SYNTHESIS OF TiO_2-PVDF MEMBRANE WITH ENHANCED WETTING RESISTANCE FOR MEMBRANE DISTILLATION APPLICATION

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SYNTHESIS OF TIO$_2$-PVDF MEMBRANE WITH ENHANCED WETTING RESISTANCE FOR MEMBRANE DISTILLATION APPLICATION

by

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LIST OF ABREVIATIONS

AGMD	Air-gap membrane distillation
APTES	3- aminopropyltriethoxysilane
AFM	Atomic force microscopy
BOD	Biological oxygen demand
BCA	Bicinchoninic acid assay
B.Subtilis	*Bacillus Subtilis*
COD	Chemical Oxygen Demand
CA	Contact angle
CB	Cassie-Baxter
DCMD	Direct-contact membrane distillation
DMF	Dimethyl formamide
DMAC	N, N-dimethyl acetamide
EE	Energy efficiency
E.Coli	*Escherichia coli*
ENM	Electron nanofibre membrane
FTCS	Fluorosilane , 1H,1H,2H,2H-Perfluorooctyltriethoxysilane
LMH	L/ m^2/ hr
LEPw	Liquid entry pressure of water
MD	Membrane distillation
MF	Microfiltration
MAPTMS	3-methacryloyloxypropyl trimethoxysilane
MMDES	methacryloyloxy methylenemethyl diethoxysilan
M-12	Neat Membrane with polymer concentration of PVDF in 12%w/v

M-16	Neat Membrane with polymer concentration of PVDF in 16%w/v
M-20	Neat Membrane with polymer concentration of PVDF in 20%w/v
M-PVDF	Neat PVDF Membrane
MT-0	Neat PVDF Membrane without TiO_2
MT-0.01	Nano-composite membrane with 0.01g dosage TiO_2
MT-0.1	Nano-composite membrane with 0.1g dosage TiO_2
MT-0.5	Nano-composite membrane with 0.5g dosage TiO_2
MT-1.0	Nano-composite membrane with 1g dosage TiO_2
MT-UT	Nano-composite membrane with untreated TiO_2
MT-AC	Nano-composite membrane with acid treated TiO_2
MT-AL	Nano-composite membrane with alkali treated TiO_2
MT-Si-2	Nano-composite membrane with silane treated TiO_2 at pH 2
MT-Si-7	Nano-composite membrane with silane treated TiO_2 at pH 2
MT-Si-12	Nano-composite membrane with silane treated TiO_2 at pH 12
NF	Nanofiltration
NMP	N-methyl-2-pyrrolidone
NIPS	Non-solvent induced phase separation
OMW	Olive mill wastewater
PMR	Photocatalytic membrane reactor
PTFE	Polytetrafluoroethylene
PVDF	Poly(vinylidene fluoride)
PP	Polypropylene
PE	Polyofelin
POME	Palm oil mill effluent
PMSE	Paper mill SBR effluent

PBS	Phosphate buffer saline
RO	Reverse Osmosis
RE	Renewable energy
SGMD	Sweep Gas membrane distillation
SEM	Scanning electron microscopy
T-AC	TiO_2 treated with acid
T-AL	TiO_2 treated with alkali
T-Si-2	TiO_2 treated with silane at pH 2
T-Si-7	TiO_2 treated with silane at pH 7
T-Si-12	TiO_2 treated with silane at pH 12
TE	Thermal efficiency
TEM	Transmission electron microscopy
TIPS	Thermally induced phase separation
TiO_2	Titanium dioxide
TPC	Temperature polarization coefficient
UF	Ultrafiltration
UT	Untreated TiO_2
VMD	Vacuum membrane distillation
VIP	vapor induced phase separation
XRD	X-ray diffraction

