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A novel in situ membrane cleaning method using periodic electrolysis

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ABSTRACT

Membrane fouling is the major problem during the practical application of membrane separation processes in industry and water treatment. Therefore a search for novel efficient methods of membrane cleaning is currently of crucial importance for membrane-based technologies. The paper describes a new method of membrane cleaning, which is based on periodic electrolysis using a novel electrically conductive membrane to remove/prevent membrane fouling. The membrane consists of a thin electrically conductive layer of multi-walled carbon nanotubes (MWCNTs) deposited on the membrane's surface. The deposited MWCNTs allow the membrane to function as a cathode in an electrochemical system that includes the electrically conductive membrane, the salt water as an electrolyte and a stainless steel counter anode. The efficiency of the cleaning procedure in the flux recovery has been proved with typical bio- and inorganic membrane foulants such as $CaCO_3$ and yeast suspensions. The cleaning mechanism during the electrolysis process is explained by the evolution of gases forming micro-bubbles at the membrane surface which remove the foulant material out from the membrane. The proposed method enables in situ membrane self-cleaning, thus providing a non-destructive, continuous and renewable approach for the mitigation of the different types of membrane fouling.

1. Introduction

During the last few decades, pressure-driven membrane processes such as reverse osmosis, nanofiltration, ultrafiltration and microfiltration have been widely used in water treatment, biotechnology, the food industry, medicine and other fields [1]. However, the main problem arising upon the operation of the membrane units is membrane fouling, which seriously hampers the application of membrane technologies [2].

Membrane fouling is an extremely complex phenomenon that has not yet been defined precisely. In general, the term is used to describe the undesirable deposition of retained particles, colloids, macromolecules, salts, etc., at the membrane surface or inside the pores. Depending on the membrane process and chemical/biological nature of foulants, several types of fouling can occur in membrane systems, e.g. inorganic fouling or scaling, organic fouling colloidal fouling and biofouling [3–6].

Membrane fouling, as well as its prevention, has been a subject of many studies since the early 1960s when industrial membrane separation processes emerged. Membrane fouling can be partially controlled by the selection of an appropriate membrane, adjustment of the operating conditions in a membrane element, including hydrodynamics and operating pressure, and appropriate pretreatment of the feed solutions [7,8]. Unfortunately, very often these actions are not sufficient to cope with fouling. As fouling progresses, membrane flux declines; higher operating pressures and thus more energy must be expended to achieve the desired throughput.

Usually, membrane cleaning is applied to remove the foulants and restore the membrane flux. A number of physical and chemical techniques have been used for membrane cleaning including backwashing, pulsing, forward flushing with air, sonification and chemical cleaning [9–12]. However, these operations fail to recover the membrane flux without deteriorating the membrane material and interrupt the water treatment process [13]. In many cases, the membrane elements must be replaced, which sharply increases the treatment costs [8]. Therefore the development of novel efficient methods of membrane cleaning at lower cost is of crucial importance for the wider use of membrane technologies in industry and water treatment.

Electrolytic cleaning is a common method used for metal surface cleaning before galvanizing and electroplating [14]. Electrolytic cleaning is an electrolysis process in which a direct voltage

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is applied between an anode and a cathode dipped in an electrolyte that consists of free ions for conducting the electric current [15]. During the electrolysis process gases are produced and bubbled at the electrodes' surfaces. The generation and evolution of gases has been found to be effective in removing the tiniest remaining amounts of dirt from the surface of electrically conductive materials [14–17]. The application of this technique to pressure-driven membrane processes is hindered by the inherent insulating nature of polymeric membranes. Over the years, attempts have been made to use electrically conducting polymers to form membranes for different purposes [18,19]. However, traditional conducting polymers are notoriously difficult to process, and membranes made from these materials suffer from low selectivity, low flux, and often, low conductivity [19,20]. Recently, it has been reported that carbon nanotubes (CNTs) possess good electrical conductivity [21]. Because of their electrical properties CNTs have been proposed as functional electrodes in electrochemical systems such as: oxygen reduction in fuel cells; hydrogen production; photo-assisted water electrolysis etc [21–24]. Additionally it was shown that CNTs deposited on a porous support layer [25] or embedded into polymer membranes are capable of bacterial inactivation and bio-fouling prevention once an electrical bias is applied [26].

In this paper, we have studied the possibility of using electrolytic cleaning for polymer membranes modified with multi wall carbon nanotubes (MWCNTs) to develop a membrane cleaning process, which might be used in situ in membrane modules. The polymer membrane has been coated with a thin electrically conductive MWCNTs layer and acts as an electrode during the periodic electrolysis. The efficiency of membrane cleaning has been studied during membrane filtration of calcium carbonate and yeast suspensions, which are typical membrane foulants for membrane-based desalination processes.

