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Research Progress on Catalytic Ceramic Membrane Degradation of Phenol Containing Wastewater

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Abstract

In recent years, ceramic membrane supported catalysts for catalytic ozonation have made certain progress in the treatment of organic wastewater. This process has the advantages of simple operation, high oxidation efficiency, high catalyst utilization, ceramic membrane resistance to pollution, and no secondary pollution. However, the large-scale promotion and use of this process still rely on the development of highly active and stable heterogeneous catalysts. Therefore, it is crucial to summarize the development status of ceramic membrane supported ozone catalysts at home and abroad in recent years. This article first summarizes the recent research on catalytic membranes; Secondly, the production method of catalytic ceramic membrane is elaborated; Finally, the research significance of catalytic ceramic membranes is discussed.

Keywords

Ceramic Film; Ozone Catalysis; Catalyzer; Phenolic Wastewater.

1. Introduction

With the rapid development of industrialization in our country, the consumption of clean water has increased rapidly, while the discharge of industrial sewage and wastewater has also increased sharply. Phenolic wastewater is a major category of industrial pollution, mainly present in the emissions of various industries such as coking, petroleum, paint, etc. Due to the diverse industrial fields involved and the large water consumption of related industries, phenol containing wastewater has a wide range of sources, complex components, and a large pollution area. This type of wastewater has strong toxicity. Once directly discharged without corresponding treatment, it will pose great harm to the living environment and healthy growth of various organisms and even humans[1]. Therefore, seeking suitable methods to achieve efficient treatment of phenol containing wastewater has always been a research hotspot in recent years.

At present, most sewage treatment plants in China often use chemical methods, physical methods, biochemical methods, etc. when treating sewage. And the advanced oxidation technology in chemical methods has attracted widespread attention from many scholars [2]. Advanced oxidation technologies include ozone oxidation, wet oxidation, Fenton oxidation, photocatalytic oxidation, electrocatalytic oxidation, etc. The use of advanced oxidation methods greatly improves the removal rate of difficult to degrade pollutants such as colloids and dissolved substances in wastewater.

However, using advanced oxidation alone is not enough to achieve national standards for effluent quality, so combining advanced oxidation with other treatment processes will be more practical. Taking ozone oxidation technology as an example, this technology is based on the strong oxidizing property of ozone (redox potential of 2.07V) to oxidize and degrade organic matter in wastewater. Due to its advantages of easy operation and low operating costs, it is widely used in the field of industrial wastewater treatment. However, it has problems such as low ozone utilization rate and inability to deeply mineralize organic matter. In recent years, membrane separation technology has received widespread attention as an energy-saving and environmentally friendly efficient separation technology. It achieves effective filtration of pollutants based on different pore sizes. Among them, ceramic membranes have attracted more and more attention due to their higher mechanical strength and chemical stability compared to traditional polymer membranes[3]. However, organic matter inevitably adheres and deposits on the membrane surface or pores during the membrane separation process, making membrane fouling a major obstacle to the development and application of membrane technology. Research has shown that combining ozone oxidation with membrane separation technology, using ceramic membranes as ozone catalysts or catalyst carriers, can effectively accelerate ozone decomposition, generate highly oxidizing hydroxyl radicals (•OH), and degrade organic wastewater, while achieving the goal of alleviating membrane pollution. Therefore, several catalysts were selected to be loaded onto ceramic membranes, taking into account issues such as pollutant removal efficiency, operating costs, and catalyst recovery. The most suitable catalyst was chosen to complete the loading of the ceramic membrane on the catalyst, and the experimental rationality, catalyst recovery issues, and stability of the coupling technology were studied.

