Supporting Material

Insights into the Electron Transfer Mechanisms of Permanganate Activation by Carbon Nanotube Membrane for Enhanced Micropollutants Degradation

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Supporting Information: 5 Texts, 3 Tables, and 10 Figures.

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Text S1. Chemicals and reagents.

Sulfamethoxazole (SMX, 98.0%), bisphenol A (BPA, >99.8%), p-Nitrophenol (PNP, 98.0%),benzoic acid (BA, ⩾ 99.5%), 2,2,6,6-tetramethylpiperidine (TEMP, ≥98.0%), 5,5-dimethyl-1-pyrrolidine-N-oxide (DMPO, 97.0%), pyrophosphate (PP, 99.0%), and methyl phenyl sulfoxide (PMSO, >98.0%) were obtained from Shanghai Aladdin Biological Technology Co., Ltd. (China). Permanganate ($KMnO_4$), sodium chloride (NaCl, ≥98.0%), sodium sulfate (Na_2SO_4, ≥99.0%), potassium nitrate (KNO_3, ≥98.5%), and ethanol (≥96.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Methanol (≥99.9%), phosphoric acid, formic acid and acetonitrile (≥99.9%, chromatographic grade) were purchased from Titan Scientific Co., Ltd. (China). Multiwalled carbon nanotubes (CNT) (<d> = 10-20 nm and <l> = 0.5-2.0 μm) were supplied by Nanjing XFNANO Materials Tech Co., Ltd. (China). The 5 μm polytetrafluoroethylene (PTFE) support membranes (<d> = 47 mm) were purchased from Millipore (Omnipore JWMP, USA).

Text S2. Preparation of CNT filters.

The CNT filter can be fabricated by a facile vacuum filtration route. Briefly, 25 mg of CNT powders were dispersed into 40 mL N-mmethyl-2-pyrrolidinone (NMP) and probe-sonicating for 40 min (100 W, LABSONIC® M, Sartorius) to achieve a homogeneous suspension solution. The mixture was then vacuum-filtered onto a PTFE membrane and washed sequentially with 100 mL of ethanol and 200 mL of DI-H_2O before use.

Text S3. Calculation of oxidation flux.

Oxidation flux was used to quantify the filtration performance according to the following equation. (Guo et al., 2021)

$$\text{Oxidation Flux} = \frac{(EACTC_{inf} - EACTC_{eff})(\text{mmol}\cdot L^{-1}) \times \text{flow rate}(L\cdot h^{-1})}{\text{effective filter area } (m^2)} \quad (1)$$

where $EACTC_{inf}$ and $EACTC_{eff}$ correspond to the influent and effluent concentrations of EACTC, respectively. An Effective filter area represents the area that is permeable to a solution *i.e.* 7.1×10^{-4} m^2.

Text S4. Computational methods.

The theoretical calculations were performed via the Gaussian 16 suite of programs. The structure of the studied systems was optimized at the B3LYP-D3BJ/6-311G(d) level of theory. The solvent effect (H_2O) was included in the calculations using the solvation model based on the density (SMD) model. The vibrational frequencies of the optimized structures were carried out at the same level. The structures were characterized as a local energy minimum on the potential energy surface by verifying that all the vibrational frequencies were real. The molecular orbital levels of studied compounds were investigated via theoretical calculations, including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The Visual Molecular Dynamics (VMD) program(William Humphrey, 1996) was used to plot the color-filled iso-surface graphs to visualize the molecular orbitals.

Text S5. Toxicity Estimation of Intermediates.

