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Effects of transmembrane pressure and ozonation on the reduction of ceramic membrane fouling during water reclamation

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ABSTRACT

The effects of transmembrane pressure (TMP) and ozonation on the reduction of ceramic membrane fouling were investigated to reclaim and reuse secondary treated wastewater. A tubular ZnO_3/TiO_2 ceramic membrane with a molecular weight cutoff of 300 kD was used for filtration tests at different TMPs of 1, 2, and 3 bar. Pre-ozonation at 3, 6, and 9 mg/L O_3 followed by membrane filtration at 1 bar were also conducted to assess the effect of ozonation on the reduction of membrane fouling and the improvements of water qualities. Ceramic membrane filtration removed large size of molecules, which were mostly aromatic and hydrophobic compounds. However, hydrophobic fractions of organics caused the irreversible fouling of the ceramic membrane; the irreversible fouling increased as TMP increased. Molecular weight distribution and fluorescence excitation emission matrix verified the results. Ozonation improved water quality and membrane permeability, regardless of the doses, but it could not decrease the relative ratio of irreversible fouling to reversible fouling of the ceramic membrane filtration system.

Keywords: Ceramic membrane; Membrane fouling; Irreversible fouling; Ozonation; Water reuse

1. Introduction

Membrane filtration is one of the promising technologies for water reclamation and reuse, because it can provide effective separation of bacteria from wastewater thus meeting tight water quality standards in many countries. However, membrane fouling is a main obstacle to the wide application of membrane filtration for water reclamation, which causes declining permeate flux and increasing operation costs [1–4].

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Various types of pollutants, such as particles, organic and inorganic compounds, and microbes, can be accumulated on membrane surface, and some enter the membrane pores, stuck to the pore wall and make its passages narrow. Treated wastewater is characterized by organic foulants that interact with the high concentrations of colloids and microparticles in the feed water and membrane surfaces [5]. Many previous studies have focused on reducing membrane fouling by changing or optimizing membrane materials and/or characteristics, membrane modules, process designs, operation/backwash schemes, physical/chemical cleaning, etc.

The application of ozonation prior to membrane filtration can reduce membrane fouling and improve membrane permeability [6]. In addition, intermittent ozonation can prevent membrane fouling caused by particle accumulation on the membrane surface [6,7]. Although few studies were conducted using ozone-resistant polyvinylidene fluoride and polysulfone (PS) membranes reporting that using pre-ozonation enhanced the permeability and reduce membrane fouling [8,9], the use of ozonation in combination with polymeric membranes has been limited because ozone is a strong oxidant that preferentially oxidizes electron-rich moieties containing carbon–carbon double bonds and destruct polymeric membranes [8,10].

Unlike polymeric membranes, ceramic membranes are ozone-resistant and can achieve a high-permeate flux without membrane damage combining with ozonation [7]. Since ceramic membranes are physically superior to polymeric membranes, their durability to strong chemicals and maximum operation pressures are higher than polymeric membranes [11]. Due to these advantages, ceramic membranes have attracted much attraction for an alternative to conventional polymeric membranes to produce potable water. However, few researchers have investigated the application of ozonation to ceramic membrane filtration for water reclamation and reuse [12]. This study assessed the effects of pre-ozonation on the reduction of ceramic membrane fouling by changing ozone dosages and transmembrane pressures (TMP). The effects of characteristics of organics in reclaimed water on membrane fouling were also investigated.

2. Materials and methods

2.1. Feed water

The feed water for the filtration tests was taken from secondary effluents of a wastewater treatment plant in South Korea. Table 1 summarizes the typical characteristics of the feed water. Water samples were collected in 20-L high-density polyethylene carboys and stored at 4°C before experiments. All the filtration tests were conducted at 20°C in a temperature controlled water tank and room, unless otherwise stated.

