1. Introduction

Plenty of organic pollutants were generated with the growing rate of urbanization, such as phenolic compounds, antibiotics, dyes, pesticides, etc \([1,2]\). Some of these pollutants are biodegraded into harmful compounds, while others are inherently difficult to degrade, leading to environmental accumulation \([3–5]\). There is an urgent need to find effective ways to eliminate toxic pollutants that strike a balance between economic feasibility and environmental friendliness to eliminate the threats to humans, animals, and plants \([6]\).

In recent years, many researchers have reported that manganese oxides and their composites are effective adsorbents and catalysts for removing organic pollutants from wastewater compared with other metal oxides \([7–12]\). Manganese is a transition metal that occurs widely in nature (the tenth most abundant element in the earth’s crust) \([13,14]\). Manganese exists in nature mainly in the form of manganese oxide and other compounds. The nano-sized manganese metal oxides have many advantages, such as large specific surface area, porous structure, many active sites, good thermal stability, easy recovery, high environmental compatibility, and low toxicity \([2,15–17]\). The crystalline phase MnO\(_2\) material consists of \(\text{MnO}_6\) octahedral units in various tunnel-like and laminar structures, which are one-dimensional tunnel structure, two-dimensional lamellar structure, and three-dimensional mesh structure, respectively. Due to its special structure, single MnO\(_2\) species can be modified by element doping, morphology control, facet engineering, structure construction. In addition, MnO\(_2\)-based composites can be prepared using homojunction and heterojunction structures \([2]\). Due to their unique physicochemical properties and synergistic effects with other metals or metal oxides, they have received extensive attention as excellent adsorbents and catalysts for organic pollutants \([18–20]\).

In this paper, different phase and morphological structures of MnO\(_2\) are reported (Figure 1). The application, degradation mechanism, and development status of MnO\(_2\)-based materials on organic pollutants are described. The organic pollutants were divided into phenolic compounds, antibiotics, dyes, and pesticides. The review provides an overview of the research related to manganese oxides and their application, including future areas of research and limitations in the current body of research.

2. Physical structure

2.1 Phase structure

There are many kinds of MnO\(_2\) in the environment, including \(\alpha\)-MnO\(_2\), \(\beta\)-MnO\(_2\), \(\gamma\)-MnO\(_2\), \(\delta\)-MnO\(_2\), \(\varepsilon\)-MnO\(_2\), and \(\lambda\)-MnO\(_2\) \([14,21]\). The six main types of crystalline...
MnO$_2$ can be classified into three categories, namely, 1D tunnel structures, 2D layer structures, and 3D mesh structures, respectively [2,22].

α-MnO$_2$ belongs to the tetragonal crystal system, which is widely found in nature. It has (2 × 2) tunnels of large square vacancies, which can be partially occupied by K$^+$, Na$^+$, Ba$^+$, Mg$^{2+}$ or Ca$^{2+}$ ions and water molecules [23]. This structure would increase the adsorption ability of α-MnO$_2$. β-MnO$_2$ belongs to the tetragonal system and its structure is relatively stable. The narrow tunnel of β-MnO$_2$ (1 × 1) can only accommodate small ions such as H$^+$ or Li$^+$, which is not conducive to ion diffusion [24]. γ-MnO$_2$ has a hexagonal dense row structure with alternating growth of (1 × 1) and (1 × 2) tunnels. The disorderly and irregular alternating growth of γ-MnO$_2$ tunnels leads to low crystallinity and the generation of defects and vacancies. This structural feature enhances its electron exchange capacity and thus improves the catalytic performance [25]. The two-dimensional layered δ-MnO$_2$ belongs to a typical monoclinic system with a large interlayer distance, which can accommodate many water molecules, metal cations, and other substances [26,27]. λ-MnO$_2$ is a typical spinel structure. Its 3D (1 × 1) tunnel structure is conducive to electron transfer [2]. ε-MnO$_2$ has a polycrystalline structure with hexagonal symmetry and many cationic vacancies [28]. Therefore, the difference in the phase structure of MnO$_2$ also determines the difference in its properties.

