

Surface and pore co-functionalized ceramic membrane with Zr doped Co₃O₄ for SMX degradation through coupling peroxymonosulfate activation

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Abstract: Peroxymonosulfate (PMS) based advanced oxidation has emerged as a promising strategy to decompose sulfamethoxazole (SMX). However, traditional powder catalysts commonly suffer from severe agglomeration and poor recyclability. In this work, Zr-doped Co_3O_4 serving as an efficient PMS catalyst, was immobilized onto both surface and pore channels of an Al_2O_3 ceramic membrane, generating a dual functional CoZr@CM composite membrane. Such simultaneous surface-pore functionalization delivers abundant accessible active sites, prolongs reactant retention duration and facilitates interfacial mass transfer. Benefiting from these merits, 97.1% SMX was degraded in optimized CoZr@CM and the first-order kinetic constant of SMX degradation was 90 times higher than that for powder catalyst. Moreover, the CoZr@CM/PMS system exhibited satisfactory removal capacity toward multiple recalcitrant organic contaminants including phenol, bisphenol A and rhodamine B. Long-term continuous experiment demonstrated robust operational stability, with 87.5 % SMX removal maintained after 17 h run time. Water-matrix variables including solution pH and ubiquitous background anions were further evaluated for their influences on SMX degradation. Quenching experiment and electron paramagnetic resonance (EPR) test confirmed $\text{SO}_4^{\bullet-}$ as dominant species, accompanied by a small amount of $\cdot\text{OH}$ and $^1\text{O}_2$. Based on the liquid chromatography mass spectrometry (LC-MS) results, three plausible degradation pathways of SMX were proposed and the trends in toxicity changes of intermediate products were analyzed. This research offers an alternative route to mitigate the application bottlenecks of powder catalysts for wastewater remediation.

Key word: Catalytic membrane; Zr-doped Co_3O_4 ; PMS activation, sulfamethoxazole degradation

1. Introduction

Excessive antibiotic consumption over the past decades has resulted in increasing discharge of antibiotics into water bodies, posing a severe threat to public health and ecological stability (Li et al., 2025; Wang et al., 2024; Zhi et al., 2025). Sulfamethoxazole (SMX), a prevalent sulfonamide antibacterial agent frequently detected in water matrices, tends to accumulate within organisms along food chains and disturbs the normal structure of aquatic plant communities (Qin et al., 2023; Xin et al., 2023). However, conventional wastewater treatment technologies represented by biological treatment fail to achieve satisfactory elimination of SMX due to its strong hydrophilicity, high stability and antibacterial nature (Shang et al., 2022).

Advanced oxidation technologies (AOTs) are considered as an efficiency method to eliminate antibiotics by generating the powerful oxidizing species (Anjali and Shanthakumar, 2019; Xiao et al., 2023). Among various AOTs, Sulfate radical based advanced oxidation processes (SR-AOPs) stand out among diverse AOTs and have garnered massive research interest recently due to the higher oxidation potential of $\text{SO}_4^{\bullet-}$ (2.5–3.1 V NHE VS. 2.7 V NHE) than $\bullet\text{OH}$, wide pH range (2–8), comparatively longer radical lifetime (30–40 μs) (Ma et al., 2022). $\text{SO}_4^{\bullet-}$ can be produced by peroxymonosulfate (PMS) activation. At present, heterogeneous PMS catalysts has been extensively studied and a broad range of heterogeneous catalysts have been developed for PMS activation, mainly including transition-metal oxides (e.g., Co_3O_4 , Fe_3O_4 , CuO , Mn_3O_4) as well as metal-free carbon materials (Huang et al., 2023; Wu et al., 2024; Zhang et al., 2022; Zhao et al., 2022). Compared to metal-free carbon catalysts, transition metal catalysts have sustainability due to their excellent redox properties. In particular, Co_3O_4 stands out in PMS activation because of its prominent catalytic activity, acceptable stability and cost-effectiveness. To further improve the

catalytic activity of Co_3O_4 , heteroatom doping strategy has been proposed (Gao et al., 2022; Li et al., 2021a; Pan et al., 2025; Tan et al., 2026). Heteroatom doping could reconfigure the 3d band center of active sites and affect adsorption of PMS on active sites, hence improving the catalytic performance (Zhang et al., 2023). Previous investigations reported that Zr doping shifts the d-band center of Co sites from -0.27 eV (pure Co_3O_4) to -0.20 eV for Zr- Co_3O_4 . Such shift strengthens PMS adsorption and accelerates interfacial electron transfer during PMS activation. Correspondingly, Zr doped Co_3O_4 delivers roughly 10 times higher catalytic activity than pristine Co_3O_4 . Additionally, Zr-doped Co_3O_4 outperforms many previously reported Co-containing oxide catalysts and demonstrates enhanced structural stability relative to conventional metal-oxide powders (Zhang et al., 2023)

However, traditional powdered catalyst for example Zr- Co_3O_4 still suffers intrinsic drawbacks: particle agglomeration, insufficient mass transfer and difficulties in solid-liquid separation after reaction. Immobilizing powdered catalysts onto porous membrane substrates to construct catalytic filtration membranes provides a feasible strategy to resolve these limitations (Li et al., 2021b). First, PMS activation proceeds in-situ during membrane filtration, enabling continuous water treatment operation (Wang et al., 2020). Second, under the pressure-driven flow mode, the target pollutants and PMS are more likely to approach the catalytic site on the catalytic membrane, thereby enhancing the reaction substance contact. Alao, it is reported that the mass transfer capacity is significantly enhanced within the confined space of the membrane pore channels (Ma et al., 2020). Therefore, it is feasible to construct catalytic filtration membrane to solve the problem of powder catalysts. The choice of catalytic membrane support is crucial. Ceramic membranes are widely applied due to their high water permeability, robust mechanical strength and low fouling tendency. Their

interconnected porous architecture with large specific surface area also makes them ideal supporting hosts for catalyst loading. Commonly, Most reported catalytic membranes only anchor active substances on the membrane surface (Huang et al., 2025). This configuration suffers limited active site density and short contact duration between reactants and the catalytic layer, especially under high-flux operational conditions. To tackle this issue, loading both membrane surface and pore channel with catalytic layers can supply more exposed active centers and extend reactant-catalyst contact time, hence improving the performance of PMS catalytic membrane. Furthermore, in the confined spacing of pore channels, the mass transfer and reaction kinetics could be substantially improved compared with the surface reaction due to the confinement effect. Therefore, it is feasible to construct surface and pore co-functionalized ceramic membrane with Zr-Co₃O₄ for SMX degradation through coupling PMS activation.

