1 **A pilot-scale coupling catalytic ozonation-membrane filtration**
2 **system for recirculating aquaculture wastewater treatment**

3 Shuo Chen¹, Jinqi Yu¹, Hua Wang^{1,2}, Hongtao Yu¹, Xie Quan^{1*}

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5 1. Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of
6 Education, China), School of Environmental Science and Technology, Dalian
7 University of Technology, Dalian 116024, China.

8 2. School of Fisheries and Life Science, Dalian Ocean University, Dalian 116023,
9 China.

10

11 Corresponding author's name: Xie Quan

12 Mail address: School of Environmental Science and Technology, Dalian University of
13 Technology, Dalian, China, 116024.

14 Tel: +86-411-84706140; Fax: +86-411-84706263; E-mail: quanxie@dlut.edu.cn

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1. Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education, China), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China.

2. School of Fisheries and Life Science, Dalian Ocean University, Dalian 116023, China.

Abstract

A pilot-scale coupling catalytic ozonation-membrane filtration system was designed for the recirculating aquaculture wastewater treatment at a fish farm. The ceramic membranes were coated with Ti-Mn/TiO₂ oxide for both catalytic ozonation and filtration. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) images showed that the Ti-Mn oxides were distributed smoothly over both the membrane surface and the inner walls of the pores. Compared with the TiO₂/Al₂O₃ membranes, the Ti-Mn/TiO₂/Al₂O₃ membranes exhibited better catalytic ozonation capability with enhanced membrane antifouling (a normalized permeate flux obtained after 2 h operation was 0.56) and higher removal efficiency of organic matters (52.1%). The ozone dose has an important effect on the degradation of organic matters and ammonia. At an ozone dose of 52 mg/min (stable permeate was

1 obtained after 1 h operation), turbidity and nitrite were almost completely removed,
2 and the concentration of total ammonia nitrogen (TAN) dropped to less than 0.1 mg/L.
3 The permeate quality satisfied the water quality requirement for aquaculture. The
4 recovery ratio of the aquaculture seawater was as high as 95.8%.

5 **Keywords:** pilot-scale, catalytic ozonation, membrane filtration, ceramic membranes,
6 aquaculture water treatment

7 1. Introduction

8 The limited suitable water supplies, the absence of land sources and concerns over
9 the environmental pollution are regarded as key obstacles to further expansion of
10 traditional flow-through aquaculture systems [1]. Thus, recirculating aquaculture
11 systems, which can remove solids, organic matters and total ammonia nitrogen, and
12 can kill microbes to realize low water exchange compared with flow-through systems,
13 are of great interest in aquaculture water treatment. Conventionally, a good
14 recirculating aquaculture system should incorporate unit processes to remove
15 suspended solids and organic matters, add oxygen, and control ammonia, nitrite, pH
16 and pathogenic bacteria [2]. However, the present recirculating aquaculture systems,
17 which are mainly based on the biological method, suffer some problems, such as
18 frequent backwashing of the biofilter [3], complex biological denitrification process
19 [4], changeable biological nitrification beds [5], long hydraulic retention time or large
20 area occupied, and the long start-up period (3 or 4 weeks) [6].

21 Alternatively, membrane filtration is effective at removing particles and organic

1 matters from wastewater in aquaculture process [7,8]. However, the fouling of
2 membranes caused by inorganic or organic matters retained on the membrane surface
3 is inevitable during the operation and decreases the membrane filtration capacity
4 [9,10]. The general approaches to solve the membrane fouling problem are chemical
5 cleaning and back washing. Nevertheless, the periodical chemical cleaning or
6 backwashing of the membranes can generate additional wastewater and increase
7 economic costs. In recent years, the integration of advanced oxidation processes
8 (AOP) in the membrane filtration process to repress membrane fouling has become a
9 popular topic. Ozonation, one kind of AOP, is frequently used in aquaculture systems
10 for water quality improvements and disinfection [11,12]. The combination of
11 ozonation with the membrane filtration process is an effective approach to mitigating
12 membrane fouling in treating surface water [13-15]. In this process, the contaminants
13 (suspended and colloidal inorganic or organic substances) are intercepted and
14 deposited on the membrane surface by membrane separation, then the enriched
15 contaminants are degraded by ozonation. In the meantime, the membrane fouling can
16 be reduced to some extent and the water quality can be improved. Catalytic ozonation
17 by catalysts can promote the decomposition of ozone and the formation of hydroxyl
18 radicals ($\cdot\text{OH}$) or other radicals [16,17]. $\cdot\text{OH}$ can react with almost all types of
19 contaminants due to their high reactivity. Consequently, coating ozone catalysts on the
20 membrane is a more promising subject for improving water quality and alleviating
21 membrane fouling [18-20].

