Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Zhu, Hongtao , Wen, Xianghua , Huang, Xia , Noguchi, Motoharu and Gan, Yiping(2009) 'Membrane Fouling in the Reclamation of Secondary Effluent with an Ozone-Membrane Hybrid System', Separation Science and Technology, 44: 1, 121 — 130

To link to this Article: DOI: 10.1080/01496390802391171

URL: http://dx.doi.org/10.1080/01496390802391171

Separation Science and Technology, 44: 121–130, 2009

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802391171

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Abstract: The current research is a pilot scale study on membrane fouling in an ozone-ceramic membrane hybrid system, aiming at the reclamation of secondary effluent which contains abundant organic substances and bacteria. Compared with the microfiltration process with 30 mg O_3/L feed, the microfiltration without ozone sustained for a longer period of time and produced greater filtrate volume, while all other conditions were kept constant. The results of size exclusive chromatography (SEC) show that the number of large molecules increases after ozonation; this part of organic molecules may contribute more to 0.1 μm membrane fouling. Other evidence proves that ozone brings about the lysis of bacteria. This may account for the increase in the number of large organic molecules after ozonation.

Keywords: Ceramic membrane, membrane fouling, microfiltration, ozonation, secondary effluent

Received 2 April 2008; accepted 9 June 2008.

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INTRODUCTION

Water scarcity is becoming a global and urgent issue worldwide. Therefore, many researchers have focused their attention to studies on the advanced treatment of secondary effluent from wastewater treatment plants for reuse purposes (1–5). In this regard, membrane filtration is one of the most promising treatment technologies as it is highly efficient, easy, and economical to operate (3). However, membrane fouling is still a main obstacle to the practical applications of membrane filtration processes because the mechanisms of it are not well understood yet and the method to control it is limited. Four categories of methods have been studied and adopted to mitigate and control membrane fouling, i.e.

1. Pretreatment of feed;
2. Membrane materials/surface modification;
3. Operating parameters; and
4. Cleaning procedures (6), and one of these methods that has recently received attention is the ozonation of the suspension.

Some researchers have found that pre-ozonation can reduce membrane fouling to some extent; however, its mechanism stays vague (7–13). Organic matter plays an important role in membrane fouling in filtration of the secondary effluent (14). Therefore, the effect of ozone on organic matter in secondary effluent might be an important factor in using ozone to mitigate membrane fouling. Organic mass loading in terms of COD and TOC can decrease 10% to 90% after ozonation (11,13,15). The removal rate of organic substances maybe varies as with ozone dosage, ozone contact time, and types of organic matter. However, most of researchers have also reported that aside from TOC (total organic carbon) removal, the ozone's effect also includes changes in the characteristics of organic molecules, such as polarity and apparent molecule weight distribution (5,12,13,16–18). It has been shown through experiments that the apparent molecule weight distribution (AMWD) of organic substances has a greater influence over the content of organic substances (13). Moon explained that fouling reduction by ozone is a result of the decrease in NOM's (natural organic matter) molecular weight and the increase in the inner adsorptive ability of hydrophilic matter (9). However, under certain conditions, ozonated water can increase membrane fouling due to its organic substance (19).

Besides organic substances, secondary effluent is a type of water abundant in bacteria. At the same time, ozonation is known as a potential disinfection method because of its high oxidation-reduction potential (20). It is reported that ozone can kill bacteria by increasing the membrane permeability of cells, which will lead to leakage of cytoplasm and organelle from cells (21,22). Therefore, it will increase the mass of organic matter in the secondary effluent.

There are a limited number of studies on membrane fouling in hybrid ozonation and ceramic membrane microfiltration systems, especially with the pilot scale system. Also, it is unknown about what happens when ozone is applied to secondary effluent with both organic matter and bacteria. Therefore, the aim of this study which was conducted in a waste water treatment plant is to explore the effects of ozone addition on ceramic membrane fouling in filtration of the secondary effluent.

MATERIALS AND METHODS

Experimental Setup and System Operation

The experimental setup (as shown in Fig. 1) consisted of (1) a flocculation tank, (5) an ozone contact tower, and (6) the ceramic membrane module. The ceramic membrane modules used in the study were supplied by NGK Ltd, Japan. The pore size and filtration area of the ceramic membrane were 0.1 μm^2 and 0.48 m^2. Data were obtained from (10) pH sensor, (11) temperature sensor, (4) flow meter, and (8) pressure sensors. The pressure data monitored by the sensor were recorded using a personal computer.

