Effect of Pre-Ozonation and UF Membrane Modification with CNT on Fouling Control

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Abstract. The effect of carbon nanotubes (CNT) modification on ultrafiltration membrane fouling control was explored. Three kinds of base membrane were chosen in the study: 20 kDa polysulfone (PS) membrane, 20 kDa and 100 kDa polyethersulfone (PES) membrane. Besides, the effect of pre-ozone on the three CNT modified membranes for fouling alleviation was further studied. CNT modification presented antifouling properties at the beginning of filtration, while the recoverability of the CNT modified membranes are relatively lower as for the blocking of CNT layer by foulants. Pre-ozonation with a lower ozone concentration (0.25 mgO₃/mgDOC) did not efficiently alleviate the fouling of CNT modified membranes. With the ozone concentration increased to 0.81 mgO₃/mgDOC, the CNT modified membranes exhibited their higher antifouling properties. Water quality analysis results showed that CNT modification presented a higher capture ability for the humic-like and protein-like substances. After pre-ozone, more organic materials could be retained in the interior of CNT layer, which decreased the fouling of base membranes and increased the permeate quality as well. Base membrane with large molecular size cut-off is more helpful for the synergistic effect of pre-ozone and CNT modification.

1. Introduction

Ultrafiltration process is widely used in water and wastewater treatment and shows outstanding advantages for its low energy cost, low capital investment and high degree of automation [1]. Nevertheless, the sustainability of UF in water treatment is limited by its fouling, as fouling causes severely decline of membrane permeability during filtration process [2].

Ozonation was investigated as a pretreatment method of membrane filtration. It was reviewed that the positive effect of pre-ozone on membrane fouling derived from the substantial structural changes to the organic materials present in the feed water [3]. The study made by Zhu et al.[4]showed that breaking of large molecules by ozonation was the dominant criteria for fouling reduction. However, large pollutants degraded into small ones could penetrate into permeate, which caused an increase of TOC concentration. Guo et al. [5] demonstrated that the component transformation of sewage effluent after activated carbon catalytic ozonation pretreatment caused the alleviation of membrane fouling.

Recently, carbon nanotubes (CNT) have attracted high interest in the preparation and modification of membrane for fouling control [6]. Many studies found that the addition of CNT to polymeric membrane can improve the membrane permeability, rejection and antifouling property effectively [7]. Besides, recent investigation demonstrated that pre-deposited the CNT layer on membrane surface could improve the fouling resistance ability of membrane [8]. The hybrid process of pre-ozone and UF membrane modification with CNT has never been investigated for fouling control.
The aim of this paper was to investigate the recoverability of CNT modified UF membrane, and the synergistic effects of pre-ozonation and CNT modification on fouling control. Three kinds of base UF membranes: (1) 20 kDa polyethersulfone (PES) membrane, (2) 20 kDa polysulfone (PS) membrane, and (3) 100 kDa polyethersulfone (PES) membrane were chosen in the study.

2. Materials and Methods

2.1. Water Samples
Actual sewage effluent was selected as water samples, which were taken from a pilot-scale sequence batch reactor (SBR) reactor. The sewage effluent was pre-filtered with 0.45 μm micro-membrane and then stored in refrigerator at 4°C.

Table 1. Water qualities of sewage effluent.

|            | TOC (mg/L) | COD (mg/L) | UV$_{254}$ (cm$^{-1})$ | pH       | TN(mg/L) | TP(mg/L) |
|------------|------------|------------|-----------------------|----------|----------|----------|
| Sewage effluent | 8.5-10.02  | 30.6~54    | 0.15-0.21             | 7.54-8.04| 18.10~25.85| 2~5.42  |