Combined catalytic ozonation and membrane filtration was applied for surface water [13,14] or tertiary effluent [15] treatment. However, no special attention was paid to the removal of TAN and nitrite nitrogen (NO_2^- -N) in this process. TAN and NO_2^- -N are toxic to fish even at a low concentration. Long-term exposure of TAN or NO_2^- -N would significantly inhibit the growth of fish because of a decrease in food intake. Although TAN, NO_2^- -N and dissolved organic matters are difficult to be removed by membrane filtration alone, they are expected to be removed by catalytic ozonation. There has been no reports about combination of catalytic ozonation with membrane separation for aquaculture wastewater treatment till now. In the present study, a pilot-scale coupling catalytic ozonation-ceramic membrane filtration system was established for recirculating aquaculture wastewater treatment at a fish farm. This study focused on the feasibility of the coupling system, the permeate flux of catalytic membranes, the recovery ratio of the aquaculture wastewater and the water quality which should meet the water quality requirement for aquaculture. The performances of Ti-Mn/ $\text{TiO}_2/\text{Al}_2\text{O}_3$ and $\text{TiO}_2/\text{Al}_2\text{O}_3$ catalytic membranes in terms of antifouling and removal of total ammonia nitrogen and chemical oxygen demand (permanganate index, COD_{Mn}) was also investigated.

2. Experiential section

2.1. Membrane preparation

2.1.1. Preparation of intermediate layer ($\text{TiO}_2/\text{Al}_2\text{O}_3$ membranes)

1 Commercial tubular ceramic membranes (α -Al₂O₃, 30 mm (D) $\times$ 1016 mm (L)
2 $\times$ 19 channels, Jiexi Lishun technology, Inc., China) were first coated with rutile TiO₂
3 (with a particle size of approximately 200 nm) (JinZhou PengDa Titanium Dioxide
4 Manufacturing Co., Ltd., China) by a dip-coating method to form the TiO₂
5 intermediate layer. A home-made dip-coating system was used to coat the membranes.
6 In the coating procedure, a cylindrical vessel was first filled with TiO₂ suspension (8
7 wt.%), and then the tubular ceramic membranes were immersed in the suspension for
8 2 min. Afterwards, the TiO₂ suspension was discharged by a peristaltic pump at a
9 velocity of 200 μ m/s. This process was repeated twice. Subsequently, the coated
10 membranes were dried at 80 °C for 12 h and sintered at 1000 °C for 1 h in air with a
11 heating and cooling ramp of 10 °C/min.

12 2.1.2. Preparation of Ti-Mn oxide layer (Ti-Mn/TiO₂/Al₂O₃ membranes)

13 The Ti-Mn oxide layer was prepared as follows: Ti-Mn sol was prepared as
14 introduced in our previous work [21]. Pluronic F127 (45 g) was dissolved in 1000 mL
15 ethanol, and then 250 mL titanium (IV) isopropoxide, 71.5 mL acetic acid, 38.45 mL
16 manganese (II) nitrate solution (50%), and 75 mL pure water were added to the
17 solution dropwise under vigorous stirring to obtain a light yellow transparent Ti-Mn
18 sol with a Ti/Mn molar ratio of 1:0.1. The TiO₂/Al₂O₃ membrane channels were filled
19 with Ti-Mn sol for 2 min, and then the Ti-Mn sol was extracted at a velocity of 200
20 μ m/s. This dip-coating process was also repeated twice. After coating, the
21 Ti-Mn/TiO₂/Al₂O₃ membranes were sintered in air at 550 °C for 1 h to fuse the Ti-Mn

1 catalyst to the underlying $\text{TiO}_2/\text{Al}_2\text{O}_3$ ceramic membranes.

