



Article Enhanced Ozone Oxidation by a Novel Fe/Mn@γ–Al₂O₃ Nanocatalyst: The Role of Hydroxyl Radical and Singlet Oxygen

Chen Liang ^{1,2}, Xinhao Luo ^{1,2} and Yongyou Hu ^{1,2,*}

- ¹ Guangzhou Higher Education Mega Centre, School of Environment and Energy, South China University of Technology, Guangzhou 510006, China; scuterlc@163.com (C.L.); 2615390@163.com (X.L.)
- ² Guangzhou Higher Education Mega Centre, The Key Lab of Pollution Control and Ecosystem Restoration in Industry Clusters, Ministry of Education, Guangzhou 510006, China
- * Correspondence: ppyyhu@scut.edu.cn; Tel.: +86-13602746125

Abstract: Catalytic ozonation is a potential alternative to address the dye wastewater effluent, and developing an effective catalyst for catalyzing ozone is desired. In this study, a novel Fe/Mn@ γ -Al₂O₃ nanomaterial was prepared and successfully utilized for catalytic ozonation toward dye wastewater effluent components (dimethyl phthalate and 1–naphthol). The synthesized Fe/Mn@ γ -Al₂O₃ exhibited superior activity in catalytic ozonation of dimethyl phthalate and 1–naphthol in contrast to Fe@ γ -Al₂O₃ and Mn@ γ -Al₂O₃. Quench and probe tests indicated that HO° contributed to almost all removal of dimethyl phthalate, whereas O₃, HO°, and singlet oxygen participated in the degradation of 1–naphthol in the Fe/Mn@ γ -Al₂O₃/O₃ system. The results of XPS, FT–IR, and EPR suggested that HO° and singlet oxygen were generated from the valence variations of Fe(II/III) and Mn(III/IV). Moreover, the Fe/Mn@ γ -Al₂O₃/O₃ system could also have excellent efficacy in actual water samples, including dye wastewater effluent. This study presents an efficient ozone catalyst to purify dye wastewater effluent and deepens the comprehension of the role and formation of reactive species involved in the catalytic ozonation system.

Keywords: catalytic ozonation; reactive species; singlet oxygen; dye wastewater

1. Introduction

Advanced oxidation processes (AOPs) gained much attention as powerful techniques to mineralize the pollutants in water treatments [1]. Catalytic ozonation is a promising technology for efficiently removing refractory pollutants, especially in the advanced treatment of wastewater. Heterogeneous catalytic ozonation can minimize the dissolving of toxic metal cations in contrast to homogeneous catalyzing.

Many metal oxides have been utilized in the heterogeneous catalytic ozonation process, including manganese oxides, iron oxides/oxyhydroxide, aluminum oxides, and bimetallic/polymetallic oxides. MnO_X supported by granular activated carbon or alumina catalyzed ozone to generate hydroxyl radical (HO°) and efficiently degrade benzenes [2,3]. The surface hydroxyl groups of hydroxylated synthetic α –FeOOH can promote catalyzing ozone to yield HO° [4], and surface MeO–H weak bonds were the favorable sites for accelerating HO° generation. The complex of oxalic acid and iron (Fe₂O₃/Al₂O₃) reacted with ozone and accelerated the degradation of oxalic acid [5]. In addition to Mn and Fe, TiO₂ and MgO nanoparticles were also investigated and used to catalyze ozone [6,7].

Bimetallic nanostructured materials hold promise for improving catalyst activity and selectivity [8]. Mesoporous bimetallic catalysts, such as Ru–Cu/SBA–15, Co–Mn–MCM–41 catalysts, accelerated catalytic ozonation to generate more HO° to degrade dye industry effluent or dimethyl phthalate (DMP) in contrast to single metal loading [9,10]. Fe–Ni/activated carbon also exhibited high performance for degrading 2,4–dichlorophenoxyacetic acid compared to single metal or activated carbon [11]. The micron–sized Fe⁰/Cu/O₃ process



Citation: Liang, C.; Luo, X.; Hu, Y. Enhanced Ozone Oxidation by a Novel Fe/Mn@ γ -Al₂O₃ Nanocatalyst: The Role of Hydroxyl Radical and Singlet Oxygen. *Water* 2022, 14, 19. https://doi.org/ 10.3390/w14010019

Academic Editor: José Alberto Herrera-Melián

Received: 12 November 2021 Accepted: 20 December 2021 Published: 22 December 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). enhanced *p*-nitrophenol mineralization more than twice the sum of ozone and Fe^0/Cu alone [12]. The ratios of surface defective oxygen/lattice oxygen and Mn(III)/Mn(IV) of Mn-M bimetallic HZSM-5 (M: Fe, Cu, Ru, Ag) catalysts were higher than that of Mn-only catalyst, of which Ru-Mn/HZSM-5 showed the highest efficiency in degrading toluene [13,14].

Ozonation, radical oxidation, and nonradical reaction in the catalytic ozonation system mainly contributed to contaminant degradation [15–17]. In addition to HO°, reactive oxygen species (ROS), including singlet oxygen (¹O₂) and superoxide radical (O₂°⁻), were also involved in contaminant degradation during catalytic ozonation [18]. Oxygen vacancies and multi–valence Mn were the main Lewis acidic sites for Mn₂O₃/LaMnO_{3-δ} perovskite composites during catalytic ozonation, and the generated HO°, ¹O₂, and O₂°⁻ were possibly responsible for the degradation of 1H–benzotriazole [19]. As bimetallic nanoparticles and Fe– and Mn–based materials exhibited excellent performance on catalytic ozonation, however, Fe/Mn bimetallic material in catalytic ozonation has not been reported so far. Consequently, the performance of Fe/Mn bimetallic nanoparticles on catalyzing ozone and the corresponding reactive species in such systems needs further evaluation.

This study aims to investigate the performance of catalytic ozonation by synthesized Fe/Mn@ γ -Al₂O₃ nanoparticles. A modified evaporation—induced self—assembly method was employed to fabricate Fe/Mn@ γ -Al₂O₃ nanoparticles, and SEM, TEM, XRD, XPS, FTIR, and BET were utilized to characterize the morphology, crystal form, element distribution, and composition. DMP and 1–naphthol (1–NP), dye precursors and intermediates, were selected as model compounds. Their removal performance, reactive species, reaction mechanism, degradation pathway, and matrix factors were investigated in catalytic ozonation system in the presence of Fe/Mn@ γ -Al₂O₃ nanoparticles.

2. Materials and Methods

2.1. Catalyst Preparation

Al₂O₃ – based catalysts were prepared by a modified evaporation – induced self – assembly process as described previously for pure γ – Al₂O₃ [20]. Aluminum isopropoxide [Al(O₁Pr)₃], Fe(NO₃)₃·9H₂O, and Mn(NO₃)₂ were selected as the sources of Al, Fe, and Mn. [Al(O₁Pr)₃] (8.4 g), glucose (7.2 g), and a required dosage of Fe(NO₃)₃·9H₂O and Mn(NO₃)₂ were dissolved thoroughly in ultrapure water at 35 °C. The pH value of the mixture was adjusted to 5.5 using formic acid (10 wt.%), and the mixed solution was ultrasonicated for 4 h and heated at 105 °C. The final solid after grinding was calcined at 600 °C for 6 h, and a series of γ -Al₂O₃-based catalysts were obtained and termed as Fe@ γ -Al₂O₃ Mn@ γ -Al₂O₃ and Fe/Mn@ γ -Al₂O₃.

