ENHANCEMENT OF ANTIFOULING PROPERTIES USING RICE HUSK SILICA PARTICLES IN POLYSULFONE MEMBRANE AND OPTIMIZATION OF ITS OPERATING CONDITION

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SPECIAL GRATITUDES TO:

Special for my parent,

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Especially for my kindly supervisor that give encouragement and support,

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ABSTRACT

This study investigates the effects of rice husk silica (RHS) as additive in the polysulfone membrane to enhance antifouling properties in membrane separation process. The flat sheet PSf/RHS membrane was prepared via phase inversion technique. The characterization and performance test were conducted on PSf ultrafiltration membrane prepared from a different additive concentration. The thermal stability of prepared membrane was observed by using thermogravimetric analysis (TGA). The cross section area and particles distribution of additive were carried out by using the scanning electron microscope (SEM) while the surface morphology was investigated via field emission scanning electron microscope (FESEM). The surface roughness and hydrophilicity were also determined by using Atomic force microscopy (AFM) and contact angle measurement respectively. Meanwhile, the performance was evaluated in term of pure water flux (PWF), rejection and antifouling properties. The optimized of normalized flux (J_f /J_o) at different parameter filtration condition (pH, ionic strength and tranmembrane-pressure) was carried out by using the response surface methodology (RSM). From the analysis of SEM, FESEM and AFM, results showed that the microstructure of the membrane especially at top layer and sub layer obviously changed with the incorporation of RHS. The results also demonstrated that the mean pore size was decreased and hyrophilicity was increased as increased RHS particles in PSf membrane. The performance of the membrane was analyzed by using distilled water for permeation test and humic acid for the rejection test. The results also showed that the hydrophilic PSf/RHS membrane has significantly improved the permeation and rejection performance after the addition of RHS. The results showed that the addition of 4 wt. % RHS give the highest flux at 300.50 L/m^2.hour (LMH). The highest rejection was found at 3 wt. % of RHS membrane with value 98% for UV_{254} and 96% for TOC. The optimal value of J_f/J_o was found at 0.62 with the parameter condition pH: 6.10, ionic strength: 0.05 mol/L and transmembrane-pressure: 2.67 bars. Optimize of RSM analysis also proved that the error of model is less than 0.05% which indicates that the model is significant.

ABSTRAK

Kajian ini menyiasat kesan silika sekam padi (RHS) sebagai bahan tambah dalam membran polisulfon untuk ciri-ciri anti-kekotoran di dalam proses pemisahan membran. Lembaran rata daripada membran PSf/ RHS telah disediakan melalui teknik fasa balikan. Pencirian dan ujian prestasi telah dijalankan ke atas penapisan ultra membran yang disediakan daripada kandungan RHS yang berbeza. Kestabilan terma membran dikaji dengan menggunakan analisis Termogravimetri (TGA). Kajian ke atas keratan rentas dan taburan zarah pada membran telah dijalankan dengan menggunakan mikroskop imbasan elektron (SEM) manakala morfologi permukaan telah disiasat melalui bidang pelepasan mikroskop imbasan elektron (FESEM). Kekasaran permukaan dan sifat hidrofilik juga ditentukan melalui daya Atom mikroskopi (AFM) dan ukuran sudut sentuh. Sementara itu, prestasi aliran air tulen (PWF), penolakan dan pencirian anti-kekotoran juga dijalankan. Proses mengoptimumkan fluks normal (J_f /J_o) pada keadaan penapisan yang berbeza parameter (pH, kekuatan ionik dan membran tekanan membran) telah dijalankan dengan menggunakan kaedah gerak balas permukaan. Keputusan yang ditunjukkan oleh SEM, FESEM dan AFM bahawa mikrostruktur membran terutama di lapisan atas dan lapisan sub telah berubah. Keputusan kajian juga menunjukkan bahawa saiz purata liang menurun dan peningkatan sifat hidrofilik meningkat disebabkan peningkatan kuantiti RHS dalam membran PSf. Prestasi membran dianalisa dengan menggunakan air suling untuk ujian penyerapan dan asid humik untuk ujian penolakan. Keputusan juga menunjukkan bahawa membran prestasi penyerapan dan penolakan PSf/RHS hidrofilik telah meningkat selepas penambahan RHS. Hasil kajian menunjukkan bahawa dengan tambahan 4 wt. % daripada RHS memberi fluks tertinggi iaitu 300.50 L/m^2.jam (LMH). Penolakan tertinggi ditemui dengan 3 wt. % daripada RHS membran dengan nilai 98% untuk UV_{254} dan 96% untuk TOC . Nilai optimum J_f / J_o ditemui pada nilai 0.62 dengan keadaan parameter pH: 6.1, kekuatan ionik 0.05 mol/L dan tekanan membran: 2.67 bar. Analisa optimum dengan menggunakan RSM juga membuktikan bahawa ralat model adalah kurang daripada 0.05% dan menunjukkan bahawa model adalah boleh diterima pakai.

