BORON NITRIDE NANOCOMPOSITE MEMBRANE FOR ORGANIC POLLUTANT AND SALT REMOVAL FROM WATER

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ABSTRACT

A desalination plant consists of pretreatment and the main salt rejecting units. A pretreatment unit consists of ultrafiltration membranes for filtering organic matter from water. While the salt rejecting unit, the heart of desalination process, consists of reverse osmosis (RO) membranes. In this study, a potential membrane material to be used for pretreatment and desalting units in the desalination plant. Ultrafiltration polysulfone-based mixed matrix membranes (MMMs) incorporated with two-dimensional boron nitride nanosheet (BNNS) were prepared via phase inversion method. The amount of BNNS incorporated was varied and the influence on membrane morphology, contact angle, surface charge, as well as water permeability and organic matter rejection were investigated. Results revealed that the addition of BN to the membrane matrix resulted in profound increase in water permeability (almost tripled to that of neat polysulfone membrane (PSf) , as increase from 50 L/m^2.h.bar for neat PSf to 110 L/m^2.h.bar for PSf/BN 1.0%) and humic acid rejection due to the increase in pore size and surface negative charge (94% of humic acid rejection for PSf/BN 1.0%). Beyond the morphological changes imparted by the inclusion of BNNS, the presence of BNNS within the membrane matrix also contributed to the enhancement in flux and humic acid rejection based on surface-slip and selective interlayer transport in the membrane. Despite the favourable augmentation of water transport and filtration performance, the MMMs suffered from fouling problem due to the entrapment of foulant within the enlarged pores and the membrane valleys. Inherent adsorptive character of BNNS could be a disadvantage when utilized as a membrane filler without proper modification. Next, raw BNNS and chemically activated BNNS (A-BN) were used as a nanofiller for the development of thin film nanocomposite (TFN) membrane. TFN membranes were synthesized via interfacial polymerization reaction between 1,3-Phenylendiamine (MPD) and trimesoyl chloride (TMC) monomer to form ultra-thin polyamide layer on PSf porous substrate. TFN membrane was responsible for desalination through RO process. Results showed that TFN membranes consisted of BNNS and A-BN as nanofillers have shown improvement in water permeability (33.9% higher than TFC membrane), with a minor loss in sodium chloride (NaCl) rejection (89.84% NaCl rejection for TFN-4). A comparative study with TFN membrane consisted of A-BN revealed a strong influence in improving water permeability with a minimal loss in salt rejection compared to TFN membrane with raw BNNS.

ABSTRAK

Loji penyahgaraman terdiri daripada unit prarawatan dan unit penyahgaraman utama. Dalam unit prarawatan, ia terdiri daripada membran ultrapenapisan bertujuan untuk menyingkirkan bahan organik yang terdapat dalam air. Manakala unit penyahgaraman, proses penyahgaraman terdiri daripada membran osmosis balikan (RO). Dalam kajian ini, bahan membran berpotensi akan digunakan untuk unit prarawatan dan penyahgaraman dalam loji penyahgaraman. Membran matriks tercampur berasaskan ultrapenapisan polisulfona (MMMs) digabungkan dengan nanokepingan boron nitrida dua-dimensi (BNNS) disediakan melalui kaedah balikan fasa. Kandungan gabungan BNNS dipelbagaikan bagi mengkaji kesannya ke atas morfologi membran, sudut sentuh, caj permukaan, kebolehtelapan air dan penolakan bahan organik. Keputusan menunjukkan bahawa penambahan BN di dalam membran matrik mengakibatkan peningkatan kebolehtelapan air yang ketara (hampir tiga kali ganda daripada membran polisulfona (PSf) yang tulen, iaitu peningkatan daripada 50 L/m2.h.bar untuk PSf tulen kepada 110 L/m^2.h.bar untuk PSf/BN 1.0%) dan penolakan asid humik disebabkan oleh peningkatan saiz liang dan caj negatif permukaan membran (94% penolakan asid humik untuk PSf/BN 1.0%). Selain daripada perubahan morfologi permukaan yang disebabkan oleh kemasukan BNNS, kehadiran BNNS dalam membran matrik juga menyumbang kepada peningkatan fluks dan penolakan asid humik berdasarkan slip permukaan dan pengangkutan antara lapisan terpilih dalam membran. Walaupun terdapat peningkatan pengangkutan dan penapisan air yang menggalakkan, MMMs mengalami masalah pemendakan kotoran disebabkan oleh pemerangkapan kotoran dalam liang yang besar dan celah membran. Sifat penyerapan yang tinggi adalah penyebab kelemahan BNNS apabila digunakan sebagai pengisi membran tanpa pengubahsuaian yang betul. Seterusnya, BNNS dan pengaktifkan kimia BNNS (A-BN) digunakan sebagai pengisi nano untuk membina membran nanokomposit filem tipis (TFN). Membran TFN disintesis melalui tindak balas pempolimeran antara muka antara 1,3-fenilendiamina (MPD) dan monomer trimesoil klorida (TMC) bagi membentuk lapisan poliamida ultra-nipis pada substrat berliang PSf. Membran TFN bertanggungjawab untuk penyahgaraman melalui kaedah RO. Keputusan menunjukkan bahawa membran TFN yang mempunyai BNNS dan A-BN sebagai nanopengisi telah menunjukkan peningkatan dalam kebolehtelapan air (33.9% lebih tinggi daripada membran TFC), dengan kehilangan kecil dalam penolakan natrium klorida (NaCl) (89.84% penolakan NaCl untuk TFN-4). Kajian perbandingan dengan membran TFN yang terdiri daripada A-BN menunjukkan bahawa pengaruh yang kuat pada A-BN telah meningkatkan kebolehtelapan air dengan kehilangan minimum dalam penolakan garam berbanding dengan membran TFN dengan BNNS sahaja.

