Effects of ozonation and coagulation on effluent organic matter characteristics and ultrafiltration membrane fouling

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A B S T R A C T

Effluent organic matter (EfOM) is the major cause of fouling in the low pressure membranes process for wastewater reuse. Coagulation and oxidation of biological wastewater treatment effluent have been applied for the fouling control of microfiltration membranes. However, the change in EfOM structure by pre-treatments has not been clearly identified. The changes of EfOM characteristics induced by coagulation and ozonation were investigated through size exclusion chromatography, UV/Vis spectrophotometry, fluorescence spectrophotometry and titrimetric analysis to identify the mechanisms in the reduction of ultrafiltration (UF) membrane fouling. The results indicated that reduction of flux decline by coagulation was due to modified characteristics of dissolved organic carbon (DOC) content. Total concentration of DOC was not reduced by ozonation. However, the mass fraction of the molecules with molecular weight larger than 5 kDa, fluorescence intensity, aromaticity, highly condensed chromophores, average molecular weight and soluble microbial byproducts decreased greatly after ozonation. These results indicated that EfOM was partially oxidized by ozonation to low molecular weight, highly charged compounds with abundant electron-withdrawing functional groups, which are favourable for alleviating UF membrane flux decline.

Introduction

Ultrafiltration (UF) membranes are generally used for wastewater reclamation and reuse (Wintgens et al., 2006). However, deposition and adsorption of soluble and solid components of the wastewater treatment effluent cause membrane fouling, which results in the reduction of productivity and increase in backwashing and membrane replacement cost (Le-Clech et al., 2006). It is generally known that the less charged macromolecular and/or colloidal organic components in effluent organic matter (EfOM) are the major foulants of UF membranes (Shon et al., 2006; Guo et al., 2011). EfOM is a highly heterogeneous mixture of natural organic matter (NOM) such as humic acid (HA) and fulvic acid (FA), soluble microbial products (SMP) and other organic compounds generated during water use and wastewater treatment (Shon et al., 2006). The molecular weight (MW) of EfOM especially increases after aerobic biological treatment by the aggregation of humic substances and SMP, accelerating UF membrane flux decline (Guo et al., 2011).

Many pre-treatment processes, such as coagulation, adsorption, prefiltration and oxidation, have been investigated for the removal and/or transformation of EfOM to prevent fouling (Huang et al., 2009). Among them, oxidation of EfOM by oxidants (e.g., ozone) has shown a good potential for the reduction of UF membrane flux decline by organic foulants (Wu et al., 2011). Genz et al. (2011) reported that the flux decline of a ceramic UF membrane was reduced significantly by the ozonation of EfOM. It was thought that the decreased flux decline could be attributed to the reduction of MW and aromaticity of EfOM, which was evidenced partially by analyzing

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dissolved organic carbon (DOC) and spectroscopy. Wu et al. (2011) reported that the pre-ozonation of municipal wastewater treatment effluent decreased the specific UV absorbance at 254 nm (SUVA$_{254}$) from (2.2 ± 0.2) to (0.8 ± 0.3) L/(mg·m). DOC was slightly changed from (6.5 ± 1.1) to (6.4 ± 1.3) mg/L. Pisarenko et al. (2011) observed a decrease in the UV/Vis absorbance at 254 nm and fluorescence intensity after ozonation of EfOM, but DOC did not decrease significantly. However, it is necessary to investigate the relationships between the change in EfOM characteristics after oxidation and flux decline, based on a wide range of analytical methods.

Therefore, the objective of this study was to investigate the EfOM characteristics affected by pre-treatments such as ozonation and its effects on UF membrane flux. The characteristics of EfOM were widely evaluated with size exclusion chromatography, UV/Vis spectrophotometry, fluorescence spectrophotometry; acidity measurements and Fourier transform infrared spectroscopy (FT-IR). Changes induced by coagulation were also investigated for comparison.

1 Materials and methods

1.1 Pre-treatment of wastewater treatment effluent

Wastewater treatment effluent was obtained from a local biological municipal wastewater treatment plant in Kyung-gi Province, Korea. The effluent, hereafter designated as RAW, was pre-treated by coagulation (COA) at 2.5 mg/L Fe^{3+} (FeCl$_3$), with rapid mixing at 120 r/min for 1 min, followed by slow mixing at 60 r/min for 4 min or ozonation with 4 mg/L ozone (AOP), or both of them (AOP+COA). All reagents in this study were purchased from Aldrich (USA).