The toxicity assessment of SMX intermediates is also a manifestation of application potential of the CNT/$KMnO_4$ system, the quantitative structure activity relationship (QSAR) approach was executed to analyze the mutagenicity, acute toxicity, bioaccumulation factor and developmental toxicity of SMX and its intermediates via using Toxicity Estimation Software Tool (T.E.S.T., US, EPA). From Fig. S6(a), all the intermediates have the negative mutagenicity, including SMX. In addition, for oral rat LD_{50} and bioaccumulation factor, all the intermediates have lower toxicity than SMX (Fig. S6(b) and Fig. S6(c)). For developmental toxicity, SMX is 0.85, some intermediates

have lower toxicity than SMX (Fig. S6(d)). But only one toxic intermediate is produced, especially, the developmental toxicity of TP4 is 0.95. In all, the above results show that the CNT/$KMnO_4$ system cannot only accomplish the oxidation of SMX but also the decreases the toxicity of SMX.

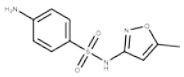
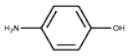
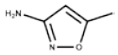
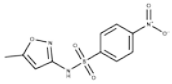
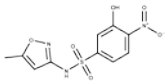
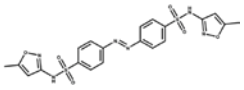
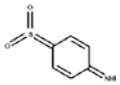
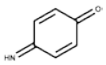
Table S1. HPLC operation parameters for different substrates.

Substrates	Methanol	Acetonitrile	DI (0.1% phosphoric acid)	DI (0.1% phosphoric acid)	DI	Detection wavelength (nm)	Flow rate (mL/min)
SMX	30	-	70	-	-	300	1.0
BPA	70	-	-	-	30	230	1.0
PNP	-	60	-	40	-	250	0.5
BA	-	50	-	50	-	227	1.0

Table S2. The molecular orbital energy of SMX, $KMnO_4$ and CNT.

Samples	E_{HOMO} (eV)	E_{LUMO} (eV)	The different of HOMO and LUMO	HOMO-LUMO gap
SMX	-6.108563	-1.015086	5.093477	5.093477
CNT	-3.532174	-3.008827	0.523347	0.523347
$KMnO_4$	-6.235399	-2.585211	3.650188	3.650188

Table S3. Transformation intermediates of SMX detected by UPLC-QTOF-MS/MS.

Product number	ESI (+/-)	Rt (min)	m/z	Molecular formula	Proposed structure
SMX	+	6.465	254.0607	$C_{10}H_{11}N_3O_3S$	
TP1	+	6.216	110.0606	C_6H_7NO	
TP2	+	2.97	99.0558	$C_4H_6N_2O$	
TP3	-	8.8	284.0348	$C_{10}H_9N_3O_5S$	
TP4	+	8.022	300.0296	$C_{10}H_9N_3O_6S$	
TP5	+	9.777	503.0816	$C_{20}H_{18}N_6O_6S_2$	
TP6	+	2.788	155.003	$C_6H_5NO_2S$	
TP7	+	6.216	108.0451	C_6H_5NO	