2.2. Ozonation Procedure
Ozonation experiment was carried out in a semi-continuous flow reactor (figure 1). The cylindrical reactor is made of glass with volume of 350mL. O$_3$ was generated by a ozone generator (ZR-C-5, Beijing Zhong Rui Yi Jia Technology Co., Ltd., China) using pure oxygen as the feed gas. Ozone dosage was controlled through adjusting the feeding time of ozone gas, and the residual ozone in the off-gas was absorbed by the Potassium Iodide solution (KI). By using the iodinetry, gaseous ozone dosage (consumption of ozone) was calculated as the difference between the inlet ozone and the residual ozone in off-gas. After the feeding of ozone gas, water sample was continuously contacted with ozone for 1 min, and then pure N$_2$ was used to blow off the residual ozone. In the experiment, ozone concentration of 0.25, 0.81 mgO$_3$/mgTOC (mg of gaseous O$_3$ per mg of dissolved organic matter) on fouling alleviation was evaluated.

Figure 1. Schematic diagram of Pre-ozonation

2.3. UF Experiment
All ultrafiltration experiments were conducted at room temperature. The experiments were conducted in a 50 mL-stirring cell (Amicon 8050, Millipore, USA) and operated in down flow dead-end filtration mode, as shown in figure 2. The flat sheet of membranes had an effective filtration area of 13.4 cm$^2$. Nitrogen gas at a constant pressure of 0.1 MPa was used to drive the feed solution through the membrane.

The pure water flux of each membrane was measured and named Jp(0). Every UF experiment had 3 filtration cycles. The starting and ending flux in the filtration of synthetic solution were named Js(n) and Je(n), respectively. The flux of filtration with DI water after rinse was named Jp(n). The number n
represented the cycle number. Then, reversible fouling (RF), irreversible fouling (IF) and total fouling (TF) could be calculated as follows.

\[
IF_n = \frac{J_{p(n-1)} - J_{p(n)}}{J_{p(0)}}
\]

(1)

\[
RF_n = \frac{J_{s(n+1)} - J_{v(n)}}{J_{p(0)}}
\]

(2)

\[
TF_n = IF_n + RF_n
\]

(3)

1. \(N_2\) pressure cylinder; 2. Liquid storage tank; 3. Filtration cell; 4. Membrane; 5. Stirrer; 6. Magnetic stirrer; 7. Beaker; 8. Electronic balance; 9. Computer (for data collection)

**Figure 2.** Down flow dead-end UF scheme

2.4. Membrane Modification

Three kinds of base membrane were chosen in the study: 20 kDa PES membrane (PES900C/D, Sepro, America), 20 kDa PS membrane (PS35, Sepro, America), 100 kDa PES membranes (OM100076, Pall, USA). The basic properties of them were listed in table 2.

**Table 2.** The basic characteristics of membranes.

| Membrane | Materials          | MWCO | \(J_0\) (L/m²/bar) | Zeta values | Contact angle |
|----------|--------------------|------|-------------------|-------------|---------------|
| PES20    | polyethersulfone   | 20kDa| 1200              | -58.01      | 75.3          |
| PS35     | polysulfone        | 20kDa| 1600              | -84.1       | 61.5          |
| PES100   | polyethersulfone   | 100kDa| 3000             | NA          | 59.8          |

Multi-walled carbon nanotubes with diameters of 30-50nm and length of 5-20 μm were obtained from Beijing Nachen Tech Co. Ltd. China. Membrane modification was performed in the 50 mL stirring cell (Amicon 8050, Milli-pore, USA). The CNT suspension (10mg CNT suspended in 50mL ethanol solution with a concentration of 50%, corresponding to the CNT loading of 7.5 g/m²) was dispersed by sonication for 10 min and immediately filtered through the original membrane under \(N_2\) with a pressure of 0.1 MPa. Then a layer of CNT was loaded on the base membrane. Immediately, 100mL DI water was filtered through the membrane to stabilize the CNT layer on the membrane surface.
2.5. Analytical Methods
DOC was measured with a TOC analyzer (Elementar, Germany). The UVA analysis was performed with a UV-3900PC spectrophotometer (Hitachi, Japan) at a wavelength of 254 nm using a 1 cm quartz cell. Fluorescence Excitation-Emission Matrix Spectroscopy (EEM) was measured using a Fluorescence Spectrophotometer (F-7000, Hitachi, Japan). The surface and cross-sectional images of the membranes were analyzed with a scanning electron microscope (SEM) (S-4300, Hitachi, Japan).

