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# Efficient removal of sulfamethazine by a magnetic recoverable $CeO_2/Fe_3O_4$/natural zeolite catalyst in catalytic ozonation process

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In order to realize the efficient removal of sulfamethazine (SMZ) and overcome the recycling difficulty of catalysts in a heterogeneous catalytic ozonation process, low-cost natural zeolite loaded with $CeO_2$ and $Fe_3O_4$ (FC/HZ) was synthesized by the co-precipitation method. The FC/HZ catalyst could completely degrade SMZ and realize 39.6% removal of TOC through catalytic ozonation. Moreover, the FC/HZ catalyst exhibited high catalytic ozonation activity under a wide pH range and possessed excellent recyclability (>90%) and stability with a magnet. Based on experiment and material characterization, the possible catalytic mechanism and degradation pathway of SMZ was revealed. In brief, this study offered an effective strategy for preparing recyclable catalysts and eliminating SMZ in aqueous solution.

KEYWORDS

**catalytic ozonation, cerium oxides, natural zeolite, magnetic, sulfamethazine**

## 1 Introduction

Antibiotics are widely used in pharmaceutical and aquaculture industries for the treatment of various non-viral infections (Zhou et al., 2012; Wang et al., 2021; Wu et al., 2022). However, the abuse of antibiotics causes serious threats to ecological environment and human health, due to their persistence and drug resistance (Zhang et al., 2015; Zsirka et al., 2016; Jallouli et al., 2017; Wu et al., 2021). Sulfamethazine (SMZ) is a typical antibiotic, which has been widely used to treat *Staphylococcus*, lytic *Streptococcus*, and other infections. Recently, SMZ was detected in some kinds of water. Its threats cannot be ignored (Wehrhan et al., 2010; Xu et al., 2011; Cui et al., 2021; Fu et al., 2022). Owing to the complex intermediates and poor biodegradability of SMZ, it is difficult to effectively remove SMZ with traditional treatment technologies. The heterogeneous catalytic ozonation technology, a representative of advanced oxidation technology, can overcome the selectivity of ozone and improve the mineralization efficiency of organic pollutants, especially the removal of toxic and non-biodegradable substances (Baciogliu and Otker, 2003; Slomczynska et al., 2004; Andreozzi et al., 2005; Dantas et al., 2008). However, the complex preparation methods, high cost, and low recycling of $O_3$ catalysts have restricted the development and application of the technology (Xie et al., 2020; Chen et al., 2021).

Zeolite is a porous aluminosilicate with a framework structure. It has excellent ion exchange, surface activity, adsorption, and chemical stability, which are widely used in the field of adsorption and catalysis (Cheng et al., 2000), wherein most research studies are based on the artificial zeolite due to its controllable material. However, the enormous production cost has become the obstacle for further application. Natural zeolite possesses extremely low production cost, in addition to the similar structure and performance with artificial zeolite (Lu et al., 2007; Sivaguru and Lalitha, 2014). It can promote the adsorption of organic pollutants and the exposure of active sites in the catalytic ozonation process. Moreover, high-purity natural zeolite can be developed into high-efficiency catalysts *via* appropriate modifications. Therefore, using natural zeolite is a potential and feasible synthesis strategy of $O_3$ catalysts.

In addition, magnetic carrier technology has been applied to the separation and fixation of biological cells, wastewater treatment, and mineral processing (Takafuji et al., 2004; Galindo-González et al., 2005). It can improve the recycling of catalysts *via* loading the magnetic materials on natural zeolite. Researchers have prepared magnetic adsorbents with different characteristics by combining zeolite and magnetic iron oxide (Bourlinos et al., 2003). However, the prepared catalysts had limited ozone catalytic activity. Also, the complicated process of preparation increased the cost. According to previous studies, catalysts loaded with $CeO_2$ (labeled as Ce/HZ) exhibited high catalytic ozonation activity (Zhang et al., 2020). Therefore, the combination of natural zeolite, magnetic materials, and $CeO_2$ was likely to simultaneously solve the complexity of the complex preparation methods, high cost, and low recycling of $O_3$ catalysts.

