DEVELOPMENT OF POLYACRYLONITRILE/POLYACRYLONITRILE-*g*-POLY(VINYL ALCOHOL) HOLLOW FIBER ULTRAFILTRATION MEMBRANES WITH ENHANCED ANTI-FOULING PROPERTIES

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Dedicated to my beloved parents

(*Mohd Nazri bin Alias and Faizatun Zarila binti Mohamad*)

my husband

(*Mohd Iliyas Zukhry bin Mohd Nasir*)

my siblings

(*Nadzirah, Adilla, Syazwani, and Nazrul Haffis*)

and friends for their encouragement and support

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ABSTRACT

The objective of this study is to develop polyacrylonitrile (PAN)-based hollow fiber ultrafiltration (UF) membranes with improved anti-fouling properties for wastewater treatment. The prepared membranes were characterized with respect to their morphological structure, surface chemical composition, surface roughness, and hydrophilicity to investigate the impact of the membrane properties on the separation and anti-fouling performance. In the first stage of this study, PAN-based hollow fiber membranes incorporated with polyvinyl alcohol (PVA) were fabricated. Experimental results indicated that the resultant membranes demonstrated a trade-off between their separation and anti-fouling performances. Therefore, for the second stage, PAN-*g*-PVA graft copolymers of different properties (i.e. CP5, CP10 and CP15) were synthesized via ceric ($Ce^{(IV)}$)-initiated free radical polymerization by using different acrylonitrile (AN) monomer weights (5, 10, 15 g of AN per 10 g of PVA) and incorporated in the hollow fiber membranes. Obtained results revealed that the copolymer properties (i.e. number of PVA repeating units (n_{PVA})) significantly influenced the overall membrane properties. The highest pure water flux (179 L/m^2.h.bar) was achieved by the membrane incorporated with graft copolymer of the highest n_{PVA} of 70 due to the increase in hydrophilicity, pore size and porosity, and surface roughness. Thirdly, the investigation on the effect of the graft copolymer compositions in dope solution on the membrane properties and performances was carried out by using the best performance graft copolymer (CP10). The membrane properties and performance were significantly altered using the different copolymer composition. Membranes with the highest copolymer content demonstrated the highest water flux of 297 L/m^2.h when tested at 1 bar which attributed to the changes in the membrane morphology, surface roughness and hydrophilicity. Overall, it was summarized that the UF performance and fouling property were mostly affected by the pore structure of the membrane and partly by the membranes physical properties (i.e. degree of PVA surface coverage and surface roughness) during filtration of bovine serum albumin (BSA), albumin from chicken egg white (EA) and trypsin. In the final stage, three different membranes; CP5 (incorporated with graft copolymer with n_{PVA} of 68 at PAN:PAN-*g*-PVA weight ratio of 90:10), CP10-10 (incorporated with CP10 graft copolymer with n_{PVA} of 25 at PAN:PAN-*g*-PVA weight ratio of 90:10) and CP10-5 (incorporated with CP10 graft copolymer with n_{PVA} of 25 at PAN: PAN-*g*-PVA weight ratio of 95:5), which demonstrated among the highest flux recovery during proteins filtration, were subjected to a feasibility study for natural rubber (NR) effluent treatment. The highest flux recovery of 84% could be achieved by CP10-10 membrane using hydraulic cleansing and its properties are summarized as follows: 62.73º contact angle, 34.3% degree PVA surface coverage, 43.5 nm root mean square surface roughness (R_q), 30-72 nm pore size and 23% porosity. It can also be inferred that the pore size and pore size distribution gave profound influence on the membrane fouling resistance during NR filtration. In addition, all the membranes showed remarkable performances in reducing turbidity (> 99%) and colour (>97%). Reduction of 68-70% total proteins, 29-38% chemical oxygen demand (COD), 14-32% total organic carbon (TOC), 8-11% total dissolved solid (TDS) and 7-8% conductivity were achieved by the membranes depending on the membrane properties.

