



# Does pre-ozonation or *in-situ* ozonation really mitigate the protein-based ceramic membrane fouling in the integrated process of ozonation coupled with ceramic membrane filtration?



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## ABSTRACT

The integrated process of ozonation coupled with ceramic membrane filtration has been actively utilized to alleviate membrane fouling in water/wastewater treatment, however, the effect of ozonation on protein-based ceramic membrane fouling is still contradictory. Herein, for the first time, we reported the severe protein-based ceramic membrane fouling at high ozone dosage in the integrated process of ozonation coupled with ceramic membrane filtration and the related fouling mechanism was systematically explored. Ozonation at low dosage slightly mitigated membrane fouling, whereas severe membrane fouling occurred at high ozone dosage (10 mg/L for pre-ozonation; 4 and 10 mg/L for *in-situ* ozonation). At high ozone dosage, the trans-membrane pressure (TMP) remarkably increased ( $> 40$  kPa) within 90 min and both hydraulically reversible and irreversible fouling contributed to the total membrane fouling resistance. Electro kinetic potential and particle size of the bovine serum albumin (BSA) solution were not the key factors affecting the aggravated membrane fouling at high ozone dosage. The remarkably deteriorated membrane fouling at high ozone dosage can be accounted for the formation of BSA crosslinks ascribed to the oligomerization and agglomeration of BSA and the intermolecular disulfide bridge formation with the crosslinks progressively accumulating on the membrane surface and in the membrane pores during filtration. The modeling results confirmed that the BSA-based membrane fouling mechanism was changed from cake-intermediate to cake-standard with ozonation at high ozone dosage. Meanwhile, the cake layer and/or gel layer played a more important role for the aggravated membrane fouling at high ozone dosage even though the contribution of pore blocking was also significant.

## 1. Introduction

Membrane processes are considered to be the state-of-the-art technology in filtration applications, such as water/wastewater treatment [1]. However, membrane fouling is still a big issue in the filtration applications. Recently, the integrated processes of pre-ozonation/*in-situ* ozonation coupled with membrane filtration have been actively utilized in water/wastewater treatment for membrane fouling control [2–18].

However, discrepancies still exist in terms of the effect of ozonation on membrane fouling control. For instance, Stylianou et al. [2], Sklari et al. [3], Zouboulis et al. [4] and Szymanska et al. [5] showed that a combined process of ozonation and ceramic membrane filtration had high efficiency on trans-membrane pressure (TMP) reduction in wastewater and surface water treatment. Park et al. [6] indicated that the

hybrid process of ozonation and ceramic membrane filtration enhanced the destruction of natural organic matters (NOM) and reduced membrane fouling. Meanwhile, it was also reported that ozonation reduced membrane fouling in the integrated process of pre-ozonation/*in-situ* ozonation coupled with ceramic membrane filtration in algal-rich water and wastewater treatment [7–11]. The degradation of organic matters by ozonation was supposed to be responsible for the mitigation of membrane fouling [8,12–15]. However, membrane fouling was not always mitigated by pre-ozonation and the performance of membrane fouling control was closely related to ozone dosage. Byun et al. [16] observed that pre-ozonation at low ozone dosages ( $< 1$  mg(O<sub>3</sub>)/mg dissolved organic carbon (DOC)) led to the formation of cake layer with higher specific resistance on the membrane surface. Karnik et al. [17] observed that increasing the ozone concentration from 5.0 to 12.5 g/m<sup>3</sup>

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### Nomenclature

BSA	bovine serum albumin
DOC	dissolved organic carbon
EEM	Excitation-emission matrix spectra
IEP	isoelectric point

MW	molecular weight
NOM	nature organic matters
TMP	transmembrane pressure
TOC	total organic carbon
UF	ultrafiltration

had no beneficial effect on permeate flux recovery. Meanwhile, Oh et al. [18] found that pre-ozonation at ozone dosages of 2, 4 and 10 mg/L induced much higher TMP during the microfiltration process than filtration of non-ozonated bacteriophage did. Tang et al. [9] also found that membrane fouling was mitigated after pre-ozonation ( $\leq 5$  mg/L) while the pre-ozonation dosage above 10 mg/L resulted in deteriorated membrane fouling.

Protein is one of the major foulants among the complex mixture of NOM [19–22] and biopolymers [23–25]. Protein-based fouling occurs due to the deposition and adsorption of proteins on the surface and the pore walls of membranes [26], which mainly formed irreversible fouling [27]. It has been demonstrated that the interactions between the protein functional groups and membrane *via* van der Waals forces, electrostatic attraction, hydrogen bonding and hydrophobic interactions determined the early stage of membrane fouling [28,29], and the fouling performance at the later stage was dependent on the protein-protein and protein-membrane electrostatic interaction [30–34]. For example, Kelly and Zydney [35] have demonstrated that the non-aggregated bovine serum albumin (BSA) only fouled the membrane by chemical attachment to an existing protein deposit *via* the formation of intermolecular disulfide linkages. Hadidi and Zydney [36] showed that the extent of membrane fouling was strongly affected by the electrostatic and hydrophobic interactions between the protein and membrane.

