Overview of advanced oxidation technology based on sulfate radical in water treatment

Junfei Wang, Yongli Zhang *
School of Environmental and Chemical Engineering, Foshan University, Foshan, China

*Corresponding author e-mail: 670511263@qq.com

Abstract. with the rapid development of industry and agriculture, the pollution of organic pollutant wastewater to the environment is becoming more and more serious. This paper introduces the classification of traditional water treatment method and advanced oxidation method, introduces their mechanism, advantages and disadvantages, and puts forward some research directions.

1. Introduction

Water is a necessary resource for human survival and development. In recent years, with the rapid development of industry and agriculture, the pollution of water resources is becoming more and more serious, and has brought all kinds of hazards. Among them, organic pollution is the most harmful and difficult to deal with, which is the focus of water pollution treatment. Due to its complex composition and unstable chemical properties, refractory organic wastewater is often treated with different treatment methods to meet the purpose of high treatment efficiency and low cost. Generally, wastewater treatment techniques can be divided into biological, physical and chemical methods.

2. Traditional water treatment technology

2.1. Biological methods

Biological method refers to a method of using microorganisms to degrade and adsorb pollutants in wastewater. Many microorganisms have been found to be effective in degrading organic wastewater, including bacteria, fungi and algae. However, due to the difficulty of organic wastewater, it is difficult for microorganisms to effectively destroy its toxicity and structure in normal time and environment. Therefore, how to select dominant microorganisms and apply them to degrade organic wastewater is the current research direction and hotspot.

2.2. Physical methods

Physical method is a method to separate organics from wastewater by physical methods such as adsorption, coagulation and membrane separation. Physical method is the most traditional method of wastewater treatment, which has the advantages of simple and effective. However, the treatment effect of refractory organic wastewater is general and easy to cause secondary pollution. The research direction is how to reduce the process cost and enhance the degradation effect.

2.3. Chemical methods

Chemical method refers to the use of chemical reagents to oxidize or reduce the pollutants in waste water, into low-toxic or non-toxic molecules. Among them, oxidation technology can make organic
wastewater odor, chroma, COD and other indicators decreased significantly, especially outstanding degradation ability. Common oxidants are hydrogen peroxide (H₂O₂), ozone (O₃), potassium permanganate (KMnO₄) and so on. However, with the improvement of industrial and agricultural level, a variety of organic wastewater, such as agricultural wastewater, printing and dyeing wastewater, pharmaceutical wastewater, cosmetics wastewater, etc. are produced in large quantities and pollute the water body, and ordinary chemical REDOX technology cannot meet the degradation requirements. Therefore, advanced oxidation processes (AOPs) has been widely studied for its various advantages. Traditional wastewater treatment methods are shown in Table 1.

| methods           | Concepts and Principles | Advantages and disadvantages | Research Trends                        |
|-------------------|-------------------------|------------------------------|----------------------------------------|
| biological methods| Use microorganisms to degrade and adsorb pollutants in wastewater | It is economical and efficient, but not completely degraded | Select dominant microorganisms for cultivation |
| physical methods  | Organic compounds in wastewater are separated by physical methods such as adsorption coagulation and membrane separation | Simple and effective, but easy to cause secondary pollution | Reduce process cost and enhance degradation effect |
| chemical methods  | Use chemical reagents to oxidize or reduce the pollutants in wastewater and convert them into low-toxic or non-toxic molecules | Strong degradation ability and high efficiency | Ordinary chemical REDOX techniques cannot meet the degradation requirements |

3. Advanced oxidation processes

Advanced oxidation processes, first proposed by Glaze et al. [1], is a treatment technology that generates free radicals with strong oxidation ability by transferring external energy or introducing catalysts, so as to oxidize or mineralize refractory organic substances into small molecules. Since its development in the 1980s, advanced oxidation technology has gradually shown its wide application range, fast reaction rate, strong oxidation ability and other advantages. Compared with traditional biochemical and physical water treatment processes, advanced oxidation technology has a strong ability to degrade organic wastewater with high toxicity and poor biodegradability, and has obvious advantages.

3.1. AOPs based on hydroxyl radicals

Wet oxidation (WAO) refers to the chemical process of oxidizing organic pollutants into water, CO₂ or other inorganic substances and small molecular organic compounds in liquid phase with oxygen or ozone as oxidant under high temperature (125~320 °C) and high pressure (0.5~10 MPa).

Photocatalytic oxidation is an advanced oxidation technology that uses ultraviolet or visible light to illuminate semiconductor catalysts to produce •OH degradation of organic pollutants. Under the irradiation of light, common photocatalysts, such as TiO₂, SiO₂ and ZnO, can generate photogenerated electrons (e⁻) and photogenerated holes (h⁺) on the surface. Photogenic holes can produce •OH, and photogenic electrons can produce radicals such as O₂•⁻ and HO₂•, which have strong mineralization
ability and can decompose organic pollutants into harmless small molecules to achieve the purpose of degradation.

Fenton method refers to the process of \( \cdot \text{OH} \) degradation of organic wastewater by using mixed solutions of Fe\(^{2+} \) and H\(_2\)O\(_2 \) under acidic conditions.

Ozonation refers to the water treatment technology that, under the combined action of catalyst or other conditions, O\(_3 \) molecules decompose to induce \( \cdot \text{OH} \) to degrade organic pollutants.