LIST OF SYMBOLS

a	Air
A	Membrane area (m^2)
α_a , α_w	Collision water for air and water vapor
b	Bulk
δ, b	Thickness of membrane (m)
C_F	Initial COD in the feed (mg/L)
d	Mean pore size or nominal pore diameter (m)
d_m	Membrane thickness (m)
ε	Membrane porosity (%)
f_s & f_v	Area fractions of the solid and vapor (m^2)
F	Feed-side
H_g	Enthalpy of vapor (Jkg^{-1})
ΔH_v	Enthalpy of vaporization of water (Jkg^{-1})
ΔH_{LV}	Latent heat of vaporization (J/kg)
h_f	Feed-side heat transfer coefficient (Wm^{-2} K^{-1})
h_m	Membrane heat transfer coefficient (Wm^{-2} K^{-1})
h_p	Permeate-side heat transfer coefficient (Wm^{-2} K^{-1})
J	Mass flux of water vapor across the membrane (kgm^{-2} s^{-1})
ΔJ	Average mass flux of water vapor across the membrane (kgm^{-2} s^{-1})
K_n	Knudsen number
K_B	Boltzman constant
k	Combined thermal conductivity of membrane (Wm^{-1} K^{-1})
k_f , k_p,	Thermal conductivity feed and permeate (Wm^{-1} K^{-1})
λ, K_m	Thermal conductivity of membrane material (Wm^{-1} K^{-1})
l	Mean free path of molecule

M_{tank}	COD in the permeate solution tank (mg/L)
m	Membrane-solution interface
m_p	Mass of the dry membrane
m_n	Mass of the absorbed butanol
M_i	Mass flow rate of stream (kg s^{-1})
Mi	Molar mass of species (kg kmol^{-1})
n	Molecular concentration (m^{-3})
N_i	Molar flux of species (kmolm^{-2} s^{-1})
Nu	Nusselt numbers
σ_i	Molecular diameter of species (m)
Θ_c	Intrinsic contact angle (^{o})
Θ_{CB}	Apparent contact angle (^{o})
Θ	Contact angle (^{o})
P	Bulk pressure in membrane pores (Pa)
P	Permeate-side
P_i	Partial vapor pressure of species (Pa)
Pr	Prandtl number
ρ_p	Density of the PVDF (1.78 g/cm^3)
ρ_n	Density of butanol (0.81 g/cm^3)
ΔQ	Average heat flux across the membrane (Wm^{-2})
Q	Heat flux across the membrane (Wm^{-2})
Q_c	Heat rejected to environment (W)
Q_1	Heat flux from feed (W)
Q_2	Heat flux from permeate (W)
Re	Reynolds number
R_{sw}	Rejection of synthetic nutrient water (%)
R_{rej}	Rejection ratio (%)

$\dot{S}_{gen}$	Rate of entropy generation (WK^{-1})
Sc	Schmidt number
Sh	Sherwood number
T	Mean Temperature (^{o}C or K)
T_H	Hot temperature, temperature of heater or heat source (K)
T_c	Cold temperature, temperature of cooler or heat sink, temperature of environment (K)
τ	Membrane tortuosity
ΔT_{min}	Minimum approach temperature in the heat exchanger (^{o}C or K)
Δt	Sampling time (h)
T_1, T_p	Temperature at membrane surface hot side (K)
T_2, T_f	Temperature at membrane surface permeate side (K)
V_{tank}	Volume of permeate reservoir (m^3)
w	Water vapor
$\hat{W}_{in}$	Work input (W)
ΔW	Quantity of distillate (L)

