Research Progress of Advanced Oxidation Technology for Drinking Water Treatment

lixi LIU¹, zhili CHEN^{1*}

¹ Guilin University of Technology, Environmental Science and Engineering, 541006, Guilin, Guangxi

Abstract. Advanced oxidation technology is attracting attention as an effective method of water treatment that can degrade various organic pollutants. The combination of photocatalysis (UV) and ozone (O₃) and titanium dioxide (TiO₂) is a promising advanced oxidation technology. The combination of ozone, hydrogen peroxide, ultraviolet light and other oxidants for catalytic oxidation is also the current mainstream advanced oxidation technology. They can effectively degrade emerging water pollutants and alleviate water pollution problems. Titanium dioxide, hydrogen peroxide, and ozone are all popular catalysts because of their low cost, non-toxicity, strong oxidizing ability, and easy contact with various surfaces.

1 Introduction

At present, my country's water supply treatment process cannot effectively remove refractory organics in drinking water. Process technologies such as chlorine disinfection and ozonation usually produce some disinfection by-products such as organic halides and bromates, which are likely to cause secondary pollution problems. Ultraviolet disinfection has very low efficiency in removing organic pollutants. Emerging advanced oxidation technology can effectively deal with the difficult-to-degrade toxic organic pollutants treatment problem, and can bridge the gap between the maximum treatability achieved by traditional treatment processes and the increasingly stringent standard limits of environmental laws and regulations. High attention from environmental engineering scholars.

Advanced oxidation technology (AOTs) is a new technology developed on the basis of traditional chemical water treatment principles. Advanced oxidation processes (AOPs) are derived from advanced oxidation technologies (AOTs). Glaze proposed the generally accepted definition of advanced oxidation in 1987 and it was first applied to the degradation of organic pollutants in groundwater. After that, AOPs have been extensively studied in the field of water treatment. At present, most of the high-level oxidation processes successfully applied in water treatment are to use extremely oxidizing free radicals (OH[•], SO₄^{•-}, etc.) to finally mineralize organic pollutants with strong toxic and stable chemical properties in the water. It is CO₂, H₂O and other inorganic small molecular substances, or converts pollutants into low-toxic, easily biodegradable small molecular organic substances. And its reaction with organics has very low selectivity, and the overall rate constant is mostly 10⁸~10¹⁰M⁻¹·S⁻¹. Throughout the oxidation process, the advantages of AOPs, such as high efficiency, universal applicability and low secondary pollution, have gradually attracted people's

attention, and they hope to carry out more efficient and thorough oxidation.

2 Definition, classification and hazards of emerging pollutants

International organizations are dedicated to defining and characterizing emerging pollutants. "Emerging" refers to new pollutants found in aquatic media and organisms, or new characteristics and effects of compounds that already exist in the environment. Norman Network defined emerging pollutants as harmful substances detected in the environment in 2016. Currently, more than 1,000 substances can be detected, mainly in 16 categories: algal toxins, defoaming agents, complexing agents, antioxidants, detergents, disinfection by-products, plasticizers, flame retardants, fragrances, gasoline additives, nanoparticles, perfluoroalkylates substances, personal care products, pharmaceuticals, pesticides, preservatives.

For all emerging pollutants, their impact on the environment and human health risks have not been fully studied, but this issue has received extensive attention from various fields. Compounds that can be produced by the conversion of emerging pollutants through drinking water treatment processes may have higher toxicity, persistence and lower biodegradability than before. The most important environmental and human impacts of emerging pollutants are: bioaccumulation, persistence, toxicity, endocrine disorders, carcinogenicity, mutagenicity and teratogenicity. Some emerging pollutants may be harmful to humans and aquatic organisms, and have endocrine disrupting effects, leading to estrogen or hormone destruction, fetal malformations and even DNA damage.

* Corresponding author: zhilichen518@foxmail.com

3 Ultraviolet combined photochemical advanced oxidation technology

The photochemical advanced oxidation technology based on UV combined use includes photo-excited oxidation technology and photocatalytic oxidation technology. Among them, light-excited oxidation technology mainly uses H_2O_2 , Fenton, sulfate (SP), O_3 , HClO , etc. as oxidants, and generates strong oxidizing free radicals such as $\text{OH}\cdot$ and $\text{SO}_4\cdot^-$ under the action of UV radiation, and then Attack the refractory organic pollutants in the water, and finally mineralize them into small-molecule inorganic substances (CO_2 , H_2O , etc.).

