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Efficient and Thorough Oxidation of Bisphenol A via Non-Radical Pathways Activated by Sulfur-Modified Mn_2O_3

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Article

Efficient and Thorough Oxidation of Bisphenol A via Non-Radical Pathways Activated by Sulfur-Modified Mn_2O_3

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Abstract

It is generally found that enhancement in catalytic activity comes at the expense of selectivity or stability. In this study, a sulfur-modified Mn_2O_3 (S- Mn_2O_3) solid catalyst was prepared using a simple oxalate precipitation method. This catalyst exhibited not only high catalytic activity but also high selectivity and good cycling stability. The degradation ratio of bisphenol A (BPA) under S- Mn_2O_3 activated peroxymonosulfate (PMS) achieved over 99% within 10 minutes, and the mineralization ratio increased to 83.2%. Particularly, the degradation rate for BPA under of S- Mn_2O_3 /PMS system was 15 times that of Mn_2O_3 . Furthermore, the degradation ratio remained at 93.3% after five consecutive cycles. Multiple experimental characterizations confirmed that the introduction of S into Mn_2O_3 shifted the oxidative degradation pathway from a mixture of radical and non-radical routes to a predominantly non-radical pathway. This suppressed radical generation promoted the selective formation of high-valence metallic oxygen (HVMO) species and singlet oxygen ($^1\text{O}_2$), thereby significantly enhancing the catalytic activity. In addition, the S- Mn_2O_3 /PMS system exhibited broad applicability towards the degradation of other phenolic pollutants, strong anti-interference capability against complex water matrices, and suitability for efficient removal of organic contaminants in such environments. This research offers new perspectives for the design of selective catalysts for PMS activation.

Keywords: sulfur modification; PMS activation; high selectivity; high-valent metallic oxygen species

1. Introduction

The deep treatment of persistent organic pollutants (POPs) in aquatic environments represents a pressing global challenge because it has posed severe threats to human health and ecological security. Peroxymonosulfate-based advanced oxidation processes (PMS-AOPs) have emerged as a promising technology for water treatment and are widely employed for organic pollutant removal [1-3]. However, highly reactive sulfate radical ($\text{SO}_4^{\cdot-}$) and hydroxyl radical ($\cdot\text{OH}$) suffer from significant matrix interference (e.g., inorganic anions, humic acid) during practical water treatment applications, leading to drastically reduced treatment efficiency in real water systems [4-6]. Consequently, non-radical oxidation pathways—characterized by strong matrix interference resistance and high selectivity—are better suited for organic pollutant degradation in complex aqueous matrices.

Developing novel solid catalysts to activate PMS for the efficient and selective generation of non-radical oxidizing species is critically important for wastewater remediation. High-valent metallic oxygen (HVMO) species and singlet oxygen ($^1\text{O}_2$) represent highly effective non-radical reactive species with significant promise for organic wastewater treatment. These species exhibit extended lifetimes, high oxidant utilization efficiency, and strong resistance to interference from non-target

substrates, particularly demonstrating high selectivity toward recalcitrant organic pollutants bearing electron-donating groups [7-10]. Metallic elements, such as Co and Fe, have been extensively applied in developing catalyst for PMS activation, while they predominantly trigger Fenton-like reactions via radical pathways [11-13]. Manganese (Mn), offers abundant natural reserves, environmental compatibility, and redox versatility. Particularly, manganese oxides (MnOx) exhibit exceptional sensitivity in modulating PMS activation modes toward non-radical species (HVMO and $^1\text{O}_2$) in contrast to Co and Fe [14-18]. Recent studies confirmed that surface-modified MnOx via defect engineering or heteroatom doping facilitated $^1\text{O}_2$ generation from PMS [19-22]. However, the incorporation of guest metal atoms induces undesirable side reactions. For instance, the insertion of Fe into manganese oxides (MnFeO) promoted $^1\text{O}_2$ production but simultaneously resulted in the formation of radical species ($\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$) during PMS activation [23]. Similar phenomenon were found in other metal-modified MnOx systems [21].