2.2 Morphological structure

In addition to the phase structure, the morphology structure also has a great influence on the properties of MnO$_2$. The morphological structures of MnO$_2$ include nanorods, nanotubes, nanowires, nanofibers, nanoribbons, nanosheets, and nanoflowers. As shown in Figure 1.

Figure 1. A brief description of manganese dioxide and organic pollutants.
MnO$_2$ nanosheets have a large specific surface area and are highly porous, which provides more active sites for methylene blue molecules [32]. Nanoflower ε-MnO$_2$ exhibited the best removal efficiency of trielson because of its high oxygen vacancy and Mn$^{3+}$ content, easily released lattice oxygen, and unique tunnel structure [33,34]. The crystal defects in the amorphous structure in MnO$_2$ nanoflowers facilitated the absorption and oxidative degradation of Rhodamine [35]. The catalytic properties of MnO$_2$ nanotubes are like nanorods but have a larger surface area than nanorods for degradation of phenol with higher charge transfer rate [36]. Nanofibers had the higher activity and stable properties, which have good adsorption performance in addition to excellent catalytic oxidation performance for propane [37,38]. MnO$_2$ nanowires can effectively degrade methylene blue at low temperatures, with only a slight decrease in the generation of free radicals and degradation efficiency after recycling [39].

The morphological structure control can determine the specific surface area, low-temperature reducibility, oxygen vacancies, surface defects, mass transportation, and charge motion electron-hole pairs, which have a great influence on the adsorption and catalytic oxidation properties of MnO$_2$-based materials.

3. Doping and composite of MnO$_2$-based materials

With the application of MnO$_2$ in environmental protection, the demand for catalytic properties of MnO$_2$ is gradually increasing too. However, the specific surface area, crystal structure, oxygen-manganese bond strength, and other aspects of MnO$_2$ are not ideal for some substances that are difficult to degrade. To cope with different organic pollutants, MnO$_2$ has been doped and compounded to improve its catalytic capacity.

3.1 Doping of MnO$_2$-based materials

Elemental ion doping can adjust or change the intrinsic properties of MnO$_2$, including morphology, specific surface area, oxygen vacancy formation energy, and oxygen mobility [40]. Hence, many researchers have endeavored to dope alkali and alkaline earth metal ions, other metal ions, and nonmetal anions into MnO$_2$, as shown in Figure 2.

Alkali metals and alkaline earth metal ions can change the morphology and lattice structure of MnO$_2$, which in turn affect their adsorption and catalytic properties. It has been reported that K$^+$ and Tb$^{3+}$ doped MnO$_2$ materials have higher specific surface area, Mn$^{3+}$ content, surface oxygen vacancy, and lattice oxygen activity for methyl blue [41]. The addition of K$^+$, Mg$^{2+}$, Ca$^{2+}$, and Na$^+$ can affect the specific surface area, the binding energy of lattice oxygen, the oxygen vacancy, and the interlayer space of MnO$_2$ materials [42–44].

Besides, other metal ions were doped with MnO$_2$, such as Ag$^{+}$ [45], Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$ [46], Fe$^{3+}$ [47], Sn$^{2+}$ [48], Cr$^{3+}$ [49], W$^{6+}$ [50], V$^{3+}$ [51], Ce$^{4+}$ [52], and Eu$^+$ [53]. The doping of metal ions can improve the performance of MnO$_2$: 1) the concentration of holes and oxygen vacancies; 2) the electrical conductivity; 3) the lattice surface activity; 4) the crystal defects; 5) the specific surface area; 6) the charge transfer and electron-hole dissociation; 7) the oxygen-manganese bond length.

In addition to metal anion doping, nonmetal anion (N [54], B [55]) doping has also been investigated. Non-metal anion doping can reduce the energy of oxygen vacancy formation and bandgap, promote the formation of oxygen vacancy, and electron transport thus improving the optical and electrical catalytic activity of the catalyst.

3.2 Fabrication of MnO$_2$-based composites

Combining with other substances is a good way to improve the catalytic performance of MnO$_2$. So far, MnO$_2$ composite catalysts can be divided into four types: MnO$_2$/MnO$_2$, metal/MnO$_2$, metal oxide/MnO$_2$, and carbon materials/MnO$_2$. MnO$_2$-based composites have a larger surface area, faster electron-hole dissociation efficiency, stronger light absorption, and charge separation efficiency compared to MnO$_2$ catalysts alone.