To address the problem that powder catalysts were difficult to recover and kept high catalytic ozonation activity, magnetic catalysts based on natural zeolite were prepared. The magnetic component, $Fe_3O_4$, and the active substance, $CeO_2$, were loaded on the natural zeolite by the co-precipitation method. The morphology, specific surface area, and element valence changes of the prepared catalyst were systematically studied. The degradation performance of SMZ was evaluated in the catalytic ozonation process with prepared catalysts. The degradation mechanism and pathway of the target pollutant SMZ in the heterogeneous catalytic ozonation system were discussed.

# 2 Methods

## 2.1 Experimental material

Natural zeolite (clinoptilolite, 200 mesh), $Ce(NO_3)_3\bullet 6H_2O$, $Fe(NO_3)_3\bullet 9H_2O$, nitric acid ($HNO_3$), and ammonia water were purchased from Sinopharm Group.

## 2.2 Catalyst preparation

The natural zeolite was added into $HNO_3$ solution (1 mol/L) and stirred at room temperature for 4 h, and then the precipitate was washed with deionized water and dried in an oven at 60°C for 12 h. The prepared material was labeled as HZ. Then, the HZ was added to the $Ce(NO_3)_3$ solution (0.029 mol/L) and stirred at room temperature for 6 h. The pH was adjusted to 7–8 with $NH_3\bullet H_2O$ (2.0 mol/L). Then, the obtained cerium loading catalyst (Ce/HZ) was dried at 12°C for 12 h and calcined at 450°C for 4 h.

$FeSO_4\bullet 7H_2O$ and $Fe(NO_3)_3\bullet 9H_2O$ with a molar ratio of 1: 2 were added. Then, the mixed solution was stirred, and the $NH_3\bullet H_2O$ was added until the solution became black. The solution was aged for 2 h at 70°C. The obtained magnetic material (FC/HZ) was dried in an oven at 80°C for 4 h.

## 2.3 Characterization

The morphologies of the catalyst were analyzed using a cold-field emission scanning electron microscope (SEM, Jeol JSM-7500F). The chemical states of catalysts were obtained by X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Kratos Co., United Kingdom). The specific surface and pore distribution of the catalysts were measured by nitrogen adsorption–desorption on Brunauer–Emmett–Teller (BET, Micromeritics ASAP2460, United States). An X-ray diffractometer (XRD, PANalytical B.V., Holland) was used to analyze the composition of the catalysts.

## 2.4 Experimental method

All the ozonation experiments were conducted in a 1-L glass reactor. The concentrations of SMZ and catalysts were 50 mg/L and 2 g/L, respectively. The gas flow rate and concentration were 600 mL/min and 6 mg/L, respectively. In degradation experiments, the samples were withdrawn from the reactor at predetermined intervals and filtered through a 0.22-μm PTFE filter into a plastic bottle.

The SMZ concentration of the samples was determined by high-performance liquid chromatography (HPLC, Agilent 1260 Infinity, Agilent Technologies Co., Ltd.). Detection conditions: The chromatographic column was an Eclipse XDB-C18 column. The ratio of pure water and methanol was 50:50, with a liquid flow rate of 1.0 mL/min. Detection was performed at 275 nm. TOC of the samples were measured using a TOC analyzer (TOC-L-CPH-CN200, Shimadzu, Japan). An ultrahigh performance liquid chromatograph (Agilent, 1290 Infinity II) equipped with the Eclipse plus-C18 column and an AgilentG6545 Q-TOF mass spectrometer (UPLC-QTOF-MS/MS) were used to analyze the degradation intermediates of SMZ. The mobile phase A was the mixing solution of acetonitrile and water (V/V 55%/45%). The mobile phase B was the mixing solution of 0.1% formic acid and 5 μM ammonium formate aqueous solution. The injection volume was 20 μL, and the pump flow was 1.0 mL/min.