### 3.2. AOPs based on sulfate radical

Advanced oxidation processes based on sulfate radical is a new technology developed in recent years to treat refractory organic pollutants. The main ways of producing SO\(_4^{•−} \) are activated S\(_2\)O\(_8^{2−} \) and HSO\(_5^{−} \). S\(_2\)O\(_8^{2−} \) and HSO\(_5^{−} \) are structurally similar to H\(_2\)O\(_2 \), both containing O-O bonds. The O-O bond in H\(_2\)O\(_2 \) breaks to produce \( \cdot \text{OH} \), and in S\(_2\)O\(_8^{2−} \) and HSO\(_5^{−} \) it breaks to produce SO\(_4^{•−} \). Under normal conditions, persulfate (PS) and persulfate (PMS) are stable, and a series of activation measures are required to break the O-O bond to produce SO\(_4^{•−} \). The activation methods include thermal activation, ultraviolet activation, alkali activation and transition metal ion activation.

At high temperatures, the O-O bonds in persulfate break to form SO\(_4^{•−} \), Thermal activation is an important method for persulfate to produce free radicals to degrade organic pollutants. Waldemar [2] compared the degradation of ethylene chloride in groundwater by potassium permanganate and persulfate, it was found that the degradation rate of trichloroethylene was nearly 100% when heated to 60 °C, but not nearly when heated to 20 °C.

UV activation refers to the process in which the O-O bond in PS breaks to produce SO\(_4^{•−} \) after UV irradiation on PS. The sulfate radical generated by the activation of PS by ultraviolet light can degrade the organic pollutants well. Hori et al. [3] studied the photoactivated persulfate degradation effect of perfluorooctanoic acid. The results show that perfluorooctanoic acid can be completely degraded into non-toxic small molecules under UV irradiation.

Alkali activation refers to the process in which PS reacts with OH\(^− \) to form SO\(_4^{•−} \) under alkaline conditions. Currently, the generally accepted mechanism was proposed by Furman [4], HUANG et al. [5] found that under acidic and neutral conditions, PS was relatively stable, mainly producing SO\(_4^{•−} \). When pH > 8.5, SO\(_4^{•−} \) gradually turns into \( \cdot \text{OH} \). Under the strong alkaline condition of pH > 12, the degradation performance becomes stronger and stronger.

Transition metal ions activate PS by transferring an electron to break its O-O bond. When the molar ratio of transition metal ions to persulfate is 1:1, the activation effect is the best.

When the molar ratio of metal ions to persulfate is greater than 1, the degradation efficiency of organic pollutants will be reduced. This is because excessive metal ions will react with sulfate radicals generated.

Compared with other activation methods of PS, transition metal activation of PS has obvious advantages. However, some soluble transition metals are toxic and cause environmental damage and secondary pollution, which limits the application of this activation method. Therefore, the development of heterogeneous catalytic systems is the focus of current research. Anipsitakis et al. [6] used Co\(_2\)O\(_4 \), CoO and Co\(_2\)O\(_3 \) as heterogeneous catalysts to activate PMS, and the results showed that all three had certain effects.

A brief introduction to various advanced oxidation wastewater treatment methods is shown in Table 2.
| methods                      | Concepts and Principles                                                                 | Advantages and disadvantages                                                                 | Research Trends                                                                                  |
|------------------------------|------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|
| Wet Air Oxidation            | The chemical process of oxidizing organic pollutants to water, CO<sub>2</sub> or other inorganic substances and small molecular organic compounds in liquid phase under high temperature and pressure with oxygen or ozone as oxidant | It has good degradation effect for high concentration, high toxicity and high hazard organic wastewater, but the conditions are harsh | To find a catalyst with better cost performance to reduce the reaction conditions                  |
| photo-catalytic oxidation process | An advanced oxidation technique for •OH degradation of organic pollutants by irradiation of semiconductor catalysts with ultraviolet or visible light | The reaction speed is fast, the reaction time is short, the reaction condition is mild, the operation condition is easy to control, but the low efficiency of catalyst limits its application | Better catalysts and carriers should be selected to improve the efficiency of their utilization of light energy |
| Fenton and fenton-like methods | Under acidic conditions, organic wastewater was degraded by •OH using mixed solutions of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> | With high reaction rate and wide range of degradable substances, it is easy to cause secondary pollution due to acidic conditions | Fenton-like method with ultraviolet, ultrasonic and other methods                                 |
| Ozone oxidation method       | Under the combined action of catalysts or other conditions, O<sub>3</sub> molecules decompose to induce the production of •OH and degrade organic pollutants | The reaction conditions are mild, and there is basically no secondary pollution, but the degradation efficiency is low | Combined with H<sub>2</sub>O<sub>2</sub>, UV binding, improved catalyst and other technical methods |
| Advanced oxidation based on sulfate radical | Through various ways, persulfate is activated to produce sulfate radical, thus degrading pollutants | The degradation effect is good, the utilization rate is high, the condition is mild, the groundwater remediation effect is remarkable | The catalyst needs to be selected and improved to improve its activation performance and degradation effect |
4. Conclusion

The key of persulfate advanced oxidation technology is to efficiently and rapidly activate persulfate to produce sulfate radical to degrade organic pollutants. Common activation methods such as thermal activation, UV activation, alkali activation and transition metal activation can effectively activate persulfate, but there are some limitations in application: (1) Both thermal activation and photoactivation require additional energy, and low activation efficiency is difficult to meet practical application requirements under dark or low temperature conditions. (2) Alkali activation needs to consider the influence of alkaline conditions on the environment. (3) The pollution of heavy metal ions should be considered in transition metal ions and secondary pollution should be avoided. Therefore, the development of new activator with high efficiency, economy and environmental protection is the main research direction of persulfate advanced oxidation technology.

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