ABSTRAK

Objektif kajian ini adalah untuk membangunkan membran turasan-ultra (UF) gentian geronggang berasaskan poliakrilonitril yang mempunyai sifat anti-kotoran yang lebih baik untuk rawatan air sisa. Membran yang disediakan dianalisa berdasarkan struktur morfologi, komposisi kimia permukaan, kekasaran permukaan, dan kehidrofilikan untuk mengkaji kesan sifat-sifat membran terhadap prestasi pemisahan dan anti-kotoran. Pada fasa pertama kajian ini, membran gentian geronggang berasaskan PAN yang dimasukkan dengan polivinil alkohol telah disediakan. Keputusan eksperimen menunjukkan membran terhasil menunjukkan kesan gangguan keseimbangan di antara prestasi pemisahan dan anti-kotoran. Oleh itu, pada fasa kedua, kopolimer cangkuk PAN-*g*-PVA (cth. CP5, CP10, CP15) yang mempunyai sifat-sifat berbeza telah disintesis melalui pempolimeran radikal bebas yang dimulakan oleh serik ($Ce^{(IV)}$) dengan menggunakan berat monomer akrilonitril (AN) yang berbeza dan dimasukkan ke dalam membran gentian geronggang. Keputusan menunjukkan sifat-sifat kopolimer (cth. nombor unit-unit berulang PVA (n_{PVA})) mempengaruhi keseluruhan sifat-sifat membran dengan ketara. Fluks air tulen tertinggi (179 L/m^2.jam) telah dicapai oleh membran yang dimasukkan dengan kopolimer cangkuk dengan n_{PVA} sebanyak 70 disebabkan oleh peningkatan kehidrofilikan, saiz liang dan keliangan, dan kekasaran permukaan. Ketiga, kajian tentang kesan komposisi kopolimer cangkuk di dalam larutan dop terhadap sifat-sifat dan prestasi membran telah dijalankan dengan menggunakan kopolimer cangkuk yang mempunyai prestasi terbaik (CP10). Sifat-sifat membran dan prestasinya berubah dengan ketara dengan komposisi kopolimer yang berbeza. Membran dengan kandungan kopolimer tertinggi menunjukkan fluks air tulen tertinggi sebanyak 297 L/m^2.jam apabila diuji pada 1 bar disebabkan oleh perubahan morfologi membran, kekasaran permukaan dan kehidrofilikan. Keputusan keseluruhan meringkaskan bahawa prestasi UF dan sifat anti-kotoran kebanyakannya bergantung kepada struktur liang membran dan sebahagiannya terkesan daripada sifat fizikal membran (cth. darjah liputan PVA pada permukaan dan kekasaran permukaan semasa turasan albumin daripada serum lembu (BSA), albumin daripada telur putih ayam (EA) dan tripsin. Pada fasa terakhir, tiga membran; CP5 (dimasukkan kopolimer cangkuk dengan 68 n_{PVA} pada nisbah berat PAN:PAN-*g*-PVA 90:10), CP10-10 (dimasukkan dengan kopolimer cangkuk CP10 dengan 25 n_{PVA} pada nisbah berat PAN:PAN-*g*-PVA 90:10) dan CP10-5 (dimasukkan dengan kopolimer cangkuk CP10 dengan 25 n_{PVA} pada nisbah berat PAN:PAN-*g*-PVA 95:5), yang telah menunjukkan di antara pemulihan fluks tertinggi semasa turasan protein diuji untuk kajian kemungkinan untuk rawatan sisa buangan getah asli (NR). Pemulihan fluks air tertinggi sebanyak 84% boleh dicapai oleh membran CP10-10 yang mempunyai sifat-sifat seperti berikut: 34.3% darjah liputan permukaan PVA, 43.5 nm punca kuasa dua kekasaran permukaan, 30-72 nm saiz liang dan 23% keliangan. Boleh disimpulkan bahawa saiz liang dan agihan saiz liang mempengaruhi rintangan kotoran semasa turasan NR. Sebagai tambahan, kesemua membran menunjukkan prestasi yang sangat baik dalam menurunkan kekeruhan (>99%) dan warna (>97%). Penurunan sebanyak 68-70% jumlah protein, 29-38% keperluan oksigen kimia (COD), 14-32% jumlah karbon organik (TOC), 8-11% jumlah pepejal terlarut (TDS) dan 7-8% konduktiviti telah dicapai bergantung kepada sifat-sifat membran.