2 **2.2 Membrane module**

3 The characteristics of the membrane module are listed in Table 1. Every tubular
4 ceramic membrane had a filtration area of 0.1 m^2 , and seven membranes were
5 assembled into one module (Fig. 1). Two modules were connected in parallel to obtain
6 the desired treatment capacity.

7

Table 1 Characteristics of membrane module

Parameters	
Type	Tubular
Pore size	$2 \mu\text{m}$
Material	Ceramic
Porosity	40%
Effective filtration area per module	0.7 m^2
Initial seawater flux (20°C)	Ti-Mn/ $\text{TiO}_2/\text{Al}_2\text{O}_3$ membrane: $269.6 \pm 4.6 \text{ (L/m}^2 \text{ h bar)}$
	$\text{TiO}_2/\text{Al}_2\text{O}_3$ membrane: $340.5 \pm 5.7 \text{ (L/m}^2 \text{ h bar)}$
Membrane dimension	$30 \text{ mm (D)} \times 1016 \text{ mm (L)} \times 19 \text{ channels}$

8

9 A schematic diagram and photographs of the membrane module are shown in Fig. 1.

10 A cross-flow filtration mode at a flow velocity of $\sim 1.04 \text{ m/s}$ was adopted in all

11 membrane tests.

Fig. 1. A schematic diagram and photographs of the membrane module

2.3 Pilot-scale system

Fig. 2a shows the process flow diagram of the pilot-scale coupling ozonation-membrane filtration system. The coupling system was operated in a recycling mode as follows: The permeation was recycled to the culture pond with a booster pump. The retentate was recirculated in the loop using a gas-liquid mixing pump, and was discharged every 4 h. In the coupling system, the fish (*Paralichthys lethostigma*) was cultured in a pond with 7 m³ of water. The water was discharged from a bottom-centered drain of the pond, then passed through a sand filter and got into a buffer tank. After that, the water flowed into the membrane module where ozone was injected. Finally, the water flowed through an activated carbon filter for removing residual ozone, and then was recycled in this system. In this system, a gas-liquid mixing pump was used for mixing ozone and seawater adequately, and a

1 backwash pump was used for back flushing. In addition, the backwash water was
2 stored in a storage tank. The membrane operating pressures were adjusted by the
3 concentrate control valve. The flow rate of the ozone gas was controlled by a flow
4 controller. The dissolved ozone concentration in the permeation was continuously
5 monitored by the iodometry method (GB/T 5750.11-2006, China). Temperature, water
6 yield, cross flow rate and pressure were monitored continuously using a
7 multifunctional sensor and were recorded using a data acquisition system. Fig. 2b
8 shows the major parts of the pilot-scale coupling ozonation-membrane filtration
9 system, including the membrane modules, pumps, an ozone generator (NP010-S-2,
10 Shandong NIPPON Photoelectricity Equipment co., Ltd, China), a data acquisition
11 system and a buffer tank. The operating conditions for the coupling
12 ozonation-membrane filtration system are summarized in Table 2.

13

14

15 Fig. 2. Process flow diagram (a) and photograph (b) of the coupling ozonation-membrane
16 filtration system

17

18 **Table 2 Operating conditions for the coupling ozonation-membrane filtration system**

Membrane filtration	Transmembrane pressure (TMP)	2.22 - 2.30 bar
	Cross flow velocity	1.04 ± 0.04 m/s
Ozonation	Applied ozone dosage	52 (mg O ₃ /min)
	Gas flow rate	0.6 L/min
Coupling system	Seawater recirculation rate	4000 L/h
	Temperature	17 - 19 °C

1

2 **2.4. Aquaculture wastewater**

3 The **aquaculture wastewater** was from an aquaculture farm in Dalian, China near
4 Bohai Bay producing *Paralichthys lethostigma* with a load of 12-15 kg/m². The
5 **aquaculture wastewater** was initially filtered with a sand filter prior to the treatment.
6 The water quality of the seawater after sand filtration is presented in Table 3. These
7 fish are very sensitive to total ammonia nitrogen (the lower the better) which should
8 normally be below 0.1 mg/L. Nitrite nitrogen is also a key parameter and should
9 normally be controlled below 0.01 mg/L.

