SYNTHESIS AND CHARACTERIZATION OF SKINNED-ORIENTED ASYMMETRIC LOW PRESSURE NANOFILTRATION MEMBRANE

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ABSTRACT

Nanofiltration is the most popular developed pressure-driven membrane process for liquid-phase separations. As continuous developed of new membranes process, special features including a nanometer ranges of pore radius, high retention of charged particles, inherent charges and lower operating pressure, its applications are rapidly increased especially in the field of process water, drinking water and wastewater treatment. This thesis is focused on the novel and significant study on the synthesis and characterization of skinned-oriented asymmetric low pressure nanofiltration membrane. In this study a new formulation of dope solution consisting of polyethersulfone, N-methyl-2-pyrrolidone and water were formulated from 19 to 27 wt% of PES concentration. In order to prepare a smooth, even and thin asymmetric nanofiltration membrane, high precision auto casting machine was developed based on the main concept of a simple dry/wet phase inversion technique. The polymeric additive (PVP K15) was added into the dope solution as pore former to improve the membrane porosity. Moreover, to synthesis the skinned-oriented nanofiltration membrane, the rheological factors (shear rate and evaporation time) were induced during the casting process. At the operating pressures ranging from 100 to 500 kPa and Sterlitech filtration cell, the membranes performance were evaluated in terms of pure water permeability, water flux, salts rejection and neutral solutes separation under the. Employing of the Spiegler-Kedem, SHP and TMS models, the membranes parameter, structural details and key properties (r_p, $\Delta x / A_k$ and ζ) were characterized. Analysis on the morphologies and pore size distribution led to the verification the optimum preparation conditions and the finest nanofiltration membranes. From this study, the membrane prepared from polymer concentration of 20.42 wt% (optimum) exhibited of high water flux ranging from 6.30 x 10^{-6} m^3/m^2s to 8.94 x 10^{-6} m^3/m^2s, 3.26 x 10^{-6} m^3/m^2s of salt permeation and good NaCl rejection of 43.10%. Meanwhile, the addition of 2 wt% of PVP K15 additive produced higher salt permeation (3.61 10^{-6} m^3/m^2s) and more selective membrane (46.94%). Besides that, membranes performance-properties data revealed that the rheological factors induced molecular orientation in polymeric membrane were found to be very significant and strongly affected toward separation improvement and properties enhancement. The highest salt rejection of about 49.55% and 59.38% achieved at shear rate of 233.33 s^{-1} and evaporation time of 20s indicated that the skinned-oriented asymmetric nanofiltration membrane was succefully synthesized. In relations to the attained high separation performance, the newly synthesized ALP-NF membrane was having of narrow pore size, good pore size distribution, high surface charge and fine asymmetrical structures. Modeling data revealed that the membranes key properties (r_p, $\Delta x / A_k$ and ζ) were found to evolute from the ranges of 0.91 to 1.41 nm, 2.56 to 9.05 µm and -1.56 to -2.34, respectively. Finally, the synthesized ALP-NF membranes were found to be comparable and in the range of the 29 available commercial nanofiltration membranes. Therefore, with the packages of high separation performance, good properties and fine structural details, the synthesized ALP-NF membrane also provided the excellent technical potentials towards membranes development and a great platform for the production of locally novel high performance nanofiltration membranes for various applications in the future.