SINTESIS MEMBRAN TiO_2-PVDF DENGAN SIFAT RINTANGAN PEMBASAHAN TAMBAHAN UNTUK APLIKASI MEMBRAN PENYULINGAN

ABSTRAK

Membran penyulingan (MD) merupakan teknologi yang penting di dalam industri seperti penyulingan air laut dan rawatan sisa air kerana membran penyulingan memerlukan tenaga yang lebih rendah dan secara teorinya berkecenderungan pengotoran yang rendah. Bagi mengelakkan berlakunya pembasahan membran, kaedah rendaman dua kali diperkenalkan bagi menyesuaikan morfologi membran untuk meningkatkan keliangan, kekasaran permukaan serta kristalisasi polimer. Hidrofobisiti membran boleh ditingkatkan dengan menambah kekasaran permukaan membran melalui penambahan zarah bersaiz nano TiO_2. Namun begitu, penambahan TiO_2 pada membran mengurangkan keliangan disebabkan oleh penyekatan liang dan juga merendahkan hidrofibisiti akibat kehadiran kumpulan hidroksil. Masalah penghalang liang boleh diatasi dengan meminimumkan saiz zarah melalui penggunaan bahan kimia iaitu asid pada membran. Akan tetapi, sifat hidrofilik intrinsik TiO_2 yang berterusan yang menyebabkan masalah pembasahan yang tidak diingini. Dengan mengurangkan saiz liang, sifat-sifat antibakteria pada membran terhadap *E.Coli* dapat ditingkatkan di mana masalah penyumbatan oleh bakteria pada membran dapat dikurangkan dengan menambahkan asid pengubah suai membran TiO_2/PVDF. Bagi meningkatkan hidrofobisiti membran, TiO_2 dirawat dengan flurosilan yang diubahsuai di bawah keadaan asid, neutral dan alkali. TiO_2 yang dirawat silan pada pH 7 meningkatkan sudut sentuhan (131.7 ± 4), peningkatan penyerapan fluks (12kg/m^2.h), nilai LEPw yang tinggi, pengurangan nutrien sehingga 99.65%, dan saiz liang yang lebih kecil yang dapat mengurangkan kemungkinan pembasahan liang. Membran yang paling optimum ini diuji dengan sisa air yang mempunyai kandungan pepejal yang tinggi iaitu sisa air dari kilang kertas SBR (PMSE) dan air sisa dari kilang minyak kelapa sawit (POME) selama 7 jam. Nilai fluks stabil sekitar 6 kg/m^2.h untuk air sisa dari kilang kertas SBR (PMSE) boleh dicapai dan menunjukkan pembasahan membran dan rintangan penyumbatan adalah baik. Kecekapan sistem adalah sekitar 55% boleh dibandingkan dengan proses air tulen (50%). Walaubagaimanapun, membran tersebut tidak sesuai digunakan untuk merawat sisa air dari kilang minyak kelapa sawit yang kaya dengan minyak kerana fluks telah menurun dari 6 hingga 2 kg/m^2.h selepas 7 jam beroperasi. Didapati bahawa sisa air dari kilang minyak kelapa sawit memberikan kecekapan terma terendah iaitu 26% berbanding dengan proses-proses lain kerana gejala pengotoran.

SYNTHESIS OF TIO_2-PVDF MEMBRANE WITH ENHANCED WETTING RESISTANCE FOR MEMBRANE DISTILLATION APPLICATION

ABSTRACT

Membrane distillation (MD) has emerged as an important technology for applications in industries such as seawater desalination and wastewater treatment due to lower energy requirement and theoretically low fouling propensity. However, the main obstacle to obtain high separating efficiency in MD lies on the availability of porous hydrophobic membrane that can withstand pore wetting and membrane fouling. A dual coagulation bath method was introduced to fine tune the membrane morphology to increase its porosity, surface roughness as well as polymer crystallinity. To increase the membrane hydrophobicity, membrane roughness was induced by adding TiO_2 nanoparticles. However, this brought concomitant impacts on lower porosity due to the pore blocking and it also reduces hydrophobicity due to availability of hydroxyl group. The pore blocking problem can be solved by minimizing the particle size via surface acid modification. Nonetheless, the intrinsically hydrophilic nature of TiO_2 still persist which brings unwanted wetting problem. By decreasing the particle size, it was interesting to note that the antibacterial properties on membrane towards *E.Coli* also improved, which means that the membrane bio-fouling problem can be mitigated by incorporating acid modified TiO_2/PVDF membrane. To further enhance the hydrophobicity of the membrane, TiO_2 was treated with flurosilane which was modified under acid, neutral and alkaline conditions. Silanized TiO_2 with pH 7 gave higher contact angle