Study on Catalytic Ozone Oxidation with Nano-TiO₂ Modified Membrane for Treatment of Municipal Wastewater

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This study reports the application of nano-TiO₂ modified membrane technology in municipal wastewater treatment. Ozone aeration can produce a large numbers of high oxidizing free radicals (hydroxyl radical HO·) to degrade organic matters when ozone contacts with nano-TiO₂ modified membrane. This is called catalytic ozone oxidation process. This approach is a new frontier of municipal wastewater treatment, which has excellent reactive activity and degradation of organic compounds without the need for catalyst recycling. Our purpose is to remove organic matters by ozone aeration pre-treatment and nano-TiO₂ modified membrane. In this study, municipal sewage is raw water, polyvinylidene fluoride (PVDF) and the nano-TiO₂ modified polyvinylidene fluoride ultra-filtration membranes are experimental materials. Results suggest that new method (TiO₂ + O₃) removal rate of organic matters is 66.4 %, which is 13.3 % higher than original membrane with O₃ (PVDF + O₃) under the same condition. Compared with traditional polyvinylidene fluoride membrane filtration whose removal rate is 38.7 %, this novel approach is 27.7 % higher.

Keywords: Catalytic ozone oxidation, Modified ultra-filtration membrane, Nano-TiO₂, Membrane fouling.

INTRODUCTION

In recent decades, membrane separation technology as one of new high-efficiency separation techniques has developed rapidly. Compared with traditional separation techniques (UF, MF, MBR), it is highly efficient, energy-saving and easy to operate. Membrane separation technology has been widespread used and considered to be "one of the most promising high-techs from 20th century to the 21st century medium-term"¹.

In the past decades, many reports indicated that ozone was used as pretreatment because of its strong oxidizing property², but this process is expensive and difficult to control³. Currently, several studies used catalytic ozone oxidizing with metal oxides as catalysts for ozone degradation of water is a new trend of advanced oxidation technology⁴.

Polyvinylidene fluoride (PVDF) ultra-filtration membrane is in good chemical stability and fiber durability, which is widely used in membrane separation. Nano-TiO₂ modified membrane is a new membrane of nano-TiO₂ coating on constituent particles of the PVDF membrane through micro-electrophoresis, which can catalyze ozone to produce a large numbers of high oxidizing free radicals (hydroxyl radical HO·)^{5,6} to degrade organic matters inside/on the surface of membrane. In addition, the product of ozone oxidation is oxygen, accordingly catalytic

ozone oxidation reaction is highly active and without secondary pollution oxidants⁷. This experimental application of catalytic ozone oxidation in water treatment is mainly based on characteristics such as strong oxidizing property and non-secondary pollution.

In this paper, we use the a new method of catalytic ozone oxidation with nano-TiO₂ modified PVDF membrane for treatment of municipal wastewater. The research puts emphases on two aspects as follows: (1) Analyze molecular weight distribution of organic matters in different water samples by molecular sieving membrane, compare efforts of removal rate of catalytic ozone oxidation approach with traditional ones and (2) Characterize the mechanism of catalytic ozone oxidation by molecular weight distribution.

EXPERIMENTAL

Mechanism of ozone oxidation for degradation of organic matters

Ozone oxidation: Ozone is a strong oxidant, research shows that ozone has strong oxidizing property and fast reaction ability, in the treatment of industrial wastewater. Ozone oxidation is available for a variety of organic compounds. Why dose ozone have such a strong oxidizing property? Because

the oxygen atom in the molecule has strong electrophilicity or protophilia and the nascent oxygen atom which ozone decomposition produced also has high oxidation activity⁸.

In aqueous solutions, ozone reacts with organic compounds in two ways⁹: ozone molecules direct attack and the free radical reactions by decomposition of ozone.

Reactions of molecular ozone: Ozone has triangular molecular structure, central oxygen atom has equidistant distance between the other two oxygen atoms and there is a domain key (π) in the molecule, this special structure allows itself to be used as ozone molecules dipole reagent, nucleophilic and electrophilic reagents¹⁰. Reactions of ozone with organic compounds are divided into three categories¹¹.

(a) Addition reactions (opening double bond): Because ozone has a dipole structure, so it can happen to 1- β key dipolar cycloaddition reaction with the unsaturated organic compounds, ozone-forming of intermediate products and further broken down to form aldehydes, ketones and other carbonyl compounds.

(b) Electrophilic reactions: Electrophilic reactions happen in the high density point of molecular electron cloud. For aromatic family compounds, when the replaced group is electronic giving group ($-\text{OH}$, $-\text{NH}_2$) and C nearby has high electronic cloud density, ozone oxidation usually occurs in these locations. When the replaced group is electronic catching group ($-\text{COOH}$, $-\text{NH}_2$), ozone has weak oxidation ability.