In this work, a novel Zr-Co₃O₄ coated ceramic membrane (CoZr@CM) with PMS activation capability was successfully synthesized by a simple impregnation calcination method for the degradation of the typical antibiotic sulfamethoxazole. Zr-Co₃O₄ possessing high PMS activation ability was coated onto the surface and pores simultaneously to construct surface and pore co-functionalized ceramic membrane. The degree of functionalization of CoZr@CM was adjusted by optimizing the precursor concentration. A series of experiments were carried out to explore the effect of PMS dosage, hydraulic conditions, initial pH and background anions on the catalytic filtration performance of CoZr@CM. The stability of the catalytic membrane was tested. The main active species and reaction mechanisms were investigated. The synergistic effect between membrane and catalytic oxidation was discussed. Finally,

SMX degradation products were characterized, plausible degradation pathways were proposed, and the ecotoxicity of resulting intermediates was evaluated.

2. Experiment section

2.1 Chemicals and materials

Materials and chemical analysis are presented in the Text S1-S3 (Supporting information).

2.2 preparation of Zr-Co₃O₄ catalyst and ZrCo@CM

ZrCo@CM was synthesized by impregnation-calcination method and the preparation process is illustrated in Figure 1. Firstly, the precursor solution is prepared by dissolve Co(NO₃)₂·6H₂O, ZrO(NO₃)₂·xH₂O and citric acid. CMs were submerged inside the precursor solution and subjected to 30 min sonication. Sonication facilitates inward diffusion of metal ions and enables sufficient penetration of precursor liquid throughout the CM. Afterwards, the soaked CMs were dried at 100 °C for 12 h to eliminate residual water. Finally, the ZrCo@CM was obtained by calcining in a muffle furnace at 200 °C for 2 h, followed by another 2 h calcination at 500 °C, with a heating ramp of 2 °C min⁻¹. The CoZr@CM was treated with PMS solution to remove the unstable cobalt. The degree of functionalization for the surface and pore of membrane was controlled by adjusting the concentration of the precursor solution. The precursor solution concentrations were 5, 10 and 20 mmol L⁻¹, respectively, and the catalyst loading amounts 0.79、2.19 and 6.29 mg g⁻¹. For comparison, pure Co₃O₄ and Zr-Co₃O₄ powder catalysts were synthesized by aging the precursor solutions and applying the same calcination protocol. The detailed preparation process can be found in the supporting information Test S4.

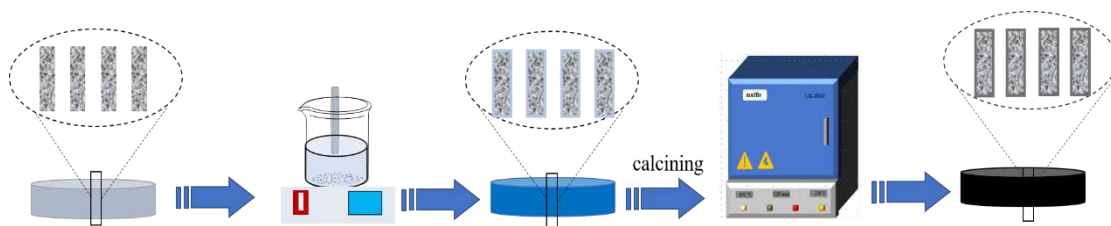


Figure 1 Illustration of preparation process for CoZr@CM

2.3 Catalytic degradation experiments

The specific details of batch experiment were presented in Test S5. The catalytic performance of the as-prepared ZrCo@CM was assessed using a dead-end filtration setup, whose schematic drawing is shown in Figure S1. The mixed solution of SMX and PMS was filtrated through the membrane using a peristaltic pump. The permeate was collected, filtered and quenched for test. The test method for SMX and other target contaminants are summarized in Table S1. The membrane flux (J , $L\ m^{-2}\ h^{-1}$) was computed using the following formula:

$$J = \frac{V}{S \times t}$$

where V (L) is the volume of the membrane permeate, S (m^2) is the membrane effective filtration area, and t is the filtration time.

3 Results and discussion

3.1 Characterization of Zr-Co₃O₄@CM

X-ray diffractometer (XRD) was used to illustrate the crystalline phase and crystal structure. The XRD patterns of CM, Zr-Co₃O₄ and CoZr@CM were presented in Figure 2. For CM, the major peaks at 25.7° (012), 35.3° (104), 43.5° (113), and 57.6° (024), 61.19° (116), 66.41° (421) and 68.11° (300) were well indexed as the standard diffraction patterns of Al₂O₃ (PDF#10-0173) (Xu et al., 2024). For Zr-Co₃O₄, the

diffraction peaks located at 31.2° , 36.8° , 44.8° , 59.4° and 65.2° belonging to (220) (311) (531) (511) (440) crystal facets of Co_3O_4 (Zhang et al., 2026), indicating that Zr is successfully doped into Co_3O_4 . For $\text{Zr-Co}_3\text{O}_4@\text{CM}$, it can be seen that the peak intensity of Al_2O_3 weakened compared with CM, and a weak peak owing to Co_3O_4 was observed, which could be caused by the less impregnated amount of Co_3O_4 as well as extremely high signal of Al_2O_3 (Bao et al., 2019).

