Supporting Information

Revealing the influencing pathways and mechanisms of inorganic salts on the catalytic ozonation of petrochemical wastewater

Zhikai Qin [a, b, c], Fang Wang [b, c], Yue Yuan [b, c, *], Guoxin Ma [d], Yin Yu [b, c], Yutong Duan [b, c, e], Ruiling Bao [a], Changyong Wu [a, b, c, *]

[a] College of Hydrology and Water Resources, Hohai University, Nanjing 210098, China

[b] State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

[c] Research Center of Environmental Pollution Control Technology, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

[d] Environmental Technology Engineering Co Ltd., Chinese Research Academy of Environmental Sciences, Beijing 100012, China

[e] College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

[*] Corresponding author: Yue Yuan: yuan.yue@craes.org.cn Changyong Wu: wu.changyong@craes.org.cn

Text S1 Optimization experiment of catalyst dosage

Catalyst dosage experiments (Fig. S3) showed a clear increase in TOC removal with higher catalyst dosage from 200 g/L to 400g/L. At 400 g/L, the effluent TOC concentration and TOC removal was 6.1 mg/L and 59.89%, respectively. Further increasing the catalyst dosage to 500g/L, there is a slight improvement in the TOC removal effect. Therefore, a dosage of 400 g L-1 was selected for the experiment in this study (section 2.2).

Text S2 Preparation and characterization of catalyst

The catalysts preparation process is as follows: 1) The γ-Al_2O_3 balls was cleaned with deionized water to neutral, and dried at 105 °C, cool them for use. 2) Prepared a certain amount of mixed solution of manganese and copper nitrate, and immersed γ-Al_2O_3 balls in a mixed solution for a period of time.) The impregnated material was dried at 105 °C, cooled to room temperature and calcined in a Muffle oven at 400 °C for 4 h.

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analyses of the catalysts were carried out on a Hitachi Su 8020 (HITACHI, Japan) system. The BET specific surface area of the catalysts was determined from nitrogen adsorption used a Tristar II 3020 (Micrometritics, USA) surface area analyzer. Thermogravimetric Analysis of the catalysts was tested by a Hitachi STA200 (HITACHI, Japan) thermal gravimetric analyzer. Atomic force microscope (AFM) of the catalysts was carried out on a Bruker Multimode 8 (BRUKER, USA) system. Surface functional groups of the catalysts was tested by a IS50 (Thermo Fisher Scientific, USA) Fourier transform infrared spectrometer.

Text S3 Calculation of ozone mass transfer coefficient

The ozone mass transfer coefficient was calculated by Eq. (S1):

$$\ln\frac{[O_3]_\infty}{[O_3]_\infty-[O_3]_t}=K_L at \tag{S1}$$

Here, $[O_3]_\infty$ is the liquid phase ozone saturation concentration, mg/L; $[O_3]_t$ is the liquid phase ozone concentration at time t, mg/L; t is time, s. According to Henry's law, the saturation concentration of ozone in water $[O_3]_\infty$ can be expressed as Eq. (S2):

$$[O_3]_\infty=\frac{[O_3]_{gas}}{1.59e^{(0.0437T)}} \tag{S2}$$

Here, T is temperature, °C; $[O_3]_{gas}$ is the concentration of ozone gas phase, mg/L.

Text S4 Inorganic salt adsorption experiment

1 L of 10 g/L NaCl solution, a petrochemical wastewater with 10 g/L NaCl, 10 g/L Na2SO4 solution, and a petrochemical wastewater with 10 g/L Na_2SO_4 were added into the reactor, respectively. The catalyst dosage was 400 g/L, and the flow rate of the oxygen gas was 20 mL/min, and samples were taken for measurement after 60 minutes of reaction. A Dionex series DX 100 ion chromatography (IC) and conductivity detector and a Dionex AG4A-SC column were used to determine the concentration of inorganic ions (Cl^- and SO_4^{2-}) in the aqueous solution. The eluent was a mixture of Na_2CO_3 (2.0 mmol/L) and $NaHCO_3$ (0.75 mmol/L). The flow rate of the eluent was 1.0 mL/min.

Text S5 Detection methods of ·OH

The Electron Paramagnetic Resonance method: add 50 mM DMPO (5,5-dimethyl-1-pyrroline N-oxide) in 100 mL of pure water, 10 g/L Na_2SO_4 and NaCl solution, respectively. Then add 0.5 g/L Cu & Mn/γ-Al_2O_3 catalyst powder, inject ozone gas (6.25 mg/L) for 10 min. The samples were detected by Electronic Paramagnetic Resonance Spectrometer (Bruker EMXnano, Germany).

The fluorescent marker method: add 60 mL of 100 mg/L coumarin solution, 100 mg/L coumarin-containing NaCl solution, and 100 mg/L coumarin-containing Na_2SO_4 solution to the conical flask, respectively. Then add 0.1 g of Cu & Mn/γ-Al_2O_3 catalyst powder, and finally, add 45 mL of ozone saturated solution. The reaction was shaken under light protection for 10 minutes. Fluorescence images were obtained using a fluorescence microscope (Olympus BX51, tungsten lamp, 200x) and ToupView software.