# 3 Results and discussion

## 3.1 Characterization of the catalysts

The morphology of the FC/HZ catalyst was shown in Figure 1A. The fine particles uniformly covered the surface of the modified zeolite, indicating the introduction of $CeO_2$ and $Fe_3O_4$. The

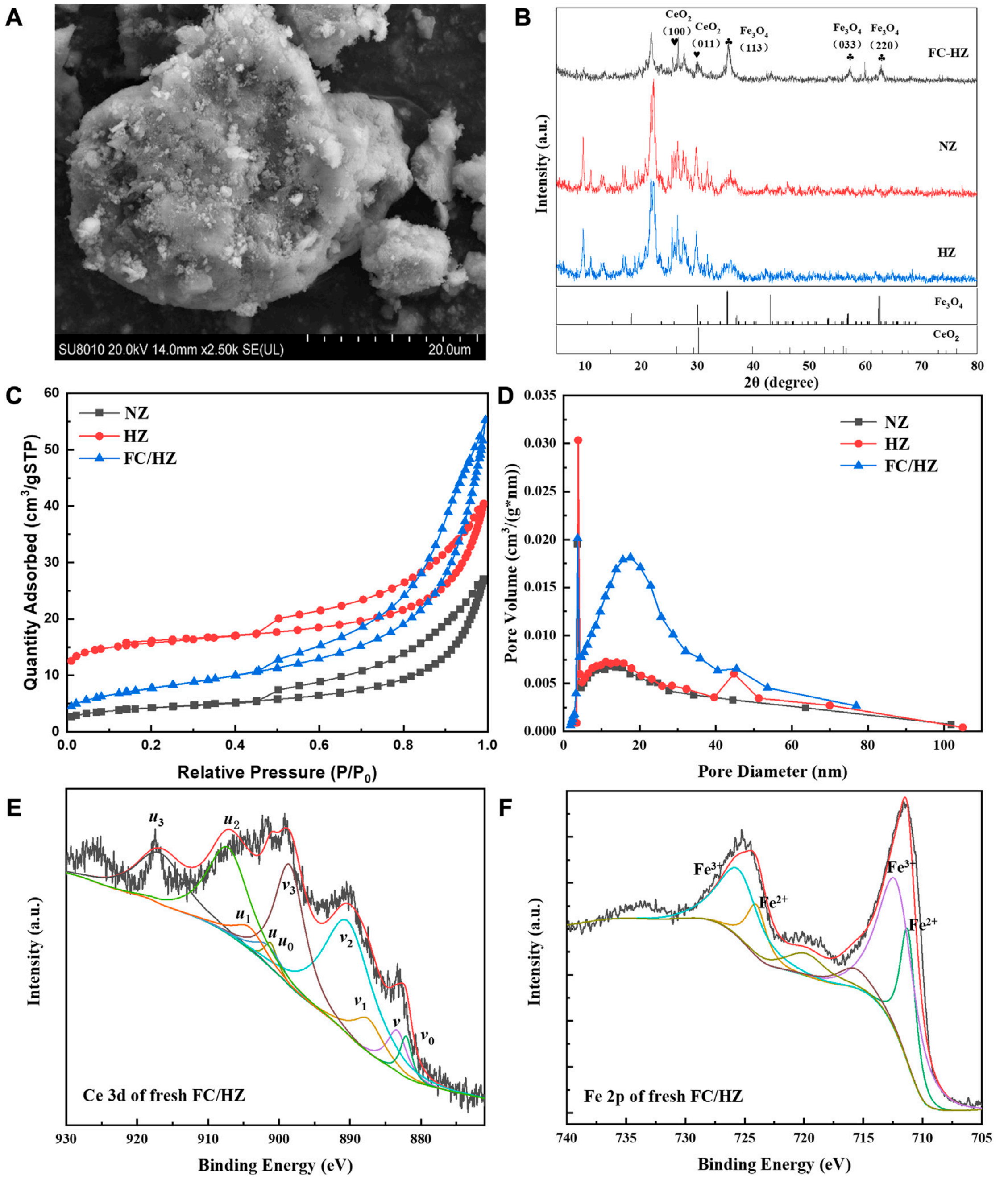

FIGURE 1
Morphologies, crystalline structures, pore size distribution, and chemical states of the FC/HZ catalyst. **(A)** SEM image. **(B)** XRD spectra. **(C)** and **(D)** show BET data. **(E)** and **(F)** show the spectrum of Ce 3d and Fe 2p.

crystalline structures of FC/HZ, NZ, and HZ catalysts were analyzed by XRD. Figure1B shows that the diffraction peaks at 35.5°, 57.0°, 62.4°, and 64.8° of the FC/HZ catalyst were ascribed to (212), (232), (400), and (308) of $Fe_3O_4$ (PDF-# 97-009-2356), respectively. Moreover, the characteristic diffraction peaks of $CeO_2$ could be observed in the XRD pattern of FC/HZ, according to the standard card of $CeO_2$ (PDF-#44-1086). These results further confirmed that $CeO_2$ and $Fe_3O_4$ were loaded, and the designed catalyst was successfully prepared by the method of ultrasonic impregnation and heat-treatment.

