



Exploring phase effects and ROS contributions in catalytic ozonation of polymorphic MnO₂-Oxalic acid complexes

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ABSTRACT

This study investigated the pivotal role of oxalic acid (OA) in promoting the formation of multi-phase MnO₂-OA complexes (α -MnO₂-OA, β -MnO₂-OA, and δ -MnO₂-OA), significantly enhancing the efficiency of catalytic ozonation efficiency for pollutants degradation. At a catalyst-to-OA molar ratio of 1:0.8, the ATZ (5 mg L⁻¹) degradation efficiencies within 3 min were 95.09 %, 93.43 %, and 96.71 % for the α -MnO₂/OA/O₃, β -MnO₂/OA/O₃, and δ -MnO₂/OA/O₃ systems, respectively—approximately twice as high as that of O₃ alone. Pyrophosphate experiments verified that the formation of MnO₂-OA complexes relied on the presence of Mn³⁺ on the surface of catalysts, which exhibited higher stability and catalytic ozonation ability in acidic conditions. Further probe experiments quantified the contributions of various reactive oxygen species (ROS) in the MnO₂-OA complexes mediated catalytic ozonation system. The results indicated that O₂^{•-} as dominant species responsible for ATZ removal, followed by [•]OH, while O₃ and ¹O₂ played comparatively minor roles. Notably, multi-phases MnO₂-OA complexes revealed distinct active sites during the catalytic ozonation processes, as identified through a series of characterization techniques. For the α -MnO₂-OA complex, more oxygen vacancies were generated on the surface, adsorbing O₃ and pollutants for further reaction. For the β -MnO₂-OA complex, more manganese vacancies and enhanced lattice oxygen (O_L) mobility were key factors contributing to ROS production. As for the δ -MnO₂-OA complex, the surface -OH groups acted as the main active site, reacting with O₃ to generate more ROS, thus improving ATZ degradation. Overall, this study provides innovative insights into the application of MnO₂ in catalytic ozonation.

1. Introduction

Ozone (O₃), a strong oxidant with an oxidation potential of 2.07 eV, can effectively destroy various types of organic compounds in water [1]. This process occurs either directly through molecular O₃, or indirectly through the highly reactive hydroxyl radical ([•]OH, E₀ = 2.8 eV) that is generated from O₃ decomposition [2]. Considering several disadvantages of single ozonation like low efficiency, high selection, and long reaction time, heterogenous catalytic ozonation (HCO) has drawn increasing attention owing to its benefits of high O₃ availability, low energy consumption, mild operate conditions, and easier separation of the catalyst [3,4]. The presence of catalyst could strengthen O₃ decomposition to generate more [•]OH through enhancing the adsorption and reaction of compound and O₃ on the catalyst surface [5]. Thus, making the process non-selective, stable, and more efficient. Therefore, selecting catalysts that are highly stable, cost-effective, and exhibit

strong catalytic activity has become crucial for advancing HCO technology.

Manganese (Mn), as a cheap metal, constitutes approximately 0.10 % of the earth's crust [6], and its oxides (MnO_x) are widely used as catalysts in HCO owing to their low cost, easy availability, and environmental friendliness [7]. Manganese dioxide (MnO₂) is a common MnO_x and has multiple valence Mn species (Mn²⁺, Mn³⁺, and Mn⁴⁺). Lattice oxygen (O_L) migration and electron transfer frequently occur during the redox reaction between Mn²⁺/Mn³⁺ and/or Mn³⁺/Mn⁴⁺, which can promote O₃ decomposition to generate more reactive oxygen species (ROS), thus increasing the catalytic performance of MnO₂ [8]. Generally, there are six main types of crystalline MnO₂ (α -, β -, γ -, δ -, ϵ -, and λ -), which are composed of [MnO₆] octahedral basic units and combined by different rectangular configurations, resulting in different activities for various reaction system [9]. Nawaz et al. [10] prepared a nanowire cluster-like α -MnO₂ with high specific area (387.7 m² g⁻¹), which

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achieved 98.4 % of 4-nitrophenol degradation and 75.3 % of total organic carbon removal in the HCO system. Scavenger tests demonstrated that superoxide radicals ($O_2^{\bullet-}$), rather than $\bullet OH$, were mainly responsible for the pollutant elimination. However, Ma et al. [11] revealed that $\bullet OH$ and singlet oxygen (1O_2) might be more significant for sulfachloropyridazine degradation (63 %) than $O_2^{\bullet-}$ in δ -MnO₂ catalytic ozonation process. Moreover, Zhao et al. [6] reported that the $\bullet OH$, $O_2^{\bullet-}$, and surface atomic oxygen ($\bullet O$) were not mainly involved in the catalytic ozonation of phenol (94.9 %). The oxidation of O_L enhanced the reversion of Mn^{4+} to Mn^{3+} , with electrons from the surface Mn^{3+} being the primary factor for the strong interaction between O_3 and α -MnO₂. Whereas, Zhang et al. [12] illustrated that the high catalytic ozonation activity of β -MnO₂ for COD removal of bio-treated coking wastewater (47.39 %) was attributed to more crystal defects and adsorbed oxygen on the surface. Obviously, the catalytic mechanisms of various crystal MnO₂ catalysts are complicated and controversial.

Apart from the use of MnO₂ alone in HCO, our previous study [13] found that the addition of oxalic acid (OA) in the solution could promote the formation of β -MnO₂-OA complex, which enhanced not only k value of β -MnO₂/OA/ O_3 process for pBCA degradation (1.541 min^{-1}) by 4 times that of ozonation alone, but also achieved co-degradation of contaminant (90.4 %) and OA (65.2 %). The construction of β -MnO₂-OA complex could enhance electron transfer ability and the redox property of catalyst, as well as availability of O_3 . Other researchers have drawn different conclusions regarding the performance and mechanisms of MnO₂/acid system in the removal of pollutants. For example, Wang et al. [14] described that δ -MnO₂-OA complex could effectively degrade 67.83 % of methyl parathion (MP). First, the excess OA combined with Mn^{3+} produced by the reduction of δ -MnO₂ to form Mn^{3+} -OA complex. Then, the Mn^{3+} -OA complex combined with MP or its hydrolysis products to generate new active complexes, which, as primary active substances, reduced MP or its hydrolysis products. Sun et al. [15] constructed MnO₂/organic acid systems using MnO₂ colloid for tetracyclines (TC) degradation. The results showed that 62.5 % of TC degradation in the OA system was due to the Mn^{3+} -oxalate complex, while 90.7 % of TC removal in L-tartaric acid system was due to direct oxidation by Mn (III). To date, there are few studies discussing the effects of OA as a complex agent on the catalytic ozonation of pollutants by MnO₂ [16,17]. Levanov et al. [16] found the presence of an oxalate complex of tetravalent manganese in catalytic ozonation and mineralization of OA. Qin et al. [17] indicated high activities of Mn(III)-OA at acidic pH in transformation of phenolic compounds. Additionally, the catalytic efficiencies and mechanisms of multi-phase MnO₂-OA complexes have not been studied and compared. Therefore, it is attractive to explore the complexity between different crystalline MnO₂ and OA and the HCO mechanism.

In this study, α -, β -, and δ -MnO₂ materials were synthesized via a modification hydrothermal-calcination method and used for constructing MnO₂-OA complexes. Atrazine (ATZ) degradation was chosen to compare the catalytic ozonation activity of MnO₂-OA complexes. A series of characterization techniques was used to analyze the influence of different MnO₂ structures and surface properties on the formation of MnO₂-OA complexes. Subsequently, a low concentration probe method was adopted to quantify the ROS produced in the catalytic ozonation and evaluate the contribution to ATZ degradation. Finally, the feasible catalytic ozonation mechanisms involving various MnO₂-OA complexes reaction were elaborated and discussed, presenting a potential strategy improving catalytic ozonation performance.

2. Material and methods

2.1. Chemicals

All chemicals including atrazine (ATZ), 2,4-dichlorophenoxyacetic acid (2,4-D), terephthalic acid (TA) and metronidazole (MDE), were provided by Merck. NaOH (pharma grade), acetonitrile (for HPLC super gradient grade), phosphoric acid (H₃PO₄, pharma grade) and

hydrochloric acid (HCl) were supplied by Panreac. More details were exhibited in the supporting information (Text S1).

2.2. Preparation of catalysts

A modified hydrothermal-calcination method was used to synthesize α -MnO₂, β -MnO₂, and δ -MnO₂ catalysts. For α -MnO₂, KMnO₄ and MnSO₄ were dissolved in 80 mL deionized water with magnetic stirring for about 1 h to form precursor solution. Then the liquids were transferred into 100 mL Teflon-lined stainless-steel autoclaves and sealed. The autoclave kept at 160 °C for 14 h, then cooled down to room temperature. The resulting precipitates were dried at 100 °C for 24 h after being collected, filtered, and washed by deionized water. The obtained solid was finely ground and transferred to a ceramic crucible, then heated in a muffle furnace at 360 °C for 2 h with a temperature ramp of 180 °C per hour.

The other MnO₂ catalysts are prepared through the same procedure as α -MnO₂, except for the precursor, hydrothermal temperature and hydrothermal duration. All details are included in Table S1.

2.3. Characterization

The catalysts were characterized through the Fourier transform infrared (FT-IR) spectra, X-ray powder diffraction (XRD) patterns, the X-ray photoelectron spectra (XPS), scanning electron microscope (SEM), Brunauer-Emmett-Teller (BET) analysis, and the oxygen temperature programmed desorption (O_2 -TPD). More parameters and procedures are presented in supporting information (Text S2).

2.4. Experiment procedure

2.4.1. Catalytic activity experiments

Batch ozonation experiments were conducted in a 250 mL glass beaker. Ozone stock solution was prepared using the same method as in a previous study [13]. Typically, a certain quantity of catalyst (α -/ β -/ δ -MnO₂) was added to a mixture of OA and ATZ solution. Then, catalytic ozonation reaction was initiated by the addition of the O_3 stock solution with an initial reaction concentration of 5 mg L⁻¹. Samples (1.5 mL) were taken at specified time intervals under stirring (400 rpm) and then quenched with excess Na₂S₂O₃ (0.01 M) to remove residual O_3 . After filtering through a 0.45 μm filter, the samples were analyzed using High Performance Liquid Chromatography (HPLC). Each experiment was performed at least in duplicate. More details are illustrated in supporting information (Text S3).