MnO$_2$/MnO$_2$ materials with different crystalline phases or morphologies form synergistic interactions, which increase the surface active oxygen and specific surface area of MnO$_2$. Various similar materials have been reported, such as Mn$_2$O$_3$/Mn$_3$O$_4$/MnO$_2$ [56], α-MnO$_2$/β-MnO$_2$ [57], δ-MnO$_2$/δ-MnO$_2$ [58], Mn$_3$O$_4$/MnO$_2$ [59], MnO$_2$ nanotube/MnO$_2$ nanosheet [60], and core-shell δ-α-MnO$_2$ [61].

The combination of metal monomer (Ag [62], Pd [63], Au [64], Fe [65], Mg [66], Ni [67]) and MnO$_2$ is common to improve the catalytic efficiency by increasing the surface oxygen defects, specific surface area, reactive oxygen concentration, lattice defects, and active sites of MnO$_2$.

A variety of composites can be synthesized by combining metal oxides and MnO$_2$. The addition of metal oxides and the generation of special structures can increase the concentration of oxygen vacancies on the surface of manganese oxide, which forms a low resistance electron-defective surface and promotes the rapid transfer of carriers, giving the catalyst a high oxidation potential and a high photocurrent reaction. Metal oxides/MnO$_2$ catalyst also has special structures, such as hollow sphere structures, intercalation structures, hollow tube structure, etc. Many metal oxides have been reported, such as Bi$_2$WO$_6$ [68], ZnO [69], Co$_3$O$_4$ [70], Fe$_3$O$_4$ [71], SiO$_2$ [72], CuO [73], SnO$_2$ [74], Cu$_2$B$_2$O$_4$ [75], Al$_2$O$_3$ [76], TiO$_2$ [77] etc.
Carbon materials are widely applied to enhance the catalytic performance of MnO2 due to their lightweight, high strength, high electrical conductivity, and chemically stable. In recent years, nanotube, nanosphere, nanofiber, and graphene have been used for enhancing the activity of MnO2. The combination of carbon material increased the surface area, the active site of manganese dioxide, more surface oxygen-containing functional groups, and the carrier mobility of MnO2 [78–81].

The Layered Double Hydroxides (LDH) is so known as a hydrotalcite-like material. Recently, MnO2-based LDH materials have been widely used for the catalytic degradation of pollutants. Due to its unique structure, MnO2-based LDH materials have a large specific surface area and more exposed active groups. The characteristics of its adsorption and catalytic degradation of pollutants are improved. Chen et al. prepared FeMn-LDH by co-precipitation method and used it to activate the peroxymonosulfate (PMS) for octadecylamine degradation [82]. Kabel et al. synthesized a novel manganese oxide FeMnO3 as a heterogeneous catalyst for Methylen Blue (MB) degradation [83]. FeMn-LDH synthesized by Hou et al. could effectively activate PMS and remove 97.56% of the organic pollutant Acid Orange 7 [84].

4. Organic pollutant degradation

Organic pollutants widely exist in water and soil environment. Some of them are highly toxic, easily accumulative, and difficult to degrade. Organic pollutants can be divided into phenolic compounds, antibiotics, dyes, pesticides, etc.

4.1 Phenolic compounds

Phenolic compounds are aromatic organic compounds. And most of them have acute toxicity, genotoxicity, and endocrine-disrupting effects. Many common phenol derivatives, such as biphenol A, chlorophenols, nitrophenols, and aminophenols, can be detected in the environment [85–87]. In recent years, advanced oxidation methods have been proposed to remove toxic phenolic compounds from wastewater. Advanced oxidation methods belong to redox reactions that can generate hydroxyl radicals (•OH), sulfate radicals (SO42−), and other radicals (e.g. O2−) in situ. MnO2-based materials act as important catalysts in advanced oxidation [88].

4.1.1 Hydroxyl radical oxidation methods

•OH are the most common advanced oxidative radicals. Generally, the degradation of phenolic compounds by •OH is a continuous process. With the attack of •OH, aromatic rings undergo a ring dissociation reaction and various functional groups of phenolic compounds undergo substitution and addition reactions. In this process, intermediate products such as aminophenols, phenols, hydroquinones, benzoquinones, and carboxylic acids will be formed. With the involvement of other conditions, the degradation reaction may eventually produce carbon dioxide and water [89–91].

