An Overview of Advanced Oxidation Process and Outlook

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Abstract. With the development of industry and agriculture, water contamination comes more and more serious even threatens human health. Advanced oxidation processes are widely used in waste water treatment because of their high efficiency, among them peroxymonosulfate (PMS) activate by catalysts to release sulfate radicals and hydroxyl radicals is the best way of removing recalcitrant organic pollutants in water. Cobalt ion and cobalt oxides can activate PMS efficiently, however their high toxicity will contaminate the environment terribly and even cause human cancer, which restrains the extensive utilization. Compared with cobalt, manganese is more environment-friendly with low toxicity and abundant content, meanwhile manganese oxides are given excessive focus due to its high catalytic efficiency, which makes it can be used in practical situations.

1. Research background

Water is an essential resource in human life. Although earth's water reserves are quiet abundant, there is little water that can be directly used. According to the World Health Organization, the total global water volume is about 1.36 billion cubic kilometers. However, the sea water is about 1.32 billion kilometers, accounting for 97 percent of the world's total water. But the sea water is salt water which cannot be used directly by human beings. The remaining 3% water, including ice and snow melt water in high mountains areas polar regions which accounts for 2.14% of the earth’s total water, cannot be used directly either. The groundwater, rivers and lakes and other fresh water that can be directly used by human is about 8.5 million cubic kilometers, accounting for about 0.64% of the total water volume in the world [1].

Figure 1. (a) Overview of the distribution of Earth's water resources; (b) Different uses of freshwater.

Before the beginning of global industrialization, the water pollution can be naturally degraded by the self-purification ability of the environment. However, due to the development of industrialization,
many cannot naturally degradable pollutants are discharged into water bodies. At the same time, these pollutants will also cause serious harm to human production, life and health, which seriously affect social development [2].

Traditional methods of sewage treatment include physical method, chemical method and biological method. However, in recent years, there is no good way to deal with organic pollutants. Such organic pollutants generally include antibiotics, endocrine disruptors and so on. These chemical substances are detrimental to human health, even cause huge social and financial burden.

For example, Bisphenol A (BPA) is widely used in plastic production, so it is inevitable that a large amount of BPA will be discharge into the water. Bisphenol A is harmful to organisms and will be accumulated by the food chain. It has been reported that BPA will have impact on biological sex ratio and reproductive behavior. The European Union believes that BPA can lead to precocious puberty. Animal experiments have found that even a small amount of bisphenol A can lead to prostate growth, precocious puberty in female animals and a decline in sperm count. BPA also causes fetal toxicity and teratogenicity, increasing the risk of diseases such as ovarian cancer [3].

Antibiotics are widely used in biopharmaceuticals and can be used as growth agents for animals. However, the overuse and leakage of antibiotics are very serious, which will lead to microbial drug resistance and increase the difficulty of treating corresponding diseases. Antibiotics can also damage human cells and even produce irreversible damage to human nerves. For example, in the 1980s, the abuse of antibiotics has caused huge amounts of adverse reactions and even death in patients [4]. Therefore, it is urgent to find an effective method to dispose organic pollutants in the environment.

2. The research status of sewage treatment technology

Traditional sewage treatment methods can be divided into physical methods, chemical methods and biological methods. The physical methods mainly depend on adsorption, precipitation, filtration to deal with the large particles in the water, which can deal with a huge amount of water. However, its purification degree is lower than other methods. Chemical methods can dispose pollutants dissolved in water through chemical reactions. Although it can effectively degrade organic pollutants, it requires a large amount of chemical reagent, which makes it difficult to be used in practical applications. The biological methods mainly use the micro-organisms including bacteria to deal with the pollutants in the water. The purification degree is higher than physical methods, but it is necessary to control water temperature and pH to keep the bio-activity and ensure the chemical agents in the water will not kill the bacteria in the water, which makes the condition of using biological method much more restrictive. The new method such as ion exchange, electrodialysis and electrolysis, which can effectively remove the pollutants in the water. However, the high cost and the complex facilities with difficult operation makes it hard to be used widely [5]. Thus, it is urgent to find a cheaper, convenient and large-scale sewage treatment method.

