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Supplementary Material

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Text S1. Reagents

Multi-walled carbon nanotubes (CNTs, OD 3–15 nm, length 15–30 μ m, special surface area: 210–280 m² g⁻¹, purity >97 wt.%) was obtained from Guosen Linhang Technology Co., Ltd. (China). Tetrabutyl titanate (Ti(OC₂H₅)₄, 99.0%), cetyltrimethyl ammonium bromide (CTAB, 99.0%), ibuprofen (IBP, 98.0%), and silver nitrate (AgNO₃, 99.8%) were supplied by Aladdin Company (China). Diclofenac (DCF, 99.0%) were obtained from the Chengdu Micxy Chemical Co., Ltd. (China). Superoxide dismutase (SOD, 2000 u mg⁻¹), catalase (CAT, 2000 u mg⁻¹), and humic acid (HA, 98.0 %) were purchased from Sigma-Aldrich Company (China). Nitrobenzene (NB), phenol (99.5%) and tert-butanol (TBA, 99.0%) were obtained from Chengdu Kelong Chemical Co., Ltd. (China). Other chemicals were purchased from Chongqing Chuandong Chemical Co., Ltd. (China). All the chemicals used in this study were analytical grade or higher and used without further purification.

For water matrix experiment, surface water was collected from the Yangtze River in Chongqing and tap water was taken from the laboratory of Chongqing University. Other aqueous solutions and mobile phase were prepared with ultrapure water (resistivity of $18.2 \text{ M}\Omega$ cm).

Text S2. The calculation formula of hydraulic gradient

Re

$$=\frac{nd_j^2\rho}{\mu}$$

$$P_{h} = N_{p}\rho n^{3}d_{j}^{5}$$

$$G = \sqrt{\frac{P_{h}}{\mu}}$$

where Re is the Reynolds number, n is rotation speed (r s⁻¹), d_j is blade diameter (m), ρ is density of solution (kg m⁻³), μ is liquid viscosity coefficient (Pa s), P_h is the power provided by the agitator (W), N_p is the power number, ρ is the density of the solution (kg m⁻³), n is the rotation speed (r s⁻¹), d_j is the blade diameter (m), *G* is the hydraulic gradient (s⁻¹).

Text S3. Model dimension and Simulation Settings

A. Model dimension for ansys fluent

The size of the reaction container: R=7 cm; H=12 cm; the size of the rotor: r = 3.5 cm, h = 8 mm. Adopt sliding mesh.

B. Simulation Settings for ansys fluent

Set gravity along y axis (~ 9.81m s^{-2}), and selected transient state for calculation in General term. There was air and water in the container. Thus, multi-Fluid VOF model was selected. The surface tension of the gas-liquid phase was set to a constant value of 0.073. Moreover, realizable k-epsilon and scalable wall functions were chosen as the viscous model. Inner fluid adopted mesh motion, and set rotation axis direction as (0, 1, 0). Under the boundary conditions, the turbulent intensity was 5%, hydraulic diameter was 25 mm. The rest of the options took the default values.

C. Detailed description of the COMSOL simulation

The combination of solid mechanics field and static electric field was used to simulate piezoelectric effect. The model consisted of a cubic-like BT crystal with the side length of 100 nm. The other material parameters used in this simulation, such as density ($\rho = 6020$ kg m⁻³), elasticity matrix (*cE*), coupling matrix (*eES*), and relative permittivity (ε_r) of BT were available as predefined material parameters in COMSOL Multiphysics. The polarization was aligned along the global co-ordinate z axis, while the center was fixed and grounded. It was assumed that the analog pressure on the cube was the maximum dynamic pressure under the specific hydraulic gradient.

Text S4. Characterization structure and morphology characterization

Phase composition and crystal structure were analyzed using X-ray diffraction (XRD, Cu Kα source, 40 kV-40 mA, Spectris Pte. Ltd) over the 2θ range from 20° to 80° at a scan rate of 7° min⁻¹, and Raman spectroscopy was carried out using a 100 mW laser with a wavelength of 532 nm equipped at room temperature to further analyze the phase of BT (HORIBA Jobin Yvon S.A.S company, France). Changes of elements and their chemical states of BT were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo, USA).

Text S5. Synergistic index (SI)

SI

$$= \frac{k (PE - O_3)}{k (PE) + k (O_3)}$$

where SI denotes the synergetic index, k (PE-O₃), k (O₃), and k (PE) denote the

pseudo-first-order rate constants of PE-O₃, O₃, and PE processes, respectively (min⁻¹).