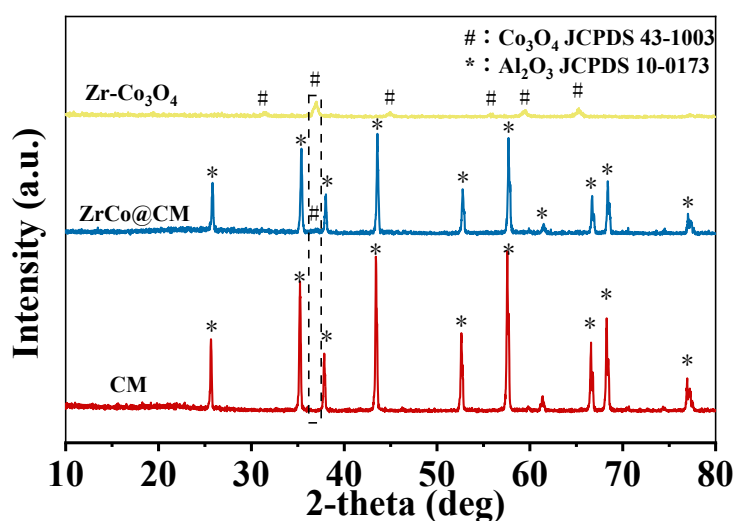


Figure 2 XRD patterns of $\text{Zr-Co}_3\text{O}_4$, CoZr@CM and CM

Scanning electron microscope (SEM) was used to observe the morphologies of CM support and CoZr@CM , which was displayed in Figure 3. The CM support with porous structure was composed of irregular Al_2O_3 (Figure 3a-c). The surface and cross-section of CM support are smooth and there are no obvious particles presented. The surface of CoZr@CM appears dark black (the inset of Figure 3d), and abundant solid particles are attached to the membrane surface and the membrane cross-section (Figure 3d-f), indicating that the catalyst has been successfully loaded onto the CM support. Energy dispersive X-ray (EDS) mapping in Figure 3g-j indicate that the elements of O, Co, and Zr are uniformly distributed on the CM support.

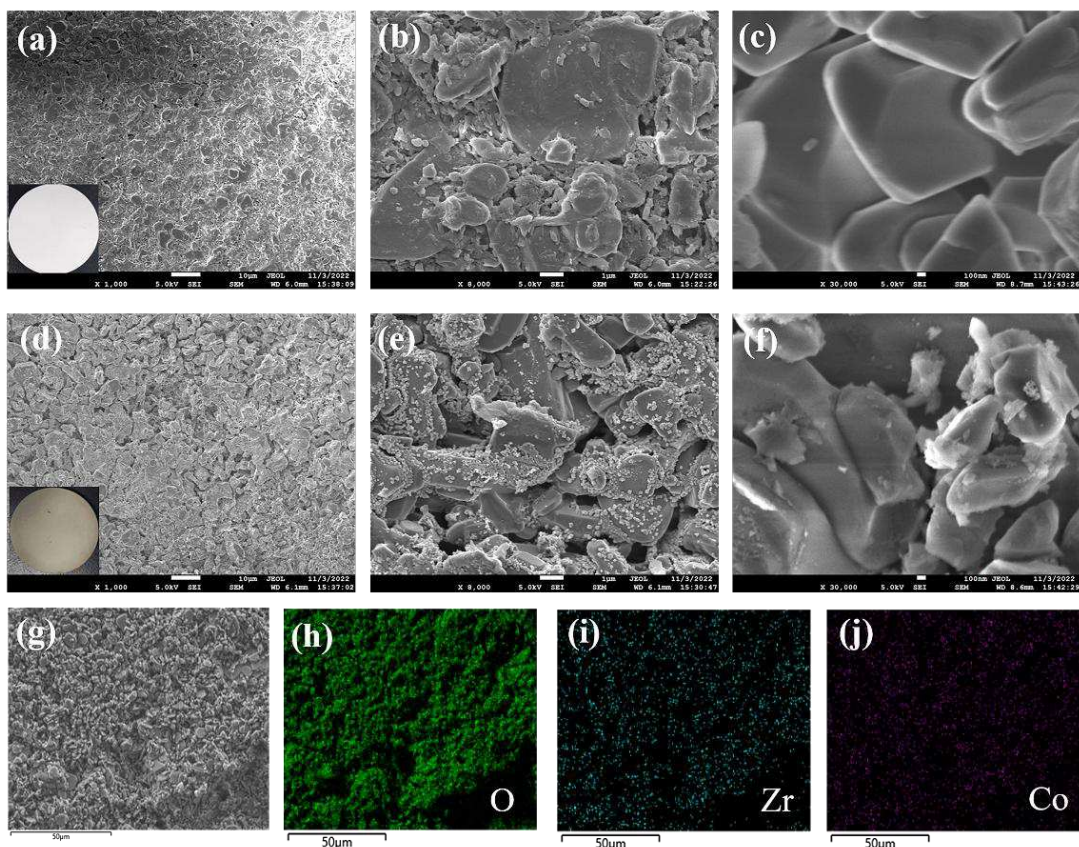


Figure 3 SEM images of (a) (b) ceramic membrane surface and (c) ceramic membrane cross-section; SEM images of (d) (e) CoZr@CM surface and (f) CoZr@CM cross-section; (g-j) EDS of CoZr@CM

X-ray photoelectron spectroscopy (XPS) tests were conducted to further identify catalyst chemical composition and interfacial bonding between Zr-Co₃O₄ and CM. Full rang XPS spectra for CoZr@CM and CM are given in Figure S2. The signals assigned to Co, Zr, Al, O and C are detected for CoZr@CM sample. High resolution Al 2p spectra of CM and CoZr@CM are presented in Figure 4a-b. The 74.0 eV peak for bare CM originates from Al-O-Al bonds belonging to ceramic substrate. Two peaks at 74.0 eV and 74.4 eV appear for CoZr@CM, which correspond to Al-O-Al and Al-O-Co bonds (Bao et al., 2019), respectively. The presence of Co-O-Al can alleviate the aggregation of Zr-Co₃O₄, reduce the leaching of Co during the experiment, and improve the stability of CoZr@CM. The high resolution XPS spectra of Co 2p (Figure 4c-d) and Zr 3d

(Figure 4e-f) is not detected for CM. The Co 2p and Zr 3d peaks for CoZr@CM further demonstrate that Zr-Co₃O₄ has been successfully loaded onto the ceramic membrane.