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LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
ASTM	American Society for Testing and Materials
A	Membrane Area (m^2)
C_p	Solute Concentration in permeate stream
C_f	Solute Concentration in Feed
CA	Cellulose Acetate
FTIR	Fourier transform-infrared
FESEM	Field Emission Scanning electron microscopy
HA	Humic Acid
J_{wf}	Total of pure water flux
J_{cp}	Total of filtration
J_c	Total of pure water flux after physical cleaning
J_a	Total of pure water flux after chemical cleaning
J_O	Pure Water Flux of clean Membrane
J_f	Pure Water Flux of Fouled Membrane
J_f/J_o	Normailzes flux (initial flux / final flux)
LMH	L/m^2. h
MD	Membrane Distillation
MF	Microfiltration
NF	Nanofiltration
NMP	N-methyl-2-pyrrolidone
PEG	Polyethylene glycol
PWF	Pure Water Flux
PSf	Polysulfone
Q	Permeate volume (L)
R	Rejection of feed components
R_t	Total resistance

R_m	Membrane resistance
R_a	Resistance due to absorption
R_c	Resistance due to cake layer
R_{cp}	Resistance due to cake polarization
RHS	Rice husk silica
RSM	Response surface methodology
RO	Reverse osmosis
SEM	Scanning electron microscope
SiO_2	Silica Oxide
UF	Ultrafiltration
Wt.%	Weight Percentage
XRD	X-ray diffraction
Δt	Time (h)

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CHAPTER 1

INTRODUCTION

1.1 Introduction

In recent years, water pollution has become a serious issue that need to be discussed and attract attention from all over the world. Based on World Health Organization society, the worst situation that facing by most people in the world is the lack of access to get clean water. As the world population is going to be increased to 1.1 billion by year 2015, the contamination problem from all sources of clean water i.e. river water, rain water, sea, lake are with unwanted material such as bacteria, floating debris and dust is becoming a serious problem that need to be handled (Tebbutt *et al*., 1998). Thus, many researches have been conducted recently to treat the water medium via different approaches such as activated carbon, activated alumina, aeration, ion exchange, neutralizing filter and membrane. Based on extensive study that reported in source articles, membrane technology offer much easiest way.

Basically, a membrane is divided into several types of separation such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Ultrafiltration can be used to remove contaminants from the polluted water with the intense regulatory activity and scarce high quality source water. These stages of separation can be considered as a very promising process for drinking water production due to its pore sizes range that is between 2 - 100 nm. Ultrafiltration is able to remove viruses, bacteria, colloids, and larger particulate matter from suspensions (Dorgan, 1992). According to Haijun *et al.*, (2009) polysulfone (PSf) is a very popular polymer and widely used in the fabrication of ultrafiltration membrane due to its good mechanical, thermal and chemical stability. However, because of its hydrophobic nature, PSf membranes are susceptible to membrane fouling by the adsorption of proteins and other biomolecules from the feed stream (Yan, Xiang, and S. Xianda, 2006). This fouling mechanism causes the flux decline by concentration polarization where a membrane undergoes plugging or coating by some element in the stream being treated, in such a way its output or flux is reduced. In general, when fouling occurs in separation process it can affect the performance of membrane such as flux permeation, water permeability, surface porosity and morphological (Mansourizadeh and Ismail, 2010).