2.1. A brief introduction to Advanced Oxidation Technology

At present, the advanced oxidation technology is used to treat organic pollutants in water. And the equipment is simple, cheap and easy to operate. Moreover, the advanced oxidation technology has low requirements for reaction conditions, is easy to control, has various ways, has good chemical stability, does not produce secondary pollution, and has low cost. These are much better than the tradition methods [6].

Advanced oxidation technology refers to the efficient treatment of organic pollutants in water through generating huge amounts of strong oxidizing free radicals. These radicals generally have high redox potentials and large reaction rate constants, so they are very active and can quickly and effectively attack organic pollutants in water, such as phenols, dyes, and antibiotics. Free radicals can oxidize them to smaller molecular fragments and even be completely oxidized to water and carbon dioxide.

As for the hydroxyl radical, the mainstream fenton oxidation technology (Fe$^{2+}$+H$_2$O$_2$→Fe$^{3+}$+OH$^-$ +·OH) can be widely used as it can produce hydroxyl radical with high strong oxidizing property.
Comparing with other oxidants, the hydroxyl radical has higher Oxidation electrode potential (2.7 V) which means it can deal with most organic pollutants with simple operation and mild reaction condition. Though this method can remove the pollutant in the water, the selectivity of the reaction is usually poor and it is susceptible to the reaction system. There are many disadvantages such as a need of a large amount of iron ions as catalyst, and a narrow range of reaction pH value, which result in a need to adjust the pH value, the production of iron hydroxide sludge [7], and so on. It is the disadvantages above make this reaction system requires extra separation facilities, increases the cost of the reaction, restricts its wildly use.

Sulfate radical can be generated through the decomposition of peroxymonosulfate (PMS, HSO$_5^-$) and persulfate (PS, S$_2$O$_8^{2-}$). Because PMS has asymmetric molecular structure and relatively large O-O bond lengths in molecules, it is the best choice to produce sulfate radical. Therefore, PMS is also the best choice for advanced oxidation treatment of sewage. The salt sold on the market that can produce PMS are almost the PMS composite salt oxone ($2\text{KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4$), which is a white solid powder, nontoxic, cheap and easy to obtain. Also, it is relatively stable and easy to transport, which makes it has a larger application property [8]-[9].

2.2. Activation technology of PMS

However, the activation energy of peroxymonosulfate is relatively high, thus, it needs to provide additional energy to help it to start the reaction. The tradition methods include ultraviolet radiation, ultrasonic wave, and high temperature methods.

Nie et al. proved that increasing temperature can decrease the activation energy of PMS activation. As showed in Figure 2, the horizontal axis represents the reaction time, and the vertical axis represents the logarithm of the proportion of remaining organic pollutants in the reaction. Through the image, we know that the higher the temperature, the greater the slope of the image, and the faster the reaction rate, which proves that increasing the temperature can reduce the activation energy of the reaction [10].

![Figure 2. Degradation rate at different temperatures.](image)

Liu et al. used ultrasound to help the decomposition of PMS. They have proved that ultrasound can promote the decomposition of PMS. In Figure 3, the horizontal axis represents the reaction time and the vertical axis represents the decomposition efficiency. It can be seen from the diagram that the organic pollutants are not decomposed by only ultrasonic wave without oxidant, which proves that ultrasonic wave can not decompose the oxides in water by itself. After the oxidant is added, the higher the ultrasonic power, the higher the decomposition efficiency, which proves that ultrasonic wave can promote the PMS decomposition [11].
He et al. only used ultraviolet radiation to promote the decomposition of PMS, experiments have proved that ultraviolet radiation can promote the decomposition of PMS. In Figure 4, the vertical axis represents the proportion of remaining pollutants and the horizontal axis represents the amount of ultraviolet radiation. It can be seen from the figure that ultraviolet rays can not decompose organic pollutants in water alone, and under the same ultraviolet intensity, PMS shows the strongest oxidizing ability [12].