(c) Nucleophilic reaction: Nucleophilic reactions only occur on the C with the electronics catching group. The reaction of ozone has strong selectivity, only occurs on unsaturated aromatic, aliphatic compounds and particular groups.

Free radical reaction: The stability of ozone has relationships with pH, UV, ozone concentrations and the capture concentration of free radicals. The formation of free radicals depends on the ozone decomposition which causes free radical reactions¹².

Ozone decomposition reaction carried out in a chain reaction, involves the following basic steps. Free radicals reaction is the rate-limiting step. In addition, the steps of producing and HO_2 are also important, because these substances can increase the stability of ozone in the water. This machine includes a two-electron transfer process or one oxygen atom transfers from the ozone molecule to hydrogen peroxide ion processes.

Experimental design and method

In the research, experimental devices are divided into three main groups, as shown in Fig. 1 for membrane filtration, Fig. 2 for ozone aeration pretreatment of raw water, Fig. 3 for molecular weight sieving, respectively.

The experimental device is shown in Fig. 1. It is used for raw water filtration and the water filtration after ozone aeration pretreatment.

Experimental device (Fig. 2) used for raw water ozone pretreatment. It can reach the target of pretreatment by ozone aeration gas processing removal part organic matters, meanwhile, extra ozone can also dissolve in the water and through the pipe. Catalytic ozone oxidation with nano- TiO_2 modified membrane will remove organic matters that stick to the membrane (physical trapping and catalytic ozone oxidation).

Fig. 1. Membrane filtration device-water sample goes from 1 to 3 by 2. There is a piece of membrane (PVDF/ nano- TiO_2 modified) in 3. The organic matters will be trapped and get into 4 and the filtrated water will be collected in 5

Fig. 2. Raw water ozone aeration pretreatment- The oxygen goes from 1 to 3 and 3 converts oxygen to ozone. There are ozone and water sample mixture in 4

Device shown in Fig. 3 is mainly used for molecular sieving with raw water and percolates after different membranes (PVDF and nano- TiO_2 modified membranes). In the research, we use molecular sieve membranes of different apertures in order to trap organic matters of different molecular weights. In the end, molecular weight distributions are determined by COD_{Mn} ¹³.

We sieve molecular weight distributions by plate Ultra-filtration membranes in different pore sizes as Table-1.

TABLE-1
MATERIAL AND MOLECULAR WEIGHT
CUT-OFF OF THE MEMBRANE

Membrane size	Material	Range of molecular wight, Dalton
0.45 μm	Cellulose acetate	Diameter > 0.45 μm
100,000 (100 K)	Polysulfone	> 100,000
30,000 (30 K)	Polysulfone	> 30,000
10,000 (10 K)	Polysulfone	> 10,000
3000 (3 K)	Polysulfone	> 3000
1000 (1 K)	Polysulfone	> 1000

Note. 1 Daltan (Da) = 1.66×10^{-27} kg

1. Nitrogen cylinder; 2. Screening equipment; 3. Molecular sieve membrane

Fig. 3. Molecule sieve device-water sample is filtered under the pressure of nitrogen, with the aid of membranes in different sizes. Molecular weight distributions of water sample can be exhibited

Analysis method of the molecular weight distribution of water: On the first stage, Fig. 1 showing, we filter raw water (water in wastewater treatment plant after primary treatment, meaning sinking sand and primary sedimentation) directly by PVDF membrane and TiO₂ modified membrane until the membrane is blocked up and then trap percolates through molecular sieve membranes of 1, 3, 10, 30 and 100 kDa apertures, respectively. After that, we determine COD_{Mn} of percolates. On the second stage, as Fig. 2 showing, under the operating condition of 1.34 mg/L ozone dosage and after aeration of 5 min, we make the samples go through PVDF and TiO₂ modified membranes and repeat the first stage experiment after this ozone aeration pretreatment.

Identification of catalytic ozone oxidation function: In order to confirm the effect of catalytic ozone oxidation, we performed comparison experiment on PVDF + O₃ and (TiO₂ + O₃) as Fig. 2 and under the operating condition of 1.34 mg/L ozone dosage from 0 to 10 min. We recorded the COD_{Mn} removal rate per 2 min. Under the same condition, we added tertiary butyl alcohol (an inhibitor of HO[•]) to avoid the reaction of catalytic ozone oxidation. Catalytic ozone oxidation function can be verified from both above comparison experiments.

RESULTS AND DISCUSSION

The molecular weight distribution of organic matters is shown in Fig. 4 as follows: According to Fig. 4, in the raw water, the main organic matters are centered on >100 k and 30 k-100 k scales and COD of raw water reduced 2.5 % by ozone aeration treatment, so we can infer that, after a short time, the ozone aeration does not reduce the COD significantly. As shown in Fig. 4, the large organic matters reduces while the small ones get increased and the >100 kDa ones make the main contribution to COD reduction. Meanwhile, the 3 k to 100 k ones grow and others are not very obviously. That is mainly due to the strong selectivity of ozone reaction. This

effort is only limited to unsaturated aromatic, aliphatic compounds and certain special groups. But ozone has little effect on low molecular weight organic acids such as acetic acid, various types of compounds such as alkanes which almost have no response¹⁴. Thus, molecules of ozone play the main role in pre-treatment. This process is affected by ozone aeration time and concentration strongly.