Sulfur modification can modulate redox processes by altering the surface microenvironment of metal oxides (e.g., surface electronic structure, lattice strain, and molecular dynamics) [24-27]. Typically, changes in the surface microenvironment of metal oxides induce modifications in electronic structure and crystal lattice, thereby influencing the adsorption behavior of guest molecules and ultimately determining the catalytic reaction pathways on the surface [28-30]. Notably, PMS activation pathways and its molecular adsorption configuration are intrinsically linked to metal centers, particularly oxygen sites of PMS [31,32]. Thus, tailoring the structure and chemical properties of manganese oxides through sulfur modification represents an attractive strategy for regulating non-radical oxidation pathways in PMS-AOPs systems.

Herein, a sulfur-modified manganese trioxide (S-Mn₂O₃) solid catalyst was constructed for PMS activation to selectively generate non-radical oxidizing active species (Mn-oxo species and $^1\text{O}_2$), achieving efficient degradation and deep oxidation of phenolic organic pollutants. The removal ratio of bisphenol A (BPA) increased by 15 times under the catalysis of S-Mn₂O₃ in comparison to that catalyzed by Mn₂O₃, achieving a mineralization ratio exceeding 80% within 10 minutes. The S-Mn₂O₃ catalyst also demonstrated superior anti-interference capability and reusability, being bound to become a promising catalyst in wastewater treatment in practical applications.

2. Materials and Methods

2.1. Reagents

Sodium thiosulfate (Na₂S₂O₃), BPA (C₁₅H₁₆O₂), manganese(II) acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O), phenol (C₆H₆O), 4-chlorophenol (4-CP), 2,3-dichlorophenol (2,3-DCP), PMS (O₅S), oxalic acid (H₂C₂O₄), tert-butanol (TBA), potassium thiocyanate (KSCN), methanol (CH₃OH), sodium azide (NaN₃), potassium iodide (KI), terephthalic acid (TPA), methyl phenyl sulfoxide (PMSO), p-hydroxybenzoic acid (HBA), and 9,10-anthracenediyl-bis(methylene) dimalonic acid (ABDA) were all analytical grade and purchased from China National Medicines Chemical Reagents Co., Ltd.

2.2. Synthesis and characterization of S-Mn₂O₃

A homogeneous solution (solution A) was prepared by dissolving 2.3 g of Mn(CH₃COO)₂·4H₂O and 4.92 g of Na₂S₂O₃ in 50 mL of ultrapure water. Solution B was obtained by dissolving 5.2 g of H₂C₂O₄ in 50 mL of ultrapure water. Then the solution B was maintained at 60°C under magnetic stirring. Solution A was added dropwise into solution B, and the reaction proceeded for 30 min. The resulting suspension was filtered, thoroughly washed and dried in sequence. Subsequently, the solid products was calcined at 500°C for 2 h to and S-Mn₂O₃ was obtained. For comparison, pristine Mn₂O₃ was synthesized following an identical procedure without Na₂S₂O₃ addition. Detailed characterization methods of both Mn₂O₃ and S-Mn₂O₃ catalysts were provided in Supporting Information.

The samples were systematically characterized using the following instruments: D8 Advance X-ray powder diffractometer (XRD), Bruker, Germany, Cu K α radiation $\lambda = 0.15406$ nm, tube voltage 40 kV, tube current 40 mA, wide-angle scanning range $2\theta = 10\sim 80^\circ$, step size 0.020° , scanning speed $5^\circ/\text{min}$; JEM-2100 transmission electron microscope (TEM), JEOL, Japan, operating voltage 150 kV; ASAP-2460 specific surface area tester, Micromeritics, USA; Auto Chem II 2920 fully automated temperature-programmed chemisorption analyzer, Micromeritics, USA, carrier gas He flow rate 30 mL/min, desorption temperature range from room temperature to 500°C ; U-3900 ultraviolet-visible spectrophotometer, Hitachi, Japan; RF-5301PC fluorescence spectrophotometer, Shimadzu, Japan, excitation wavelength 412 nm, slit width 2 nm; Agilent 1100 high-performance liquid chromatograph (HPLC), Agilent, column Hypersil ODS, column temperature 40°C , detection wavelengths 254 nm and 280 nm; mobile phase: acetonitrile and water (volume ratio) 20:80; flow rate 1 mL/min.