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LIST OF ABBREVIATIONS

^{1}H NMR	-	Nuclear magnetic resonance proton spectra
AFM	-	Atomic force microscope
AGS	-	Aerobic granular sludge
AGWSP	-	Attached-growth waste stabilization pond
AN	-	Acrylonitrile
ANT	-	Ammoniacal nitrogen
ASP	-	Activated sludge process
ATRP	-	Atomic transfer radical polymerization
BOD	-	Biological oxygen demand
BSA	-	Bovine serum albumin
CAN	-	Ceric ammonium nitrate
CCD	-	Central composite design
COD	-	Chemical oxygen demand
CW	-	Constructed wetland
DMAC	-	N,N-dimethylacetamide
DMF	-	Dimethylformamide
DMMSA	-	*N*,*N*-dimethyl-*N*-methacryloxyethyl-*N*-(3 sulfopropyl)
DMSO	-	Dimethylsulfoxide
DO	-	Dissolved oxygen
DSC	-	Differential scanning calorimeter
EA	-	Albumin from chicken egg white
FESEM	-	Field emission scanning electron microscope
FPE	-	Fermented pineapple extract
FTIR	-	Fourier transform infrared
GA	-	Glutaraldehyde
HA	-	Humic acid
HCL	-	Hydrochloric acid

HRT	-	Hydraulic retention time
IEP	-	Isoelectric point
MBR	-	Membrane bioreactor
MD	-	Molecular dynamic
MF	-	Microfiltration
MW	-	Molecular weight
MWCNT	-	Multiwalled carbon nanotube
MWCO	-	Molecular weight cut-off
NF	-	Nanofiltration
NMP	-	*N*-methyl-2-pyrolidone
NOM	-	Natural organic matter
NR	-	Natural rubber
P_4VP	-	Poly(4-vinylpyridine)
PAA	-	Poly(acrylic acid)
PAN	-	Polyacrylonitrile
PBMA	-	Poly(butyl methacrylate)
PDMS	-	Poly(dimethyl) siloxane
PEG	-	Poly(ethylene glycol)
PEGMA	-	Poly(ethylene glycol) methyl ether methacrylate
PEO	-	Polyethylene oxide
PES	-	Polyethersulfone
PES-c	-	Phenolphthalein polyethersulfone
PET	-	Polyethylene terephthalate
PHFBM	-	Poly(hexafluorobutyl methacrylate)
PMMA	-	Poly methyl methacrylate
PNMGA	-	*N*-methyl-*D*-glucamine
PNSB	-	Purple non-sulphur photosynthetic bacteria PNSB
PPESK	-	poly(phlazinone ether sulfone ketone)
PSBMA	-	Poly(sulfobetaine methacrylate
PSF	-	Polysulfone
PSR	-	Polystyrene
PVA	-	Poly(vinyl alcohol)
PVC	-	Poly(vinyl chloride)

PVDF	-	Poly(vinylidene fluoride)
PVP	-	Poly(vinyl pyrrolidone)
RDF	-	Radial distribution function
RO	-	Reverse osmosis
SA	-	Sodium alginate
SEM	-	Scanning electron microscope
SMR	-	Standard Malaysian Rubber
SS	-	Suspended solid
TDI	-	Diisocyanate
TDS	-	Total dissolved solid
TEOS	-	Tetraethoxysilane
TFC	-	Thin film composite
TGA	-	Thermal gravimetric analysis
TKN	-	Total Kjeldahl nitrogen
TOC	-	Total organic carbon
TS	-	Total solid
TSS	-	Total suspended solid
UF	-	Ultrafiltration
WSP	-	Waste stabilization pond
XPS	-	X-ray photoelectron spectrometer