10

11 **Table 3 Aquaculture wastewater quality parameters (after sand filtration)**

Parameters	values
COD _{Mn} (mg/L)	2.1-4.1
UV ₂₅₄ (cm ⁻¹)	0.073-0.095
Turbidity (NTU)	1.2-1.6
Total ammonia nitrogen (mg/L)	0.2-0.4
Nitrite nitrogen (mg/L)	0.03-0.04

Dissolved Oxygen (mg/L)	6.5-8.2
Average particle size distribution (nm)	~ 900
pH	7.7-8.1

1

2 **2.5. Analytical methods**

3 The morphology of the surface and cross section of the membranes was observed
4 using a scanning electron microscope (SEM, S4800, Hitachi, Japan) equipped with an
5 energy dispersive X-ray spectroscopy (EDX). The total ammonia nitrogen
6 concentration was determined by Nessler's reagent colorimetric method (Water
7 quality standard for fisheries GB11607-89, China) and the nitrite nitrogen (NO₂⁻-N)
8 concentration was determined by the ultraviolet spectrophotometry method (GB/T
9 5750.5-2006, China) using a UV-visible spectrophotometer (JASCO V-550, Japan).
10 COD_{Mn} measurement was performed according to GB 17378.4-2007 (China) using
11 KMnO₄ as oxidants. The average particle size of the fine solids in the [permeation](#) was
12 tested using a nano laser granulometer (Zetasizer ZS90, Malvern Instruments Ltd.,
13 Britain). Turbidity was detected using a turbidity meter (WGZ-200, Shanghai Xirui
14 instrument meter co., Ltd., China), and pH was detected using a digital pH meter
15 (PB-20, Sartorius, Germany).

16

17 **3. Results and discussion**

18 **3.1. Characterization of membranes**

1 The Al_2O_3 tubular membrane and the Al_2O_3 membranes coated with TiO_2 or
 2 Ti-Mn/TiO_2 are displayed in Fig. 3a. The SEM images of these three membrane
 3 samples (Fig. 3b, c, d) showed that the TiO_2 particles on the $\text{TiO}_2/\text{Al}_2\text{O}_3$ membrane
 4 were 100-300 nm (Fig. 3c). After being coated with Ti-Mn sol, the particles on the
 5 membrane surface (Fig. 3d) became denser and the membrane surface seemed more
 6 coarsened. The cross section of the $\text{Ti-Mn/TiO}_2/\text{Al}_2\text{O}_3$ membrane (Fig. 3e) showed
 7 that the coating thickness varied from 4.5 μm to 6 μm .

8

9

10 Fig. 3. (a) photograph of tubular ceramic membranes with different catalysts; SEM images of
 11 surface of Al_2O_3 membrane (substrate) (b), surface of $\text{Al}_2\text{O}_3/\text{TiO}_2$ membrane (c), surface of
 12 $\text{Ti-Mn/TiO}_2/\text{Al}_2\text{O}_3$ membrane (d), cross section of $\text{Ti-Mn/TiO}_2/\text{Al}_2\text{O}_3$ membrane (e)

13

14 The EDX images of the $\text{Ti-Mn/TiO}_2/\text{Al}_2\text{O}_3$ membranes (Fig. 4a) showed that the
 15 Mn and Ti were distributed uniformly on the membrane surface. The low Al content

1 (3.763wt.%) and high Ti contents (92.92%) suggested that the membrane surface was
 2 almost completely covered by the catalysts. The EDX analysis on its cross section
 3 (Fig. 4b) also indicated that the porous Al-based substrate was coated by a
 4 mesoporous Ti-Mn layer, and some of the Ti and Mn even penetrated into the
 5 membranes. The well-distributed catalyst indicated it likely played an important role
 6 in the ozonation-membrane process.

7

8

9 Fig. 4. EDX images of (a) surface of Ti-Mn/TiO₂/Al₂O₃ membrane and the content of three
 10 elements, and (b) cross section of Ti-Mn/TiO₂/Al₂O₃ membrane.

