DEVELOPMENT OF FLAT SHEET THIN FILM COMPOSITE NANOFILTRATION MEMBRANE FOR SEPARATION OF ACETIC ACID INHIBITOR AND SUGAR FROM BIOMASS HYDROLYSATE

SITI NORMUNIRA BINTI RAMLI

Master of Science

UNIVERSITI MALAYSIA PAHANG

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science.

_____

(Supervisor's Signature)
Full Name : DR SYED MOHD SAUFI BIN TUAN CHIK
Position : ASSOCIATE PROFESSOR
Date :

_____

(Co-supervisor's Signature)
Full Name : DR MAZRUL NIZAM BIN ABU SEMAN
Position : ASSOCIATE PROFESSOR
Date :

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

_____

(Student's Signature)

Full Name : SITI NORMUNIRA BINTI RAMLI

ID Number : MKC15006

Date :

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SITI NORMUNIRA BINTI RAMLI

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ABSTRAK

Proses pemisahan yang berkesan diperlukan dalam pemprosesan biojisim hidrolysate untuk memulihkan xilosa dan glukosa untuk tahap penapaian selanjutnya dan untuk mengeluarkan perencat yang tidak diingini seperti asid asetik. Kaedah pemisahan konvensional seperti penyejatan, kromatografi dan pemanasan adalah rumit, melibatkan masa pemprosesan yang panjang dan kehilangan gula yang dapat ditapai. Oleh itu, filem komposit nipis (TFC) penurasan nano (NF) dipilih sebagai proses pemisahan biorefineri kerana kelebihan teknikal dan ekonomi. Kesan membran sokongan terhadap prestasi membran TFC disiasat dalam kajian ini kerana kemungkinan membran sokongan memberi kesan kepada prestasi membran TFC. Empat jenis membran sokongan polyethersulfone (PES) disediakan dengan mengubah kepekatan PES dalam larutan dop dari 17 wt.% PES hingga 23 wt.% PES. Membran TFC disediakan dengan menggunakan 0.2 % w/v piperazine (PIP) dan 0.2 % w/v tri-mesoyl klorida monomer (TMC). Membran TFC yang disediakan dari 23 wt.% PES membran sokongan menunjukkan prestasi terbaik. Faktor pemisahan untuk xilosa/glukosa, asid asetik/glukosa dan asid asetik/xilosa adalah masing-masing 1.45±0.06, 1.86±0.05 and 1.29±0.09. Seterusnya, kesan jenis monomer dan parameter-parameter semasa IP telah dikaji untuk penyingkiran asid asetik dan pemisahan xilosa/glukosa. Membran TFC disediakan dengan melakukan pempolimeran antara muka (IP) pada membran sokongan untuk membentuk lapisan pemisahan filem nipis yang aktif. Menggunakan membran sokongan yang terbaik yang mana PES 23, tiga jenis monomer yang berbeza dalam proses IP diteliti iaitu PIP, m-phenylene diamine (MPD) dan triethanolamine (TEOA). Membran PIP TFC menunjukkan fluk air tertinggi iaitu xilosa (4.80±0.97 L/m^2.h), glukosa (5.48±0.00 L/m^2.h) dan asid asetik (5.82±0.48 L/m^2.h) . Faktor pemisahan untuk PIP TFC membrane adalah terbaik di antara monomer yang diuji iaitu 1.45 ± 0.06, 1.86 ± 0,05 dan 1.29 ± 0,09 untuk xylose/glukosa, asid asetik/glukosa dan asid asetik/xylose, masing-masing. Faktor pemisahan untuk MPD TFC membrane ialah 0.90±0.07, 0.74±0.11 and 0.83±0.18 untuk xilosa/glukosa, asid asetik/glukosa dan asid asetik/xilosa, masing-masing. Sementara itu, factor pemisahan untuk TEOA TFC membran ialah 0.94±0.12, 1.12±0.11 dan 1.21±0.27 untuk xilosa/glukosa, asid asetik/glukosa dan asid asetik/xilosa, masing-masing. Pada bahagian terakhir, kesan monomer PIP (0.15 - 3.0 % w/v) dan masa reaksi larutan akueus (45 saat - 15 minit) telah dikaji. 2.0% PIP dan 2 minit masa tindak balas larutan akueus dipilih sebagai syarat terbaik untuk menyediakan membran PIP TFC dengan factor pemisahan 1.06±0.23, 1.59±0.39 dan 1.64±0.05 untuk xilosa/glukosa, asid asetik/glukosa and asid asetik/xilosa, masing-masing. Dengan menggunakan 23 wt. % kepekatan PES sebagai sokongan kepada 2.0 % w/v PIP pada 2.0 minit masa reaksi dalam larutan akueus membran TFC NF memastikan bahawa membrane TFC NF yang dihasilkan dalam kajian ini menunjukkan potensi untuk aplikasi di biorefineri.

