Journal of Industrial and Engineering Chemistry 29 (2015) 366–374

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Preparation of high antibiofouling amino functionalized MWCNTs/PES nanocomposite ultrafiltration membrane for application in membrane bioreactor

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ARTICLE INFO

Article history:
Received 7 August 2014
Received in revised form 20 February 2015
Accepted 21 April 2015
Available online 1 May 2015

Keywords:
Amino functionalized MWCNTs
Antibiofouling membrane
Membrane bioreactor (MBR)

ABSTRACT

Membrane bioreactor (MBR) is an innovative hybrid biotechnology for wastewater treatment. However, its application is constrained by its tendency to fouling. Various procedures are applied to reduce membrane fouling. In this work, nanocomposite membranes were prepared by embedding amino functionalized multi-walled carbon nanotubes (NH_2-MWCNTs) and were used for improving membrane surface hydrophilicity and subsequently the reduction of the membrane biofouling. The NH_2-MWCNTs were synthesized and used as nanofiller in preparation of polyethersulfone (PES) ultrafiltration (UF) membrane. The modified MWCNTs were blended with different weight percentage in the casting solution, i.e. 0.05, 0.1 and 1 wt.%. In this study, the effect of the NH_2-MWCNTs on membrane morphology and antibiofouling property was investigated. The Fourier transform infrared (FT-IR) spectra analysis showed that the –NH_2 functional groups formed on the surface of MWCNTs. The nanocomposite membranes prepared with different contents of NH_2-MWCNTs nanofiller were characterized using contact angle, scanning electron microscopy (SEM), and permeation tests. The SEM images displayed a finger-like and porous structure for all synthesized UF membranes. Contact angle measurements indicated that NH_2-MWCNTs nanofiller improved the hydrophilicity of the obtained membranes. Fouling resistances of the membranes elucidated by activated sludge suspension filtration and measurements of flux recovery ratio (FRR). The results of the experiments revealed that the 0.1 wt.% NH_2-MWCNTs membrane had the best permeability, hydrophilicity and antibiofouling properties. It was quite a surprise to discover that inclusion of only about 0.1 wt.% of the amino functionalized MWCNTs in the fabrication of membrane could spring up a generation of membrane with antibiofouling capability for MBRs.

Introduction

Membrane bioreactor (MBR) has attracted very much interest in recent years, for wastewater treatment that necessitates high effluent quality, e.g. water reuse or water recycling [1–5]. The advantages of using MBR technology for wastewater treatment comprises excellent effluent quality, low surplus sludge production, high metabolic activity, and small footprint demand [6–8]. However, the large-scale application of the MBR is constrained by their tendency to foul [9–11]. Membrane fouling occurs due to biofilm formation and deposition of soluble and particulate materials onto the membrane surface and into the membrane pores [10] which leads to reduction in permeate flux [12], decrease in membrane performance [7], increase in operational cost and shortening of the membrane lifetime [7].

The fouling in MBRs can be divided into three major categories, e.g. biofouling, organic fouling, and inorganic fouling [13]. Complex interactions between membrane material and components of activated sludge lead to biofouling of the membrane [36]. Biofouling can damage membrane surface, thus increasing membrane replacement costs and contributing to reduce membrane flux, which resulting in higher operational costs [14]. Unlike other fouling, biofouling is much more difficult to clean and often causes permanent permeability loss as well as irreversible damage of the membranes [15]. Therefore, it is highly desirable to have a membrane with antifouling or antibiofouling capability.

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http://dx.doi.org/10.1016/j.jiec.2015.04.017

Several approaches have been applied to control the membrane fouling, which generally include modification of the feed solution, surface modification of membrane like hydrophobic or hydrophilic and electropositive or electronegative modification, changing operating conditions, and periodic cleaning [16–19]. Due to interaction of hydrophobic between the membrane surface and foulant, surface modification of membrane and increasing of membrane hydrophilicity appears to be a suitable approach to diminish membrane fouling.

Polyether sulphone (PES) is known as an organic polymer which is used in manufacturing of different types of membrane, such as microfiltration [20], ultrafiltration [21,22] and nanofiltration [23] membranes. It has been widely used in membranes preparation because of remarkable chemical and thermal stability, environmental tolerance, wide pH endurance as well as wider range of pore size and good mechanical properties. Despite the advantages mentioned above, the major disadvantage of the PES is high hydrophobicity and low biofouling resistance properties of the prepared membranes. Many methods were used to enhance the hydrophilicity of membranes such as grafting of hydrophilic monomers onto the membrane surface [24], interfacial polymerization with hydrophilic monomers [25], functionalization of polymer [26], embedding with nanoparticles [27,28] or hydrophilic monomers and polymers [29], etc. Recently, incorporation of hybrid materials such as TiO_2 [30], Al_2O_3 [28,31], SiO_2 [27,32], Fe_3O_4 [33], and carbon nanotubes [23,34] have been tried as membrane forming materials to attain high permeability, selectivity, and antifouling property in membrane applications. Akar et al. [35] used selenium and copper nanoparticles in order to preparation of ultrafiltration membrane. These nanoparticles showed superior antioxidant activity and acted as an antimicrobial agent. The blended membranes with nanoparticles are considered to be suitable for the prevention of biofouling. The 0.05 wt.% Cu/PES membrane exhibited highest protein rejection (86.3%) and Se/PES membranes showed better antifouling performance (lower flux decline). Lee et al. [36] prepared the composite membrane blended with graphene oxide (GO) nanoplatelets with hydrophilic and antifouling properties in order to investigate the membrane antifouling capability for MBR. The results indicated that 1 wt.% of graphene oxide in the fabrication of membrane showed good antifouling capability for MBRs. Zhao et al. [37] fabricated GO/PVDF composite membrane with effective antifouling performance for application in MBR system. The GO/PVDF composite membrane demonstrated sustained permeability, lower cleaning frequency, and filtration time that were three times longer than that of the PVDF membrane.