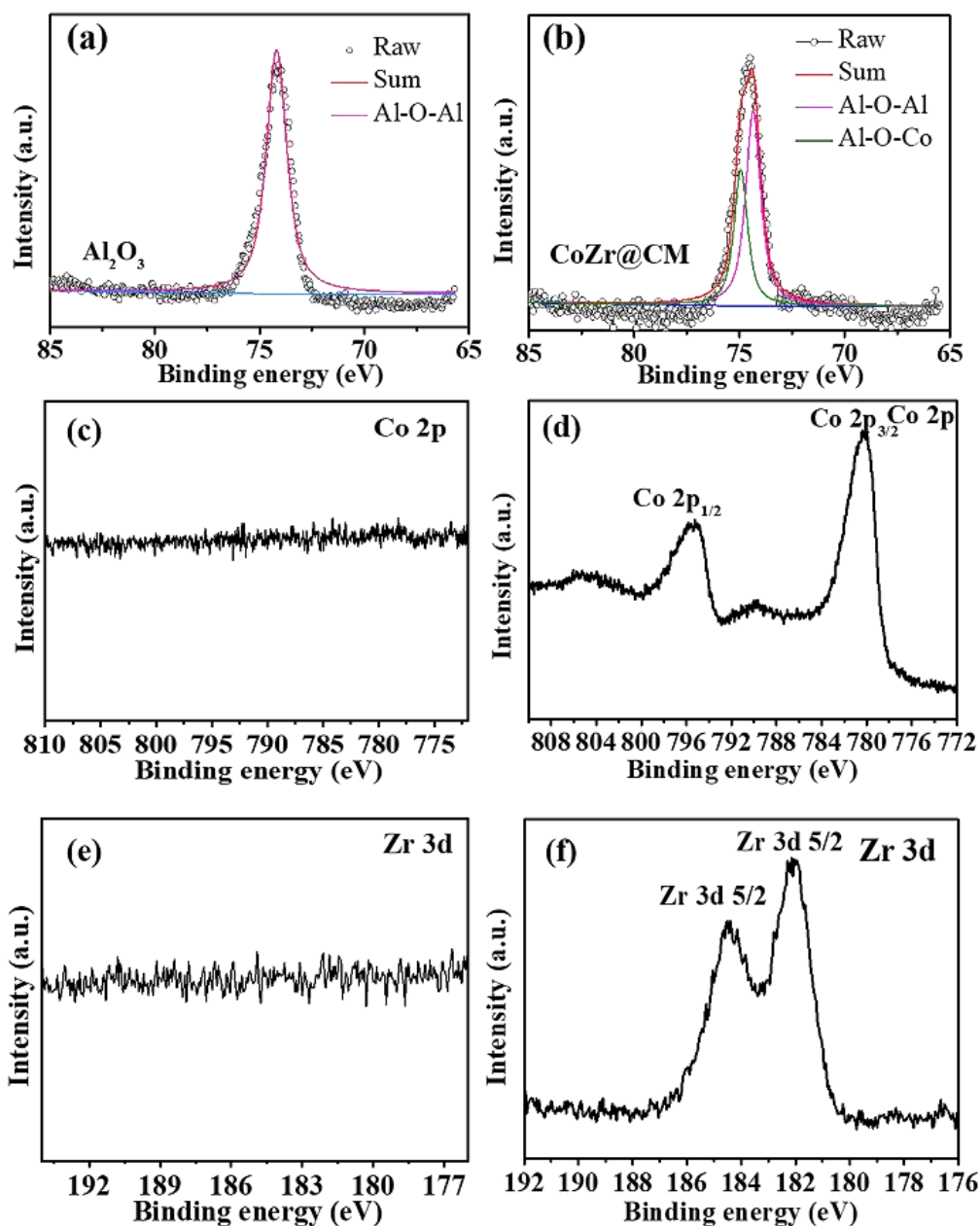


Figure 4. XPS spectra of (a-b) Al 2p, (c-d) Co 2p and (e-f) Zr 3d for CM and CoZr@CM

The membrane physicochemical properties of CM and CoZr@CM are shown in Table 1. The average pore diameters of CM and CoZr@CM are 296.5 nm and 283.9 nm respectively, and the porosities are 34.9% and 31.6% respectively. The fluxes are 3090.3 L m⁻² h⁻¹ bar⁻¹ and 2912.0 L m⁻² h⁻¹ bar⁻¹, respectively. Compared with CM, the

slight decrease in porosity, average pore diameter and flux of CoZr@CM may be due to the catalyst loading on the membrane pore, but it did not cause membrane pore blockage.