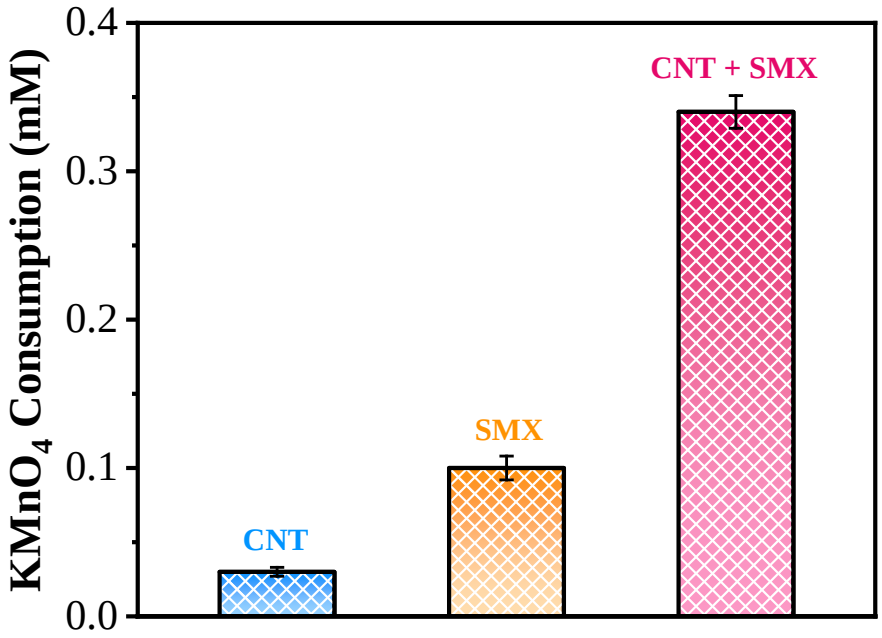


Fig. S1 The consumption of $KMnO_4$ in different system. Experimental conditions: $[SMX]_0$ = 80 μM, $[KMnO_4]_0$ = 1.0 mM, flow rate = 0.5 mL/min, and pH = 6.2.

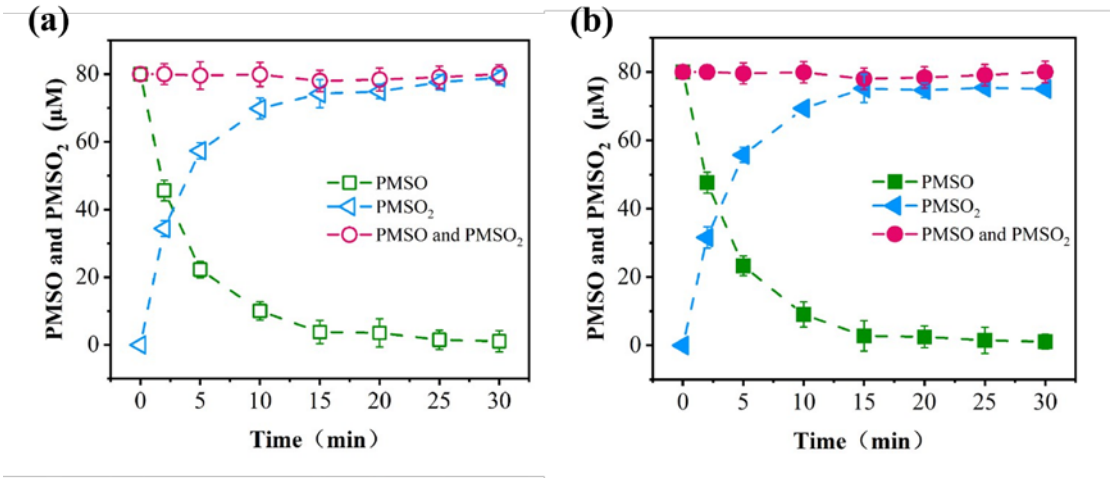


Fig. S2 The variation of PMSO and $PMSO_2$ in the (a) $KMnO_4$ alone system and (b) CNT/$KMnO_4$ system. Experimental conditions: $[PMSO]_0$ = 80 μM, flow rate = 0.5 mL/min, and pH = 6.2.

