Low-toxicity and efficient removal of emerging contaminants in marine aquaculture wastewater by hydrodynamic cavitation/calcium peroxide Fenton-like system

Yiying Lv[a,b], Wei Ding[a], Jianxing Liang[a,c], Diwen Ying[a], Jinping Jia[a,c,*]

[a] State Key Laboratory of Green Papermaking and Resource Recycling, Shanghai Engineering Research Center of Solid Waste Treatment and Resource Recovery, School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

[b] Hainan Research Institute, Shanghai Jiao Tong University, Sanya 572024, China

[c] State Key Laboratory of Synergistic Chem-Bio Synthesis, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

[*]Corresponding author E-mail: jpjia@sjtu.edu.cn

This file contains 4 texts, 3 tables and 9 figures.

Fig. S1. Hydraulic cavitation device.

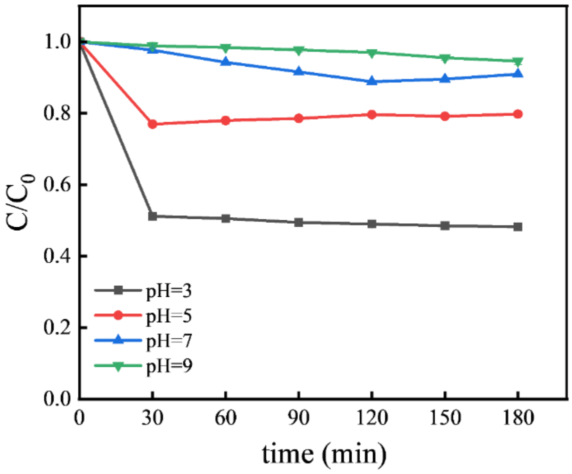

Fig. S2. The degradation of TC in the Fe^{2+}/CaO_2 system under different pH conditions.

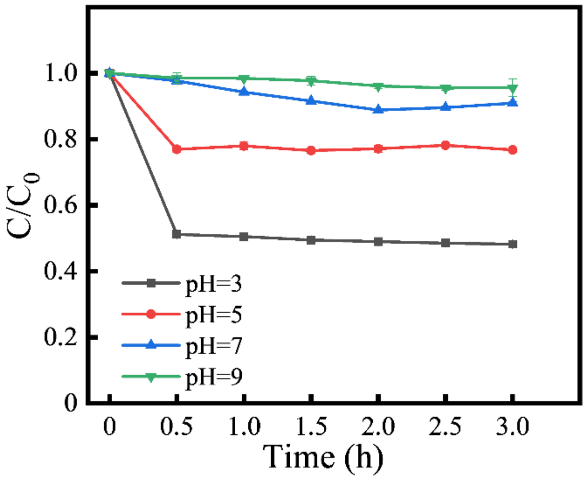

Fig. S3. The degradation of TC in the Fe^{2+}/H_2O_2 system under different pH conditions.

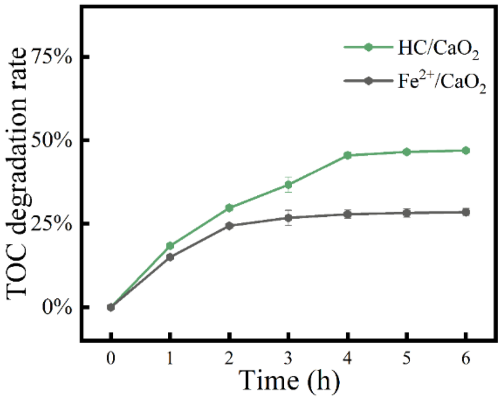

Fig. S4. The changes in TOC during the degradation of TC by Fe^{2+}/CaO_2 system and Fe^{2+}/H_2O_2 system.

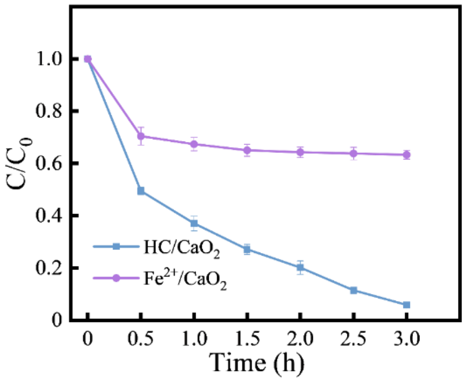

Fig. S5. The degradation effects of Fe^{2+}/CaO_2 system and Fe^{2+}/H_2O_2 system on ciprofloxacin (CIP).