LIST OF SYMBOLS

A	-	Area (m^2)
C	-	Degree of PVA surface coverage (%)
C_f	-	Feed concentration ($mg.L^{-1}$)
C_p	-	Permeate concentration ($mg.L^{-1}$)
G	-	Percentage of grafting (%)
GE	-	Grafting efficiency (%)
J_p	-	Constant flux ($L.m^{-2}.h^{-1}$)
J_{W1}	-	Initial pure water flux ($L.m^{-2}.h^{-1}$)
J_{W2}	-	Final pure water flux (after cleansing) ($L.m^{-2}.h^{-1}$)
M_o	-	Theoretical oxygen molar ratio (dimensionless)
n_{PVA}	-	Number of PVA repeating units (dimensionless)
R	-	Rejection (%)
R_a	-	Mean roughness (nm)
R_{FD}	-	Flux decline (%)
R_{FR}	-	Flux recovery (%)
R_{ir}	-	Irreversible fouling (%)
R_q	-	Root mean square of Z data (nm)
R_r	-	Reversible fouling (%)
R_t	-	Total fouling (%)
R_z	-	Mean difference between five highest peaks and five lowest valleys (nm)
t	-	Time (h)
T_g	-	Glass transition temperature (°C)
T_o	-	Oxygen molar ratio on membrane surface (dimensionless)
v	-	Volume (L)
Wt_f	-	Final weight of hollow fiber (mg)

Wt_i	-	Initial weight of hollow fiber (mg)
Wt_{loss}	-	Weight loss (%)

Greek letters

δ	-	Chemical shift in NMR spectra (ppm)
θ	-	Take-off angle (°)

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CHAPTER 1

INTRODUCTION

1.1 Membrane Separation Processes

Over the past decade, declining water quality is inevitably a growing global concern. Increasing global population, evolving urbanization, and accelerating economic activities are among the leading factors in the degradation of water quality. Major pollutants sources which include domestic sewage, industrial effluent, and agriculture runoff have been known to release notorious anthropogenic pollutants to the aquatic system. This is most probably due to poor treatment and management of the effluents, which adversely posing serious threat to environment and health (Kumar Reddy and Lee, 2012). As a result, this deprivation in water quality will consequently cause water scarcity. By year 2025, it is expected that water scarcity will become a major issue when global water consumption would reach to 3800 km^3/year (Jury and Vaux, 2005).

To address the increasing need of clean water, various water treatment technologies have been proposed and implemented from small to big-scale. However, conventional treatment methods are always hampered by the lack of skilled personnel, expensive cost, long retention time, requirement of ample land, and also failure to meet safe discharge limits (Mohammadi *et al.*, 2010). In this regard, membrane technology is a promising candidate in wastewater treatment due to advantages offered by this process which include high efficiency, ease of operation, low operating cost, and also low energy requirements (Baker, 2004). Recently, membrane technologies have been greatly progressed in various industrial processes and have shown very promising outcomes in various wastewater treatments.

In general, membrane is a selective barrier which allows one selective component of a mixture to pass through while rejecting others (Baker, 2004). In this regard, pressure-driven membrane processes such as ultrafiltration (UF), microfiltration (MF), and reverse osmosis (RO) have received significant attention due to low operating and maintenance cost, high efficiency, low energy requirement, and also ease of operation (Chen *et al*., 2011).

Of the membrane technologies used in water and wastewater treatment, low pressure driven membranes (MF and UF) are commonly used to remove microorganisms and colloidal particles present in the wastewater. Since mid-1990s, the installations of UF and MF have increased in capacity from ca. 1000 m^3/day in 1997 to 10,000,000 m^3/day in 2003 (Kennedy *et al*., 2008). The UF and MF have also been continuously developed in terms of their modules, materials and characteristics at both laboratory and commercial scale (Baker, 2004). Currently, UF is accepted as a reliable and efficient technology for many domestic and industrial processes. In fact, UF membrane technology has been also widely applied in water and wastewater treatments. It is believed that tougher environmental legislation and also water scarcity issue are probably the main factors behind the rapid development of UF membrane in wastewater treatment.

Currently, low-pressure driven UF membrane process has been proposed as a potential alternative for various wastewater treatments. However, better understanding on the improvement of the membrane fouling resistant and optimization of the membrane properties for filtration of heavily polluted effluent is of crucial importance in order to achieve desired separation and anti-fouling performance. Although great deals of studies have been reported so far in fundamental and practical manners, material development of UF membrane particularly to improve fouling resistance is still inadequate.