2.3. Catalytic Degradation and Quenching Experiments

Catalytic degradation experiments were conducted in 150 mL glass reactors containing 100 mL of phenolic solutions under dark conditions at 25°C . The S-Mn $_2$ O $_3$ catalyst was dispersed in solutions of different target phenolics (bisphenol A, phenol, 4-CP, or 2,3-CP) under magnetic stirring, respectively. After reaching adsorption equilibrium, PMS was introduced to initiate catalytic degradation. During degradation process, 3.0 mL of the above solution were collected at 2-min intervals using a syringe, immediately filtered through PTFE-membrane filter, and then quenched with 0.01 mL of 0.1 M sodium sulfite (Na $_2$ SO $_3$). The quenched solutions were analyzed by high performance liquid chromatography (HPLC) to determine the degradation ratio of phenolics. Quenching experiments followed identical procedures except that PMS and radical scavengers were added simultaneously into the catalytic systems. Detailed analytical methods are provided in the Supporting Information.

2.3.1. active oxidizing species detection

The concentration of organic compounds was analyzed using an Agilent 1100 high-performance liquid chromatograph (HPLC) equipped with a Hypersil ODS column. The mobile phase and detection wavelength were set as follows: acetonitrile and water (20:80 v/v), detection wavelength $\lambda=254$ nm. Degradation kinetics were fitted using the pseudo-first-order model, and the reaction rate constant was calculated according to Equation 1:

$$\ln(C_t / C_0) = -kt \quad (1)$$

where C_t is the concentration of the target pollutant at a given reaction time (t), and C_0 is the initial concentration of the target pollutant.

2.3.2. Detection of $\bullet\text{OH}$ radicals

Fluorometric method: 20 mg of catalyst was dispersed in 50 mL of an aqueous terephthalic acid solution (0.2 mmol/L). The mixture was sonicated for a period of time (generating 2-hydroxyterephthalic acid, with an absorption peak at 425 nm). The solution was filtered (sampled every 2 min for testing), and its fluorescence spectrum (PL) was measured using a fluorescence spectrophotometer. The amount of OH was indirectly measured using PL emission spectroscopy (excitation wavelength 412 nm).

2.3.3. Detection of Singlet Oxygen ($^1\text{O}_2$)

Ultraviolet-visible spectrophotometry: 20 mg of catalyst was dispersed in 50 mL of an aqueous solution of 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA: 5×10^{-5} mol/L) (DMSO/water (V:V):1/100). The mixture was sonicated for a period of time. The solution was filtered and measured using an ultraviolet-visible spectrophotometer, with a test wavelength range of 200–800 nm. Its absorption peak is located between 350–410 nm.

2.3.4. Detection of $\text{SO}_4^{\bullet-}$ radicals

The concentration of $\text{SO}_4^{\bullet-}$ was indirectly quantified using benzoquinone (BQ), the main degradation byproduct of p-hydroxybenzoic acid (HBA). 20 mg of catalyst was dispersed in 50 mL of an aqueous HBA solution, followed by the addition of 10 mg PMS. The mixture was stirred and reacted for a period of time (PMS:HBA molar ratio 1:2). Catalyst particles were removed by filtration using a PTFE syringe filter disk (0.22 μm). The sample was immediately quenched with 0.1 mM $\text{Na}_2\text{S}_2\text{O}_3$ solution, and then the benzoquinone (BQ) content in the sample was determined by ultraviolet-visible spectrophotometry.

2.3.5. Detection of High-Valent Metal Ions

20 mg of catalyst was dispersed in 50 mL of an aqueous methyl phenyl sulfoxide (PMSO: 20-500 $\mu\text{mol/L}$) solution, followed by the addition of 10 mg PMS. The mixture was stirred and reacted for a period of time. The solution was filtered, and the PMSO_2 produced in the sample was determined using high-performance liquid chromatography (HPLC). The mobile phase and detection wavelength were set as follows: acetonitrile and water (20:80 v/v), detection wavelength $\lambda=254$ nm.