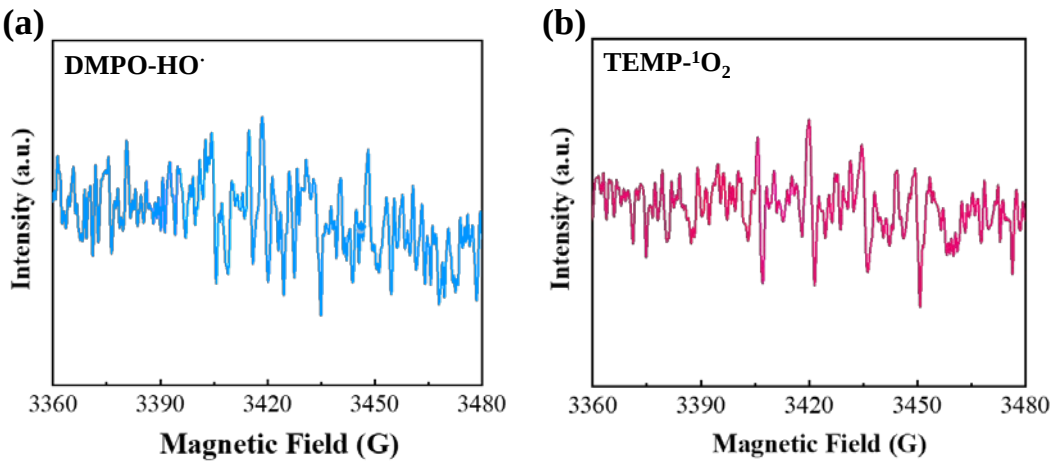


Fig. S3 Identification of ROS: (a) EPR characterization using DMPO; (b) EPR characterization using TEMP.