2. Research Progress of Catalytic Ceramic Membranes

The combination of catalytic ozone oxidation technology and ceramic membrane separation technology can achieve simultaneous separation and decomposition of organic pollutants, which not only improves the removal efficiency of organic pollutants, but also helps alleviate membrane fouling. It has potential application value in the treatment of low concentration and high toxicity wastewater and micro polluted surface water. Currently, research in this field has gradually become a new hotspot. Hyung et al. [4] applied ozone oxidation as a pretreatment for membrane separation technology in the treatment of drinking water. By adjusting the ozone dosage and pollutant concentration in the raw water, it was found that ozone oxidation can significantly improve the membrane's anti pollution ability and increase the removal rates of UV_{254} and trihalomethanes. Lehman and Zhu et al. applied the coupling technology of ozone pretreatment and ceramic membrane separation to the treatment of secondary effluent from wastewater. The experimental results showed that the addition of ozone could maintain a high membrane flux, reduce the number of backwashing or chemical cleaning, and prolong the service life of the membrane during long-term operation. Janknecht et al. designed an ozone membrane coupling process using ceramic membranes as ozone distributors. Ozone gas and water pass through both sides of the ceramic membrane, and the ozone is dispersed through the ceramic membrane before coming into contact with the water, reducing the size of ozone bubbles and facilitating the dissolution of ozone in the water, thereby enhancing the removal efficiency of pollutants. Heng et al. [5] established another novel reactor structure using ceramic membranes as carriers for ozone catalysts. Ozone and water are mixed and reacted in contact within the membrane, and the products are separated by a zeolite membrane layer. This design effectively utilizes the catalyst loading capacity of the ceramic membrane support layer and improves the catalytic ability of the membrane structure through modification of mesoporous catalysts, providing new ideas for the development of ozone membrane coupling processes with ceramic membranes as the main unit. Karnik and Corneal loaded catalysts (MnO_2, Fe_2O_3, Tio_2) onto the surface of ceramic ultrafiltration membranes through layer by layer deposition, achieving the catalytic function of ceramic membranes, improving the utilization efficiency of ozone, and enhancing the production of hydroxyl radicals in the reaction system. The experimental results showed that this coupling process can not only effectively improve water pollution in the treatment of drinking water, but also increase the removal rate of humus in the water, and effectively kill pathogenic bacteria in the water. By coupling catalytic ozone oxidation with reverse osmosis technology, experimental results show that catalytic ozone oxidation technology can be used as an effective technique for treating intercepted pollutants in membrane separation processes. It can not only improve membrane fouling, but also effectively remove organic pollutants in the concentrated phase.

3. Preparation Method of Catalytic Ceramic Membrane

The current technology for preparing ceramic membranes mainly includes two types: one is membrane surface coating technology, and the other is to infiltrate the catalyst into the membrane substrate. Due to the difficulty of embedding the catalyst into the membrane matrix, the overall catalytic activity of the prepared catalytic membrane is limited; In addition, integrating catalysts into the membrane matrix may impair the performance and functionality of the original membrane, such as physical structure, porosity, mechanical strength or elasticity, and chemical selectivity. Therefore, surface coating of catalysts is often an ideal method for preparing catalytic membranes, which not only allows the catalyst to be directly exposed to the system with reactants, but may also improve mass transfer and reaction rates through forced convection effects. So far, various surface coating technologies for innovative and intelligent catalytic membranes have been developed. However, a comprehensive review of these surface coating technologies is still lacking, and more importantly, due to the complex procedures and some negative effects on membrane permeability or catalyst activity, coating catalysts on membrane filtration materials seems immature and cannot achieve industrial mass production [6].

3.1. Surface Coating Method

Surface coating refers to a method of coating catalyst solution, suspension or colloidal particles on the surface of a membrane to achieve surface functionalization. Coating methods typically include spin coating, immersion deposition, and vacuum filtration. The prepared membrane flux, anti fouling ability, and catalytic performance are significantly correlated with the type of catalyst coated, the surface roughness of the base film, and the coating method. The spin coating process can be controlled by adjusting the rotation time, speed, solution concentration, and viscosity. Zhao et al. used a mixture of copper nitrate, iron nitrate, citric acid, and ethylene glycol with a molar ratio of 1.0:2.0:3.6:7.2, spin coated at 300r/min for 12 seconds, and then calcined at 500 ℃ to obtain $CuFe_2O_4$ catalytic ceramic film. It couples with persulfate to degrade humic acid (HA), significantly increasing efficiency by 70%. Immersion deposition is the process of immersing a base film in a prepared catalyst solution or suspension, and connecting the catalyst through physical adsorption or chemical bonding[7].

A catalytic film is formed on the surface of the membrane. The base film is generally made of ceramic film, but PVDF film, polypropylene (PP) film, polyacrylonitrile (PNA) film, or nylon film can also be used. The catalyst loading can be adjusted by immersion time, immersion frequency, and immersion solution concentration. Bao et al. successfully prepared $CoFe_2O_4/Al_2O_3$ ceramic membranes by immersing Al2O3 ceramic membranes in a mixed solution containing urea, $Co(NO_3)_2 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$ for 30 minutes, followed by calcination. The membranes exhibited excellent catalytic activity and permeation flux. Catalytic ceramic membranes not only have higher permeation flux and superior anti fouling ability, but also have excellent high temperature resistance, solvent resistance, and acid alkali corrosion resistance. However, due to the high cost of preparing ceramic membranes, their application is limited. The vacuum filtration method involves a negative pressure state (vacuum) on one side of the filter medium, and the filtrate is separated into solid and liquid through a membrane, leaving the catalyst on the membrane surface. Vacuum filtration usually requires drying treatment to remove residual water from the catalytic membrane. Bao et al. prepared $Fe_2O_3/TiO_2/GO$ photocatalytic membranes through vacuum filtration and found that the catalytic degradation performance of the membrane was optimal when the molar ratio of Fe_2O_3: TiO_2: GO was 50:100:5. The spin coating method for preparing catalytic membranes by surface coating is simple and the coating thickness is uniform. However, it is only suitable for simple planar base films and cannot be coated with film materials with complex geometric shapes. The immersion deposition method is simple to operate and the preparation conditions are easy to control. However, due to the limitation of the "wedge effect", the thickness of the catalytic film is uneven. Moreover, the catalyst may detach from the membrane surface, leading to a gradual decrease in the catalytic performance of the catalytic membrane during long-term operation. The vacuum filtration method has a simple process and fast manufacturing speed, but its high energy consumption limits its use [8].