ABSTRAK

Nanoturasan adalah prosess membran paling popular yang dibangunkan untuk pemisahan fasa cecair. Sebagai proses membran terbaru yang dibangunkan secara berterusan, ciri-ciri istimewa seperti jejari liang berjulat nanometer, penolakan tinggi partikel-partikel bercas, cas tersedia dan tekanan operasi yang rendah, aplikasinya berkembang pesat terutama dalam bidang proses air, air minuman dan rawatan air sisa. Tesis ini memfokuskan kajian terbaru dan signifikan dalam sintesis dan pencirian ke atas membran lapisan nipis terorientasi asimetrik nanoturasan tekanan rendah. Dalam kajian ini, formulasi baru larutan polimer yang terdiri daripada polyethersulfone, 1-methyl-2-pyrrolidone dan air telah diformulasikan dengan kepekatan polimer sebanyak 19 hingga 27 peratus berat (wt%). Untuk menghasilkan membran asimetrik nanoturasan yang lembut, rata dan nipis, mesin penuangan berketepatan tinggi telah dibangunkan berasaskan konsep utama teknik fasa balikan kering/basah. Untuk menyediakan membran yang poros, bahan tambah polimerik (PVP K15) telah ditambah ke dalam larutan polimer sebagai pembentuk liang untuk menambahbaik keporosan membran. Selain itu, untuk menghasilkan membran nanoturasan kulit nipis terorientasi, faktor-faktor reologikal (kadar ricih dan masa pemeruwapan) telah dikenakan semasa proses penuangan. Pada julat tekanan operasi daripada 100 hingga 500 kPa dan sel penelapan Sterlitech, prestasi membran telah dinilai dari segi penelapan air tulen, penelapan air, penolakan garam dan pemisahan bahan-bahan neutral. Menggunakan model-model Spiegler-Kedem, SHP dan TMS, parameter membran, perincian struktur dan sifat-sifat utama ((r_p, $\Delta x / A_k$ and ζ) telah dicirikan. Analisis ke atas struktur–struktur morfologikal dan pengagihan saiz keliangan berjaya mengesahkan keadaan penyediaan optimum dan membran nanoturasan terbaik. Daripada kajian ini, di dapati bahawa membran yang di hasilkan daripada kepekatan polimer pada 20.42 wt% menunjukkan penelapan air yang tinggi dari julat 6.30 x 10^{-6} hingga 8.94 x 10^{-6} m^3/m^2s dan penelapan garam serta penolakan garam, masing-masing kira-kira 3.26 x 10^{-6} m^3/m^2s dan 43.10%. Sementara itu, penambahan bahan penambah PVP K15 sebanyak 2 wt% menghasilkan membran dengan kebolehtelapan garam lebih tinggi (3.61 10^{-6} m^3/m^2s) dan lebih selektif (46.94%). Selain itu, data prestasi-sifat-sifat membran menunjukkan bahawa faktor-faktor reologikal berserta orientasi molekul di dalam membran polimer adalah sangat signifikan dan sangat memberikan kesan kepada perubahan pemisahan dan peningkatan dalam pencirian. Penolakan garam tertinggi kira-kira 49.55% dan 59.38% yang dicapai pada kadar ricih optimum (233.33 s^{-1}) dan masa pemeruwapan (20s) menunjukkan bahawa membran asimetrik nanoturasan lapisan nipis terorientasi tinggi telah berjaya disintesis. Sehubungan dengan itu, membran ALP-NF terbaru yang disintesis juga mempunyai saiz liang kecil dan penyerakkan keliangan yang baik, caj permukaan tinggi dan struktur asimetrik sempurna. Data-data permodelan bagi sifat-sifat utama membran (r_p, $\Delta x / A_k$ and ζ) didapati telah berubah masing-masing dari julat 0.91 kepada 1.41 nm, 2.56 kepada 9.05 µm dan -1.56 kepada -2.34. Akhir sekali, membran yang disintesis juga didapati setanding dan berada di dalam julat 29 membran komersial. Maka, dengan pakej baik seperti prestasi pemisahan tinggi, ciri-ciri baik dan percirian struktur sempurna, membran ALP-NF yang disintesis juga menyediakan potensi teknikal yang sangat baik ke arah pembangunan membran dan juga platfom terbaik untuk penghasilan membran nanoturasan berprestasi tinggi terbaru untuk pelbagai aplikasi pada masa hadapan.

