EMERGING MATERIALS AND MATERIALS

ADVANCED MATERIALS FOR WASTEWATER TREATMENT AND DESALINATION

Fundamentals to Applications

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Preface

Water is a key component of living organisms. With more human activities, industrialization and urbanization, the demand for clean water is also increasing. On the other hand, the reduction of reliable water sources and increasing water pollution are known as one of the key global environmental issues of the 21st century. Water reclamation is an important strategy to resolve the water shortage issue. Wastewater treatment and desalination have shown great potential to provide sustainable clean water to meet water requirements. In the past few decades, a wide variety of treatment technologies and materials have been studied and applied for wastewater treatment and desalination. Tremendous efforts have been made in these aspects, and this book aims to make a compilation in the state-of-the-art progress made in the development of advanced materials for wastewater treatment and desalination application. This book, entitled *Advanced Materials for Wastewater Treatment: Fundamental to Application*, aims to bring together the ideas of researchers working in this field. Through contributions from leading experts from around the world, the book offers a detailed overview of the principles and applications of advanced materials in wastewater treatment.

This edited book is divided into two major sections: (a) Fundamentals and (b) Applications. The first part encompasses the synthesis and modification of advanced materials to eliminate any pollutants from wastewater and for desalination purpose. This includes the revolutionary material synthesis, modification, and characterization techniques. Advanced materials synthesized in different dimensions such as metal oxide, carbon-based materials, perovskite-based materials, polymer-based composite materials, and advanced nanocomposites are discussed. New fabrication techniques, including green synthesis, solvent-free, energy-saving synthesis approaches, are elaborated. The relevant synthesis route and mechanisms as well as the correlation of materials properties with their characterization are also included in the discussions. The second section of this book highlights the potential applications by advanced materials in water treatment technologies and desalination. The applications of a wide spectrum of functional and advanced materials in the removal of organic contaminant, discoloration of dye wastewater and agricultural wastewater reclamation, just to name a few, are discussed in this section. With further advancement, the innovations made in material advancement are expected to fulfill today's wastewater treatment demand with better quality.

hoped that this edited book serves as a reference for this targeted group to provide useful information on the progresses made in this field.

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5 Investigating Thin-Film Composite Membranes Prepared by Interaction between Trimesoyl Chloride with M-Phenylenediamine and Piperazine on Nylon 66 and Performance in Isopropanol Dehydration

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5.1 INTRODUCTION

Isopropanol (IPA) is produced by indirect hydrogenation or fermentation of cellulosic materials [1]. IPA is widely used in modern semiconductor and microelectronic industries as the solvent and cleaning solution [2]. It is also utilized as a chemical intermediate to produce mono-isopropyl amine or isopropyl acetate, weed killer, rubbing alcohol, vitamin B12 and many others. In the aforementioned applications, there are by-products in many other processes where IPA is involved, which generate the IPA and water mixtures. Consequently, IPA waste recycling is extremely significant from both environmental and economic perspectives. Thus, to conserve the environment with low overall cost treatment, many studies have been carried out and proposed throughout the years. Several experiments have taken off and intended over the years in an attempt to protect the ecosystem [3]. Although distillation is more favorable for purifying IPA waste, attention should be focused on the fact that industrial wastes can produce azeotropes, suggesting that pervaporation (PV) is more appropriate [4].

Pristine hydrophilic membranes were mainly used in the IPA dehydration process. However, it is found to be limited in mechanical strength, low thermal stability, change of the surface integrity, low yield as well as swelling. To overcome these limitations, thin-film composite (TFC) membrane can be very effective in enhancing the membrane flux and selectivity performance. The substrate layer of TFC membrane demonstrates mechanical stability and does not interfere with the mass transport. Prior to TFC formation, the support membrane has to act as a platform intended for aqueous and organic monomers for interfacial polymerization (IP) reaction to occur and form a thin layer known as polyamide (PA).