All the methods above can promote the decomposition of organic pollutant, but they all need the extra facilities to help with the reaction, increasing the cost of the reaction. As the catalyst can directly contact the reactant without additional equipment, scientists started to study the methods of using catalysts to decrease the activation energy.

The electron layer of the transition metal has electron-filled or empty d-orbitals, which can provide electrons or act as electron-accepting ligands, thereby promoting the generation of intermediate products, reducing the activation energy of the reaction, and exhibiting a good catalytic effect. Therefore, transition metal ions were first used in aqueous solutions to activate PMS generate free radical ions. As early as 2004, Dionysios used nine transition metal ions as catalysts to activate PMS, PS and hydrogen peroxide respectively to degrade organic pollutants in water, and the catalytic activity of these transition metal ions on PMS is as follows: Ni^{2+} < Fe^{3+} < Mn^{2+} < V^{3+} < Ce^{3+} < Fe^{2+} < Ru^{3+} < Co^{2+} [13].
Kim et al found that the chain reaction mechanism of sulfate radical is shown in Figure 5 [14]. Cobalt ions (Co^{2+}) is only used as a catalyst to participate in the reaction, by generating CoOH\(^+\) and HSO\(_5^-\) to generate sulfate radical, after that the generated CoOH\(^+\) is converted to Co\(^{3+}\), and then reacts with HSO\(_5^-\) to generate persulfate radicals (SO\(_5^•^-\)), and at the same time Co\(^{3+}\) is reduced to the original Co\(^{2+}\). Throughout the reaction process, Co\(^{2+}\) is only act as a catalyst to participate in the reaction, and without any change before and after the reaction. However, the entire reaction can proceed smoothly and quickly through the introduction of Co\(^{2+}\), and a large number of free radicals can be generated to degrade organic pollutants.

Figure 5. Schematic diagram of the chain reaction mechanism of Co\(^{2+}\) catalyzed PMS to produce sulfate radicals.

In 2009, Dionysios and his teammates start to use Fe\(^{2+}\) to activate PMS to degrade dichlorobiphenyl. They found that Fe\(^{2+}\) also has a pretty good activation properties that can activate PMS to generate sulfate radical, degrade almost all of the dichlorobiphenyl. They also find that the need of Fe\(^{2+}\) have a optimal value. At that value, the Fe\(^{2+}\) can promote the reaction to the greatest extent. If the concentration of Fe\(^{2+}\) is higher than the optimal value, it will block that reaction. At that time, the surplus Fe\(^{2+}\) will become radical scavenger and react with sulfate radical to form Fe\(^{3+}\), which will hinder the reaction by consuming free radicals. The Fe\(^{3+}\) catalytic activity is not as good as Fe\(^{2+}\), so it shows a decrease in catalytic activity [15].

The transition metal ions above can show good catalytic activity which benefits from their high solubility make them can be evenly distributed in solution and have enough possibility to get touch with the PMS in the solution to make the reaction more efficient. However, it is precisely because these transition metal ions can be completely dissolved in the solution to form a homogeneous system, which also makes the subsequent recovery and use difficult to achieve. At the same time, the transition metal ions also have biotoxicity, which can easily cause the secondary pollution, especially the cobalt ion with the best catalytic activity, which has been reported in the literature that cobalt ions may cause a series of diseases such as cancer, asthma and pneumonia [16]. These shortcomings seriously hinder the wide use of transition metal ions in the field of advanced oxidation, and make people try to study and use heterogeneous catalysts with good catalytic performance and easy separation. It has been found that after the metal ions are fixed, the leakage rate of metal ions can be greatly degraded, thereby reducing the degree of secondary pollution to the environment [17].

