



## Fouling control mechanisms in filtrating natural organic matters by electro-enhanced carbon nanotubes hollow fiber membranes



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### ABSTRACT

Membrane fouling is a ubiquitous and costly problem for membrane bioreactor (MBR) that usually deteriorated membrane performance. Applied voltage on membrane is an important strategies mitigating the fouling. To evaluate antifouling mechanisms of electro-enhanced carbon nanotubes hollow-fiber membranes (CNTs-HFMs), the removal of bovine serum albumin (BSA), sodium alginate (SA) and supernatant of anaerobic bioreactor (SAB) were performed. The results showed that the optimal applied voltage ( $-1.2$  V) could effectively reduce membrane fouling from excluding the negative pollutants far away from the membrane surface, offering an impediment on forming gel layer and controlling the formation of high-molecular-weight pollutants. The effluent COD removal efficiencies by filtrating BSA (92.1%), SA (87.3%) and SAB (56.8%) at  $-1.2$  V were 3.3, 1.4 and 1.5 times higher than that of membrane filtration alone. Then, a short-term experiment (30 days) was performed, where CNTs-HFMs served dual function as the cathode and filtration function in an electro-enhanced anaerobic bioreactor (AnEMBR). The results presented that a low transmembrane pressure of 0.35 bar was obtained compared to the control reactor (0.60 bar), implying that applied voltage on CNTs-HFMs contributed to alleviate membrane fouling. This work implied that electrochemical control might provide a promising avenue to mitigate membrane fouling in MBR.

### 1. Introduction

Anaerobic membrane bioreactor (AnMBR) systems as essential wastewater treatment processes have presented much superiority, including small foot print requirements, superior effluent quality, higher volumetric loading and less sludge production [1]. In addition, it can retain all of the biomass in the reactor more effectively without any fear of sludge washout irrespective of short hydraulic retention time [2]. However, due to the high sludge concentration and membrane pore blocking, the membrane fouling of AnMBR (in general, to all processes using membrane separation) is an inevitable phenomenon, which is the main technical obstacle [3–5]. Membrane fouling contributes significantly to both capital and operation costs that arise from the need to clean or replace membranes. From a physicochemical point of view, membrane fouling in AnMBR has been found to be seriously influenced by a number of abiotic parameters, such as, concentration of microorganisms which have a hydrophobic surface, causing them to adhere to hydrophobic membranes [6]. Extracellular polymeric substances (EPS), including bound and soluble EPS (also known as soluble microbial products, SMP), are products of the metabolism of

microorganisms [7] and are also considered as the main ingredient of pollutants. SMP and EPS are prevalent in the interior and surface of biomass flocs. They are polymer of some macromolecules such as polysaccharides, proteins and nucleic acids, most of which have negative charges [8]. In fact, many studies have identified SMP and EPS as the most significant biological factor responsible for membrane fouling [9]. Therefore, the control of membrane fouling was the urgent need in order to accelerate the application and development of MBR in full-scales.

Membrane cleaning is a necessary part of operation in AnMBR, which significantly influences membrane filtration performance. It is well accepted that membrane cleaning can be categorized into physical and chemical cleaning [10]. Physical cleaning removes loosely attached materials on membrane surfaces (generally termed ‘reversible fouling’) but with low efficiency, while chemical cleaning removes more tenacious materials (often termed ‘irreversible’ fouling) but with harmful residual chemical substances [11,12]. Nevertheless, both physical and chemical cleaning can not help to solve the membrane fouling problems comprehensively. Therefore, membrane fouling control is a considerable challenge in anaerobic membrane-based bioreactors.

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The key to membrane fouling control is to mitigate the deposition of various foulants on membrane and/or to timely remove them from the membrane surface. Recently, various novel membrane materials were used to evaluate the antifouling performance of membranes [13–16]. Among them, conductive materials modified on membrane surface or direct application as the membrane materials has shown great prospects, since charge repelling action could prevent EPS attachment and electrochemical action might degrade the attached pollutants on the membrane surface. Wang et al. [13] reported an antifouling electrochemical membrane bioreactor based on in-situ utilization of the generated electricity for fouling control. The membrane fouling was mitigated by in-situ removing the membrane foulants. Meanwhile, 93.7% COD removal and 96.5%  $\text{NH}_4^+$ -N removal in average as well as a low effluent turbidity of below 2 NTU were achieved. Katuri et al. [16] used electrically conductive nickel-based hollow-fiber membranes as membrane separation system to treat low organic strength solution. The experimental results demonstrated that the membranes at a voltage of 0.9 V can obviously mitigate the membrane fouling, because the gas bubble formation could provide a means of scouring (self-cleaning) the surface of the membranes. Dudchenko et al. [17] synthesized electrically conductive films ( $2500 \text{ S m}^{-1}$ ) made of cross-linked poly (vinyl alcohol) and carboxylated multi-walled carbon nanotubes. Electrostatic interactions produced significant repulsive forces between the membrane surface and the charged organic foulant (3–5  $\text{g L}^{-1}$  of pure alginate acid). Pure alginate acid aggregates would be strongly repulsed away from membrane surface, resulting in overall reduced fouling inhibition. Although previous studies explored many novel conductive membrane materials with improved antifouling performance, the reports are very scarce regarding the antifouling properties for carbon nanotube-based membrane by electrostatic repulsion in AnMBR.