Table 1
Characteristics of feed water

Parameter	Unit	Value
TOC	mg/L	6.2
DOC	mg/L	5.6
UVA_{254}	1/cm	0.135
SUVA	$m^{-1}/(mg/L)$	2.4
Turbidity	NTU	1.6
pH	s.u.	7.3

2.2. Ozonation and membrane filtration system

A schematic flow chart of the ozonation and membrane filtration system is shown in Fig. 1. A tubular ceramic membrane (CeRAM Inside, TAMI Industries, France) with a molecular weight cutoff (MWCO) of 300 kD was used. The ceramic membrane was monolith type with seven channels and consisted of active layer (ZnO_3–TiO_2) and support layer (TiO_2). The external diameter and length of the membrane were 10 and 250 mm, respectively. The total filtration area of the membrane was 0.013 m^2.

Ozone gas was injected into the water stream through an inline mixer just before entering the membrane module. To generate ozone, pure oxygen gas from a pressurized cylinder was fed to the ozone generator (LAB2B, Ozonia, USA). The gaseous ozone concentration was controlled by varying the voltage applied to the ozone generator.

2.3. Filtration experiments

Effects of the TMP on water quality and flux of permeates were compared by varying TMPs (1, 2, and

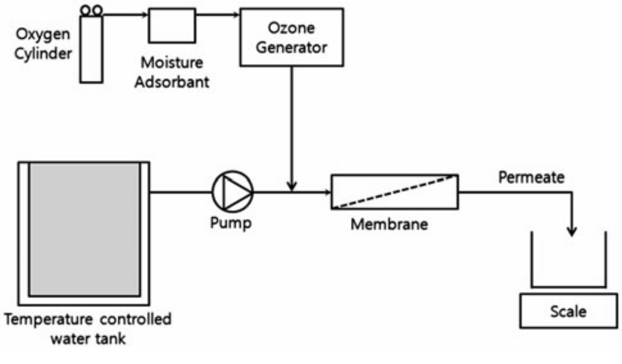

Fig. 1. Schematic diagram of the experimental system.

3 bar). All other conditions except TMP were the same for the membrane filtration tests. Effect of ozonation on the permeate flux was tested at ozone doses of 3, 6, and 9 mg/L by comparing water quality of permeate and the permeability. These tests were conducted at a steady TMP of 1 bar. At the completion of each filtration test, the membrane is hydraulically backwashed and chemically cleaned to calculate fouling resistance. The backwash flow rate was three times higher than operational flow rate, and the backwash phase lasted for one minute. Chemical cleaning involved soaking of the membranes in solutions of sodium hydroxide (NaOH) and nitric acid (HNO_3) based upon a procedure developed by Xing et al. [13]: soaked in a 15 g/L NaOH solution at 85°C for 30 min and then rinsed with deionized water; soaked in a 0.1 M HNO_3 solution at 50°C for another 30 min and then rinsed with deionized water. The cleaning activities ensured the same initial membrane flux in all experiments.

2.4. Water viscosity and fouling resistance calculation

The resistances-in-series model was employed to calculate fouling resistances:

$$J = \frac{\Delta P}{\mu \times R_t} = \frac{\Delta P}{\mu \times (R_m + R_r + R_{irr})} \tag{1}$$

where J is the permeate flux, ΔP is the TMP, μ is the viscosity of raw water, and R_t is the total resistance to filtration (i.e. apparent resistance of the fouled membrane). Filtration adds to the initial hydraulic resistance of the membrane (R_m) a filtration cake with a specific resistance R_r, as this cake formation is reversible by backwash and a gel layer or fouling by adsorption with a specific resistance R_{irr} which is irreversible (or nonreversible) by hydraulic backwash and reversible by chemical cleaning [14].

