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Application of Ozone-catalyzed Oxidation Process for Degradation of Pharmaceuticals and Personal Care Products

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Abstract

Pharmaceuticals and personal care products (PPCPs) continue to be detected in water sources with far-reaching negative impacts, and removing these emerging contaminants has become a top priority. Conventional water treatment technologies make it difficult to effectively remove these contaminants. As an advanced oxidation technology, ozone-catalyzed oxidation has attracted attention for its efficient degradation of PPCPs. This paper reviews the basic principles of the ozone-catalyzed oxidation process in removing PPCPs. Compared with homogeneous catalytic ozonation technology, multiphase catalytic ozonation technology has the advantages of easy recycling, lower cost of water treatment, higher activity, and improved mineralization of organic matter, etc., and these catalysts improve the removal efficiency of PPCPs by promoting the decomposition of ozone to produce reactive oxygen species (ROS). This paper also discusses typical examples of degradation of PPCPs by ozone-catalyzed oxidation processes, including gemfibrozil(GMF), ibuprofen (IBP), and ciprofloxacin (CIP). Finally, limitations of existing studies and future research directions are presented.

Keywords

Ozone; Catalytic Oxidation; Pharmaceuticals and Personal Care Products (Ppcps); Water Treatment Technology.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) are emerging micropollutants that are abundant in the environment. Even at low doses, they can cause adverse effects on ecosystems and human health. PPCPs are widely used in daily life, including various types of pharmaceuticals (e.g., antibiotics, non-steroidal anti-inflammatory drugs, anti-epileptic drugs, β-blockers, lipid regulators, etc.) and personal care products (e.g., perfumes, skin lotions, sunscreens, surfactant, etc.). Their presence in water bodies is mainly attributed to effluent from sewage treatment plants.

Studies have shown that ozone can react with a wide range of pollutants in water. However, due to its selective oxidation properties, the oxidation of some organic pollutants is relatively slow, resulting in low pollutant removal rates or the production of toxic intermediate substances. Moreover, during the degradation of some organic pollutants by molecular ozone, intermediates such as carboxylic acids and aldehydes accumulate, which cannot react with ozone, resulting in low mineralization efficiency. In addition, the low solubility of ozone in water reduces the efficiency of ozone utilization, leading to high operating costs. Catalyzed catalysts were used to solve the above problems, and an advanced ozone-catalyzed oxidation process was developed. Preliminary studies have shown that this process can remove organic compounds, including PPCPs, from wastewater with high degradation efficiency. In ozone-catalyzed oxidation, the addition of catalysts is expected to improve the decomposition of molecular ozone, generate highly reactive free radicals, and promote the adequate mineralization of PPCPs. Various metals, metal oxides, activated carbons, and minerals are used

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as catalysts to improve the removal efficiency of PPCPs. In addition, the addition of catalysts further improved the efficiency of ozone utilization.

2. Overview of Ozone Catalytic Oxidation Technology

Ozone is an unstable gas with a characteristic penetrating odour partially soluble in water. Ozone is also a powerful oxidizing agent with a redox potential in alkaline solutions of 2.07 V. Thus, ozone is capable of oxidizing a large number of inorganic and organic substances. In general, ozone oxidation of pollutants can occur in two ways: direct reaction of ozone molecules and indirect oxidation through hydroxyl groups produced by ozone decomposition. In order to make up for the shortcomings of the performance of ozone oxidation in the water treatment process, some catalysts are added to promote the decomposition of oxidizing agents (O3) to produce reactive radicals, such as hydroxyl radicals (-OH). Generally speaking, the ozone catalytic oxidation process can be divided into homogeneous catalytic ozone oxidation and multiphase catalytic ozone oxidation, depending on the different catalysts used in the system.

The ozone catalytic oxidation process can efficiently degrade difficult-to-degrade PPCPs through the synergistic action of ozone oxidation and catalysts; meanwhile, ozone catalytic oxidation has particular applicability to a variety of organic pollutants, including dissolved organics, volatile organics, and toxic organics, etc.

Ozone will be decomposed into oxygen in the catalytic oxidation process, and there is no problem of secondary pollution; ozone catalytic oxidation technology can be applied alone or in combination with other water treatment technologies to meet different water quality and treatment requirements.

3. Types of Catalysts and Mechanisms of Action

(1) Homogeneous Catalytic Ozonation

Homogeneous catalytic ozone oxidation is a catalytic reaction carried out in solution, in which both the catalyst and the reactants are in the same phase. Commonly used catalysts include transition metal ions Mn, Fe, Co, Cu, Ni, Zn, Cr, Ce, etc., which are completely soluble in aqueous solution and can react with ozone and promote its decomposition to produce reactive oxygen species.

(2) Heterogeneous Catalytic Ozonation

Heterogeneous catalytic ozone oxidation uses solid-state catalysts that are immobilized on solid carriers in different phases from the reactants. The catalysts promote ozone decomposition by providing surface active sites to generate ROS, which oxidize organic pollutants. Commonly used catalysts include the following:

Metal oxides: These include Fe2O3, CoO, MoO3, CuO, NiO, Al2O3, MnO, ZnAl2O4, CuFe2O4, CoFe2O4, Mn-Ce-O, etc., which act as solid-state catalysts to provide surface active sites to promote ozonolysis.