In terms of the effect of ozonation on protein-based membrane fouling, whether ozonation mitigates or deteriorates protein-based membrane fouling remains contradictory and how ozonation affects the BSA-based reversible and irreversible fouling also needs further study even though the protein-based membrane fouling mechanisms without ozonation have been studied for a long time. Ozone can cause denaturation of proteins and introduce change in their secondary and tertiary structure, while the polyamide bond of the protein main chain is not degraded by the oxidation of ozone [37]. After ozonation, only cysteine and the aromatic amino acids including tryptophan, tyrosine and phenylalanine were oxidized, but crosslinks between adjacent protein chains were formed, which might in turn deteriorate protein-based membrane fouling [37,38]. Ozonation could change C-OH to C=O and it has been proved that the carbonylation can induce protein misfolding and aggregation even with the formation of visible aggregates by inducing carbonyl stress and recapitulating in the increased protein accumulation [39]. Yu et al. [40] indicated that the ozonated BSA had the size of aggregates similar to the ultrafiltration (UF) pore size (100 k Dalton), which resulted in deteriorated fouling with ozone dosage increased from 0.1 to 1.0 mg/L. Most recently, however, Cheng et al. [41] demonstrated that pre-ozonation (0.5, 1.5 and 4 mg/L) had negligible effect on membrane fouling during BSA filtration.

In this study, BSA was chosen to represent protein and the main objective of this work was to obtain a more fundamental understanding of the influence of ozone dosage (1, 2, 4, 10 mg/L) on ceramic membrane fouling in BSA filtration with pre-ozonation and *in-situ* ozonation. The membrane fouling mechanism was systematically explored from the perspective of TMP, reversible and irreversible fouling resistances, BSA characteristics (morphology, viscosity, zeta potential, particle size and EEM spectra), DOC removal and the fitted results of five combined fouling models.

## 2. Materials and methods

### 2.1. Ceramic membrane and BSA raw water

Flat sheet  $\text{Al}_2\text{O}_3$  ceramic membrane (Meidensha Co., Japan) was used for filtration experiments with a total filtration area of  $0.042 \text{ m}^2$  (250 mm (length)  $\times$  80 mm (width)  $\times$  6 mm (thickness)). The membrane structure is showed in Fig. S1. The average membrane pore size is 100 nm (Supplied by Meidensha).

BSA (Sigma-Aldrich, USA) was chosen to represent protein. The isoelectric point (IEP) of BSA is about pH 4.7 and its typical molecular weight (MW) is about 67 kDa [42]. The Stokes radius of BSA is 3.48 nm [43]. The BSA stock solution was prepared by dissolving 10.0 g BSA into 1.0 L Milli-Q water (Millipore, USA) and then the prepared solution was stirred for 24 h (300 rpm, Jintan, China) to guarantee the complete dissolution of BSA. The stock solution was then stored at 4 °C. The BSA raw water samples (25 mg/L) (pH 5.6 without buffer) used for filtration experiments were prepared by dissolving BSA stock solution (25 mL) into 10.0 L Milli-Q water. The equivalent DOC concentration of the BSA raw water samples was 13.3 mg-C/L, which was similar as the DOC concentration in the micro-polluted surface water in the local Shenzhen River with the purpose that the results obtained from the BSA filtration experiments can be helpful to understand the filtration performance in the micro-polluted surface water treatment.

### 2.2. Membrane filtration process

The BSA raw water samples (10 L) were pre-ozonated in a 20 L batch reactor both for pre-ozonation and *in-situ* ozonation tests (Fig. S2). The desired aqueous ozone dosage was calculated by the following equation:

$$C_{\text{water}} = \frac{C_{\text{air}} \times v_{\text{air}} \times t}{V_{\text{water}}} \quad (1)$$

Where  $C_{\text{water}}$  is the desired aqueous ozone dosage, mg/L;  $C_{\text{air}}$  is the gaseous ozone concentration, mg/L;  $v_{\text{air}}$  is the flowrate of gaseous ozone, 11.2 mL/min;  $t$  is the ozonation time, min;  $V_{\text{water}}$  is the volume of the raw water, 10 L.

The effective pre-ozonation period was 180 min and the gaseous ozone concentrations were set to 5, 10, 20 and 50 mg/L to achieve the desired aqueous ozone dosages of 1, 2, 4 and 10 mg/L, respectively. Then the pre-ozonated solution (3.0 L) was quickly pumped (within 3 min) to the membrane tank (10 L) to conduct the filtration tests. Ozone was produced from ultrapure oxygen by an ozone generator (Guolin, China) and was injected at the bottom of the reactor through a titanium alloy aeration rod. The concentration of gaseous ozone was measured by an online ozone monitor (IDEAL-2000, Aidier, China) and adjusted by varying the electric current of the generator. More details about ozone generation and concentration control can be found in our very recent paper [8].

The filtration experiments were conducted with the same protocol with filtration flux of  $80 \text{ L/m}^2\text{-h}$ , aeration rate of 11.2 mL/min and a running period of 180 min (Fig. 1). The cubic plexiglass membrane tank (inner dimension of 500 mm (length)  $\times$  150 mm (width)  $\times$  50 mm (thickness)) was fixed on a magnetic stirring apparatus (Jintan, China) with the rate of 300 rpm. A pressure gauge (GC31-174, Nagano keiki Japan) mounted between the membrane tank and the peristaltic pump

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