Table 1 Physicochemical properties of CM and CoZr@CM membranes

Membrane	Weight (g)	Mean pore width (nm)	Porosity (%)	Permeability (L m ⁻² h ⁻¹ bar ⁻¹)
CM	8.2396	296.5	34.9	3090.3
CoZr@CM	8.2577	283.9	31.6	2912.0

3.2 Catalytic performance

SMX, one widely detected antibiotic pollutant in aquatic environments, was chosen as the target contaminant for evaluating the catalytic capabilities of CoZr@CM. It can be seen from Figure S3 that 100% SMX was degraded and the first-order kinetic constant (k) is 0.14 for Zr-Co₃O₄, while only 27.8% SMX was degraded and the k is 0.0085 min⁻¹ for Co₃O₄. These findings demonstrate that Zr doping effectively boosts the catalytic capacity of Co₃O₄ for PMS activation for SMX degradation. The catalytic performance of CoZr@CM was presented in Figure 5a. It can be seen that only 15.4% SMX was degraded by PMS oxidation alone, which is due to the low redox potential of PMS. Only 8.5% of SMX was removed by membrane retention alone. This phenomenon arises from the fact that the average pore size of CoZr@CM (283.9 nm) greatly exceeds the molecular dimension of SMX (1.33 nm). Once PMS was introduced into the CoZr@CM membrane system, the removal rate of SMX increased to 97.1%, indicating that CoZr@CM can efficiently activate PMS to degrade organic pollutants. The catalytic performance was compared with that of the best-performing PMS catalytic membrane reported, as shown in Table S2, CoZr@CM demonstrated excellent

permeation rate and pollutant degradation performance. The degradation performance of CoZr@CM membrane towards other refractory organic pollutants such as methylene blue (MB), rhodamine b (RHB), phenol and bisphenol A (BPA) was also investigated. As shown in Figure 5b, the removal rates of RHB, MB, phenol, and BPA were 95.1%, 92.7%, 100%, and 72.8%, respectively. This result indicates that CoZr@CM activated PMS can efficiently degrade a variety of refractory organic pollutants.

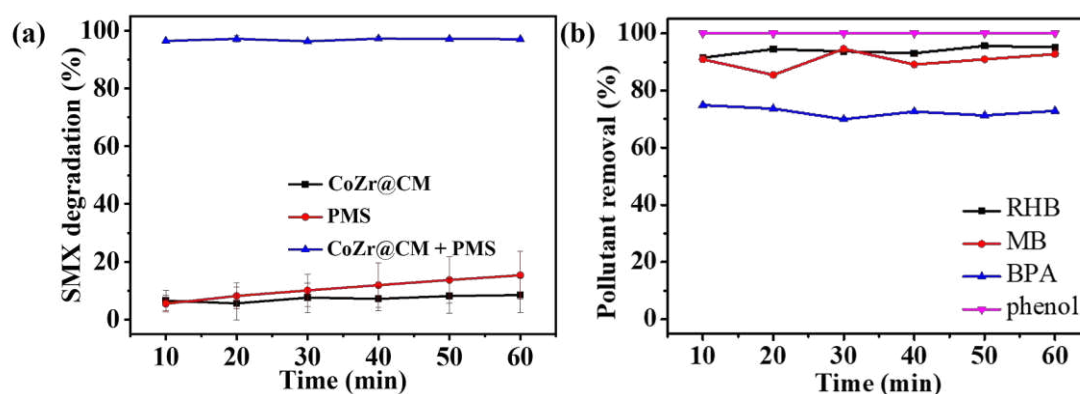


Figure 5 (a) SMX removal by CoZr@CM adsorption, PMS and CoZr@CM/PMS (b)

Performance of CoZr@CM in the degradation of different pollutants ($[PMS] = 0.25 \text{ g L}^{-1}$, $[SMX] = 10 \text{ mg L}^{-1}$, $T = 25 \text{ }^{\circ}\text{C}$, flow rate $= 2.019 \text{ mL min}^{-1}$, $P = 0.52 \text{ bar}$)

The degree of functionalization for the surface and pore of membrane is a crucial factor influencing the performance of the ZrCo-CM membrane. Hence, the effect of degree of functionalization for ZrCo-CM on performance was evaluated in Figure 6a, which was adjusted by changing the catalyst loading amounts. The loading amount of the catalyst on the ceramic membrane was regulated by adjusting the concentration of the impregnated metal salt. When the metal salt concentration of the impregnation solution was 5, 10, and 20 mmol L⁻¹, the catalyst loading amounts were 0.79, 2.19, and 6.29 mg g⁻¹ (calculated as loaded catalyst mass divided by membrane mass of CoZr@CM), respectively. The SMX removal efficiency is 73.2%, 97.1 % and 98.9% when catalyst area density was 0.79, 2.19 and 6.29 mg g⁻¹. Given that the removal rates of SMX were comparable when the impregnation liquid concentrations were 10 and 20

mmol L⁻¹, the concentration of the ceramic membrane impregnation liquid was selected as 10 mmol L⁻¹ for subsequent experiments.

Figure 6b describes how PMS dosage affects SMX degradation. When the PMS concentration increased from 0.10 g L⁻¹ to 0.25 g L⁻¹, the SMX removal rate rose from 37.9% to 97.1%. However, when the PMS concentration was further increased to 0.50 g L⁻¹, there was no significant increase in the degradation rate of SMX. Therefore, the PMS concentration was selected as 0.25 g L⁻¹.

Hydraulic residence time is another significant factor affecting the overall performance of catalytic membranes. To clarify its influence, SMX degradation was measured under varied hydraulic retention time, which corresponds to different flow rates (Figure 6c). At the retention time of 5.03 s (flow rate of 686.0 L m² h⁻¹), SMX removal stood at 26.6%. SMX removal was further enhanced to 54.0, 91.4 and 97.1% when the retention time increased to 6.68, 9.14 and 19.9 s (flow rate of 549.3, 346.2 and 173.1 L m² h⁻¹). Longer retention time (lower flow velocity) facilitates sufficient interaction between SMX and the catalytic membrane, thus improving degradation efficiency. Nevertheless, continuously increasing the retention time to 39.4, the removal of SMX almost unchanged (from 97.1% to 97.5%), indicating that the extra prolonged retention time barely further contributes to pollutant degradation. The kinetic constant of SMX degradation in the CoZr@CM membrane was calculated (Figure 6d), which is 0.21 s⁻¹, 90 times larger than that of the powder catalyst ($k = 0.14 \text{ min}^{-1}$). This may be due to the confinement effect occurred in the ceramic membrane pores, promoting the mass transfer of reactants and thereby enhancing the degradation of pollutants (Huang et al., 2025; Meng et al., 2022).