Most previous studies have shown that incorporation of additive into membrane formulation can play an important role in preventing the fouling problem which may cause improper morphology structure including its pore and skin layer (Vatanpour *et al*, 2011; Nghiem *et al.*, 2008). The incorporation of different material or additive have contribute to significant effect to membrane performance by reducing fouling and increasing rejection. The incorporation of additives in membrane formation is expected to add value to membrane properties to make porous, increase hydrophilicity, induced antibacterial properties and enhanced membrane performances (Saljoughi *et al*, 2010; B.Torrestinana-Sancheza *et al*., 1998; Basri *et al*., 2010). The incorporation of most inorganic fillers such as polymeric additive, silica, aluminum, zeolite, and titanium dioxide to dope solutions is able to produce membranes with higher porosity and hydrophilicity (Ma *et al*, 2011; Idris *et al*., 2011; Jian *et al*., 2012 and Arthanareeswaran *et al*., 2007).

The potential of organic fibers from natural sources (non-hazardous element) for example rice husk (which has high silica content) was being considered due to its biodegradable properties and green technology. In fact, some inorganic additives are able to suppress the formation of macrovoids, enhance pore formation and improve pore interconnectivity and hydrophilicity of the membranes. The inorganic additive also can increase membrane permeability and control membrane surface properties (Chakrabarty *et al*, 2008). As reported by Yan *et al*., the additive of aluminum oxide (inorganic) used as additive in membrane dope formulation has improved the antifouling properties (Yan *et al*., 2007). By improving membrane hydrophilicity it can reduce the membrane fouling to some extent.

The addition of additive in membrane formulation is expected to change the characteristic such as pore sizes, pore distribution, physical properties and mechanical characteristic. As reported in many papers, silica can suppress the formation of amphiphilic component and macrovoids, enhance the pore formation, improve pore interconnectivity and hydrophilicity for the membrane (He *et al*, 2002;

Qu *et al*., 2010; Hero *et al*., 2006; Huang *et al*., 2012 and Arthanareeswaran *et al*., 2007). The incorporation of potential organic fibres from natural sources (non-hazardous element) i.e. rice husk was considered as its contain high silica compound. Besides that it also has biodegradable properties and offers green technology. Hopefully, the incorporation of this additive will improve the antifouling mechanism of the membrane and membrane performance at the same time reduces the costs.

1.2 Problem Statement

Most applications in membrane separation process i.e. chemical, food, petroleum, mining etc. having a critical problem with fouling mechanism. Membrane fouling is characterized in general as a reduction of permeate flux through the membrane, as a result of increased flow resistance due to pore blocking, concentration polarization, cake formation and absorption. Membrane fouling gives a negative impact on filtration performance as it decreases the permeate flux or increases the transmembrane-pressure (TMP). The effect of this fouling mechanism on the decrease of flux depends on factor such as membrane pore size, solute loading and pore size distribution, membrane material and operating conditions. In addition, the efficiency of membrane separation process is highly dependent on fouling effect of natural organic matter (NOM) that present in surface water. Humic substance is a major component in NOM and generally categorized into humic acid (HA) (Combe *et al*., 1999). Al-Amoudi reported that pH and ionic strength affect the molecular size distribution of HA (Al-Amoudi, 2010). This NOM can change the molecule to be large, flexible and linear shape at high and low pH (Al-Amoudi, 2010). In addition, the high ionic strength and concentration in HA water also accelerate the fouling formation on membrane (Wang *et al*, 2001). Thus it is necessary to study the anti-fouling mechanism of membrane in membrane separation process. The good and potential additive which can enhance the antifouling performance will be determined. The addition of suitable additive is wisely needed in order to modify membrane structure and properties to overcome this fouling phenomena. The modification of suitable additive in membrane formulation will be carried out and the effect of membrane properties and structure will be investigated. Silica from rice husk is highly potential as additive that induced hydrophilicity properties can enhance the antifouling agent.