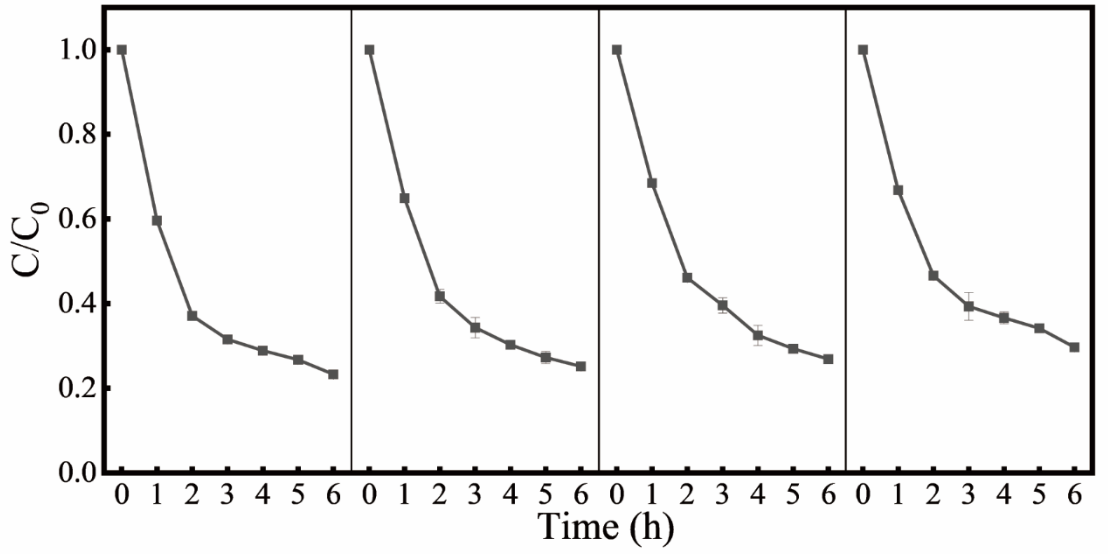

Fig. S6. Experimental study on the removal of total chromium (TC) from actual seawater aquaculture wastewater under continuous flow conditions (24 hours).

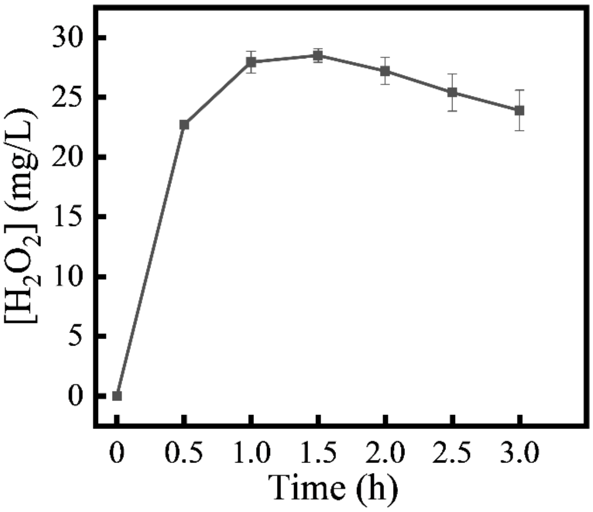

Fig. S7. The production of H_2O_2 in the HC/CaO_2 system.

Text. S1. The detection method of COD.

The chemical oxygen demand (COD) of actual aquaculture wastewater was measured following the alkaline potassium permanganate method specified in *GB 17378.4-2007*. Briefly, a fixed volume of the sample was oxidized by $KMnO_4$ under alkaline conditions with heating. The excess $KMnO_4$ was then reduced with KI under acidic conditions (H_2SO_4), and the liberated iodine was titrated with a standard $Na_2S_2O_3$ solution. The COD concentration was calculated according to Eq. S1. All water used in this part of the experiment was distilled.

$$\mathrm{COD}=\frac{c(V_2-V_1)\times 8.0}{V}\times 1000 \tag{S1}$$

Among them, COD represents the chemical oxygen demand of the water sample, with the unit being mg/L. c is the concentration of the $Na_2S_2O_3$ solution (mol/L), V_2 is the volume of $Na_2S_2O_3$ solution consumed during the blank value titration (mL), V_1 is the volume of $Na_2S_2O_3$ solution consumed during the titration of the sample (mL), and V is the volume of the water sample taken (mL).