2.4.2. The identification and quantification of ROS

In HCO processes, the O_3 , $\bullet OH$, $O_2^{\bullet-}$, and 1O_2 are generally considered to play important roles in contaminant degradation. In the study, 2,4-dichlorophenoxyacetic acid (2,4-D), terephthalic acid (TA) and metronidazole (MDE) as $\bullet OH$, $O_2^{\bullet-}$, and 1O_2 probes, were added into the same catalytic ozonation system with ATZ and OA at low concentration (0.1 mg L⁻¹) to identify and quantify ROS (Fig.S1). Moreover, the adsorption of the probes and ATZ on the surface of catalysts was determined to be negligible. Therefore, the degradation of ATZ, TA, 2,4-D, and MDE in HCO system can be illustrated as Eqs. (1)–(4).

$$\ln\left(\frac{[ATZ]_0}{[ATZ]_t}\right) = k_{\bullet OH, ATZ} \int [\bullet OH] dt + k_{O_2^{\bullet-}, ATZ} \int [O_2^{\bullet-}] dt + k_{^1O_2, ATZ} \int [^1O_2] dt + k_{O_3, ATZ} \int [O_3] dt \quad (1)$$

$$\ln\left(\frac{[TA]_0}{[TA]_t}\right) = k_{\bullet OH, TA} \int [\bullet OH] dt + k_{O_2^{\bullet-}, TA} \int [O_2^{\bullet-}] dt + k_{^1O_2, TA} \int [^1O_2] dt + k_{O_3, TA} \int [O_3] dt \quad (2)$$

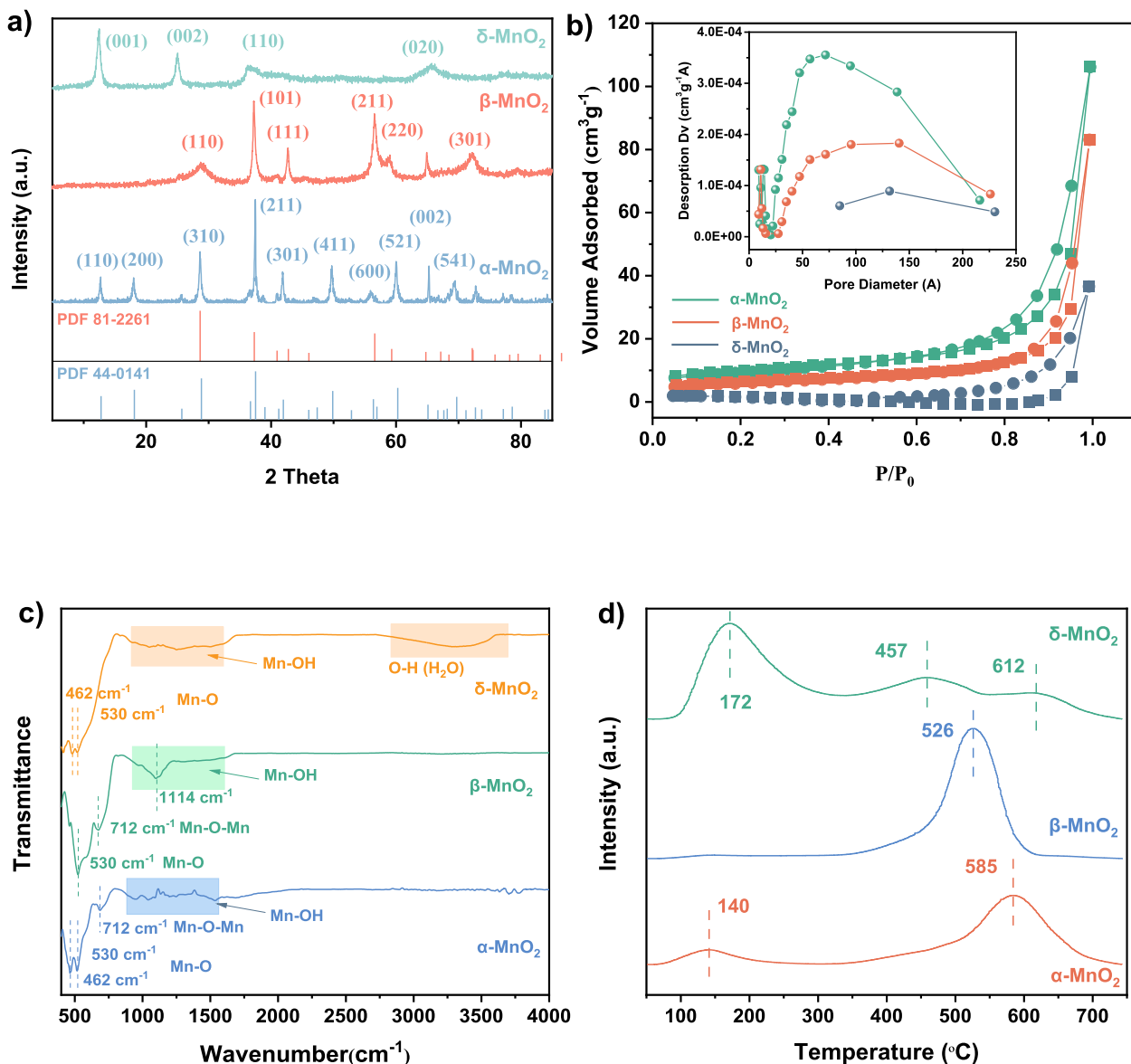


Fig. 1. XRD patterns of different MnO₂ composites a), N₂ adsorption/desorption isotherm b), FT-IR spectrum c) and O₂-TPD profiles d) of α-MnO₂, β-MnO₂, and δ-MnO₂.

$$\ln\left(\frac{[MDE]_0}{[MDE]_t}\right) = k_{\bullet OH, MDE} \int [\bullet OH] dt + k_{O_2^{\bullet-}, MDE} \int [O_2^{\bullet-}] dt + k_{^1O_2, MDE} \int [^1O_2] dt + k_{O_3, MDE} \int [O_3] dt \quad (3)$$

$$\ln\left(\frac{[2, 4-D]_0}{[2, 4-D]_t}\right) = k_{\bullet OH, 2, 4-D} \int [\bullet OH] dt + k_{O_2^{\bullet-}, 2, 4-D} \int [O_2^{\bullet-}] dt + k_{^1O_2, 2, 4-D} \int [^1O_2] dt + k_{O_3, 2, 4-D} \int [O_3] dt \quad (4)$$

$$O_{3, exp} = \int [O_3] dt \quad (5)$$

$k_{O_3, compound}$, $k_{\bullet OH, compound}$, $k_{O_2^{\bullet-}, compound}$, and $k_{^1O_2, compound}$ are the second-order rate constants for the reaction of probe compounds and ATZ with O₃, $\bullet OH$, O₂^{•−}, and ¹O₂, respectively, which are listed in Table 1. O₃ exposure ($\int [O_3] dt$) was determined from the time integrated O₃ concentration during the treatment time Eq. (5) [18]. The exposures of $\bullet OH$, O₂^{•−}, and ¹O₂ were calculated through Eqs. (2)–(4), which were described as $\int [\bullet OH] dt$, $\int [O_2^{\bullet-}] dt$, and $\int [^1O_2] dt$, respectively, based on

the observed abatement efficiency of TA, 2,4-D, and MDE in the same HCO system [19].

2.5. Analysis methods

The concentration of ATZ was analyzed by an Infinity 1260 HPLC from Agilent Technologies (USA) equipped with a Mediterranean Sea18 column (250 mm × 4.6 mm with a particle size of 5 μm) from Teknokroma (Spain). The concentrations of TA, 2,4-D, and MDE were separated by Vanquish HPLC-MS 137, equipping with Orbitrap IQ-X detector. 0.1 % formic acid water and acetonitrile were used as the mobile phases and the samples (2 μL) were measured at a constant flow rate of 0.5 mL min⁻¹. More analysis details were provided in supporting information (Text S4).

3. Results and discussion

3.1. The structural properties of various MnO₂

The XRD patterns of three as-prepared samples are shown in Fig. 1

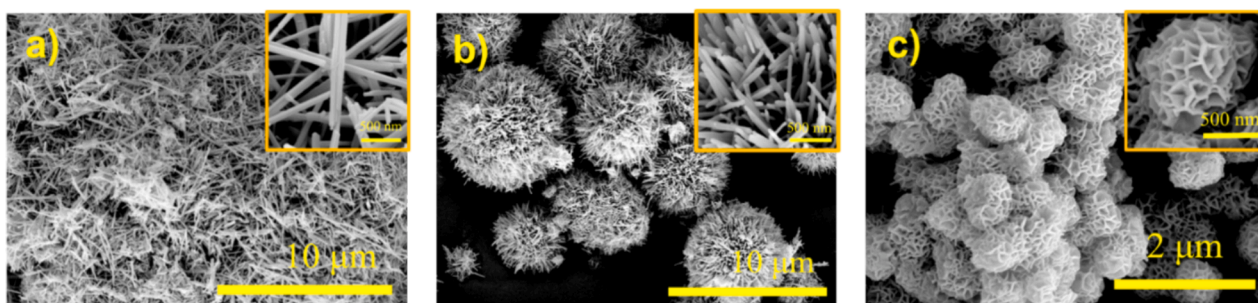


Fig. 2. SEM images of α -MnO₂ a), β -MnO₂ b), and δ -MnO₂ c).