1.2 Problem Statements

UF membrane has been widely applied in various separation processes. However, it should be emphasized that reports addressing fouling issue of the UF membrane particularly during filtration of heavily polluted effluent treatment are scarcely reported in open literature (Delgado Diaz *et al*., 2012; Hilal *et al*., 2005). Susanto and Ulbricht (2009b) pointed out that several factors such as the use of feed pre-treatment, advanced membranes and module design, as well as process condition optimization could enhance UF membrane performance. Another important factor which could play a significant role in UF membrane fouling is the membrane material itself (Susanto and Ulbricht, 2009b).

Polyacrylonitrile (PAN) is a common material used to fabricate UF membrane owing to its high chemical stability, hydrophilicity and high solubility to common solvents. Although PAN is hydrophilic in nature, several modification methods have been proposed to further improve its anti-fouling resistance and permeation properties (Lohokare *et al*., 2011; Jung, 2004). Blending the dope solution with hydrophilic components is the simplest modification method, yet efficient, to enhance a membrane morphological properties as well as its filtration performance (Alsalhy, 2012; Amirilargani and Mohammadi, 2012). For example, Li *et al*. (2010) reported that addition of PVA to polyvinylidene fluoride (PVDF) via blending method leads to improvement of the membrane surface hydrophilicity, pure water flux as well as the membrane anti-fouling properties. The enhanced performance of the membrane is attributed to hydrophilic nature of PVA, revealing the influential role of PVA in improving both filtration and anti-fouling performance. Although a great numbers of studies have reported on the viability of blending method in improving properties of membranes, several drawbacks such as compatibility problem, leaching out of the additive during phase inversion process and/or filtration require further address (Chen *et al*., 2011; Su *et al*., 2009).

To address the currently existing problems associated with blending approach, blending with amphiphilic copolymers is introduced. Such blending have received considerable attention due to its unique self-assembly behaviour that can impart excellent hydrophilicity to membrane and enhance fouling resistance (Asatekin *et al*., 2007; Liu *et al*., 2009; Nie *et al*., 2011). However, only several reports are found available in open literature for PAN membrane modification with amphiphilic copolymer.

Poly(vinyl alcohol) (PVA) is a hydrophilic polymer commonly used in membrane fabrication. It possesses excellent film forming ability, and also excellent physical and chemical stability, which have made it as a good choice for membrane fabrication (Na *et al*., 2000; Zhang *et al*., 2006; Ahmad *et al*., 2012). However, only few studies have been reported on the modification of UF membranes with PVA, probably due to complicated and difficult preparation procedures (Gohil and Ray, 2009; Guo *et al*., 2007). Nevertheless, it is necessary to fully understand the impact of modification using PVA on UF membrane properties and performances.

In view of this, efforts have been made to investigate the potential of PAN-based hollow fiber UF membranes incorporated with PAN-*g*-PVA amphiphilic copolymers to treat heavily polluted NR effluent. It is noted that despite those mentioned advantages of UF membrane, the practical application of UF for NR effluent treatment is scarcely reported in literature. It is also acknowledged that the presence of various toxic and hazardous constituents in NR effluent has led to the searching of new and innovative methods to produce quality-complied and safely dischargeable NR effluent. In this regard, various treatment methods such as biological methods, chemical methods and also integrated methods have been implemented to treat the NR effluent. However, it remains challenging to develop treatment methods that would be cost-effective, simple in operation, environmentally friendly and also efficient (Mohammadi *et al*., 2010). In Malaysia, mostly the wastewater is treated by biological methods, but results have shown that this method alone is not effective enough to completely degrade all the pollutants to acceptable safe level of discharge. Besides, it also suffers from several drawbacks such as unpleasant odour, large land area requirement, high cost, high retention time and sludge problem (Chaiprapat and Sdoodee, 2007; Rosman *et al*., 2013). Such deficiencies have prompted the seeking of more viable and innovative approaches to achieve higher separation efficiencies for various pollutants.