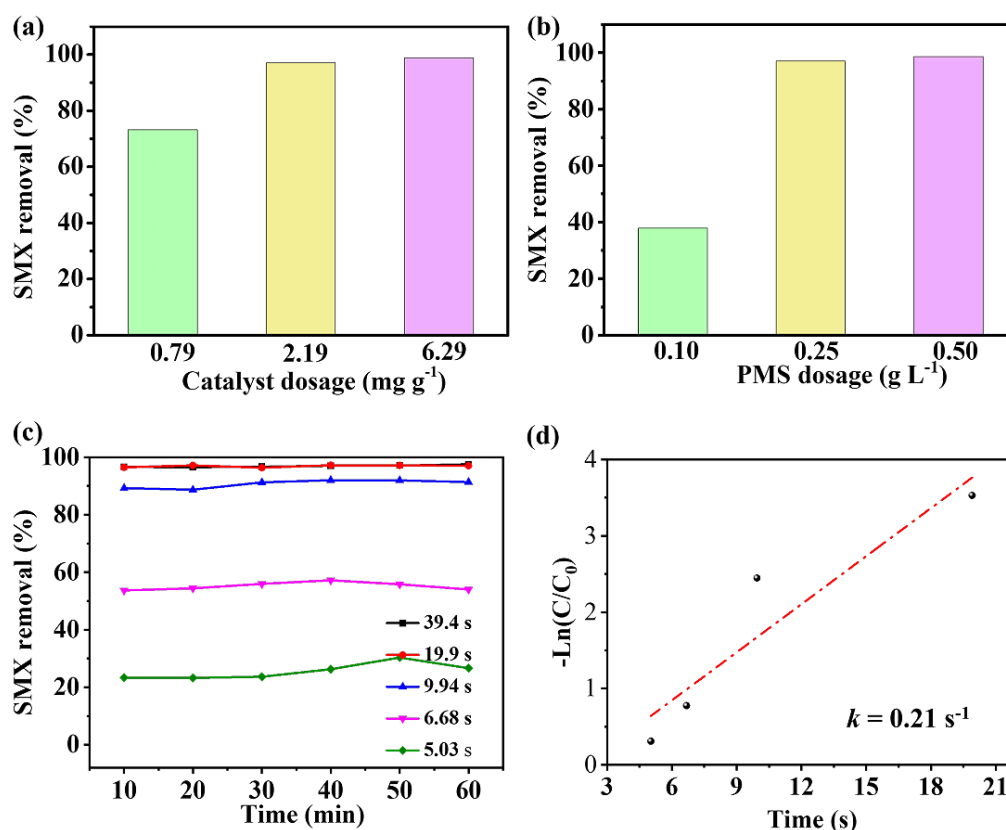


Figure 6 The influence of (a) catalyst loading, (b) PMS concentration and (c) reaction time on SMX degradation; (d) Pseudo-first-order kinetic modeling of SMX in CoZr@CM

3.4 Stability and potential for practical application

The stability of CoZr@CM was investigated through long-term continuous flow experiments. As shown in Figure 7a, when the operation time continued to be extended to 17 hours, the removal rate of SMX still reached 87.5%. Such minor decline in degradation performance could stem from the coverage of SMX-derived oxidative transformation products over the active sites on CoZr@CM membrane (Ma et al., 2020; Zhang et al., 2023). This finding proves that the CoZr@CM catalytic membrane holds great promise for long-term utilization. Additionally, the morphology of used membrane was further characterized. The corresponding results reveal that the membrane surface remained intact after prolonged running (Figure S4), confirming favorable structural stability. The leached cobalt concentration reached only

0.053 mg L⁻¹, far below the permissible cobalt discharge limit (1 mg L⁻¹) for aqueous environments (Li et al., 2020).

Abundant inorganic anions and natural organic substances were widely present in real wastewater, which should be taken into account when evaluating practical application prospects. Figure 7b displayed the influence of inorganic ions such as Cl⁻, H₂PO₄⁻, HCO₃⁻, NO₃⁻ and organic matters such as humic acid (HA) on SMX degradation. SMX degradation efficiency reached nearly 100 % and was further improved with the addition of Cl⁻. This improvement is ascribed to reactive chlorine radicals yielded from the reaction between chloride ions and PMS (Peng et al., 2021). The H₂PO₄⁻ exerted negligible interference toward SMX degradation, with removal efficiency staying at 92.5 %. However, the SMX removal decreased to 83.3% and 84.1% in the existence of HCO₃⁻ and HA, respectively. This inhibitory effect could originate from the scavenging and consumption of reactive species by HCO₃⁻ and HA. Figure 7c presents SMX degradation performance across pH 3–11, a range representative of most practical wastewater. It can be the 94.3%, 96.5%, 97.1%, 93.5% and 90.7% SMX were removed when pH was 3, 5, 7, 9 and 11. The above experiment outcomes verify that the CoZr@CM catalytic membrane system possesses considerable feasibility for real wastewater treatment.