1.3 Research Objectives

The objective of this work were:

i. To prepare ultrafiltration composite membrane with silica from rice husk as an additive at different weight percentage.
ii. To study the effect of rice husk silica (RHS) as additive towards polysulfone (PSf) membrane characteristic and performance.
iii. To determine the fouling properties of prepared membrane.
iv. To optimize normalized flux of PSf/RHS membrane at three difference parameter filtration such as pH, ionic strength and transmembrane-pressure by using response surface modeling (RSM).

1.4 Research Scope

In order to achieve the above mentioned objectives, the following scopes of study were drawn.

i. Preparing the silica from rice husk at burning temperature 600 ºC as an additive and characterize in term of XRD pattern, particles content and size of particles.
i. Fabricating composite membrane by preparing dope solutions from PSf as polymer material, N-Methyl-2-pyrrolidone (NMP) as solvent, PEG 400 as pore forming agent and RHS as additive at different concentration (0 – 6 wt. %) via phase inversion technique.
ii. Characterizing the prepared membrane in terms of its cross section area, surface morphology, surface roughness, particles distribution, hydrophilicity, porosity, mean pore sizes and tensile strength.
iii. Measuring performance of prepared the membrane via pure water flux (PWF) and rejection of humic acid (HA) solution by using ultrafiltration permeation testing unit.
iv. Evaluating fouling performance filtration of HA by using the ultrafiltration permeation testing unit in term of membrane resistance, normalized flux, and flux recovery after membrane chemical and physical cleaning.

v. Optimizing of PSf/RHS membrane performance on final normalized flux at three difference operating condition (pH, Ionic strength and transmembrane-pressure by using Response Surface Methodology (RSM).

1.5 Research significance

Due to the nature of current polysulfone membranes that has hydrophobic properties and tends to absorb foulants at top and inside the pore structure, therefore the enhancement of membrane to increase antifouling properties is crucially needed. In this study, the use of silica that poseses strong hydrophilicity had proven can increase membrane structure and performance. In fact, the synthesization of silica from agro waste material which is rice husk not only can minimize the pollution but also introduce green materials to membrane technology. Furthermore, the use of RSM also provides the variable response in getting the optimized range of filtration operation which benefit to membrane technology

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter will discuss on previous related works on the membrane separation process. This section will explain the effect of fouling towards membrane performance. Further explanation on membrane modification and fabrication will also be highlighted.

2.2 Membrane Separation Process

Membrane separation can be defined as the filtration of two or more components from a fluid stream based on size difference (Munir, 2000). According to Mulder the definition of membrane is a selective barrier between two phases (Marcel Mulder, 1991). The term ‘selective’ being inherent to a membrane or a membrane process. Membrane separation describes the ability of a membrane to control the permeation rate of particles and molecules passing through the membrane. The membrane has the ability to transport one component more readily than the other because of differences in physical or chemical properties between the membrane and the permeating components. The movements of those components across the membrane need a driving force. Figure 2.1 shows the schematic diagram of membrane separation concept. The diagram demonstrated that phase 1 is that usually considered as feed or upstream side while phase 2 is considered as permeates or downstream side (Marcel Mulder, 1991). The solute bigger particle has tendency to foulant and blocked the inner pore, meanwhile the smaller particle will pass through the membrane which is called permeates. The concentration bigger particle of blocked by the membrane calculated to get rejection data.

Nowadays, membrane widely used in river water filtration, waste water treatment, desalination of sea water, purification of food, gas separation, pharmaceutical product and etc. Hence, membranes are developed individually in different industrial field in order to fulfill the current needs. In membrane fabrication, there are two factors that determine the performance of a membrane separation process; selectivity and productivity. Selectivity is expressed as a parameter called retention or separation factor. Productivity is expressed as a parameter called flux (Marcel Mulder, 1991). However, membrane fouling is one of constrain in membrane separation and give negative effect on membrane performance.