Fig. 4. COD_{Mn} of different levels of treatment of water as a result of molecular sieve membranes

After filtration of PVDF membrane, the reduction of COD in raw water is only 27.6 %, but we can find the concentrations of macro-molecular organic compounds (mainly in molecular weight between >100 kDa, 30 to 100 kDa organic compounds) reduce significantly. Therefore, traditional membrane filtering only has effect on large molecular weight organics, but the membrane fouling occurs soon, membrane pore is blocked, that means PVDF membranes need to clean or replace frequently.

After ozone aeration pre-treatment, removal of COD is obviously (above 50 %). Organic compounds of molecular weight > 100 kDa reduce obviously (84.8 %), the removal rate of smaller organic compounds (molecular weight 30 kDa-100 kDa) reaches 45.9 %. Ozone makes macro-molecules organic compounds degrade into smaller ones. That is why organic compounds of > 100 kDa removal rate rises significantly. Additionally, organic compounds of 30 to 100 kDa and 10 to 30 kDa can be removed by PVDF membrane mostly. Micro-molecules and macro-molecules degradation organic compounds (< 10 kDa) can not be removed by PVDF membrane clearly.

After filtration of nano-TiO₂ modified membrane, COD of raw water totally fell 42.4 %. TiO₂ modified membrane can remove organic matters of molecular weight above 10 kDa mostly while it has only a little effect on smaller ones (< 10 kDa).

After ozone aeration pre-treatment and filtration of nano-TiO₂ modified membrane, we can gain the best removal result of organic matters-total removal rate reaches 66.4 %. Compared with PVDF + O₃, total removal rate rises 13.3 %. It is suggested that the contribution comes from catalytic ozone oxidation on TiO₂ modified membrane. That is because after ozone aeration, there is still some ozone dissolved in the water.

When dissolved ozone goes through TiO_2 modified membrane, catalytic ozone oxidation helps to degrade organic matters. Compared with molecular ozone oxidation, ozone catalytic oxidation is speedy, full and non-selective. This process ($\text{TiO}_2 + \text{O}_3$) is better than others (raw water + O_3 , PVDF, PVDF + O_3 , TiO_2). There may be two processes existed in nano- TiO_2 catalytic ozone oxidation process: (1) Nano-organics adsorbed on the surface. Adsorptive organic molecules, due to the changes in the electron cloud distribution, are easily to be oxidated. (2) Nano- TiO_2 catalytic ozone oxidation produces more $\text{HO}\cdot$, which is useful to removal of more organic matters than molecular ozone oxidation.

Fig. 5 verifies the effect of catalytic ozone oxidation as follows: as the input of ozone aeration is increased, the removal rate of organic matters climbs up, which confirms that ozone can remove organic matters effectively. Meanwhile, process ($\text{TiO}_2 + \text{O}_3$) is better than PVDF + O_3 under the same consideration which means that catalytic ozone oxidation has contributed that part.

Fig. 5. COD_{Mn} removal rates of PVDF + O_3 and $\text{TiO}_2 + \text{O}_3$ vs. ozone aeration time

With the addition of tertiary butyl alcohol, there is not clear different between PVDF + O_3 and $\text{TiO}_2 + \text{O}_3$ as Fig. 6 showing. Without free radical reaction of $\text{HO}\cdot$, there is only reaction of molecular ozone in the water samples. This result proves our opinion that catalytic ozone oxidation process did take place and remove organic matters effectively.

Conclusion

After ozone aeration pre-treatment and filtration of nano- TiO_2 modified membrane, we can gain the best removal result of organic matters-total removal rate reaches 66.4 %. Compared with PVDF + O_3 , total removal rate rises 13.3 % under the same condition.

Fig. 6. COD_{Mn} removal rates of PVDF + O_3 and $\text{TiO}_2 + \text{O}_3$ with the addition of *tert*-butyl alcohol

It is verified by comparison experiments that new method ($\text{TiO}_2 + \text{O}_3$) can remove organic matters better than traditional membrane separation process. It is more efficient, which combines catalytic ozone oxidation, ozone oxidation and physical filtration.

Consequently, catalytic ozone oxidation joint ozone aeration pre-treatment process can receive better treatment effect than traditional process. Compared with traditional process (PVDF membrane filtration) whose removal rate is 38.7 %, this novel approach is 27.7 % higher. Meanwhile, ozone catalytic oxidation removes the organic matters sticking to the membrane, which is an effective way to prevent membrane fouling.

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