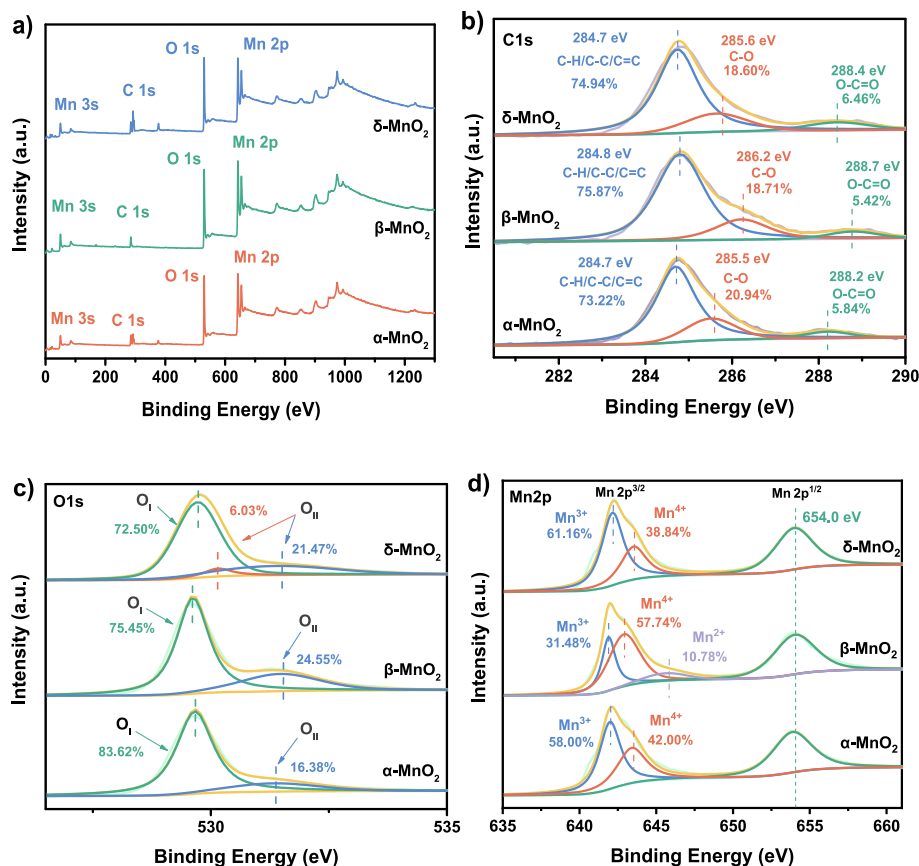


Fig. 3. XPS spectrum for α -MnO₂, β -MnO₂, and δ -MnO₂ composites: survey spectra a), C 1 s b), O 1 s c), and Mn 2p d).

(a). The diffraction peaks were identified with 2θ at 22.5°, 28.7°, 37.5°, 42.0°, 49.9°, 56.6°, 59.9°, 65.3° and 68.9° (PDF 44-0141), which could be assigned to the (110), (200), (310), (211), (301), (411), (600), (521), (002), and (541) planes of α -MnO₂ indicating the presence of manganese oxide with a tetragonal structure [20]. Furthermore, low intensity and broad diffraction peaks of δ -MnO₂ were also detected at $2\theta = 12.5^\circ$, 25.1°, 37.2°, and 65.5° corresponding to the (001), (002), (110), and (020) crystal planes [21]. The evident peaks at 28.6°, 37.3°, 40.9°, 42.8°, and 56.7° were related to the (110), (101), (111), (211), (220), and (301) crystal planes, respectively, representing the rutile structure of β -MnO₂ (PDF 81-2261) [22]. The XRD results clearly revealed the successful preparation of varied MnO₂ crystallographic forms.

Fig. 1(b) exhibits the N₂ adsorption-desorption isotherms of as-prepared MnO₂ samples. The three catalysts presented similar characteristic type IV adsorption curves with a hysteresis loop at about relative pressure (P/P_0) between 0.4 and 1.0, suggesting the presence of mesopores [5]. The specific surface areas, pore size distributions, and pore

volumes are summarized in Table 1. Due to differences in morphological structure, the catalysts displayed varying specific surface areas in the following order: α -MnO₂ (33.23 m² g⁻¹) > β -MnO₂ (21.67 m² g⁻¹) > δ -MnO₂ (6.30 m² g⁻¹). Moreover, the SEM images of the various crystal structures of catalysts are shown in Fig. 2. α -MnO₂ exhibited a uniform shape of nanowires with the width of 50–70 nm and length of 0.5–3 μ m [11]. β -MnO₂ had dandelion-like nanospheres with a diameter of 2–8 μ m, consisting of nanorods with the width of 40–60 nm on the surface. And δ -MnO₂ exhibited a flower-like sphere morphology consisting of nanoflakes.

The FT-IR analysis in the range between 400 and 4000 cm⁻¹ is shown in Fig. 1(c). Same peaks of three samples appeared at 462 cm⁻¹, and 530 cm⁻¹ could be indexed to the vibrations of Mn-O bonds [23] and the absorption band at 712 cm⁻¹ was ascribed to the Mn-O-Mn stretching vibration, indicating the successful formation of octahedral [MnO₆] [24]. Several small peaks in the range of 1000–1500 cm⁻¹ of three composites could be attributed to the bending vibrations of hydroxyl

Table 1
XPS results of different catalysts.

Catalyst	O 1 s		O _{II}		O _{III}		O _{II} /O _I		Mn 2p	
	O _I		O _{II}		O _{III}		O _{II} /O _I		Mn ³⁺ /Mn ⁴⁺	
	Peak (eV)	Area (%)	Peak (eV)	Area (%)	Peak (eV)	Area (%)	ratio		ratio	
α-MnO ₂	529.7	83.62			531.3	16.38		0.20		1.38
β-MnO ₂	529.6	75.45			531.5	24.55		0.32		0.54
δ-MnO ₂	529.7	72.50	530.2	6.03	531.4	21.47		0.38		1.58
α-MnO ₂ -OA	529.6	55.96	530.2	15.92	531.5	28.12		0.79		1.52
β-MnO ₂ -OA	529.3	60.96			531.0	19.83	532.4	0.33		1.65
δ-MnO ₂ -OA	529.8	58.69	530.3	16.19			532.3	0.28		1.60

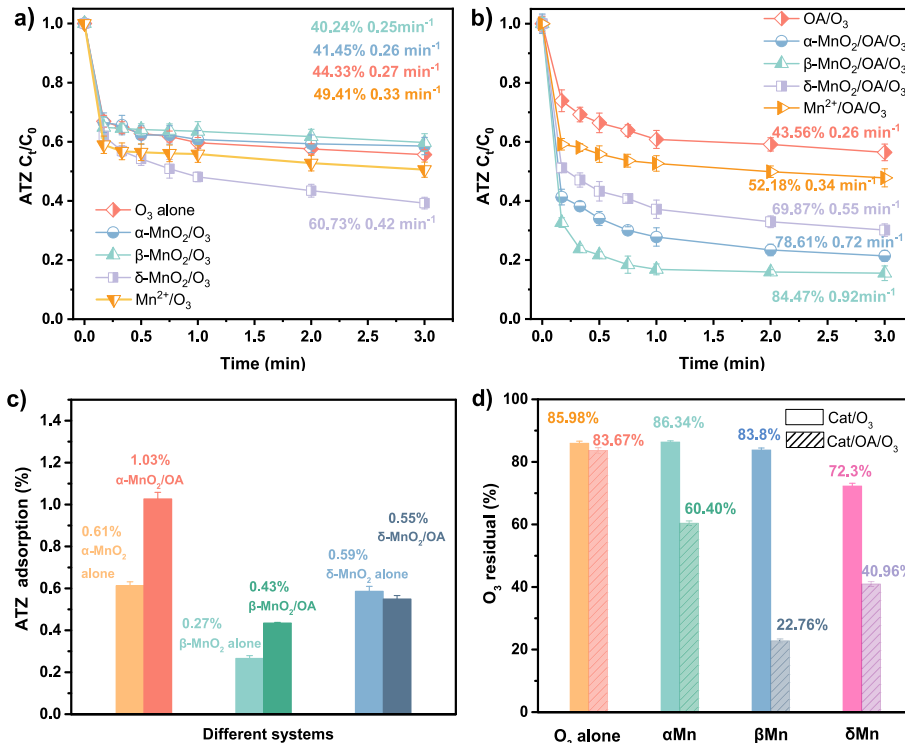


Fig. 4. ATZ removal efficiency in different Cat/O₃ systems a), Cat/OA/O₃ systems b), catalyst alone c), and depletion of O₃ in different processes d). Experimental conditions: [ATZ]₀ = 5 mg L⁻¹, [Cat] = 50 mg L⁻¹, [OA]₀ = 10 mg L⁻¹, [O₃]₀ = 5 mg L⁻¹, pH₀ = 4.0 ± 0.2.

(-OH) groups connected with Mn atoms [25,26]. In the case of δ-MnO₂, a broad peak at 3400 cm⁻¹ was associated with O – H bonds stretching vibrations originating from water adsorbed on the surface of catalyst [26]. Furthermore, it could be observed that β-MnO₂ possessed a strong intensity band at 1114 cm⁻¹, which usually appears in low temperature hydrothermal synthesis of nanostructured materials [27].

The O₂-TPD experiments were conducted to explore the mobility of oxygen species (Fig. 1(d)). The desorption peaks below 300 °C correspond to the surface-adsorbed oxygen species (O_S). The second desorption peaks, observed in 300–500 °C range, could be ascribed to subsurface lattice oxygen (O_{SL}), which is correlated with the reduction of Mn⁴⁺ to Mn³⁺. While the third peaks, occurring above 500 °C, are assigned to the release of lattice oxygen (O_L) [28,29]. Compared to α-MnO₂ and β-MnO₂, larger desorption peak of O_S was found over δ-MnO₂ (172 °C). This means that more active oxygen species were detected on the catalyst surface. As the generation, activation, and migration of reactive Os typically relied on oxygen vacancies (Vo), the result suggested that δ-MnO₂ contained the highest activity of mobile oxygen and the largest amount of Vo [29,30].

The surface chemical element states of three types of MnO₂ were determined by XPS. Based on Fig. 3(a), the investigated scan spectrum

suggests that the catalysts consist mainly of Mn and O. After calibrating the binding energies, The C 1 s spectrum (Fig. 3(b)) was divided into three peaks at ~ 288.4, ~285.6, and ~ 284.7 eV, which could be ascribed to C–C/C=C/C–H bonds, C–O, and O–C=O, respectively [31]. For the O 1 s spectra in Fig. 3(c), the peak at lower binding energy (<530.3 eV) could correspond to lattice oxygen (O_I: O₂⁻), and the peak at 530.0 ~ 531.8 eV (donated O_{II}) could be assigned to the adsorbed oxygen (O₂⁻, O₂⁻, O⁻) and –OH groups [6,20,29]. As presented Table 1, the O_{II}/O_I ratio of δ-MnO₂ (0.38) was higher than that of α-MnO₂ (0.20) and β-MnO₂ (0.32), indicating δ-MnO₂ had the most abundant surface adsorbed oxygen due to the presence of Vo on the catalyst surface [32]. Moreover, the Mn 2p_{3/2} signal (Fig. 3(d)) fitting for catalysts could be deconvoluted into three peaks with binding energy at ~ 641.9, 643.4, and 645.3 eV attributed to Mn³⁺, Mn⁴⁺, and Mn²⁺, respectively [33]. δ-MnO₂ showed the highest (1.57) Mn³⁺/Mn⁴⁺ ratio whereas β-MnO₂ exhibited the lowest (0.54) (Table 1). The existence of Mn³⁺ in the MnO₂ catalyst would produce Vo to maintain electrostatic balance [21]. In general, compared to α-MnO₂ and β-MnO₂, δ-MnO₂ had the highest amount of Mn³⁺ and Vo, which could enhance the adsorption of O₃ on catalyst surface and then decompose into more ROS.

