Desalination 360 (2015) 8–12

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Electrically conductive membranes based on carbon nanostructures for self-cleaning of biofouling

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HIGHLIGHTS

- Highly electrically conductive CNS/PVDF membrane
- Periodic electrolysis for membrane surface cleaning
- Formation of microbubbles on membrane surface during electrolysis

ARTICLE INFO

Article history:
Received 11 November 2014
Received in revised form 4 January 2015
Accepted 5 January 2015
Available online 12 January 2015

Keywords:
Carbon nanostructure membrane
PVDF binder
Self-cleaning
Electrolysis
Fouling

ABSTRACT

Although membranes are widely employed in separation processes, their performance can be severely deterred by fouling due to organic, inorganic and biological foulants. Periodic electrolysis is a fast and simple technique for membrane cleaning, but requires membranes with high electric conductivities. In this work, novel electrically conductive CNS/PVDF membranes were fabricated via vacuum filtration, followed by heat treatment above the melting point of PVDF, such that PVDF acts as a binder inside the CNS structure, resulting in better mechanical properties and greater wettability. Membranes that were subjected to periodic electrolysis were able to sustain higher flux through multiple filtration cycles of yeast suspensions as compared to those without electrolysis, indicating the efficiency of this technique using electrically conductive CNS/PVDF membranes. Electrolysis led to the formation of micro-bubbles on the membrane surface, which removed foulants. These self-cleaning membranes can be used to mitigate the effects of fouling in different types of separation processes.

1. Introduction

Despite the rapid rise in the development of new membranes, attempts to minimize problems related to fouling have been largely insufficient. Fouling refers to loss of performance due to the deposition of suspended or dissolved substances, either on the external surface of the membrane or inside its pores i.e. pore constriction and pore clogging. Fouling affects all membrane-based separation processes including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Although operating conditions and feed characteristics determine the fouling propensity of a membrane for a certain process, fouling also depends greatly on the membrane material, specifically its surface chemistry and structure. In recent years, many new materials have been developed with enhanced anti-fouling and/or self-cleaning properties [1]. Much of the focus has been geared towards enhancing the hydrophilicity of membranes. Hydrophilicity of polymers can be improved by plasma treatment, surface graft copolymerization or hydrophilic coatings [2–6]. The impact of fouling can also be reduced by introducing a negative surface charge density to the membrane surface [7]. The use of negatively charged membranes deters fouling as the charged membrane repels similarly charged foulants via electrostatic repulsion.

Recently, attention has shifted to electrically conductive membranes that make use of their high electrical conductivity to either prevent fouling, or to remove foulants from used membranes. The mechanism of cleaning in conductive membranes can be simple electrostatic interactions or electrochemical redox reactions at the membrane surface. Electrochemical recovery of conductive membranes via bubble generation has previously been found to be an effective cleaning method [8,9].

Although intrinsically conductive polymers are promising for various applications such as sensors, coatings and solar cells [10], they are not widely used in membrane separation due to their relatively low selectivity and flux [11,12]. On the other hand, incorporating carbon nanotubes (CNTs) in typically insulating polymeric membranes not only results in high electrical conductivity, but it also leads to improved

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http://dx.doi.org/10.1016/j.desal.2015.01.006
0011-9164/

mechanical properties. Fast water transport through CNTs as well as strong antimicrobial properties has stimulated interest for their use in membrane materials [13–18].

Previously, Zhang and Vecitis used a CNT–PVDF cathode with a UF membrane to mitigate fouling by generating negative surface charges through capacitive charging [19]. A similar mechanism based on electrostatic repulsion was used by Dudchenko et al., who developed CNT–PVA composite membranes for UF [20]. However, electrochemical defouling using redox reactions on CNT-based electrodes is an area of growing interest. In electrochemical defouling, the membrane can act either: (1) as the anode where direct oxidation of foulants takes place at the membrane surface; or (2) as the cathode, in which foulants are removed via bubble generation at the surface. Vecitis's group was able to remove foulants through oxidation at the surface of CNT membranes [21]. However, it was recently found that bubble generation through electro-reduction is a more non-destructive mechanism for cleaning membranes, as oxidation at the surface may damage the membrane itself [22]. We recently reported periodic electrolysis as a fast and efficient cleaning technique for CNT-coated membranes via bubble generation [23]. However, the limited conductivity of coated membranes required silver mesh to be pasted on the surface for better charge distribution during electrolysis.

Carbon nanostructures (CNS) have been developed by Applied Nanostructured Solutions (ANS), a subsidiary of Lockheed Martin [24], USA. CNS consists of highly entangled CNTs characterized by improved processability, high electrical conductivity and large surface area. CNS is a relatively low cost material developed from a process free of volatile organic compounds.

In this work, we developed self-supporting CNS/PVDF membranes in which PVDF acted as a binding agent in the CNS membrane. The performance of these membranes was studied for in-situ surface cleaning using electrolysis with a typical biofoulant solution as feed. The membranes were also characterized for mechanical stability, surface area and hydrophilicity.

