The Preparation of Double Layers Low Pressure Carbon Nanotubes Membrane

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Abstract. Double layers low pressure carbon nanotubes (CNTs) membrane was prepared by pre-depositing CNTs on the Polyethersulfone (PES) flat membrane by pressure-assisted membrane filtration technology. Ethanol and Triton X-100 (TX-100) were used as dispersant to disperse two kinds of CNTs. By filtering two kind of CNTs dispersions in sequence, double layers CNTs were distributed on the surface of a PES membrane. With the proportion of the CNTs using TX-100 as dispersant increasing, the pure water flux of the double layers CNTs membrane will decrease. Normally, a membrane’s upper layer using ethanol as CNTs’ dispersant have higher pure water flux. Overall, almost all the double layers low pressure CNTs membrane realized the higher HA removal rate than single layer. By using CNTs with a diameter of 10-20 nm and length of 10-30 μm, the membrane with upper layer of 70% CNTs using ethanol as dispersant and 30% CNTs using TX-100 as dispersant can removal over 95% HA.

1. Introduction
Effluent organic matter (EfOM) from the urban sewage treatment plants includes natural organic matter, microbial metabolites and artificially synthesized refractory organic matter [1]. Membrane filtration technology is widely used in advanced treatment of sewage for its advantages of not introducing secondary pollution and not changing the nature of pollutants. Traditional low-pressure membranes can remove larger-sized pollutants, but have a mediocre removal effect on low molecular weight pollutants [2]. Membrane fouling also limit the using of low-pressure membranes. CNT is a one-dimensional carbon nanomaterial, which not only has a high specific surface area, but also has excellent mechanical properties, electrical conductivity, and hydrophobicity. By loading CNTs on the surface of organic membrane, it can effective improve the ability of the membranes to remove small molecule pollutants and antifouling ability [3]. Pressure-assisted membrane filtration technology are widely used for its easy operation to fabricate CNTs pre-deposited membranes. Generally, CNTs pre-deposited membranes were single layer, the CNTs layer have a uniform structure in the vertical direction. In this study, by using ethanol and TX-100 as CNTs dispersant, a double layers low pressure CNTs membrane was obtained by sequence filtration. To characterize the performance of the double layers low pressure CNTs membrane, humic acid (HA) was chosen as the representative pollutant in surface water or sewage effluent. Comparing with the single layer CNTs membrane, double layers CNTs membranes has better removal effect and antifouling performance.
2. Materials and Methods

2.1. Materials

Multi-wall carbon nanotube (OD >50nm, length<10μm; OD:10-20nm, length:10-30μm, purity>95% wt%) was purchased from Beijing Nachen Tech Co. Ltd. China. Ethanol was supplied by MACKLIN (Analytical purity). TX-100 was supplied by Tianjin Guangfu Fine Chemical Research Institution. Humic Acid (HA) was supplied by SigmaAldrich (China). Polyvinylidene fluoride (PVDF) was supplied by Ande Membrane Separation Technology & Engineering (Beijing) Co., Ltd. AMFOR INC. Ultrapure water was made in the laboratory by the Milli-Q water purification system (Millipore, USA).

2.2. Dispersion preparation

CNTs with an outer diameter of 10-20 nm, length 10-30 μm and CNTs with an outer diameter of greater than 50 nm, length less than 10 μm were selected in our experiment. Ethanol and TX-100 (0.5% w/v) were selected to disperse CNTs. These two kinds of dispersants were common in disperse CNTs [4]. Mixing 100mg carbon nanotubes and 300 mL dispersant in a beaker. Then using ultrasonic breaker treat the mixture 15 min in 350W in ice bath (SCIENTZ-950E, Ningbo Xinzhi Biological Technology Co., Ltd.).

2.3. Fabrication of membranes

The schematic of membrane manufacturing is shown in Figure 1. The membrane is made by dead-end filtration, and the air compressor supplies 0.1 MPa pressure. The CNTs in the two dispersions were sequentially filtered onto the PES membrane. Before filtration, a PES membrane (pore size is 0.45μm) was placed in the ultrafiltration cup. To build different double layers CNTs membrane, a series of ethanol dispersion and TX-100 dispersion with different proportion were selected to filter in sequence, listed in Table 1. After the sequenced filtrations, the membrane was rinse with MilliQ water until the effluent TOC is less than 0.2 mg/L.

![Figure 1. Schematic diagram of method of CNTs membrane](image)

Table 1. The volumes of two dispersions during filtration

| Label | Dispersion 1 Volumes of dispersion 1 (mL) | Dispersion 2 Volumes of dispersion 2 (mL) |
|-------|----------------------------------------|----------------------------------------|
| E     | 0                                      | 300                                    |
| 9E1T  | CNTs dispersed by TX-100               | 30                                     |
| 7E3T  | 90                                     | CNTs dispersed by Ethanol              |
| 5E5T  | 150                                    | 150                                    |
| 1T9E  | 270                                    | 30                                     |
| 3T7E  | CNTs dispersed by Ethanol              | 210                                    |
| 5T5E  | 150                                    | 150                                    |
| T     | 0                                      | 300                                    |

*E means. Ethanol as the dispersant. T means. TX-100 as the dispersant. 9E1T means. The membrane prepared by filter 30 mL TX-100 dispersion, and then filter 270 mL ethanol dispersion.

2.4. Constant flow membrane filtration experiment

The constant flow membrane filtration system was shown in Figure 2. The peristaltic pump is used to control the constant flow, the pressure sensor monitors the pressure, and connecting the pressure sensor with the computer to record the pressure value in real-time. Using this constant flow membrane filtration
The system can monitor transmembrane pressure (TMP). UV-spectrophotometer (UV-1200) were used to determine the HA concentration. The effective filtration area of the membrane module is 7.07 cm². The flow rate is 106 L/(m²·h). And the concentration of HA solution is 5ppm.