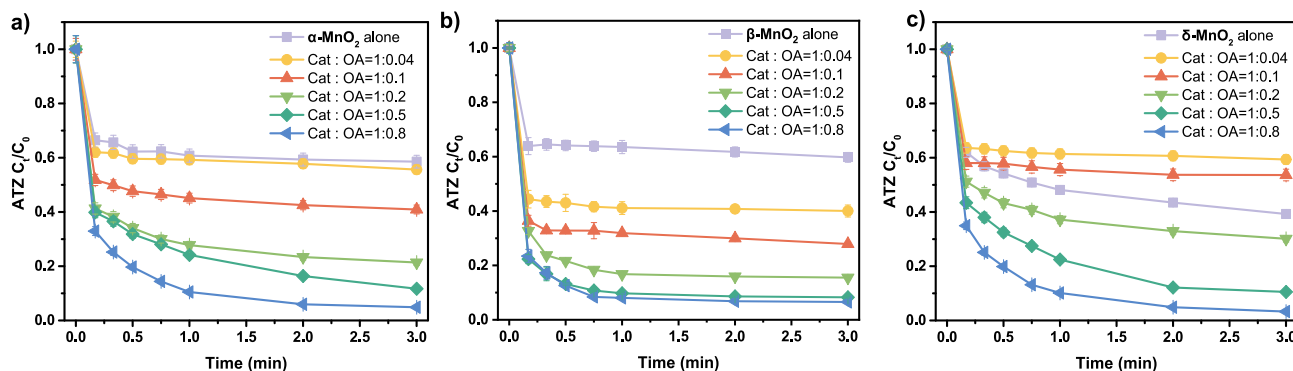


Fig. 5. The effects of molar ratios (1:0.04–1:0.8) of α -MnO₂ to OA a), β -MnO₂ to OA b), and δ -MnO₂ to OA c) on ATZ removal efficiency in catalytic ozonation systems. Experimental conditions: [ATZ]₀ = 5 mg L⁻¹, [Cat] = 50 mg L⁻¹, [OA]₀ = 2–40 mg L⁻¹, [O₃]₀ = 5 mg L⁻¹, pH₀ = 4.0 ± 0.2.

3.2. Enhanced catalytic ozonation mediated by MnO₂-OA complexes

As illustrated in Fig. 4(a), the ATZ removal in sole O₃ was 44.33 % and it was slightly inhibited in the α -MnO₂/O₃ (41.45 %) and β -MnO₂/O₃ (40.24%) processes. However, the presence of δ -MnO₂ enhanced the ATZ degradation (60.73%) and corresponding rate constant (*k*) increased from 0.25 min⁻¹ to 0.42 min⁻¹. Despite having the lowest BET surface area and smallest pore size (5.85 nm), δ -MnO₂ exhibited a unique layered structure, which is rich in structural defects and Vo. Vo possesses the ability to both accept and donate electrons facilitating electron transfer across the catalyst, thereby supporting the redox cycle of Mn species [34]. Moreover, Vo integrated into the crystal structure of MnO₂ catalysts can modulate the intrinsic electronic configuration, which ultimately enhances the exposure of catalytic sites. Additionally, owing to the high energy of Vo, the adsorption of O₃ and H₂O on the catalyst surface could be improved, thus enhancing the utilization of O₃ to generate more ROS, which are essential for the degradation of ATZ [35]. These findings indicated that catalytic performance was not solely dependent on surface area and pore volume but is also significantly influenced by the structural, electronic, and chemical properties of MnO₂ phases.

Our previous study [13] confirmed that a complex can form between OA and MnO₂, enhancing the catalytic ozonation efficiency. To investigate the role of OA in complex generation with various MnO₂, the ATZ degradation in α -MnO₂/OA/O₃, β -MnO₂/OA/O₃, and δ -MnO₂/OA/O₃ systems was compared. As exhibited in Fig. 4(b), ATZ was significantly degraded in 0.25 min with the addition of OA (10 mg L⁻¹) in three systems, achieving removal rates of 78.61 %, 84.47 %, and 69.87 %, respectively. The rapid formation of MnO₂-OA complex in short time facilitated O₃ decomposition, generating more active species and thereby enhancing ATZ degradation. However, as O₃ was consumed, the degradation slows down. The surface adsorption of ATZ (<2 %) (Fig. 4(c)) by the complexes can be considered negligible.

Furthermore, as shown in Fig.S2(a), the adsorption efficiencies of OA on α -MnO₂, β -MnO₂, and δ -MnO₂ were 10.25 %, 12.94 %, and 11.82 %, respectively. However, in α -MnO₂/OA/O₃, β -MnO₂/OA/O₃, and δ -MnO₂/OA/O₃ systems, the OA degradation increased significantly to 51.78 %, 67.09 %, and 33.99 %, respectively—at least three times higher than that achieved with O₃ alone (Fig.S2(b)). The results confirmed that the Cat/OA/O₃ system enables the co-degradation of OA and ATZ. Meanwhile, Fig. 4(d) revealed the rate of O₃ depletion, which was distinctively enhanced by α -MnO₂/OA/O₃ (39.60 %), β -MnO₂/OA/O₃ (77.24 %), and δ -MnO₂/OA/O₃ (59.04 %). This further verified that the formed α -MnO₂-OA, β -MnO₂-OA, and δ -MnO₂-OA complexes promote the effective utilization of O₃, thereby producing more active substances to enhance ATZ degradation in the solution.

The concentration of Mn ion in the solution after ozonation was quantified in different systems. In α -MnO₂/O₃, β -MnO₂/O₃, and δ -MnO₂/O₃ processes, the release of Mn ion in the solution is less than

0.35 mg L⁻¹. In α -MnO₂/OA/O₃, β -MnO₂/OA/O₃, and δ -MnO₂/OA/O₃ processes, Mn ion remained low (< 0.4 mg L⁻¹). To clarify the contribution of homogeneous Mn species in the system to the degradation of ATZ, two additional systems including Mn²⁺(0.4 ppm)/O₃ and Mn²⁺(0.4 ppm)/OA/O₃ were conducted. As shown in Fig. 4(a) and (b), the degradation of ATZ in two systems were 49.41 % and 52.18 %, respectively. It was clear that the contribution of Mn ions in the solution to catalytic ozonation of ATZ degradation was not the most important. Moreover, to investigate the potential formation of Mn²⁺/OA complexes, the reaction solutions were further analyzed using UV-Vis spectrophotometer (Fig.S3). Levanova et al [16] found that the addition of Mn²⁺ ion in catalytic ozonation system for OA degradation would promote the formation of Mn²⁺/OA complex, which exhibited characteristic absorption peaks (high-intensity shoulder at 385–390 nm and a less intense peak with a maximum at 645 nm). However, as displayed in Fig.S3, no such characteristic absorption peaks were found in α -MnO₂/OA/O₃, β -MnO₂/OA/O₃, and δ -MnO₂/OA/O₃ systems. These findings confirm that homogeneous Mn²⁺-mediated ozone activation played an insignificant role in our system, and the observed catalytic activity was primarily attributed to heterogeneous reactions.

To clarify the effect of complexation between OA and MnO₂ on the catalytic ozonation system, the ATZ removal efficiency under various molar ratios of catalyst to OA was evaluated in Fig. 5. As exhibited in Fig. 5(a), the ATZ removal at molar ratios of α -MnO₂ to OA from 1:0.04 to 1:0.8 was 44.35 %, 59.07 %, 78.61 %, 88.27 %, and 95.09 % after 3 min reaction. Similar removal trends were observed in β -MnO₂/OA/O₃, where the degradation of ATZ was gradually promoted from 59.96 % to 93.43 % (Fig. 5(b)) as molar ratios rose to 1:0.8. The introduction of OA would promote the rapid formation of α -MnO₂-OA and β -MnO₂-OA complexes, impacting the removal of ATZ. As for the δ -MnO₂/OA/O₃ process displayed in Fig. 5(c), δ -MnO₂ catalytic ozonation achieved 60.73 % of ATZ degradation, while it was slightly reduced at molar ratio of 1:0.04 (40.63 %) and 1:0.1 (46.35 %). The inhibition was due to the competition between ATZ and OA for the ROS and O₃. However, when the ratio of OA continuously increased up to 1:0.8, the elimination of ATZ increased to 96.71 %. The generation of δ -MnO₂-OA complex depended on the content of OA. Moderately increasing the OA dose would enhance formation of α -MnO₂-OA, β -MnO₂-OA, and δ -MnO₂-OA complexes, which might generate more ROS through strengthening reaction with O₃, thereby boosting the catalytic ozonation performance.

Considering the conditions for complex generation, the influence of various pH values was explored in Fig.S4, for the catalyst (Fig.S4(a)) and the complex (Fig.S4(b)) ozonation systems. With the increase of pH value from 3.0 to 7.0, the catalytic ozonation removal of ATZ showed no significant changes in the presence of only the catalyst (α -MnO₂ or β -MnO₂), remaining around 43 % (Fig. S4(a)). In the case of δ -MnO₂, the removal efficiency of ATZ was reduced from 63.27 % to 48.29 %, which may be related to the charge of catalyst surface and O₃ utilization efficiency [36]. As compared in Fig. S4(b), more than 95 % of ATZ was

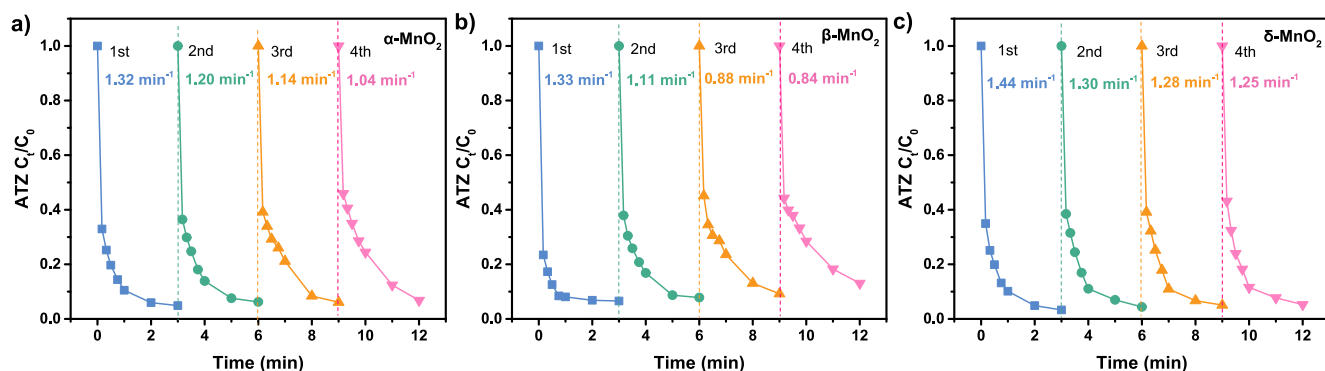


Fig. 6. The recycling experiments of α -MnO₂ a), β -MnO₂ b), and δ -MnO₂ c). Experimental conditions: [ATZ]₀ = 5 mg L⁻¹, [Cat] = 50 mg L⁻¹, [OA]₀ = 40 mg L⁻¹, [O₃]₀ = 5 mg L⁻¹, pH₀ = 4.0 ± 0.2.