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A_k	Membrane porosity
c	Concentration (mol/m^3)
c_i	Concentration of component i (mol/m^3)
$c_{p,i}$	Concentration of component i in the permeate (mol/l)
$c_{r,i}$	Concentration of component i in the rejection (mol/l)
C_i	Concentration in the bulk solution (mol/m^3)
C_{total}	Total charge concentration in bulk solution mol/m^3)
D_i	Diffusivity of ion i in free solution (m^2/s)
D_s	Solute diffusivity for neutral molecules
F	Faraday constant (=96487)(C/mol)
H_D , H_F	Steric parameters related to wall correction factors under diffusion and convection conditions, respectively (-)
J_s	Averaged solute flux over membrane surface (mol/m^{2}s)
J_v	Averaged volume flux over membrane surface (m^3/m^2.s)
k_i	Averaged distribution coefficients of ion i by the electrostatic effects
P	Permeability (m/s)
P_s	Solute permeability (m/s)
r	Pore size (nm)
r_s	Solute radius (nm)
R_i	Rejection of component i (%)
R	Gas constant (8.314)(J/mol^3 K)
R_{obs}	Observed rejection (%)
R_{real}	Real rejection (%)

S_D , S_F	Distribution coefficients of solute by steric-hindrance effect under diffusion and convection condition, respectively (-)
u_x	Velocity in the axial direction to the membrane (m/s)
X_d	Effective membrane charge density (mol/m^3)
z_i	Valences of ion
ΔP	Applied pressure (kPa)
Δx	Membrane thickness (m)
$\Delta x / A_k$	Ratio of membrane thickness to membrane porosity
ε	Membrane porosity (dimensionless)
ζ	Ratio of fixed charge density to salt concentration
λ	Ratio of solute radius to membrane pore radius
σ	Reflection coefficient
η	Viscocity of solution (Pa.s)
τ	Tortuosity (dimensionless)

LIST OF ABBREVIATIONS

ATR-FTIR	Attenuated Total Reflection Fourier Transform Infrared
ALP-NF	Asymmetric low pressure nanofiltration
CA	Cellulose acetate
D	Dialysis
DMAc	Dimethylacetamide
DMF	Dimethyformamide
DIPS	Diffusion induced phase separation
DSPM	Donnan steric pore model
ED	Electrodialysis
GS	Gas separation
LM	Liquid membranes
MD	Membrane distillation
MW	Molecular weight
MF	Microfiltration
MWCO	Molecular weight cut-off
NF	Nanofiltration
NG	Nucleation growth
NMP	1-Methyl-2-pyrrolidone
NSA	Non-solvent additive
OSW	Office of Saline Water
PA	Polyamides
PEG	Polyethyleneglycol
PES	Polyethersulfone

PD	Piezodialysis
PSf	Polysulfone
PWP	Pure water permeation
PVP	Polyvinyl-pyrrolidone
RIPS	Reaction induced phase separation
RO	Reverse osmosis
SD	Spinodal decomposition
SEM	Scanning Electron Microscopy
SHP	Steric-Hindrance Pore Model
TDS	Total Dissolved Solids
TFC	Thin film composite
THF	Tetrahydofuran
TIPS	Temperature induced phase separation
TMS	Teorell-Meyer-Sievers
UF	Ultrafiltration
ULPRO	Ultra low pressure reverse osmosis

CHAPTER 1

INTRODUCTION

1.1 MEMBRANE SEPARATION TECHNOLOGY

Membrane separation technology is a highly innovative process in engineering operations. Since the 1960's, new technology of membrane processes have been developed rapidly due to the tremendous increases in the growth of the new separation based industries. Practically, membranes separation offered the most economical separation technique with the advantages of ambient temperature operation, low capital and running costs, and modular construction. As the most important and effective engineering component in used today, membranes processes also gained wide acceptance and significance due to flexibility and performances. This technology has broad industrial applications including in the petro-chemical, oil and gas, environmental, water and wastewater treatment, pharmaceutical, medical, biotechnology, paper, textile, and electronic industries with the growing rate of 10% to 20% per year. Thus, as continuous and highly stable based operations, membranes technology could offer an alternative to the conventional industrial separation methods.