2. Methods

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) (Cheaptubes.com, USA) (outer diameter 13–18 nm, purity > 99 wt%), microfiltration polyvilidefluoride Millipore membranes (GSWP, 0.22 μm), sodium lauryl sulfate (SDS, surfactant), sodium chloride (NaCl, Aldrich), yeast (Baker's yeast, DCL, France), calcium carbonate ($CaCO_3$, Aldrich) were used as received.

2.2. MWCNTs coating on the membrane

Millipore membranes were coated using vacuum filtration technique reported elsewhere [27]. 0.05 wt% MWCNTs powder was dispersed in an aqueous solution of 1 wt% SDS in water using probe sonicator (Hielscher, UP400S, 400 W, 24 kHz) at 50% amplitude and 0.5 cycle for 10 min to obtain a homogeneous ink-like suspension. Then 4 ml of MWCNTs suspension was filtered through the membrane with an active area of 9.34 cm^2 using vacuum filtration at 30 kPa pressure. Thereafter the membrane sample was carefully washed three times with Milli-Q water to remove any excessive MWCNTs from the membrane surface. Optical images of MWCNTs coated microfiltration membranes were shown in Fig. 1(a–c). First the membranes were coated with MWCNTs and then silver electrodes were printed on the coated membrane to improve the electric charge distribution of the membranes (Fig. 1c). Thickness of the MWCNTs coating on the surface was measured from the cross-sectional SEM images and found to be 3–4 μm. After drying the MWCNTs coated membrane at room temperature, silver electrodes were coated on the membrane surface (Fig. 1c) to improve the electrical contacts and charge distribution on the surface of membrane.

2.3. Membrane characterization

Scanning electron microscopy (FEI Quanta FEG 250) was used to image the surface and cross-section of the membrane in high vacuum. Prior to imaging, samples were first coated with a thin gold layer of 5–8 nm thickness. Optical images of the membrane surface were obtained by the optical microscope (Olympus-DP21). Surface resistivity of the MWNTs coated membrane was measured by using four point probe (LakeShore, USA) according to Van der Pauw method [28]. 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 and current is passed through 1 and 2 electrodes and potential is measured between 3 and 4 electrodes. Four consecutive measurements were done by applying current between 2 and 3, 3 and 4, 4 and 1 and potential was measured between 4 and 1, 1 and 2 and 2 and 3 respectively.

2.4. A membrane cleaning setup

A custom made cross flow filtration setup was used in this study. A schematic design of the filtration setup is shown in Fig. 2. MWCNTs coated surface acts as a negative electrode (cathode) in electrochemical system using stainless steel of diameter 15 mm as

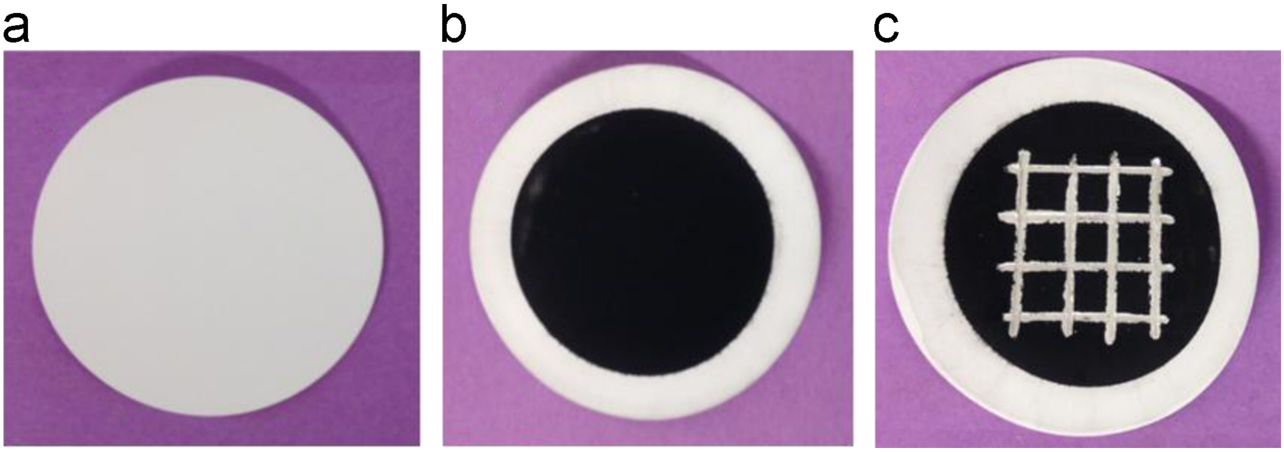

Fig. 1. Optical images of (a) pristine Millipore membrane, (b) coated with MWCNTs using vacuum filtration, (c) MWCNTs coated membrane with silver electrodes.