PERVAPORATION MEMBRANE CONTAINING ELECTROSPUN POLY(VINYL ALCOHOL) COMPOSITE NANOFIBRE LAYER FOR DEHYDRATION OF 1,4-DIOXANE

YEANG QIAN WEN

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by

YEANG QIAN WEN

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LIST OF ABBREVIATIONS

[Bmim][BF_4]	1-butyl-3-methylimidazolium tetrafluoroborate
3D	3-dimensional
ABE	Acetone-butanol-ethanol
Al_2O_3	Aluminum oxide
Al-MCM-41	Alumina-containing mobile composition matter-41
BDC	Benzene dicarboxylate
BET	Brunauer-Emmett-Teller
BP	Buckypaper
BSA	Bovine serum albumin
BTC	Benzene-1,3,5 tricarboxylic acid or trimesic acid
CNT	Carbon nanotube
$Co(HCOO)_2$	Co(II)-formate
COOH-MWCNT	Carboxyl multi-walled carbon nanotube
CS	Chitosan
Cu-BTC	Cu_3(1,3,5-benzenetricarboxylate)$_2$
CVD	Chemical vapour deposition
DMF	N,N-dimethylformamide anhydrous
Fe_3O_4	Magnetite
FTIR	Fourier transform infrared
GPU	Gas permeation units
IPA	Isopropanol
M_0	Asymmetric membranes with electrospun PVA nanofibres as pre-selective layer
$M_{COOH\text{-}MWCNT}$	Asymmetric membranes with electrospun COOH-MWCNT/PVA nanofibres as pre-selective layer
M_{CuBTC}	Asymmetric membranes with electrospun Cu-BTC/PVA nanofibres as pre-selective layer
MMM	Mixed matrix membrane
MOF	Metal organic framework
MWCNT	Multi-walled carbon nanotube
PA	Polyamide

PAH	Poly(allylamine hydrochloride)
PAN	Poly(acrylonitrile)
PANI	Polyaniline
PBI	Polybenzimidazole
PDMS	Polydimethylsiloxane
PEBA	Poly(ether block amide)
PEC	Polyelectrolyte–polyelectrolyte complex
PEI	Polyethyleneimine
PES	Polyethersulfone
PET	Polyethylene terephthalate
PHB	Poly(3-hydroxybutyrate)
PI	Polyimide
PS	Polystyrene
PSF	Polysulfone
PSI	Pervaporation separation index
PSSA	Poly(styrene sulfonic acid)
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
SEM	Scanning electron microscope
SILM	Supported ionic liquid membrane
SPES	Sulfonated polyethersulfone
SPES-C	Sulfonated polyarylethersulfone with cardo
SWCNT	Single-walled carbon nanotube
TED	Triethylenediamine
TEM	Transmission electron microscopy
TiO_2	Titanium dioxide
ZIF	Zeolitic imidazolate framework
β-CD	β-cyclodextrin

LIST OF SYMBOLS

$\bar{\gamma}_i$	Average activity coefficient of component *i* at the feed side and permeate side
$Đ_i^*$	Relative transport coefficient of component *i*
ΔH_{Si}	Enthalpy of sorption of component *i*
A	Effective membrane area
A_{ij}	Wilson parameter
A_{ji}	Wilson parameter
$Đ_i$	Transport coefficient of component *i*
E_{Di}	Activation energy for diffusion of component *i*
E_{Ji}	Activation energy for the permeation of component *i* which takes into account the impact of the driving force
E_{Pi}	Permeation activation energy, which characterises the dependence of the membrane permeance on the temperature
J	Permeation flux
J_{io}	Pre-exponential factor of the permeation flux
M_d	Weight of the dry membrane
M_s	Weight of the swollen membrane
MW_i	Molar mass of component *i*,
P	Permeance
p_{i1}	Partial pressure of component *i* at the liquid phase side of the membrane
p_{i2}	Partial pressure of component *i* at the vapour phase side of membrane
P_{io}	Pre-exponential factor of the permeance
p_i^{sat}	Saturated vapour pressure of component *i* at the feed side
p_p	Downstream pressure at permeate side
Q	Amount of permeate collected
Q_0	Permeability of the porous layer of membrane
R	Universal gas constant
T	Absolute temperature
T^*	Reference temperature, equal to 293K

X_i	Weight fraction of component *i* in the feed
x_i	Molar fraction of component *i* at the feed side
x_j	Molar fraction of component *j* at the feed side
Y_i	Weight fraction of component *i* in permeate
y_i	Molar fraction of component *i* at the permeate side
Y_{im}	Weight fraction of component *i* in the membrane
α	Separation factor
β	Membrane selectivity
β_{diff}	Diffusion selectivity
β_{sorp}	Sorption selectivity
γ_{i1}	Activity coefficient of component *i* at the feed side
γ_{i2}	Activity coefficient of component *i* at the permeate side
γ_{j1}	Activity coefficient of component *j* at the feed side
δ	Thickness of the asymmetric membrane
Δt	Time interval

