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Preparation and performance evaluation of high-density polyethylene/silica nanocomposite membranes in membrane bioreactor system

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ABSTRACT

In this study, in order to improve the antifouling properties of high-density polyethylene (HDPE) membrane in the membrane bioreactor (MBR) system, HDPE/SiO_2 nanocomposite membrane was developed and evaluated for its physicochemical changes with different contents (0, 0.25, 0.5, and 1 wt.%) of SiO_2 nanoparticles (NPs). Flat sheet membranes were fabricated via thermally induced phase separation (TIPS) method and characterized by field emission scanning electron microscopy (FESEM), contact angle, energy dispersive X-ray analysis (EDX), tensile test and pure water flux. The filtration experiments and FESEM confirmed that certain dosages of SiO_2 NPs (0.5 wt.%) can increase the membrane porosity. Fouling analysis revealed that the presence of SiO_2 NPs in the membrane matrix results in respectively 27% and more than 70% reduction in the total fouling ratio (TFR) and irreversible fouling ratio (IFR) and a little bit increase (16%) in the reversible fouling ratio (RFR). The obtained results showed high efficiencies of chemical oxygen demand (COD) removal rates like more than 95% for both membranes coupled biological filtration tests. In order to identify the most likely fouling mechanism, Hermia's model was used and the obtained results revealed the existence of two fouling phases; in the first phase, cake filtration is the main fouling mechanism for both membranes, while complete blockage model is the prevailing fouling mechanism in the second phase.

1. Introduction

Population growth and industrial development are the two main influential parameters affecting the ever-increasing water demand, which push water purification/reclamation industries to explore effective and efficient methods for producing water from non-conventional resources in developing countries located in the Middle East and North Africa (MENA). Among several wastewater reclamation and water recycling processes, membrane-based technologies show great potential to overcome water scarcity in MENA. Membrane technology generally refers to an advanced separation process which produces treated effluent without any addition of chemicals. Recently membrane technology has become economically reliable due to lower energy consumption and membrane costs [1]. In the membrane separation technology, energy consumption is very low as there is no phase change. Also, this process can be done in low-temperature operation.

According to several reports, membrane bioreactor (MBR) has gained popularity due to several unique advantages such as less area requirement, self-governing sludge retention time (SRT) and hydraulic retention time (HRT), less HRT, less sludge production and high quality of effluent compared to other conventional wastewater treatment systems [2–10].

Membrane fouling, including internal blocking or external deposition of mixed liquor constituents [11–15], however, is an inevitable phenomenon in MBRs that limits their commercialization due to decreased productivity and increased operational costs as well as energy intake [7,16].

Fouling in membrane bioreactors usually takes place due to effective physicochemical interactions between the membrane surface and biomass ingredients [17,18]. The latter comprises microbial cells and metabolites such as soluble microbial products (SMP) and extra-cellular polymeric substances (EPS). Their hydrophobic adsorption on the membrane surface is usually considered as an irreversible phenomenon due to the self-perpetuating

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nature of living components and microorganisms [19–22]. It is well documented that reversible fouling can be easily eliminated by implementation of hydraulic cleaning such as cross-section flushing and backwashing, while irreversible fouling needs chemical cleaning to be removed [23,24]. In recent publications, numerous studies have been intensively conducted and various strategies such as adjustment of operation conditions, membrane manipulation and biomass specifications have been introduced to overcome membrane fouling [18,24–28]. On the other hand, membranes with the hydrophobic surface are more vulnerable to fouling with respect to the hydrophilic membrane [29,30].

In comparison with other commercial polymers, high - density polyethylene (HDPE) is a good choice to prepare membrane with several excellent properties such as good mechanical strength, great chemical resistance and thermal stability. However, its wider application has been restricted because of its inherent hydrophobicity, non-wettability, absence of any active functional groups and high fouling affinity [30–33].

Therefore increasing the membrane hydrophilicity seems to be a suitable method to overcome severe fouling. Many efforts such as physical blending with hydrophilic polymers or inorganic fillers, plasma treatment, grafting hydrophilic species to the membrane surface and chemical reaction have been dedicated to improving the HDPE membrane hydrophilicity [32,34–36]. Among these methods, preparation of membranes embedded with uniformly dispersed inorganic nanoparticles (NPs) in a polymer matrix has attracted great attention in membrane technology owing to the unique physicochemical properties of NPs [24,27]. Incorporation of inorganic NPs in the membrane matrix can alter the porous structure and improve the relative hydrophilicity, mechanical properties, water permeability and also antifouling properties [34]. Nanoparticles including TiO_2 [37,38], ZnO [31,39], SiO_2 [17], GO have been widely used in polymer-inorganic membranes [35,40]. Thus, NPs utilization can be regarded as an effective method in the fouling reduction of used membrane in MBR [35,40–44].