2.2. Catalyst Characterization

The morphology and chemical composition of catalysts were characterized by transmission electron microscope (TEM, Talos L120C) and scanning electronic microscopy—energy dispersion spectroscopy (SEM—EDS, Merlin, Carl Zeiss AG, GER). The powder X-ray diffraction (XRD, Empyrean, NL) spectra of the obtained catalysts were collected with *Cu*-K α radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA operating from the 20 angle of 10–90. The specific surface area and pore size distribution of the catalysts were calculated from the N₂ adsorption/desorption isotherms at 77 K (ASAP2020, Micromeritics, Norcross, GA, USA). X-ray photoelectron spectroscopy (XPS, EscaLab Xi⁺, ThemoFisher Scientific, Leicestershire, UK) spectra were recorded by using *Al*-K α radiation at 15 kV and 51 W, and the binding energies were calibrated with C1s at 284.8 eV. Fourier transform infrared spectra (FT–IR) were recorded using a CCR–1 (Thermo–Nicolet, Waltham, MA, USA).

2.3. Catalytic Ozonation Procedure

The catalytic ozonation experiments of target contaminants were performed in a 1.2 L column reactor at a temperature of 25 °C. Ozone was produced in situ from pure oxygen by a ZA–1G laboratory ozone generator (Guangzhou Zeao Ozone Equipment Co., Ltd.,

Guangzhou, China) and continuously bubbled into the reactor through the reactor's porous plate at a bottom 200 mL min⁻¹ flow rate (6 mg L⁻¹). Catalyst powder (200 mg L⁻¹) was mixed in the reactor under continuously magnetically stirring. Target compounds (DMP/1–NP, 50 mM) with/without quenchers (*p*–benzoquinone (*p*–BQ), nitrobenzene (NB), furfuryl alcohol (FFA)) or probes (NB, FFA) were added in the catalytic ozonation system. The same procedures were carried out for the control experiments, including ozone alone, catalyst without ozone, and catalyst with oxygen. All solutions were prepared with ultrapure water (\geq 18.2 M Ω ×cm). Samples were taken at regular intervals, filtered by a Millipore filter (0.45 µm), and quenched by Na₂S₂O₃, then DMP, 1–NP, NB, and FFA were analyzed. All experiments were conducted in duplicate.

2.4. Analytic Methods

DMP, 1–NP, NB, and FFA concentrations were quantified using high–performance liquid chromatography (UPLC, Agilent 1200) equipped with a PDA 2998 detector and a C–18 column (Agilent Eclipse, 5 µm, 4.6 mm × 250 mm). The mobile phase was acetonitrile/0.02% phosphoric acid water (60:40, v/v) with a flow rate of 0.1 mL min⁻¹. The analytical wavelengths of DMP, 1–NP, NB, and FFA were set at 228 nm, 210 nm, 265 nm, and 204 nm at 30°C. The electron paramagnetic resonance (EPR) spectra were measured by Bruker EMX plus instrument (Karlsruhe, Germany). The compound 2,2,6,6–Tetramethylpiperidine (TEMP) was used to capture ${}^{1}O_{2}$, and 5,5–dimethyl–1–pyrroline–N–oxide (DMPO) was applied to capture HO° and $O_{2}^{\circ-}$. In detail, the samples for EPR tests were dispersed in a 100 mM DMPO/TEMP solution (2 mL) with O_{3} purging, and the solvent was H₂O for trapping ${}^{1}O_{2}$ and HO° and methanol for trapping $O_{2}^{\circ-}$. The concentration of leached metals was determined by graphite furnace atomic absorption spectrometry (AAS, Pin AAcle 900T, Perkin Elmer, Waltham, MA, USA). The intermediates of DMP and 1–NP during catalytic ozonation were identified by using LC–MS (Thermo Fisher Scientific, Q Exactive Plus, Waltham, MA, USA).

3. Results

3.1. Characterization

A series of γ -Al₂O₃-based nanocatalysts were synthesized using the glucose template method [20]. SEM images (Figure 1A–D) show amorphous particle structure for all materials, and Fe/Mn@ γ -Al₂O₃ was more compact compared to others. TEM images (Figure S1) displayed the nanoscale structure of Fe/Mn@ γ -Al₂O₃ with a thickness of 5–10 nm. The element mapping of Fe/Mn@ γ -Al₂O₃ indicated that four elements were distributed uniformly (Figure 1E,F), and the element composition of Fe/Mn was 1.3, which corresponded to the nominal loading molar ratio (1.5). Figure 1G shows the XRD patterns of γ -Al₂O₃-based nanomaterials, and five broad peaks (39.4°, 45.9°, 66.9°, 80.5°, 84.9° of 20) were observed and related to γ -Al₂O₃ phase [21]. The peaks of Fe/Mn oxide alloy (35° of 20), Fe₂O₃ (33° of 20), and MnO₂ (21° of 20) were not observed, which might be affected by γ -Al₂O₃ peaks [22]. FT–IR spectroscopy at approximately 575, 748, and 819 cm⁻¹ derived from the Al–O vibrations confirmed the formation of γ -Al₂O₃ (Figure S2) [23]. Additionally, XPS full spectra of γ -Al₂O₃-based nanomaterials identified O, Al, Fe, and Mn, indicating Fe and Mn oxides grew on the γ -Al₂O₃ (Figure S3).

The nitrogen sorption isotherm of Fe/Mn@ γ -Al₂O₃ is shown in Figure 1H, exhibiting a type IV N₂ sorption isotherm with an H3 hysteresis loop, which is a typical characteristic of a mesoporous material [24]. The BET surface area, total pore volume, and median mesopore diameter of Fe/Mn@ γ -Al₂O₃ were 304.2 m² g⁻¹, 0.416 cm³ g⁻¹, and 3.830 nm (Figure S4), which were similar to γ -Al₂O₃-based materials (Sasol product) [21]. This result indicates that the Fe-Mn catalyst was impregnated well into the γ -Al₂O₃ without pore blocking. Overall, the Fe/Mn@ γ -Al₂O₃ catalyst was a mesoporous nanomaterial with uniform iron-manganese oxide growing on the surface.



Figure 1. The SEM of γ -Al₂O₃ (**A**), Fe@ γ -Al₂O₃ (**B**), Mn@ γ -Al₂O₃ (**C**), Fe/Mn@ γ -Al₂O₃ (**D**); the EDS spectra of the synthesized catalysts (**E**); the elemental mapping of the Fe/Mn@ γ -Al₂O₃ (**F**); the powder XRD patterns (**G**); the N₂ adsorption–desorption isotherms (**H**).

3.2. Degradation of DMP and 1-NP

DMP and 1-NP, the precursor or intermediate of dyes, were selected as model compounds (Figure S5), and Figure 2 illustrates their degradation in the catalytic ozonation system. The observed first-order rate of 1-NP (4.13 \times 10⁻³ s⁻¹) under ozonation alone was higher in contrast to DMP ($6.64 \times 10^{-4} \text{ s}^{-1}$) (Figure 2A,B). This result corresponds with the fact that the reactivity of DMP with O_3 alone was relatively low $(0.2 \text{ M}^{-1} \text{ s}^{-1})$ compared with $1-\text{NP} (\sim 10^2 \text{ M}^{-1} \text{ s}^{-1})$ (Table 1). Note that the second-order rate of 1-NP with O₃ was estimated roughly using the quench test (Figure S6), and the value was in the range of $\sim 10^2$ –3 $\times 10^3$ M⁻¹ s⁻¹ for naphthalene, 2–methylnaphthalene, and 1-chloronaphthalene [25–27]. Similarly, the observed first-order rate constants of 1–NP under each catalytic ozonation treatment (i.e., Fe@ γ –Al₂O₃/O₃, Mn@ γ –Al₂O₃/O₃, Fe/Mn@ γ -Al₂O₃/O₃) were higher than those of DMP. Specifically, the Fe/Mn@ γ -Al₂O₃ catalytic was the most effective to catalyze ozone for removing DMP or 1-NP (2.04 \times 10⁻³ s⁻¹ for DMP, $2.25 \times 10^{-2} \text{ s}^{-1}$ for 1–NP), followed by Fe@ γ –Al₂O₃, Mn@ γ –Al₂O₃. Figure S7 shows that the catalytic activity decreased less than 10% after five cycles of use, and the concentration of leached—out Fe and Mn increased slightly during the cycling use (Table S1), implying that $Fe/Mn@\gamma-Al_2O_3$ was relatively stable during the ozonation reactions. Overall, the catalytic ozonation by Fe/Mn@ γ -Al₂O₃ catalytic was feasible and efficient in removing O_3 -resistant compounds.