Lv et al. found that •OH were the main active agents in the degradation of phenol by carbon aerogel doped with MnO2 [6]. Ponnusamy et al. synthesized 6-MnO2 on carbon fiber, which could effectively degrade 90% of ibuprofen with the •OH radicals [92]. Guo et al. reported that the degradation rate of benzophenone-3 was 92.0% with •OH radicals from MnO2-Co3O4 nanoparticles [93]. Zhang et al. found that the •OH concentration was increased by a factor of two when using the prepared MnO2 with mesoporous structure and high specific surface area to degrade phenolic acid [94]. MnO2 can also generate •OH to participate in the degradation of phenolic compounds when used as electrode materials, such as MnO2 electrodes, polypyrrole/β-MnO2 modified graphite electrodes [95], and MnO2/Nano-G|Foam-Ni/Pd composite cathodes [67].

4.1.2 Sulfate radical oxidation methods

More recently, SO42− have been proposed as an alternative to •OH for organic oxidation. The SO42−
can be obtained by heating, light radiation, and metal activation from sulfate oxidizers such as persulfate and PMS [96]. The degradation of phenols by SO₄²⁻ presumably undergoes substitution, addition, hydroxylation, ring-opening, C-C bond breaking, and decarboxylation. The intermediates of the degradation reaction are complex. Generally, there are phenol, hydroquinone, quinones, and other substances [97,98].

It was found that SO₄²⁻ generated from a three-dimensional γ-MnO₂@ZnFe₂O₄/rGO nanohybrid catalyst could completely degrade 50 mL/20 ppm phenol solution within 30 min [99]. Saputra et al. found that the nanowire α-MnO₂ in the crystalline state had the highest activity in generating SO₄²⁻ [16]. Liang et al. synthesized mesoporous α-MnO₂ nanoparticles loaded with Co₃O₄, which could degrade 100% of phenol within 20 min [21]. In addition, metal oxides/MnO₂ composites have higher efficiency in degrading quinones, nitrophenols, and bisphenols under acidic conditions through SO₄²⁻ [100,101].

4.1.3 Other radical and nonradical oxidation methods
In addition to -OH and SO₄²⁻, superoxide radical (O₂⁻•⁻) is also produced in some cases. Wang et al. found that δ-MnO₂ crystals with high exposure surfaces promoted the formation of O₂⁻•⁻ and accelerated the degradation of phenol [102]. Another process is the mechanical ball milling of oxygen vacancy enriched manganese dioxide. It was found that the obtained BM20-MnO₂ produced O₂⁻•⁻ and the degradation rate of tetrabromobisphenol was increased by 22 times [4]. Bisphenol A was oxidized by a non-radical mechanism using the formation of reactive complexes between amorphous MnO₂ and PMS. The amorphous MnO₂ could activate PMS, and the generated active MnO₂/PMS system degraded about 94% of bisphenol A within 60 min [103].

4.1.4 Reaction mechanism
Manganese oxides based catalysts activate different oxidizing substances (PMS, peroxydisulfate (PDS), H₂O₂, O₂, etc.) to produce -OH, SO₄²⁻, and O₂⁻•⁻. Free radicals directly participate in the degradation of organic pollutants. After a few steps of reaction, CO₂, H₂O, inorganic ions (SO₄²⁻), and low molecular organics are eventually generated (Figure 3) [21,83,89,92].

4.2 Antibiotics
Antibiotics are widely used around the world to treat infectious diseases, and they enter soils and water systems through leachates of sewage, manure, and leachate from pharmaceutical waste. They are persistent in the environment and remain toxic to the hematopoietic system, posing a serious threat to the environment and humans. Therefore, it is urgent to develop effective and economical methods to eliminate antibiotics, considering their chemical and biological stability [75,104]. Antibiotics mainly include ciprofloxacin, tetracycline, sulfa antibiotics, and other antibiotics. Most of the degradation of antibiotics is accomplished by oxidative free radicals. -OH, SO₄²⁻, and O₂⁻•⁻ are the main active species.