Text. S2. Economic feasibility analysis.

Economic feasibility is the key indicator for evaluating the engineering potential of water-treatment technologies. Based on bench-scale results, this section compares the HC/CaO_2 system with conventional processes, focusing on reagent costs and the resulting economic viability for mariculture applications.

(1) pH-adjustment cost

The HC/CaO_2 process (hereafter “this process”) operates at the raw-water pH without any adjustment.Conventional Fe^{2+}/CaO_2 and Fe^{2+}/H_2O_2 processes require pH ≈ 3 for appreciable degradation; the culture water must therefore be isolated, acidified, and re-neutralised after treatment.

Reagent doses for pH control:

- This process (HC/CaO_2)
  - Lab: HCl 0.07 g/L
  - Full-scale: 70 g/t
- Fe^{2+}/CaO_2
  - Lab: HCl 0.13 g/L + NaOH 0.04 g/L
  - Full-scale: HCl 130 g/t + NaOH 40 g/t
- Fe^{2+}/H_2O_2
  - Lab: HCl 0.12 g/L + NaOH 0.04 g/L
  - Full-scale: HCl 120 g/t + NaOH 40 g/t

(2) Advanced-oxidation reagent cost

The core oxidant in this process is CaO_2 activated by hydrodynamic cavitation; no catalyst is required.Conventional processes use CaO_2 or H_2O_2 as the oxidant and $FeCl_2$ as the catalyst.

CaO_2 dose calculation:

Lab effective dose: 100 mg/L × 75 % = 75 mg/L = 75 g/t (≈ 1 mM)

Industrial dose (56 % purity): 75 g/t ÷ 0.56 = 134 g/t

H_2O_2 dose calculation:

Lab effective dose (pure H_2O_2): 1 mM = 34 g/t

Industrial dose (27 % w/w): 34 g/t ÷ 0.27 = 125.9 g/t

Catalyst ($FeCl_2$) dose calculation:

Lab effective dose: 30 mg/L = 30 g/t

Industrial dose (58 % purity): 30 g/t ÷ 0.58 = 51.7 g/t

(3) Waste-disposal cost

This process generates no solid residue.Conventional processes produce $Fe(OH)_3$ sludge that must be treated as hazardous waste.

$Fe(OH)_3$ sludge production:

Fe mass per tonne water: 30 g/t × (55.85 / 126.75) = 13.22 g/t

Dry $Fe(OH)_3$: 13.22 g/t × (106.85 / 55.85) = 25.29 g/t

Wet sludge (85 % moisture): 25.29 g/t ÷ (1 – 0.85) = 0.17 kg/t

Table. S1. Pharmaceutical Cost summary.

Reagent / item	Unit price (CNY/t)	HC/CaO_2	Fe^{2+}/CaO_2	Fe^{2+}/H_2O_2
HCl	150	70 g/t	130 g/t	120 g/t
NaOH	3 000	—	40 g/t	40 g/t
CaO_2	5 000	134 g/t	134 g/t	—
H_2O_2	1 800	—	—	125.9 g/t
$FeCl_2$	900	—	51.7 g/t	51.7 g/t
Hazardous-waste disposal	2 340 (Shanghai) 3 508 (Jiangsu) 3 405 (Hainan)	0	0.17 kg/t	0.17 kg/t

The total treatment cost is:

- This process: 0.68 Yuan/t
- Fe^{2+}/CaO_2: 1.25–1.45 Yuan/t
- Fe^{2+}/H_2O_2: 0.81–1.01 Yuan/t

Thus, this process offers a clear economic advantage. Note: the comparison is based on 50 % removal for conventional systems at pH 3 versus 60.9 % removal for this process at pH 7, demonstrating superior degradation performance as well as lower cost.

Moreover, existing recirculation and aeration equipment in farms can be retrofitted with negligible amortised capital, adding virtually no extra energy demand. CaO_2 is already a common aquaculture chemical, so on-site dosing can simply supplement prior additions, avoiding redundant oxidant consumption. We have previously achieved low-cost synthesis of CaO_2 (Wang et al., 2025), providing a technical basis for further cost reduction at scale. Overall, the process shows strong potential for practical deployment.

Table. S2. Comparison of Energy Consumption for Different H_2O_2 Activation Methods (Gągol et al., 2018).