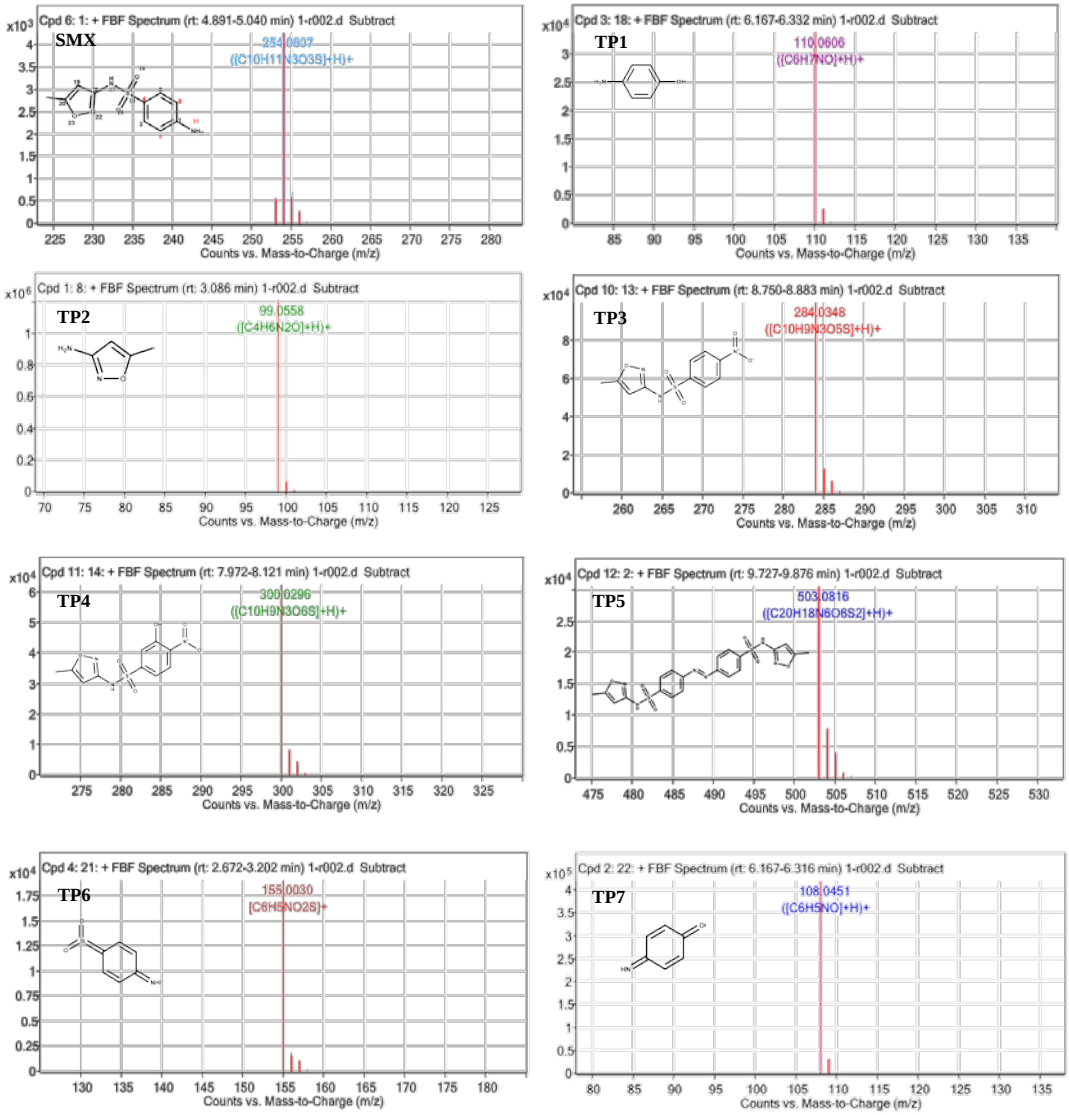


Fig. S4 Mass spectrum of SMX and intermediates during the SMX oxidation in the $KMnO_4$/CNT system.

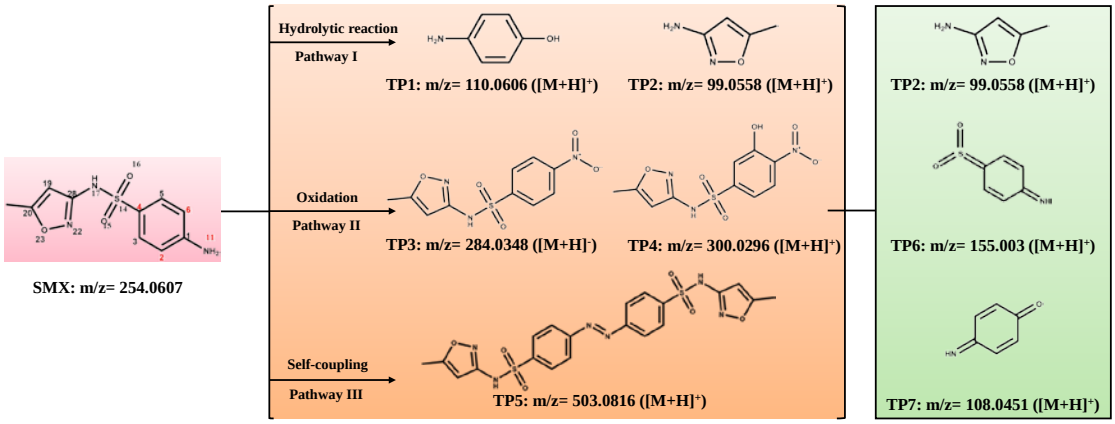


Fig. S5 Possible degradation pathways of SMX in the $KMnO_4$/CNT system.