3. Results

3.1. Structure and chemical composition of Mn_2O_3 and S- Mn_2O_3

Transmission electron microscopy (TEM) images of Mn_2O_3 (Figure S1a) and S- Mn_2O_3 (Figure 1a) demonstrated that both type of nanoparticles with irregular morphology and particle sizes of 20~40 nm were aggregated. The lattice fringes of Mn_2O_3 (Figure S1b) and S- Mn_2O_3 (Figure 1b) with spacing of 0.27 nm and 0.38 nm, respectively, correspond to the (222) and (211) crystal face of Mn_2O_3 . Elemental mapping images (Figure 1c) exhibited that S atoms distributed homogeneously. X-ray photoelectron spectroscopy (XPS) spectra of S- Mn_2O_3 (Figure 1d) indicated that a peak assigned to S existed with an atomic ratio of 2.1%. The S 2p peak at 168.8 eV (Figure 1e) was assigned to SO_x^{2-} ($x=3, 4$) [26,27]. X-ray diffraction (XRD) patterns (Figure 1f) confirmed both samples were bixbyite-type crystal structure (JCPDS no. 41-1442) with other impurities [18]. The above results verified the successful S incorporation into Mn_2O_3 via forming SO_x^{2-} species and the crystal structure of Mn_2O_3 was well-maintained after S modification. The intensity of diffraction peak for S- Mn_2O_3 decreased compared to Mn_2O_3 and the peaks shifted toward lower angles, which were attributed to increased oxygen vacancies induced by sulfur modification [33,34].

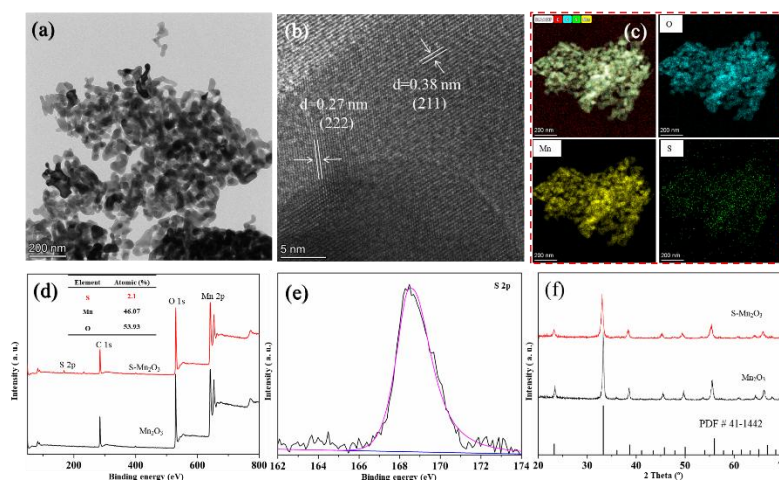


Figure 1. (a,b) TEM images and (c) Elemental mapping images of S- Mn_2O_3 sample. (d) XPS spectra of Mn_2O_3 and S- Mn_2O_3 samples. (e) S 2p core-level spectrum of S- Mn_2O_3 sample. (f) XRD patterns of Mn_2O_3 and S- Mn_2O_3 sample.

The peaks at the binding energies of 640.2 eV, 641.6 eV, and 644.1 eV in XPS Mn 2p fine spectra of the Mn_2O_3 and $\text{S-Mn}_2\text{O}_3$ samples (Figure 2a) were assigned to Mn(II), Mn(III), and Mn(IV), respectively [35]. Moreover, an increase in Mn(II) content and a decrease in Mn(IV) content in the $\text{S-Mn}_2\text{O}_3$ sample compared to that of Mn_2O_3 indicated that the incorporation of S promoted an increase in low-valence manganese species. Previous studies have shown that the $\text{Mn}^{4+}\text{-O}$ bond are stronger than $\text{Mn}^{2+}\text{-O}$ and $\text{Mn}^{3+}\text{-O}$ bonds [36]. Consequently, the presence of a large amount of low-valence Mn species weakened the Mn-O bond strength in $\text{S-Mn}_2\text{O}_3$ [37]. The peaks at 341 cm^{-1} and 634 cm^{-1} in the Raman spectra of the Mn_2O_3 and $\text{S-Mn}_2\text{O}_3$ samples (Figure 2b) were attributed to the deformation vibrations and lattice vibrations of the Mn-O-Mn and Mn-O bonds, respectively [38]. The results demonstrated that the transfer of electron cloud density from surface oxygen atoms in Mn_2O_3 to the electron-withdrawing SO_x^{2-} groups weakened their interaction with adjacent Mn atoms, thereby lengthened the Mn-O bond and reduced its strength, being beneficial for lowering the energy barrier for the formation of Mn-oxo species [37, 39].