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LIST OF ABBREVIATIONS

A-BN	-	Chemically activated boron nitride
AFM	-	Atomic force microscopy
BN	-	Boron nitride
BNNS	-	Boron nitride nanosheet
BNNT	-	Boron nitride nanotube
Ca^{2+}	-	Calcium ion
CA	-	Cellulose acetate
Cl^{-}	-	Chloride ion
CNs	-	Carbon nanomaterials
CNT	-	Carbon nanotubes
ED	-	Electrodialysis
EDR	-	Electrodialysis reversal
FTIR	-	Fourier transform infrared spectroscopy
h-BN	-	Hexagonal boron nitride
HCl	-	Hydrochloric acid
K^{+}	-	Potassium ion
MED	-	Multi-effect distillation
Mg^{2+}	-	Magnesium ion
MMMs	-	Mixed matrix membrane
MPD	-	m-phenylenediamine
MSF	-	Multi-stage flash distillation
Na^{+}	-	Sodium ion
NaCl	-	Sodium chloride
NMP	-	1-methyl-2-pyrrolidinone
PA	-	Polyamide
PES	-	Polyethersulfone
PSf	-	Polysulfone
RO	-	Reverse osmosis
SWRO	-	Seawater reverse osmosis

TEM	-	Transmission electron microscopy
TFC	-	Thin film composite
TMC	-	Trimesoyl chloride
TFN	-	Thin film nanocomposite
UF	-	Ultrafiltration
VCD	-	Vapor compression distillation
XRD	-	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Research Background

Globally, fresh water scarcity has become the main issue due to the increase of world demand. Human population is estimated to increase from 7 to 10 billion by 2050. Without contaminant-free water, those disease-causing germs or chemicals will affect human health. Seawater desalination has the potential to become a solution for water shortage issue as seawater volume accounted for 98 % of water on Earth. Water desalination is a process that used to separate those dissolved ions and minerals from water (Sheikholeslami, 2009).

To date, apart from membrane technology, there are various techniques to extract potable water from the seas such as boiling, distillation, in situ chemical oxidation, and gas hydrate crystal centrifuge method. Among all, membrane filtration is one of the most known methods and many people had done a lot of research regarding water purification by membrane filtration. It has been proved that membrane technology is a fast, liable, better removal of contaminants, high efficiency, low operating and production cost method (McCutcheon and Elimelech, 2008).

The development and implementation of membranes was traced back to 1748, where Jean-Antoine Nollet outlines the permeation of water through osmosis phenomenal by using a semipermeable membrane (Brazier, 2009). Nollet was the first to coin the term “osmosis”. Traube and Pfeffer further discussed osmosis phenomenon in 1860. Their work led to the osmotic pressure relationship known as van’t Hoff (Singh, 2015). The term ultrafiltration has been introduced by Bechold in 1906, which using filter papers that was impregnate with acetic acid collodion. Bechold has successfully synthesized the membranes with pore size smaller than 0.01 µm. (Friedrich *et al.*, 1981). Michaels (1968) further developed ultrafiltration membranes. Further in 1960, with the discovery of asymmetric membrane for desalination has opened door for UF membranes. The growth of UF membrane goes parallel with asymmetric membrane and begins to make in industrial scale membrane filtration.