The quench and probe tests were conducted to investigate the reactive species involved in catalytic ozonation. As noted in previous studies, HO° played the dominant role in removing organic compounds [28–31]. Moreover, other ROS (*e.g.*, ${}^{1}O_{2}$, $O_{2}^{\circ-}$) also participated in the chemical oxidation during catalytic ozonation [32]. Thus, two model compounds with different reactivity toward HO° and ROS (Table 1) were selected to distinguish their roles in the contaminant removal during catalytic ozonation.



Figure 2. The degradation of DMP (**A**) and 1–NP (**B**) during the catalytic ozonation. The degradation of DMP or 1–NP during the Fe/Mn@ γ –Al₂O₃/O₃ system in presence of different quenchers (NB/FFA/p–BQ, 100 mM) (**C**) or different probes (NB/FFA, 5 μ M) (**D**). Conditions: [O₃] = 0.02 mM, [catalyst] = 200 mg L⁻¹, the molar ratio of Fe/Mn = 1.5, [DMP]/[1–NP] = 50 μ M, pH = 7.0 \pm 0.1 with 2 mM phosphate buffer. The probe test is detailed in Text S1.

Table 1. The estimated and experimental observed removal rate constants of DMP/1–NP.

Compound _	Rate Constant (M ⁻¹ s ⁻¹)			Exp. k (s ⁻¹)	Fet k * (e-1)
	O ₃	HO°	¹ O ₂		L31. K (3)
DMP	0.2 [33]	$3.7 imes10^9$ #	<10 ³ [34]	$3.0 imes10^{-3}$	$2.1 imes 10^{-3}$
1–NP	$\sim 10^{2}$ \$	$1.3 imes 10^{10}$ [35]	$7.6 imes 10^{6}$ [36]	$3.3 imes10^{-2}$	$2.2 imes 10^{-2}$

* The observed rate constant of DMP and 1–NP (Est. k) were estimated as described in Text S1. # The second–order rate constant of HO° with DMP was determined using laser flash photolysis technology and competitive kinetics detailed in Text S2 and Figure S10. \$ The second–order rate constant of O3 and 1–NP was estimated roughly based on the quench test and other naphthalenes.

NB, FFA, and p–BQ at a high level (100 mM) were chosen to selectively quench HO°, ¹O₂, and O₂°⁻, and their second–order rate constants are listed in Table S2. Figure 2C shows that NB can inhibit most DMP removal (> 99%), and the removal efficiency of DMP with the presence of FFA or p–BQ was almost the same as that with the presence of NB. This result indicated that HO° was the main contributor to DMP degradation under the Fe/Mn@ γ –Al₂O₃/O₃ system, whereas ¹O₂ or O₂°⁻ was not involved in DMP degradation. Being different from DMP, the removal of 1–NP was not inhibited by NB completely (Figure 2C), and the removal rate constant decreased by 50% in contrast to that without NB. Both FFA and p–BQ almost inhibited the degradation of 1–NP completely. This result indicated that in addition to HO°, ¹O₂, or O₂°⁻ also played a significant role in the degradation of 1–NP. EPR spectroscopy was employed to characterize ROS and demonstrated that HO°, ¹O₂, and O₂°⁻ was relatively low (detailed in Section 3.3).

The probe test was conducted to specify the contributions of diverse reactive species to DMP and 1–NP degradation under the Fe/Mn@ γ –Al₂O₃/O₃ system. NB and FFA were selected as the probes of HO° and ¹O₂, and the modeled steady–state concentrations of HO° and ¹O₂ ([HO°]_{SS}, [¹O₂]_{SS}) are listed in Table S3. The estimated observed first–order

rate constants of DMP ($3.0 \times 10^{-3} \text{ s}^{-1}$) or 1-NP ($3.3 \times 10^{-2} \text{ s}^{-1}$) were calculated based on Equations (1)–(3), which were nearly the same as the experimental ones ($2.1 \times 10^{-3} \text{ s}^{-1}$ or $2.2 \times 10^{-2} \text{ s}^{-1}$) (Figure 2D).

$$\mathbf{k}' = \mathbf{k}'_{O_3} + \mathbf{k}'_{HO^\circ} + \mathbf{k}'_{1O_2} \tag{1}$$

$$k' = k_{O_3,DMP}[O_3] + k_{HO^{\circ},DMP}[HO^{\circ}] + k_{1O_2,DMP} \begin{bmatrix} {}^{1}O_2 \end{bmatrix}$$
(2)

$$k' = k_{O_3,1-NP}[O_3] + k_{HO^{\circ},1-NP}[HO^{\circ}] + k_{1O_2,1-NP} \begin{bmatrix} 1 O_2 \end{bmatrix}$$
(3)

Specifically, $[HO^{\circ}]_{SS}$ and $[{}^{1}O_{2}]_{SS}$ were 8.1×10^{-13} M and 1.8×10^{-9} M during the degradation of DMP in catalytic ozonation system. The estimated first–order rate constant of DMP with HO^o was 3.0×10^{-3} s⁻¹. Note that $[{}^{1}O_{2}]_{SS}$ was as high as $[HO^{\circ}]_{SS}$ but can rarely contribute to the degradation of DMP (1.8×10^{-6} s⁻¹) due to the relatively low reactivity ($k_{1O_{2},DMP} < 10^{3}$ M⁻¹ s⁻¹). The DMP degradation during catalytic ozonation was consequent on the HO^o–mediated oxidation. As for the 1–NP–involved system, $[HO^{\circ}]_{SS}$ and $[{}^{1}O_{2}]_{SS}$ were 1.2×10^{-12} M and 2.0×10^{-9} M (Table S3), which were comparable with the DMP involved system. However, the degradation of 1–NP was not only contributed to by HO^o, but ${}^{1}O_{2}$ and O_{3} also participated in its removal. The estimated rate constant of each reactive species ($k'_{O_{3},1-NP}$, $k'_{HO^{\circ},1-NP}$, $k'_{1O_{2},1-NP}$) accounted for 7.51%, 46.85%, and 45.65% of the total 1–NP removal rate constant, respectively.

The above results suggested that the Fe/Mn@ γ -Al₂O₃/O₃ system can provide comparable levels of HO° (10⁻¹² – 10⁻¹³ M) and ¹O₂ (10⁻⁹ M) that were involved in removing different pollutants. HO° ($E^0 = 2.7$ V) is non–selective thus reacts with both DMP and 1–NP at considerably high second–order rate constants (10⁹ – 10¹⁰ M⁻¹ s⁻¹) [37–40]. O₃ and ¹O₂ are more selective to naphthalenes (e.g., naproxen and propranolol) than DMP. Therefore, the inherent O₃ and the yielded ¹O₂ in the Fe/Mn@ γ –Al₂O₃/O₃ system made contributions to the degradation of 1–NP (> 40%).

3.3. Catalytic Ozonation Mechanism

HO° and ¹O₂ were identified and involved in degrading pollutants in the Fe/Mn@ γ –Al₂O₃/O₃ system. XPS and EPR spectra were utilized to explore their formation and catalytic mechanisms in such a system.