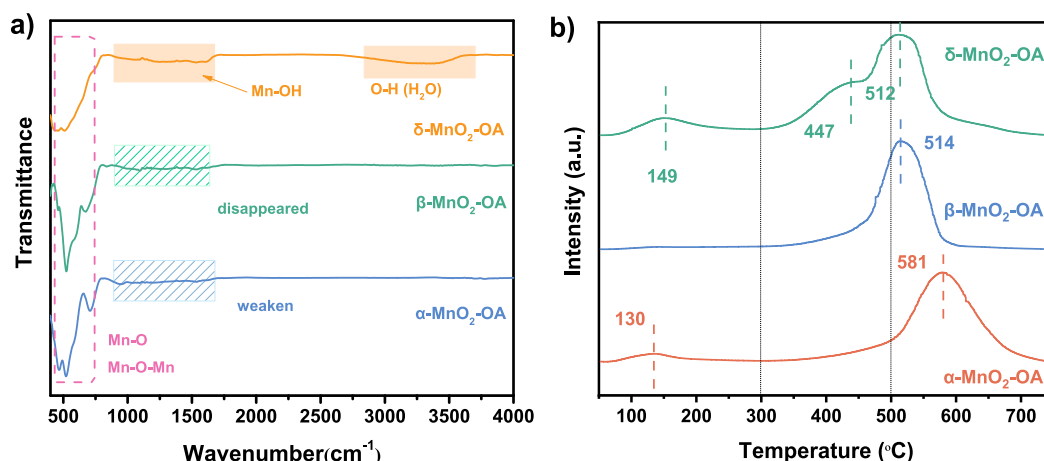


Fig. 7. FT-IR spectrum a) and O₂-TPD profiles b) of α -MnO₂-OA, β -MnO₂-OA, and δ -MnO₂-OA complex.

degraded within 3 min by the formed complexes at pH 3.0. Subsequently, the catalytic ozonation activities of three complexes were obviously restrained (<40 %) as pH increased to 7.0. These results can be primarily explained by the increased solubility of MnO₂ in OA at acidic pH, which facilitated the production of Mn³⁺. Additionally, Mn³⁺ complex formed with OA exhibited higher stability and catalytic ozonation ability in acidic conditions, but lower under alkaline pH conditions [17].

The recycling experiments were conducted using α -MnO₂, β -MnO₂, and δ -MnO₂ catalysts, which were separated, washed 4 times with Milli-Q water, dried at 60 °C for 12 h. As shown in Fig. 6, the degradation efficiency of ATZ remained around 90 % even after the 4th cycle. However, the observed pseudo-first-order rate constant (k_{obs}) values for the α -MnO₂/OA/O₃, β -MnO₂/OA/O₃, and δ -MnO₂/OA/O₃ processes decreased from 1.32 to 1.04 min⁻¹, 1.33 to 0.84 min⁻¹, and 1.44 to 1.25 min⁻¹, respectively. By the end of the cycles, the Mn ion concentration in the solution increased to approximately 2.62 mg L⁻¹, 2.58 mg L⁻¹, and 3.27 mg L⁻¹ in α -MnO₂/OA/O₃, β -MnO₂/OA/O₃, and δ -MnO₂/OA/O₃ processes, respectively. The increased dissolution of Mn ions likely reduced the active Mn species on the catalyst surface, affecting the formation of the MnO₂-OA complex and subsequently inhibiting its reaction rate. Additionally, it has been reported that the deposition of reaction intermediates on the catalyst surface, blocking active sites [37], could also contribute to the decline in the corresponding k_{obs} values. On the other hand, Graham et al [38] reported that the introduction of a small amount of Mn²⁺ in O₃/Mn²⁺ oxidation process can directly promote the decomposition of O₃, generating •OH. Therefore, the increase in the dissolved amount of Mn ions in the Cat/OA/O₃ system could promote the generation of •OH, which might be one of the reasons why

the degradation of ATZ remains around 90 % after four cycles.

To further study the stability of the catalysts, the phase structure of reacted α -MnO₂, β -MnO₂, and δ -MnO₂ were examined by XRD. As illustrated in Fig.S5, the baseline of spectrum shifts upward due to the dissolution Mn ions. The typical crystal planes were observed in the XRD spectrum of reacted catalysts, which were the same characteristic peaks as those in original α -MnO₂, β -MnO₂, and δ -MnO₂ catalysts (Fig. 1). These results demonstrated the structural stability of the catalysts. The reusability tests of the α -MnO₂, β -MnO₂, and δ -MnO₂ catalysts provided new insights into the application of Cat/OA/O₃ system for water purification

3.3. Characterizations of MnO₂-OA complexes

The addition of OA in the solution facilitated the formation of the MnO₂-OA complex, which affected the catalytic ozonation efficiency. To compare the structures, surface properties, and chemical composition of the formed α -MnO₂-OA, β -MnO₂-OA, and δ -MnO₂-OA complexes, the FT-IR, O₂-TPD, and XPS characterizations were further conducted.

In the FT-IR spectrum (Fig. 7(a)), several high-frequency modes of the three samples below 750 cm⁻¹ represented the vibrations of Mn-O-Mn and Mn-O bonds, illustrating that the newly formed complexes had not altered the fundamental unit structure of MnO₂ [39]. However, the peak intensity decreased, signifying the weakened Mn-O bonds. Compared to the initial MnO₂ catalysts (Fig. 1(c)), the peaks in the range of 1000–1500 cm⁻¹ were weakened in the spectra of the α -MnO₂-OA complex. Moreover, the peak at 1114 cm⁻¹ had completely disappeared in the case of the β -MnO₂-OA complex. The results indicated that the complexation of OA with α -MnO₂/ β -MnO₂ occurred by replacing some

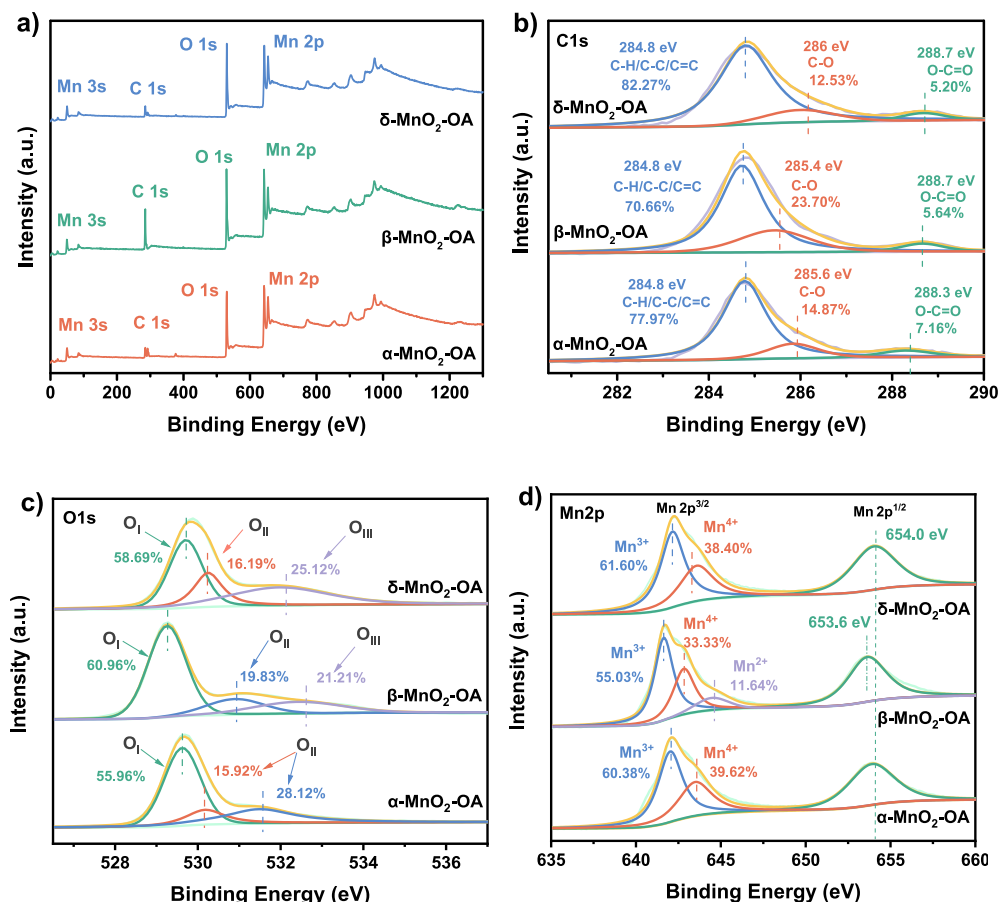


Fig. 8. XPS spectrum for α -MnO₂-OA, β -MnO₂-OA, and δ -MnO₂-OA complexes: survey spectra a), C 1 s b), O 1 s c), and Mn 2p d).

–OH groups on the catalysts (α - and β -MnO₂) surface [40,41]. However, peaks in the 1000–1500 cm^{−1} range as well as a broad peak around 3400 cm^{−1} were still observed in the spectra of the δ -MnO₂-OA complex. This implied that –OH groups remained and an amount of H₂O was adsorbed on the catalyst surface after δ -MnO₂ complexation with OA [25].