In the late of the 1940s, the idea of extracting pure water from salty water had been examined. Desalination of water through a semipermeable membrane was suggested by Hassler, Reid and Breton (1998). His team had developed the first reverse osmosis (RO) membrane systems in the 1950. They dissolved cellulose acetate polymer with appropriate acetyl content in acetone to synthesis a homogeneous cellulose acetate membrane (Malshe, 2008). In the early 1970s, desalination had come to a new era due to the development of new class membrane, thin-film composite (TFC) membrane for reverse osmosis. Cadotte and his teammates (1980) was the founder of the TFC membranes. They synthesized TFC membrane by deposit a thin layer of PA onto finely porous polysulfone membrane through interfacial polymerization reaction. TFC membrane fabricated by them showed high salt rejection with high flux.

Most of the present technologies have undergone a series of modifications to improve the effectiveness and so as membrane technology. Membrane technology is a separation process by using a semi permeable membrane to selectively permit substances across the membrane by pressure driven flow system. Up to the present, membrane technology has been used widely in a broad range of applications including RO plant.

Up to now, RO has become the main desalting water technology as RO is the most energy-efficient technology. In a RO plant, membrane technology is the main component as increase in membrane selectivity results in enhancement of water quality (Yang et al., 2018). Most of the RO desalination plant consists of various components including feed intake, pretreatment, reverse osmosis, post-treatment and waste discharge. Membrane technology can be applied into the pretreatment and RO section. In the pretreatment section, it aids to remove those foulants mainly suspended solid and organic matter from the feed. Nowadays, UF has been used widely in pretreatment of water as UF is effective in removing those suspended solid and organic matter. Moreover, membrane filtration tends to provide a better quality of water compared to those conventional pretreatment methods (Kabsch-Korbutowicz et al., 2006). In the RO system, the feed water flow through a semipermeable membrane by pressure driven flow and left over the dissolved salt. (Elimelech et al., 2011). The key properties that determine the membrane efficiency are the selectivity and flux of membrane.

In a RO plant, UF as pretreatment technology has become the preferred choice due to the advancement provided by ultrafiltration technology. Nowadays, many of the RO systems are facing the same challenges in regard to RO membrane fouling and UF membranes as pretreatment tend to increase the fouling resistances of RO system. Natural organic matter (NOM) is one of the most found organic compounds in natural water resources and the main NOM component is attributed to humic substances. Humic substances presented in water bodies mainly consist of humic acid, fulvic acid and humin, which can affect the water quality (Mamba et al., 2008). Hence, humic acid (HA) which often presented in the water bodies was chosen as the model pollutant for the evaluation of UF membrane filtration performance. For the RO membrane, NaCl solution was chosen as the feed solution to evaluate the performance of TFC and TFN membranes.

1.2 Problem Statement

Membrane technology has proven its effectiveness in ultrafiltration pretreatment and desalination. However, most of the polymeric membrane constrained by the trade-off effect in between selectivity and permeability. In order to overcome the trade-off effect between selectivity and permeability, the integration of nanomaterials into membrane for the development of nanocomposite membrane has been identified as one of the solutions to increase the selectivity and permeation flow of membranes.

The development of nanocomposite membrane needs to design to meet the specific requirement or specific water treatment application such as MF, UF, NF, RO and FO. The incorporation of nanomaterials into membrane tends to alter the structural and surface chemistry of membrane, which can aid to increase the performance of the membrane. However, the selection of nanomaterials is greatly depending on the type of feed used. Based on previous literatures, there are various types of nanomaterials been used as filler for the development of nanocomposite membranes.