Activation Method	Energy Consumption (kWh/m³)	Characteristics	Applicable Scenarios
Hydrodynamic Cavitation (HC)	0.1~8.01	High efficiency, low energy consumption	Large flow rates, low temperatures, requires simultaneous disinfection, low operating costs
Ultrasonic Cavitation	2~10	Highly efficient locally, strong mass transfer	Small-scale research; energy consumption and equipment costs increase sharply for large flows
Thermal Activation	100~500	Fast reaction rate	High-temperature industrial wastewater treatment
Photo Activation	0.242~50	Good selectivity, no secondary pollution	Drinking water disinfection, trace pollutant removal

Remark: Venturi reactors are more energy-efficient than orifice plate reactors.

Text. S3. The method for extracting intermediate products of TC using solid-phase extraction.

For the identification of TC degradation intermediates, a 200 mL aliquot of the reaction mixture was loaded onto a C18 SPE cartridge previously conditioned with 5 mL of HPLC-grade methanol, 5 mL of ultrapure water and 5 mL of acidified water (pH 3.0). The loading flow rate was maintained at 5 mL/min, after which the cartridge was successively rinsed with 10 mL of ultrapure water and 10 mL of 5 % (v/v) methanol to remove inorganic salts and matrix impurities. The retained analytes were eluted twice with 4 mL of methanol (total 8 mL), and the combined eluate was gently concentrated to ~1 mL under a mild nitrogen stream at room temperature. The final concentrate was transferred into an LC-MS vial and stored at 4 °C until analysis.

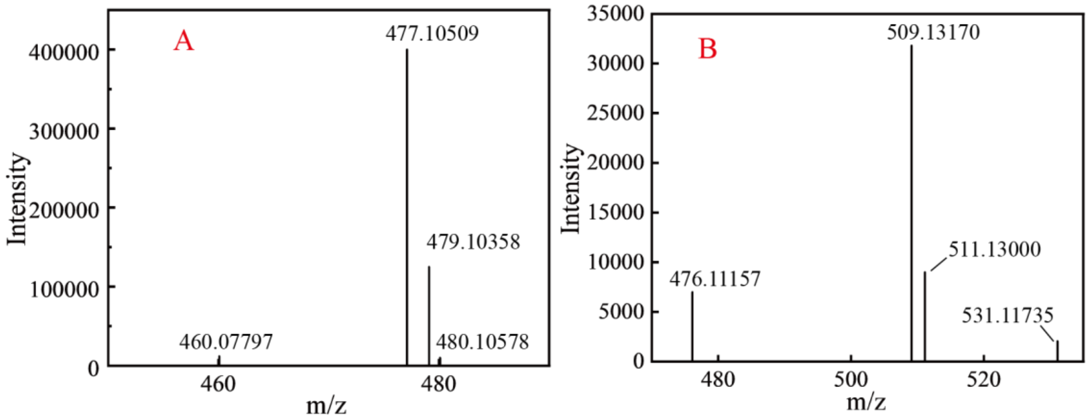

Fig. S8. The chlorinated products detected in the Fe/CaO_2 system.

Text. S4. Identification of chlorinated products.

For Byproduct A (molecular mass 477), the mass difference from the parent is 33. A plausible explanation is the addition of one chlorine atom (+35) to the molecule alongside the loss of two hydrogen atoms (-2), yielding a net increase of +33. Thus, the possible molecular formula is $C_{22}H_{22}ClN_2O_8$ (original H_{24} minus 2 H gives H_{22}, plus one Cl atom). This byproduct is likely a monochlorinated tetracycline, formed through a single electrophilic substitution reaction where a chlorine radical attacks an electron-rich site on the tetracycline molecule.

For Byproduct B (molecular mass 509), the mass difference from the tetracycline parent (molecular mass 444) is 65. This mass increase can be reasonably explained by the introduction of two chlorine atoms to the tetracycline molecule (each Cl atom has a mass of ~35.5, approximated to 35 for calculation, thus two Cl atoms contribute +70), concurrent with the loss of 5 mass units, likely corresponding to the loss of five hydrogen atoms (i.e., -5). This results in a net increase of +65. Consequently, the possible molecular formula is inferred to be $C_{22}H_{19}Cl_2N_2O_8$ (based on the original number of H atoms being 24, minus 5 H gives H_{19}, plus the addition of 2 Cl atoms).

Regarding the formation mechanism, this byproduct is likely a dichlorinated tetracycline. It is formed via two electrophilic substitution reactions where chlorine radicals or active chlorine species attack electron-rich sites on the tetracycline molecule (e.g., the phenolic ring), each replacing one hydrogen atom, potentially accompanied by further dehydrogenation to maintain structural stability.