The XPS spectra of Fe 2p, Mn 2p, and O 1s for Fe/Mn@ γ -Al₂O₃ before/after catalytic ozonation are shown in Figure 3A–C. As described in previous studies, the Fe 2p_{3/2} and Fe 2p_{1/2} peaks could be deconvoluted into three peaks, including Fe(II) (711.7 eV and 725.3 eV), Fe(III) (712.9 and 726. eV), and satellite (719.6 and 732.8 eV), respectively (Figure 3A) [41,42]. The Mn 2p_{3/2} and Mn 2p_{1/2} peaks could be deconvoluted into two peaks, including Mn(III) (642.2 eV and 653.9 eV) and Mn(IV) (643.8 eV and 654.8 eV) (Figure 3B) [22,43]. The contents of the high valence of both Fe and Mn (i.e., Fe(III) and Mn(IV)) increased slightly after ozonation (Table S4), indicating the conversion between Fe(II))/Mn(III) and Fe(III)/Mn(IV) in the Fe/Mn@ γ -Al₂O₃/O₃ system. The previous studies also found valence metals resulted in the transformation of oxygen vacancy (V_O) to lattice oxygen (O_{lat}) due to the strong storing/releasing oxygen nature of the metal redox couple [46]. Moreover, oxygen mobility by electron transfer caused the valence variation of doping metals [47–49].

Three characteristic peaks were identified in the O 1s spectrum of Fe/Mn@ γ -Al₂O₃ and regarded as adsorbed oxygen (O_{ads}, 530.3 eV), O_{lat}, (532.4 eV), and oxygen of metal oxide (O_{MO}, 531.2 eV), respectively (Figure 3C) [42,50]. After ozonation, the relative contents of O_{lat}/O_{ads} significantly increased from 1.32 to 1.64 (Table S4), whereas a subtle increase in that of Mn(IV) or Fe(II) was observed, indicating the prominent role of O_{ads} in reacting with pollutants rather than high valence metal. Specifically, the increase in O_{lat} contributed to the metal valence change and the formation of Mn(IV) or Fe(III). However, O_{ads} declined slightly after ozonation, which might have resulted from the replenishment



of V_O [51,52]. Overall, the continuous catalytic activity of Fe/Mn@ γ -Al₂O₃ originated from the interaction among V_O, O_{lat}, and the transformation of Fe(II)/(III)and Mn(III)/(IV) redox couple.

Figure 3. XPS spectra of Fe 2p (**A**), Mn 2s (**B**), and O 1s (**C**) for Fe/Mn@ γ -Al₂O₃ before/after catalytic ozonation; oxygen vacancy of γ -Al₂O₃ and Fe/Mn@ γ -Al₂O₃ (**D**); the EPR spectra of HO° and O₂°⁻ using DMPO in water and methanol respectively, and the EPR spectra of ¹O₂ using TEMP from single ozonation and catalytic ozonation processes (**E**); the proposed catalytic ozonation mechanism of Fe/Mn@ γ -Al₂O₃ (**F**).

Solid EPR was applied to directly and accurately detect the unpaired electron information of Fe/Mn@ γ -Al₂O₃ for identifying V_O (Figure 3D). Note that the EPR signal of Fe/Mn@ γ -Al₂O₃ at g = 2.095 was more intensive than others, demonstrating that the introduction of Fe and Mn led to more formation of V_O on the Fe/Mn@ γ -Al₂O₃ surface [45]. V_O contained many unpaired electrons and preferred to serve as active sites for the adsorption of oxygen (e.g., molecule O₂, molecule O₃), thereby facilitating the formation of ROS (HO°, ¹O₂, O₂°⁻, etc.) [53].

The reactive species in the Fe/Mn@ γ -Al₂O₃/O₃ system was identified by EPR tests, as illustrated in Figure 3D. Generally, DMPO and TEMP are typical trapping chemicals for HO°, O₂°⁻, and ¹O₂. The characteristic signal of DMPO-HO° ($A_H = A_N = 14.9$ G), with a peak intensity ratio of 1:2:2:1, was obtained in both ozonation alone and Fe/Mn@ γ -Al₂O₃/O₃ systems, but no signal was observed in pure water. Moreover, the intensity of DMPO-HO° adduct elevated significantly under the Fe/Mn@ γ -Al₂O₃/O₃ system, implying Fe/Mn@ γ -Al₂O₃ dramatically enhanced ozone decomposition to generate more HO°. TEMP was applied as the capture agent for ¹O₂. The typical signal of TEMP-¹O₂ ($A_N = 16.9$ G) in the Fe/Mn@ γ -Al₂O₃/O₃ catalytic ozonation system was more intensive than that in the ozonation alone system. The results implied that ¹O₂ was generated in the ozone-based systems and enhanced in the Fe/Mn@ γ -Al₂O₃/O₃ systems were also captured using DMPO to form DMPO-O₂°⁻ ($A_H = 10.2$ G, $A_N = 12.9$ G), but the intensity was very weak and not promoted in the catalytic system, indicating the neglectable role of ¹O₂ in the catalytic ozonation system.

As illustrated in Figure S2, FT–IR spectroscopy of Fe/Mn@ γ –Al₂O₃ at ~3460 cm⁻¹ and ~1634 cm⁻¹ corresponded to the surface hydroxyl group and the chemisorbed water, respectively [24,54]. Metal oxides adsorbed water molecules further dissociated to hydroxyls,

generating the surface hydroxyl groups at Lewis acid sites of metal oxide surfaces [55–59]. The surface hydroxyl group functioned as Brønsted acid for catalytic ozone decomposition and promoted HO° generation [55–59].

The catalytic ozonation mechanism of Fe/Mn@ γ -Al₂O₃ was proposed and illustrated in Figure 3F. First, O₃ was adsorbed at the surface hydroxyl group of metal oxide and interacted with Vo. The V_O was replenished with O donated by O₃ and produced an O₂ molecule releasing into the environment and active oxygen (O²⁻) to form adsorbed oxygen (O_{ads}) [60,61]. The O²⁻ further reacted with O₃ to generate O₂²⁻ (peroxide) [50]. The yielded O²⁻/O₂²⁻ (i.e., O_{ads}) then reacted with water molecules to generate ROS, including HO°, ¹O₂, and O₂°⁻ via charge–transfer interactions. Thereinto, O₂°⁻ underwent self–quenching to form ¹O₂ or react with O₃ to yield HO° ($k = 1.6 \times 10^9$ M⁻¹ s⁻¹) [62]. V_O also converted to O_{lat}, leading to the metal valence increase. The interaction among V_O, Fe(II/III)/Mn(III/IV), and O_{lat} of Fe/Mn@ γ -Al₂O₃ resulted in the circulation of metal valence, thus constantly catalyzing O₃ [63].

3.4. Proposed Degradation Pathways of DMP and 1-NP

The intermediates of DMP and 1–NP during Fe/Mn@ γ –Al₂O₃ catalytic ozonation were analyzed using LC–MS, and their identified intermediates are detailed in Figures S8 and S9. As previously noted, the degradation of DMP was dominated by HO°–induced reaction, and that of 1–NP resulted from O₃, HO°, and ¹O₂ oxidation. Their degradation pathways are proposed and illustrated in Figure 4.



Figure 4. Degradation pathways of DMP (A) and 1-NP (B) during Fe/Mn@ γ -Al₂O₃ catalytic ozonation.

The degradation of DMP during Fe/Mn@ γ -Al₂O₃ catalytic ozonation (Figure 4A) was initiated by HO° to attack the ester group to form P₁₈₀ and further oxidized to generate 1,2–benzenedicarboxylicacid [64], or to undergo addition on the benzene ring to yield HO–adducts (P₂₁₀, P₂₂₆, P₂₄₂) [65]. The formed 1,2–benzenedicarboxylicacid reacted with HO° to yield HO–adducts (P₁₈₂) or transform to phthalic anhydride via dehydration. The adducts P₂₁₀, P₂₂₆, and P₂₄₂ were oxidized by HO° to form P₁₉₆, P₁₈₂, and P₁₉₈. 1,2–benzenedicarboxylicacid and its HO–adducts (P₁₈₂ and P₁₉₈) underwent a ring–opening reaction to generate maleic acid and phenols. Phthalic anhydride and maleic acid were decomposed to yield low molecular weight organic acids (e.g., acetic acid, oxalic acid) via ring–opening reactions, which were finally mineralized to CO₂ and H₂O [66].