Carbon nanotubes (CNTs) have been reported as a promising material for constructing membranes owing to their outstanding properties including high surface area, high mechanical strength, excellent chemical inertness, and water-transport. [18–23] Because of the overlap and interpenetration of CNTs, as-constructed CNT membranes with mesh like structures usually present plentiful interconnected pores and high porosities ( $> 70\%$ ) [24–26]. These properties further endow CNT membranes with a high flux even at a low operating pressure. Importantly, CNTs exhibit encouraging electrochemical performances and the ability of fast electron transfer kinetics. The CNTs membranes by the electro-assistance can further enhance their wastewater treatment efficiency and antifouling abilities [27–30].

Herein, the electro-conductive carbon nanotube hollow fiber membranes (CNTs-HFMs) were prepared as a separation material in AnMBR for wastewater treatment. The electro-assistance is an effective method for improving the separation performances of CNTs-HFMs through affecting the membrane surface charges. The membrane fouling can be alleviated by reducing the deposition of negative charged contaminants onto the negative charged membrane surface. Hence, the objectives of this work was to evaluate the effect of different applied voltages ( $-0.4$ ,  $-0.8$ ,  $-1.2$  and  $-1.4 \text{ V}$ ) on the separation performance of electrically enhanced CNTs-HFMs. The antifouling mechanisms of electro-assisted CNTs-HFMs were explored by separating natural organic matters (NOMs), such as bovine serum albumin (BSA), sodium alginate (SA) and supernatant of anaerobic bioreactor (SAB). Meanwhile, a novel electrically enhanced anaerobic membrane bioreactor (AnEMBR) using CNTs-HFMs as basic separation unit was firstly built in this study. We investigated the system performance in terms of membrane fouling mitigation and contaminant removal, and elucidated how the membrane fouling was suppressed in this system. This work provides a theoretical basis and technical support for AnEMBR with the special electrochemical environment.

## 2. Materials and methods

### 2.1. Materials

The pristine multi-walled CNTs (purity  $> 98\%$ ) were supplied by Shenzhen Nanotech Port Co., Ltd., China and used as received. And the membranes fabrication chemicals, such as polyvinyl butyral (PVB) and polyvinyl alcohol (PVA) were both obtained from Sinopharm Chemical Reagent Co., Ltd, China. N,N-Dimethylformamide (DMF) was obtained from Xilong Chemical Company Co., Ltd., China. Bovine serum albumin (BSA) and sodium alginate (SA) were purchased from Sigma-Aldrich Chemical Company, USA. Other chemicals, such as sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98%) and nitric acid ( $\text{HNO}_3$ , 65%) were all analytical grade and supplied by Bench Chemicals (Tianjin, China). At last, the ultrapure water (resistivity  $> 18 \text{ M}\Omega \text{ cm}^{-1}$ ) used in this study was produced by a purification system (Beijing Purkinje General Instrument Company Co., Ltd., China).

### 2.2. Membrane fabrication and characterization

The CNTs-HFMs were prepared based on wet-spinning technologies [31]. Firstly, surface-functionalized CNTs and PVB were well dispersed in DMF solution under sonication and stirring. Then the spinning solution and water were subsequently squeezed into water using a coaxial two capillary spinneret by a constant-flow pump to form the hollow fiber structure. To eliminate the influence of DMF, the prepared CNT/PVB hollow fiber membranes were submerged in pure water for 24 h and dried overnight at room temperature. Subsequently, the products were calcinated in a flow of argon (40 sccm) at  $600 \text{ }^\circ\text{C}$  for 2 h at a heating rate of  $2 \text{ }^\circ\text{C min}^{-1}$ . Finally, the membranes were immersed in 1% PVA for 4 h to change its toughness, and naturally dried at room temperature ( $20 \text{ }^\circ\text{C}$ ).

The morphologies of the membrane was observed with SEM (FESEM, Hitachi S-8010) on a microscope with 1.0 nm resolution. Automatic contact angle meter (SL200B, Kono Industrial Co., Ltd., USA) was used to record contact angle ( $\theta$ ) of membranes. Membrane pore size was measured using the pore size tester (POROLUX™1000, POROMETER, Germany). The pure water flux of membrane was calculated as follows:

$$J = \frac{V}{A \cdot \Delta t} \quad (1)$$

where  $J$  is the permeation flux ( $\text{L m}^{-2} \text{ h}^{-1}$ ),  $V$  is the volume of the permeate (L),  $A$  is the membrane area ( $\text{m}^2$ ) and  $\Delta t$  is the permeate collection interval (h).

The porosity of membrane was determined by gravimetric method and calculated using the following formula:

$$\varepsilon = \frac{4m_2 - 4m_1 - \pi l \rho d_{inner}^2}{\pi l \rho (d_{outer}^2 - d_{inner}^2)} \quad (2)$$

where  $\varepsilon$  is the porosity of the membrane (%);  $m_1$  and  $m_2$  are the mass of dry and wet membrane, respectively;  $l$  is the effective length;  $\rho$  is the water density;  $d_{outer}$  and  $d_{inner}$  are the outer and inner diameter of the membrane, respectively.

### 2.3. Membrane performance tests

#### 2.3.1. Electrically enhanced filtration experiments

The filtration experiments of electrically enhanced membranes were carried out in a dead-end cell with 80 mL working volume as displayed in Fig. S1. The distance between membrane component and titanium mesh was 2 cm in all works to keep electric field strength ( $E$ ) constant. Each tests were run in three parallel sets at  $25 \text{ }^\circ\text{C}$ .  $1 \text{ g L}^{-1}$  BSA,  $1 \text{ g L}^{-1}$  SA and SAB (COD was average  $503 \text{ mg L}^{-1}$ , pH was approximately 7.1, polysaccharides concentration was average  $9.0 \text{ mg L}^{-1}$  and protein concentration was average  $94 \text{ mg L}^{-1}$ ) were used as the target organic

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