Text S6 Calculation of the integral standard volume of EEM

The excitation and emission wavelengths were simultaneously scanned at 5 nm intervals with a 12 000 nm/min scan speed. The EEM spectroscopy was normalized, and region-specific EEM volume ($\Phi_{i,5}$) was calculated as follows:

$$\Phi_{i,5} = MF\Phi_i \sum_{Ex} \sum_{Em} I_{\lambda_{Ex}\lambda_{Em}} \Delta\lambda_{Ex}\lambda_{Em} \tag{S3}$$

$$\Phi_{T,5} = \sum \Phi_{i,5} \tag{S4}$$

here, $\Phi_{i,5}$ represents cumulative volume beneath the EEM; MF is each region multiplication factor for each region (equal to the inverse of the fractional projected Excitation-emission area); $I_{\lambda_{Ex}\lambda_{Em}}$ is the fluorescence intensity at each excitation-emission wavelength pair; and $\Delta\lambda_{Ex}$ and $\Delta\lambda_{Em}$ are the excitation wavelength interval and emission wavelength interval (5 nm), respectively.

Text S7 Molecular weight classification of organic matters

The filter membrane was pretreated before the experiment: the filter membrane was first immersed in 5% NaCl solution for 30 min (smooth side down), and then washed with deionized water for 3 times for 1 h each time. The ultrafilter cup contains a magnetic stirring device, the speed was set to 90 r/min, the use of high purity nitrogen pressure drive, the pressure was 0.1~0.5 MPa, in order to prevent excessive pressure caused by filter membrane damage. Before each water sample filtration, it is necessary to filter 100 mL of deionized water first, and then added the waste water filtered by 0.45μm filter membrane. Discarded the first 50 mL of filtrate and stopped filtering when the remaining solution is about 30 mL each time, dump the residual water sample, and add new water sample to continue filtering. The filtering sequence is 10, 5, 3, and 1 kDa.

Text S8 Estimation of reactive chlorine species (RCS)

Under neutral condition, the reaction of Cl- with O3 as follows:

$$Cl^- + O_3 \rightarrow ClO^- + O_2 \qquad \text{(S5)}$$

and the RCS generation rate equation is:

$$\frac{d[\mathrm{ClO}^-]}{dt} = k[\mathrm{O}_3][\mathrm{Cl}^-] \qquad \text{(S6)}$$

here, $[\mathrm{ClO}^-]$ is the concentration of ClO^-, mM, $[\mathrm{O}_3]$ is the concentration of O_3, mM, $[\mathrm{Cl}^-]$ is concentration of Cl^-, mM, k is the second order reaction rate constant of Cl^- with O_3, $1.2 \times 10^{-3}\ M^{-1}s^{-1}$, t is the reaction time, s.

Text S9 Calculation of TOC removal kinetics

The degradation rate of TOC during the reaction was simulated using the pseudo-first-order kinetic model. The calculation formula is as follows:

$$-\ln\left(\frac{[\mathrm{TOC}]_t}{[\mathrm{TOC}]_0}\right) = kt \qquad \text{(S7)}$$

Here, $[\mathrm{TOC}]_0$ and $[\mathrm{TOC}]_t$ is the TOC concentration at 0 and *t*, respectively, mg/L; k is the pseudo-first-order rate constant, min^{-1}; t is the reaction time, min.

Text S10 Calculation of energy consumption

The energy consumption of the catalytic ozonation system was typically measured by electrical energy per ln order (EE/O), which was defined as the electrical energy (kWh) required to degrade one order of magnitude in 1 m^3 of water to be treated (Eq (S8)).

$$\mathrm{EE/O}=\frac{1000\times \mathrm{P}\times \mathrm{t}}{60\times \mathrm{V}\times \ln([\mathrm{TOC}]_0/[\mathrm{TOC}]_f)} \tag{S8}$$

Here, P is the electrical power, kW; t is the reaction time, min; V is the volume of wastewater treated, L; $[TOC]_0$ and $[TOC]_f$ are the initial and final concentrations of TOC, respectively, mg/L.

Table. S1 Water quality of petrochemical wastewater.

Water quality	Unit	Value
Total organic carbon (TOC)	mg/L	13.0~19.8
Chemical oxygen demand (COD)	mg/L	54~70
BOD_5	mg/L	4.65~6.12
TN	mg/L	9.7~14.5
TP	mg/L	0.1~0.75
pH	/	6.0~8.5
UV_{254}	cm^{-1}	0.4~0.6
Cl^-	mg/L	400~800
SO_4^{2-}	mg/L	200~500

Table. S2 Excitation and Emission (E_x/E_m) wavelengths of the fluorescent regions.

Regions (i)	Substances	E_x/E_m wavelength (nm)
I	Tyrosine-like substances	200 ~ 250/280 ~ 330
II	Tryptophan-like substances	200 ~ 250/330 ~ 380
III	Fulvic acids-like substances	220 ~ 250/380 ~ 500
IV	Dissolved microbial products-like substances	250 ~ 350/280 ~ 380
V	Humic acid-like substances	250 ~ 400/380 ~ 500

Table. S3 Proportion of element content of fresh and used catalysts.

Element	Proportion (%)		
	Fresh catalyst	Used catalyst (0)	Used catalyst (10)
C 1s	20.79	14.99	38.53
O 1s	50.06	52.79	40.03
Na 1s	0.31	0.14	0.35
Al 2p	28.17	31.61	20.73
S 2p	0.08	0.10	0.08
Mn 2p	0.37	0.11	0.17
Cu 2p	0.22	0.25	0.11

Table. S4 Physical properties of fresh and used catalysts.

	Specific surface area (m^2/g)	Average pore size (nm)	Average pore volume (cm^3/g)
Fresh catalyst	227.19	7.5857	0.4308
Used catalyst (0)	235.37	7.5034	0.4415
Used catalyst (10)	233.27	7.4021	0.4316

Table. S5 Anion adsorption by catalysts under different conditions.