Figure 4B shows the degradation pathway of 1–NP under the Fe/Mn@ γ –Al₂O₃/O₃ system. Ozone quickly reacted with the naphthalene group as electron–rich moieties to produce hydroxy–1,4–naphthoquinone (P₁₇₄) that was oxidized to yield 1,4–naphthoquinone (P₁₅₈) [67]. The initial attack of HO° on 1–naphthol generated transient naphthyloxy radical (1–NP°(–H)) via H–abstraction and transformed to 1,4–naphthoquinone (P₁₅₈) [68]. ¹O₂ readily added to 1–NP to form P₁₇₆, and P₁₇₆ rearranged and dehydrated to yield 1,4–naphthoquinone (P₁₅₈) [69]. The generated 1,4–naphthoquinone was further oxidized to 1,2–benzenedicarboxylicacid and phthalic anhydride by ozone and HO°, which were finally mineralized to CO₂ and H₂O [67].

3.5. Effects of Water Matrix

The performance of the synthesized catalyst in the complex water matrix was evaluated to investigate its potential application, especially for dyeing wastewater effluent. Thus, the effects of ions, pH, and actual water samples on the degradation efficacy of DMP and 1-NP were investigated (Figure 5).

Carbonate, sulfate, chloride, and nitrate were widely detected in dyeing wastewater. Figure 5A,D show their effects on the performance of catalytic ozonation in the ultrapure water system. As seen, sulfate, chloride, and nitrate cannot distinctly inhibit the degradation of DMP and 1–NP (< 5%) because sulfate and nitrate barely consumed the reactive species (<10 M⁻¹ s⁻¹) involved in the Fe/Mn@ γ –Al₂O₃/O₃ system. Chloride reacts with HO° but cannot accelerate forward reaction at a low concentration (2 mM) ($k_{+/-} = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}/6.10 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) intensively scavenged [HO°], thus impeding their removal (> 50%). The formed CO₃°⁻ ($E^0 = 1.63$ V) was much less reactive than HO° ($E^0 = 2.7$ V) [37,72].

The pH value affects the concentration and speciation of reactive species during catalytic ozonation and thus leads to the variation in pollutant removal efficiency. The removal rate increased from $1.83 \times 10^{-3} \text{ s}^{-1}$ to $2.46 \times 10^{-3} \text{ s}^{-1}$ for DMP and from 1.90×10^{-2} to $2.72 \times 10^{-2} \text{ s}^{-1}$ for 1–NP within pH 5–8 (Figure 5B,E). Their removal efficiencies exceeded 90% within 30 min, indicating that the synthesized Fe/Mn@ γ –Al₂O₃ catalyst had a good ozone–catalyzing performance at a wide pH variation. Specifically, the alkali condition was more suitable for the contaminant degradation in the Fe/Mn@ γ –Al₂O₃/O₃ system as OH⁻ is mainly hydroxyl radical initiator in ozonation [73], corresponding with previous studies [74,75].

To further investigate the effect of the water matrix on the removal of 1–NP and DMP with the Fe/Mn@ γ –Al₂O₃/O₃ system, DMP/1–NP (50 µM) was spiked in printing and dyeing industrial park (PDIP) effluent, wastewater treatment plant (WWTP) effluent, and river water (RW). The water quality parameters of three water samples are listed in Table S5. The removal rate constants of 1–NP and DMP in all actual water samples decreased by 50–60% in contrast to ultrapure water (Figure 5C,F). This decrease resulted from the competition of reactive species by dissolved organic matter (DOM) in the actual water samples. In contrast, the Fe/Mn@ γ –Al₂O₃/O₃ system accelerated the DOC and UV₂₅₄ decrease in the actual water samples compared with ozonation alone (Figure S11).



Overall, the synthesized Fe/Mn@ γ -Al₂O₃ can be potentially applied in the catalytic ozonation of actual water.

Figure 5. The degradation of DMP and 1–NP in presence of different ions (CO_3^{2-} , SO_4^{2-} , Cl^- , NO_3^- , 2 mM) (**A**,**D**), at pH of 6–9 (**B**,**E**), in different real water samples (ultrapure water, PDIP effluent, WWTP effluent, RW) (**C**,**F**). Conditions: $[O_3] = 0.04$ mM, [catalyst] = 200 mg L⁻¹, the molar ratio of Fe/Mn = 1.5, [DMP]/[1–NP] = 50 μ M, 2 mM phosphate buffer. Details are described in Text S3.

4. Conclusions

A novel Fe/Mn@ γ -Al₂O₃ nanocatalyst was successfully synthesized and utilized for catalytic ozonation of DMP and 1–NP. Their removal rate constants could elevate 3–5 times with Fe/Mn@ γ -Al₂O₃/O₃ system compared to ozonation alone due to more yield of HO° and ¹O₂ involved in their degradation. The characterization of Fe/Mn@ γ -Al₂O₃ suggested that the formation of HO° and ¹O₂ possibly resulted from the transformation of O₃ from V_O to O_{ads} with the circulation of Mn(III)/(IV) and Fe(II)/(III). The degradation pathways of DMP and 1–NP were proposed based on the mechanisms and the identified intermediates. Additionally, the Fe/Mn@ γ -Al₂O₃/O₃ system could be applied in removing pollutants at pH 6–9, in the presence of different ions, and dealing with actual dye wastewater effluent samples. The performance and practicability of the Fe/Mn@ γ -Al₂O₃/O₃ system on the treat-

ment of dye wastewater effluent should be further evaluated in a pilot-/full-scale experiment.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.339 0/w14010019/s1, Text S1: Steady-state concentrations of different reactive species, Text S2: Determination of the rate constant of DMP with HO°, Text S3: Factors influencing catalytic performance, Figure S1: TEM images of Fe/Mn@ γ -Al₂O₃ (A) and a partial enlargement (B), Figure S2: FT-IR spectra of γ -Al₂O₃, $Fe@\gamma-Al_2O_3$, $Mn@\gamma-Al_2O_3$, and $Fe/Mn@\gamma-Al_2O_3$, Figure S3: The survey spectrum of XPS spectra of NiCo2O4 before catalytic ozonation, Figure S4: The corresponding pore size distribution in nitrogen adsorption and desorption isotherms, Figure S5: Influence of (A,C) Fe/Mn@ γ -Al₂O₃ dose and (B,D) the ratio of iron to manganese in the catalyst on DMP and 1-NP decomposition. Conditions: $[O_3] = 0.04 \text{ mM}$, $[\text{catalyst}] = 50-300 \text{ mg L}^{-1}$, the molar ratio of Fe/Mn = 0.3-1.5, $[DMP]/[1-NP] = 50 \mu M$, 2 mM phosphate buffer, Figure S6: The degradation of 1-NP under ozonation in presence of FFA. Conditions: $[O_3] = 0.02$ mM, [FFA] = 100 mM, $[1-NP] = 50 \mu$ M, $pH = 7.0 \pm 0.1$ with 2 mM phosphate buffer, Figure S7: DMP and 1–NP removal rate constants during the reuse of Fe/Mn@ γ -Al₂O₃ in catalytic ozonation system, Figure S8: LC-MS total ion chromatograms for DMP degradation products, Figure S9: LC-MS total ion chromatograms for 1-NP degradation products, Figure S10: Growth kinetics of DMP-OH adducts at 320 nm with different concentrations of DMP (0.02–0.3 mM) determined by using a laser flash photolysis system. The inset is the plot of the first-order formation rate constants of DMP-OH adducts vs. DMP concentrations, Figure S11: The removal of UV₂₅₄ and DOC during the catalytic ozonation in the real water samples. Conditions: $[O_3] = 0.02 \text{ mM}$, $[\text{catalyst}] = 200 \text{ mg L}^{-1}$, the molar ratio of Fe/Mn = 1.5, Table S1 Dissolution of metal ions in Fe/Mn@ γ -Al₂O₃ catalytic ozonation, Table S2: The steady-state concentrations of different reactive species, Table S3: The reactivity of different probes/quenchers with reactive species, Table S4: XPS parameters of high-resolution Mn $2p_{3/2}$, Fe $2p_{3/2}$, and O 1s regions, Table S5: Parameters of different real water samples.