The analysis of O₂-TPD spectra is shown in Fig. 7(b). In comparison with α -MnO₂ (Fig. 1(d)), the desorption peaks of the α -MnO₂-OA complex shifted from 140 °C to 130 °C (O_S). Theoretically, O_S as labile oxygen, the lower the temperature of O_S release was, the looser they had been adsorbed on the catalyst surface, which indicated more Vo existed in the catalyst [29]. In the spectra of the β -MnO₂-OA complex, the peak of O_L moved towards a lower temperature (514 °C) from 526 °C (Fig. 1(d)), implying the lattice oxygen in the framework had become more unstable [42]. This phenomenon was explained by increased Mn vacancies (V_{Mn}), which weakened Mn–O bonds in the crystal framework and thus enhanced lattice oxygen mobility [29,43]. Moreover, upon forming the δ -MnO₂-OA complex, the peak intensity of O_S (149 °C) decreased, while those of O_{SL} (447 °C) and O_L (512 °C) increased, indicating a substantial rise in O_L content [30]. Meanwhile, the O_L shifted sharply from 612 °C to 512 °C, suggesting a notable enhancement in O_L activity within the δ -MnO₂-OA complex.

The complete XPS survey spectrum of the complex is revealed in Fig. 8(a). It was observed that the peak intensity of C 1s in the β -MnO₂-OA complex had increased significantly, suggesting a stronger combination ability between β -MnO₂ and OA. Meanwhile, the O–C=O and C–O ratios of the β -MnO₂-OA complex increased from 5.42 % to 5.64 % and from 18.71 % to 23.70 %, respectively (Fig. 9(b)).

In the O 1 s signals of the α -MnO₂-OA, β -MnO₂-OA, and δ -MnO₂-OA complexes, the binding energy of the peak above 532.0 eV could be

associated with adsorbed molecular water (O_{III}) [6]. As shown in Fig. 8c and Table 1, the O_I peak of the three complexes decreased compared to original MnO₂, which confirmed the weakened Mn–O bonds during the formation process of complex. Moreover, in the case of the α -MnO₂-OA complex, two peaks at 530.2 and 531.5 eV could be assigned to O_{II}, whose intensity rose to 15.92 % and 28.12 %, respectively. The improved O_{II}/O_I ratio (0.79) indicated the generation of more Vo during the combination of α -MnO₂ and OA [31]. For the β -MnO₂-OA complex, the O_{II} peak (531.0 eV) decreased from 24.55 % to 19.83 % further verifying the substitution of surface –OH groups. Due to the weakened Mn–O bonds of the β -MnO₂-OA complex, the Mn–O coordination configuration changed, which could induce the formation of V_{Mn}, thus enhancing the adsorption of O₃ and water molecules (H₂O) on the catalyst surface [29]. That could be the reason for the appearance of the peak at 532.4 eV (21.21 %). In terms of the δ -MnO₂-OA complex, the peak at 530.3 eV increased markedly from 6.03 % to 16.19 %, implying the creation of a large amount of surface –OH [40]. However, the O_{II}/O_I ratio of the δ -MnO₂-OA complex decreased from 0.38 to 0.28, indicating that the formation of the complex did not lead to an increase in Vo.

The Mn 2p_{3/2} spectra of the α -MnO₂-OA complex in Fig. 8(d) were deconvoluted into two peaks assigned to Mn³⁺ (642.0 eV) and Mn⁴⁺ (643.05 eV) [6]. It was noted that the Mn³⁺/Mn⁴⁺ ratio (1.52) was higher than that of pristine α -MnO₂ (1.38) (Table 1), suggesting the much larger content of Mn³⁺ on the surface of the complexation catalyst, which could promote the formation of surface Vo over the α -MnO₂-OA complex to preserve charge balance [37]. Three peaks were found in the Mn 2p_{3/2} spectra of the β -MnO₂-OA complex at 641.6 (Mn³⁺), 642.8 (Mn⁴⁺), and 644.5 eV (Mn²⁺) [33]. The percentage of Mn⁴⁺ decreased and that of Mn³⁺ and Mn²⁺ increased. During the complexation process, Mn⁴⁺ in the frameworks was progressively reduced to Mn³⁺ and

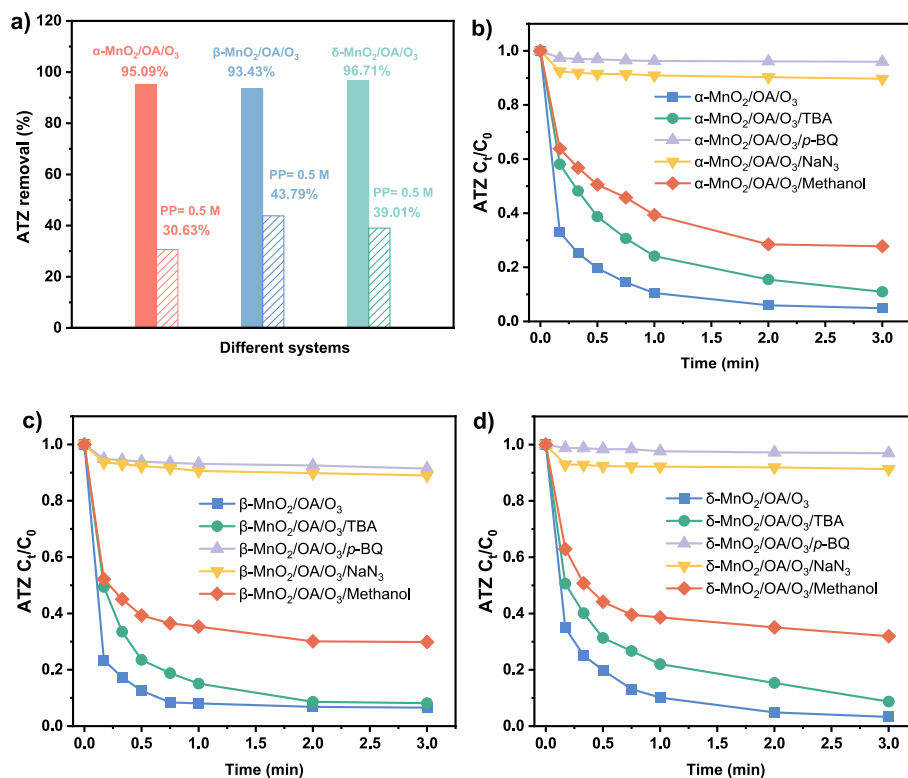


Fig. 9. Effects of sodium pyrophosphate on ATZ removal efficiency a), effects of various scavengers on ATZ removal efficiency in α -MnO₂/OA/O₃ b), β -MnO₂/OA/O₃ c), and δ -MnO₂/OA/O₃ d) systems. Experimental conditions: [ATZ]₀ = 5 mg L⁻¹, [Cat] = 50 mg L⁻¹, [OA] = 40 mg L⁻¹, [O₃]₀ = 5 mg L⁻¹, [PP]₀ = 0.5 mM, [TBA] = [p-BQ] = [NaN₃] = [Methanol] = 1 mM.

subsequently to Mn²⁺, with its two 3 s electrons being transferred to Mn–O orbitals [44]. This reduction led to an increase in V_{Mn} and the Mn³⁺/Mn⁴⁺ ratio (1.65) [29]. Besides, the relative Mn³⁺/Mn⁴⁺ ratio of the δ -MnO₂-OA complex did not distinctly change (1.60), suggesting the excellent stability of the catalyst in the combination process with OA [45].

3.4. Identification of reactive species

3.4.1. Role of Mn³⁺ species

Based on the XPS analysis, after forming complexes by adding OA into the solution, the amount of Mn³⁺ in the α -MnO₂-OA, β -MnO₂-OA, and δ -MnO₂-OA complexes increased. In order to investigate the role of Mn³⁺ in the complexation processes, pyrophosphate (PP) was introduced to the catalytic ozonation systems, which could act as a scavenger of Mn³⁺ (log *k*_{apparent} = 31.35). As shown in Fig. 9(a), the ATZ (5 mg L⁻¹) degradation efficiencies of the α -MnO₂/OA/O₃, β -MnO₂/OA/O₃, and δ -MnO₂/OA/O₃ systems were restrained by 64.46 %, 49.64 %, and 57.70 %, respectively, with PP concentration of 0.5 mM. PP could complex with Mn³⁺, which would inhibit the complexation between MnO₂ and OA. The reduction of complexes limited further reactions with O₃, resulting in less ROS production, thus hindering the degradation of ATZ. These findings indicated that the formations of the α -MnO₂-OA, β -MnO₂-OA, and δ -MnO₂-OA complexes depended on the presence of Mn³⁺ in the system.

3.4.2. Roles of ROS via scavenger experiments

Compared to O₃ alone (44.33 %), α -MnO₂/O₃ (41.45 %), and β -MnO₂/O₃ (40.24 %), the δ -MnO₂/O₃ process achieved the highest performance (60.73 %) for ATZ degradation. In this study, 1 mM of TBA, *p*-BQ, and NaN₃ were introduced to the catalytic ozonation system as quenchers of •OH, O₂^{•-}, and ¹O₂, respectively. As shown in Fig.S6, the degradation of ATZ was inhibited by the presence of TBA (31.41 %), *p*-

BQ (7.02 %), and NaN₃ (5.17 %) in the δ -MnO₂/O₃ system. Considering that TBA as a scavenger could quench •OH in the bulk liquid phase (•OH_L), methanol (1 mM) was used to further evaluate the role of both •OH_L and surface-bound •OH (•OH_S) in ATZ degradation [46]. It was found that the ATZ removal in the presence of methanol (31.12 %) was similar to that in the presence of TBA. The results implied that the degradation of ATZ in the δ -MnO₂/O₃ process relied on the presence of •OH, O₂^{•-}, and ¹O₂.

As investigated in Fig. 9(b-d), the addition of TBA in the α -MnO₂/OA/O₃, β -MnO₂/OA/O₃, and δ -MnO₂/OA/O₃ systems inhibited ATZ removal by less than 5 %. For comparison, the presence of methanol could hinder ATZ degradation by more than 20 %, which indicated that •OH_S participated in the reaction, improving catalytic efficiency. Furthermore, the presence of *p*-BQ, and NaN₃ almost completely restrained the degradation of ATZ in the catalytic ozonation system. This suggested that both O₂^{•-} and ¹O₂ were also important ROS in the process. However, as illustrated in Fig.S7, when the scavengers were added to the O₃ alone process, the ATZ elimination was significantly suppressed. In particular, more than 20 % of ATZ degradation was inhibited by *p*-BQ and NaN₃. Guo et al pointed out that conventional radical scavengers with high concentrations can significantly interfere with O₃ decomposition and the chain reaction involving free radicals, making it challenging to accurately assess the contribution of ROS to catalytic ozonation efficiency [18]. Therefore, a probe approach was employed in the study to measure the exposures of various ROS in the reaction.