	Anion adsorption amount (mg/g)
Na_2SO_4 solution (in pure water)	5.58
Na_2SO_4 in petrochemical wastewater	4.29
NaCl solution (in pure water)	2.31
NaCl in petrochemical wastewater	0.02

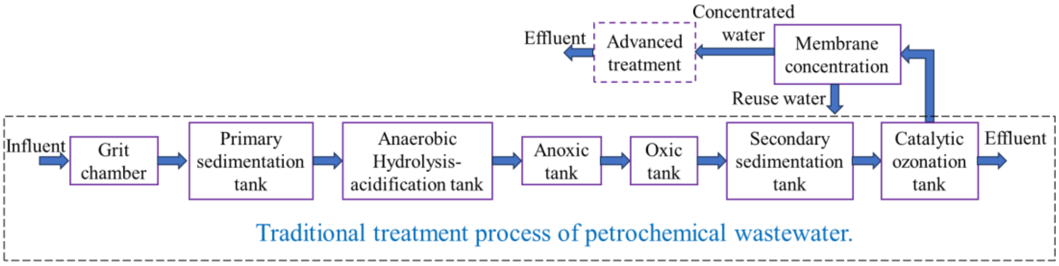


Fig. S1 Petrochemical wastewater treatment process.

*The secondary effluent was used as the research object because it mainly contains complex organic matters that are difficult to biodegrade, which is the best match for catalytic ozonation object when studying real wastewater. Besides, compared to real high-salinity wastewater like the RO concentrate, the concentration of inorganic salts in secondary effluent is low, which allowed us to regulate the salt concentration for better study of the mechanisms.

*Prior to the experiment, no pretreatment work was carried out on the experimental water except adding the required inorganic salts to the wastewater.

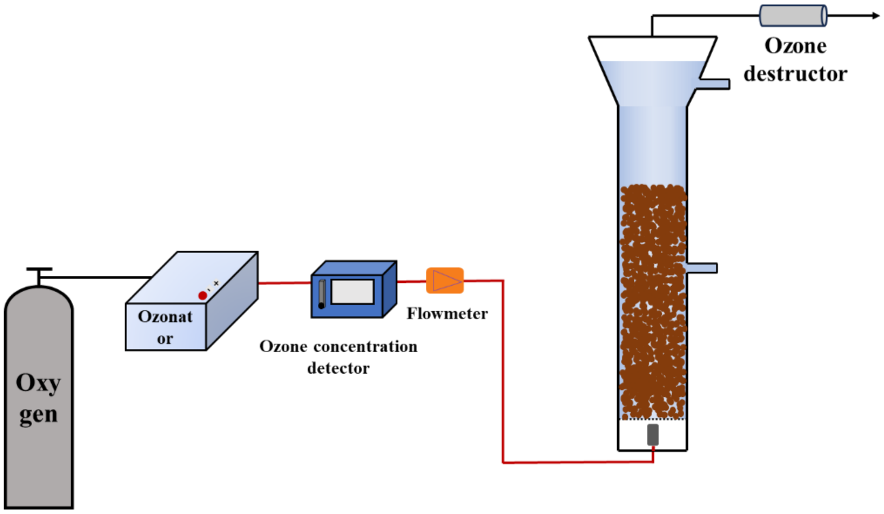


Fig. S2 The experimental setup for catalytic ozonation.

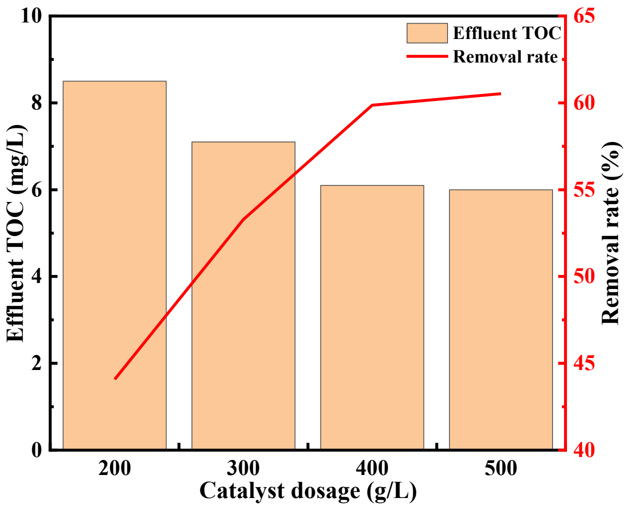


Fig. S3 Effluent TOC concentration and TOC removal rate after 60 min treatment with different catalyst dosage.