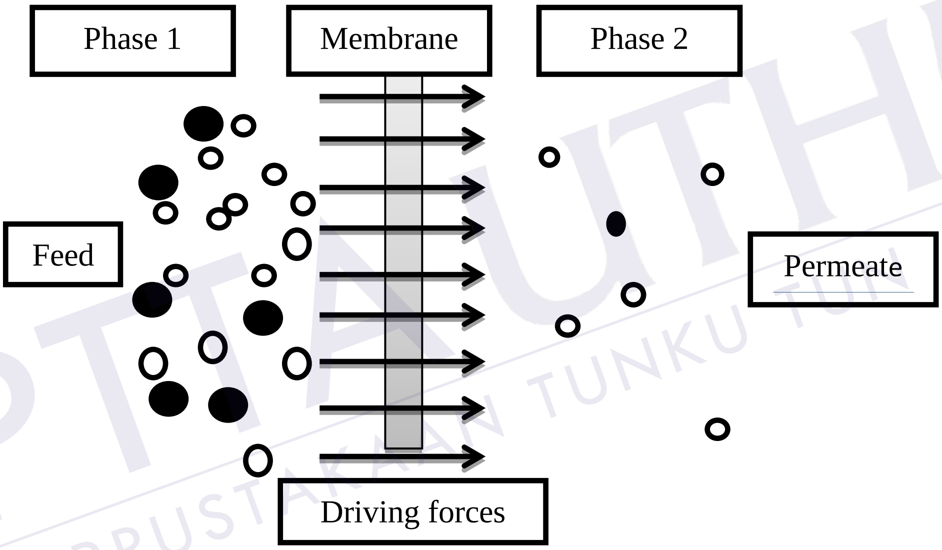

Figure 2.1: Two phase system separated by membranes (Mulder, 1991).

2.3 Membrane process

Membrane is the important element in every membrane separation process. It can be considered as a perm selective barrier of interface between two phases. Separation happens due to the ability of membrane to transfer one or more selected component of the feed mixture to permeate. Membrane filtration which is classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) is a pressure process. Table 2.1 discusses a different membrane process between ultrafiltration (UF), nanofiltration (NF) microfiltration (MF) and reverse osmosis (RO). The process difference depending on the component retained, trans-membrane pressure and process application.

In this study, ultrafiltration (UF) is typically used to separate macromolecules and colloids from a solution, e.g. water or micro-solutes. The average pore size of the membranes used is in the 2-100 nm range. In general, UF has been used in a wide field of applications such as food and dairy industry, pharmaceutical and biotechnology industry, textile industry, chemical industry and so on. UF is a pressure driven process, freely permeable to the solvent but impermeable to the concentrated solutes (Yanlei *et al*, 2008). The solvent molecules flow through the membrane pores and can be collected on the downstream side of the system.

In addition, UF processes are also used to remove low molecular weight materials from solutions, such as in the desalting of macromolecular solutions. UF membranes are also used to fractionate different sized molecular species, by virtue of the fact that these membranes have very well defined pore diameter distributions. UF membranes are available in a variety of configurations, the operating pressures of 2 to 9 bars are usual and its water fluxes vary widely, but can be as high as 5000 L/m^{2}h in some systems (Marcel Mulder, 1991 and Wang *et al*., 2006).

REFERENCES

Ahmad A. L, Majid M A., Ooi BS. Functionalized PSf/SiO2 nanocomposite membrane for oil-in-water emulsion separation. *Desalination*. 2011.268(1-3):266–269.

Al-Amoudi AS. Factors affecting natural organic matter (NOM) and scaling fouling in NF membranes: A review. *Desalination*. 2010. 259(1-3):1–10.

Armesto, L.; Bahillo, A.; Veijonen, K.; Cabanillas, A. and Otero, J. Combustion Behaviour of Rice Husk in a Bubbling Fluidised Bed. *Biomass and Bioenergy*. 2002. 23:171-179.

Arthanareeswaran, G., D. Mohan, and M. Raajenthiren. Preparation and performance of polysulfone-sulfonated poly(ether ether ketone) blend ultrafiltration membranes. *Part I. Applied Surface Science*, 2007. 253 (21). 8705-8712.

