V}{\int_0^t Idt} \times 100 \quad (S4)$$

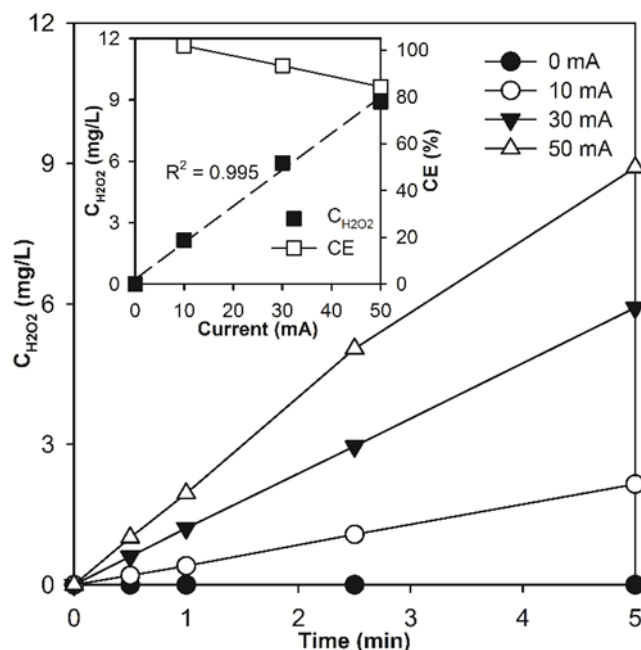


Figure S4. Electro-generation of H₂O₂ from cathodic O₂ reduction in the surface water at different currents. The inset plot shows H₂O₂ concentration at 5 min and H₂O₂ electro-generation current efficiency (CE) as a function of applied currents. (Reaction conditions: volume = 250 mL, current = 30 mA, Pt anode = 2 cm × 2 cm, carbon-PTFE cathode = 2 cm × 5 cm).

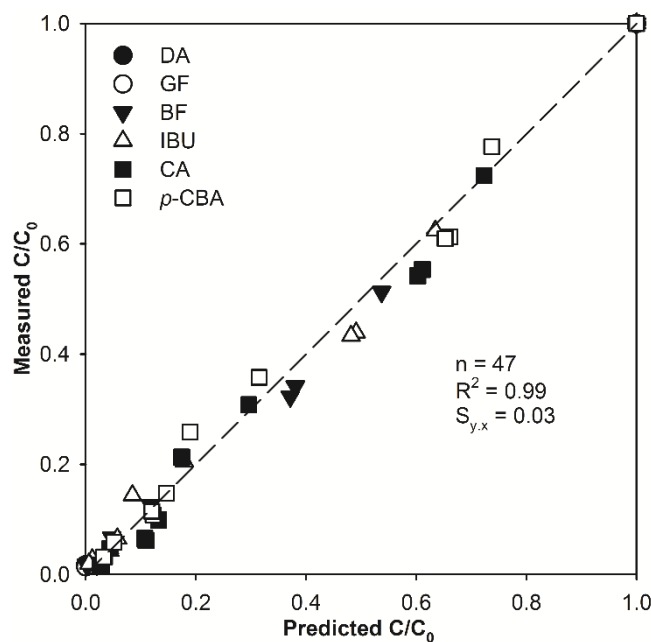


Figure S5. Correlation analysis between experimentally measured and model predicted micropollutant abatement by the E-peroxone process at different specific ozone dose (0.5, 1.0, and 1.5 mg O₃/mg dissolved organic carbon (DOC)). *n* is the number of data points, R² is the correlation coefficient, and S_{y,x} is the standard deviation of the linear regression with an equation *y* = *x*. (Reaction conditions: each micropollutant concentration ~150 μg/L, and current = 30 mA).