The N_2 adsorption/desorption isotherms and corresponding structure characteristics (Figure 2c) revealed that the specific surface area of $\text{S-Mn}_2\text{O}_3$ ($33.8\text{ m}^2\text{ g}^{-1}$) is 2.2 times that of Mn_2O_3 ($15.6\text{ m}^2\text{ g}^{-1}$), indicating that S modification increases the specific surface area of the Mn_2O_3 catalyst, which could provide more adsorption and catalysis sites [33,34]. The hysteresis loop in the range of P/P_0 between 0.8~1.0 suggested that the materials possesses aggregated pore structure, which is consistent with the TEM results.

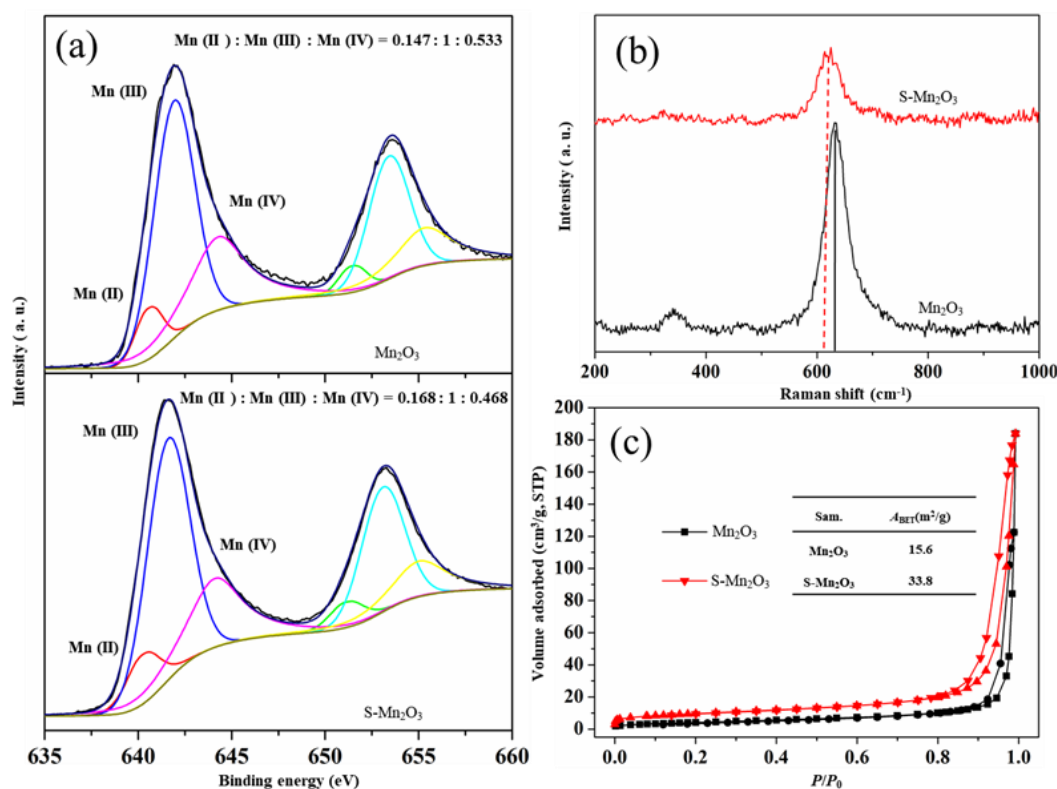


Figure 2. (a) XPS Mn 2p fine spectra, (b) Raman spectra and (c) N_2 adsorption-desorption isotherms of the Mn_2O_3 and $\text{S-Mn}_2\text{O}_3$ samples.

3.2. Catalytic performance of Mn_2O_3 and $\text{S-Mn}_2\text{O}_3$

The catalytic performance of Mn_2O_3 and $\text{S-Mn}_2\text{O}_3$ catalysts was evaluated by activating PMS for BPA degradation (Figure 3a). Before adding PMS, $\text{Mn}_2\text{O}_3/\text{BPA}$ and $\text{S-Mn}_2\text{O}_3/\text{BPA}$ systems reached adsorption-desorption equilibrium within 10 min, with an adsorption ratio of approximately 6% and 14%, respectively. The results are aligned with the fact that a larger specific surface area favors the adsorption of more pollutant molecules. In particular, PMS alone could hardly degrade BPA in the