Author Contributions: Conceptualization, C.L. and X.L.; methodology, C.L.; writing—original draft preparation, C.L.; writing—review and editing, X.L. and Y.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Not applicable.

Acknowledgments: This work was supported by the National Natural Science Fund of China (NO. 21477039, No. U1401235).

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Coha, M.; Farinelli, G.; Tiraferri, A.; Minella, M.; Vione, D. Advanced oxidation processes in the removal of organic substances from produced water: Potential, configurations, and research needs. *Chem. Eng. J.* **2021**, *414*, 128668. [CrossRef]
- Pearce, C.I.; Lloyd, J.R.; Guthrie, J.T. The removal of colour from textile wastewater using whole bacterial cells: A review. *Dye. Pigment.* 2003, 58, 179–196. [CrossRef]
- McMullan, G.; Meehan, C.; Conneely, A.; Kirby, N.; Robinson, T.; Nigam, P.; Banat, I.; Marchant, R.; Smyth, W.F. Microbial decolourisation and degradation of textile dyes. *Appl. Microbiol. Biotechnol.* 2001, 56, 81–87. [CrossRef] [PubMed]
- Lara-Ramos, J.A.; Figueroa Angulo, M.A.; Machuca-Martínez, F.; Mueses, M.A. Sensitivity Analysis of the Catalytic Ozonation under Different Kinetic Modeling Approaches in the Diclofenac Degradation. *Water* 2021, 13, 3003. [CrossRef]
- 5. Beltrán, F.J.; Rivas, J.; Montero-De-Espinosa, R. Iron type catalysts for the ozonation of oxalic acid in water. *Water Res.* 2005, *39*, 3553–3564. [CrossRef] [PubMed]
- 6. Sun, Q.; Yang, L. The adsorption of basic dyes from aqueous solution on modified peat-resin particle. *Water Res.* **2003**, *37*, 1535–1544. [CrossRef]
- 7. Kumar, M.; Sridhari, T.; Bhavani, K.; Dutta, P. Trends in color removal from textile mill effluents. Colourage 1998, 45, 25–34.
- Zugic, B.; Wang, L.C.; Heine, C.; Zakharov, D.N.; Lechner, B.A.J.; Stach, E.A.; Biener, J.; Salmeron, M.; Madix, R.J.; Friend, C.M. Dynamic restructuring drives catalytic activity on nanoporous gold–silver alloy catalysts. *Nat. Mater.* 2017, 16, 558–564. [CrossRef]
- Ghuge, S.P.; Saroha, A.K. Catalytic ozonation of dye industry effluent using mesoporous bimetallic Ru–Cu/SBA–15 catalyst. Process. Saf. Environ. Prot. 2018, 118, 125–132. [CrossRef]
- Tang, Y.M.; Pan, Z.Q.; Li, L.S. pH-insusceptible cobalt-manganese immobilizing mesoporous siliceous MCM-41 catalyst for ozonation of dimethyl phthalate. J. Colloid Interf. Sci. 2017, 508, 196–202. [CrossRef]