Photocatalytic oxidation technology uses semiconductors in water as photocatalysts. When irradiated with UV energy equal to or greater than the band gap of the semiconductor catalyst, the semiconductor absorbs photons and causes photon transitions, thereby generating oxidizing holes (h^+) It is paired with reducing photogenerated electrons (e^-) to oxidize or reduce the water molecules, oxygen and other substances adsorbed on the surface of the semiconductor, and produce strong oxidizing $\text{OH}\cdot$, and finally realize the degradation and mineralization of organic matter.

3.1 UV/ H_2O_2

In the advanced oxidation process that combines UV and H_2O_2 , UV can directly photodegrade organic matter, and at the same time, the large amount of $\text{OH}\cdot$ produced by UV irradiation of H_2O_2 can efficiently oxidize difficult-to-biodegradable organic matter, so that the treatment of pollutants achieves an ideal effect. The UV/ H_2O_2 process has become a classic oxidation process in the field of water treatment due to its high degradation and mineralization rate, simple operation, and low secondary pollution. It has a high removal ability for a wide range of organic pollutants. TAK^[1] took anabaena toxin a as the target pollutant, and explored the degradation of anabaena toxin a by the UV/ H_2O_2 process under UV-A and UV-C UV wavelengths. The results showed that when $\text{pH}=6.7$, when the UV irradiance is 3.5 mW/cm^2 and the H_2O_2 dose is 0.01 mmol/L , the removal rate of anabaena toxin a can reach 99% when the UV-C/ H_2O_2 reaction reaches 30 minutes. Chuang^[2] compared the degradation of 26 kinds of low molecular weight halogenated disinfection by-products (DBPs) by UV direct photolysis and UV/ H_2O_2 process respectively. The data shows that UV/ H_2O_2 process can quickly decompose through electron transfer, addition, and hydrogen abstraction. Halogenated disinfection by-products, thereby greatly reducing the potential toxicity of DBPs in water treatment. It can be seen that the UV/ H_2O_2 process is an efficient treatment method for the treatment of toxic and emerging micro-polluting organic matter in the water supply.

The research on the combined UV/ H_2O_2 process has been relatively mature. At present, the process has achieved pilot scale applications. For example, PWN Technology Company in the Netherlands has achieved good treatment effects on the pesticides detected in drinking water such as polyacetaldehyde, clopyralic acid,

and propionic acid. (After treatment, the single mass concentration is close to the EU legislative allowable limit of $0.1 \mu\text{g/L}$). On the basis of the UV/ H_2O_2 process, a variety of degradation prediction models and economic evaluation methods have been developed and applied, such as the group contribution method (GCM), the unit electric energy method (EE/O), etc., to optimize the UV dose and H_2O_2 dosage. Dosage and other operating parameters to achieve the maximum economy and effectiveness of the actual application of the UV/ H_2O_2 process. The above research shows that the UV/ H_2O_2 process is feasible as a green and safe environmental water treatment technology, but the technology still faces many challenges in the practical application of degradation and removal of organic pollutants, such as H_2O_2 is easy to decompose and store Difficulty in transportation, scattering and high optical density effects caused by natural organic matter (humic acid, fulvic acid, etc.), inorganic anions (Cl^-), metal cations (Cu^{2+} , Ca^{2+} , Mg^{2+} , etc.) in the water body, alkalinity, hardness Inhibition of degradation rate. Taking appropriate technical means to solve the above-mentioned problems, so as to promote the in-depth research work of the UV/ H_2O_2 process in actual water samples, is the prerequisite for realizing the engineering application of this process in the water treatment industry.

3.2 UV/ TiO_2

The UV/ TiO_2 process is a typical representative technology of photocatalytic oxidation technology. The process relies on the aforementioned technical principles to generate hydroxyl radicals to rapidly degrade organic compounds in water, and can efficiently inactivate pathogenic microorganisms, which significantly improves the efficiency of water supply treatment. In this process, compared to UVC, UVA is widely used in TiO_2 photocatalysis research due to its small light scattering effect.