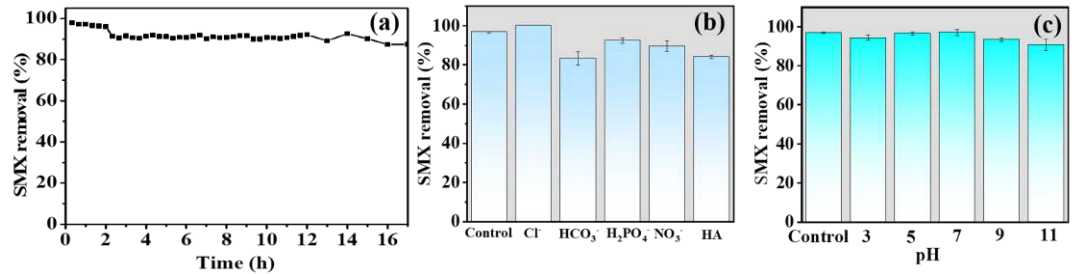


Figure 7 (a) Degradation of SMX during a long-term operation of CoZr@CM; The effect of inorganic ions (10 mmol L⁻¹) and HA (20 mg L⁻¹) on SMX degradation; (c) The influence of pH on SMX degradation

3.5 The identification of active species and mechanism analysis

To clarify the dominant reactive species responsible for SMX elimination within the CoZr@CM catalytic membrane system, quenching experiment were carried out. Tert-butyl alcohol (TBA) serves as a scavenger for $\bullet\text{OH}$ owing to the high reaction rate constant ($k(\bullet\text{OH}) = (3.8\text{--}7.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Methanol can trap both $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$, with corresponding rate constants of $k(\bullet\text{OH}) = (1.2\text{--}2.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k(\text{SO}_4^{\bullet-}) = (1.6\text{--}7.7) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. L-histidine was selected as an efficient quencher for $^1\text{O}_2$ ($3.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), while p-benzoquinone (p-BQ) was applied to capture $\text{O}_2^{\bullet-}$ ($9.0 \times 10^8\text{--}1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). As demonstrated in Figure 8a, SMX removal efficiencies dropped to 82.1%, 23.4%, 80.3% and 90.1% upon adding TBA, methanol, L-histidine and p-BQ, respectively. These outcomes suggest $\text{SO}_4^{\bullet-}$ acts as the primary reactive species, accompanied by the participation of $\bullet\text{OH}$, $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$. Electron paramagnetic resonance (EPR) tests were further implemented to verify these reactive intermediates. As shown in Figure 8b, no obvious characteristic signals were observed for isolated PMS or CoZr@CM. Distinct strong peaks with an intensity ratio of 1:2:1:2:1:2:1, which correspond to DMPOX (oxidized derivative of DMPO), emerged when PMS and CoZr@CM co-existed. This seven-line fingerprint signal of DMPOX originates from rapid DMPO oxidation induced by $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ (Bu et al., 2021; Pang et al., 2021). Singlet oxygen was also detected using TEMP (2,2,6,6-tetramethylpiperidine) as the trapping agent. Although the triplet TEMP- $^1\text{O}_2$ adduct signal (intensity ratio 1:1:1) could be detected for single PMS or CoZr@CM systems, this characteristic signal was substantially intensified in the combined CoZr@CM+PMS setup relative to individual components. This result confirms the generation of $^1\text{O}_2$ in the CoZr@CM/PMS system. By contrast, no characteristic peaks assigned to superoxide radicals were detected (Figure S5). Based on the above results, it can be concluded that $\text{SO}_4^{\bullet-}$ represents the

major reactive species in this system, alongside the generation of $^1\text{O}_2$ and $\cdot\text{OH}$.

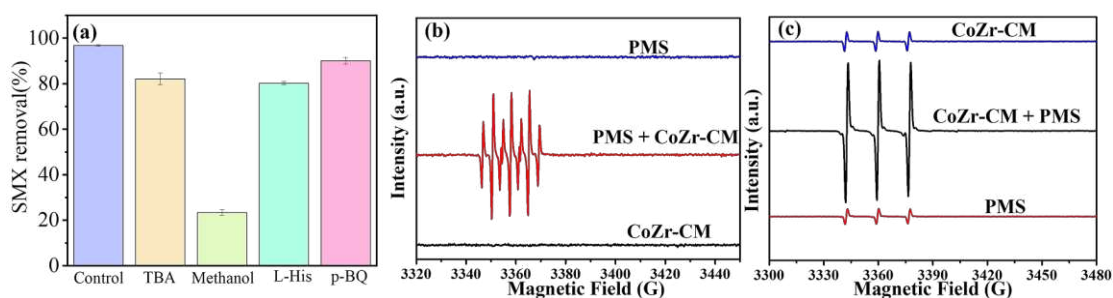


Figure 8 (a) Quenching experiment; EPR spectra in DMPO solutions (b) and in (c) TEMP solutions

On the basis of above mechanistic investigations, a plausible mechanism for the CoZr@CM/PMS catalytic membrane is proposed (Figure 9). Driven by transmembrane pressure, PMS molecules and target pollutants rapidly migrate toward and penetrate into the membrane pore of CoZr@CM. Inside these regions, PMS interacts with catalysts anchored on membrane surfaces and inner pore channels to produce multiple reactive oxygen species such as $\text{SO}_4^{\cdot-}$, $\cdot\text{OH}$ and $^1\text{O}_2$, which further degrade organic pollutants. Benefiting from membrane pore functionalization, more catalytic active sites become accessible, and mass contact duration is prolonged. Moreover, spatial confinement effects formed within pore channels greatly boost mass-transfer performance. Such effects facilitate higher yields of reactive species and ultimately achieve superior pollutant removal.

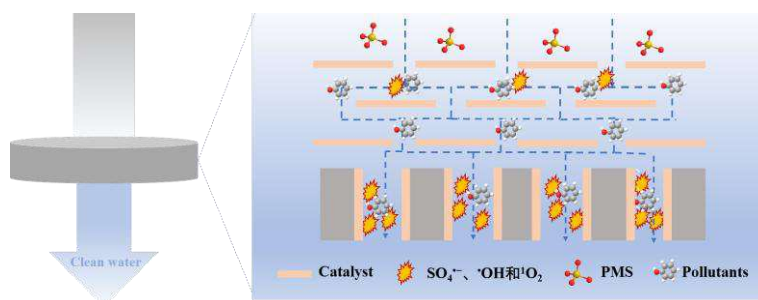


Figure 9 The mechanistic diagram of PMS activation coupled membrane separation process