4.2.1 Ciprofloxacin
Ciprofloxacin is a quinolone antibacterial drug with strong penetrating properties. Many researchers have explored the degradation of ciprofloxacin. 98.3% of ciprofloxacin was degraded within 30 min in a visible light/PMS system mediated by magnetic γ-Fe₂O₃-MnO₂ with many oxygen vacancies [105]. Wang et al. synthesized copper-based bimetallic oxides to decompose ciprofloxacin in wastewater by activating H₂O₂ to produce -OH. The degradation efficiency was up to 100% [106]. The degradation efficiency of ciprofloxacin by α-MnO₂ combined with dielectric barrier discharge could reach 93.1% after 50 min [107]. In summary, MnO₂ has an important effect in the degradation of ciprofloxacin.

4.2.2 Tetracycline
Tetracycline is a very common antibiotic in polluted environment. And its contamination area is very large. Tetracyclines also induce resistance in microorganisms and their metabolic intermediates are more toxic [108]. The α-MnO₂/ZnO-C z-type photocatalyst degraded 96.69% of tetracycline within 60 min with O₂⁻•⁻ and -OH [109]. The adsorption capacity of Erdite/MnO₂ nanorods on tetracycline was 2613.3 mg/g, which was due to the coordination reaction between the -NH₂ group of tetracycline and the hydroxyl group [110]. Minale et al. degraded 91.46% of oxytetracycline at pH 5 by using a sodium polyacrylate hydrogel loaded with MnO₂ [111].

4.2.3 Sulfa antibiotics
Sulfa antibiotics are typical toxic antibiotics. Khan et al. found that the ε-MnO₂/PMS system could effectively activate sodium persulfate and degrade 99% of sulfamethoxazole. Besides, the degradation rates of sulfachlorpyridazine, sulfamethazine, ciprofloxacin, and azithromycin were 100%, 88%, 100%, and 25%, respectively [112]. Wang et al. immobilized Co₃O₄ on different MnO₂ crystals for the degradation of sulfisoxazole. The γ-MnO₂@Co₃O₄ system showed the highest removal rate of more than 97% [113]. Jiang et al. found that Co₃O₄-MnO₂/biochar catalyst with PMS could completely degrade sulfadiazine, and the O₂⁻•⁻ and SO₄²⁻ were the main active substances [114].

4.2.4 Other antibiotics
Many other types of antibiotics can also be harmful to the environment and humans, such as ceftiofur (CEF),
norfloxacin (NOF), metoprolol (MET), and ibuprofen (IBU), etc. Zhang et al. prepared CuBi\textsubscript{2}O\textsubscript{4}/MnO\textsubscript{2} composite by two-step hydrothermal method. 93.6% of CEF was decomposed over 40 min with 0.4 g·L\textsuperscript{−1} PMS and 0.3 g·L\textsuperscript{−1} CuBi\textsubscript{2}O\textsubscript{4}/MnO\textsubscript{2} at pH 11 [75]. Xu et al. found that NOF was completely degraded when α-MnO\textsubscript{2}/MnFe\textsubscript{2}O\textsubscript{4} catalyst was dosed at 0.2 g/L, PMS of 1 mmol/L, pH of 7, room temperature, and NOF of 20 mg/L [115]. He et al. investigated the oxidative reactivity of α-MnO\textsubscript{2}, β-MnO\textsubscript{2}, and γ-MnO\textsubscript{2} concerning MET and IBU. It was found that α-MnO\textsubscript{2} had the highest degradation efficiency of 99% for IBU and MET [116].

4.3 Dyes

Water pollution resulted from organic dyes and their residues with the rapid growth of textile and dye industries has become a major environmental problem [72,117,118]. In addition to traditional adsorption methods, advanced oxidation technologies (i.e. photocatalytic oxidation, Fenton, and Fenton-like reactions) have been widely applied to eliminate dyes from wastewater [119].