3.2. Sol Gel Method

Sol gel technology is a well researched technology to synthesize solid materials from small molecules. It usually starts from the hydrolysis of liquid precursor (sol) and forms gel through polycondensation. A typical sol-gel process consists of four stages, including: (1) hydrolysis, (2) monomer condensation to form chains and ions, (3) particle growth, and (4) tight aggregation of polymers. Mamane et al. used the sol gel technology to coat the N-doped TiO_2 photocatalysis film on the commercial α-Al_2O_3 photocatalysis film, while performing bottom-up filtration and photocatalytic oxidation. 80% of the membrane surface is covered by N-doped TiO_2 film, but it reduces the permeability of the membrane substrate by more than 50%. However, the superior photocatalytic activity of the "in pore" catalyst significantly increased the degradation rate of carbamazepine (90%), as it promoted the contact between molecules and active sites in the flow mode. Grilli et al. [9]deposited a thin photocatalytic active coating of N-doped TiO_2 onto Al_2O_3 film through the sol-gel process. The results showed that the degradation rate of carbamazepine (CBZ) by the photocatalytic film was 58.6%, while in the absence of photocatalytic degradation, the adsorption and removal of CBZ by the N-doped TiO_2 coating film could be neglected. However, sol gel technology is usually time-consuming and not cost-effective in industrial production. In addition, the sol-gel coating may be affected by delamination, cracking and adhesion limits. For example, cracks and large capillary stress are caused by the shrinkage of wet gel after drying, which makes it difficult to form large blocks. In addition, when drying or sintering is incomplete, organic matter or carbon residues may be left behind, which can have a negative impact on the quality of the coating [10].

3.3. Chemical Vapor Deposition Method

Chemical vapor deposition (CVD) is a popular surface coating technique suitable for various applications, in which volatile coating precursors are evaporated in an inert atmosphere through heating, light, and/or plasma discharge, and then react on a solid substrate surface to produce the desired deposition. The modification process is similar to PVD technology, except that the precursor in CVD is usually in an evaporated state (as a compound), while the precursor in PVD is usually in an elemental state (as a pure metal), with no chemical reaction on the surface [11]. CVD has become one of the most promising technologies for large-scale production of functional materials such as semiconductors, optics, and electronics, and provides excellent control over coating properties such as thickness and density. In addition, CVD can coat functional layers at the nanoscale and typically does not involve the use of various toxic organic solvents (especially suitable for insoluble material coatings). CVD is one of the most promising and extensively studied methods for depositing catalysts onto films. Itoh et al. reported a catalytic palladium membrane prepared by CVD for the reduction and oxidation of benzene to phenol. The membrane activates hydrogen atoms to react with oxygen molecules, generating reactive free radicals that further attack benzene for hydroxylation. According to reports, the yield of phenol has increased by over 20% and the selectivity has increased by 77%.

Photocatalysts such as ZnO and TiO_2 have also been successfully deposited on inorganic films by CVD for advanced oxidation processes. For example, Athanasekou et al. developed a composite photocatalytic ultrafiltration membrane by coating TiO_2 nanoparticles on a gamma alumina film through chemical vapor deposition layer by layer (LBL/CVD). In the layer by layer CVD process, titanium tetraisopropoxide and oxygen are used as TiO_2 precursors and oxidants, respectively. The retention rate of methyl orange by the dual function ultrafiltration membrane/photocatalytic composite membrane under ultraviolet light is 5 times that of the nanofiltration membrane.

4. The Significance of Catalytic Ceramic Membrane

The ceramic membrane supported catalyst process has broad application prospects in the treatment of wastewater. The deep decontamination technology of organic wastewater combining catalytic membrane and AOPs has become a cutting-edge technology in sewage treatment. The catalytic membrane/AOPs system can not only reduce membrane fouling, but also significantly improve the degradation of pollutants in wastewater. In addition, the catalytic membrane can be directly recycled and reused, making it less prone to secondary pollution. Currently, heterogeneous catalysts can still achieve good treatment effects for wastewater by catalyzing ozone, especially supported catalysts have shown excellent catalytic efficiency. However, finding suitable ozone catalysts and ceramic membrane loading methods is still the main focus of this process. Issues such as catalyst particle size, loading stability, and loading uniformity urgently need to be addressed. Additionally, due to the complex reaction mechanism of the ceramic membrane loaded catalyst system, optimizing this process will be difficult. Therefore, these will be urgent issues that need to be addressed in future research and development in this field.

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