11

12 3.2. The effects of catalysts on the permeate flux

1 The performance of the membranes with different catalysts in the aquaculture
2 seawater treatment was investigated. The flux data were unified to a standard
3 temperature of 20 °C using the following formula for eliminating the interference of
4 the water viscosity varying with temperature [22].

$$5 \quad J(20^{\circ}\text{C}) = [Q_p \times 1.024^{(20-T)}] / S$$

6 Where J = filtrate flux (L/(h m²)), Q_p = measured filtrate flow (L/h) at temperature T
7 (°C), S = membrane surface area (m²).

8 Permeate flux is a very important parameter in membrane filtration. The pollutants
9 intercepted by membranes cause the membrane fouling and the degree of membrane
10 fouling could be characterized by the flux decline. The effects of the catalysts on the
11 normalized permeate flux are shown in Fig. 5. It is obvious that the Ti-Mn catalyst
12 coating improved the anti-fouling capacity of the membrane. In the presence of ozone,
13 the Ti-Mn/TiO₂/Al₂O₃ membranes present a much higher permeate flux, with the
14 normalized permeate flux remaining stable at 0.56 until the test end at 4 h, whereas
15 the permeate flux of the system with the TiO₂/Al₂O₃ membranes kept decreasing. This
16 indicates that the Ti-Mn catalyst at the membrane surface had a stronger catalytic
17 ozonation capacity than TiO₂, resulting in a better antifouling performance. The
18 antifouling performance of Ti-Mn membranes with ozone is due to the excellent
19 catalytic ozonation of Ti-Mn for effective degradation of the pollutants. As reported
20 by Ma et al., surface hydroxyl groups is considered to be the initiation for catalytic
21 ozonation or catalytic ozone decomposition to generate ·OH [23]. The point of zero

charge of Mn oxide is relatively low ($pH_{ZPC} = 2.8-4.5$), and at the pH of the aquaculture water, the H_2O molecules will be strongly adsorbed on the surface of Mn oxides, and dissociates into OH^- and H^+ , forming surface hydroxyl groups which are active sites for catalytic ozonation [24]. The ozone is catalytically transformed into $\cdot OH$ and other active species, resulting in its high activity for degradation of pollutants.

Fig. 5. Effects of the catalysts on normalized permeate flux (J/J_0)

(Conditions: TMP = 2.22-2.30 bar, Ozone dose = 52 mgO₃/min, J_0 = initial seawater flux).

Because of the accumulation of pollutants at the membrane surface, the permeate flux dropt rapidly for the membrane filtration alone. When the ozone was applied,

some of the pollutants at the membrane surface could be decomposed, alleviating the membrane fouling.

3.3. Suspended solids removal

Suspended solids can increase turbidity and worsen the water quality, so they should be removed from the water before reuse in aquaculture. In this study, the turbidity and the average particle size of solids in the permeation were determined to assess the removal of suspended solids. As shown in Fig. 6a, during the first half hour, the removal of turbidity rose rapidly in each test because the foulants on the membrane surface lowered the porosity and pore size of the membrane, causing it to retain more suspended substances. These retained matters could function as filter layers to intercept the suspended solids. The turbidity removal efficiency for the TiO₂/Al₂O₃ membranes without ozone was only 55%, while it was up to 100% for both the TiO₂/Al₂O₃ and Ti-Mn/TiO₂/Al₂O₃ membranes with ozone.

The membranes coated with Ti-Mn oxide showed the stronger ability to decompose fine solids than the membranes coated with TiO₂. As shown in Fig. 6b, the average particle size of the fine solids in the permeation was ~20 nm for the Ti-Mn/TiO₂/Al₂O₃ membranes with ozone, which is smaller than that for the TiO₂/Al₂O₃ membranes (~100 nm). This result can be explained by Nawrocki's work [17], in which metal oxide promoted the decomposition of ozone and enhanced the generation of hydroxyl radicals or other radicals. Ti-Mn oxide, as a mixed catalyst, exhibited greater capacity to catalyze ozone for producing hydroxyl radicals or other

radicals than TiO_2 in the membrane surface. Hydroxyl radicals can decompose various pollutants into small structures [25] as well as break larger solids into smaller solids. Accordingly, the average particle size of the fine solids in the permeation was ~ 400 nm for $\text{TiO}_2/\text{Al}_2\text{O}_3$ membranes without ozone, nearly four times that with ozone.