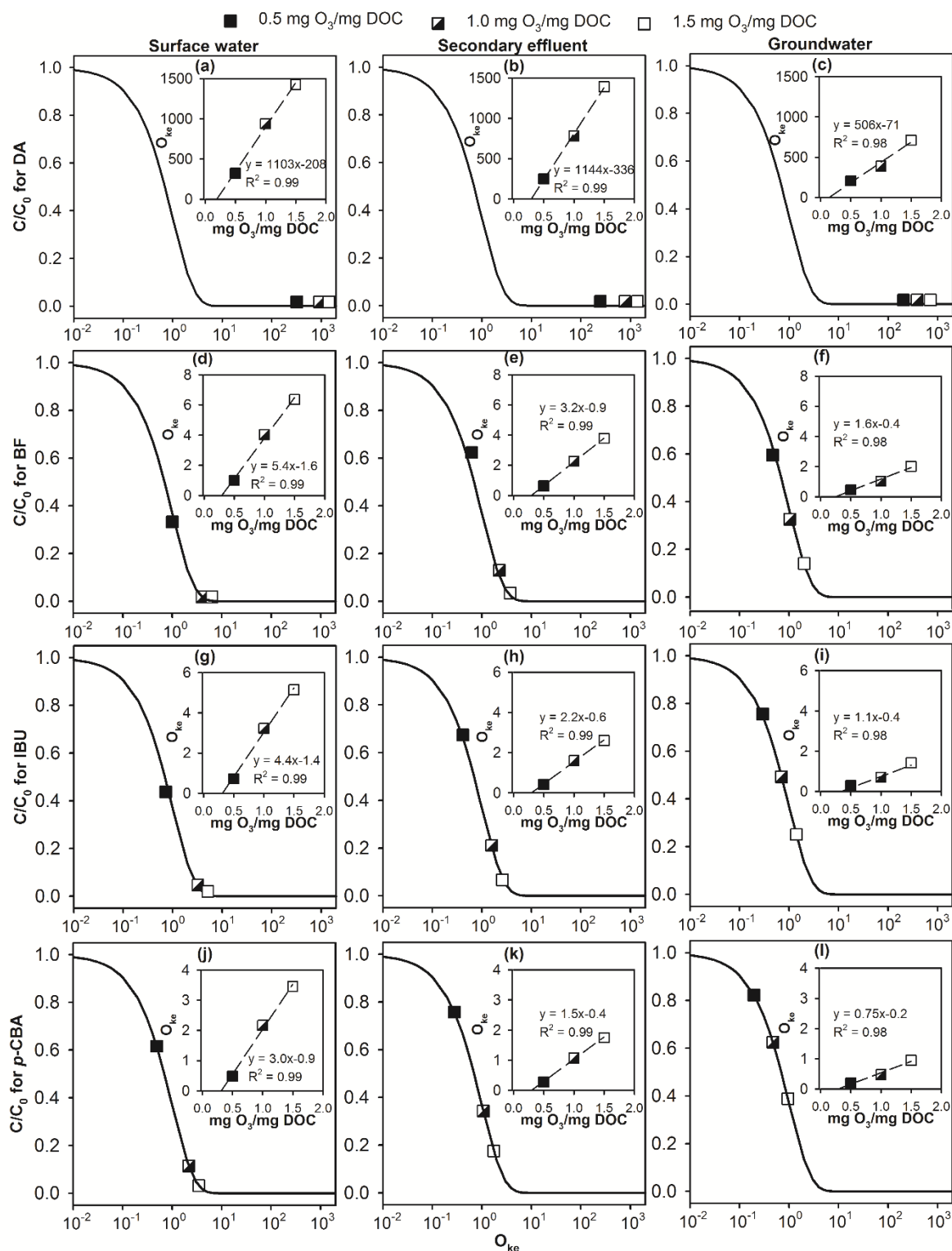


Figure S6. Abatement efficiency of (a–c) diclofenac (DA), (d–f) bezafibrate (BF), (g–i) ibuprofen (IBU), and (j–l) para-chlorobenzoic acid (*p*-CBA) as a function of their O_{ke} values during the E-peroxone treatment of surface water (left column), secondary effluent (middle column), and groundwater (right column) with varying specific ozone (O_3) doses. The symbols in the plot represent experimentally measured results; the solid lines are model simulation using Equation (3). The inset plot shows linear regression between specific O_3 dose and the O_{ke} value observed for selected micropollutant during the E-peroxone process. (Reaction conditions: current = 30 mA, and each micropollutant concentration ~150 $\mu\text{g/L}$).

Table 1. Model compounds used in this study and their second-order reaction rate constants with O₃ and •OH.

Compound	k_{O_3} (M ⁻¹ s ⁻¹)	$k_{\bullet OH}$ (M ⁻¹ s ⁻¹)
Diclofenac (DA)	6.8×10^5 [3]	7.5×10^9 [3]
Gemfibrozil (GF)	5×10^4 [4]	10×10^9 [4]
Bezafibrate (BF)	590 [3]	7.4×10^9 [3]
Ibuprofen (IBU)	9.6 [3]	7.4×10^9 [3]
Clofibric acid (CA)	< 20 [5]	5.2×10^9 [5]
<i>para</i> -chlorobenzoic (<i>p</i> -CBA)	≤ 0.15 [6]	5×10^9 [6]

Table 2. Main water quality parameters of the surface water, secondary effluent, and groundwater used in this study.

Parameter	Surface water	Secondary effluent	Groundwater
pH	8.2	8.0	8.1
DOC (mg/L)	4.0	6.2	1.2
HCO ₃ ⁻ (mg/L)	131	196	295
CO ₃ ²⁻ (mg/L)	2	3	6
Alkalinity (mg/L as CaCO ₃)	110	165	248
Conductivity (µS/cm)	272	857	683
TDS (mg/L)	102	522	371

Table 3. Operational parameters for UPLC/MS-MS analysis and the limits of detection (LOD) and quantification (LOQ) of the tested micropollutants.

Compound	Precursor ion (<i>m/z</i>)	Product ion (<i>m/z</i>)	Declustering potential (V)	Collision energy (eV)	LOD (µg/L)	LOQ (µg/L)
DA	293.9	250.0	-15.0	-12.0	0.8	2.6
GF	249.3	121.0	-25.0	-18.0	0.6	2.1
BF	360.0	274.0	-40.0	-16.0	0.8	2.6
IBU	204.9	161.0	-24.0	-16.7	0.9	2.9
CA	212.8	126.9	-15.0	-20.0	0.8	2.6
<i>p</i> -CBA	154.9	111.0	-35.0	-18.0	1.4	4.7

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