



EMERGING MATERIALS AND MATERIALS

# ADVANCED MATERIALS FOR WASTEWATER TREATMENT AND DESALINATION

Fundamentals to Applications

EDITED BY

A.F. Ismail • P.S. Goh

H. Hasbullah • F. Aziz



CRC Press  
Taylor & Francis Group

First edition published 2023  
by CRC Press  
6000 Broken Sound Parkway NW, Suite 300, Boca Raton, FL 33487-2742

and by CRC Press  
4 Park Square, Milton Park, Abingdon, Oxon, OX14 4RN

*CRC Press is an imprint of Taylor & Francis Group, LLC*

© 2023 Taylor & Francis Group, LLC

Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, access [www.copyright.com](http://www.copyright.com) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. For works that are not available on CCC please contact [mpkbookspermissions@tandf.co.uk](mailto:mpkbookspermissions@tandf.co.uk)

*Trademark notice:* Product or corporate names may be trademarks or registered trademarks and are used only for identification and explanation without intent to infringe.

ISBN: 978-0-367-76516-3 (hbk)  
ISBN: 978-0-367-76517-0 (pbk)  
ISBN: 978-1-003-16732-7 (ebk)

DOI: 10.1201/9781003167327

Typeset in Times  
by codeMantra

---

# Contents

Preface.....	vii
Editors.....	ix
List of Contributors.....	xi

## **SECTION 1 Fundamentals**

<b>Chapter 1</b>	Graphitic Carbon Nitride (g-C <sub>3</sub> N <sub>4</sub> )-Based Photocatalysts for Wastewater Treatment .....	3
	<i>Nur Aqilah Mohd Razali, Wan Norharyati Wan Salleh, Farhana Aziz, Ahmad Fauzi Ismail, and Wan Mohd Asyraf Wan Mahmood</i>	
<b>Chapter 2</b>	Metal-Organic Frameworks for Wastewater Treatment.....	25
	<i>Nur Azizah Johari, Nur Fajrina, and Norhaniza Yusof</i>	
<b>Chapter 3</b>	Impact of Metal Oxide Nanoparticles on Adsorptive and Photocatalytic Schemes.....	53
	<i>Muhammad Ikram, Usman Qumar, Salamat Ali, and Anwar Ul-Hamid</i>	
<b>Chapter 4</b>	2D Nanostructures for Membrane-Enabled Water Desalination: Graphene and Beyond .....	79
	<i>Muhammad Ikram, Anwar Ul-Hamid, and Ali Raza</i>	
<b>Chapter 5</b>	Investigating Thin-Film Composite Membranes Prepared by Interaction between Trimesoyl Chloride with M-Phenylenediamine and Piperazine on Nylon 66 and Performance in Isopropanol Dehydration .....	99
	<i>Wan Zulaisa Amira Wan Jusoh, Sunarti Abdul Rahman, Abdul Latif Ahmad, Nadzirah Mohd Mokhtar, and Hasrinah Hasbullah</i>	
<b>Chapter 6</b>	Sustainable Carbonaceous Nanomaterials for Wastewater Treatment: State-of-the-Art and Future Insights.....	113
	<i>Muhammad Ikram, Ali Raza, Salamat Ali, and Anwar Ul-Hamid</i>	

- Chapter 7** Magnetic Materials and Their Application in Water Treatment ..... 139  
*Muhammad Ikram, Syed Ossama Ali Ahmad, Atif Ashfaq,  
 and Anwar Ul-Hamid*

## **SECTION 2 Applications**

- Chapter 8** Direct Membrane Filtration for Wastewater Treatment ..... 167  
*Elorm Obotey Ezungbe, Emmanuel K. Tetteh,  
 Sudesh Rathilal, Edward K. Armah, Gloria Amo-Duodu,  
 and Dennis Asante-Sackey*

- Chapter 9** 3D Printing Technology for the Next Generation of Greener  
 Membranes towards Sustainable Water Treatment ..... 195  
*Mohammadreza Kafi, Mohammad Mahdi A. Shirazi,  
 Hamidreza Sanaeepur, Saeed Bazgir, Paria Banino,  
 Nur Hidayati Othman, Ahmad Fauzi Ismail, and Ahmad Fauzi Ismail*

- Chapter 10** Nanohybrid Membrane for Natural Rubber  
 Wastewater Treatment ..... 243  
*Tutuk Djoko Kusworo and Dani Puji Utomo*

- Chapter 11** Mixed Matrix Membrane (MMM) in the Agriculture Industry ..... 279  
*E. Yuliwati, S. Martini, Ahmad Fauzi Ismail, and Pei Sean Goh*