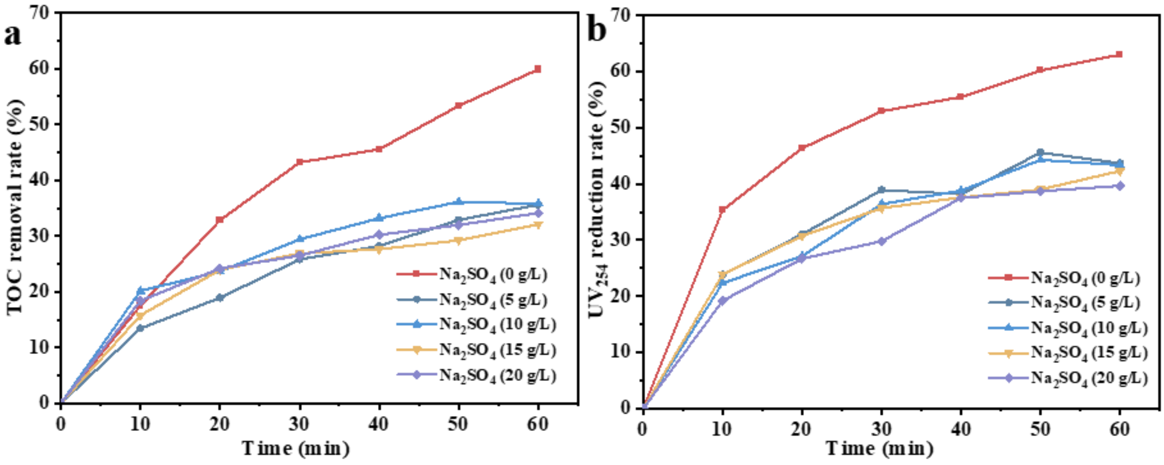


Fig. S4 (a) TOC removal and (b) UV$_{254}$ reduction rate through catalytic ozonation under different Na$_2$SO$_4$ concentrations.

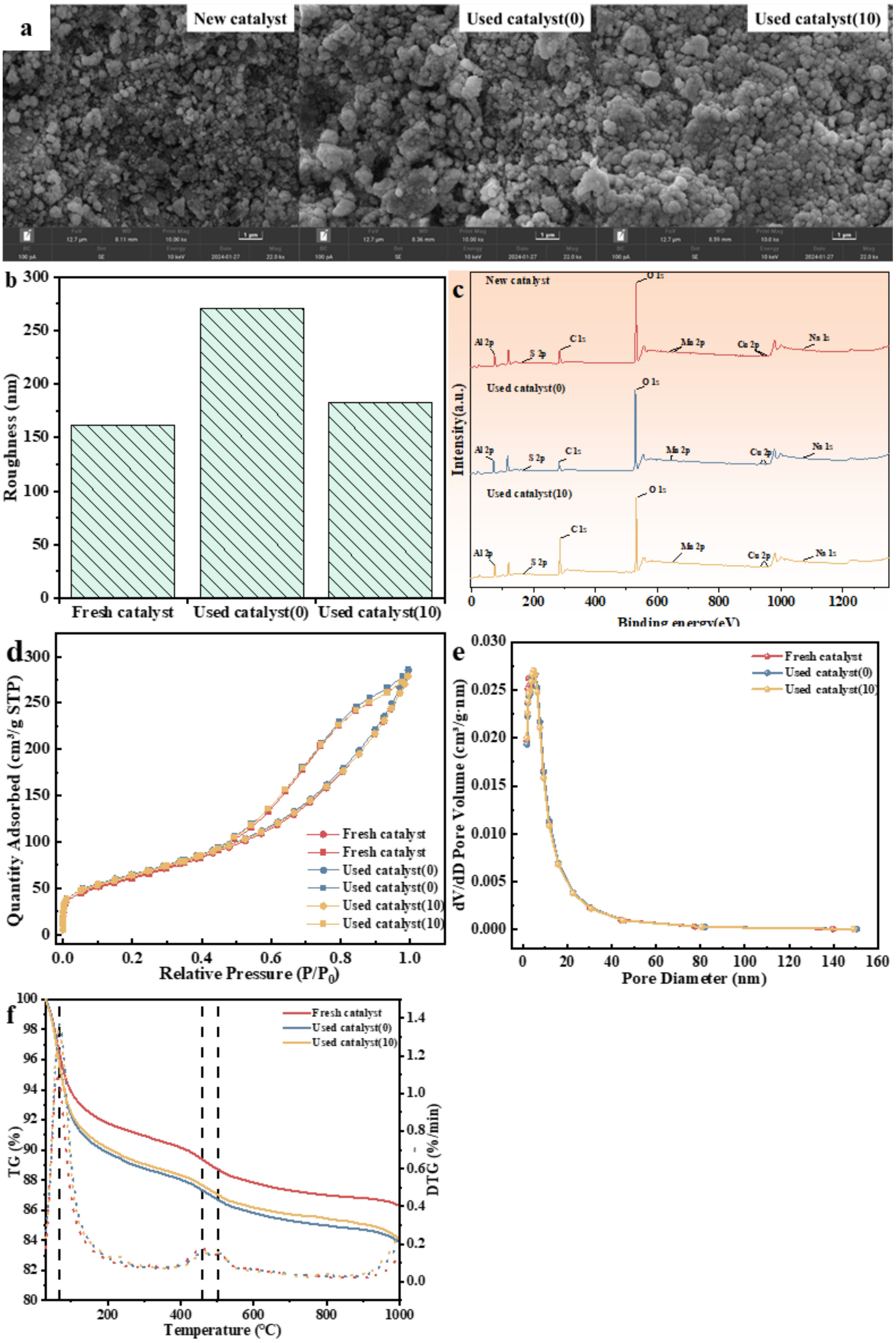


Fig. S5 (a) SEM, (b) AFM and (c) XPS of fresh and used catalyst; (d, f) Absorption and desorption curve and Pore size distribution of fresh and used catalyst; (f)TGA of fresh and used catalyst.