The isotherm of the FC/HZ catalyst showed type IV characteristics with hysteresis loops of type H3 (Figure 1C). The type IV isotherm indicated the FC/HZ catalyst was mesoporous. The specific surface area of the FC/HZ catalyst was 27.78 $m^2/g$. In comparison with HZ, the specific surface area decreased after loading $CeO_2$ and $Fe_3O_4$. This might be attributed to $CeO_2$ and

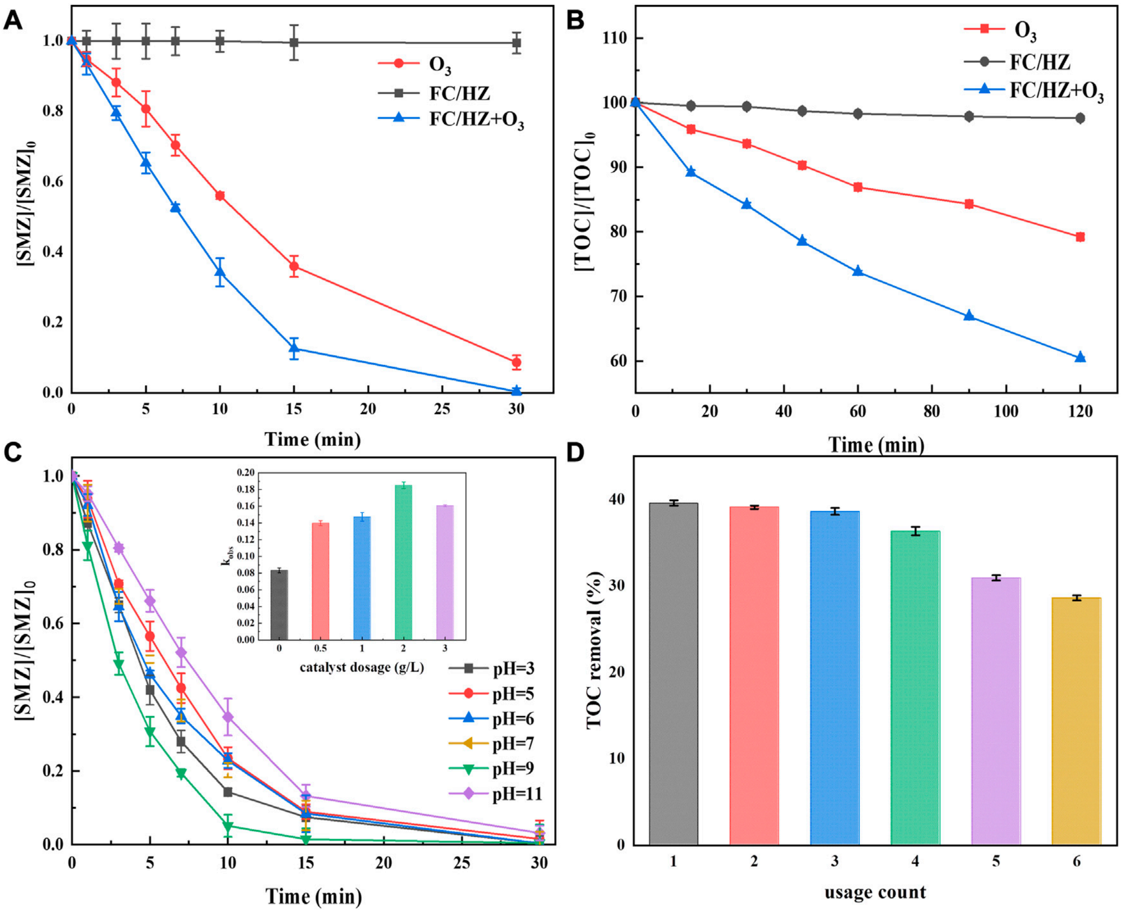

FIGURE 2
**(A)** and **(B)** show the degradation efficiencies of SMZ and removal efficiencies of TOC in various processes. **(C)** Degradation efficiencies of SMZ under various pH in the catalytic ozonation process with the FC/HZ catalyst (inset: the effect of catalyst dosage). **(D)** Stability and recyclability of the FC/HZ catalyst.