2.5. Analytical methods

A Shimadzu TOC analyzer (Shimadzu Corp., Japan) was used to measure TOC and DOC. UV/Vis spectroscopy was conducted using a Shimadzu UV/Vis spectrophotometer, MultiSpec-1501 (Shimadzu Corp., Japan). Fluorescence spectroscopy was obtained using a Shimadzu RF5301 Fluorescence Spectrophotometer according to the method developed by Chen et al. [15]. The excitation and the emission slits were maintained at 10 nm, and the scan speed was set at 1,000 nm/min during all measurements. To obtain fluorescence excitation–emission matrix (FEEM), excitation wavelengths were incrementally increased from 200 to 400 nm at 5-nm steps. To limit second-order Raleigh scattering, a 290 nm cutoff was used for all samples. To account for the absorbance of light from the lamp by DOC molecules, an inner-filter correction was applied to these data using UV–vis spectra data. Molecular weight distributions of samples were determined using high-performance size-exclusion chromatography (HPSEC). As pretreatment for the HPSEC fractionation, water samples were filtered through a GF/F filter (pore size 0.7 μm). Molecules were separated with the Waters Protein-Pak 125 column (7.8 mm × 300 mm) (Waters, MA, USA). The column was connected to an Agilent high-performance liquid chromatograph (Agilent Technologies, CA, USA) consisting of a pump and UV detector operating at 254 nm. The eluent was reagent-grade water buffered at pH 6.75 with 2 mM K_2HPO_4 and 2 mM KH_2PO_4. The flow rate was 1 mL/min.

3. Results and discussion

3.1. Effect of TMP

A study was conducted to compare the changes in water quality and filterability by varying TMPs. Fig. 2 presents the remaining of organics, represented by UVA_{254} and DOC, after ceramic membrane filtration tests at different TMPs. Regardless of changes in TMPs, water qualities of permeates filtrated at TMPs of 1, 2, and 3 bar were statistically not different (significance level = 0.05). Removal of DOC was minimal (6–7%) with ceramic membrane filtration only. The removed fractions were mostly large size of molecules that are aromatic and hydrophobic, because the removals of UVA_{254} were higher than DOC. The percent removal of UVA_{254} ranged 28–30%. Analysis results of molecular weight distribution confirmed the removal of large molecular weight compounds as shown in

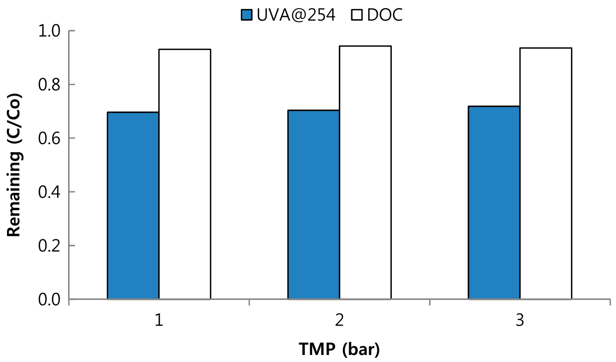

Fig. 2. Water quality changes on various TMP conditions.

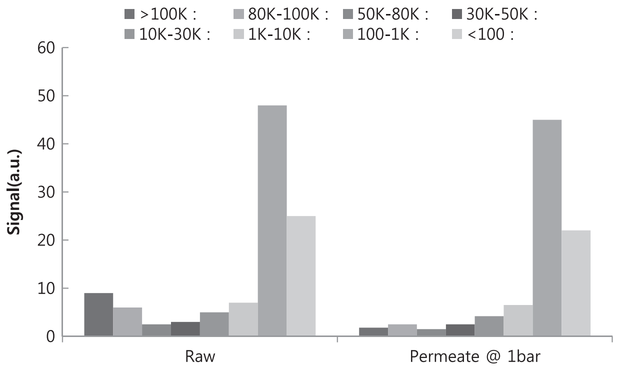

Fig. 3. Molecular weight distribution of raw water and permeate at TMP of 1 bar.

Fig. 3. The MWCO of the ceramic membrane was 30 kDa. Organics with molecular weight > 30 kDa were significantly removed through the ceramic membrane filtration: 80% removal for > 100 kDa, 58% removal for 80–100 kDa, 40% removal for 50–80 kDa, and 17% removal for 30–50 kDa. Organic compounds with smaller than 30 kDa were also removed but the percent removals were lower, ranging from 6 to 16%.