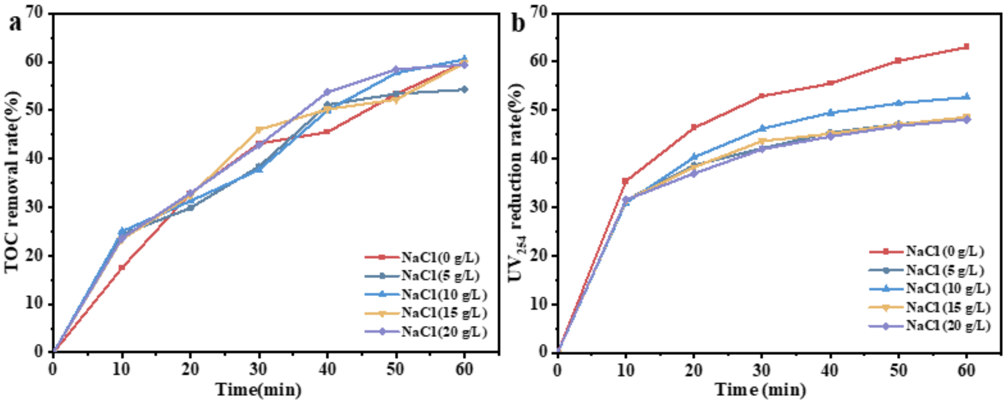


Fig. S6 (a) TOC removal and (b) UV_{254} reduction rate under different NaCl concentrations.

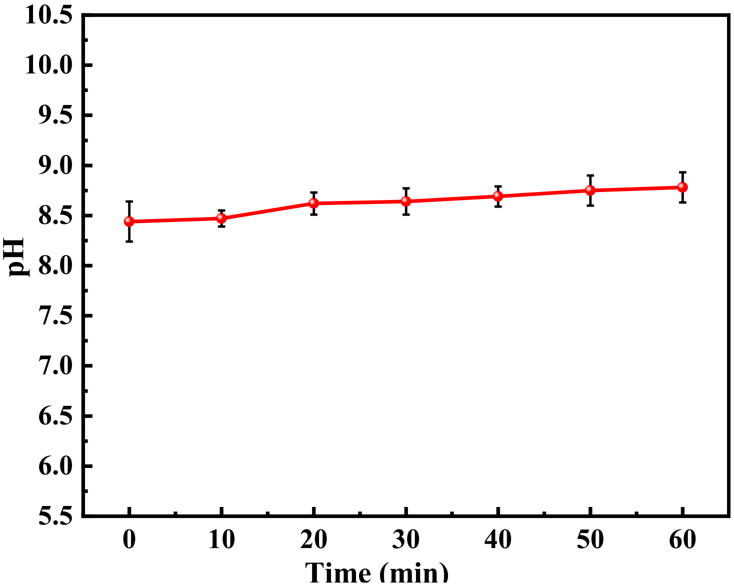


Fig. S7 pH changes during the catalytic ozonation process of petrochemical wastewater under different NaCl concentration (5~20 g/L) conditions.

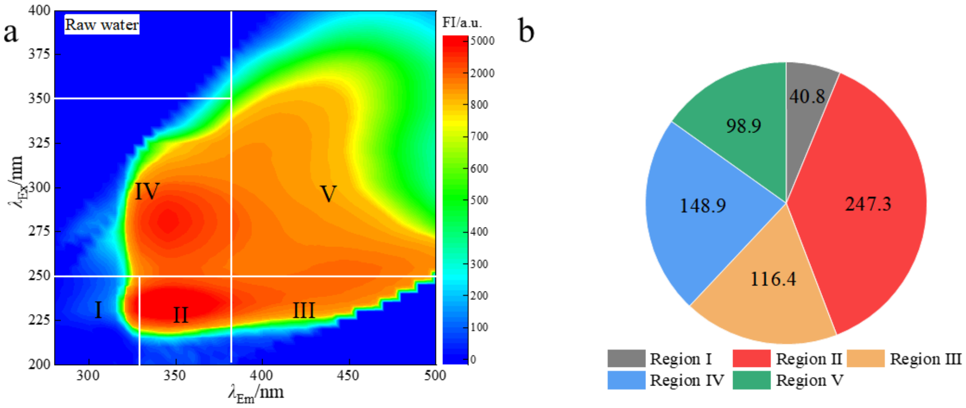


Fig. S8 (a) 3D-EEM and (b) the integrated volumes (×10^4) of raw petrochemical wastewater.