- Lu, X.H.; Zhang, Q.Y.; Yang, W.Q.; Li, X.K.; Zeng, L.X.; Li, L.S. Catalytic ozonation of 2,4–dichlorophenoxyacetic acid over novel Fe–Ni/AC. *Rsc. Adv.* 2015, *5*, 10537–10545. [CrossRef]
- 12. Xiong, Z.K.; Cao, J.Y.; Lai, B.; Yang, P. Comparative study on degradation of p-nitrophenol in aqueous solution by mFe/Cu/O₃ and mFe0/O₃ processes. *J. Ind. Eng. Chem.* **2018**, *59*, 196–207. [CrossRef]
- Ma, J.; Sui, M.; Zhang, T.; Guan, C. Effect of pH on MnOx/GAC catalyzed ozonation for degradation of nitrobenzene. *Water Res.* 2005, *39*, 779–786. [CrossRef]
- 14. Einaga, H.; Futamura, S. Catalytic oxidation of benzene with ozone over alumina—supported manganese oxides. *J. Catal.* 2004, 227, 304–312. [CrossRef]
- 15. Beltran, F.J.; Rivas, F.J.; Montero–De–Espinosa, R. Ozone–Enhanced Oxidation of Oxalic Acid in Water with Cobalt Catalysts. 1. Homogeneous Catalytic Ozonation. *Ind. Eng. Chem. Res.* **2003**, *42*, 3210–3217. [CrossRef]
- 16. Pines, D.S.; Reckhow, D.A. Effect of Dissolved Cobalt(II) on the Ozonation of Oxalic Acid. *Environ. Sci. Technol.* 2002, 36, 4046–4051. [CrossRef] [PubMed]
- Ma, J.; Graham, N.J.D. Degradation of atrazine by manganese-catalysed ozonation—Influence of radical scavengers. *Water Res.* 2000, 34, 3822–3828. [CrossRef]
- 18. Cao, H.; Xing, L.; Wu, G.; Xie, Y.; Shi, S.; Zhang, Y.; Minakata, D.; Crittenden, J.C. Promoting effect of nitration modification on activated carbon in the catalytic ozonation of oxalic acid. *Appl. Catal. B Environ.* **2014**, *146*, 169–176. [CrossRef]
- Wang, Y.X.; Chen, L.L.; Cao, H.B.; Chi, Z.X.; Chen, C.M.; Duan, X.G.; Xie, Y.B.; Qi, F.; Song, W.Y.; Liu, J.; et al. Role of oxygen vacancies and Mn sites in hierarchical Mn₂O₃/LaMnO₃-delta perovskite composites for aqueous organic pollutants decon-tamination. *Appl. Catal. B–Environ.* 2019, 245, 546–554. [CrossRef]
- Xu, B.J.; Xiao, T.C.; Yan, Z.F.; Sun, X.; Sloan, J.; Gonzalez–Cortes, S.L.; Alshahrani, F.; Green, M.L.H. Synthesis of mesoporous alumina with highly thermal stability using glucose template in aqueous system. *Micropor. Mesopor. Mat.* 2006, *91*, 293–295. [CrossRef]
- Cho, K.; Rana, B.S.; Cho, D.W.; Beum, H.T.; Kim, C.H.; Kim, J.N. Catalytic removal of naphthenic acids over Co–Mo/gamma–Al2O3 catalyst to reduce total acid number (TAN) of highly acidic crude oil. *Appl. Catal. A–Gen.* 2020, 606, 117835. [CrossRef]
- 22. Teng, Y.; Wang, X.-D.; Liao, J.-F.; Li, W.-G.; Chen, H.-Y.; Dong, Y.-J.; Kuang, D.-B. Atomically Thin Defect–Rich Fe–Mn–O Hybrid Nanosheets as High Efficient Electrocatalyst for Water Oxidation. *Adv. Funct. Mater.* **2018**, *28*, 28. [CrossRef]
- 23. Naskar, M.K. Hydrothermal Synthesis of Petal-Like Alumina Flakes. J. Am. Ceram. Soc. 2009, 92, 2392-2395. [CrossRef]
- 24. Zhu, L.; Pu, S.; Liu, K.; Zhu, T.; Lu, F.; Li, J. Preparation and characterizations of porous γ–Al₂O₃ nanoparticles. *Mater. Lett.* **2012**, 83, 73–75. [CrossRef]
- 25. Zhu, S.Y.; Zheng, X.S.; Li, D.T. Ozonation of naphthalene sulfonic acids in aqueous solutions. Part I: Elimination of COD, TOC and increase of their biodegradability. *Water Res.* 2002, *36*, 1237–1243.
- 26. Wang, P.; Matta, H.; Kuo, C.-H. Kinetics of ozonation of naphthalene and anthracene. J. Chin. I. Ch. E 1991, 22, 365–371.
- 27. Hoigné, J.; Bader, H.; Haag, W.; Staehelin, J. Rate constants of reactions of ozone with organic and inorganic compounds in water—III. Inorganic compounds and radicals. *Water Res.* **1985**, *19*, 993–1004. [CrossRef]
- Huber, M.M.; Canonica, S.; Park, G.-Y.; von Gunten, U. Oxidation of Pharmaceuticals during Ozonation and Advanced Oxidation Processes. *Environ. Sci. Technol.* 2003, 37, 1016–1024. [CrossRef] [PubMed]
- Zhang, T.; Li, C.; Ma, J.; Tian, H.; Qiang, Z. Surface hydroxyl groups of synthetic α–FeOOH in promoting OH generation from aqueous ozone: Property and activity relationship. *Appl. Catal. B Environ.* 2008, *82*, 131–137. [CrossRef]
- Ma, J.; Graham, N.J. Degradation of atrazine by manganese-catalysed ozonation: Influence of humic substances. Water Res. 1999, 33, 785–793. [CrossRef]
- 31. Sui, M.; Liu, J.; Sheng, L. Mesoporous material supported manganese oxides (MnOx/MCM-41) catalytic ozonation of nitrobenzene in water. *Appl. Catal. B Environ.* **2011**, *106*, 195–203. [CrossRef]
- 32. Yu, G.; Wang, Y.; Cao, H.; Zhao, H.; Xie, Y. Reactive Oxygen Species and Catalytic Active Sites in Heterogeneous Catalytic Ozonation for Water Purification. *Environ. Sci. Technol.* **2020**, *54*, 5931–5946. [CrossRef]
- 33. Yao, C.C.D.; Haag, W.R. Rate constants for direct reactions of ozone with several drinking water contaminants. *Water Res.* **1991**, 25, 761–773.
- 34. Lei, Y.; Lu, J.; Zhu, M.; Xie, J.; Peng, S.; Zhu, C. Radical chemistry of diethyl phthalate oxidation via UV/peroxymonosulfate process: Roles of primary and secondary radicals. *Chem. Eng. J.* **2020**, *379*, 122339. [CrossRef]
- 35. Kanodia, S.; Madhaven, V.; Schuler, R. Oxidation of naphthalene by radiolytically produced OH radicals. *Int. J. Radiat. Appl. Instrumentation. Part. C. Radiat. Phys. Chem.* **1988**, 32, 661–664. [CrossRef]
- 36. Darmanyan, A.P.; Moger, G. Interaction of singlet oxygen with nitroso- and phenol-type inhibitors. *Magy. Kem. F.* **1988**, *94*, 282–284.
- 37. Zuo, Z.; Cai, Z.; Katsumura, Y.; Chitose, N.; Muroya, Y. Reinvestigation of the acid–base equilibrium of the (bi)carbonate radical and pH dependence of its reactivity with inorganic reactants. *Radiat. Phys. Chem.* **1999**, *55*, 15–23. [CrossRef]
- 38. Buxton, G.V.; Greenstock, C.L.; Helman, W.P.; Ross, A.B. Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/O– in Aqueous Solution. *J. Phys. Chem. Ref. Data* **1988**, 17, 513–886. [CrossRef]
- Zhao, L.; Sun, Z.; Ma, J. Novel Relationship between Hydroxyl Radical Initiation and Surface Group of Ceramic Honeycomb Supported Metals for the Catalytic Ozonation of Nitrobenzene in Aqueous Solution. *Environ. Sci. Technol.* 2009, 43, 4157–4163. [CrossRef]