Text S6. Electrical energy per order (EEO)

The electrical energy per order (EEO) during NB degradation was calculated according to Eq. S5–S6.

$$EEO = \frac{P_{in}t + rC_{O_3}}{Vlog(C_0/C_t)}$$
(5)
$$C_{O_3} = Q_g \int_0^t ([O_3]_{inlet} - [O_3]_{outlet})dt$$
(6)

EEO here is the electrical energy per order (kWh·m⁻³·order⁻¹) with the subscripts identifying the various processes. Where P_{in} denotes the input power provided by hydroenergy (kW), t is the reaction time (h), r is the energy required to produce the O₃ used. The energy required to generate 1 g of O₃ was assumed to be 0.012 kWh¹. ^CO₃ is the consumption of O₃ (g). TOC₀ and TOC_t represent solution TOC concentrations at times t = 0 and t (g L⁻¹), V is the solution volume (L). ^CO₃ is the consumption of O₃ (g). V is the volume of reaction solution (L), C₀ is the initial concentration of contaminant (μ M), C_t is the contaminant concentration at time t (μ M). Q_g is the gas flow rate (L min⁻¹). [O₃]_{inlet} and [O₃]_{outlet} are the gas phase O₃ concentration (mg L⁻¹) at the gas inlet and outlet of the reactor, respectively.

Text S7. Inhibitory efficiency

The inhibitory efficiency was used to further explore the role of each reactive species.

η

$$=\frac{k_0 - k_{\rm s}}{k_0} \times 100\%$$

where η represents the inhibition efficiency, k_0 represents the pseudo-first-order rate constants of the PE-O₃ process without scavenger (min⁻¹), k_s denotes the pseudofirst-order rate constants of the PE-O₃ process with a certain scavenger (min⁻¹).



Fig. S1. The schematic of the reactor for piezoelectric catalysis, ozonation, and piezocatalysis ozonation treatment for NB.



Fig. S2. The adsorption of NB by BT (initial NB concentration = 100 μ M, BT dosage = 3 g L⁻¹, rotation rate = 100 rpm; pH₀ = 9.6 (without adjustment); T = 298 ± 1 K).



Fig. S3. NB removal ratio in PE, O₃, and PE-O₃ processes (inlet O₃ gas phase concentration = 14 mg L⁻¹; sparging gas flow rate = 0.3 L min⁻¹, initial NB concentration = 100 μ M, BT dosage = 3 g L⁻¹, G = 15.82 s⁻¹; pH₀ = 9.6 (without adjustment); T = 298 ± 1 K).



Fig. S4. The change of pH under different initial pH in PE-O₃ process. (inlet O₃ gas phase concentration = 14 mg L⁻¹; sparging gas flow rate = 0.3 L min⁻¹, initial NB concentration = 100 μ M, BT dosage = 3 g L⁻¹, G = 15.82 s⁻¹, T = 298 ± 1 K).



Fig. S5. The inhibition ratio of different scavengers for NB removal in PE-O₃ process (inlet O₃ gas phase concentration = 14.0 mg L⁻¹, sparging gas flow rate = 0.3 L min⁻¹, initial NB concentration = 100 μ M, BT dosage = 3.0 g L⁻¹, initial TBA concentration = 100 mM, initial AgNO₃ concentration = 1 mM, initial AO concentration = 10 mM, initial SOD concentration = 500 u mL⁻¹, initial CAT concentration = 500 u mL⁻¹, T = 298 ± 1 K).



Fig. S6. Comparison of NB degradation by PE-O₃ process in ultrapure water, tap water and surface water (inlet O₃ gas phase concentration = 14 mg L⁻¹; sparging gas flow rate = 0.3 L min⁻¹, initial pollutant concentration = 100 μ M, BT dosage = 3 g L⁻¹, $G = 15.82 \text{ s}^{-1}$; pH₀ = 9.6 (without adjustment); T = 298 ± 1 K).



Fig. S7. (a) Stability tests of BT for the degradation of NB in PE-O₃ process (inlet O₃ gas phase concentration = 14 mg L⁻¹; sparging gas flow rate = 0.3 L min⁻¹, initial NB concentration = 100 μ M, BT dosage = 3 g L⁻¹, *G* = 15.82 s⁻¹, pH₀ = 9.6 (without adjustment), T = 298 ± 1 K) and (b) Typical XPS survey spectra of Ti in BT crystallites (the virgin BT and the BT reused for 10 times).