3. Results and Discussion

3.1. Double layers membranes pure water flux

Figure 1. a) shows the pure water flux of double layers membranes made by CNTs with an outer diameter of 10-20 nm and length of 10-30 μm; b) shows the pure water flux of the double layers membranes made by CNTs with an outer diameter greater than 50 nm and length less than 10 μm. Comparing the membranes prepared by two kinds of CNTs, the results showed that pure water flux of the membranes produced by CNTs with an outer diameter greater than 50 nm were higher than the membranes produced by CNTs with an outer diameter of 10-20 nm. CNTs membranes’ pores are formed by the gaps between the CNTs bundles. Therefore, the double layers CNTs membranes manufactured by the CNTs with an outer diameter greater than 50 nm have a larger pore size than the membranes manufactured by the CNTs with an outer diameter of 10-20 nm. Using CNTs of the same outer diameter, the pure water flux of the membranes will decrease with the increasing of the proportion of the CNTs dispersed by TX-100. For example, 9E1T, 7E3T, 5E5T, the membranes’ upper layer all using ethanol as CNTs’ dispersant. With the proportion of CNTs using TX-100 as dispersant increasing, the pure water flux decreased. Compared with ethanol, TX-100 has a better dispersion effect. The membranes prepared by the CNTs dispersed by TX-100 are more uniform and denser. The CNTs layer dispersed with TX-100 has smaller pore size. Therefore, the proportion of CNTs dispersed by the two dispersants will affect the pure water flux of the membranes. In addition, when the proportion of CNTs dispersed by the two dispersants is fixed, membrane with the upper layer using ethanol as CNTs’ dispersant have higher pure water flux.
3.2. HA removal rate
The results of the HA removal rate of the double layers CNTs membranes were shown in Figure 4. Overall, the constant flux experiment showed that the membrane made by the CNTs with an outer diameter of 10-20 nm have a higher HA removal rate. As the pore size of the membrane made by the CNTs with an outer diameter of 10-20 nm is smaller and the specific surface area is higher, it showed better adsorption and retention effect for HA. As for the membranes prepared by the CNTs with an outer diameter greater than 50 nm, it had an excellent HA removal rate at the beginning period, then rapidly reduced. The pore size of the membranes manufactured by CNTs with an outer diameter greater than 50 nm were not small enough to exclude HA molecules. Consequently, HA molecules were mainly adsorbed on the surface of CNTs membranes [5]. After adsorption saturation, the CNTs membranes were difficult to realize further HA removal. By using CNTs with a diameter of 10-20 nm and length of 10-30 μm, the membrane with upper layer of 70% CNTs using ethanol as dispersant and 30% CNTs using TX-100 as dispersant can removal over 95% HA. When the upper layer is CNTs dispersed by ethanol, the upper layer of the membranes’ structure is loose and the lower layer is dense. When the HA solution flow through the membrane, it is adsorbed by the upper layer, and the remaining HA be retained by the lower layer.

3.3. TMP change in constant flux experiment
Figure 5. shows the TMP change of the double layers membranes in constant flux experiment. As shown in Figure 5, the membranes made of CNTs with an outer diameter greater than 50 nm have a lower TMP than the membranes made by CNTs with an outer diameter of 10-20 nm. The pore size of the membranes manufactured by the CNTs with an outer diameter great than 50 nm are larger. The TMP of the single layer membranes prepared by the CNTs dispersed by TX-100 (T) increases most rapidly, and the TMP of the single layer membranes prepared by CNTs dispersed by pure ethanol (E) least increase. By using CNTs with a diameter of 10-20 nm and length of 10-30 μm, the membranes with the upper layer of 70% CNTs using ethanol as dispersant and 30% CNTs using TX-100 as dispersant, can remove over 95% HA in a relatively low TMP (less than 100 kPa). The membranes exert the ability of adsorption and retention at the same time, so it has a higher removal rate (higher than 95%) with a low TMP (less than 100 kPa).
4. Conclusion
Preparing double layers low pressure CNTs membranes by pressure-assisted membrane filtration technology. Compared with single layer low pressure CNTs membrane, the double layers membrane has better HA removal effect. The membranes exert the ability of adsorption and retention at the same time. With the proportion of CNTs using TX-100 as dispersant increasing, the pure water flux decreased. In all the membranes manufactured, by using CNTs with a diameter of 10-20 nm and length of 10-30 μm, the membrane with upper layer of 70% CNTs using ethanol as dispersant and 30% CNTs using TX-100 as dispersant showed the best performance. This membrane can removal 95% HA during the constant flux experience in a relatively low TMP range.

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References
[1] Labbs, C.N., Amy, G.L., Jekel, M. (2006) Understanding the size and character of fouling-causing substances from effluent organic matter (EfOM) in low-pressure membrane filtration. Environment Science Technology., 40(14):4495-4499.
[2] Zheng, X., Zhang, Z.X., Yu, D. (2015) Overview of membrane technology applications forindustrial wastewater treatment in China to increase water supply. Conservation and Recycling 105:1–10.
[3] Chen, H., Zhang, L., Chen, J., Becton, M., Wang, X., Nie, H. (2016) Effect of CNT length and structural density on viscoelasticity of buckypaper: A coarse-grained molecular dynamics study. Carbon 109:19-29.
[4] Oxana, V., Kharissova, B.I., Kharisov (2013) Dispersion of carbon nanotubes in water and non-aqueous solvents. RSC Advances. 3: 24812–24852.
[5] Ajmani, G.S., Cho. H.H., Abbott, C.T.E., (2014) Static and dynamic removal of aquatic natural organic matter by carbon nanotubes. Water Research, 59:262-270.