The system was run with and without ozone addition. The operational mode consisted of 90 minutes filtration followed by 5 minutes of enhanced back washing at a pressure of 500 kPa. The flux was 3 m/d. Once the TMP (trans-membrane pressure) increased to 350 kPa, the

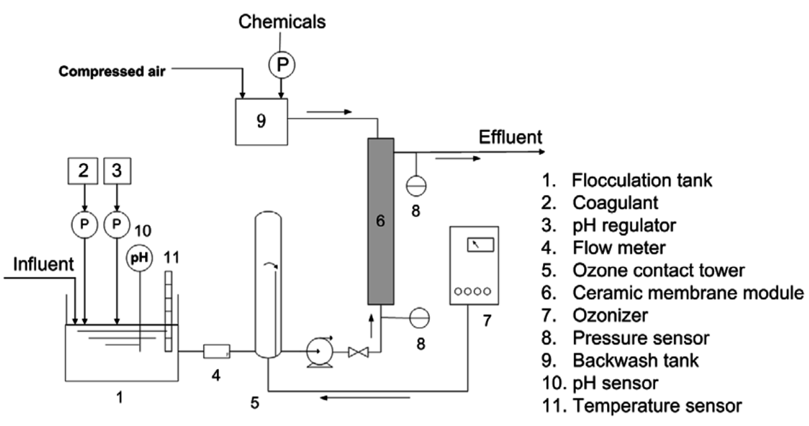

Figure 1. Schematic diagram of the coagulation-O_3-MF ceramic membrane system.

Table 1. Average characteristics of the secondary effluent used in this study

Parameters	Units	Values	Parameters	Units	Values
pH	—	6.8–7.0	Ammonia nitrogen	mg/L	31
Turbidity	NTU	7.3	Total nitrogen	mg/L	44
Suspended solids	mg/L	25.6	Total phosphorus	mg/L	2.24
COD_{Cr}	mg/L	45.6	Total coliform	Cfu/ml	38000
UV_{254}	1/cm	0.1401			

Note: Average values calculated from 6 months data.

membrane was cleaned off line using 1% citric acid solution (soaked in 24 h) and 3g/L sodium hypochlorite solution (soaked in 24 h) sequentially in order to recover its filtration ability. The washed off pollutants were analyzed using SEC, UV-VIS spectrum and ICP.

Raw Water Quality

The secondary effluent employed in this study came from a WWTP located in Beijing, which utilized a traditional active sludge process. The characteristics of the secondary effluent are given in Table 1.

Analytical Methods

Analyses of COD (chemical oxygen demand), ammonia nitrogen, total nitrogen, total phosphorus, and total coliform bacteria were performed according to the standard methods proposed by SEPA of China. TOC was analyzed using a TOC analyzer (Shimadzu, Japan). The AMWD of organic substances was monitored by SEC (Shodex OHpak SB-804HQ, Showa Denko, Japan). Measurement of absorptance at 540 nm and 254 nm was carried out with a UV-VIS Recording Spectrophotometer (UV-2401PC, Shimadzu, Japan). Viscosity value was obtained using a viscometer from BrookField, USA.

RESULTS AND DISCUSSION

Evaluation of Ozone Effect

The addition of ozone has been thought to be useful in delaying the development of membrane fouling, but the experimental results did not verify this. The filtration process without O_3 addition revealed a longer period of time before membrane fouling developed, and therefore, more

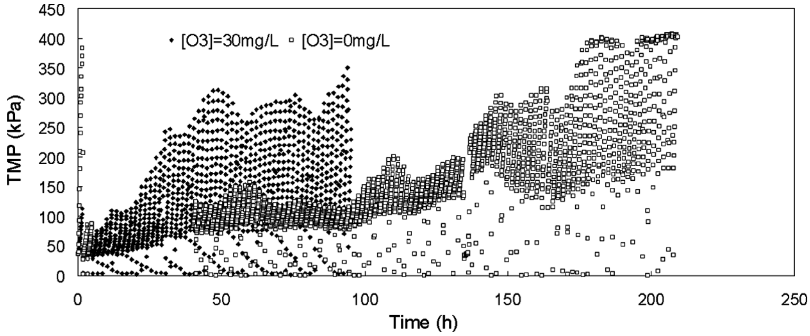

Figure 2. Comparison of TMP variation between tests with and without O_3.

filtrate volume was produced, while all other conditions such as flux were kept constant. As shown in Fig. 2, the steady run time without O_3 is about 2 times of that with 30 mg O_3/L added when the filtration process was stopped at a TMP of 350 kPa.