ABSTRACT

Effective separation process is required in processing biomass hydrolysate to recover xylose and glucose for further fermentation stage and to remove undesired inhibitor such as acetic acid. The conventional separation methods such as evaporation, chromatography and heating are complicated, involve long processing time and extensive loss of the fermentable sugar. Thus, thin film composite (TFC) nanofiltration (NF) was chosen as biorefinery separation process due to its technical and economic advantages. The effect of the support membrane on the TFC performance was investigated in this study as the support membrane influence the performance of TFC membrane. Four different types of the polyethersulfone (PES) support was prepared by varying the PES concentration in dope solution from 17 wt.% PES to 23 wt.% PES. TFC membrane was prepared by performing interfacial polymerization (IP) on the support membrane to form an active thin film separation layer. TFC membrane was prepared by using 0.2 % w/v piperazine (PIP) and 0.2 % w/v tri-mesoyl chloride monomers (TMC). TFC membrane prepared from 23 wt.% PES support membrane showed the higher separation factor. The separation factor for xylose/glucose, acetic acid/glucose and acetic acid/xylose were 1.45±0.06, 1.86±0.05 and 1.29±0.09, respectively. Next, the effects of monomer type and parameters during IP were investigated for acetic acid removal and xylose/glucose separation. Using the best support membrane which is PES 23, three different types of monomers in IP process was studied which are PIP, m-phenylene diamine (MPD) and triethanolamine (TEOA). PIP TFC membrane showed the highest water flux of xylose (4.8±0.97 L/m^2.h), glucose (5.48±0.00 L/m^2.h) and acetic acid (5.82±0.48 L/m^2.h). The separation factor for the PIP TFC membrane was the best among the monomer tested which are 1.45±0.06, 1.86±0.05 and 1.29±0.09 for xylose/glucose, acetic acid/glucose and acetic acid/xylose, respectively. The separation factor for MPD TFC membrane was 0.90±0.07, 0.74±0.11 and 0.83±0.18 for xylose/glucose, acetic acid/glucose and acetic acid/xylose, respectively. Meanwhile, the separation factor for TEOA TFC membrane was 0.94±0.12, 1.12±0.11 and 1.21±0.27 for xylose/glucose, acetic acid/glucose and acetic acid/xylose, respectively. The effect of PIP monomer concentration (0.15 – 3.0 % w/v) and aqueous solution reaction time (45 second – 15 minutes) was studied. 2.0 % w/v of PIP and 2 minutes of aqueous solution reaction time were selected as the best condition to prepare the PIP TFC membrane with separation factor of 1.06±0.23, 1.59±0.39 and 1.64±0.05 for xylose/glucose, acetic acid/glucose and acetic acid/xylose, respectively. By using 23 wt.% PES concentration as a support to 2.0 % w/v of PIP at 2 minutes reaction time in aqueous solution TFC NF membrane ascertained that TFC NF membrane produced in this study showed a potential for the application in biorefinery.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

A	Surface area
C	Concentration
C_m	Concentration of solute on the membrane
C_p	Concentration of solute in the permeate
C=C	Benzene group
C-O	Ester group
C=O	Ester group
Da	Daltons
$D_{i,\infty}$	Bulk diffusivity of solute
g/mol	Molar mass
i	Solute
i (j_i)	Flux of solute
J_v	Volume flux
J_w	Water flux
$K_{i,d}$ and $K_{i,c}$	Hindrance due to diffusion and convection
nm	Nanometer
pKa	Acid dissociation constatnt
Pe_m	Peclet number
Q	Volumetric flowrate
R_{obs}	Observation rejection
R_{real}	Real rejection
r_m	Mean pore size diameter
r_p	Pore size
r_r	Radius of effective membrane area
r_s	Solute radius
SO_2	Sulphone group
Wt. (%)	Mass percent
w/v (%)	Weight per volume percent
∅	Sterix terms

μ	Water viscosity
μm	Micrometer
ΔP	Operating pressure
ι	Membrane thickness
°	Angle
°C	Degree celcius
v	Velocity
$\Delta x/A_k$	Ratio of effective membrane thickness over porosity
λ	Ration of solute radius to pore size
ε	Porosity
ω	Stirring speed

LIST OF ABBREVIATIONS

DBP	Disinfection by-product
FO	Forward osmosis
HMF	Hydroxymethylfurfural
HPLC	High performance liquid chromatography
IP	Interfacial polymerisation
MF	Microfiltration
MPD	m-phenylene diamine
MW	Molecular weight
MWCO	Molecular weight cut off
NF	Nanofiltration
NMP	n-methyl-2-pyrrolidone
PEI	Polyethyleneimine
PES	Polyethersulfone
PIP	Piperazine
PSf	Polysulfone
PWP	Pure water permeability
RO	Reverse osmosis
SEM	Scanning electron microscopic
TDS	Total dissolved solids
TEOA	Triethanolamine
TFC	Thin film composite
TMC	Trimethyl chloride
UF	Ultrafiltration

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