The important remark is to ensure a good interfacial binding between aqueous and organic monomers and then with the subtract layer for improving the polymer function and properties to be applied to processes. Nevertheless, according to Tsai et al. [5], the loose PA layers are associated with the low polymerization rate and the low polymerized layer thickness formation on the final TFC membrane. Decline of crosslinking rate is due to less amount of aqueous or organic monomers molecules to complete the interfacial polymerization reaction. This would lead to TFC membranes with low crosslinking density or known as the loose formation of PA layer on the subtract. Hence, choosing strong compatibility between aqueous amine solutions and subtract is a very important step.

The morphological stability and mechanical strength of the TFC membrane play vital roles in separation. Moreover, the compatibility between aqueous solution, organic solution and support membrane is the most significant decision during preparation. However, the relationship between them is rarely reported. Among the polymers subtracts used, nylon 66 (N66) has attracted much attention in the desalination field because of its relatively high mechanical strength and very high hydrophilic nature for appropriate film formation of PA. In this research, a comprehensive study in preparing TFC membranes by using the aqueous monomer, Trimesoyl Chloride (TMC), amine monomer, M-Phenylenediamine (MPD) and Piperazine (PIP) on the N66was conducted. The effect of the immersion period in amine solution on PA formation was also discussed. The PA formation on N66, the final structure and morphology, chemical composition and roughness were observed. The mechanical strength analysis was also utilized to describe the crosslinking density on the final TFC membranes before applying in PV.

5.2 EXPERIMENTAL

The parameters and steps for interfacial polymerization to prepare the TFC membranes are discussed in this section. TFC membranes were fabricated, characterized for the final morphologies and structure, functional group identification, roughness and lastly, the mechanical strength. Finally, the performance of the fabricated membrane is tested for IPA dehydration in PV system.

5.2.1 MATERIALS

Commercial flat sheet N66 membrane (SKU: NY013001) was purchased from Sterlitech Co. (WA, USA). The N66 membranes with pores size of 0.1 µm are used as substrate for the TFC membrane in this study. All the membranes were dried in a vacuum oven at 60°C for 10 minutes and proceeded to the IP process. The reaction monomer, MPD and PIP were used as the aqueous phase, whereas TMC was used as the organic phase. Both MPD (flakes, 99.0%) and TMC (98.0%) were purchased from Sigma-Aldrich. Hexane supplied by Merck was used to prepare the organic solutions. Analytical grade IPA (≥99.8%) from Merck was employed to conduct PV experiments. All chemicals were used as received without further purification. Distilled water was used to prepare the aqueous amine solutions as well as for the preparation of PV.

5.2.2 Interfacial Polymerization Reaction on Nylon 66 Substrates

TFC membranes were prepared by the IP method provided by Hua et al. [6]. The TFC membranes were produced after exposing substrates membranes in the aqueous phase and subsequently to the TMC in the organic phase. The membranes were contacted with the 2 wt.% aqueous amine solutions for 3 and 5 minutes at 25°C as presented in Table 5.1, where TFC-MPD and TFC-PIP represent the TFC membrane prepared by MPD and PIP, respectively. After removing amine solutions excess using an air blower, the membranes were immersed into a hexane solution containing 0.1 wt.% of TMC to carry out the IP for 0.5–4 minutes. The membranes were then washed using hexane followed by distilled water before drying in a circulation oven at 70°C for 10 minutes to secure the structure of the TFC formed. Next, the fabricated TFC membrane went through post-treatment in the methanol bath for 2 minutes. The membranes were kept in DI water until it is ready to be applied in a precursory study to secure the structure and avoid defects on the membrane surfaces.

5.2.3 Characterizations

The morphologies and elements of the membrane samples were observed by FESEM. The chemical structures of the membrane surface before and after IP were analyzed by using FTIR to confirm the formation of the PA selective layer. To study the surface hydrophilicity of the resultant TFC membranes, the water contact angle was measured by the Test System of JY-82 video contact at room temperature. Meanwhile, the roughness of the TFC membranes was examined by AFM which can also confirm the hydrophilicity of the fabricated membranes. For the absorption properties, a swelling test on the TFC membrane with various IPA-water compositions was carried out. Lastly, the tensile strength was measured by CT3 Texture Analyzer for the mechanical characteristic of the membrane's samples.