Although ozone can break down large organic molecules into smaller ones because of its superior oxidation ability, the results of SEC show that the number of molecules with AMW of 400 K–2000 K Daltons increased after ozonation, while that of molecules between 150 K–400 K Daltons decreased at the same time (Fig. 3). This implies that an organic substance with an AMW between 400 K–2000 K Daltons may contribute more to 0.1 μm membrane fouling when compared to smaller molecules. The reason for this may be that small molecules can pass through the membrane; the bigger the molecule is, the more often it clogs or is adsorbed into the pore. The membrane pore size is 0.1 μm. The results in Fig. 3 show that the membrane effluent contains particles with an AMW of 2000 K Daltons.

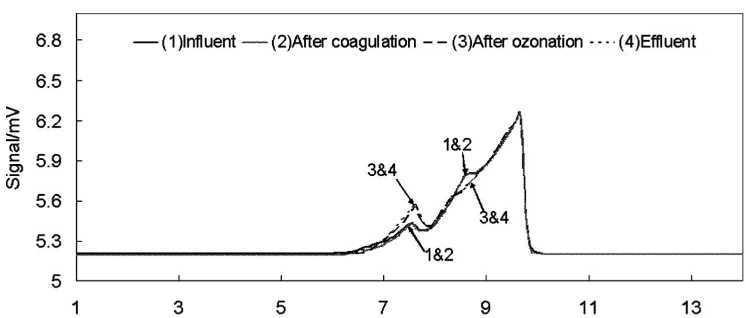

Figure 3. Change in apparent molecular size distribution after coagulation, ozonation, and micro-filtration.

Therefore, the increase in the number of molecules with MW 400 K–2000 K Daltons worsened membrane fouling. This is an interesting finding that necessitates further study.

We thought that the increase in the number of molecules with MW 400 K–2000 K after ozone addition may be related to the presence of bacteria in raw water. Total bacteria concentration in raw water was about $10^5 \sim 10^6$ cfu/ml, among which total coliform concentration in raw water was about 4×10^4 cfu/ml. In order to explore the effect of ozone addition on bacteria in raw water, a series of jar tests were conducted.

Effect of Ozone on Bacteria

Jar tests were performed to explore the effect of ozone on microbial cells. Since there exists both Gram-negative and Gram-positive bacteria in