$Fe_3O_4$ entering the slits and the pore structure of the zeolite. According to Figure 1D, the pore structure was a double-pore distribution, and the main structure was the mesoporous channel with the pore size ranging from 2.0 to 50.0 nm. The other was a microporous channel with the pore size ranging from 1.8 to 2.0 nm. Compared with NZ and HZ, the FC/HZ catalyst showed notable mesoporous distribution, indicating that the FC/HZ catalyst might be favorable to the adsorption of contaminants and catalysis of $O_3$.

XPS was used to analyze the chemical states of the FC/HZ catalyst. Figure 1E was the spectrum of Ce 3d, which was composed of 10 peaks, and the peaks of $3d_{3/2}$ and $3d_{5/2}$ were represented by $u$ and $v$, respectively (Li et al., 2015). The trivalent Ce (III) was designated as a 4-peak structure with its $v_0$ and $v_1$ peaks at 880.1 eV and 885.4 eV, and spin-orbit splitting $u_0$ and $u_1$ peaks appeared at 901.17 eV and 904.15 eV, respectively. Similarly, the tetravalent Ce (IV) showed a 6-peak structure, and its $v$, $v_2$, and $v_3$ peaks were located at 882.33 eV, 888.3 eV, and 898.5 eV, respectively. The corresponding spin-orbit splitting $u$, $u_2$, and $u_3$ peaks appear at 901.5 eV, 907.18 eV, and 916.75 eV, respectively. This indicated that Ce existed in the form of Ce (III) and Ce (IV) in the FC/HZ catalyst. Figure 1F showed the spectrum of Fe 2p. The characteristic peaks of the catalyst were located at around 711.4 and 725.3 eV, which could correspond to the complete oxidation product spectrum of Fe. The absence of satellite peaks indicated the existence of $Fe_3O_4$. In addition, the ratios of Ce (III)/Ce (IV) and Fe (II)/Fe (III) were calculated for the FC/HZ catalyst before and after the reaction, respectively. The ratio of Ce (III)/Ce (IV) changed from 0.1507 to 0.773, and the ratio of Fe (II)/Fe (III) changed from 0.3777 to 0.3155. The results indicated that they might be the active sites contributing to the catalysis of $O_3$.

## 3.2 Catalytic performance

The degradation efficiencies of SMZ were exhibited in Figure 2A. SMZ was hardly degraded during the FC/HZ catalysis alone, indicating negligible adsorption between the catalyst and SMZ due to the limited specific surface area of the FC/HZ catalyst. In comparison with ozonation alone, the degradation efficiency of SMZ improved from 65% to 90% within 15 min for the FC/HZ catalytic ozonation process. The FC/HZ catalyst exhibited better catalytic activity. Moreover, TOC result showed