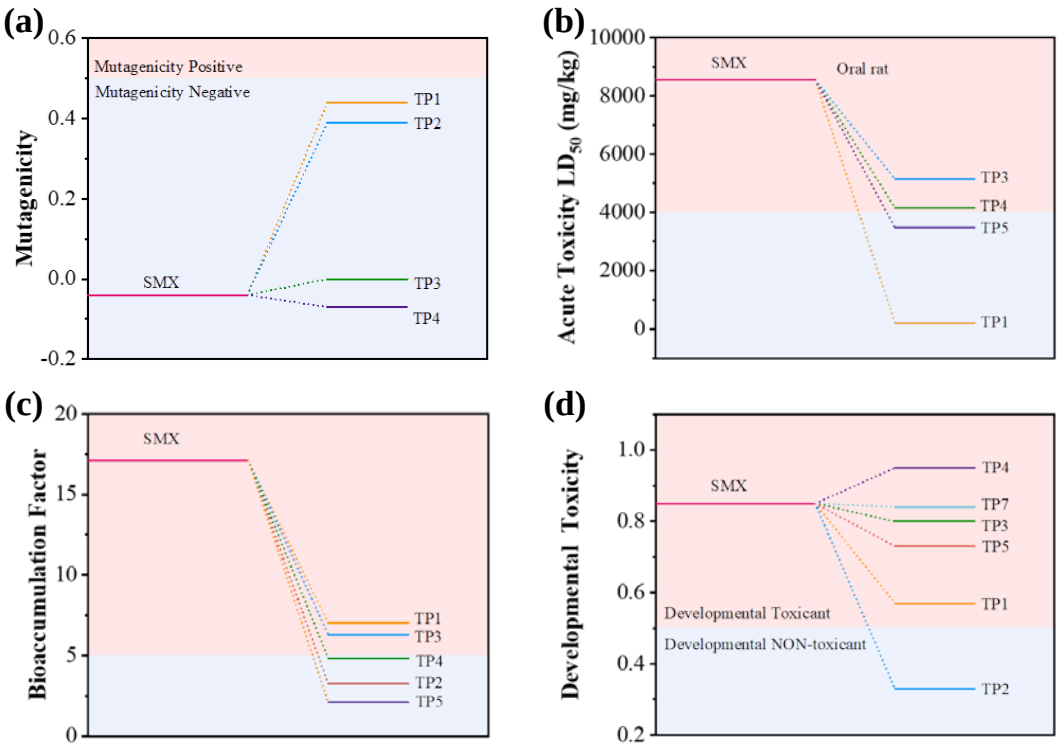


Fig. S6 (a) Mutagenicity, (b) acute toxicity, (c) bioaccumulation factor and (d) developmental toxicity of SMX and oxidation intermediates.

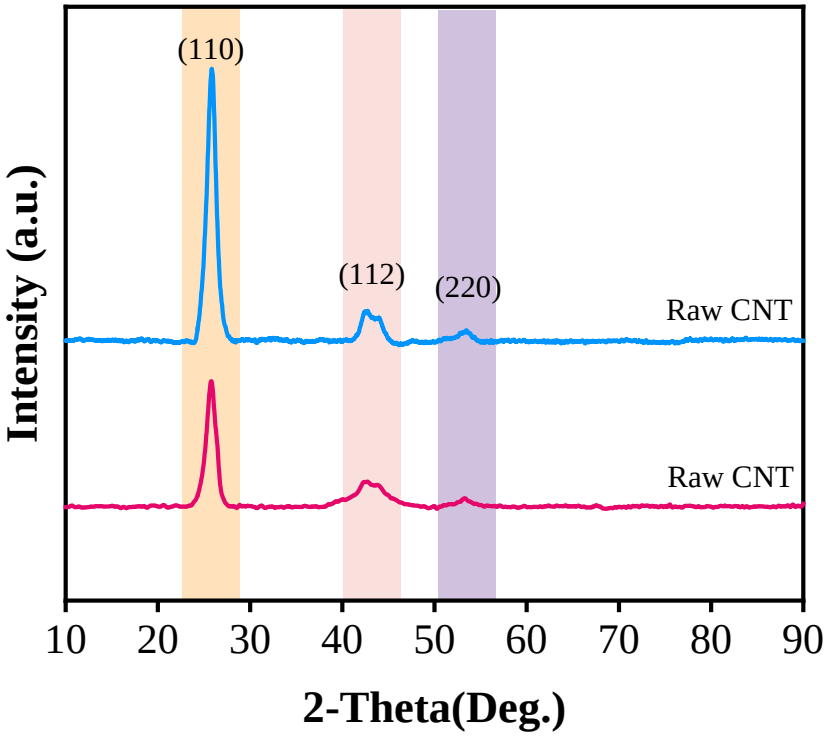


Fig. S7 Comparison of XRD patterns of raw and used CNT filter.