absence of a catalyst. While the degradation ratio of BPA was only 29.9% within 10 min under Mn_2O_3 -activated PMS system. In contrast, the degradation rate of BPA exceeded 99% within 10 min under S- Mn_2O_3 -activated PMS system. The degradation rate for BPA in the S- Mn_2O_3 /PMS system (0.434 min^{-1}) was 15 times that of Mn_2O_3 /PMS system (0.029 min^{-1}), as shown in inset of Figure 3a. The mineralization rate within 10 min increased from 19.9% to 83.2% (Figure 3b). The above results indicated that S modification significantly enhanced the oxidation and mineralization capabilities of Mn_2O_3 . Furthermore, the S- Mn_2O_3 sample exhibited good cycling stability—the degradation ratio of BPA remained at 93.3% even after 5 consecutive cycles (Figure 3c). In addition, the S- Mn_2O_3 /PMS system demonstrated excellent oxidation capability for electron-rich phenolic organic pollutants, achieving degradation ratios of 99.2%, 95.2%, 94.4% and 92.5% for bisphenol A (BPA), phenol (P), 4-chlorophenol (4-CP) and 2,3-dichlorophenol (2,3-DP) within 10 min, respectively (Figure 3d). Furthermore, the addition of Na^+ , Ca^{2+} , Mg^{2+} , Cl^- (20 mM), SO_4^{2-} (20 mM), and HCO_3^- (20 mM) had little effect on the BPA removal ratio (94%~99.2%), indicating strong resistance of the S- Mn_2O_3 /PMS system to interference from cations and anions (Figure 3e). Additionally, the removal ratio of BPA in lake water, tap water and deionized water under the S- Mn_2O_3 /PMS system were 96.5%, 96.4% and 99.2%, respectively (Figure 3f), demonstrating the strong adaptability of the S- Mn_2O_3 /PMS system for catalytic degradation of BPA in real water bodies. The high selective oxidation of electron-rich pollutants, strong adaptability to real water bodies and robust resistance to interference from anions and cations collectively demonstrated that a highly selective non-radical oxidation pathway dominated in the S- Mn_2O_3 /PMS system.

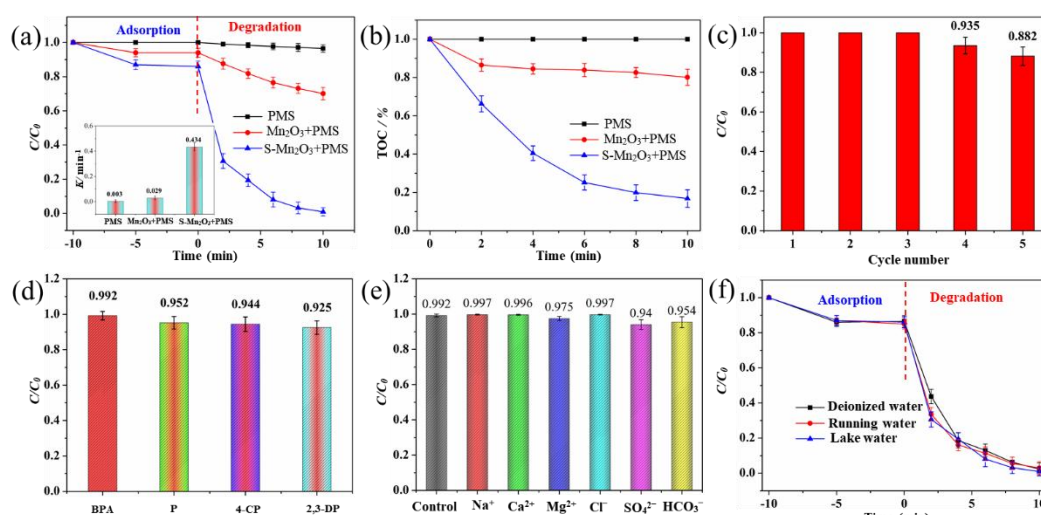


Figure 3. (a) The catalytic performance and (b) the mineralization rate of Mn_2O_3 /PMS and S- Mn_2O_3 /PMS for BPA degradation. Inset in (a) is the degradation rate. (c) Cyclic degradation performance of BPA by S- Mn_2O_3 sample. (d) The oxidation capability of S- Mn_2O_3 /PMS system for bisphenol A, phenol, 4-chlorophenol and 2,3-dichlorophenol within 10 min, respectively. (e) The effect of Na^+ , Ca^{2+} , Mg^{2+} , Cl^- (20 mM), SO_4^{2-} (20 mM), and HCO_3^- (20 mM) on the BPA removal ratio. (f) The removal ratio of BPA in lake water, tap water and deionized water under the S- Mn_2O_3 /PMS system.