Among them, metal oxides are widely used. Dionysios and others first used CoO and Co\(_3\)O\(_4\) to catalytically activate PMS, they found that the solubility of the CoO was very good, reaching 0.313 mg per 100 grams of water. Therefore, the system can be classified as a homogeneous reaction system [18]. At the same time, Chan et al. found that even the CoO filtrate has certain PMS activation ability [19], so the use of CoO can not reduce the leakage rate of metal ions. Furthermore, Dionysios et al. used Co\(_3\)O\(_4\) (CoO•Co\(_2\)O\(_3\)) to activate the PMS, and found that the leakage of cobalt ions was greatly
reduced at this time. This phenomenon may be related to the integration of CoO into the Co$_2$O$_3$ grid, making it difficult for CoO to be incorporated into the water$^{18}$. Yu et al. verified the activation mechanism of the Co$_3$O$_4$/PMS system, the original Co$^{2+}$ generated by Co$^{3+}$ participates in the homogeneous catalytic reaction and becomes Co$^{3+}$ after activation of PMS. Co$^{3+}$ will return to the crystal lattice of Co$_3$O$_4$, so that the leakage of cobalt ions can be greatly reduced. It is precisely because of the stability of Co$_3$O$_4$ that it has been widely studied and applied$^{[20]}$.

Among single metal oxide, Cobalt oxide still has the best performance, but the leakage out of cobalt is inevitable, and the Cobalt has adverse effects on the environment and human physical and mental health. Thus, people start to study other metal oxides. According to previous literature reports, manganese oxide also exhibits better catalytic performance. Compared with cobalt, manganese has much less harmful effects to human body and the environment. At the same time, manganese is quite abundant in earth’s crust, which is cheap and easy to get, made manganese has broad application prospects.

3. Persulfate activation technology based on manganese oxide

Wang et al. used manganese acetate and sodium hydroxide to react, after hydrothermal stirring, them obtain amorphous Mn$_3$O$_4$ nanoparticles with a small particle size through the thermal decomposition of the hydrothermal product. Although this product does not have a special microscopic morphology, it exhibits good catalytic activity. The 50 mg/L catalyst and 0.15 g/L PMS can degrade 81.5% of the 30 ppm orange II within two hours. The catalyst Mn$_3$O$_4$ can be considered as MnO•Mn$_2$O$_3$, in which divalent manganese and trivalent manganese generate sulfate radicals and persulfate radicals through the following two chemical formulas. In these two reactions, divalent manganese and trivalent manganese have achieved mutual conversion, and both will return to the crystal lattice, that no manganese ions will leak into the environment to cause secondary pollution. Afterwards, the persulfate radicals will be converted into sulfate radicals as shown in Figure 5, so that Orange II is completely oxidized into carbon dioxide and water which are harmless to the environment$^{[21]}$.

\[
\equiv\text{Mn}^{2+}\text{HSO}_5^-\rightarrow\equiv\text{Mn}^{3+}\text{SO}_4^{\cdot}\text{OH}^-\quad (1)
\]

\[
\equiv\text{Mn}^{3+}\text{HSO}_5^-\rightarrow\equiv\text{Mn}^{2+}\text{SO}_5^{\cdot}\text{H}^+\quad (2)
\]

Different synthesis methods can obtain manganese oxides with different microscopic morphologies, and many kinds of nanoflowers, nanospheres, nanorods and nanosheets liked manganese oxides have been reported. In 2017, Zhao et al. used methanol, polyvinylpyrrolidone (PVP) and potassium permanganate through hydrothermal and calcination to successfully prepare Mn$_2$O$_3$ nanocube with high-efficiency light-trapping properties as shown in Figure 6, which shows good performance when catalyze the degradation of ciprofloxacin in water$^{[22]}$.