- Chapter 12** Water Filtration and Organo-Silica Membrane Application for  
 Peat Water Treatment and Wetland Saline Water Desalination ..... 309  
*Muthia Elma, Fitri Ria Mustalifah, Aliah, Nurul Huda,  
 Erdina Lulu Atika Rampun, and Aulia Rahma*

- Chapter 13** Eco-Friendly Dye Degradation Approaches for Doped Metal  
 Oxides ..... 335  
*Muhammad Ikram, Jahanzeb Hassan, Anwar Ul-Hamid,  
 and Salamat Ali*

- Index** ..... 359

---

# 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.

*Editors,*

**Ahmad Fauzi Ismail**

**Pei Sean Goh**

**Hasrinah Hasbullah**

**Farhana Aziz**

*Advanced Membrane Technology Research Centre*

*School of Chemical and Energy Engineering,*

*Faculty of Engineering*

*Universiti Teknologi Malaysia*

---

# 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

*Wan Zulaisa Amira Wan Jusoh  
and Sunarti Abdul Rahman*  
Universiti Malaysia Pahang

*Abdul Latif Ahmad*  
Universiti Sains Malaysia

*Nadzirah Mohd Mokhtar*  
Universiti Malaysia Pahang

*Hasrinah Hasbullah*  
Universiti Teknologi Malaysia

## CONTENTS

5.1	Introduction .....	100
5.2	Experimental .....	101
5.2.1	Materials .....	101
5.2.2	Interfacial Polymerization Reaction on Nylon 66 Substrates .....	102
5.2.3	Characterizations .....	102
5.2.4	Pervaporation Separation Tests.....	103
5.3	Result and Discussion .....	104
5.3.1	Characterization Results of the Nylon 66 and Fabricated TFC Membranes .....	104
5.3.1.1	Morphology Structure.....	104
5.3.1.2	Chemical Composition Analysis.....	105
5.3.1.3	Surfaces Roughness .....	106
5.3.1.4	Mechanical Strength Test .....	107
5.3.2	Effect of Immersion Time in MPD Solution on the TFC Membrane .....	108
5.4	Conclusion .....	110
	Acknowledgments.....	110
	References.....	110

## 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 substrate 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 substrate. Hence, choosing strong compatibility between aqueous amine solutions and substrate 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 substrates 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 N66 was 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  $\mu\text{m}$  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 ( $\geq 99.8\%$ ) 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  $18\text{ L h}^{-1}$ . 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  $40^\circ\text{C}$ . 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  $\pm 0.001$  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  $J$  ( $\text{kg m}^{-2}\text{h}^{-1}$ ) in Equation 5.1, and the membrane selectivity,  $\alpha$ , to measure the quality of separation as Equation 5.2 [7]:

$$J = \frac{Q}{A \cdot \Delta t} \quad (5.1)$$

$$\alpha = \frac{P_{\text{water}}/P_{\text{IPA}}}{F_{\text{water}}/F_{\text{IPA}}} \quad (5.2)$$

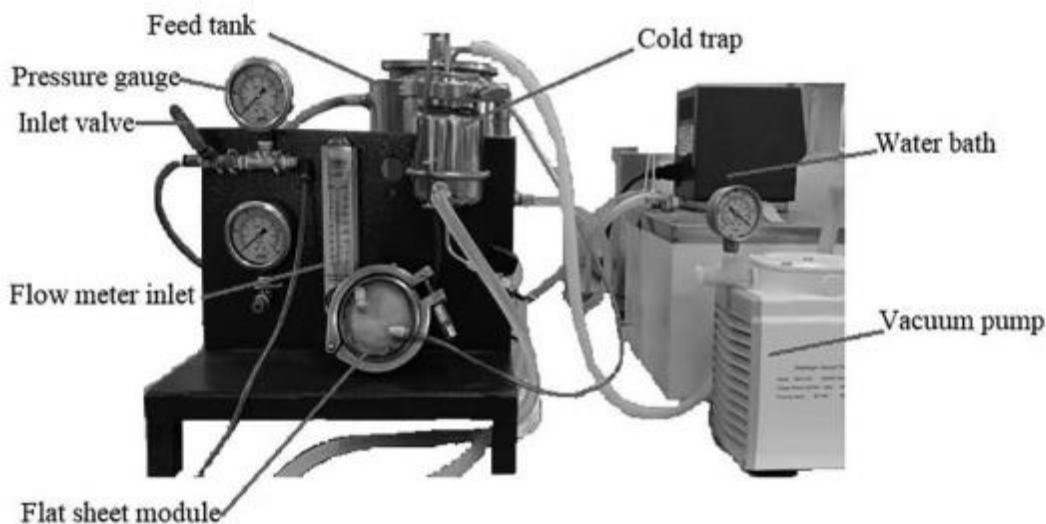


FIGURE 5.1 The pervaporation system consists of an overall pervaporation setup.