Carbon-based materials: These include activated carbon (AC), carbon nanotubes (CNTs), multi-walled carbon nanotubes (MWCNTs), graphene (GO), etc. These carbon materials excel in catalytic ozonation due to their high specific surface area and electrical conductivity.

Metal/metal oxide supports: These include Fe-MCM-48, Mn-CeO/-Al2O3, Ce/SBA-15, B-FeOOH/Al2O3, CeO2-OCNT, etc. These catalysts are made of metal or metal oxides loaded on various support materials to improve their dispersion and stability.

The homogeneous catalysts are easy to mix with the products after the reaction and are challenging to separate. In contrast, the multiphase catalysts can be separated from the reaction system after the reaction by simple filtration or sedimentation methods due to their solid state

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characteristics, which are easy to recover and reuse. Therefore, the research of multiphase catalytic ozone oxidation has received more and more attention.

4. Example of a Study on the Degradation of PPCPs by Ozone-catalyzed Oxidation

As an advanced oxidation technology, studies have shown that the ozone-catalyzed oxidation process shows excellent potential in degrading and mineralizing typical PPCPs.

Pan et al. assessed drug contamination at the Shangxi Drinking Water Treatment Plant (DWTP) in Zhejiang Province, China. They verified the feasibility and efficiency of catalytic ozonation for removing the anticancer drug Gemfibrozil (GMF) in a pilot-scale test. The results showed that the concentrations of ibuprofen (IBP) and propranolol (PLB) were effectively controlled under the existing water treatment process in different treatment units of the DWTP. However, GMF's removal efficiency was low. Pilot-scale tests showed that the removal efficiencies of 3.6 min ozonation treatment for GMF ranged from 21.1-67.9%, whereas ceramic catalyst ozonation-catalyzed oxidation treatment significantly improved the removal efficiencies to 55.6-85.2%. GMF has two degradation pathway strips in the catalytic ozonation process, firstly, through the reaction of hydroxyl radical (-OH) with aromatic ring C2; secondly, through the attack of hydroxyl radical (-OH) on aromatic ring C3.

Ibuprofen (IBP), which belongs to non-steroidal anti-inflammatory drugs (NSAIDs), is one of the most representative PPCPs and one of the most widely used analgesic drugs in human beings and is widely present in water bodies. The inefficiency of its degradation by the traditional methods has led to the development and utilization of ozone-catalyzed oxidation (OCO) technology. The CeOx/MnOx/C-MOF catalyst was constructed by interfacial oxidation reaction to create electron-deficient/enriched centres in a carbon skeleton (C-MOF) derived from a metal-organic framework (MOF), taking advantage of the electronegativity difference between cerium (Ce) and manganese (Mn). It was subjected to ozone-catalyzed oxidation for the degradation of IBPs.The study showed that the CeOx/MnOx/C-MOF/ O3 system achieved 100% IBP removal within 90 min, significantly better than ozonation alone and other catalytic ozonation processes. pH had a significant effect on the removal efficiency of IBP, with the highest removal efficiency at pH 5.

Antibiotic contamination in water bodies is a serious problem, especially fluoroquinolone antibiotics, such as ciprofloxacin (CIP), which are of great concern due to their widespread presence in the environment and potential ecological risks. Developing novel and efficient water treatment technologies to remove these structurally stable compounds is essential. A magnetic Ce-Zr bimetallic organic framework (MOF) complex (Fe3O4/CeZrUiO-66) was prepared as an efficient catalyst in the catalytic ozonation process. The complex was prepared by an interfacial oxidation reaction, which utilized the high specific surface area and designability of MOF and enhanced the electron transfer ability of the catalyst through bimetallic doping, thus significantly improving the catalytic ozonation efficiency. The experimental results showed that Fe3O4/CeZrUiO-66 exhibited excellent CIP degradation efficiency in the catalytic ozonation process, and a removal rate of 94% could be achieved in 30 min, which was significantly higher than that of 40.8% in the ozonation process alone. In addition, the catalyst showed a good mineralization effect, with a CIP mineralization rate of 54%.

5. Conclusion and Perspectives

So far, various catalysts have been studied for the catalytic oxidation process of ozone. However, some catalysts have complex processes and harsh synthesis conditions, which are not

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conducive to mass production and industrial applications. In addition, although some materials perform well in catalytic ozone oxidation systems, the reuse and stability of catalysts have not been sufficiently studied. Therefore, cheap, stable and reusable catalysts are needed. On the other hand, a systematic method for evaluating the performance of catalysts should be established.

The application of ozone-catalyzed oxidation processes for treating personal care products is still relatively small and needs further exploration.

The ozone-catalyzed oxidation process may alter the mechanisms and types of DBPs formed, with specific catalysts facilitating the reaction of ozone with PPCPs in water, thereby reducing the formation of some specific DBPs but, at the same time, potentially increasing other types of DBPs.

Combining ozone with other treatment technologies has been extensively studied. However, how the characteristics of the combined system can enhance or limit individual and overall efficiencies and control the cost of the overall treatment system in practical applications requires further research.

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