Figure 6. Scanning electron microscope (a) and transmission electron microscope (b) images of Mn$_2$O$_3$ nanocube.
Studies have found that manganese oxide with a three-dimensional structure can exhibit better catalytic activity. In 2015, Wang et al. used potassium permanganate and hydrochloric acid to obtain MnO$_2$ with a three-dimensional structure through a hydrothermal method at different temperatures. As shown in Figure 7, the product of the reaction at 100°C is δ-MnO$_2$ with the crown of nanosheets. When the temperature is increased to 110°C, a sea urchin-like α-MnO$_2$ composed of nanorods will be obtained. It can be found that during the heating process, with the occurrence of the thermal shrinkage effect, the nanosheets become much more dense, and then transformed into nanorods with a smaller specific surface area. The nitrogen adsorption test measured that the specific surface area of the product was reduced from 41.7 m$^2$/g (coral δ-MnO$_2$) to 17.5 m$^2$/g (sea urchin-like α-MnO$_2$). Along with the decrease of specific surface area, the catalytic performance is also reduced [23].

Figure 7. Scanning electron micrographs of MnO$_2$ produced by hydrothermal at 100°C (C,D) and 110°C (E,F).

In the following year, Wang et al. designed and synthesized an ellipsoidal α-Mn$_2$O$_3$@α-MnO$_2$ core-shell material. First, potassium permanganate, glucose and tartaric acid are used to synthesize MnCO$_3$ through hydrothermal method, and then the obtained potassium permanganate is dissolved in water, stirred evenly and aged, finally calcined to obtain α-Mn$_2$O$_3$@α-MnO$_2$ with a core-shell structure. As shown in Figure 8, it can be found that with the calcination temperature increases, the surface of the product becomes smoother, accompanied by a decrease in specific surface area and pore volume (Respectively reduced from 105.3 m$^2$/g to 12.73 m$^2$/g and from 0.356 cm$^3$/g to 0.029 cm$^3$/g), which followed by a decrease in catalytic activity and an increase in the activation energy of the reaction. But at the same time, it is found that the catalytic performance of the obtained catalyst is better than that of the homogeneous catalytic system based on Mn$^{2+}$, also exceeds that of a single α-Mn$_2$O$_3$ or α-MnO$_2$ [24].
Figure 8. Scanning electron micrographs of MnCO$_3$(a), 350°C (b), 400°C (c) and 550°C d) calcined products

It can be seen from the above examples that although the catalytic activities of manganese oxides with different microscopic morphologies are different, there are certain rules to follow. In 2017, Deng et al. comparatively studied the catalytic performance of several MnO$_2$ with the same α crystal form but with different microscopic morphologies. They hydrothermally heated the mixed solution of potassium permanganate and manganese sulfate for different lengths of time to obtain α-MnO$_2$ with three different microscopic morphologies of nanoparticles, nanoflowers and nanorods, as shown in Figure 9. The α-MnO$_2$ obtained above was used to catalyze the degradation of ciprofloxacin under the same conditions, and it was found that the nanoflower-shaped α-MnO$_2$ has the best catalytic effect, the nanorod-shaped second, and the nanoparticle-shaped last, but they are all better than commercial MnO$_2$. Through nitrogen adsorption test, it is found that the specific surface area and pore volume of the above three kinds of α-MnO$_2$ decrease in order of catalytic activity, but they are all much larger than commercial MnO$_2$. It can be seen that increasing the specific surface area and pore volume of manganese oxide will benefit the improvement of catalytic performance [25].

Figure 9. Nanoparticle (a), nanoflower (b) and nanorod (c) α-MnO$_2$
In 2017, Zhao et al. prepared the Mn$_3$O$_4$-MnO$_2$ catalyst by hydrothermal method, and found that the catalytic performance of manganese oxide with a non-single valence state is better than that of a single valence state. The specific principle of the reaction is shown in Figure 10. This phenomenon may be related to the mutual transformation and synergy between different valence manganese elements [26].