Based on previous literatures, diverse types of nanomaterials have been studied for the development of nanocomposite membranes and carbon based nanomaterials have hold enormous potential in water purification application (Goh et al., 2013; 2015). Another nanomaterial that has similar properties with carbon lattice nanoparticles such as CNT and graphene is BN. However, still little is known regarding the characteristics of boron nitride nanosheet (BNNS), a counterpart of graphene (Goldberg et al., 2010). BNNS possesses identical graphitic structure to that of graphite, where all carbons are fully substituted by boron and nitrogen atoms. Despite their structural similarities, in some aspects, graphene and BNNS show quite distinctive properties from each other. Carbon based materials such as graphene and graphene oxide have been proved that hold enormous potential in water purification applications (Ong et al., 2016). For instance, graphene may appear as black as coal, while BNNS is white, hence the nickname “white graphene” (Lei et al., 2013). BN nanomaterials are much more chemical and thermally robust than their carbon analogues (Goldberg et al., 2010). For instance, BN nanotubes (BNNTs) are highly resistance to oxidation and thermally stable up to 800 °C in contrast to carbon nanotubes (CNTs) which could not survive beyond 400 °C (Chen et al., 2004).

The advantage and potential applications of BN have been explored through some theoretical studies and BN show potential in desalination application. In 2009, Hilder and his teammates stated that BNNT showed superior in water flow properties and 100% of salt rejection theoretically. Under comparison, BN is expected to be more efficient water purification than CNT. There is a need to further explore the potential of utilizing newly emerging BN nanoparticles in membrane desalination application. The science behind the performance improvement needs to be elucidated.

Latest theoretical investigations also suggest that free-standing atomically thin BN membranes could efficiently reject heavy metal ions and salts for seawater desalination (Jafar et al., 2015; Gao et al., 2017). However, fabricating free standing BN membranes could impose a considerable challenge in terms of fabrication technique, reproducibility, and mechanical stability of the inorganic membrane. Preliminary attempt on exploring the applicability of BN nanomaterials for water filtration could be realized by preparing BN-based mixed matrix membranes (MMMs). The effects of BNNS on the membrane morphology and physico-chemical properties are presented. Finally, in depth discussion on the microstructural properties of BNNS and how it affects the selective permeation and water transport through BNNS MMMs are provided. A polymer composite is provided for water treatments and a nanocomposite membrane incorporated with BN nanoparticles, which is a new class of membranes fabricated by combining polymeric materials with nanomaterials. The advanced nanocomposite membrane can be designed to meet specific water treatment applications.

1.3 Objectives

The objectives of this study are:

1. To evaluate the water transport properties and humic acid rejection performance of boron nitride nanosheet mixed matrix membrane;

2. To correlate the relationship of amine-activated boron nitride nanosheet thin film nanocomposite with permeation properties.

1.4 Scope of Study

In order to achieve the objectives mentioned above, the following scope of study was drawn:

(i) Characterizing the boron nitride by X-ray diffraction (XRD), Brunauer, Emmett and Teller (BET), transmission electron microscopy (TEM).

(ii) Formulating polymer dope solution comprised of polysulfone (PSf) (Udel Polysulfone P- 3500) with molecular weight of 34,500 g/mol from Amoco Chemical (USA), N-methyl-2-pyrrolodinone(NMP) (99.5%), Polyethylene glycol 400 (PEG 400).

(iii) Preparing nanocomposite membranes with boron nitride contents ranging from 0. 5 wt % to 2.0 wt % using dry/wet phase inversion method.

(iv) Fabricating porous polymeric substrate using dry/wet phase inversion method.

(v) Activating the boron nitride chemically.

(vi) Characterizing the boron nitride by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

(vii) Preparing nanocomposite membranes with various boron nitride contents (0.5%) using dry/wet phase inversion method and incorporating both types of boron nitride into the polyamide layer of membrane.

(viii) Characterizing the membranes using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), atomic-force microscopy (AFM), contact angle, zeta potential.

(ix) Evaluating the water permeation and separation properties of the fabricated membranes using pure water, humic acid solution and sodium chloride solution.

1.5 Significance of the Study

The roles of h-BN as filler in affecting the water permeation properties of the MMMs are discussed. MMMs with different h-BN loading are incorporated into flat sheet membrane. The effects of various h-BN loading on membrane morphology were identified. The work seeks for the optimum h-BN loading in MMMs and possesses attractive permeance and selectivity. Next, chemical activation of h-BN was studied and incorporated into the TFC membrane. At the end of the study, the overview performance of TFN membranes was studied. The permeation and rejection properties of h-BN TFN membrane and activated-BN TFN membrane were compared. The project's goal is designed to identify the potential and functionality of h-BN as filler in membrane technology.

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