Arthanareeswaran G, Sriyamunadevi and T, Raajenthiren M. Effect of silica particles on cellulose acetate blend ultrafiltration membranes: Part I. *Separation and Purification Technology*. 2008. 64(1):38–47.

A. Jouyban, M. a a Fakhree, and A. Shayanfar, "Review of pharmaceutical applications of N-methyl-2-pyrrolidone. *J. Pharm. Pharm. Sci.*, 2010.13.524–35.

B.Torrestinana-Sancheza, RI. Ortiz-Basurtoa and E. Brito-De LA Fuente. Effect of non-solvents on properties of properties of spinning solution and polysulfone hollow ultra-filtration membrane. *Journal of membrane science* (1998).

Basri H, Ismail a. F, Aziz M, et al. Silver-filled polyethersulfone membranes for antibacterial applications - Effect of PVP and TAP addition on silver dispersion. *Desalination*. 2010.261(3):264–271.

Basri H, Ismail a. F, and Aziz M. Microstructure and anti-adhesion properties of PES/TAP/Ag hybrid ultrafiltration membrane. *Desalination*. 2012.287:71–77.

Basri H, A.F Ismail, and M. Aziz. Polyethersulfone (PES)-Silver Composite UF Membrane: The Effect of Silver Content and PVP of Different Molecular Weight on Membrane Morphology and Antibacterial Activity. *Desalination*. 2010. 273(1): 72-80

Bath C., M.C Goncalves, A.T.N. Pires, J. Roeder and B.A Wolf. Effects of thermodynamic conditions during formation on their performance. *Journal of membrane science*. 2000. 169. 287-299.

Chakrabarty, B., A.K. Ghoshal, and M.K. Purkait. Preparation characterization and performance studies of polysulfone membranes using PVP as an additive. *Journal of Membrane Science*. 2008. 315.36-47.

Childress AE, Elimelech M. Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *Journal Membrane. Science.* 1996. 119.253–268.

Combe, C., Molis, E., Lucas, P., Riley, R., & Clark, M.M. The effect of CA membrane properties on adsorptive fouling by humic acid. *Journal of membrane science* (1999)*154*, *73-87*.

Cui A, Liu Z, Xiao C, Zhang Y. Effect of micro-sized SiO2-particle on the performance of PVDF blend membranes via TIPS. *Journal. Membrane Science.* 2010. 360. 259–264.

Dorgan J. R. Polymer membranes for separations. In: David S. S., Polymer applications for biotechnology- Macromolecular separation and identification. New Jersey: Prentice Hall. 64-97. 1992.

Hamid N a. a., Ismail a. F, Matsuura T, et al. Morphological and separation performance study of polysulfone/titanium dioxide (PSF/TiO_2) ultrafiltration membranes for humic acid removal. *Desalination*. 2011.273. 85–92.

Haijun Yua,b, Yiming Caoa, Guodong Kanga, Jianhui Liua, Meng Li a, Quan Yuana Enhancing antifouling property of polysulfone ultrafiltration membrane by grafting zwitterionic copolymer via UV-initiated polymerization. *Journal of Membrane Science*. 2009. 342. 6–13.

Harun. Z, MR. Jamalludin., Yonus MZ. M.F Shuhor., A.F Ismail. The Effect of Amorphous Rice Husk Silica to the Polysulfone Membrane Separation Process Zawati Harun. *Advamce material research.* 2013.701. 319–322.

He, Z., Pinnau, I., and Morisato A. Nanostructured poly (4-methyl-2-pentyne)/silica hybrid membranes for gas separation. *Desalination*. 2002. 146.11-15

Heru S. and Mathias U. Insights into polysaccharide fouling of ultrafiltration membranes. *Desalination*. 2006. 181–182.

Hong J, and He Y. Effects of nano sized zinc oxide on the performance of PVDF microfiltration membranes. *Desalination*. 2012. 302.71–79.

Huang J, Zhang K, Wang K, et al. Fabrication of polyethersulfone-mesoporous silica nanocomposite ultrafiltration membranes with antifouling properties. *Journal Membrane. Science.* 2012. 362–370.