Fig. 6. Turbidity removal (a) and the average particle size of fine solids in the permeation (b) with different membranes

3.4. TAN and NO_2^- -N removal

It has been reported that TAN can be removed from seawater by ozonation [26] according to the following reactions [27]

As shown in Fig. 7, after operating for one hour with ozone, the TAN concentration

1 fell to 0.1 mg/L. The nitrite was easily removed and was nearly fully decomposed
 2 when ozone was injected into the system. Two types of membranes
 3 achieved the similar results, both meeting the water quality criterion for aquaculture
 4 water reuse (GB 3097-1997, China). Compared with the nitrogen removal
 5 performance using the two types of membranes, the predominance of the
 6 Ti-Mn/TiO₂/Al₂O₃ membranes was not significant. The most likely reason for this
 7 result may be the conversion of ammonia into nitrogen in the presence of bromide
 8 ions according to the following formula [28]

Fig. 7. TAN removal (a) and nitrite removal (b) with different membranes

14 In the membrane tests without ozone, the TAN and NO₂⁻-N concentration were
 15 only slightly decreased, meaning the adsorption and interception of TAN and NO₂⁻-N

1 with the membrane itself was negligible.

2 3.5. Effects of ozone dose on TAN and COD_{Mn} removal

3 The effect of ozone dose on the removal of TAN and COD_{Mn} was investigated in
4 this coupling ozonation-membrane filtration system. As can be seen in Fig. 8, the
5 concentration of TAN and COD_{Mn} in the permeation began to decrease with
6 increasing ozone dose. This is because the higher ozone dose injected into the system
7 yield a higher dissolved ozone concentration in the seawater [14]. The higher
8 concentration of ozone dissolved in the seawater provided more opportunities to
9 produce free radicals and decompose the contaminants.

10

11 Fig. 8. Effects of ozone dose on (a) TAN concentration and (b) COD_{Mn} concentration in a coupling
12 ozonation-membrane filtration system (membranes coated with Ti-Mn/TiO₂) at a TMP of 2.2 bar

13

14 3.6. COD_{Mn} and residual ozone removal

15 In the aquaculture systems, the presence of organic matters will consume the

1 dissolved oxygen. In this study, the concentration of COD_{Mn} in the permeation was
2 tested to evaluate the effects of catalyst coating on the removal of organic matters in
3 the aquaculture seawater. As shown in Fig. 9a, in the presence of ozone, the COD_{Mn}
4 removal of the Ti-Mn membranes was 52.1%, much higher than that of TiO₂ catalysis
5 membrane (35.7%). This phenomenon indicates that more free ·OH or other active
6 species were generated by the catalytic ozonation of Ti-Mn oxide than TiO₂ alone,
7 causing better organics removal. The structure of the Ti-Mn/TiO₂/Al₂O₃ membranes
8 may be another factor for higher COD_{Mn} removal. The Ti-Mn oxides distributed over
9 both the membrane surface and the inner walls of the pores indicated that catalytic
10 ozonation not only occurs on the surface of the membranes but also in the inner pores
11 of the membranes. COD_{Mn} removal of membrane alone was only 15.4%, meaning that
12 membrane alone for organic removal was not efficiently.

13 Considering that the residual ozone in the permeation is hazardous [29] to aquatic
14 organisms, an activated carbon filter was used to remove the residual ozone. The
15 concentration of COD_{Mn} and dissolved ozone before and after the
16 activated carbon filter was detected. We also detected the COD_{Mn} concentration and
17 residual ozone after the permeation was only kept for an hour without any other
18 treatment to determine the effects of the activated carbon. From Fig. 9b we can see
19 that the ozone concentration only decreased from 0.76 to 0.54 mg/L when standing for
20 60 min after the membrane treatment. However, the residual ozone decreased to 0.012
21 mg/L after the activated carbon filter, satisfying the aquaculture water requirements (<

0.08 mg/L). At the same time, the COD_{Mn} concentration decreased from 1.3 mg/L to 0.9 mg/L, possibly because the activated carbon served as a catalyst converting ozone into hydroxyl radicals [30,31] which can be used for the further degradation of organic matters. Taken together, the introduction of the activated carbon filter after the coupling ozonation-membrane filtration system is necessary to control the potential hazards of residual ozone.