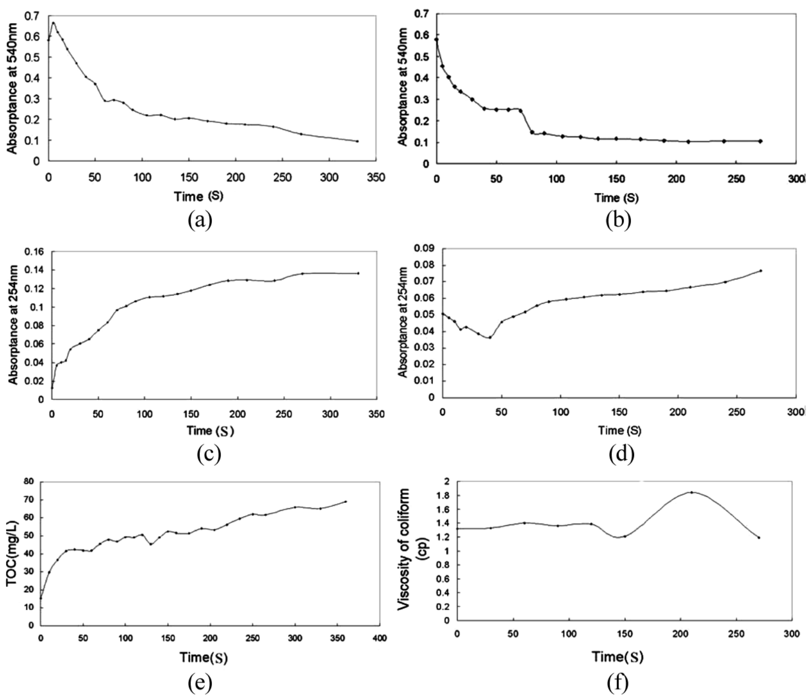

Figure 4. Parameters variation of bacteria suspension with time when ozone is added (bacteria $500\,ml \times 10^8$ cfu/ml – Ozonizer 20 mg O_3/min): (a) A_{540} of coliform; (b) A_{540} of bacillus subtilis; (c) UV_{254} of coliform; (d) UV_{254} of bacillus subtilis; (e) TOC of coliform; (f) Viscosity of coliform.

wastewater, Coliform and *bacillus subtilis* were chosen as the representatives of Gram-negative and Gram-positive bacteria, respectively. Figure 4(a) and 4(b) illustrate the variation of 540 nm absorptance of coliform and bacillus subtilis suspensions, which represents the cell concentration when a certain amount of ozone gas is added continuously. This shows that cell numbers decreased obviously with the addition of ozone, which indicates that there was lysis of bacteria. This coincides with the report of other researchers (23). Figure 4(c) and 4(e) are UV_{254} and TOC variations for coliform, respectively. Both figures demonstrate the increase in the amount of organic substances with the lysis of coliforms. The cytoplasm of coliforms increased the viscosity of the suspension (as shown in Fig. 4(f)). For *bacillus subtilis*, variations of UV_{254} have similar shapes (see Fig. 4(d)). Cell components that are cytoplasm, organelles of the cells, and cell fragments contained a large number of molecules or aggregates with AMW above 400 K (24). Jarusutthirak and Her (25,26) pointed out that cell components contribute to the organic matter in the secondary effluent to some extent. Therefore, in the ozone treated water, the occurrence of large molecules of cell components and the increase in viscosity, both of which are resulted from cell lysis, may be the fundamental reasons for the aggravated membrane fouling.

Effluent Water Quality

The effluent water quality meets the requirement for agriculture and recreation uses as stipulated in "Environmental Quality Standard for Surface Water" [GHZB 1-99, SEPA]. The existence of ozone hardly affects the effluent water quality. The average removal rates of the main pollutants are shown in Fig. 5.

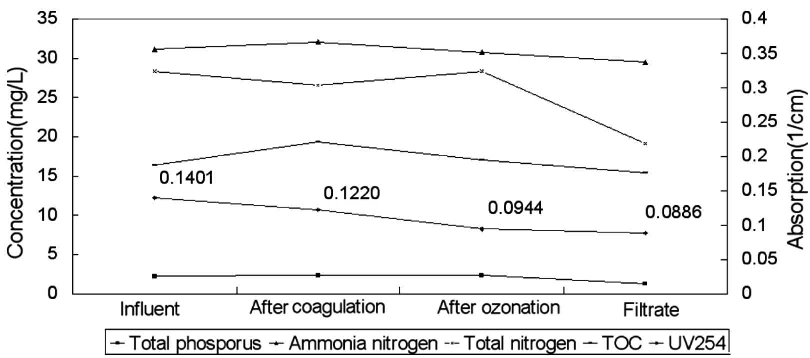

Figure 5. Removal of the main pollutants.

CONCLUSIONS

The conclusions from the study can be summarized as follows:

1. The filtration process without O_3 addition is sustained for a longer period of time, thus producing more filtrate volume, while all other conditions such as flux are kept constant.
2. The result of SEC shows that molecules with AMW of 400 K–2000 K Daltons increase after ozonation, and these molecules may be contributing more to membrane fouling.
3. Ozone causes the lysis of bacteria and increases UV_{254}, TOC, and viscosity in cell suspension. Cell components released from the broken cells after ozone treatment may lead to the increase of molecules and aggregates with molecular weight above 400 K Daltons.

ACKNOWLEDGEMENTS

This work is supported by The Chinese Ministry of Science and Technology (2007DFA91520) and the Major International Joint Research Program of NSFC(20721140019).

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