Permeability tests of reclaimed waters revealed that compositions of reversible and irreversible fouling resistances at different TMPs were different. The ratios of reversible to irreversible fouling resistances (R_r/R_{ir}) were 1.98, 1.38, and 1.33 at TMPs of 1, 2, and 3 bar, respectively. The results indicated that TMP of 1 bar was optimal to reduce irreversible fouling which requires chemical cleaning and is undesirable to operate. Therefore, further tests to find an optimum ozone dosage were conducted at TMP of 1 bar.

Hydrophobic fractions of organics possibly caused the irreversible fouling of the ceramic membrane. FEEM analysis of backwash waters after filtration at 1, 2, and 3 bar verified this hypothesis. Backwash waters contained reversible fouling materials. As shown in Fig. 4 and Table 2, backwash water after filtration at 1 bar contained more aromatic proteins (Ex < 250 nm, Em < 380 nm), soluble microbial product (SMP)-like (Ex > 250 nm, Em < 380 nm), humic acid-like (Ex > 250 nm, Em > 380 nm), and fulvic acid-like (Ex < 250 nm, Em > 350 nm) materials than those at 2 and 3 bars. Hydrophobic materials adsorbed more on the surface and/or pores of the membrane at higher TMPs, and those materials are hard to remove by backwash.

3.2. Effect of ozone doses

Following the evaluation of optimum TMP, the effect of pre-ozonation on the reduction of membrane

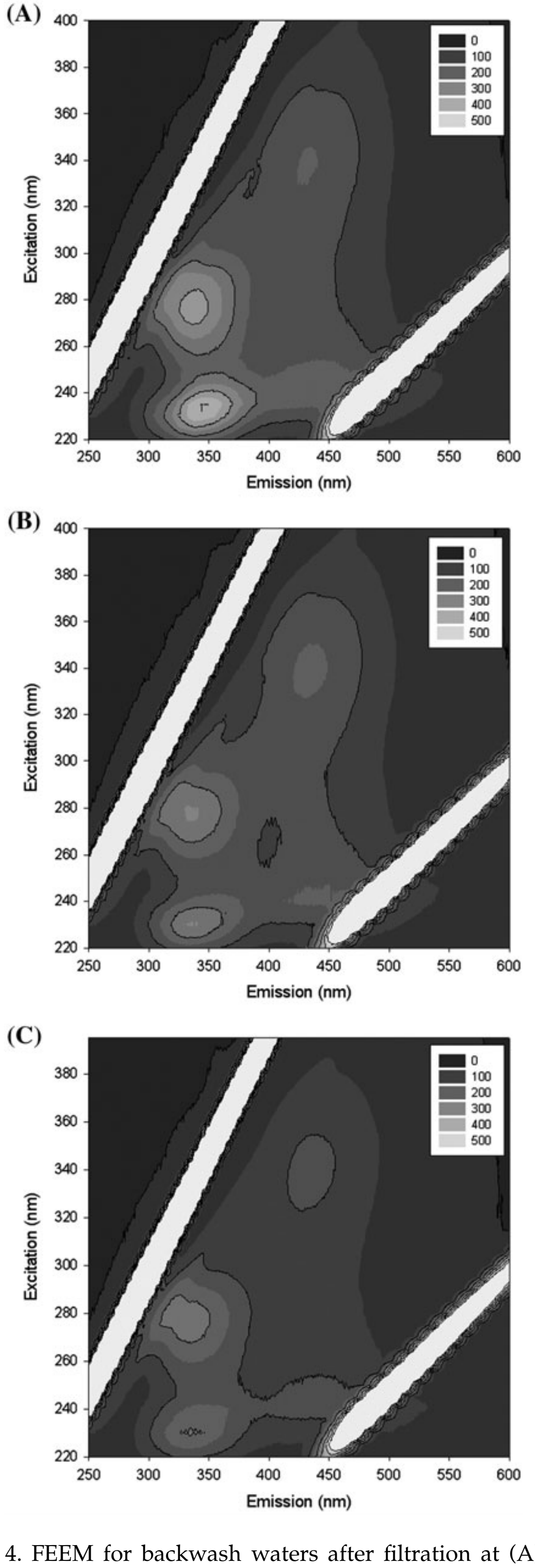

Fig. 4. FEEM for backwash waters after filtration at (A) 1, (B) 2, and (C) 3 bar.