Idris, A., Mat Zain, N., and Noordin, M.Y. Synthesis characterization and performance of asymmetric polyethersulfone (PES) ultrafiltration membranes with polyethylene glycol of different molecular weights as additives *Desalination*. 2011. 207. 324-339.

J. Taurozzi, H. Arul, V. Bosak, A. Burban, T. Voice, M. Bruening, V. Tarabara, Effect of filler incorporation route on the properties of polysulfone–silver nanocomposite membranes of different porosities. *Journal of Membrane Science*. 2008. 325.58–68.

Jamshidi Gohari R, Halakoo E, Nazri N a. M, et al. Improving performance and antifouling capability of PES UF membranes via blending with highly hydrophilic hydrous manganese dioxide nanoparticles. *Desalination*. 2014.335. 87–95.

Jian Huang, Kaisong Zhang, Kung Wang, Zongli Xie, Bradley Ladewing, Huanting Wang. Fabrication of polyethersulfone-mesoporous silica nanocomposite ultrafiltration membranes with antifouling properties. *Journal of membrane science*. 2012. 423-424.362-370

Jomekian A, Pakizeh M, Shafiee AR, and Mansoori SAA. Fabrication or preparation and characterization of new modified MCM-41/PSf nanocomposite membrane coated by PDMS. *Separation and Purification Technology.* 2011. 80. 556–565.

Jones K.L and O'Melia CR. Ultrafiltration of protein and humic substances: effect of solution chemistry on fouling and flux decline. *Journal Membrane. Science.* 2001.193.163–173.

Jung, B., J.K. Yoon, B. Kim and H.W. Rhee. Effects of molecular weight of polymeric additives on formation, permeation properties and hypochlorite treatment of asymmetric polyacrylonitrile membranes. *Journal Membrane Science*. 2004. 243: 45-47.

Kapur, P. C. Production of Reactive Bio-Silica from the Combustion of Rice Husk in a Tube-in-Basket (TiB) Burner. *Powder Technology.* 1985. 44: 63-67.

Kesting R.E., Synthetic Polymeric Membranes, McGraw- Hill, New York (1971).

Khayet.C. Cojocaru, M. & Essalhi. Artificial neural network modeling and response surface methodology of desalination by reverse osmosis. *Journal of membrane science*. 2011.368, 202–214.

Kim Y. W, Ahn W S, Kim J J, Kim Y H. Fabrication of self-transformable and hydrophilic poly (ethylene glycol) - modified polysulfone membranes. *Biomaterials*. 2005.26.2867–2875.

Koros W.J and Pinnau I., Membrane formation for gas separation processes, in: D.R Paul, Y. Yampolskii (Eds.), *Polymeric Gas Separation Membranes*, CRC, Boca Raton, FL, 209-271.1994.

Koseoglu-Imer DY, Kose B, Altinbas M, Koyuncu I. The production of polysulfone (PS) membrane with silver nanoparticles (AgNP): Physical properties, filtration performances, and biofouling resistances of membranes. *Journal Membrane Science*. 2013.428.620–628.

Lau WJ, Ismail a. F. Application of response surface methodology in pes/speek blend NF membrane for dyeing solution treatment. *Membrane Water Treatment* 2010.1. 4960.

Leo CP, Cathie Lee WP, Ahmad a. L, Mohammad a. W. Polysulfone membranes blended with ZnO nanoparticles for reducing fouling by oleic acid. *Separation Purification Technology*. 2012. 89.51–56.

Liou, Tzong-Horng. Preparation and Characterization of Nano-Structured Silica from Rice Husk. *Materials Science and Engineering*. 2004. A364: 313-323.

Liu F, Ma B, Zhou D, Xiang Y, and Xue L. Microporous and Mesoporous Materials Breaking through tradeoff of Polysulfone ultrafiltration membranes by zeolite 4A.*Microporous and mesoporous materials*. 2014. 186.113–120.

Luo, M.-L., Zhao, J.-Q., Tang, W., and Pu, C.-S. Hydrophilic modification of poly (ether sulfone) ultrafiltration membrane surface by self-assembly of TiO_2 nanoparticles. *Applied Surface Science*. 2005. 249. 76-8.