Fig. S8. Typical XPS survey spectra of (a) Ba and (b) O in BT crystallites (the virgin BT and the BT reused for 10 times).



Fig. S9. Typical XRD survey spectra of BT crystallites before and after reaction (the virgin BT and the BT reused for 10 times).

Constituent	Ultrapure water	Tap water	Surface water
рН	7.00	7.32	7.83
DOC (mg L ⁻¹)	0	1.02	11.52
UV ₂₅₄ (cm ⁻¹)	-	0.03	0.22
CO ₃ ²⁻ (mg L ⁻¹)	-	0.92	1.94
HCO ₃ - (mg L ⁻¹)	-	105.00	172.00
Cl ⁻ (mg L ⁻¹)	-	6.10	22.94
SO ₄ ²⁻ (mg L ⁻¹)	-	113.62	313.65
PO_4^{3-} (mg L ⁻¹)	-	1.56	3.86
NO ₃ ⁻ (mg L ⁻¹)	-	2.89	14.15
Ammonia (mg-N L ⁻¹)	-	-	1.75

Table S1. Water quality parameters of the ultrapure water, tap water, and surface water.

Table S2. Comparison of catalyst stability and metal leakage in ozone-based

Catalyst	Reaction conditions	Stability	Metal leaching	Ref.
MIL-88A	$[SA]_0 = 100 \text{ mg } L^{-1},$	The catalytic effect was	Fe: 0.80 mg L ⁻¹	2
$(Fe_{0.80}Ce_{0.20})$	$[O_3] = 216.0 \text{ mg h}^{-1},$	significantly reduced after	Ce: 0.60 mg L ⁻¹	
	$[catalyst]_0 = 0.1 \text{ g L}^{-1}$	4 cycles		
$MnFe_2O_4$ and	$[PNT]_0 = 0.2 \text{ mM},$	No significant change	Mn: 0.04 mg L ⁻¹	3
NiFe ₂ O ₄	$[O_3] = 21.6 \text{ mg h}^{-1},$	after 1 cycle	Ni: 0.36 mg L ⁻¹	
	$[catalyst]_0 = 2.0 \text{ g L}^{-1}$			
Cu-O-Mn/y-	$[PVA]_0 = 20 \text{ mg } L^{-1},$	The catalytic effect was	Mn: 0.03 mg L ⁻¹	4
Al ₂ O ₃	$[O_3] = 331.2 \text{ mg h}^{-1},$	reduced by 2.20% after 5	Cu: 0.01 mg L ⁻¹	
	$[catalyst]_0 = 0.1 \text{ g } L^{-1}$	cycles		
LaFeO ₃	$[BZA]_0 = 10 \text{ mg } L^{-1},$	The crystal structure was	La: 6.00 mg L ⁻¹	5
	$[O_3] = 2.0 \text{ mg } L^{-1},$	stable after 1 cycle	Fe: 2.50 mg L ⁻¹	
	$[catalyst]_0 = 0.5 \text{ g } L^{-1}$			
BaTiO ₃	$[NB]_0 = 20 \text{ mg } L^{-1},$	The catalytic effect was	Not detected	This study
	$[O_3] = 170.0 \text{ g h}^{-1},$	reduced by 4.60% after 10		
	[BT] ₀ =3.0 g L ⁻¹	cycles		

advanced oxidation processes.

References

- A. N. Pisarenko, B. D. Stanford, D. Yan, D. Gerrity and S. A. Snyder, *Water Res.*, 2012, 46, 316–326.
- D. Yu, L. Wang, T. Yang, G. Yang, D. Wang, H. Ni and M. Wu, Chem. Eng. J., 2021, 404, 127075.
- 3. F. Qi, B. Xu and W. Chu, J. Mol. Catal. A: Chem., 2015, 396, 164-173.
- Z. Yan, J. Zhu, X. Hua, D. Liang, D. Dong, Z. Guo, N. Zheng and L. Zhang, J. Clean. Prod., 2020, 272, 122856.
- Y. Zhang, Y. Xia, Q. Li, F. Qi, B. Xu and Z. Chen, Sep. Purif. Technol., 2018, 197, 261–270.