MEMBRAN PENYEJATTELAPAN DENGAN LAPISAN GENTIAN BENANG NANO KOMPOSIT POLI(VINIL ALKOHOL) HASILAN PEJAMAN ELEKTRIK UNTUK PENYAHHIDRATAN 1,4-DIOXAN

ABSTRAK

Dalam kajian ini, membran asimetri baru dengan lapisan pra-memilih hasilan pejaman elektrik yang terdiri daripada gentian benang nano poli (vinil alkohol) (PVA) dan gentian benang nano komposit PVA yang bersepadu dengan dua jenis pengisi hidrofilik iaitu kuprum benzena-1,3,5-trikarboksilat (Cu-BTC) bersaiz mikron dan tiub-nano karbon dinding berlapis berfungsikan kumpulan karboksil (COOH-MWCNT) bersaiz nano berjaya dihasilkan. Membran PVA dilapiskan dengan gentian benang nano PVA, gentian benang nano komposit Cu-BTC/PVA dan COOH-MWCNT/PVA untuk masing-masing membentuk membran asimetri M_0, M_{CuBTC} dan $M_{COOH\text{-}MWCNT}$. Semua membran asimetri mempamerkan peningkatan prestasi dalam penyahhidratan 1,4-dioxan melalui proses penyejattelapan. Kejadian ini adalah kesan daripada lapisan pra-memilih berfungsi sebagai penapis hidrofilik yang memerangkap molekul air. Prestasi penyejattelapan membran meningkat dalam susunan berikut: membran PVA < M_0 < $M_{COOH\text{-}MWCNT}$ < M_{CuBTC}. Berbanding dengan membran PVA, M_0 menunjukkan menunjukkan peningkatan hampir 50% dalam fluks penelapan air serentak dengan peningkatan dalam faktor pemisahan. Antara membran M_{CuBTC} dan $M_{COOH\text{-}MWCNT}$, membran M_{CuBTC} mempamerkan prestasi penyejattelapan yang lebih baik. Prestasi membran M_{CuBTC} meningkat dengan peningkatan kandungan Cu-BTC dari 0.5 hingga 1.0 wt.%. Di antara semua membran yang dikaji, membran M_{CuBTC} dengan 1.0 wt.% Cu-BTC ($M_{CuBTC(1.0)}$) mempamerkan fluks telapan dan faktor

pemisahan tertinggi dengan jumlah fluks penelapan sebanyak 87.69 g/m^2·j, faktor pemisahan sebanyak 1852.32, kebolehtelapan air yang bernilai 2176.20 GPU, dan kememilihan membran untuk air yang bernilai 1417.52. Fluks penelapan air yang ditunjukkan oleh membran $M_{CuBTC(1.0)}$ adalah dua kali ganda daripada membran PVA, manakala faktor pemisahan meningkat dari 392.65 hingga 1852.32. Berbanding dengan M_0, membran $M_{CuBTC(1.0)}$ menunjukkan peningkatan hampir 40% dalam fluks penelapan air bersama dengan peningkatan dalam faktor pemisahan. Walau bagaimanapun, di antara membran $M_{COOH\text{-}MWCNT}$ dengan 0.5 dan 1.0 wt.% COOH-MWCNT, iaitu $M_{COOH\text{-}MWCNT(0.5)}$ and $M_{COOH\text{-}MWCNT(1.0)}$, prestasi penyejattelapan yang lebih baik ditunjukkan oleh $M_{COOH\text{-}MWCNT(0.5)}$ dengan jumlah fluks penelapan yang bernilai 75.71 g/m^2·j, faktor pemisahan yang bernilai 605.35, kebolehtelapan air yang bernilai 1836.08 GPU dan kememilihan membran untuk air yang bernilai 462.30. Peningkatan sebanyak lebih kurang 80% dan 20% dalam fluks penelapan air ditunjukkan oleh $M_{COOH\text{-}MWCNT(0.5)}$ berbanding dengan membran PVA dan M_0 masing-masing. Walaupun faktor pemisahan $M_{COOH\text{-}MWCNT(0.5)}$ meningkat daripada 392.65 kepada 605.35 berbanding dengan membran PVA, faktor pemisahan berkurang dari 682.11 kepada 605.35 berbanding dengan M_0. Paramater yang diramal dengan menggunakan model Rautenbach menunjukkan bahawa penyahhidratan 1,4-dioxan melalui proses penyejattelapan dikawal oleh proses penyerapan.