AUTIN^[3] explored UVA/ TiO_2 and UV/ H_2O_2 processes to degrade the polyacetaldehyde in surface water and synthetic water, and found that the UV/ TiO_2 process showed a partial mineralization effect on the polyacetaldehyde. This technology has been extensively studied in the field of drinking water treatment.

Most research experiments show that the UVA/ TiO_2 process has a significant removal effect on emerging organic pollutants (such as antibiotics) that appear in the water source, such as the use of UVA/ TiO_2 technology to treat sulfamethoxazole and trimethoprim in the background of pure water Pyridine, degradation data show that the chronic toxicity of the aqueous solution is significantly reduced and the residual antibacterial activity is reduced.

At present, most of the photocatalytic degradation for the treatment of refractory organics in drinking water is based on laboratory-grade water as the research background. However, when Li^[4] and others studied the effect of humic acid on the kinetics and mechanism of photocatalytic degradation of tetracycline, they found that humic acid can drastically reduce the treatment efficiency

of tetracycline by UVA/TiO₂, and propose the free radical scavenging effect of natural organic substances such as humic acid. At the same time, natural organic substances can also cause the surface deactivation effect of TiO₂ catalyst. It can be seen that the UVA/TiO₂ technology is extremely susceptible to the influence of water quality components in the treatment of organic pollutants.

In order to improve the catalytic activity and recycling capacity of TiO₂ catalyst in drinking water treatment, ARLOS [5] and others used H₂O₂ to assist the thermal oxidation of porous TiO₂ sheets to fix TiO₂. The H₂O₂/TiO₂ catalytic material obtained in this way is irradiated by UV at 365nm. The degradation effect of estrogen is very significant. Subsequently, a variety of TiO₂ supported materials (such as activated carbon, graphene) appeared. The research and development of new types of catalysts such as supported and doped catalysts have increased the scope of practical research and application of TiO₂ catalysts in the field of drinking water treatment to a certain extent, but at the same time it has also increased the cost of catalysts. Therefore, appropriate catalyst supports and doping are selected. Materials are of great significance to the realization of engineering applications of this technology.

The hybrid process generated by combining the UV/TiO₂ process with other water purification technologies has become one of the most concerned research directions in the field of environmental pollution control, such as UV/TiO₂-ultrafiltration membrane, UV/TiO₂-ultrasound, etc., showing Has a huge research potential. In addition, the heterogeneous oxidation system formed by the combination of H₂O₂, PS, PMS and other oxidants with photocatalytic systems, such as UV/TiO₂/H₂O₂, UV/TiO₂/PS, UV/TiO₂/PMS, etc., has shown great research potential. It is worth paying attention to in the one-step exploration work. However, most of the current UV/TiO₂ photocatalysis research is still on the laboratory scale, and there are relatively few researches on refractory organics in real water samples.

Table 1. Comparative analysis of UV/H₂O₂ and UV/TiO₂ processes

process	advantages	disadvantage	application
UV/H ₂ O ₂	Low cost, simple operation	The removal efficiency is not high	Industrial wastewater,
UV/TiO ₂	Low energy consumption, secondary pollution less	difficult to recycle, high cost	Industrial wastewater

4 Advanced Ozone Oxidation Technology

4.1 O₃/H₂O₂

As a kind of strong oxidation, hydrogen peroxide is often used in wastewater treatment. In wastewater treatment, hydrogen peroxide can promote ozone decomposition to produce non-selective OH· and then mineralize organic matter in the water. O₃/H₂O₂ has the advantages of mild

conditions and simple equipment, and can increase the biodegradability of water.

Peng [6] used the O₃/H₂O₂ process to degrade the pyrimidine wastewater. When pH=11, the ozone flow rate was 4 g/h, and the reaction time was 70 min, 50 mmol/L H₂O₂ was added. The removal rates of COD and pyrimidine were 74.97% and 86.46%, respectively. The addition of tert-butanol proves that the reaction is an OH· oxidation reaction, and the composite first-order kinetic model is studied by mechanics. Yu [7] studied the degradation experiment of 2,4-dichlorophenol by O₃/H₂O₂ process. The experiment showed that the presence of H₂O₂ greatly enhanced the degradation of 2,4-dichlorophenol by ozone. With O₃/H₂O₂ and pH in a certain range, the degradation effect is gradually improved. Experimental study 2, the degradation of 4-dichlorophenol is carried out step by step and finally degraded from OH· into small molecular organic acids. Byung [8] studied the degradation effects of advanced oxidation technologies O₃/H₂O₂ and UV/H₂O₂ on endotoxins. Experiments show that the OH· produced by AOPs technology has superior degradation ability to the endotoxin in the buffer solution, and the O₃/H₂O₂ technology is better than UV/H₂O₂. Advanced oxidation technology is a gentle and effective process for degrading endotoxins to eliminate E. coli in the sample.