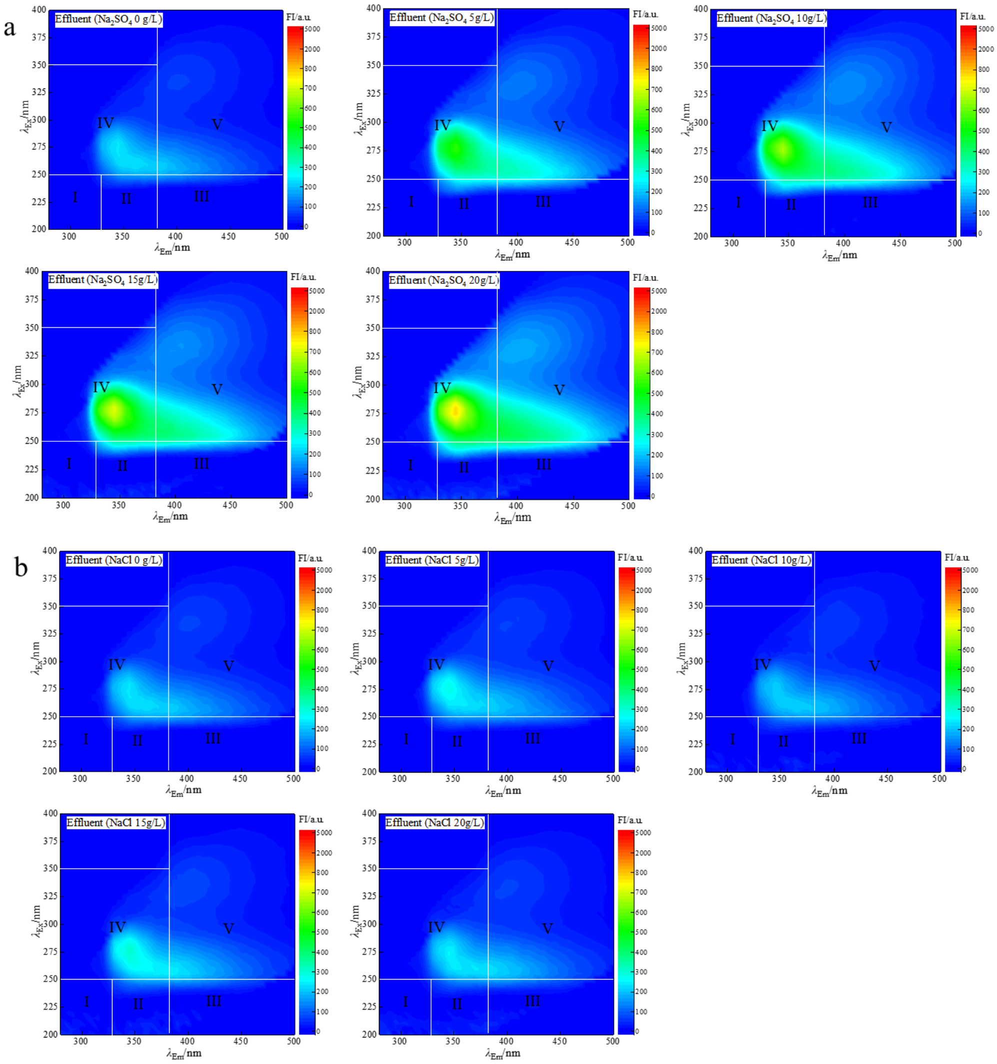
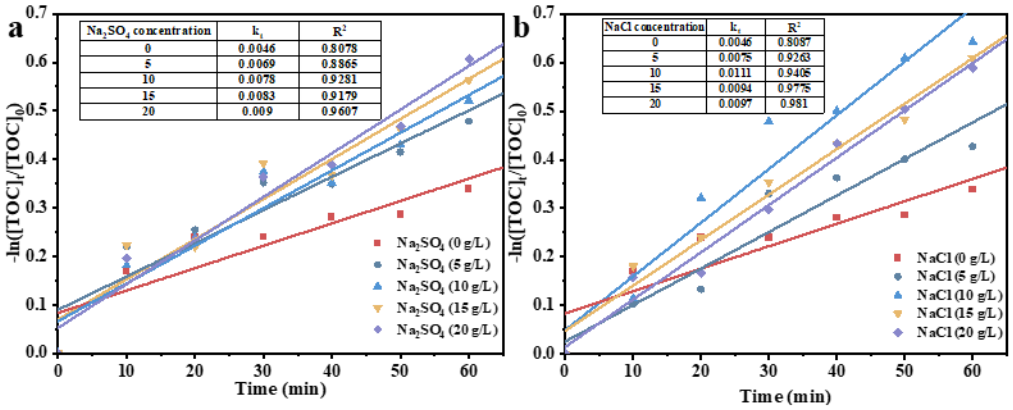


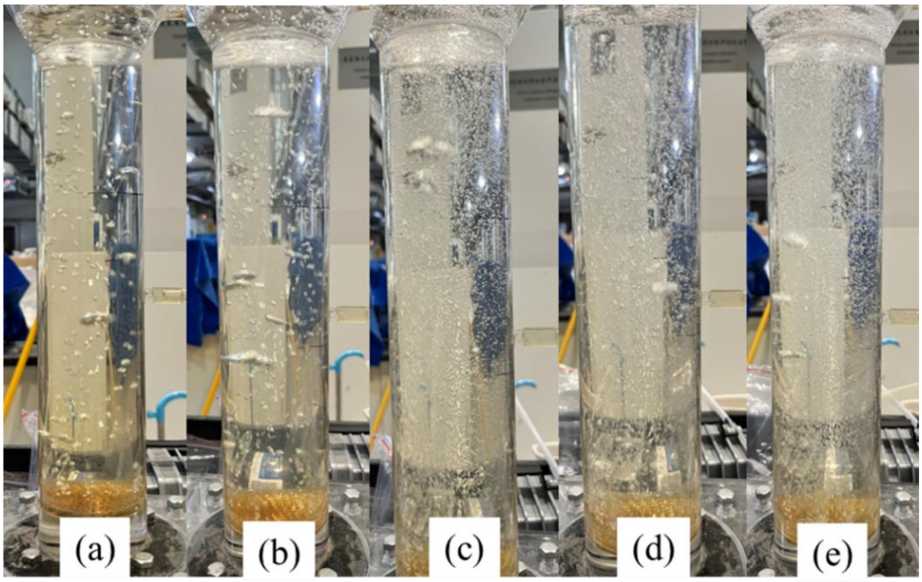
Fig. S9 3D-EEMs of effluent through catalytic ozonation under different (a) Na$_2$SO$_4$ and (b) NaCl concentrations.



Na$_2$SO$_4$ concentration	k_1	R^2
0	0.0046	0.8078
5	0.0069	0.8865
10	0.0078	0.9281
15	0.0083	0.9179
20	0.009	0.9607

NaCl concentration	k_1	R^2
0	0.0046	0.8087
5	0.0075	0.9263
10	0.0111	0.9405
15	0.0094	0.9775
20	0.0097	0.981

Fig. S10 Ozone dissolution kinetics under different inorganic salts concentrations.