3.4.3. Quantification of ROS via low concentration probe experiments

As shown in Fig.S1, the addition of trace amounts of probes (2,4-D, TA, and MDE) with a concentration of 0.1 mg L⁻¹ had little effect on the efficiency of O₃ alone (around 43 %) and catalytic ozonation (>93 %). According to the second-order rate constants of probe compounds and ATZ with O₃ and other ROS (Table 1), the exposure of O₃ and different ROS was calculated by using Eqs. (1)–(5). As shown in Fig.S8, the O₃

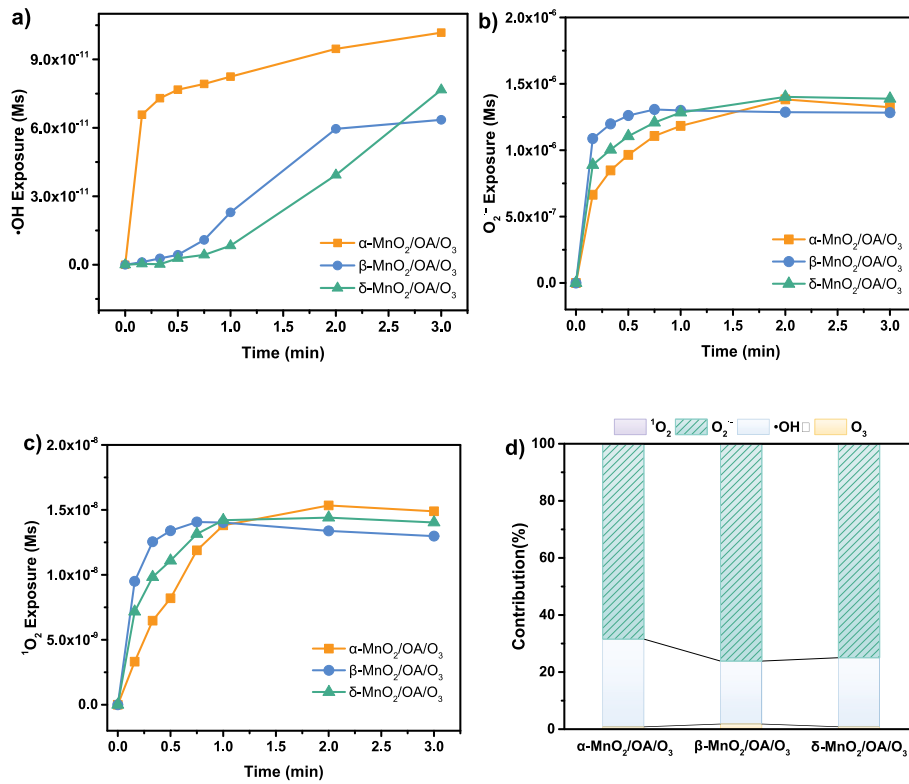


Fig. 10. The exposures of $\bullet\text{OH}$ a), $\text{O}_2^{\bullet-}$ b), and $^1\text{O}_2$ c), and the contribution rate of ROS and O_3 d) during catalytic ozonation. Experimental conditions: $[\text{ATZ}]_0 = 5 \text{ mg L}^{-1}$, $[\text{Cat}] = 50 \text{ mg L}^{-1}$, $[\text{OA}]_0 = 40 \text{ mg L}^{-1}$, $[\text{O}_3]_0 = 5 \text{ mg L}^{-1}$, $[\text{probes}] = 0.1 \text{ mg L}^{-1}$.

exposure of the $\beta\text{-MnO}_2/\text{OA}/\text{O}_3$ system was about 0.0055 Ms in 3 min, which was twice that of the $\alpha\text{-MnO}_2/\text{OA}/\text{O}_3$ and $\delta\text{-MnO}_2/\text{OA}/\text{O}_3$ processes. The higher exposure level of O_3 in the $\beta\text{-MnO}_2/\text{OA}/\text{O}_3$ system provided an explanation for the faster catalytic reaction rate of the $\beta\text{-MnO}_2\text{-OA}$ complex. Meanwhile, as displayed in Fig. 10, all three systems detected the presence of $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, and $^1\text{O}_2$, but they exhibited different exposure rates. It was evident that the $\bullet\text{OH}$ exposure level of $\alpha\text{-MnO}_2/\text{OA}/\text{O}_3$ within 1 min (8.24×10^{-11} Ms) was higher than in other systems, implying the more important role of $\bullet\text{OH}$ in $\alpha\text{-MnO}_2/\text{OA}/\text{O}_3$. As for the $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$, the $\beta\text{-MnO}_2/\text{OA}/\text{O}_3$ system presented the highest exposure rate in 1 min. In order to further investigate the roles of various ROS and O_3 in different catalytic ozonation processes, the contribution rates were simulated through Eqs. (6)–(9). Based on the

than that of the $\beta\text{-MnO}_2/\text{OA}/\text{O}_3$ (~22 %) and $\delta\text{-MnO}_2/\text{OA}/\text{O}_3$ (~24 %) processes, further verifying the significant effect of $\bullet\text{OH}$. Interestingly, the contribution column chart of O_3 and ROS also indicated that $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$ were the dominant ROS responsible for ATZ removal, rather than $^1\text{O}_2$, which differed from the conclusion of the scavenger experiments.

3.5. Mechanisms elucidation in various $\text{MnO}_2\text{-OA}/\text{O}_3$ processes

As shown in FT-IR spectra (Fig. 7(a)), the peaks of the $\alpha\text{-MnO}_2\text{-OA}$ complex in the range of $1000\text{--}1500 \text{ cm}^{-1}$ were weakened, indicating the

$$f_{\text{O}_3, \text{ATZ}} = \frac{k_{\text{O}_3, \text{ATZ}} \int [\text{O}_3] dt}{k_{\text{O}_3, \text{ATZ}} \int [\text{O}_3] dt + k_{\text{O}_2^{\bullet-}, \text{ATZ}} \int [\text{O}_2^{\bullet-}] dt + k_{^1\text{O}_2, \text{ATZ}} \int [^1\text{O}_2] dt + k_{\bullet\text{OH}, \text{ATZ}} \int [\bullet\text{OH}] dt} \quad (6)$$

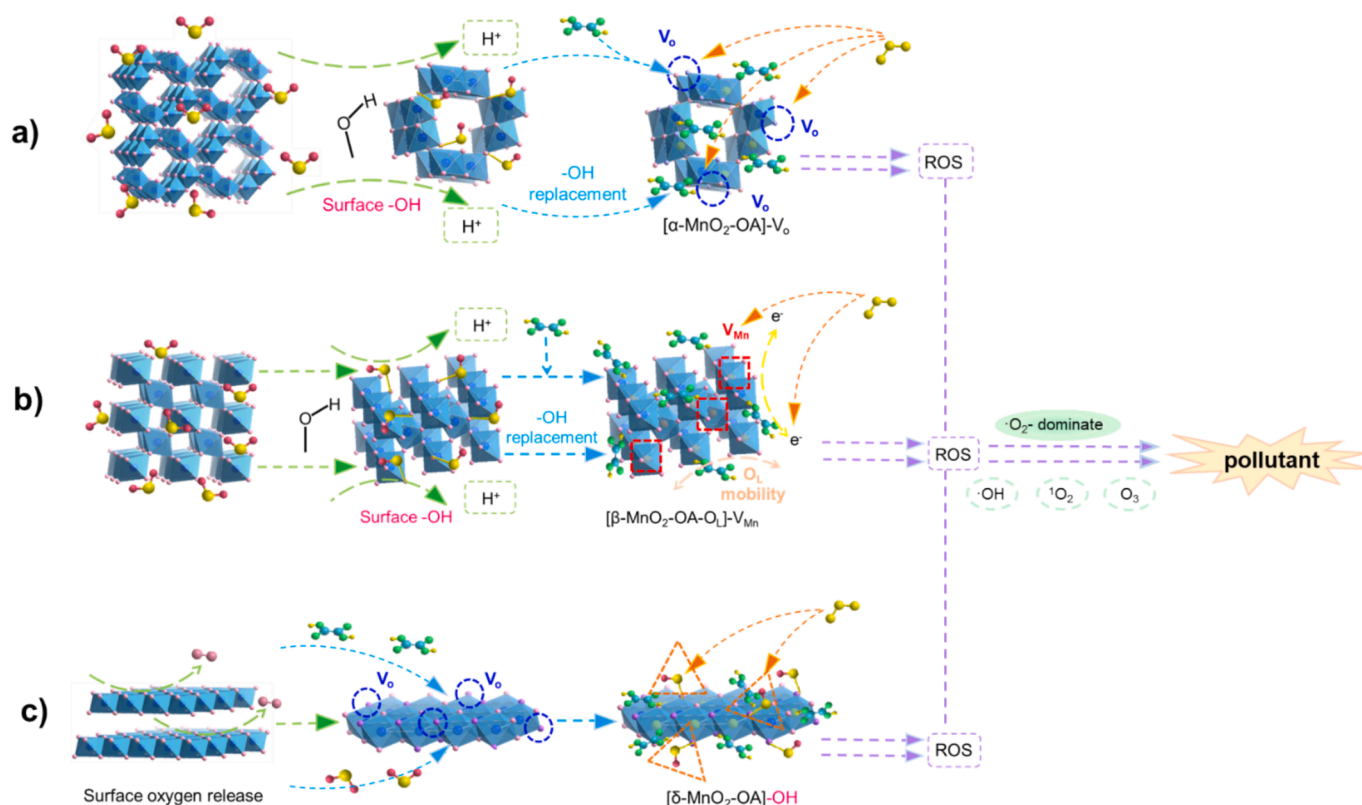
$$f_{\text{O}_2^{\bullet-}, \text{ATZ}} = \frac{k_{\text{O}_2^{\bullet-}, \text{ATZ}} \int [\text{O}_2^{\bullet-}] dt}{k_{\text{O}_3, \text{ATZ}} \int [\text{O}_3] dt + k_{\text{O}_2^{\bullet-}, \text{ATZ}} \int [\text{O}_2^{\bullet-}] dt + k_{^1\text{O}_2, \text{ATZ}} \int [^1\text{O}_2] dt + k_{\bullet\text{OH}, \text{ATZ}} \int [\bullet\text{OH}] dt} \quad (7)$$

$$f_{^1\text{O}_2, \text{ATZ}} = \frac{k_{^1\text{O}_2, \text{ATZ}} \int [^1\text{O}_2] dt}{k_{\text{O}_3, \text{ATZ}} \int [\text{O}_3] dt + k_{\text{O}_2^{\bullet-}, \text{ATZ}} \int [\text{O}_2^{\bullet-}] dt + k_{^1\text{O}_2, \text{ATZ}} \int [^1\text{O}_2] dt + k_{\bullet\text{OH}, \text{ATZ}} \int [\bullet\text{OH}] dt} \quad (8)$$

$$f_{\bullet\text{OH}, \text{ATZ}} = \frac{k_{\bullet\text{OH}, \text{ATZ}} \int [\bullet\text{OH}] dt}{k_{\text{O}_3, \text{ATZ}} \int [\text{O}_3] dt + k_{\text{O}_2^{\bullet-}, \text{ATZ}} \int [\text{O}_2^{\bullet-}] dt + k_{^1\text{O}_2, \text{ATZ}} \int [^1\text{O}_2] dt + k_{\bullet\text{OH}, \text{ATZ}} \int [\bullet\text{OH}] dt} \quad (9)$$