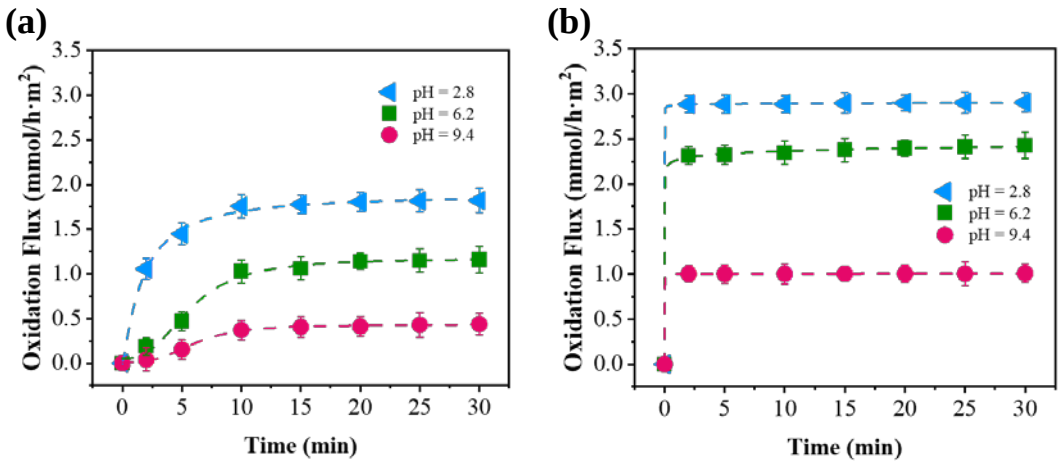


Fig. S8 Effects of solution pH on SMX oxidation in the (a) $KMnO_4$ alone system and (b) CNT/$KMnO_4$ system.

Experimental conditions: $[SMX]_0$ = 80 μM, $[KMnO_4]_0$ = 1.0 mM, flow rate = 0.5 mL/min.

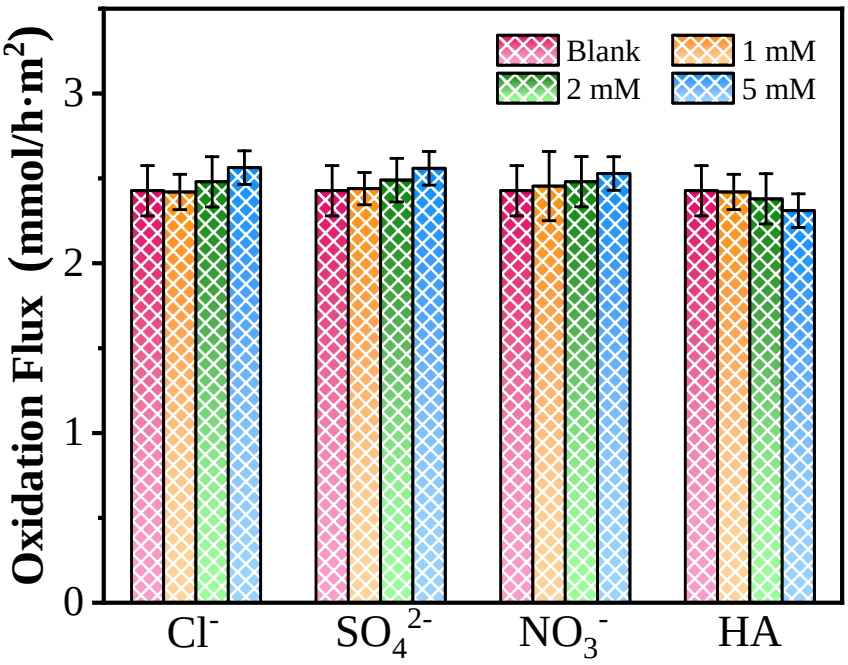


Fig. S9 Effects of (a) Cl^-, (b) SO_4^{2-}, (c) NO_3^- and (d) HA on SMX oxidation kinetics in the $KMnO_4$/CNT system.

Experimental conditions: $[SMX]_0$ = 80 μM, $[KMnO_4]_0$ = 1.0 mM, flow rate = 0.5 mL/min, and pH = 6.2.