3. Results and Discussion

3.1. Effect of Cnt Modification and Pre-Ozonation on Fouling Control
The effect of CNT modification and pre-ozonation on PES20, PS35 and PES100 membrane was shown in figure 3, 4 and 5, respectively. At the beginning of filtration, the CNT modification reduced the membrane fouling significantly, and then the fouling resistance continuously decreased. Backwash cannot alleviate the fouling process. Pre-ozonation under lower ozone concentration did not alleviate fouling of the CNT modified membrane. After backwash, the modified membrane aggravated the membrane fouling, as shown in figure 3b and 5b. However, the fouling of the CNT-PS35 membrane was slightly alleviated under lower ozone concentration. As the ozone concentration increased to 0.81 mgO₃/mgDOC, the CNT modified membrane presented antifouling properties continuously.

![Figure 3](image-url)  
Figure 3. Effect of CNT modification and pre-ozonation on fouling of PES20.
a) without pre-ozonation; b) O3=0.25 mgO3/mgDOC; c) O3=0.81 mgO3/mgDOC;

Figure 4. Effect of CNT modification and pre-ozonation on fouling of PS35.

a) without pre-ozonation; b) O3=0.25 mgO3/mgDOC; c) O3=0.81 mgO3/mgDOC;

Figure 5. Effect of CNT modification and pre-ozonation on fouling of PES100.
The fouling reversibility of CNT-PES20, CNT-PS35 and CNT-PES100 was illustrated in figure 6, 7 and 8, respectively. The recoverability of the CNT-PES100 membrane was obviously better than PES20 and PS35, which could be explained by its property of low protein binding and the large molecular size cut-off. Compared with base membrane, the CNT modified membrane caused higher irreversible fouling. Backwash cannot alleviate the fouling process. Pre-ozonation under lower ozone concentration showed a little change. With the ozone concentration increased to 0.81 mgO₃/mgDOC, the irreversible fouling and the total fouling of the modified membrane were reduced. After backwash, the recoverability of the modified membrane was highly increased. The results indicated that a higher ozone concentration could alleviate the fouling of modified membrane.

**Figure 6.** Fouling reversibility of PES20 and CNT-PES20 after pre-ozonation.

**Figure 7.** Fouling reversibility of PS35 and CNT-PS35 after pre-ozonation.
a) virgin membrane; b) CNT modified membrane; c) virgin + 0.25 mg O₃/mg DOC; d) CNT modification + 0.25 mg O₃/mgDOC; e) virgin + 0.81 mg O₃/mgDOC; f) CNT-modification + 0.81 mg O₃/mgDOC

**Figure 8.** Fouling reversibility of PES100 and CNT-PES100 after preozonation.

### 3.2. Effect of CNT Modification

#### 3.3. Modification and Pre-Ozonation on Permeate Quality

Figure 9 demonstrated the fluorescence EEM spectra of sewage effluent and that after pre-ozonation, as well as the permeates from the base membranes and CNT modification membranes. Increasing ozone concentration, the intensities of both the Peak T and Peak C were highly decreased. These results displayed that the protein-like and humic-like substances were mostly eliminated or decomposed after preozonation [9]. CNT modification further reduced the fluorescence intensity, which indicated that the layer of CNT on membrane could further trap the pollutants. Humic-like substances could agglomerate on the surface and cause some of the pores in the CNT layer to be restricted or blocked [10]. In addition, the abundant π electrons have a strong π–π coupling of aromatic or unsaturated organic compounds with the CNT surface [11,12]. And these pollutants coated on the CNT layer could easily cause high irreversible fouling, as described in the section 3.1.