TABLE 5.1
Preparation of the TFC Membrane by Varied Immersion Time in Aqueous Solution

Type	Aqueous Solution (wt.%)	Immersion Time (min) in Aqueous Solution	Organic TMC Solution (wt.%)	Reaction Time (min)	IPA Composition in Feed Solution (%)
Pristine, N66	0	0	0	0	90
TFC-MPD3	2.0	3.0	0.1	2.0	90
TFC-MPD5	2.0	5.0	0.1	2.0	90
TFC-PIP3	2.0	3.0	0.1	2.0	90
TFC-PIP5	2.0	5.0	0.1	2.0	90

5.2.4 Pervaporation Separation Tests

The PV system used in the study is shown in Figure 5.1. Five hundred milliliters of feed solution with desired IPA concentration in the mixture was circulated through the membrane, with the flow rate of 18 L h^{-1}. The concentration of the IPA feed solution was prepared using 90 wt.% of IPA solution mix with 10 wt.% of distilled water. The lumen side of the membrane was connected to a vacuum pump, which was the permeate side. The feed temperature was set at 40°C. The permeate side pressure was maintained below 50 mbar (5 kPa). The system was conditioned for 2 hours to ensure that the flux and composition of permeate were stabilized before the collection of the permeate samples as applied by Zuo et al. [2] in his research study. The sample from permeate side was condensed in a cold trap and collected at a time interval of 1 hour. The mass of the collected sample was weighed by a Mettler Toledo balance.

The compositions of the feed and permeate samples were determined by a refractive index using Abbe's refractometer (Atago-3T, Japan) with an accuracy of ±0.001 units by referring to the standard graph of refractive index versus percent composition of the water–isopropanol mixture prepared. At least three permeate samples were collected and their average was reported as the PV performance. Two main parameters should be considered when selecting a membrane for a specific mixture: the permeate flux across the membrane presented as J (kg $m^{-2}h^{-1}$) in Equation 5.1, and the membrane selectivity, α, to measure the quality of separation as Equation 5.2 [7]:

$$J = \frac{Q}{A \cdot \Delta t} \tag{5.1}$$

$$\propto = \frac{P_{water}/P_{IPA}}{F_{water}/F_{IPA}} \tag{5.2}$$

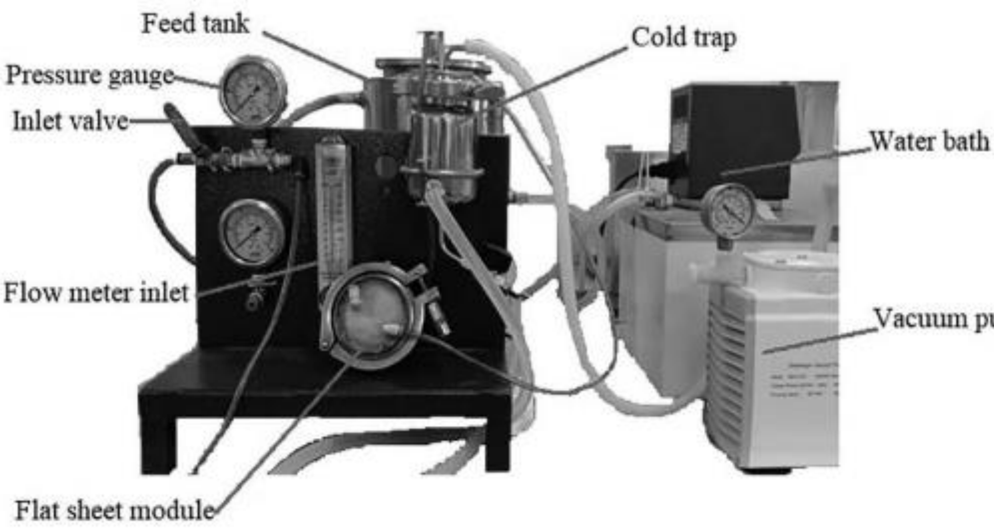

FIGURE 5.1 The pervaporation system consists of an overall pervaporation setup.