



# High flux and high selectivity carbon nanotube composite membranes for natural organic matter removal



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## ABSTRACT

Multi-wall carbon nanotubes (MWCNTs)/polyaniline (PANI)/polyethersulfone (PES) membranes were fabricated by incorporation of *in-situ* polymerised MWCNTs/PANI complex for effective removal of natural organic matter (NOM) in water. The membrane showed high permeability (1400 L/m<sup>2</sup>/h (LMH)/bar), which is 30 times greater than the PES membrane. High NOM rejection rate (80%) was also observed for the composite membrane, which is 4 times higher than PES membrane. This superior performance is attributed to the synergetic effect of increased porosity, narrow pore size distribution and hydrophilicity, and positively charged of the membranes by the inclusion of MWCNTs/PANI complex. MWCNTs/PANI electron transfer complex successfully engineered chemical/physical properties of the membrane in order to have high NOM adsorption capacity and fast water flux. It is suggested that enhanced adsorption capacity is attributed to the electrostatic interaction between NOM and the membrane surface. Key factors contributing to the fast water flux and removal mechanism were covered in depth by characterization of physical and chemical properties of the membrane. The membrane demonstrated 100% water flux recovery and 65% total fouling ratio after cleaning with 0.1 M HCl/0.1 M NaOH solution for 1 h.

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## 1. Introduction

Since membrane technology has become widely used for water treatment and wastewater recycling [1,2], ultrafiltration (UF) membranes have emerged as a promising process to produce drinking water at a relatively lower cost than nanofiltration (NF) and reverse osmosis (RO) membrane [3]. A UF membrane is defined as a low-pressure membrane with a pore diameter of 2–100 nm. Compared to the microfiltration membrane, it can reject colloids, proteins and viruses but has a relatively low flux of approximately 100 LMH/bar [4].

Even though demand for UF membranes has increased over the last decades, their separation properties are limited to certain applications. Limitations of UF membranes include low NOM removal and membrane fouling, which prevent their wide application for drinking water production [5–7]. NOM is known for carcinogenic by-products that are generated during water disinfection, and forms complex with metals [8]. It also generates odours and contributes to membrane fouling, and bacterial regrowth in the distribution system [9]. In particular, low NOM removal has been a critical issue in drinking water treatment. However, UF membranes can only reject 20–50% of NOM [10,11]. Considering the poor removal efficiency, a hybrid membrane system with chemical/physical processes might be a solution for NOM removal [12]. Such UF systems combined with coagulation have demonstrated 80% removal of NOM [13]. A UF membrane with powder activated carbon (PAC) can reject up to 90% of NOM. To save capital/operation costs and energy, a UF membrane with enhanced removal without pre/post treatment needs to be developed to deliver high water permeability.

**Abbreviations:** MWCNTs, multi-wall carbon nanotubes; PANI, polyaniline; PES, polyethersulfone; NMP, N-methyl-2-pyrrolidone; NOM, natural organic matter.

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In addition to NOM removal, membrane fouling is regarded as a challenging issue in membrane technology applications for water and wastewater treatment, as fouled membranes result in decreased water permeability, and increased chemical cleaning, and membrane replacement [3,11]. Advances in the fouling resistance membrane materials can improve the energy efficiency of water treatment plants by reducing pre/post treatment and the chemicals used for membrane cleaning [14]. Therefore, the focus of current studies has been on developing membrane materials for fouling resistance [15,16]. The latest approach to fouling reduction is the incorporation of the inorganic material into the membrane matrix. By including silica or silver nanoparticles in the membrane casting solution, the membrane increased hydrophilicity, which migrates fouling [15].

To tackle these drawbacks of conventional polymeric UF membranes, nanomaterials have been recently introduced into the membrane fabrication [17–19]. Among various nanomaterials, CNTs possess excellent adsorption capacity for organic matter. Compared to the traditional adsorbents such as activated carbon, CNTs are superior adsorbents due to their mesoporous structure and less negative surface charge [20]. Furthermore, the  $\pi$ - $\pi$  interaction between the aromatic group in NOM and CNTs contributes to the better adsorption behaviour of the CNTs [21]. Moreover, CNTs demonstrate excellent electrical and mechanical properties [22–24]. However, due to the van der Waals forces between carbon nanotubes, they are tightly bundled and insoluble in organic solvent. In order to maximize the use of CNTs over a large surface area and with high conductivity, their aggregation within the membrane casting solution has to be prevented [25–27]. There have been many studies on CNT dispersion in polymers and solvents [28–30]. The methods of CNT dispersion in these studies varied from physical treatment to chemical functionalization, which enhances compatibility between the polymer matrix and nanotubes. However, sonication disperses CNTs by breaking van der Waals forces temporarily and thus does not guarantee all CNTs are homogeneously dispersed within the polymer matrix. Functionalization by chemical oxidation of CNTs is the most commonly used method, which breaks  $sp^2$  hybrid carbon bonds on the side-walls, and attaches carboxyl/hydroxyl groups to the CNTs [31]. Functionalized CNTs with the hydrophilic group have been reported as attributing to increased flux because hydrophilic modified CNTs can make membrane more permeable [32,33]. Further, such increase to hydrophilicity is also a well-known approach to reducing membrane fouling [34,35].