To further understand the effect of pre-ozonation and CNT modification on fouling alleviation, the DOC, UV254 were analyzed. Table 3 shows the permeate DOC from different UF membranes. It revealed that pre-ozonation only achieved a little DOC removal as the O₃ preferentially reacts with unsaturated bonds to oxygenated saturated functional groups, which are hardly mineralized even after long ozonation times [19,20]. The UV254 of the sewage effluent was decreased from 0.24 to 0.147 cm⁻¹ rapidly under ozone concentration of 0.81 mgO₃/mgDOC, as shown in table 4.
a) SE; b) SE with O$_3$ of 0.25mgO$_3$/mgDOC; c) SE with O$_3$ of 0.81mgO$_3$/mgDOC; d) Permeat from PES20; e) Permeat from CNT-PES20; f) Permeat from PS35; g) Permeate from CNT-PS35; h) Permeate from PES100; i) Permeate from CNT-PES100

**Figure 9.** Fluorescence EEM spectra of SE and the permeates from different membranes.

| Ozone concentration (mgO$_3$/mgDOC) | Feed water | PES20 | CNT-PES20 | PS35 | CNT-PS35 | PES100 | CNT-PES100 |
|------------------------------------|------------|-------|-----------|------|----------|--------|------------|
| 0                                  | 8.507      | 7.058 | 6.767     | 7.751| 7.297    | 7.749  | 7.546      |
| 0.25                               | 7.876      | 7.432 | 6.105     | 7.157| 6.709    | 7.526  | 6.403      |
| 0.81                               | 7.351      | 6.746 | 6.688     | 7.026| 6.710    | 7.194  | 5.588      |

**Table 3.** The permeate DOC from different UF membranes (mgC/L).

| Ozone concentration (mgO$_3$/mgDOC) | Feed water | PES20 | CNT-PES20 | PS35 | CNT-PS35 | PES100 | CNT-PES100 |
|------------------------------------|------------|-------|-----------|------|----------|--------|------------|
| 0                                  | 0.240      | 0.227 | 0.185     | 0.227| 0.207    | 0.232  | 0.204      |
| 0.25                               | 0.211      | 0.210 | 0.176     | 0.205| 0.178    | 0.204  | 0.189      |
| 0.81                               | 0.147      | 0.143 | 0.128     | 0.129| 0.125    | 0.138  | 0.125      |

**Table 4.** The permeate UV254 from different UF membranes (cm$^{-1}$).

3.4. Formation of Foulants on the Membrane Surface with Sem

To investigate the mechanisms of pre-ozonation and CNT modification on membrane fouling, the foulants formed on the surface of CNT-PES100 were observed with SEM. As shown in figure 10a and c, there were large amount of foulants accumulated on the surface of CNT-PES100 membrane and the foulants-CNT layer was very thick, which seems that foulants stacked on the CNT layer and blocked it completely. The amount of foulants on the surface of CNT-PES100 membrane were obviously decreased and are more smoothly spread on its surface after pre-ozonation. The cross section of it also demonstrated that no obvious layer of foulants was found above on CNT layer. Previous studies also
reported that ozonation could effectively decompose large molecule pollutants to small ones [3], increase hydrophilic fraction in the EfOM [13], and decrease the hydrophobic organics [14]. The results indicated that the CNT-PES100 membranes could retain more foulants after pre-ozonation.

![SEM surface and cross section images of CNT-PES100 before and after pre-ozonation](image)

Figure 10. SEM surface and cross section images of CNT-PES100 before and after pre-ozonation

**4. Conclusions**

The effects of pre-ozonation and CNT modification on UF membrane’s fouling control were explored. Three kinds of commercialized UF base membranes were chosen. The conclusions was drawn as the follows:

As for the selected base membrane, CNT modification presented antifouling properties in the beginning, and the overall recoverability of CNT modified UF membrane is relatively lower.

With the ozone concentration of 0.81 mgO₃/mgDOC, the CNT modified membranes exhibited higher antifouling properties compared with the unmodified membranes. The foulants could be captured in the interior of CNT layer and decreased the fouling of base membranes.

Base membrane with large molecular size cut-off is more helpful for the synergistic effect of pre-ozonation and CNT modification, which had a higher effectiveness on fouling control.

**5. References**

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