PERVAPORATION MEMBRANE CONTAINING ELECTROSPUN POLY(VINYL ALCOHOL) COMPOSITE NANOFIBRE LAYER FOR DEHYDRATION OF 1,4-DIOXANE

ABSTRACT

In this study, novel asymmetric membranes with pre-selective layer consist of electrospun poly(vinyl alcohol) (PVA) nanofibres and electrospun PVA nanofibres integrated with two different types of hydrophilic fillers i.e. micron-sized copper benzene-1,3,5-tricarboxylate (Cu-BTC) and nano-sized carboxyl multi-walled carbon nanotube (COOH-MWCNT), respectively were successfully fabricated. Electrospun PVA nanofibres, Cu-BTC/PVA and COOH-MWCNT/PVA composite nanofibres were deposited on dense PVA membranes to form M_0, M_{CuBTC} and $M_{COOH\text{-}MWCNT}$ asymmetric membranes, respectively. All asymmetric membranes showed improved performance in the pervaporation dehydration of aqueous 1,4-dioxane solutions. This phenomenon is due to the electrospun hydrophilic nanofibre layer serving as a hydrophilic pre-selective barrier that traps water molecules. The pervaporation separation performance increased in the following order: dense PVA membrane $< M_0 < M_{COOH\text{-}MWCNT} < M_{CuBTC}$. Compared to dense PVA membrane, M_0 exhibited an increment of almost 50% in water permeation flux accompanied with an increase in separation factor. Between M_{CuBTC} and $M_{COOH\text{-}MWCNT}$ membranes, M_{CuBTC} membranes exhibited better separation performance. The performance of the M_{CuBTC} membranes increases with increasing Cu-BTC loading of 0.5 to 1.0 wt.%. Among all the membranes studied, M_{CuBTC} membrane incorporated with 1.0 wt.% Cu-BTC ($M_{CuBTC(1.0)}$) exhibited the highest permeation flux and separation factor with a total

permeation flux of 87.69 g/m^2·h, separation factor of up to 1852.32, water permeance of 2176.20 GPU, and water selectivity of 1417.52. The water permeation flux of the $M_{CuBTC(1.0)}$ membrane was double of that of the dense PVA membrane, while the separation factor increased from 392.65 to 1852.32. When compared to M_0, $M_{CuBTC(1.0)}$ membrane provided an enhancement of nearly 40% in water permeation flux along with an increase in separation factor. However, among the $M_{COOH\text{-}MWCNT}$ membranes integrated with 0.5 and 1.0 wt.% COOH-MWCNT, i.e. $M_{COOH\text{-}MWCNT(0.5)}$ and $M_{COOH\text{-}MWCNT(1.0)}$, respectively, better separation performance was demonstrated by $M_{COOH\text{-}MWCNT(0.5)}$ with a total permeation flux of 75.71 g/m^2·h, separation factor of 605.35, water permeance of 1836.08 GPU and membrane selectivity of 462.30 for water. An increment of around 80% and 20% in water permeation flux was achieved by the $M_{COOH\text{-}MWCNT(0.5)}$ when compared to that of the dense PVA membrane and M_0, respectively. Although the separation factor of $M_{COOH\text{-}MWCNT(0.5)}$ increased from 392.65 to 605.35 when compared to the dense PVA membrane, a slight decrease in separation factor from 682.11 to 605.35 was observed when compared to M_0. The parameters estimated using Rautenbach model showed that the dehydration of aqueous 1,4-dioxane solutions via pervaporation is dominantly governed by sorption process.

CHAPTER ONE

INTRODUCTION

An overview of the entire research project is presented in this chapter. The background and current development of pervaporation process is provided at the beginning of this chapter. In addition, electrospun nanofibres and their applications are briefly discussed. Then, the problem statement and objectives of this study are highlighted. Lastly, the scope of study and organization of the thesis are included at the end of this chapter.

1.1 Pervaporation

Pervaporation, a membrane-based separation technology, has attracted an exceptionally great amount of interest from researchers worldwide. It has been viewed as a potential alternative to the conventional separation techniques such as distillation process. In pervaporation, a dense membrane acts as a separating barrier and regulates the mass transport across the membrane. The feed liquid mixture is brought into contact with one side of the membrane where the component with higher affinity for the membrane will be preferentially transported across the membrane and removed from the other side of the membrane as a low pressure vapour. In order for separation to occur, the permeate side of the membrane is being held under vacuum or applying a sweep gas to create a chemical potential difference (Feng and Huang, 1997). The permeation of a component in membrane is driven by concentration and pressure gradients, and the overall driving force producing movement of a permeant is the chemical potential gradient. Schematic diagram of the pervaporation membrane cell operation is illustrated in Figure 1.1. The separation mechanism of the pervaporation