2. Materials and methods

Polyvinylidene fluoride (Kynar, Arkema), sodium chloride (NaCl, Aldrich), and yeast (Baker's yeast, DCL, France), were used as received.

2.1. Fabrication of CNS

Applied Nanostructured Solutions, LLC (ANS) has developed a unique Chemical Vapor Deposition (CVD) process for the growth of carbon nanotubes (CNTs) onto various fiber substrates including carbon, glass, and ceramics [24]. This process is continuous and operates at atmospheric pressures enabling high volume/low cost manufacturing. This process infuses conductive CNTs in a highly entangled form referred to as carbon nanostructures (CNS) onto the surface of the fiber. This structure can be removed and used as harvested flake which has a 3D structure with all dimension in microns.

2.2. Fabrication of the CNS/PVDF membrane

90 wt.% CNS powder and 10 wt.% PVDF powder were dispersed in a 1:1 (v/v) ethanol/water solution using a probe sonicator (Hielscher, UP400S) at 50% amplitude and 0.5 cycle for 10 min to obtain a homogeneous ink-like suspension. CNS/PVDF suspension was filtered through the filter paper using vacuum filtration. Thereafter the CNS/PVDF membrane was peeled off the filter paper and dried at room temperature. The membrane was then subjected to heat treatment at 160 °C for 1 h to melt PVDF and provide binding sites inside the entangled CNS structure to enhance the mechanical strength of the membrane.

2.3. Membrane characterization

Surface morphology of the membranes was studied using scanning electron microscopy (FEI Quanta FEG 250). Electrical conductivity of the membrane was measured using a four point probe (LakeShore, USA), according to the Van der Pauw method [25]. In this method, four electrodes were pasted on the membrane surface using silver paint dots. The electrodes were marked as 1–4 in clockwise position. Current was passed through 1 & 2 electrodes and potential is measured between 4 & 5 electrodes. Four consecutive measurements were done by applying current between 2 & 3, 3 & 4, and 4 & 1 and measuring the potential between 4 & 1, 1 & 2 and 2 & 3 respectively.

Mechanical properties of the CNS and CNS/PVDF membranes were investigated with Instron 5966 Dual Column Tabletop Testing System (Italy). A standard dog-bone specimen was stretched in tension at a strain rate of 1 mm/min and its response was recorded until failure. Stress–strain curves were generated from which tensile strength and strain at fracture were determined. Contact angle tests were carried out at room temperature using an EasyDrop Standard drop shape analysis (KRUSS, Germany). A 4 μL droplet of deionized water was produced on the membrane surface and the digital image was used to determine the water contact angle.

Surface area of the membranes was measured using Brunauer–Emmett–Teller (BET) analysis in a relative pressure of $P/P_o = 0.05$–0.30. Pore size distribution and pore volume were calculated by the Barrett–Joyner–Halenda (BJH) method.

2.4. Membrane cleaning setup

Yeast suspension used as bio-foulant was prepared by immersing 100 mg yeast in an aqueous NaCl solution with concentration of 10 g/L. NaCl solution was used to assist the electrolysis process during cleaning of the fouled membranes. The prepared yeast suspension was used as feed for the membrane in a cross-flow filtration setup operating at a pressure of 2 bar. The picture of the setup used is shown in Fig. 1. Filtration was carried out in 60 min intervals, stopping for 2–3 min for electrolysis between each run. The permeate was collected and weighed after each filtration interval. For electrolytic cleaning, the CNS/PVDF surface acted as the negative electrode (cathode) while stainless steel of diameter 15 mm was used as the positive electrode (anode) in electrochemical system. The electrolysis was performed by using

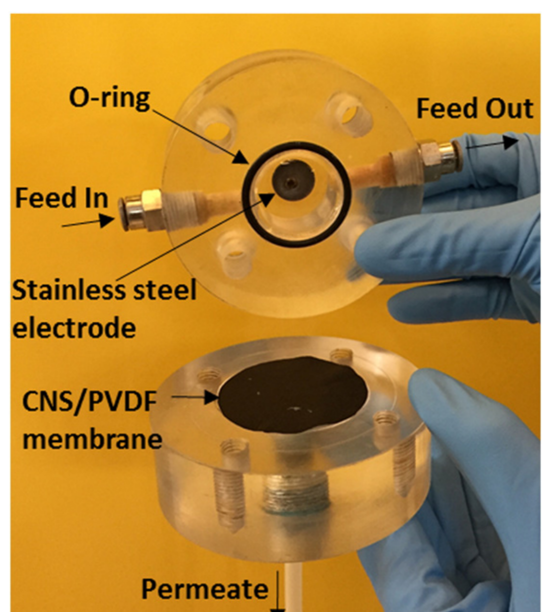

Fig. 1. Photograph of set-up used for filtration process.