Bubble size: 2.77 mm 1.83 mm 1.12 mm 1.08 mm 0.96 mm

Fig. S11 Ozone aeration conditions under different Na_2SO_4 concentrations*. (a) 0 g/L; (b) 5 g/L; (c) 10 g/L; (d) 15 g/L; (e) 20 g/L.

*Bubble size measurement method: To quantify the change in bubble size under different salt concentrations, optical images were captured during ozone aeration in the reactor. Due to the absence of specialized instrumentation for direct measurement, ImageJ software was used to process the images. The diameter of the reactor was first measured to be 6 cm, which served as a reference for all bubble size measurements. In each image, 20 bubbles were randomly selected, and their size was measured using ImageJ. To minimize the impact of irregular bubble shapes, measurements were taken in the direction parallel to the horizontal plane of the reactor. The average bubble size from the 20 measurements was then calculated and used as the representative bubble size for each image. This method provides an approximate estimate of the bubble size under varying salt concentrations.

**Similar results were observed with NaCl, thus only the pictures of Na_2SO_4 are provided as the representative.

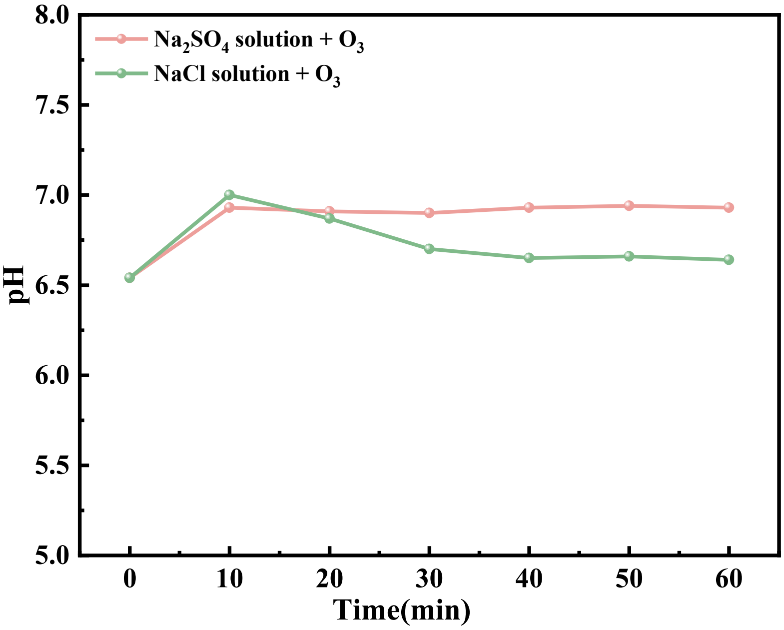


Fig. S12 pH variation in solution during aeration (Inorganic salt concentration: 10 g/L).

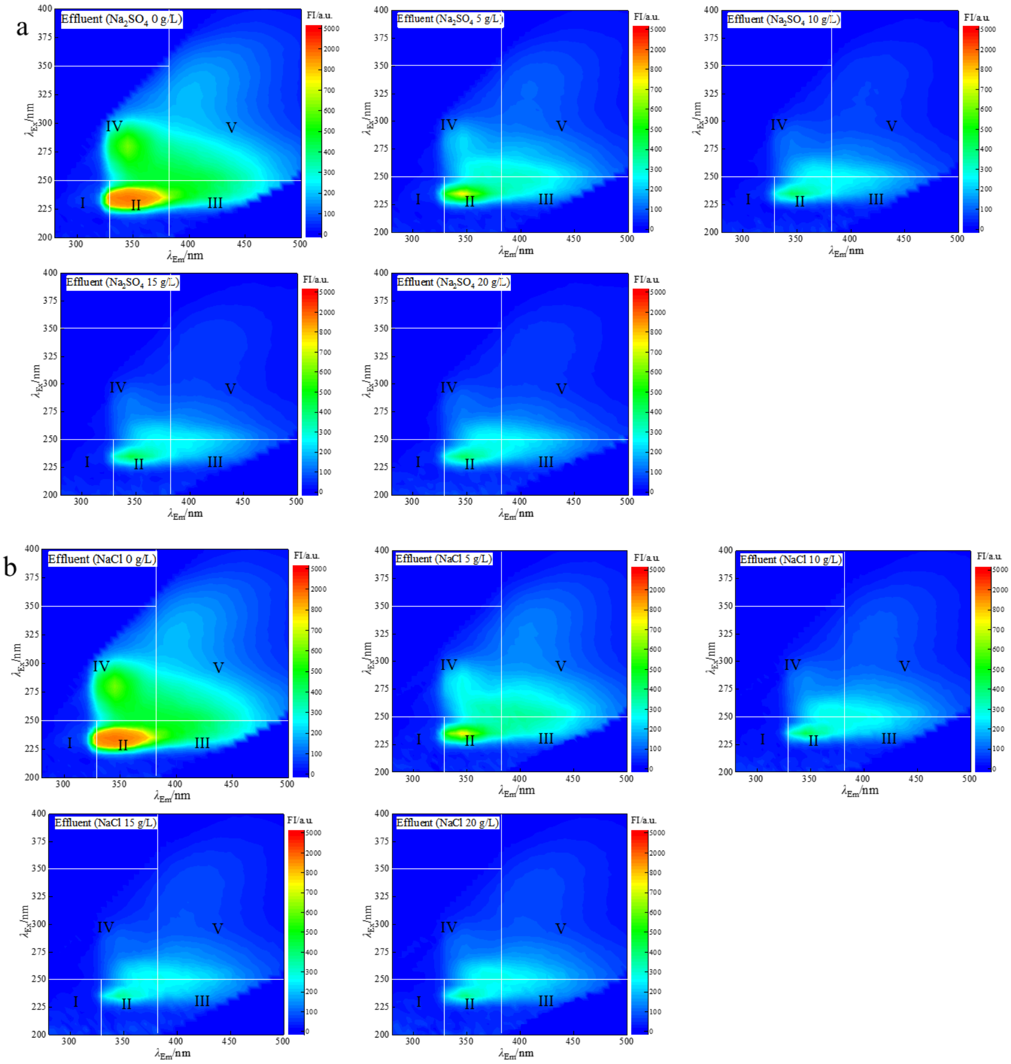


Fig. S13 3D-EEMs of effluent through single ozonation under different (a) Na_2SO_4 and (b) NaCl concentrations.