Thus, the ultimate goal is to understand the fouling behaviour and performance of the UF membranes and also the removal and reduction of organic and inorganic compounds during direct filtration of heavily polluted NR effluent. It is also essential to understand the correlation between the membranes properties (i.e. morphological structure, surface chemical composition, surface roughness, and hydrophilicity) and the membrane anti-fouling along with separation performance. In addition, present study is to provide greater understanding and highlight underlying problems associated with the membrane preparation which will contribute important insight towards the development of effective membrane for wastewater treatment.

1.3 Objectives of the Study

Based on the aforementioned problem statements, the objectives of the current study are outlined as follows:

(i) To study the effect of PVA concentration on the membrane separation and anti-fouling properties of PAN-based hollow fiber membranes,

(ii) To investigate the correlation between amounts of acrylonitrile (AN) monomer added during PAN-*g*-PVA graft copolymer synthesis and the PAN-based membrane properties and performance,

(iii) To study the effect of PAN-*g*-PVA composition on the properties and performance of PAN-based hollow fiber membranes, and

(iv) To investigate the performance of the developed membranes to treat heavily polluted NR effluent

1.4 Scopes of the Study

In order to achieve the listed objectives, several scopes of study have been identified as follows:

(i) Synthesizing PAN-*g*-PVA graft copolymer from three different AN monomer weights of 5, 10, 15 g per 10 g of PVA via $Ce^{(IV)}$-initiated free radical polymerization.

(ii) Characterizing the developed PAN-*g*-PVA copolymer by ^{1}H nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy and gravimetric analysis.

(iii) Formulating dope solution of hollow fiber UF membranes using different PVA compositions; PAN:PVA ratio of 95:5, 90:10, 85:15, and 80:20 at fixed polymer weight of 12 wt%.

(iv) Formulating dope solution of hollow fiber UF membranes using three different PAN-*g*-PVA copolymers of different properties (prepared from different AN monomer weight during synthesis; 5, 10, 15 g of AN per 10 g of PVA) at fixed polymer weight of 12 wt%.

(v) Formulating dope solution of hollow fiber UF membranes using best performance PAN-*g*-PVA copolymer (CP10) at three different copolymer composition; PAN: PAN-*g*-PVA ratio of 95:5, 90:10, and 80:20 at fixed polymer weight of 12 wt%.

(vi) Fabricating hollow fiber UF membranes by dry-wet spinning process at fixed-spinning conditions.

(vii) Characterizing the chemical and physical properties of the prepared membranes using field emission scanning electron microscope (FESEM), scanning electron microscope (SEM), atomic force microscope (AFM), X-ray photoelectron spectrometer (XPS), attenuated total reflection infrared (ATR-IR) spectroscope, thermal gravimetric analysis (TGA), differential scanning calorimeter (DSC), and contact angle analyzer.

(viii) Evaluating performance of the prepared membranes in terms of water permeation flux, proteins rejection and also anti-fouling performance during proteins filtration, i.e. BSA, EA and trypsin.

(ix) Identifying the ideal membranes for direct UF of NR effluent treatment based on their anti-fouling properties during proteins filtration.

(x) Evaluating performance of the hollow fiber membranes in terms of removal and reduction of organic and inorganic pollutants from NR effluent.

(xi) Performing membrane fouling analysis during direct UF of heavily polluted NR effluent.