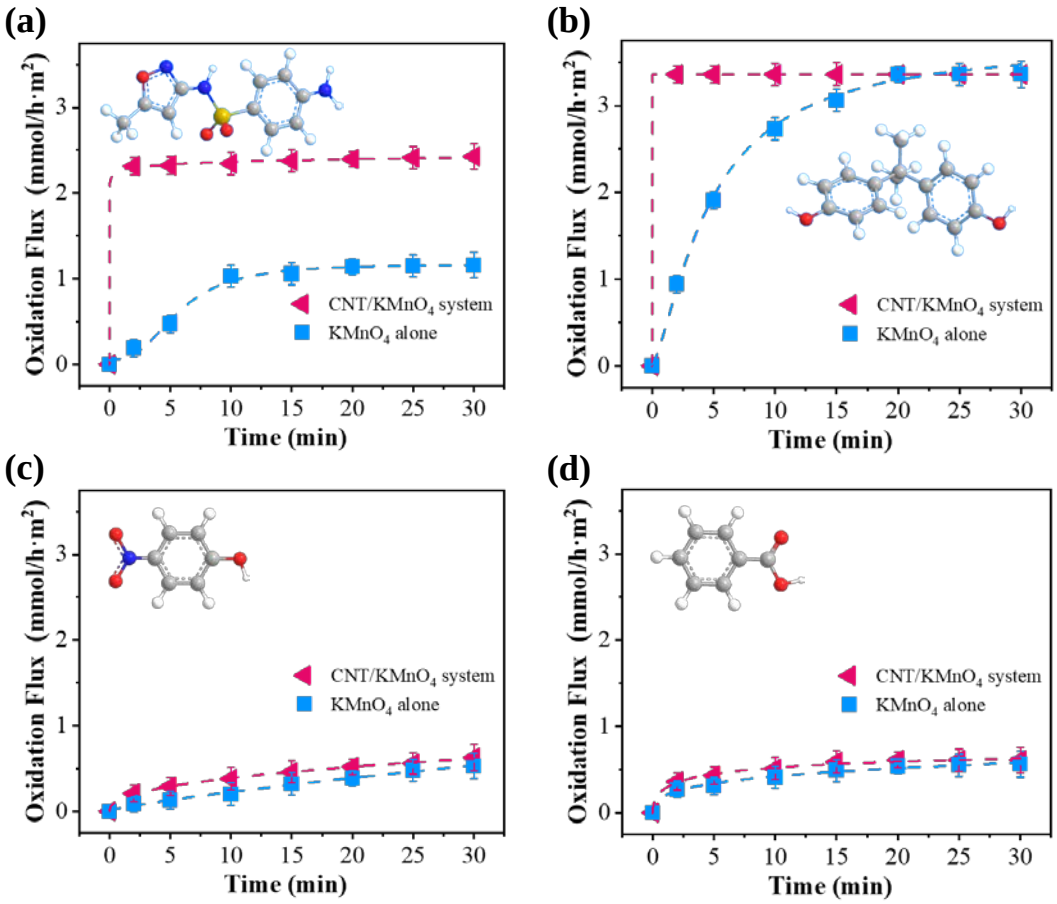


Fig. S10 The oxidation of various organic pollutants in the $KMnO_4$ alone and CNT/$KMnO_4$ system. Experimental conditions: $[SMX]_0 = [BPA]_0 = [PNP]_0 = [BA]_0 = 80$ μM, $[KMnO_4]_0 = 1.0$ mM, flow rate = 0.5 mL/min, and pH = 6.2.

References

Guo D L, Liu Y B, Ji H D, Wang C C, Chen B, Shen C S, Li F, Wang Y X, Lu P, Liu W (2021). Silicate-enhanced heterogeneous flow-through electro-Fenton system using iron oxides under nanoconfinement. Environmental Science Technology, 55(6): 4045-4053

William Humphrey A D, And Klaus Schulten (1996). VMD: Visual Molecular Dynamics. Journal of Molecular Graphics and Modelling, 14: 33-38