3.3. Catalytic mechanism of S- Mn_2O_3 /PMS system

To further verify the above conclusions, quenching experiments were conducted to identify the relative contributions of high-valence Mn-oxo species, $^1\text{O}_2$, $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$. Tert-butanol (TBA), potassium thiocyanate (KSCN), methanol (CH_3OH), sodium azide (NaN_3), and potassium iodide (KI) were selected as scavengers for $\bullet\text{OH}$, high-valent Mn-oxo, $\text{SO}_4^{\bullet-}$, $^1\text{O}_2$, and surface-adsorbed $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$, respectively [7, 9, 13, 40]. As shown in Figure S2, when TBA, KSCN, CH_3OH , NaN_3 , and KI were added separately into the Mn_2O_3 /PMS system, the degradation rate of BPA decreased from 29.9% to 23.6%, 25.4%, 11.1%, 29.5%, and 20.8%, respectively, with inhibition rates of 62.9%, 21.1%,

1.3%, 15.1%, and 30.4%. This indicated that the oxidative degradation of BPA under $\text{Mn}_2\text{O}_3/\text{PMS}$ system through both radical and non-radical pathways, with the radical species ($\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$) playing a dominant role. In the $\text{S-Mn}_2\text{O}_3/\text{PMS}$ system (Figure 4a), the presence of CH_3OH , TBA and KI had no effect on the BPA degradation ratio, while it reduced by 56.8% and 6.9% under the addition of KSCN and LH, respectively, indicating that the non-radical species high-valent Mn-oxo and $^1\text{O}_2$ played the dominant roles in BPA degradation. Furthermore, various probe compounds, including terephthalic acid (TPA), methyl phenyl sulfoxide (PMSO), p-hydroxybenzoic acid (HBA), and 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA), were used to investigate the generation process of $\bullet\text{OH}$, high-valent Mn-oxo, $\text{SO}_4^{\bullet-}$, and $^1\text{O}_2$, respectively [9,10,13,41]. In the $\text{Mn}_2\text{O}_3/\text{PMS}$ system (Figure 4b), the characteristic fluorescence signal at 425 nm gradually increased with reaction time, while no significant change were observed in the $\text{S-Mn}_2\text{O}_3/\text{PMS}$ system (Figure 4c). This indicated that $\bullet\text{OH}$ generated within the Mn_2O_3 -activated PMS systems because it can react with TPA to form the fluorescent compound (2-hydroxyterephthalic acid), and no $\bullet\text{OH}$ produced in the $\text{S-Mn}_2\text{O}_3/\text{PMS}$ system [41]. As obtained from Figure 4d and Figure 4e, the intensity of characteristic absorption peak for HBA gradually decreased with reaction time in the $\text{Mn}_2\text{O}_3/\text{PMS}$ system, whereas it almost remained unchanged in the $\text{S-Mn}_2\text{O}_3/\text{PMS}$ system. This demonstrated the generation of $\text{SO}_4^{\bullet-}$ in the $\text{Mn}_2\text{O}_3/\text{PMS}$ system and its absence in the $\text{S-Mn}_2\text{O}_3/\text{PMS}$ system [13]. It can be found from Figure 4f that the ratio of peak area for $\text{PMSO}_2/\text{PMSO}$ in the $\text{S-Mn}_2\text{O}_3/\text{PMS}$ system was 0.95, which is 16.4 times higher than that in the $\text{Mn}_2\text{O}_3/\text{PMS}$ system (0.058), indicating that S-doped Mn_2O_3 -activated PMS significantly enhanced the selective generation of high-valent Mn-oxo [9]. Additionally, the average oxidation state (AOS) of Mn species in $\text{S-Mn}_2\text{O}_3$ before and after PMS activation were calculated using the formula [42]: $\text{AOS} = 8.956 - 1.126 \Delta E$, where ΔE represents the binding energy difference between the two peaks of Mn 3s. The AOS values of $\text{S-Mn}_2\text{O}_3$ before and after the activation were calculated to be 2.521 and 2.791, respectively, further proving an increase in surface high-valent manganese content after $\text{S-Mn}_2\text{O}_3$ activating PMS (Figure 4g). Furthermore, in both the $\text{Mn}_2\text{O}_3 + \text{PMS}$ and $\text{S-Mn}_2\text{O}_3 + \text{PMS}$ systems (Figure 4h and Figure 4i), the characteristic absorption peak intensity of ABDA in the 300–450 nm range gradually decreased with reaction time, but the decrease was more significant in the $\text{S-Mn}_2\text{O}_3 + \text{PMS}$ system within the same time period. This indicates that $^1\text{O}_2$ is generated in both systems, but more is generated per unit time in the $\text{S-Mn}_2\text{O}_3 + \text{PMS}$ system [13]. The above findings demonstrate that sulfur doping modulates the PMS activation pathway, not only suppressing radical generation but also promoting the formation of high-valent Mn-oxo species and $^1\text{O}_2$ for the selective oxidative degradation of electron-rich phenolic organic pollutants, thereby enhancing catalytic activity.

