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# Effects of pre-ozonation on the ultrafiltration of different natural organic matter (NOM) fractions: Membrane fouling mitigation, prediction and mechanism

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ABSTRACT

The effects of pre-ozonation on ultrafiltration (UF) membrane fouling caused by different natural organic matter (NOM) fractions were investigated. Three typical organic model foulants, humic acid (HA), sodium alginate (SA) and bovine serum albumin (BSA) were selected as representatives of different NOM fractions in natural waters. Moreover, Songhua River water (SRW) was employed as a natural surface water. To predict membrane fouling, the dissolved organic carbon (DOC), ultraviolet absorbance ($UV_{254}$) and the maximum fluorescence intensity ($F_{max}$) were used to establish correlations with total fouling index (TFI) and hydraulic irreversible fouling index (HIFI). In addition, the fouling mechanisms were preliminarily analyzed. The results indicated that pre-ozonation significantly alleviated membrane fouling caused by HA, SA and SRW. Maximum ozone dose (4.0 mg/L) showed the best performance with approximately 39%, 78% and 42% TFI reduction, and 26%, 73% and 39% HIFI reduction for HA, SA and SRW, respectively. However, pre-ozonation exerted little influence on BSA fouling under the tested ozone exposure (0.5, 1.5 and 4.0 mg/L). TFI and HIFI were poorly correlated with the DOC contents of HA, SA, BSA and SRW, and the $F_{max}$ of BSA, whereas positively correlated with the $UV_{254}$ of HA and SRW, and the $F_{max}$ of HA and each component of SRW. The fouling mitigation mechanisms were attributed to the changes of NOM properties after pre-ozonation. The results are expected to provide relevant information on predicting and controlling UF membrane fouling according to the composition and characteristics of NOM.

## 1. Introduction

Ultrafiltration (UF) technology is one of the most promising and attractive techniques in both drinking water treatment and waste water reclamation [1–3]. On the basis of size exclusion, UF membrane acts as an effective barrier to suspended particles, colloids, viruses and the high-molecular fraction of natural organic matter (NOM) [4,5]. In spite of the excellent retention characteristics of UF, membrane fouling is still a critical impediment limiting its further widespread application [6,7]. Among numerous pollutants causing membrane fouling, NOM is one of the most problematic because it exists ubiquitously in natural waters and can cause both reversible and irreversible membrane fouling in UF processes [8,9].

One approach to mitigate UF membrane fouling caused by NOM is to adopt pretreatments, including coagulation/flocculation, adsorption, filtration and oxidation [1,2,10–12]. Ozone is an option of pretreatment because it can efficiently decompose certain organic foulants due to its strong oxidative characteristics [13]. There is an emerging use of hybrid ozonation-UF membrane for treating surface water [14–17], wastewater treatment plant effluent [18,19] and industrial wastewater [20]. Recently, the state-of-the-art knowledge in the effects of ozonation on membrane fouling by NOM has been extensively reviewed by Van Geluwe et al. [21]. However, the effect of ozonation on UF membrane fouling is difficult to predict due to the heterogeneity and variability nature of NOM, which is a complex mixture of organic materials, generally including humic substances, polysaccharides, proteins, peptides, amino acids, fatty acids, lipids, phenols, alcohols and small hydrophilic acids [21,22]. Various factors affect the interactions between diverse NOM fractions and membrane

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surface, such as their characteristics, operating conditions and solution chemistry [23]. It was manifested in several studies that ozonation efficiently reduced membrane fouling [14,16,18–20]. However, in some other studies, ozonation was reported to exert minor influence on membrane permeate flux [17]. Kim et al. [15] observed that the effectiveness of the hybrid ozonation-UF process depends upon gaseous ozone concentration and hydrodynamic conditions, including cross flow velocity and trans-membrane pressure (TMP).

Previous research on pre-ozonation for membrane fouling control emphatically studied the process efficiency for treating natural waters [14–17]. However, the complexity of NOM in natural waters may confound the interpretation of fouling mechanisms of different NOM fractions. Although some relevant studies investigated membrane fouling by different NOM fractions, these studies were mainly focused on humic acid fraction [24,25], as it is a main representative of NOM in natural water. Further systematic study on how different NOM fractions affect membrane fouling behavior after pre-ozonation should be conducted to get comprehensive understanding of the overall impacts.