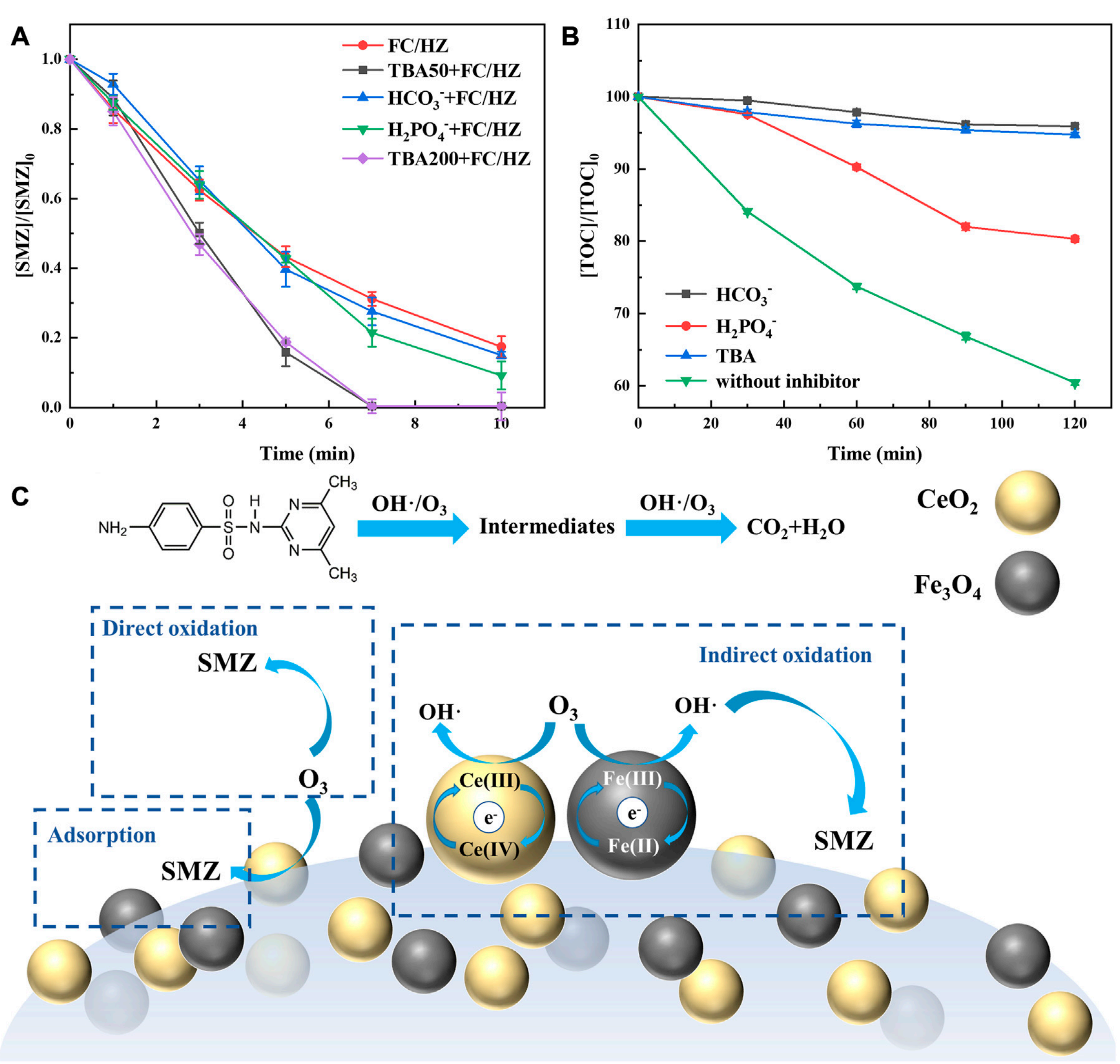

FIGURE 3
**(A)** and **(B)** show the effect of scavengers on SMZ degradation efficiency and TOC removal efficiency. **(C)** Proposed mechanism of the FC/HZ catalyst in the catalytic ozonation process.

the similar removal order of SMZ for ozonation alone and the FC/HZ catalytic ozonation process (Figure 2B), further confirming the catalytic ozonation activity of the FC/HZ catalyst. These results indicated that the FC/HZ catalyst could effectively convert $O_3$ to •OH and improve the mineralization removal efficiency of pollutants in water.

The degradation efficiencies of SMZ under different solution pH levels were evaluated in the FC/HZ catalytic ozonation process. Figure 2C showed that all the experimental groups achieved a removal rate of 97–99%, indicating that FC/HZ catalyzed $O_3$ under a wide pH range. No discernible differences between pH 3 and pH 7 were found. The highest efficiency was achieved at pH 9, and the lowest was at pH 11. When pH reached 11, the degradation efficiency decreased significantly. It was deemed that $O_3$ would react with $OH^-$ in solution. When pH reached 11, it might have caused a significant competition between the FC/HZ catalytic ozonation process and $O_3$ reaction with $OH^-$. This would cause the consumption of radicals which was used to generate •OH by chain reactions, further affecting the generation of •OH.