Fig. 9. (a) Effects of the catalysts on COD_{Mn} removal and (b) removal of residual ozone and COD_{Mn} in the permeation

After 4 h of operation, approximately 2000 L permeation was produced with 88 L of retentate discharged with the recovery ratio being up to 95.8%. For aquaculture systems, the high recovery rate could decrease the consumption of fresh water.

This study demonstrated that coupling catalytic ozonation with membrane filtration was an effective method for aquaculture wastewater treatment. Ti-Mn/TiO₂/Al₂O₃

membranes showed the better performance in permeate flux and organic removal than TiO₂/Al₂O₃ membranes. Membrane filtration alone was not feasible in the treatment of aquaculture wastewater, showing a rapid drop of membrane flux, inefficient removal of suspended solids and organic matters, and almost no degradation of TAN and NO₂⁻-N.

4. Conclusions

In this work, a pilot-scale coupling catalytic ozonation-ceramic microfiltration membrane filtration system was set up successfully for a recirculating aquaculture water treatment. This coupling system obtained satisfactory results, with the permeate quality meeting the requirement of aquaculture water reuse, the short start-up period, and the stable operation conditions. In addition, the Ti-Mn/TiO₂/Al₂O₃ membranes in the coupling system significantly reduced membrane fouling and organic matters. The ozone dose was preferable for TAN and COD_{Mn} removal. Considering the residual ozone is harmful to the aquatic organisms, an activated carbon filter is necessary after the membrane filtration to remove the residual ozone. The results showed that this coupling catalytic ozonation-ceramic membrane filtration system is expected to be a promising strategy for recirculating aquaculture water treatment.

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8 **References**

- [1] M. Badiola, D. Mendiola, J. Bostock, Recirculating aquaculture systems (RAS) analysis: Main issues on management and future challenges, *Aquacult. Eng.* 51 (2012) 26-35.
- [2] M.L. Thomas, P.M. Michael, R. James, Recirculating aquaculture tank production systems-An overview of critical considerations, *SRAC Publication No. 451*, 1998.
- [3] L. Yang, L.S. Chou, W.K. Shieh, Biofilter treatment of aquaculture water for reuse applications, *Water Res.* 35 (2001) 3097-3108.
- [4] G. Ruiz, D. Jeison, R. Chamy, Nitrification with high nitrite accumulation for the treatment of wastewater with high ammonia concentration, *Water Res.* 37 (2003) 1371-1377.
- [5] D.W. Graham, C.W. Knapp, E.S.V. Vleck, K. Bloor, Experimental demonstration of chaotic instability in biological nitrification, *The ISME Journal* 1 (2007) 385-393.
- [6] M.P. Masser, J. Rackocy, T.M. Losordo, Recirculating aquaculture tank production systems: Management of recirculating systems, *Management of*