To the best of our knowledge, fabrication of HDPE/SiO_2 membrane and investigation of its antifouling performance in the membrane bioreactor have not been reported yet.

In the present work, SiO_2 NPs embedded HDPE membranes with different weight fractions of SiO_2 NPs were prepared via thermally induced phase separation (TIPS) method. This method was widely used in the fabrication of other types of membranes such as polyvinylidene fluoride (PVDF) [45] and cellulose acetate [46]. However, these membranes have not been used in MBR systems. A set of structural and operational analyses including field emission scanning electron microscopy (FESEM), energy dispersive X-ray analysis (EDX), contact angle measurements, tensile test and pure water flux experiment were conducted to characterize the membranes and identify the impact of NPs content on the membrane properties and performances.

In order to clarify the performance of nanocomposite membranes, neat and SiO_2 NPs embedded nanocomposite membranes were used in a lab-scale immersed MBR to treat the real industrial wastewater supplied by Daana Pharmaceutical Company of Tabriz, Iran. This study has mainly focused on such points as the effect of SiO_2 NPs concentration on the structure of SiO_2 embedded HDPE nanocomposite membrane, the impact of membrane characteristics on the critical flux, comparing the antifouling performance of neat and SiO_2 embedded HDPE membranes and finally analysis of fouling mechanisms that commonly occur in MBR systems. In this case, the only models which describe individual different fouling mechanisms under constant pressure filtration circumstances are those shown by Hermia's model. Generally, Hermia's model is the most useful and applicable models for microfiltration flux decline prediction.

2. Materials and methods

2.1. Materials

High-density polyethylene, commercial grade and 119,500 g/mol molecular weight, was purchased from Amirkabir Petrochemical Company and used as polymer. Mineral oil (MO) from Acros Organics, acetone from Merck and SiO_2 NPs (particle size less than 100 nm) from Sigma Aldrich were used as diluent, extractant and inorganic filler, respectively. Deionized (DI) water was used in the sample preparation and throughout the experiments for pure water flux measurements.

2.2. Preparation of membranes

Neat and SiO_2 embedded HDPE nanocomposite membranes were prepared via TIPS method. In order to prepare SiO_2 embedded membrane, silica NPs with different weight fractions including 0.25, 0.5, 1 wt.% (based on the weight of HDPE) were accurately weighed and dispersed in MO, followed by sonication by probe system (Sonopuls HD 3200, Bandelin) for 30 min. Subsequently, HDPE (20 wt.% based on the weight of MO) was added to the MO-NP suspension and melt-blended at 160 °C and 450 rpm for 90 min in a sealed glass vessel, kept in the silicon oil bath. Dope solution was cast with 400 μm thickness on a pre-heated glass sheet. The plate was immediately soaked in the DI coagulation bath (27 °C ± 3) to start phase separation. The membrane was then immersed in acetone for 24 h to extract its diluent. Finally, the prepared membrane was dried at room temperature to remove acetone. In order to prepare neat membrane, HDPE and MO were melt-blended at 160 °C for 90 min in a sealed glass vessel kept in a silicon oil bath, followed by a similar procedure described above for the SiO_2 embedded HDPE membrane.

2.3. Membrane characterization

2.3.1. Field emission scanning electron microscopy (FESEM)

FESEM analysis is an important technique in the qualitative study of membrane morphology. The top surface and cross-sectional morphologies of membranes were characterized by FESEM (MIRA3 FEG-SEM, Tescan). The samples were cut into pieces of small size and then fractured in liquid nitrogen in order to prepare cross-section samples. All samples were coated by gold using sputtering machine before observation to make them conductive.

2.3.2. Energy dispersive X-ray (EDX) analysis

In order to get a deep understanding of a certain part of the membrane, EDX analysis was also performed to confirm the presence of the Si element on the membrane top surface as well as pore walls. In this research, EDX analysis was carried out with Energy Dispersive X-ray Spectroscope (Vega/BSE DETECTOR, TESCAN).

2.3.3. Contact angle measurement

A contact angle goniometer (PGX, Thwing-Albert Instrument Co.) was used to measure the contact angle between the membrane surface and water droplet to determine the membrane hydrophilicity. The average of five measurements at different locations of each membrane was reported.

2.3.4. Tensile test

The membranes' mechanical strength and elongation at the break point were measured using tensile measurement machine (STM-5, SANTAM). The small test samples of neat and SiO_2 embedded HDPE membranes were prepared in the size of 5.0 cm × 0.5 cm and were stretched with the strain rate of 10 mm/min. At least three