4.3.1 Adsorption and oxidation method

The conventional adsorption-oxidation method is a more economical, mature, and environment friendly technology compared to other technologies. It can be used for degrading most dyes, such as RhB, Reactive Blue 19 (RB19), and so on. Core-shell MnO\textsubscript{2}-SiO\textsubscript{2} nanorods were synthesized by Gong et al. It was found that the final decolorization rate of RhB was 98.7% under the action of the absorption and oxidation [120]. Fathy et al. synthesized a novel and efficient nanocomposite catalyst γ-MnO\textsubscript{2}/MWCNT by in situ co-precipitation method. The results showed that the degradation rate of RB19 dye was 100% under the combined effect of adsorption and catalytic oxidation [121]. Adsorption oxidation is widely used in the field of organic dye degradation and has a large potential for development.

4.3.2 Photocatalytic reaction

In recent years, more and more studies have been applied to the photocatalysis technology for the degradation of dyes. Chiam et al. synthesized MnO\textsubscript{2} nanoflowers as photocatalysts to degrade RhB, the degradation rate was 99.0% under acidic conditions because of the formation of •OH catalyzed by Mn\textsuperscript{2+} [35]. 98.35% of Coomassie Brilliant Blue R-250 was degraded in 30 min by α-MnO\textsubscript{2}/TiO\textsubscript{2} heterostructured photocatalysts with narrow band gap [72]. Ma et al. found that the degradation rate of MB solution by flower-shaped Fe\textsubscript{3}O\textsubscript{4}/SiO\textsubscript{2}/MnO\textsubscript{2}/BiOBr-Bi photocatalyst was 95.23% within 150 min [122].

4.3.3 Fenton reaction

The Fenton reaction is often used for treating organic matter by generating •OH through H\textsubscript{2}O\textsubscript{2}. The laminated hollow Fe\textsubscript{3}O\textsubscript{4}/Fe\textsubscript{1−x}S\textsubscript{x}/MnO\textsubscript{2} composite was able to degrade 20 mg/L of RhB solution within 4 min, where •OH was the main active substance. And the maximum adsorption capacity of tetracycline reached 748.9 mg/L [123]. Sabbaghan et al. found that the degradation rate of MB reached 90% in 60 min with H\textsubscript{2}O\textsubscript{2} and needle ferrite/MnO\textsubscript{2} catalyst [124]. Li et al. removed 99.13% of acidic red 73 in 40 min by synthesizing coal fly ash supported MnO\textsubscript{2}. •OH and SO\textsubscript{4}\textsuperscript{2−} were considered as the main reactive radicals in the degradation process [125].

4.3.4 Fenton-like reaction

With the development of the Fenton reaction, Fenton-like reaction has been gradually applied to the prevention and control of dye pollution. MnO\textsubscript{2}@ZIF-8 core-shell nanoparticles were synthesized by Cao et al. The nanoparticles were used as photocatalysts to degrade RhB in a Fenton-like process and the final degradation rate was greater than 96.0% [126]. Yu et al. prepared a series of β-MnO\textsubscript{2} macro catalysts for the degradation of some dyes (MB, methyl orange (MO), RhB, and acid orange II (AOII)) under hydrothermal conditions. After
40 min of reaction, the degradation rates of MB, MO, RhB, and AOII were 95%, 45%, 52%, and 63%, respectively [127].

4.4 Pesticides

As food production increases, the use of pesticides is also growing rapidly. Of the total pesticide use, about 0.1% meets the target, and the rest remains in the environment. This led to the deterioration of soil quality and following crop yield reduction with poor quality, and water pollution. Ultimately, it poses a threat to animals and humans [128–130]. Pesticides can generally be classified as phenols, organophosphates, and other types.

4.4.1 Organophosphorus pesticides

Among the common pesticide contaminants, organophosphorus pesticides are the most commonly used agricultural pesticides, most of which are highly or moderately toxic [131]. Manganese (IV) oxide prepared by homogeneous hydrolysis of KMnO₄ and 2-chloroacetamide degraded 90% of methyl parathion (MP) within 2 h [132]. Li et al. found that the removal of glyphosate by ferricydrite/δ-MnO₂ composites was dominated by degradation when the ratio of Mn/Fe was greater than 0.0167, and mainly by adsorption when the ratio was less than 0.0167 [133]. Wang et al. studied the degradation efficiency of MP in the MnO₂-HSO₄⁻-reaction system. The results showed that the maximum degradation rate of MP reached 97% [134]. MnO₂ plays an important role in the degradation of organophosphorus pesticides.