- recirculating systems, SRAC Publication no. 452, 1999.
- [7] R.C. Viadero, J.A. Noblet, Membrane filtration for removal of fine solids from aquaculture process water, *Aquacult. Eng.* 26 (2002) 151-169.
 - [8] B. Gemende, A. Gerbeth, N. Pausch, A.V. Bresinsky, Tests for the application of membrane technology in a new method for intensive aquaculture, *Desalination* 224 (2008) 57-63.
 - [9] S. Hong, M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes, *J. Membr. Sci.* 132 (1997) 159-181.
 - [10] K.J. Howe, M.M. Clark, Fouling of microfiltration and ultrafiltration membranes by natural waters, *Environ. Sci. Technol.* 36 (2002) 3571-3576.
 - [11] M.S. Tango, G.A. Gagnon, Impact of ozonation on water quality in marine recirculation systems, *Aquacult. Eng.* 29 (2003) 125-137.
 - [12] S.T. Summerfelt, Ozonation and UV irradiation-an introduction and examples of current applications, *Aquacult. Eng.* 28 (2003) 21-36.
 - [13] B. Schlichter, V. Mavrovb, H. Chmiel, Study of a hybrid process combining ozonation and microfiltration/ultrafiltration for drinking water production from surface water, *Desalination* 168 (2004) 307-317.
 - [14] S.H. You, D.H. Tseng, W.C. Hsu, Effect and mechanism of ultrafiltration membrane fouling removal by ozonation, *Desalination* 202 (2007) 224-230.
 - [15] J. Kim, S.H.R Davies, M.J. Baumann, Effect of ozone dosage and hydrodynamic conditions on the permeate flux in a hybrid ozonation-ceramic ultrafiltration system treating natural waters, *J. Membr. Sci.* 311 (2008) 165-172.
 - [16] B.K. Hordern, M. Ziólek, J. Nawrocki, Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, *Applied Catalysis B: Environmental*. 46 (2003) 639-669.
 - [17] J. Nawrocki, B.K. Hordern, The efficiency and mechanisms of catalytic ozonation, *Appl. Catal., B.* 99 (2010) 27-42.

- [18] B.S. Karnik, S.H. Davies, M.J. Baumann, S.J. Masten, Fabrication of catalytic membranes for the treatment of drinking water using combined ozonation and ultrafiltration, *Environ. Sci. Technol.* 39 (2005) 7656-7661.
- [19] B.S. Karnik, S.H.R. Davies, K.C. Chen, D.R. Jaglowski, M.J. Baumann, S.J. Masten, Effects of ozonation on the permeate flux of nanocrystalline ceramic membranes, *Water Res.* 39 (2005) 728-734.
- [20] L.M. Corneal, M.J. Baumann, S.J. Masten, Mn oxide coated catalytic membranes for hybrid ozonation-membrane filtration: Membrane microstructural characterization, *J. Membr. Sci.* 369 (2011) 182-187.
- [21] Y.Q. Zhu, S. Chen, X. Quan, Y.B. Zhang, C. Gao, Y.J. Feng, Hierarchical porous ceramic membrane with energetic ozonation capability for enhancing water treatment, *J. Membr. Sci.* 431 (2013) 197-204.
- [22] S.G. Lehman, L. Liu, Application of ceramic membranes with pre-ozonation for treatment of secondary wastewater effluent, *Water Res.* 43 (2009) 2020-2028.
- [23] J Ma, N.G.D Graham, Degradation of atrazine by manganese-catalysed ozonation: Influence of humic substances. *Water Res.* 33 (1999) 785-793.
- [24] L Yang, C Hu, Y.L Nie, J.H Qu, Catalytic ozonation of selected pharmaceuticals over mesoporous alumina-supported manganese oxide, *Environ. Sci. Technol.* 43 (2009) 2525–2529
- [25] C.P. Huang, C.D. Dong, Z.H. Tang, Advanced chemical oxidation: Its present role and potential future in hazardous waste treatment, *Waste Manage.* 13 (1993) 361.
- [26] S.H. Lin, Y.L. Yen, Ammonia and nitrite removal from sea water by ozonation, *Environ. Technol.* 18 (1997) 65-73.
- [27] M. Yang, K. Uesugia, Ammonia removal in bubble column by ozonation in the presence of bromide, *Water Res.* 33 (1999) 1911-1917.
- [28] S. Khuntia, S.K. Majumder, Removal of ammonia from water by ozone

- microbubbles, *Ind. Eng. Chem. Res.* 52 (2013) 318-326.
- [29] J.P. Schroeder, P.L. Croot, B. Von Dewitz, Potential and limitations of ozone for the removal of ammonia, nitrite, and yellow substances in marine recirculating aquaculture systems, *Aquacult. Eng.* 45 (2011) 35-41.
- [30] U. Jans, J. Hoigne, Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH-Radicals, *OS&E*, 20 (1998) 67-90.
- [31] M.S. Polo, U.V. Gunten, J.R. Utrill, Efficiency of activated carbon to transform ozone into $\cdot\text{OH}$ radicals: Influence of operational parameters, *Water Res.* 39 (2005) 3189-3198.