4.2 O₃/UV

O₃/UV is an advanced oxidation technology that combines ozone and ultraviolet irradiation. Ozone degrades organic matter under ultraviolet light. In the reaction, it can produce OH· with stronger oxidizing ability, which can deeply mineralize organic matter in wastewater. Therefore, OH· degradation wastewater has been used in the degradation process of a variety of organic substances. Li [9] compared the degradation of salicylic acid (SA) synthetic wastewater by O₃, UV, and O₃/UV, and discussed the influence of ozone dosage, the initial pH value, and the reaction time. The experimental results showed that SA degradation by different methods the efficiency is O₃/UV>O₃>UV. When the dosage of ozone is 7 mg/L, the initial concentration of salicylic acid is 40 mg/L, and the initial pH=4, the degradation rate of O₃/UV is nearly 97% when the reaction is 15 min. And verified that the reaction mechanism is OH·. Cui [10] studied printing and dyeing wastewater under optimal conditions. The photocatalytic COD removal rate of ozone is 9% higher than that of pure ozone, and the biodegradability of water can be improved. The best ozone release intensity is 60%, HRT=21 min.

Table 2. Comparative analysis of O₃/H₂O₂ and O₃/UV processes

process	advantages	disadvantage	application
O ₃ /H ₂ O ₂	Increase biodegradability	Poor oxidation of halogenated hydrocarbons	refractory organic matter
O ₃ /UV	Deep mineralization of organic matter	Instrument is vulnerable, consumes energy	Dye wastewater

5 Conclusion

Compared with the conventional drinking water treatment process, the advanced oxidation technology based on the combination of UV/O₃ and catalyst has become a hot research topic in the field of water supply treatment at home and abroad because of its high efficiency, universality and thoroughness of oxidation. The strong oxidizing free radicals produced by this process can efficiently remove refractory organics to reduce their toxicity, can effectively deal with emerging pollutants in drinking water sources and control disinfection by-products, and can make up for the technical defects of other conventional water supply processes. However, advanced oxidation processes also have some shortcomings, such as oxidizers, high catalyst consumption, susceptibility to water quality, high operating costs, secondary pollution, etc. These disadvantages make the practical application of these processes subject to certain restrictions. Some results of these studies are summarized as follows:

(1) Carry out special research and development for new oxidants, catalysts and catalyst carriers that are cheap, stable and efficient, to reduce the application cost of this technology and increase the possibility of its practical application.

(2) Strengthen the research on the degradation kinetics and mass transfer mechanism of organic refractory pollutants based on actual water bodies, and provide references for evaluating the effectiveness and feasibility of advanced oxidation processes based on UV combined.

(3) Design and develop a systematic photoreactor that is suitable for different water quality conditions by combining UV and TiO₂ with advanced oxidation integrated process, focusing on exploring the efficiency of photoreaction instruments on the use of natural light such as sunlight, and promoting advanced UV-based combined use the oxidation technology realizes the practical engineering application.

(4) The combined use of ozone and UV/H₂O₂ has a better effect on the treatment of specific organic substances. With the in-depth study of catalysts, the combined use of transition metal ions and transition metal oxides and ozone will affect some high-stability organic pollutants (insecticides), Herbicides, and nitrobenzene and titanate) and other oxidation efficiency is significantly improved. Ozone can be combined with a variety of catalysts to treat more and more complex organic pollutants.

For the removal of difficult-to-degrade and toxic organic pollutants in drinking water, the advanced oxidation process based on the combination of UV/O₃ and catalyst has shown a broad research and application prospect. While in-depth understanding of the mechanism of this type of advanced oxidation technology, according to the water quality characteristics of different water bodies, selecting an appropriate oxidation process and other water supply treatment processes will be the mainstream direction of development in the field of water supply treatment.

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《Study on mechanism and method of space and aerial remote sensing for characteristic pollutants in low-carbon chemicals fires》(21976043)

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