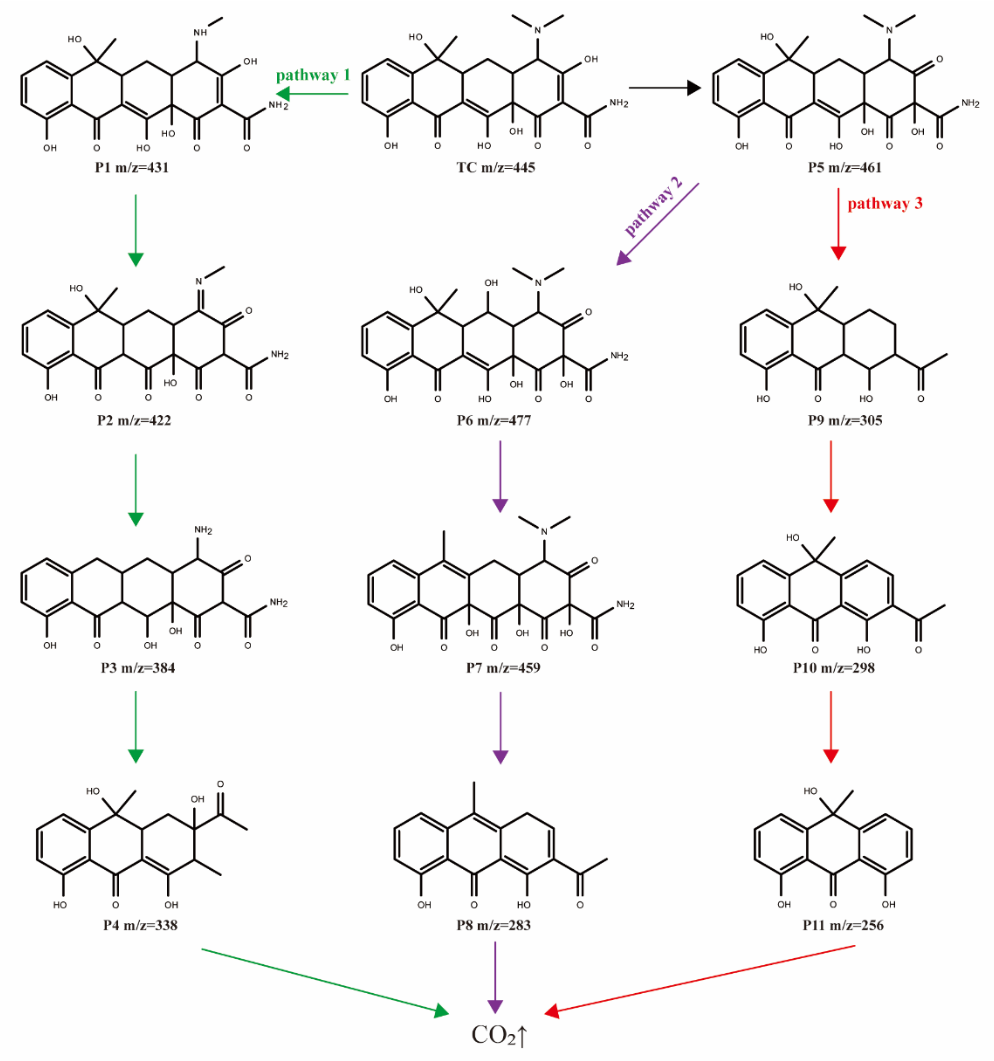

Fig. S9. The degradation pathway of TC in the Fe/CaO_2 system.

Table. S3. The LC_{50} values of zebrafish.

Disinfection byproducts		**zebrafish LC_{50} (M)**
Trihalomethanes	TCM	1.17×10^{-4}
Haloacetic acids	MCAA	3.92×10^{-3}
	DCAA	3.88×10^{-3}
	TCAA	3.06×10^{-3}

References

Gągol M, Przyjazny A, Boczkaj G (2018). Wastewater treatment by means of advanced oxidation processes based on cavitation–a review. Chemical Engineering Journal, 338: 599–627

Wang M, Cheng J, Xu W, Zhu D, Zhang W, Wen Y, Guan W, Jia J, Lu Z (2025). Self-cleaning electrode for stable synthesis of alkaline-earth metal peroxides. Nature Nanotechnology, 20(1): 67–74