Another approach to enhance the separation properties of membranes is the incorporation of nanofillers [36,37]. PANI is one of the favoured candidates due to its good environmental stability, miscibility with PES polymer and ease of synthesis [38]. Its synthesis procedure is considered as simple nonredox doping/dedoping chemistry under an acid/base reaction. PANI has been examined for potential applications for separation membranes [39], and biosensors [40] as a conductive nanofiller due to its electrical conductivity. PANI/Psf UF membranes were fabricated by an *in-situ* blending method and non-solvent induced phase inversion [41,42], and exhibited the enhancement of water permeability due to the increase in hydrophilicity and pore size of the membrane.

Several studies reported that MWCNTs/PANI can form an electron transfer complex *via* donor-acceptor interaction by *in-situ* polymerisation [43,44]; this complex showed enhanced electrical and mechanical properties, and dispersions of CNT in polymer matrices [45]. These two integrated materials were found out to have strong potential for application in functional membranes [46], conductive films, capacitors [47] and biosensors. Such attempts to the integration of an MWCNTs/PANI composite with polymer matrix have opened up the new opportunities for

advanced membrane materials for water treatment by overcoming MWCNTs aggregation and tuning membrane structure and its physicochemical properties which influences permeate flux and selectivity [48].

Even though the MWCNTs/PANI complex has a potential as a novel membrane material, the performance of the MWCNTs/PANI membrane for NOM removal and mitigation of fouling is largely unknown. Therefore, it is desirable to develop MWCNTs/PANI composite membrane, which combines advantages of these two materials in order to complement the limitations of conventional UF membrane.

While currently a UF membrane fouling under different NOM foulant model has been investigated by the modification of membrane with functionalized MWCNTs [49], this paper highlights CNTs composite membrane fabrication for advancing membrane process. We fabricated novel MWCNTs/PANI/PES membrane that showed enhanced removal efficiency and remarkably high flux compared to a PES membrane. An MWCNTs/PANI complex was synthesized by *in-situ* polymerisation and introduced to a PES matrix. The significance of this research is the development of CNTs enhanced UF membrane for effective NOM removal with high water product that requires less operating pressure. *In-situ* polymerisation was introduced to the fabrication procedure in order to overcome nanomaterial aggregation and tune the membrane structure and its physical/chemical properties. The study was aimed to determine key factors contributing to the enhanced performance, and examine the NOM removal mechanism. The chemical/physical properties of the membranes were thoroughly characterized regarding membrane morphology, pore size and its size distribution, porosity, zeta potential, and hydrophilicity. Flux decline with humic acid (HA) was conducted, and suitable cleaning methods were examined.

## 2. Materials and methods

### 2.1. Materials

The following chemicals were used for preparation of membrane casting solution: Aniline as a monomer in the PANI polymerisation (VWR International), Ammonium peroxodisulfate (APS) as an oxidant in the PANI polymerisation (Calbiochem, USA), PES (58,000 g/mol, Goodfellow Cambridge Ltd, UK), N-methyl-2-pyrrolidone (NMP) from Merck and 37% HCl from VWR International. Suwannee River humic acid (SRHA) standard II was used as a model NOM compound (International Humic Substances Society). Latex particles (hydraulic diameter = 30 nm) were purchased from Sigma-Aldrich (L5155). Hydroxylated-MWCNT was supplied from BuckyUSA, and characterized by the company as follows: purity of 98 wt% a diameter of 5–15 nm and lengths ranging from 1 to 5  $\mu$ m.

### 2.2. Fabrication of MWCNTs/PANI/PES membranes

Membrane fabrication was divided into two steps. The first step was a synthesis of the MWCNTs/PANI complex by *in-situ* polymerisation, the second step was a fabrication of the MWCNTs/PANI/PES membrane by the phase inversion method. The MWCNTs/PANI complex was fabricated into MWCNTs/PANI/PES membrane.

The first step is a synthesis of MWCNTs/PANI nanocomposite by *in-situ* polymerisation, as shown in Fig. 1(a) [43,50]. A solution of 3 mM aniline monomer and 0.8 mM APS was prepared in 1 M HCl and 99.5% NMP. MWCNTs were dispersed in 99.5% NMP solution by sonication (500 W) for 1 h. Three substances (*i.e.*, aniline, APS and MWCNTs) were mixed in a glass vessel and stirred for 48 h at 4 °C.

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