- 40. Ervens, B.; Gligorovski, S.; Herrmann, H. Temperature–dependent rate constants for hydroxyl radical reactions with organic compounds in aqueous solutions. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1811–1824. [CrossRef]
- Liu, Z.; Chen, G.; Li, X.; Lu, X. Removal of rare earth elements by MnFe2O4 based mesoporous adsorbents: Synthesis, isotherms, kinetics, thermodynamics. J. Alloys Compd. 2021, 856, 158185. [CrossRef]
- Liu, Z.; Chen, G.; Hu, F.; Li, X. Synthesis of mesoporous magnetic MnFe₂O₄@CS-SiO₂ microsphere and its adsorption performance of Zn2+ and MB studies. *J. Environ. Manag.* 2020, 263, 110377. [CrossRef]
- 43. Xia, H.; Zhang, Z.; Liu, J.; Deng, Y.; Zhang, D.; Du, P.; Zhang, S.; Lu, X. Novel Fe–Mn–O nanosheets/wood carbon hybrid with tunable surface properties as a superior catalyst for Fenton–like oxidation. *Appl. Catal. B Environ.* **2019**, 259, 118058. [CrossRef]
- 44. Shen, T.; Su, W.; Yang, Q.; Ni, J.; Tong, S. Synergetic mechanism for basic and acid sites of MgMxOy (M = Fe, Mn) double oxides in catalytic ozonation of p-hydroxybenzoic acid and acetic acid. *Appl. Catal. B Environ.* **2020**, 279, 119346. [CrossRef]
- Guan, S.; An, L.; Ashraf, S.; Zhang, L.; Liu, B.; Fan, Y.; Li, B. Oxygen vacancy excites Co3O4 nanocrystals embedded into carbon nitride for accelerated hydrogen generation. *Appl. Catal. B Environ.* 2020, 269, 118775. [CrossRef]
- Yan, H.; Lu, P.; Pan, Z.; Wang, X.; Zhang, Q.; Li, L. Ce/SBA-15 as a heterogeneous ozonation catalyst for efficient minerali-zation of dimethyl phthalate. J. Mol. Catal. A Chem. 2013, 377, 57–64. [CrossRef]
- Orge, C.A.; Orfão, J.J.; Pereira, M.F.; de Farias, A.M.D.; Fraga, M.A. Ceria and cerium-based mixed oxides as ozonation catalysts. *Chem. Eng. J.* 2012, 200-202, 499–505. [CrossRef]
- 48. 4Rui, C.M.; Quinta Ferreira, R.M. Catalytic ozonation of phenolic acids over a Mn–Ce–O catalyst. *Appl. Catal. B Environ. Ment.* 2009, 90, 268–277.
- 49. Li, L.; Ye, W.; Zhang, Q.; Sun, F.; Li, X. Catalytic ozonation of dimethyl phthalate over cerium supported on activated car—bon. *J. Hazard. Mater.* **2009**, *170*, 411–416. [CrossRef]
- He, C.; Wang, Y.; Li, Z.; Huang, Y.; Liao, Y.; Xia, D.; Lee, S.-C. Facet Engineered α–MnO₂ for Efficient Catalytic Ozonation of Odor CH3SH: Oxygen Vacancy–Induced Active Centers and Catalytic Mechanism. *Environ. Sci. Technol.* 2020, 54, 12771–12783. [CrossRef]
- He, D.; Wan, G.; Hao, H.; Chen, D.; Lu, J.; Zhang, L.; Liu, F.; Zhong, L.; He, S.; Luo, Y. Microwave–assisted rapid synthesis of CeO₂ nanoparticles and its desulfuri–zation processes for CH3SH catalytic decomposition. *Chem. Eng. J. Lausanne* 2016, 289, 161–169. [CrossRef]
- 52. Zhang, B.; Wang, L.; Zhang, Y.; Ding, Y.; Bi, Y. Ultrathin FeOOH Nanolayers with Abundant Oxygen Vacancies on BiVO₄ Photoanodes for Efficient Water Oxidation. *Angew. Chem. Int. Ed.* **2018**, *57*, 2248–2252. [CrossRef] [PubMed]
- 53. Gui, L.; Wang, Z.; Zhang, K.; He, B.; Liu, Y.; Zhou, W.; Xu, J.; Wang, Q.; Zhao, L. Oxygen vacancies-rich Ce0.9Gd0.1O2-δ decorated Pr0.5Ba0.5CoO3-δ bifunctional catalyst for efficient and long-lasting rechargeable Zn-air batteries. *Appl. Catal. B Environ.* 2020, 266, 118656. [CrossRef]
- Yan, S.; Zhang, X.; Shi, Y.; Zhang, H. Natural Fe-bearing manganese ore facilitating bioelectro-activation of peroxymonosulfate for bisphenol A oxidation. *Chem. Eng. J.* 2018, 354, 1120–1131. [CrossRef]
- Ikhlaq, A.; Kasprzyk–Hordern, B. Catalytic ozonation of chlorinated VOCs on ZSM–5 zeolites and alumina: Formation of chlorides. *Appl. Catal. B Environ.* 2017, 200, 274–282. [CrossRef]
- 56. Ikhlaq, A.; Brown, D.; Kasprzyk–Hordern, B. Catalytic ozonation for the removal of organic contaminants in water on ZSM–5 zeolites. *Appl. Catal. B Environ.* **2014**, 154–155, 110–122. [CrossRef]
- Ikhlaq, A.; Brown, D.; Kasprzyk–Hordern, B. Mechanisms of catalytic ozonation: An investigation into superoxide ion radical and hydrogen peroxide formation during catalytic ozonation on alumina and zeolites in water. *Appl. Catal. B Environ.* 2013, 129, 437–449. [CrossRef]
- Bing, J.; Hu, C.; Nie, Y.; Yang, M.; Qu, J. Mechanism of Catalytic Ozonation in Fe₂O₃/Al₂O₃@SBA-15 Aqueous Suspension for Destruction of Ibuprofen. *Environ. Sci. Technol.* 2015, 49, 1690–1697. [CrossRef] [PubMed]
- 59. Yang, L.; Hu, C.; Nie, Y.; Qu, J. Catalytic Ozonation of Selected Pharmaceuticals over Mesoporous Alumina—Supported Manganese Oxide. *Environ. Sci. Technol.* 2009, 43, 2525–2529. [CrossRef] [PubMed]
- Huang, J.; Zhong, S.; Dai, Y.; Liu, C.-C.; Zhang, H.J. Effect of MnO₂ Phase Structure on the Oxidative Reactivity toward Bisphenol A Degradation. *Environ. Sci. Technol.* 2018, 52, 11309–11318. [CrossRef] [PubMed]
- 61. Roman, P.; Veltman, R.; Bijmans, M.F.M.; Keesman, K.J.; Janssen, A.J.H. Effect of Methanethiol Concentration on Sulfur Production in Biological Desulfurization Systems under Haloalkaline Conditions. *Environ. Sci. Technol.* **2015**, *49*, 9212–9221. [CrossRef]
- 62. Buehler, R.E.; Staehelin, J.; Hoigne, J. Ozone decomposition in water studied by pulse radiolysis. 1. Perhydroxyl (HO₂)/hyperoxide (O₂-) and HO₃/O₃- as intermediates. *J. Phys. Chem.* **1984**, *88*, 2560–2564. [CrossRef]
- 63. Long, L.; Zhao, J.; Yang, L.; Fu, M.; Wu, J.; Huang, B.; Ye, D. Room Temperature Catalytic Ozonation of Toluene over MnO₂/Al₂O₃. *Chin. J. Catal.* **2011**, *32*, 904–916. [CrossRef]
- 64. Liu, Y.; Feng, Y.; Zhang, Y.; Mao, S.; Wu, D.; Chu, H. Highly efficient degradation of dimethyl phthalate from Cu(II) and dimethyl phthalate wastewater by EDTA enhanced ozonation: Performance, intermediates and mechanism. *J. Hazard. Mater.* **2019**, *366*, 378–385. [CrossRef]
- An, T.; Gao, Y.; Li, G.; Kamat, P.V.; Peller, J.; Joyce, M.V. Kinetics and Mechanism of •OH Mediated Degradation of Dimethyl Phthalate in Aqueous Solution: Experimental and Theoretical Studies. *Environ. Sci. Technol.* 2014, 48, 641–648. [CrossRef] [PubMed]

- 66. Zhang, Q.; Li, D.; Liu, Y.; Wang, H.; Zhang, C.; Huang, H.; He, Y.; Chen, X.; Du, Z.; Zheng, X. Potential anticancer activity of curcumin analogs containing sulfone on human cancer cells. *Arch. Biol. Sci.* 2016, *68*, 125–133. [CrossRef]
- 67. Wang, X.; Chen, C.; Li, J.; Wang, X. Ozone degradation of 1–naphthol on multiwalled carbon nanotubes/iron oxides and recycling of the adsorbent. *Chem. Eng. J.* **2015**, *262*, 1303–1310. [CrossRef]
- Acero, J.L.; Haderlein, S.B.; Schmidt, T.C.; Suter, M.J.-F.; von Gunten, U. MTBE Oxidation by Conventional Ozonation and the Combination Ozone/Hydrogen Peroxide: Efficiency of the Processes and Bromate Formation. *Environ. Sci. Technol.* 2001, 35, 4252–4259. [CrossRef]
- 69. Madhavan, D.; Pitchumani, K. Photoreactions in clay media: Singlet oxygen oxidation of electron-rich substrates mediated by clay-bound dyes. *J. Photochem. Photobiol. A Chem.* **2002**, *153*, 205–210. [CrossRef]
- Kim, K.-J.; Hamill, W.H. Pulse radiolysis of concentrated aqueous solutions of chloride, iodide, and persulfate ions. *J. Phys. Chem.* 1976, 80, 2325–2330. [CrossRef]
- Jayson, G.G.; Parsons, B.J.; Swallow, A.J. Some simple, highly reactive, inorganic chlorine derivatives in aqueous solution. Their formation using pulses of radiation and their role in the mechanism of the Fricke dosimeter. J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases 1973, 69, 1597–1607. [CrossRef]
- 72. Buxton, G.V.; Wood, N.D.; Dyster, S. Ionisation constants of °OH and HO°₂ in aqueous solution up to 200 °C. A pulse radiolysis study. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1988**, *84*, 1113–1121. [CrossRef]
- Kasprzyk–Hordern, B.; Ziółek, M.; Nawrocki, J. Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment. *Appl. Catal. B Environ.* 2003, 46, 639–669. [CrossRef]
- 74. Huang, Y.; Luo, M.; Li, S.; Xia, D.; Tang, Z.; Hu, S.; Ye, S.; Sun, M.; He, C.; Shu, D. Efficient catalytic activity and bromate minimization over lattice oxygen—rich MnOOH nanorods in catalytic ozonation of bromide—containing organic pollutants: Lattice oxygen—directed redox cycle and bromate reduction. *J. Hazard. Mater.* 2021, 410, 124545. [CrossRef]
- Shahmahdi, N.; Dehghanzadeh, R.; Aslani, H.; Shokouhi, S.B. Performance evaluation of waste iron shavings (Fe0) for catalytic ozonation in removal of sulfamethoxazole from municipal wastewater treatment plant effluent in a batch mode pilot plant. *Chem. Eng. J.* 2020, 383, 123093. [CrossRef]