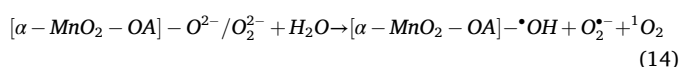
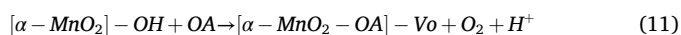
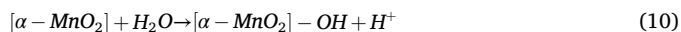
results illustrated in Fig. 10 (d), it was found that the contribution rate of $\bullet\text{OH}$ in the $\alpha\text{-MnO}_2/\text{OA}/\text{O}_3$ system reached ~31 %, which was higher

replacement of $-\text{OH}$ groups after adding OA into the solution. The $\text{O}_2\text{-TPD}$ spectra (Fig. 7(b)) of the $\alpha\text{-MnO}_2\text{-OA}$ complex verified the presence



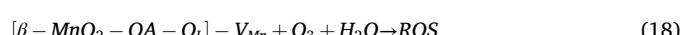
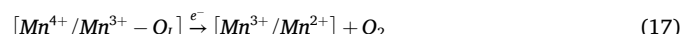
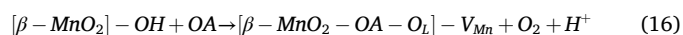
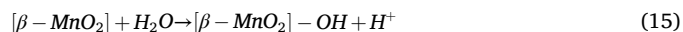
Scheme 1. Proposed mechanism for Multi-MnO₂-oxalic acid complexes mediated catalytic ozonation.

of looser O_s on the catalyst surface. Subsequently, an improvement in the O_{II}/O_I ratio (0.79) in the XPS O 1 s spectra of the α-MnO₂-OA complex was detected, which further confirmed that the combination of α-MnO₂ and OA was beneficial for the generation of more Vo on the surface of the complex. After catalytic ozonation, XPS results of O 1 s and Mn 2p (Table S4 and Table S5) showed an evident decrease in the ratio of O_{II}/O_I from 0.79 to 0.19, and a subtle decline in that of Mn³⁺/Mn⁴⁺ from 1.52 to 1.43, indicating the important role of O_{II} rather than Mn to take effect in catalytic ozonation of ATZ removal [35]. The O_{II} could occupy the Vo and then transform into ROS, resulting in a consumption of O_{II} and Vo. The above performance and characterization analysis identified the great role of Vo in catalytic ozonation for ATZ removal. Therefore, a mechanism focusing on the participation and regeneration of Vo was proposed in Eqs. (10)–(14).



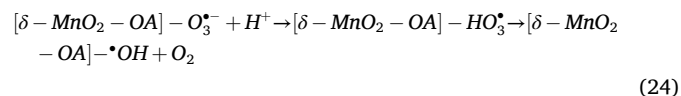
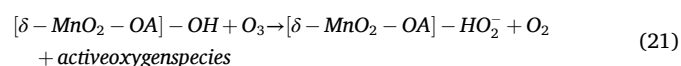
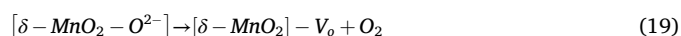
Similarly, the combination of β-MnO₂ and OA occurred through the substitution of -OH groups on the β-MnO₂, as evidenced by the disappearance of the 1114 cm⁻¹ peak in the FT-IR spectra of the β-MnO₂-OA complex (Fig. 7(a)) (Eq (15)). However, different from the α-MnO₂-OA complex, the O₂-TPD spectra illustrated that the β-MnO₂-OA complex had enhanced O_L mobility. The XPS spectra of the β-MnO₂-OA complex (Fig. 8(d)) revealed a decrease in the proportion of Mn⁴⁺ and an increase in Mn³⁺ and Mn²⁺. This indicated a transformation of Mn⁴⁺ to lower-valence Mn species with the addition of OA, leading to the generation

of more V_{Mn} and improved mobility of O_L (Eq (16)). As displayed in Table S5, the percentage of Mn³⁺ in the used β-MnO₂-OA complex declined to 45.89 %, and that of Mn²⁺ increased to 20.27 %. In β-MnO₂/OA/O₃ process, electrons from the surface of Mn²⁺ or Mn³⁺ would induce O₃ decomposition to ROS which resulted in ATZ degradation, and the oxidation of O_L promoted the reversion of Mn³⁺ to Mn²⁺. The balance between Mn³⁺/Mn²⁺ or Mn³⁺/Mn⁴⁺ and O₂⁻/O₂⁰ was an important factor for the catalytic performance of β-MnO₂-OA complex [47] (Eq (17)). Besides, the O 1 s peak appeared at 532.4 eV (Fig. 8(c)) of β-MnO₂-OA complex disappeared in O 1 s spectra of used β-MnO₂-OA complex (Fig. S9(c)). Due to the presence of V_{Mn}, O₃ and H₂O could be adsorbed on the surface of β-MnO₂-OA complex and then participated in the catalytic ozonation reaction (Eq (18)). Hence, the catalytic activity could be attributed to the more V_{Mn} and the O_L [48].



According to the characterization analysis of the α-MnO₂, β-MnO₂, and δ-MnO₂ catalysts, δ-MnO₂ exhibited the highest activity of mobile oxygen and the largest amount of Vo, which could improve O₃ adsorption and decomposition to generate more ROS, thus facilitating the degradation of ATZ (60.73 %) (Eq (19)). As OA (10 mg L⁻¹) was introduced to the solution, the formed δ-MnO₂-OA complex promoted catalytic ozonation performance achieving 69.87 % of ATZ removal. The O₂-TPD spectra (Fig. 7(b)) revealed the transition from active O_s to active O_L on the catalyst surface after δ-MnO₂ complexation with OA. Meanwhile, the FT-IR and the XPS analysis confirmed the presence of H₂O and -OH groups on the surface of the δ-MnO₂-OA complex. The results indicated that the abundant Vo of δ-MnO₂ facilitated the

adsorption of OA on the catalyst surface, accompanied by the migration of O_L to form the complex. In an aqueous environment, H_2O coordinated with Lewis active sites on the δ - MnO_2 -OA complex surface, leading to the formation of surface $-OH$ [49] (Eq (20)). As shown in Table S4, after catalytic ozonation, the O_{II}/O_I ratio of the used δ - MnO_2 -OA complex increased from 0.28 (Table 1) to 0.35. This increase is attributed to the surface $-OH$ acting as active sites, reacting with O_3 to generate more surface oxygen species, which further reacted with ATZ (Eqs. (21)–(24)). As a result, more surface Mn^{4+} was formed on the catalyst surface, converting to Mn^{3+} in order to maintain the electrostatic balance of the δ - MnO_2 -OA complex in the reaction between O_3 and ATZ species [6]. This could explain why the Mn^{3+}/Mn^{4+} ratio of the used δ - MnO_2 -OA complex increased after catalytic ozonation (from 1.60 to 1.87) (Table S5). Therefore, it could be concluded that the surface $-OH$ of the δ - MnO_2 -OA complex played a significant role in the δ - MnO_2 /OA/ O_3 process for ATZ degradation.



Based on the aforementioned analysis, in the MnO_2 -OA complexes mediated catalytic ozonation system, the different crystal phase of MnO_2 had no effect on the formation of MnO_2 -OA complexes, which relied on the presence of Mn^{3+} . However, due to the differences in the structural properties of various crystal MnO_2 , the reactive sites of the formed complexes in catalytic ozonation were different. Nevertheless, this ultimately promoted the decomposition of O_3 to generate ROS, primarily $O_2^{\bullet -}$, with $\bullet OH$ playing a secondary role, thereby enhancing the removal efficiency of pollutants. The mechanisms are elucidated in Scheme 1.

4. Conclusion

In the catalytic ozonation process, compared to α - MnO_2 and β - MnO_2 , δ - MnO_2 exhibited the highest activity with 60.73 % of ATZ degradation, which relied on the presence of $\bullet OH_L$, $O_2^{\bullet -}$, and 1O_2 in the system. However, the addition of OA (10 mg L^{-1}) to the solution could promote the formation of α - MnO_2 -OA, β - MnO_2 -OA, and δ - MnO_2 -OA complexes, which enhanced ATZ degradation to 95.09 %, 93.43 %, and 96.71 % with 3 min, respectively, when the molar ratio of MnO_2 to OA was 1:0.8. In addition, acidic conditions were shown to facilitate the formation of the complexes. The PP experiments indicated that the formation of MnO_2 -OA complexes depends on the presence of Mn^{3+} in the systems. Further scavengers and probe methods were conducted to assess the contribution of various ROS. The results implied that $O_2^{\bullet -}$ had a significant impact on the degradation of ATZ, with $\bullet OH$ playing a secondary role. Finally, based on the characterization analysis, the different catalytic mechanisms of the three systems were elucidated. In the α - MnO_2 /OA/ O_3 process, more V_o was generated on the surface of the complex, which could absorb more O_3 and pollutants for further reaction. For the β - MnO_2 -OA complex, more V_{Mn} and enhanced O_L mobility were key factors contributing to the ROS production in catalytic ozonation. As for the δ - MnO_2 /OA/ O_3 system, the main active sites were surface $-OH$ s. Overall, this study provides new insights into new water treatment technologies, offering potential pathways for enhancing catalytic

ozonation efficiency and the degradation of contaminants.

CRediT authorship contribution statement

Jing Liu: Conceptualization, Investigation, Methodology, Software, Investigation, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. **Xiangjuan Yuan:** Conceptualization, Resources, Funding acquisition, Writing – review & editing. **Carmen Sans:** Conceptualization, Visualization, Resources, Supervision, Project administration, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2025.132761>.

Data availability

Data will be made available on request.

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