![Figure 10. Synergy between manganese in different valence states](image)

In conclusion, the specific surface area and pore volume of manganese oxide, specific microscopic morphology and various valence states of manganese will all have a great influence on the catalytic activity. Inspired by this, we believe that if Mn$_3$O$_4$ with a porous hollow structure can be prepared, it should exhibit excellent catalytic performance, which can quickly activate PMS to degrade organic pollutants in water, and achieve efficient and pollution-free sewage treatment.

References

[1] GUPTA V K, CARROTT P J M, RIBEIRO CARROTT M M L, et al. Low-Cost Adsorbents: Growing Approach to Wastewater Treatment—a Review [J]. Critical Reviews in Environmental Science and Technology, 2009, 39(10): 783-842.

[2] TARICSKA J R, HUNG Y-T, LI K H. 26 - Advances in Aerobic Systems for Treatment of Food Processing Wastewater [M]. Handbook of Water and Energy Management in Food Processing. Woodhead Publishing. 2008: 54-720.

[3] CHEN P-J, LINDEN K G, HINTON D E, et al. Biological Assessment of Bisphenol A Degradation in Water Following Direct Photolysis and UV Advanced Oxidation [J]. Chemosphere, 2006, 65(7): 102-1094.

[4] FAN Y, MA W, HE J, et al. CoMoO$_4$ as a Novel Heterogeneous Catalyst of Peroxymonosulfate Activation for the Degradation of Organic Dyes [J]. RSC Advances, 2017, 7(57): 200-36193.

[5] ANDREOZZI R, CAPRIO V, INSOLA A, et al. Advanced Oxidation Processes (AOP) for Water Purification and Recovery [J]. Catalysis Today, 1999, 53(1): 9-51.

[6] TUŠAR N N, MAUČEC D, RANGUS M, et al. Manganese Functionalized Silicate Nanoparticles as a Fenton-Type Catalyst for Water Purification by Advanced Oxidation Processes (AOP) [J]. Advanced Functional Materials, 2012, 22(4): 6-820.

[7] DU Y, MA W, LIU P, et al. Magnetic CoFe$_2$O$_4$ Nanoparticles Supported on Titanate Nanotubes (CoFe$_2$O$_4$/TNTs) as a Novel Heterogeneous Catalyst for Peroxymonosulfate Activation and Degradation of Organic Pollutants [J]. Journal of hazardous materials, 2016, 308(58-66).

[8] CHEN X, WANG W, XIAO H, et al. Accelerated TiO$_2$ Photocatalytic Degradation of Acid Orange 7 under Visible Light Mediated by Peroxymonosulfate [J]. Chemical Engineering Journal, 2012, 193-194(5-290).

[9] MA W, DU Y, WANG N, et al. ZIF-8 Derived Nitrogen-doped Porous Carbon as Metal-free Catalyst of Peroxymonosulfate Activation [J]. Environmental science and pollution research international, 2017, 24(19): 88-16276.
[10] NIE M, YANG Y, ZHANG Z, et al. Degradation of Chloramphenicol by Thermally Activated Persulfate in Aqueous Solution [J]. Chemical Engineering Journal, 2014, 246(82-373).

[11] LIU Q, ZHENG Z, YANG X, et al. Effect of Factors on Decolorization of Azo Dye Methyl Orange by Oxone/natural Sunlight in Aqueous Solution [J]. Environmental Science and Pollution Research, 2012, 19(2): 84-577.

[12] HE X, DE LA CRUZ A A, DIONYSIOU D D. Destruction of Cyanobacterial Toxin Cylindrospermopsin by Hydroxyl Radicals and Sulfate Radicals Using UV-254nm Activation of Hydrogen Peroxide, Persulfate and Peroxymonosulfate [J]. Journal of Photochemistry and Photobiology A: Chemistry, 2013, 251(6): 160.