Table 2
Peak intensity of FEEM regions for backwash waters

TMP (bar)	Peak intensity of region			
	Aromatic protein	SMP-like	Humic acid-like	Fulvic acid-like
1	398	331	153	191
2	261	255	159	163
3	210	231	113	125

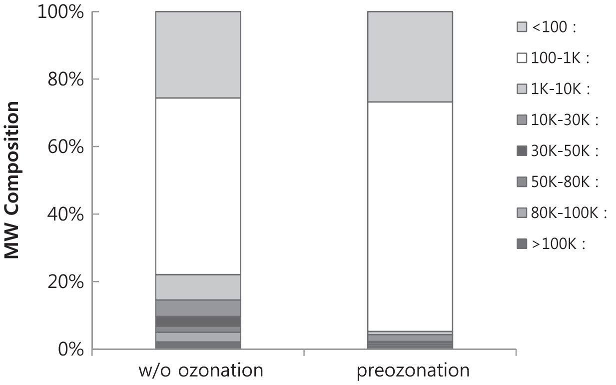

Fig. 5. Molecular weight compositions of permeates with and without pre-ozonation (9 mg/L).

fouling was also investigated. Within the ozone doses (3, 6, and 9 mg/L O_3) tested, water qualities of permeates and permeability were similar. Regardless of the ozone doses, pre-ozonation followed by ceramic membrane filtration enhanced removals of DOC and UVA_{254}. Removal of DOC increased from 6% with no ozone addition to 13, 15, and 14% with 3, 6, and 9 mg/L O_3, respectively. Removal of UVA_{254} also increased from 28% with no ozone addition to 45, 46, and 49% with 3, 6, and 9 mg/L O_3, respectively. This indicated the quality of treated water was improved when ozonation and ceramic membrane filtration were combined, and the optimal ozone dose for the tested water was 3 mg/L. Although ozonation significantly reduced portions of hydrophobic organics by breaking them down into small size and hydrophilic organics, removal of DOC was still low. For the application point of view, further removal of DOC possibly with activated carbon will be needed for better quality of reclaimed water.

In addition to the water quality improvement, preozonation also improved the permeability during ceramic membrane filtration. This was because ozonation broke down organics with larger molecular weights into smaller ones. Addition of 9 mg/L O_3 removed 81, 93, and 86% of organics with molecular weight > 100 kDa, 80–100 kDa, and 50–80 kDa, respectively. The molecular weight compositions of permeates with and without pre-ozonation are presented in Fig. 5. After pre-ozonation, 95% of organics in the permeate were less than 1 kDa. The decrease in the molecular weight of the organics would result in these compounds readily passing through the membrane.

However, the ratio of reversible to irreversible fouling resistances decreased by combining ozonation and ceramic membrane filtration. The ratio of reversible to irreversible fouling resistance (R_r/R_{ir}) was decreased from 1.98 without ozonation to 1.59 with pre-ozonation (9 mg/L). This result could be explained by the increased smaller molecular weight organics. These smaller organic matters might increase blocking of the membrane pores. The backwash flow rate was three time higher than the permeate flux (440 LMH/bar) for this study. If the backwash flux and/or backwash pressure were higher, the reversible fouling could be increased.

4. Conclusion

To assess the applicability of a combined system with pre-ozonation and ceramic membrane to reclaim and reuse wastewater, the effects of TMP and preozonation on the reduction of membrane fouling were investigated. Ceramic membrane filtration could remove larger size of molecules than the MWCO of the membrane. The large sizes of molecules were mostly aromatic and hydrophobic compounds as verified by the molecular weight distribution and FEEM analysis. However, these hydrophobic fractions of organics caused the irreversible fouling of the ceramic membrane, and the irreversible fouling increased as TMP increased. It is important to find an optimal TMP which can reduce irreversible fouling and increase backwash intervals. Ozonation improved water quality and permeability of membrane permeates, but it could not decrease the relative ratio of irreversible fouling to reversible fouling. Higher backwash flow rate and/or pressure may resolve this issue.

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