1.5 Rational and Significant of the Study

This study aims to impart better understanding on the development of hollow fiber membranes with enhanced anti-fouling properties for wastewater treatment. It is acknowledged that the membrane properties (i.e. surface roughness, hydrophilicity, pore structure) are fundamentally responsible in the extent of fouling and separation performance. Thus, by identifying the ideal properties of UF membrane, membrane with excellent anti-fouling characteristics and performances could be fabricated. In order to improve the membrane properties, blending with hydrophilic additive could offer a possible route to produce highly effective membranes with low fouling potential and excellent separation performance. Thus, efforts have been made to investigate the impact of direct blending with PVA in UF membrane properties and performance. To the best of my knowledge, none of such research has been conducted to evaluate the performance of blend membrane made of PAN/PVA. Additionally, amphiphilic copolymers has great potential to be used in making membrane with excellent anti-fouling properties, mainly due to its unique self-assembly behaviour that could impart excellent membrane hydrophilicity and subsequently enhance fouling resistance. Therefore, efforts have also been dedicated to identify the impact of copolymer bearing hydrophilic PVA (PAN-*g*-PVA) on the hollow fiber membrane properties and performance. No relevant study has been conducted so far to investigate the behaviour and performance of novel PAN/PAN-*g*-PVA particularly during direct filtration of heavily polluted effluent. Realizing the important roles of UF membranes for various industrial processes, particularly for wastewater treatment, efforts are made to investigate the membrane fouling behaviour during direct UF process of heavily polluted NR effluent. It is, thus, expected that outcomes from this study would be beneficial to further understand on the utilization of UF membrane for heavily polluted effluent treatment, which could offer great prospect for wider application of UF membrane.

1.6 Organization of the thesis

This thesis consists of 8 chapters. Chapter 1 outlines brief information on the membrane separation technology and the potential application of UF membrane for NR effluent treatment. Following this, problem statements, objectives and scopes of study are stated in detail.

Chapter 2 provides background information of UF membrane which includes the brief introduction of UF, materials used, modules, operation modes, configurations, and also fouling mechanism are elaborated. Then, attention is paid on the amphiphilic copolymers for UF membrane preparation by addressing the surface segregation mechanism, fouling mitigation by amphiphilic copolymer and also review on the recent studies of UF membranes fabrication using amphiphilic copolymer. After that, detailed discussion on UF membrane application for wastewater treatment is highlighted. Then, the potential application of UF membrane in NR effluent treatment which includes the background information of NR and NR industry as well as the characteristics of NR effluent are also provided. Additionally, an overview of treatment methods that have been recently developed to treat NR effluent is also highlighted. Chapter 3 will focus on the experimental methods and characterizations that were used in this study. The analysis methods of membrane performance and anti-fouling properties are also highlighted in detail.

Chapter 4 discusses the characterization and performances of PAN-based UF membranes incorporated with PVA as additive. The fabricated hollow fiber membranes were investigated in terms of their morphological structure, glass transition temperature, and thermal stability using FESEM, DSC and TGA. The surface properties of the membranes in terms of hydrophilicity and surface roughness were then characterized by contact angle and AFM analysis. The filtration performance by means of water permeation flux and BSA rejection are also presented in this chapter. In addition, details discussion on the anti-fouling performance of the membranes upon the addition of PVA is also addressed. The correlation between membrane properties and the membrane separation and anti-fouling performance is also discussed in detail.

Chapter 5 discusses on the fabrication, characterization and anti-fouling performance of PAN hollow fiber membranes incorporated with graft copolymer additive, prepared from different AN monomer weight during synthesis of PAN-*g*-PVA via $Ce^{(IV)}$- initiated free radical polymerization. The properties of the graft copolymers are presented in terms of their characterizations by using ^{1}H NMR, FTIR and gravimetric analysis. Then, the hollow fiber membranes are discussed in great details in terms of their morphological structure, surface properties and also water permeation flux. Additionally, rejection and filtration performance during different proteins filtration (BSA, EA and trypin) are also included. Discussion on the impact of incorporation of different copolymers prepared from different weight of AN monomer on membrane properties are also presented in this chapter. On the other hand, graft copolymer with enhanced properties and better performance for UF membranes is then presented in detail in Chapter 6. The impact of the graft copolymer composition on the UF membrane properties and performance is elaborated accordingly in this chapter.

Chapter 7 presents the performance of three membranes with the highest anti-fouling performance in the treatment of heavily polluted NR effluent. The developed membranes are discussed in terms of their efficiency in the removal of various organic and inorganic pollutants in the effluent; COD, TOC, turbidity, colour, total proteins, TDS and conductivity. In addition to this, the anti-fouling performance of the membranes during direct UF of NR effluent is also included. Finally, the general conclusions of this study and recommendations for future research works in this field are drawn in Chapter 8.

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