1.2 NANOFILTRATION MEMBRANE

According to the IUPAC recommendations (Koros et al., 1996), NF is a "pressure-driven membrane-based separation process in which particles and dissolved molecules smaller than about 2 nm are retained". The number of applications in which NF is used is growing rapidly. The reduction of hardness (removal of divalent ions like $Ca^{2+,}$ Mg^{2+}, and SO_4^{-2}) and dissolved organics from water are the most important applications (Lakshminarayan et al., 1994). Examples of other NF applications are the cleaning of water streams from metalworking plants by the removal of heavy metals (Ni, Fe, Cu, and Zn) and the cleaning up of organics, like the reportedly carcinogenic halogen compounds trihalo-methanes from contaminated groundwater. In the food industry, NF is used for the recovery of organic acids from fermentation broths, and the desalting of whey.

Among the pressure driven membranes, nanofiltration (NF) is a relatively new process in membranes separation and its applications are increasing rapidly. Due to the continuous development of new membranes materials, it has been possible to extend its application to meet new challenges of industries such as cleaning of effluent waters that contain poisonous substances and recirculation certain expensive reactants from waste stream. In many cases, the difficult circumstances are high temperatures, extreme pH or very strong solvents. From most of these situations, current membranes technology can offer new solvent resistant membranes (Nystrom et al., 2000).

NF membrane is a partly permeable membrane with the pores typically much larger than the reverse osmosis (RO) membranes so it requires lower pressures to perform the separation. The pore size of the membrane corresponds to a molecular weight cut-off value of approximately 200-500 g/mole. The separation of components within or higher than molecular weight components can be accomplished using NF membrane. NF membranes have slightly charged surface and because the dimensions of the pores are less than one order of magnitude larger than the size of ions, charge interaction plays a dominant role. This effect can be used to separate ions with different valences (Timmer et al., 1998).

Approximately 65% of NF market was accounted to have used for water treatment, 25% for the food and dairy industry, and less than 10% for the chemical industry. If the physical and chemical properties of the NF layer could be optimized to be performed at low pressure and higher flux, then only a minimum requirement of energy is needed to treat a huge volume of rinsing water. This is very promising terms of application since the cost of wastewater treatment and energy consumption is getting higher by the day (Bessarabove et al., 2002).

1.3 NANOFILTRATION MATERIALS

Most NF membranes are thin-film composites of organic (polymeric) or inorganic (ceramic) nature. A membrane top layer is responsible for the separation while the support layer provides mechanical strength. There is a large diversity of polymeric NF membranes, but mainly cellulose esters, aromatic polyamides (PA) and polyethersulfones (PES) are used (Rautenbach and Gröschl, 1990; Lakshminarayan et al., 1994; Mulder, 1998). Cellulose ester like cellulose acetate (CA) is very suitable for desalination because of its high permeability for water in combination with a very low solubility in salts (Mulder, 1998). However, the chemical and thermal stability of these membranes is quite poor and therefore cleaning of the membrane modules is very difficult. Typical operating conditions are in the pH range of 4 to 6 and at around 30 °C. The chemical stability of PA and PES membranes are much better than of CA (e.g., pH stability ≈3-10), but they are degraded by oxidizers and the feed water must therefore be dechlorinated. The PA and PES materials have a high selectivity, but their water flux is generally lower than that of the CA membranes. Inorganic NF membranes are (mixed) oxides, generally of aluminium, zirconium or titanium. Due to their material properties they all of them have good mechanical strengths and showed very good features of thermal and chemical stabilities. The latter could withstand high temperature cleaning treatments like sterilization. The pH stability of alumina membranes is similar to that of polyamides and polyethersulfones, that is, between the ranges of pH 4 to pH 10 (Kucera, 1997).