4.4.2 Other pesticides

In addition to organophosphorus compounds, some other pesticides are found in sewage and soil, such as toxaphene, DIN (difenoconazole), and DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane) and so on. 96.5% of toxaphene was removed by the MnO₂/cellulose fiber nanocomposite [135]. Zhao et al. found that α-MnO₂ could degrade 88% of DIN within 22 h, and SO₄²⁻ and OH⁻ were the main active substances [8]. Liu et al. found that the degradation efficiency of the MnO₂/PMS system for DDT was in the following order: α-MnO₂ > γ-MnO₂ > β-MnO₂. The maximum degradation rate of DDT was 97.0%, and SO₄²⁻ was the main reactant [136]. New pesticide contaminants are being discovered one after another. This is an issue that needs to be addressed urgently.

4.5 Other organic pollutants

In addition to the above pollutants, perfluorooctanesulfonic acid (PFOS), cationic blue (X-GRL), carbamazepine (CBZ), methyl benzoate, methylparaben, paracetamol, and dimethylhydrazine were also found in wastewater and contaminated soil, which can be degraded by manganese oxides. The degradation mechanisms are mostly related to free radicals. The degradation rate can reach 80–100% in a few hours (Table 1). Although manganese oxide has a good effect on the degradation of most organic pollutants, new pollutants are being discovered one after another. Therefore, we still need to continuously develop organic degradation technologies.

5. Summary and outlook

Environmental pollution caused by rapid industrialization is one of the major challenges faced by human society. Manganese oxides are one of the most promising catalytic materials at this stage due to their unique properties. In the past few years, this material has made encouraging breakthroughs in catalytic degradation of organic pollution. This paper reviews the various phase and morphological structures of MnO₂, three modification methods (self-mixing, doping, and composite) of MnO₂. In addition, the catalytic degradation effect and mechanism of phenolic compounds, antibiotics, dyes, pesticides, and other organic pollutants are also reviewed.

MnO₂ materials have been developed for the degradation of organic pollutants and their catalytic performance has been improved. However, it must be acknowledged that the application of MnO₂ materials in this field of catalytic organic degradation still faces various unresolved problems. The current problems we

| Materials     | Synthetic methods         | Target                | Degradation mechanism              | Activity     | Reference |
|---------------|---------------------------|-----------------------|------------------------------------|--------------|-----------|
| γ-MnO₂/H₂O₂   | Hydrothermal method       | perfluorooctanesulfonic acid | -OH, O₂⁻⁻                                     | 100%, 15 min | [13]      |
| δ-MnO₂/β-MnO₂ | The oxidation of permanganate | Cationic blue       | Adsorption, -OH and O₂⁻⁻              | 100%, 30 h   | [58]      |
| δ-MnO₂       | The oxidation of permanganate | Carbamazepine       | Protonation of intermediate products | 92.8%, 30 min | [137]    |
| Fe₂O₃/MnO₂   | Hydrothermal process      | Carbamazepine        | -OH, O₂⁻⁻, SO₄²⁻                      | 87.6%, 1 h   | [138]    |
| Hydrogel      | Irradiation polymerization and chemical precipitation method | Methylparaben       | -OH, O₂⁻⁻, SO₄²⁻                      | 99%, 90 min  | [139]    |
| Cationic micelles/MnO₂ | The oxidation of permanganate | Paracetamol       | Micellar osmotic oxidation            | 100%, 45 min | [140]    |
| α-MnO₂, δ-MnO₂ | Hydrothermal method       | Dimethylhydrazine    | -OH, O₂⁻⁻                          | >92%, 3.5 h  | [141]    |
need to solve or the direction we need to study in the future are: 1) To enhance the mechanical and thermo- 
dynamic stability of MnO$_2$ materials to maintain their 
structures; 2) To ensure the activity of advanced oxidation 
free-radicals catalyzed by the catalyst; 3) To explore the 
synthesis of heterotatom-doped MnO$_2$ and construction 
its composites with specific function in a controllable 
method; 4) To clarify the intermediates and reaction path 
in the catalytic process of MnO$_2$ catalyst; 5) To explore the recovery and regeneration of MnO$_2$ catalysts.

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