On the other hand, dissolved organic carbon (DOC) and ultraviolet absorbance ($UV_{254}$) have been used to reflect the concentrations of total dissolved organic matters and those containing aromatic chromophores or unsaturated bonds (primarily humics), respectively [26]. In addition, sub-fractional components of NOM can be sensitively and rapidly detected by three-dimensional excitation and emission matrix (EEM) fluorescence spectroscopy [26,27]. Previous researchers had utilized EEM to characterize the fluorescent NOM, including protein-like and humic-like compositions [28,29]. Due to the ability of identifying organic matters, fluorescence EEM has the potential to predict membrane fouling by NOM fractions. EEM coupled with parallel factor analysis (PARAFAC) was also utilized to evaluate and identify UF membrane fouling [30–32]. Shao et al. [30] utilized the PARAFAC-EEMs method coupled with adsorption pretreatment to predict UF membrane fouling. Henderson et al. [32] suggested that fluorescence EEM had a potential to be used as an indicator for UF membrane fouling caused by effluent organic matter (EfOM). Peiris et al. [33] proposed a method of principal component analysis of fluorescence EEM to monitor and control membrane fouling by natural water. It seemed that this fluorescence-based approach could provide additional information for monitoring and understanding membrane fouling. However, previous studies were mainly focused on untreated or physical treated water. It is worthy to note that pre-ozonation, which is a chemical treatment, could change the characteristics of NOM and then membrane fouling conditions. Therefore, whether EEM can be used to predict membrane fouling by different NOM fractions after pre-ozonation still needs to be figured out.

To this end, the objective of this work was to obtain a comprehensive understanding about the effects of pre-ozonation on UF membrane fouling by different NOM fractions and explore the feasibility to predict membrane fouling using several characterization methods. To elaborate the effect of different NOM fractions on membrane performance, three typical organic model foulants, humic acid (HA), sodium alginate (SA) and bovine serum albumin (BSA), as well as natural surface water were employed. A bench-scale pre-ozonation and UF system coupled with multi-cycle fouling test was adopted for membrane fouling assessment. To predict membrane fouling, DOC, $UV_{254}$ and the fluorescence EEM method were utilized to establish correlations with fouling conditions. Moreover, the mechanisms of fouling mitigation by pre-ozonation were also investigated in this study. The results were expected to illustrate the interactions between ozone, different NOM fractions and UF membrane, as well as predict membrane fouling by various characterization methods.

## 2. Materials and methods

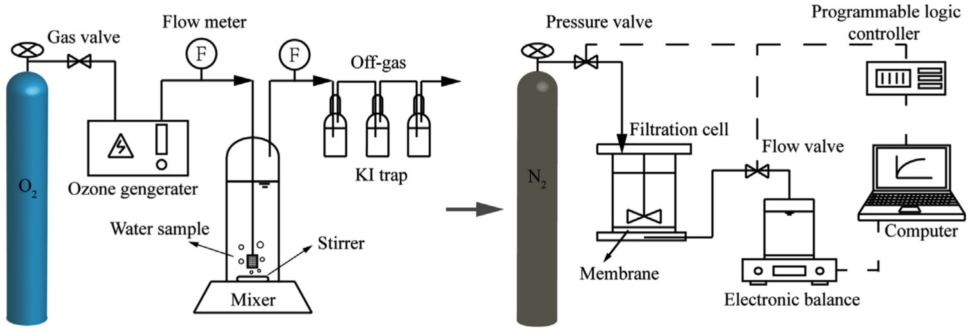
### 2.1. Feed water

HA, SA and BSA purchased from Sigma-Aldrich (USA) were chosen for preparing the model solution to represent humic substances, polysaccharides and proteins in natural waters, respectively. HA stock solution was prepared by adding 1.0 g of HA to 800 mL of 0.01 mol/L NaOH solution, followed by stirring for 24 h and adjusting pH to 7.0, and then the solution was diluted with Milli-Q water to 1000 mL to get the HA stock solution (1.0 g/L). The Milli-Q water was produced by an ultra-pure water system (Millipore, USA) equipped with a terminal 0.22 μm microfilter. The SA and BSA stock solutions (1.0 g/L) were prepared by dissolving 1.0 g of SA and BSA solid into 1000 mL Milli-Q water, respectively, and then stirring for 12 h. These stock solutions were stored at 4 °C in dark place. The water samples used in the experiment were achieved by diluting stock solutions with Milli-Q water. The concentrations of HA, SA and BSA were all 5.0 mg/L. In addition, 1.0 mmol/L $CaCl_2$ and 6.0 mmol/L NaCl were added to the model solutions, and the pH values were adjusted to $7.0 \pm 0.1$.

The natural surface water was collected from a same sampling site of Songhua River (Northeast China) during July, 2015. Water samples were pre-filtered through a 0.45 μm cellulose ester membrane (Taoyuan, China) before the experiments. The water qualities of collected Songhua River water (SRW) were as follows: DOC concentration: 7.92–9.67 mg/L, $UV_{254}$: 0.128–0.145 $cm^{-1}$, and pH: 6.9–7.3.

### 2.2. Pre-ozonation and UF experimental setup

A schematic representation of the experimental setup is illustrated in Fig. 1. The conditioned water samples were pre-



(a) Pre-ozonation (b) UF filtration

**Fig. 1.** Schematic diagram of experiment system: ozonation pretreatment and UF filtration.