[13] ANIPSITAKIS G P, DIONYSIOU D D. Radical Generation by the Interaction of Transition Metals with Common Oxidants [J]. Environmental science & technology, 2004, 38(13): 123705.

[14] KIM J, EDWARDS J O. A Study of Cobalt Catalysis and Copper Modification in the Coupled Decompositions of Hydrogen Peroxide and Peroxymonosulfate Ion [J]. Inorganica Chimica Acta, 1995, 235(1): 9-13.

[15] RASTOGI A, AL-ABED S R, DIONYSIOU D D. Sulfate Radical-based Ferrous–Peroxymonosulfate Oxidative System for PCBs Degradation in Aqueous and Sediment Systems [J]. Applied Catalysis B: Environmental, 2009, 85(3-4): 9-171.

[16] SHUKLA P, WANG S, SINGH K, et al. Cobalt Exchanged Zeolites for Heterogeneous Catalytic Oxidation of Phenol in the Presence of Peroxymonosulfate [J]. Applied Catalysis B: Environmental, 2010, 99(1): 9-163.

[17] LAI T-L, LAI Y-L, LEE C-C, et al. Microwave-assisted Rapid Fabrication of Co3O4 Nanorods and Application to the Degradation of Phenol [J]. Catalysis Today, 2008, 131(1): 10-105.

[18] ANIPSITAKIS G P, STATHATOS E, DIONYSIOU D D. Heterogeneous Activation of Oxone Using Co3O4 [J]. The Journal of Physical Chemistry B, 2005, 109(27): 5130-52.

[19] CHAN K H, CHU W. Degradation of Atrazine by Cobalt-mediated Activation of Peroxymonosulfate: Different Cobalt Counteranions in Homogenous Process and Cobalt Oxide Catalysts in Photolytic Heterogeneous Process [J]. Water research, 2009, 43(9): 2125-131.

[20] ZHIYONG Y, BENSIMON M, LAUB D, et al. Accelerated Photodegradation (minute range) of the Commercial Azo-dye Orange II Mediated by Co3O4/Raschig Rings in the Presence of Oxone [J]. Journal of Molecular Catalysis A: Chemical, 2007, 272(1): 9-11.

[21] YAO Y, XU C, YU S, et al. Facile Synthesis of Mn3O4–Reduced Graphene Oxide Hybrids for Catalytic Decomposition of Aqueous Organics [J]. Industrial & Engineering Chemistry Research, 2013, 52(10): 45-3637.

[22] ZHAO J, NAN J, ZHAO Z, et al. Facile Fabrication of Novel Mn2O3 Nanocubes with Superior Light-harvesting for Ciprofloxacin Degradation [J]. Catalysts Communications, 2017, 102(5-8).

[23] WANG Y, SUN H, ANG H M, et al. 3D-hierarchically Structured MnO2 for Catalytic Oxidation of Phenol Solutions by Activation of Peroxymonosulfate: Structure Dependence and Mechanism [J]. Applied Catalysis B: Environmental, 2015, 164(67-159).

[24] SAPUTRA E, ZHANG H, LIU Q, et al. Egg-shaped Core/shell Alpha-Mn3O4@alpha-MnO2 as Heterogeneous Catalysts for Decomposition of Phenolics in Aqueous Solutions [J]. Chemosphere, 2016, 159(8-351).

[25] DENG J, GE Y, TAN C, et al. Degradation of Ciprofloxacin Using α-MnO2 Activated Peroxymonosulfate Process: Effect of Water Constituents, Degradation Intermediates and Toxicity Evaluation [J]. Chemical Engineering Journal, 2017, 330(400-1390).

[26] ZHAO Z, ZHAO J, YANG C. Efficient Removal of Ciprofloxacin by Peroxymonosulfate/Mn3O4-MnO2 Catalytic Oxidation System [J]. Chemical Engineering Journal, 2017, 327(9-481).