Multi-walled carbon nanotubes (MWCNTs) is a very good additive in modified polymeric membranes which can ameliorate mechanical strength and antifouling property of the membrane [38] and act as extraordinary mass transport channels [39]. Considering that, biofouling of the polymeric membranes is a serious problem, particularly in water reclamation and wastewater treatment, the MWCNTs presented high bacterial adsorption capacity. The microbial adsorption ability of the MWCNTs has been reported to be higher than any other commercially available adsorbent media [40]. Despite the advantages described above, pristine MWCNTs have a tendency to self-aggregate via van der walls forces, meantime the chemically inert nature of the MWCNTs leads to poor dispersibility and weak interfacial interactions with polymer matrix [23]. The dispersing capacity of the MWCNTs in aqueous solution have a vital effect on the antimicrobial activity of the MWCNTs, as the direct contact between the MWCNTs and target pathogens was required [41–43], therefore, modification of the MWCNTs is necessary. Up to now, some of the methods which have been widely used to modify these nanofillers are; introducing hydrophilic functional groups on the surface of the MWCNTs, functionalization by chemical agents and attaching polar groups to MWCNTs sidewalls [44–46].

Salehi and his colleagues [47] synthesized amino functionalized multi-walled carbon nanotubes (NH_2-MWCNTs) and utilized it to prepare novel chitosan/PVA thin adsorptive membranes for copper ion removal from water. Results showed that the amino groups attached to the outer walls of the MWCNTs, not only can facilitate cation transport through the membrane, but also may have caused better dispersion of the functionalized MWCNTs in the polymeric matrix. Vatanpour and his coworkers [23] prepared a membrane by acid oxidized multi-walled carbon nanotubes embedded in polyethersulfone as matrix polymer. The results suggested that the hydrophilicity and antifouling properties of prepared membrane were enhanced by blending of oxidized MWCNTs in polymer matrix due to migration of functionalized MWCNTs to membrane surface. Rahimpour et al. [48] reported that appropriate amount of functionalized multi-walled carbon nanotubes can improve the performance of prepared membranes relative to unmodified membrane. Majeed et al. [39] blended hydroxyl the MWCNTs with polyacrylonitrile (PAN) to prepare ultrafiltration membranes by phase inversion method. Three different concentrations of the MWCNTs were used in PAN. The water flux of the membranes increased at 0.5 wt.% loading of MWCNTs compared to neat PAN membranes.

This research is focused on the fabrication of a nanocomposite ultrafiltration membrane by embedding the NH_2-MWCNTs in polyethersulfone (PES) matrix for application in membrane bioreactors. The membranes prepared by phase inversion method with different low concentrations of the nanofiller in order to enhance the membrane surface hydrophilicity and mitigation of membranes biofouling in membrane bioreactor. FT-IR, SEM, and water contact angle measurements are done in order to characterize the functionalized MWCNTs and the prepared membranes. Performance of the fabricated membranes was evaluated in terms of the pure water flux (PWF) and rejection of solution containing bovine serum albumin (BSA). Antibiofouling property of the membranes is also investigated on the basis of the filtration of the activated sludge suspension and flux recovery ratio (FRR) measurements.

Materials and methods

Materials

Polyethersulfone (PES ultrason E6020P with MW = 58,000 g/mol) and dimethylacetamide (DMAc) as polymer and solvent, respectively, were supplied by BASF Co., Germany. Polyvinyl pyrrolidone (PVP K30 with MW = 25,000 g/mol) was obtained from Mowiol, Germany. Raw multi-walled carbon nanotubes (length 1–10 μm, diameter 5–20 nm, number of walls 3–15), purchased from Plasma hem GmbH, Germany, was used for preparation of the amino functionalized MWCNTs. All the chemicals used in the experiments were of reagent grade. Distilled water was utilized throughout this study.

Preparation of amino functionalized MWCNTs

The used amino functionalized MWCNTs nanoparticles were synthesized according to the protocols represented in the literature [47]. Fig. 1 presents the schematic of the nonofillers synthesis. 8.55 g of raw MWCNTs was soaked in 200 ml of concentrated mixture of H_2SO_4/HNO_3 (3/1 in v/v), and completely dispersed at room temperature by a sonicator (SONREX Digit DT52 H, BAN-DELIN, Germany 240 W, 35 kHZ) for 15 min. The solution was refluxed for 7.5 h at 90 °C and then was diluted with distilled water and centrifuged for 1 h. The produced MWCNT-COOH was