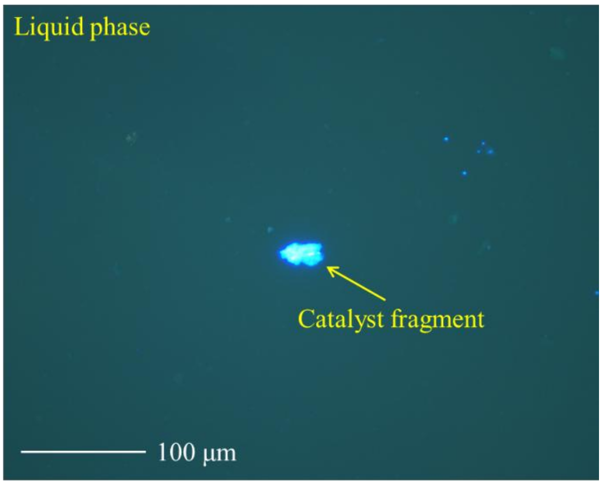


Fig. S14 Fluorescent image of ·OH by the fluorescent marker method.

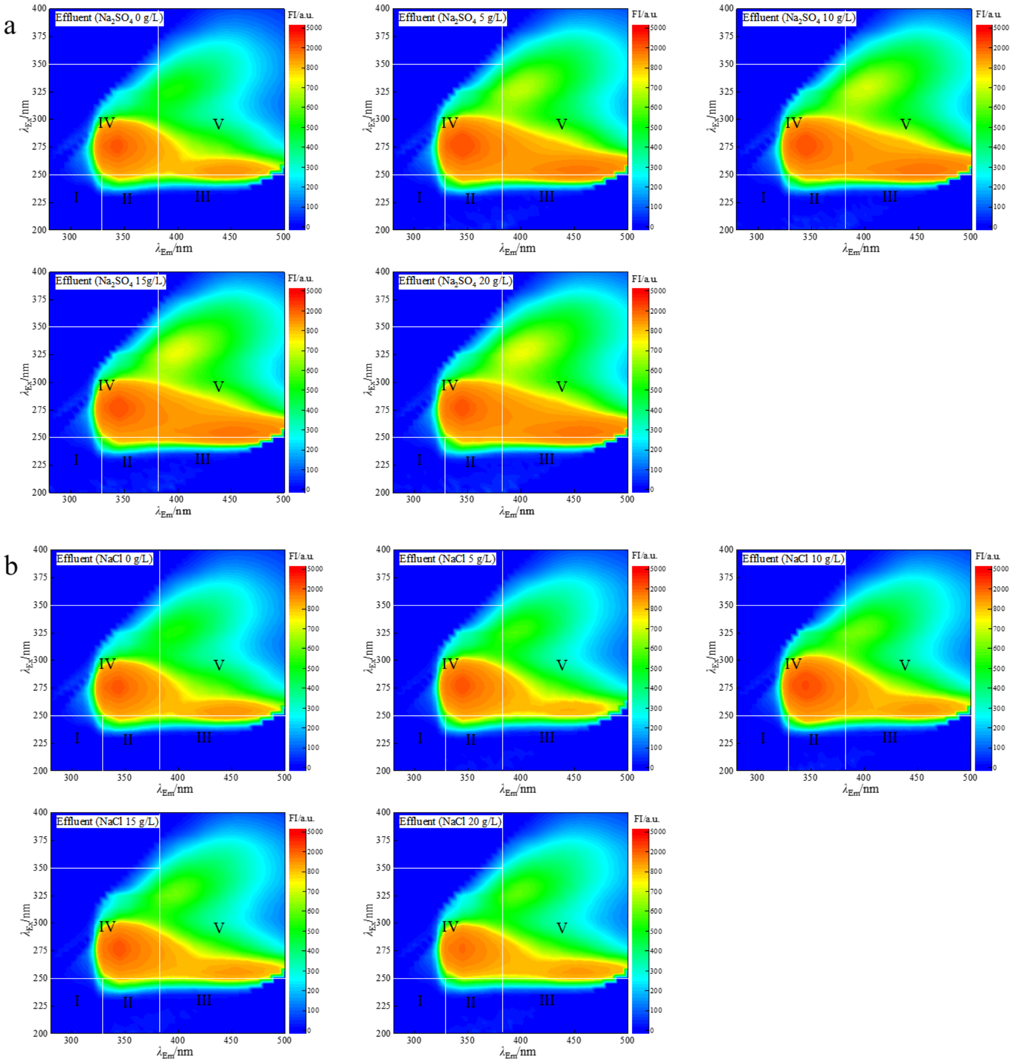


Fig. S15 3D-EEMs of effluent through adsorption process under different (a) Na$_2$SO$_4$ and (b) NaCl concentrations.