The effect of catalyst dosage was explored (Figure 2C inset). With the catalyst dosage from 0 to 2 g/L, the efficiency of SMZ removal increased significantly with the $k_{obs}$ from 0.083 to 0.185 min$^{-1}$. It was mainly found that the raised catalyst dosage increased the active sites and generated more •OH. It improved the reaction efficiency of $O_3$, SMZ, and the catalyst (Zhao et al., 2008). However, the degradation efficiencies decreased when catalyst dosage increased to 3 g/L. It might be attributed to the gas quickly turning into large bubbles after colliding with the catalyst, thus hindering the mass transfer of $O_3$ from the gas phase to the liquid phase (Lin and Gurol, 1998).

The recyclability and stability of the FC/HZ catalyst was investigated by repeating SMZ degradation tests (Figure 2D). After degradation, the catalyst was separated by an external magnet and washed with deionized water and ethanol. The

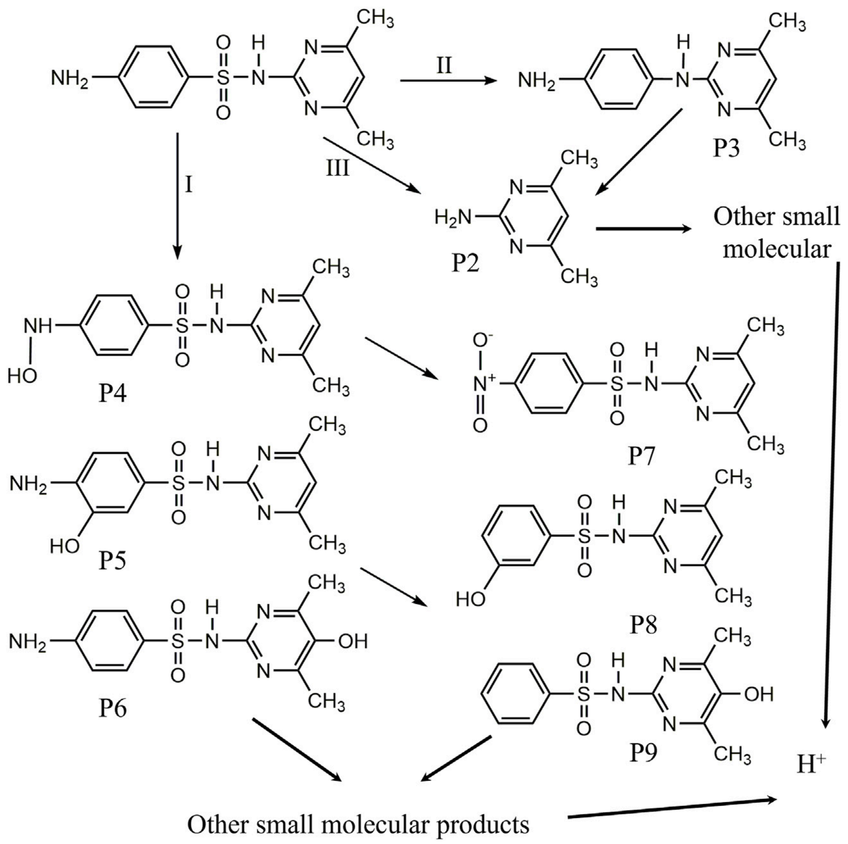

FIGURE 4
Degradation pathways of SMZ in the catalytic ozonation process.

collected catalyst was reused in the second reaction under optimum reaction conditions. This same process was repeated six times. The TOC removal efficiencies during the four cyclic experiments did not decrease significantly, confirming the catalytic stability of the FC/HZ catalyst. However, the efficiencies gradually decreased in the fifth and sixth cycles. This might be attributed to the loss of catalysts during the separation process of the catalyst and the analyzed samples in every cyclic experiment. After six cyclic experiments, the recovery efficiency of the suspension FC/HZ by magnetic force was still higher than 90%, indicating the excellent recyclability of the FC/HZ catalyst.

## 3.3 Possible reaction mechanisms

Tert-butanol (TBA) is a strong •OH radical scavenger that has a reaction rate constant of $6.0 \times 10^{8}\ M^{-1}\ s^{-1}$ with a hydroxyl radical and only $3.0 \times 10^{-3}\ M^{-1}\ s^{-1}$ with ozone (Bing et al., 2012). At the same time, TBA cannot be adsorbed on the surface of metal oxides due to its physical-chemical property (Qi et al., 2008). Furthermore, phosphate ions in water can be adsorbed on the surface of the catalyst through complexation, which will affect the catalytic activity of the catalyst. In addition, the carbonate ion is also considered a typical radical scavenger. In order to prove the generation of •OH in the catalytic ozonation process with the FC/HZ catalyst, TBA, $H_2PO_4^-$, and $HCO_3^-$ were used to explore the radicals.