3.6 Possible degradation pathways and toxicity evaluation

Intermediates generated in SMX degradation processes were identified via liquid chromatography-mass spectrometry (LC-MS). A total of seven compounds (including SMX) were identified, as summarized in Figure S6 and Table S3. Based on these LC-MS analytical results, possible transformation routes for SMX were proposed (Figure 10). Sulfamethoxazole (SMX, m/z 254) undergoes distinct degradation routes initiated by three dominant reactive including $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$ and $^1\text{O}_2$. The $\bullet\text{OH}$ attacks the benzene ring of SMX, introducing a hydroxyl (-OH) substituent onto the aromatic ring to form hydroxylated intermediate P1 ($m/z = 270$). Further oxidation of P1 by excess $\bullet\text{OH}$ breaks the benzene ring structure, generating the ring-opening diketone product P2 ($m/z = 109$). $\text{SO}_4^{\bullet-}$ induces nitration on the benzene ring of SMX, replacing the amino group with a nitro group (-NO) to produce mononitro intermediate P3 ($m/z = 268$). Continuous oxidation by $\text{SO}_4^{\bullet-}$ adds a second oxygen atom to the nitro group, forming dinitro-substituted product P4 ($m/z = 283$). $^1\text{O}_2$ selectively attacks the isoxazole heterocyclic moiety of SMX, rupturing the five-membered N-O ring and releasing heterocyclic fragment P5 ($m/z = 99$). The residual aliphatic fragment from ring cleavage is further oxidized by $^1\text{O}_2$ to form amide-diketone derivative P6 ($m/z = 99$). All intermediate products are ultimately mineralized into small inorganic molecules including CO_2 and H_2O .

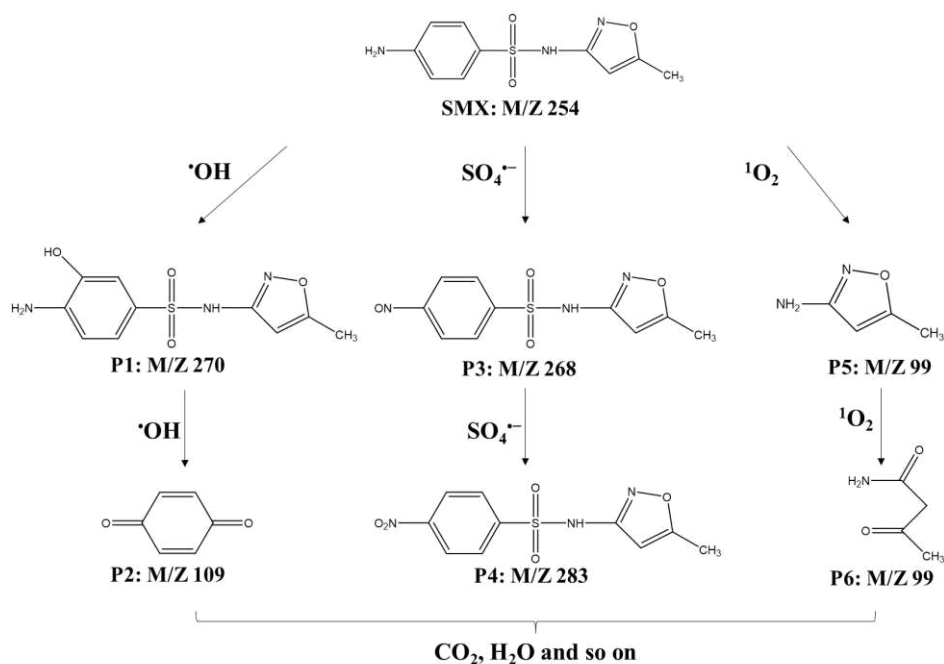


Figure 10 Possible degradation pathways of SMX in CoZr@CM catalytic membrane system

Variations in toxic properties for these transformation products were evaluated using the Toxicity Evaluation Software Tool (T.E.S.T) (Ding et al., 2022; Lian et al., 2025). As displayed in Figure S7a, the bioconcentration factors for final compounds from all three transformation pathways were below the value of parent SMX (17.11). This observation indicates that bioaccumulation risks drop as SMX degradation proceeds. Besides, nearly all detected intermediates possessed weaker developmental toxicity compared to SMX (Figure S7b). In summary, CoZr@CM/PMS system enables eco-safe degradation of SMX.

4 Conclusion

Surface and pore co-functionalized ceramic membrane CoZr@CM was successfully fabricated. The catalyst Zr-Co₃O₄ is evenly distributed in the membrane pores and surface interface. The Co–O–Al bonds CoZr@CM can suppress Co leakage. Surface and pore co-functionalized in CoZr@CM provided plentiful accessible active sites, prolonged reaction time and accelerated mass-transfer behavior. Under high water flux conditions (2912.0 L m⁻² h⁻¹ bar⁻¹), the optimized CoZr@CM achieved 97.1 %

378 SMX removal efficiency, competitive with or superior to the reported PMS catalytic
379 membrane. The k of SMX degradation in CoZr@CM was 90 times higher than that for
380 powder catalyst. The CoZr@CM/PMS system also exhibited good degrading capacity
381 toward multiple refractory organics such as phenol, bisphenol A and rhodamine B,
382 revealing universal applicability of the CoZr@CM system. CoZr@CM exhibits excellent
383 stability and 87.5% SMX degradation still was achieved after a continuous operation of
384 17 hours. The effect of solution pH and several common anions in environmental water on
385 SMX degradation was measured, providing potential practical application of
386 CoZr@CM catalytic membrane system in actual wastewater treatment. Quenching
387 experiment and EPR test confirmed $\text{SO}_4^{\bullet-}$ as dominant species, accompanied by a small
388 amount of $\cdot\text{OH}$ and $^1\text{O}_2$. The degradation pathway and toxicity analysis indicated that
389 CoZr@CM/PMS system was an eco-friendly reaction system. This study delivers a
390 feasible strategy for SMX elimination in practical wastewater.

391 Notes

392

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394

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