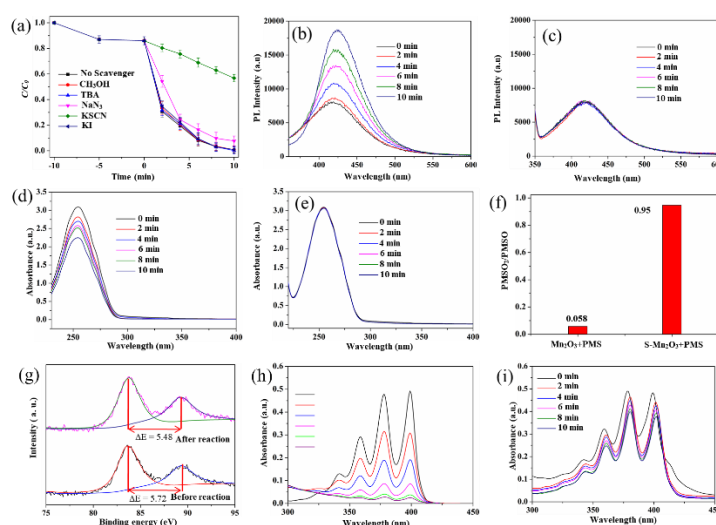


Figure 4. (a) The BPA degradation ratio by $\text{S-Mn}_2\text{O}_3/\text{PMS}$ system in the presence of TBA, KSCN, CH_3OH , NaN_3 , and KI. The characteristic fluorescence signal at 425 nm in the (b) $\text{Mn}_2\text{O}_3/\text{PMS}$ system and (c) $\text{S-Mn}_2\text{O}_3/\text{PMS}$

system under probe compounds. The intensity of characteristic absorption peak for HBA in the (d) $\text{Mn}_2\text{O}_3/\text{PMS}$ system and (e) $\text{S-Mn}_2\text{O}_3/\text{PMS}$ system. (f) The ratio of peak area for $\text{PMSO}_2/\text{PMSO}$ in the $\text{Mn}_2\text{O}_3/\text{PMS}$ system and $\text{S-Mn}_2\text{O}_3/\text{PMS}$ system. (g) The AOS values of $\text{S-Mn}_2\text{O}_3$ before and after the activation. The characteristic absorption peak intensity of ABDA between 300–450 nm in (h) $\text{Mn}_2\text{O}_3/\text{PMS}$ system and (i) $\text{S-Mn}_2\text{O}_3/\text{PMS}$ system.

4. Conclusions

A highly active and selective $\text{S-Mn}_2\text{O}_3$ solid catalyst was synthesized using a simple oxalate precipitation method + calcination method. This catalyst was used to activate PMS for the efficient oxidation and mineralization of BPA. Within 10 minutes, the degradation rate of BPA exceeded 99%, with a reaction rate constant of 0.434 min^{-1} and a mineralization rate of BPA reaching 83.2% within 10 minutes. During the oxidative degradation of electron-rich phenolic pollutants by the $\text{S-Mn}_2\text{O}_3 + \text{PMS}$ system, Mn-oxo species are the primary oxidizing species, and $^1\text{O}_2$ also plays a certain role. The rapid and sustainable generation of stable Mn-oxo species simultaneously achieves high activity, high selectivity, and high stability for phenolic pollutant degradation, which is conducive to water purification applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/doi/s1>, Figure S1: title; Figure S2: title.

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