1.2 Membrane filtration experiment

The RAW, COA and AOP+COA were used as feed water to investigate the contributions of the pre-treatments to the flux. For the pre-treatment, coagulant concentration was 2.5 mg/L and O$_3$ concentration varied from 0 to 8 mg/L. A polyvinylidene difluoride UF membrane with a molecular weight cutoff of 100 kDa, a nominal pore size of 0.01 μm and pure water permeability of 0.8 m/hr at 100 kPa was used (TORAY, Japan). A single hollow fiber module of the membrane with an active area of 0.03 m^2 was used. The experiments were carried out at (25 ± 1)°C, at a constant pressure of 0.5 and 0.75 bar for filtration and backwashing, respectively, and with a cycle of 7 min filtration and 1 min backwashing (10 mg/L NaOCl solution). The permeate weight was recorded by an electronic balance to obtain the flux (**Fig. 1**).
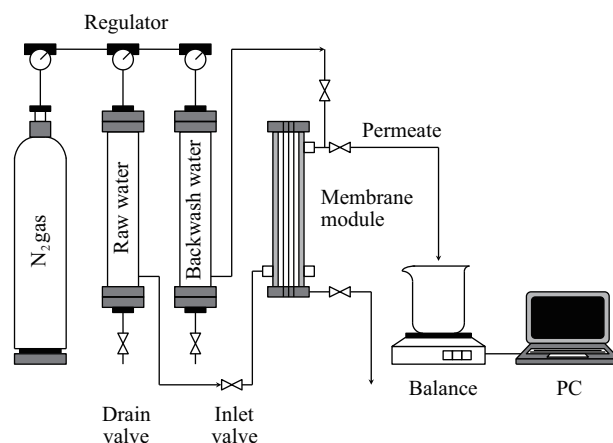

Fig. 1 Schematic of representation of membrane filtration system.

1.3 EfOM characterization

The RAW, COA, AOP and AOP+COA were filtered with 0.45 μm polyvinylidene difluoride filters. Total dissolved solids (TDS), conductivity, pH, total phosphorus (TP) and total nitrogen (TN) were measured according to standard methods (APHA et al., 1998). DOC was measured by a total organic carbon (TOC) analyzer (TOC-V CPH, Shimadzu, Japan).

UV/Vis spectra were obtained with an UV/Vis spectrophotometer (UV mini 1240, Shimadzu, Japan) at wavelengths from 800 to 200 nm. The absorbance at 254, 270, 280 and 400 nm was recorded. Fluorescence spectra were recorded using a spectrofluorophotometer (RF5301PC, Shimadzu, Japan). Excitation-emission matrices (EEMs) were obtained at excitation and emission wavelengths of 220–400 and 280–600 nm, respectively, and synchronous fluorescence (SF) spectra were obtained with constant wavelength differences (Δλ) of 21, 32, 44, 66 and 77 nm. The MW distribution was analysed with a size exclusion chromatography column (Protein Pak 125, Waters, USA), an absorbance detector (UV 730 D, Younglin, Korea), a solvent degasser (SDV 30 Plus, Younglin, Korea) and a column oven (CTS 30, Younglin, Korea). The detection wavelength was 254 nm and the flow rate of the mobile phase was 0.8 mL/min. The mobile phase was buffered at pH 6.8 by 2 mmol/L NaH$_2$PO$_4$·H$_2$O and 2 mmol/L Na$_2$HPO$_4$ to a 0.1 mol/L NaCl solution. Sodium polystyrene sulfonate standards (Polysciences, Inc., USA) and acetone were used as standards. The weight of average molecular weight (MW$_w$) and the number of average molecular weight (MW$_n$) were determined by Eqs. (1) and (2):

$$MW_w = \sum_{i=1}^{N}(h_i MW_i) \Big/ \sum_{i=1}^{N}(h_i) \qquad (1)$$

$$MW_n = \sum_{i=1}^{N}(h_i) \Big/ \sum_{i=1}^{N}(h_i / MW_i) \qquad (2)$$