1.4 TRANSPORT MECHANISMS OF NANOFILTRATION

Membrane technology has undergone a rapid development as it pertains to most applications and in particular to water and wastewater treatment. The last twenty (20) years have witnessed new membrane working at ever lower pressure and with the increasing of salt rejection from the original cellulose acetate membrane requiring 400 psi to modern polyamide thin-film membranes which only require 100 psi of net driving pressure. The above standard of operating pressure is only suitable for the process which involves high osmotic pressure and high diffusive of monovalence solute like NaCl. However, for multivalence ions like copper sulfate, the application to separate the metal salt should be developed with huge benefit to operate at the lowest possible operating pressure.

Recently, intensive study and development are being carried out on specialized membranes tailor-made for a particular application. Unfortunately, the development of high performance asymmetric nanofiltration membrane seems to be neglected due to the excessive focus on thin film composite membrane. Towards producing high performance asymmetric NF membrane, the understanding about the membranes materials, fabrication process, key and structural properties, separation process and mechanism are very critical prior to membranes optimization. Membranes separation based solely on the sieving mechanism which requires high-energy operation due to high operating pressure. NF membrane should have pores to let through the solutes that need to be retained or rejected and at the same time exhibit good rejection mechanism other than simple sieving mechanisms as Donnan exclusion, di-electric exclusion and hydration mechanism (Yaroshchuk, 2001).

The separation of NF membranes is mainly governed by electrostatic exclusion. The membranes contain ionisable groups that could charge their surface, leading to the rejection of charged solutes. The sign and magnitude of a solute's charge determine its degree of electrostatic exclusion. For polymeric membranes separation by size is also of considerable importance. Recently, another separation mechanism called dielectric exclusion has been proposed to be of importance (e.g., Bontha and Pintauro, 1994; Yaroshchuk, 2000). According to the theory of dielectric exclusion, the permittivity (of a liquid) in NF pores would be lower than the bulk permittivity, creating an additional energy barrier for solutes to enter the membrane. The growing interest in NF membranes has also lead to a tremendous increase in the development of models that describe their separation behavior.

In order to describe transport, apart from the driving forces, the diffusion coefficients, membrane pore size and thickness are required as input parameters. The diffusion coefficients at infinite dilution could be used, but in more sophisticated descriptions, they are corrected for the structure of the porous matrix (i.e., porosity and tortuosity) and the distribution of a species within a pore, which is a result of the interaction of species with the membrane pore wall. Unless the membrane top layer and the support are mixed (as with some polymers), the membrane thickness could be easily determined. It is much more difficult to accurately obtain the pore size of a membrane. Therefore this parameter is often determined by membrane separation data.

1.5 APPLICATION OF NANOFILTRATION

Recently, the environmental problems such as water, soil, air pollutions and waste pollutions have become a major problem in some countries which might be caused by human and/or industrials activities. One of the critical pollution problems arising from an electroplating industry is the generation of a large amount of rinsed water for electroplated parts. Wastewater from electroplating industry contain many heavy metals such as copper, manganese, chromium, zinc etc., and chemicals that could be detrimental to the health of organic bodies when exposed to the environment. However, these wastewater could be reuse by removing the heavy metals and toxic materials to convert it to a portable water. As for example, copper plating is very common in the production of wire brass, boiler pipe and cooking utensils. The semiconductor industry in Malaysia is one of the major industries, which generates a large portion of wastewater containing huge amount of toxic materials and heavy metals. Thus, effective techniques to remove or recover these compounds before being discharged to the environment are imperatively required.

In the conventional and traditional techniques, chemical precipitation has been widely adopted for the treatment of wastewater from electroplating wastes. However, these methods require heavy dosage of chemical addition that eliminate the possibility of direct reusing of the collected heavy metals and require the disposal of the sludge containing large amount of chemicals and heavy metal as well as ionic wastes. Hence, they are very problematic. In this case, the heavy metals in the rinsed water could be separated physically where both the filtrated water and the collected ionic metals can be reused directly. Reverse osmosis (RO) process showed a very promising data but the employment of NF are so limited and very rare. Thus, the development and fabrication of membrane separation process that is highly selective asymmetric nanofiltration (NF)