Figure 3A showed that the degradation efficiencies did not decrease with the addition of TBA, $H_2PO_4^-$, and $HCO_3^-$. However, this phenomenon could not confirm the absence of •OH because SMZ was easily degraded by $O_3$ alone. The increased degradation efficiencies might be attributed to the activation and improvement of the $O_3$ oxidation path due to the inhibition of free-radical paths. In order to confirm the •OH, the TOC was detected because some intermediates were refractory substances of $O_3$. Figure 3B shows that the removal of TOC was decreased evidently, indicating the generation of •OH in the FC/HZ catalytic ozonation process.

Based on the abovementioned analysis and experimental results, a probable catalytic ozonation mechanism was put forward, which included the radical process and direct ozonation (Figure 3C).

(1) Radical process

$CeO_2$ and $Fe_3O_4$ as the active sites catalyzed by $O_3$ to generate •OH according to the valence state change of $Ce^{3+}/Ce^{4+}$ and $Fe^{2+}/Fe^{3+}$ by the electron transfer process, respectively. The generated •OH diffused into the bulk solution to attack organic pollutants. More $O_3$ was adsorbed on the catalyst surface and converted into

•OH. The entire process was continuously circulated, and the entire oxidative degradation process was finally completed.

(2) Direct ozonation

As we all know, ozone has a strong oxidizing property and its redox potential was 2.07 V. According to the control experiment, SMZ could be removed by $O_3$ without a catalyst, indicating that $O_3$ attacked the degradable substances including SMZ and some intermediates. Therefore, the direct ozonation process existed during the removal of SMZ.

### 3.4 Degradation pathway

The degradation products of SMZ were analyzed by HPLC-MS/MS. Based on the mass spectrum fragment information, the possible pathway of SMZ was shown in Figure 4.

In pathway Ⅰ, substitution reactions occurred after •OH attacked SMZ molecules. There were three ways to replace the hydroxyl group: replacing the hydrogen in the amino group to form a hydroxylamine product, replacing the hydrogen in the benzene ring, and replacing the hydrogen in the pyrimidine ring (Seddigi et al., 2014). The hydroxylated SMZ (P4–P6) was formed by the continuous attack of the active substance. P7 was the product in which the N atom in the hydroxylamine product was further oxidized for nitrosation. P5 and P6 lost the amino to form P8 and P9, respectively.

Pathway Ⅱ showed that P3 might be the product of the cleavage of the sulfonamide bonds [S–N] and [C–S] in SMZ. Several possible pathways for the formation of extrusion products with P3 have been proposed (Guo et al., 2013; Periša et al., 2013). Subsequently, •OH attacked the carbon–nitrogen bond between the benzene and pyrimidine ring in compound P3.

Pathway III was initiated by the breaking of the sulfonamide bond [S–N]. Under the action of ozone and hydroxyl radicals, the [S–N] bond could be broken directly to form P2.

## 4 Conclusion

In this study, $CeO_2$ and $Fe_3O_4$ were loaded on the acid-washed natural zeolite by the co-precipitation method to form the FC/HZ catalyst. The FC/HZ catalyst could improve the degradation and mineralization rate of SMZ. $CeO_2$ and $Fe_3O_4$ as the active sites contributed to the rapid generation of •OH in the catalytic ozonation process. The FC/HZ catalyst exhibited high catalytic ozonation activity under a wide pH range and possessed excellent recyclability and stability. This work proposed a feasible path to prepare efficient, stable, and recyclable catalysts based on high-purity natural zeolite and realized the efficient removal of antibiotic in aqueous solution. It provided guidance for the advanced treatment of antibiotic wastewater.

## Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

## Author contributions

ZG and YL contributed to the preparation of materials, evaluation of performance, and analysis of data. JZ contributed to the analysis of data. JW and YS contributed to the supervision and modification of the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

## Publisher's note

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