Ma Y, Shi F, Ma J, et al. Effect of PEG additive on the morphology and performance of polysulfone ultrafiltration membranes. *Desalination*. 2011.272.51–58.

Ma Y, Shi F, Wang Z, et al. Preparation and characterization of PSf/clay nanocomposite membranes with PEG 400 as a pore forming additive. *Desalination*. 2012.286.131–137.

Mansourizadeh A. and A.F Ismail. Effect of additives on the structure and performance of polysulfone hollow fiber membranes for CO_2 absorption, *Journalof Membrane Science*.2010.348.260–267.

Marcel Mulder. Preparation of synthetic membrane. In: Basic Principles of Membrane Technology. Boston, London. Kluwer Academic Publisher. 54-108. 1991.

M. Lind, A. Ghosh, A. Jawor, X. Huang, W. Hou, Y. Yang, E.M.V. Hoek, Influence of zeolite crystal size on zeolite-polyamide thin film nanocomposite membranes. *Journal of Langmuir*. 2009. 10139–10145.

Mishra, P.; Chakraverty, A. and Banerjee, H.D. Production and Purification of Silicon by Calcium Reduction of Rice-Husk White Ash. *Journal. Material. Science*. 1985.20: 4387-4391.

Mollahosseini A, Rahimpour A, Jahamshahi M, Peyravi M, and Khavarpour M. The effect of silver nanoparticle size on performance and antibacteriality of polysulfone ultrafiltration membrane. *Desalination*. 2012.306:41–50.

Munir Cheryan. Membrane properties. In: Ultrafiltration and microfiltration handbook. London. RC press. 75-105.1998.

Ngang, H.P., A.L. Ahmad, S.C. Low, and B.S. Ooi. Preparation of Mixed-Matrix Membranes for Micellar Enhanced Ultrafiltration Based on Response Surface Methodology.*Desalination.* 2012. 7–20.

Nghiem, L.D. & Coleman, P.J. NF/RO filtration of the hydrophobic inorganic compound triclosan: transport mechanisms and the influence of membrane fouling. *Separation and Purification Technology*. 2008. 62 . 709 – 716.

Noordin M., Venkatesh V., Sharif S, Elting S, Abdullah a. Application of response surface methodology in describing the performance of coated carbide tools when turning AISI 1045 steel. *Journal Material Process. Technology.* 2004. 145.46–58.

P.J Shaw, H. De H. De Haan, R.I Jones. Applicability and realibility of gel filtration to styudy aquatic humic substances revisited: the effect of pH on molecular size distributuin. *Enviromental Technology.* 1994. 753-764.

Qu Y., Y. Tian, B. Zou, J. Zhang, Y. Zheng, L. Wang, Y. Li, C. Rong, and Z. Wang, A novel mesoporous lignin/silica hybrid from rice husk produced by a sol–gel method. *Bioresource Technology*. 2010. 101. 8402-8405.

Razali NF, Mohammad AW, Hilal N, Leo CP, and Alam J. Optimisation of polyethersulfone/polyaniline blended membranes using response surface methodology approach. *Desalination*. 2013.311.182–191.

Ruby Figueroa RA, Cassano A, Drioli E. Ultrafiltration of orange press liquor: Optimization for permeate flux and fouling index by response surface methodology. *Separation. Purification. Technology.* 2011. 80.1–10.

Saljoughi E., M. Amirilargani, and T. Mohammadi, Effect of PEG additive and coagulation bath temperature on the morphology, permeability and thermal/chemical stability of asymmetric CA membranes. *Desalination*, 2010. 262(1-3). 72-78.

Sentana I, De La Rubia M a., Rodríguez M, Sentana E, and Prats D. Removal of natural organic matter by cationic and anionic polyacrylonitrile membranes. The effect of pressure, ionic strength and pH. *Separation Purification Technology*. 2009.68. 305–311.

Shao J, Hou J, and Song H. Comparison of humic acid rejection and flux decline during filtration with negatively charged and uncharged ultrafiltration membranes. *Water Research.* 2011.45. 473–82.

Srisurichan S, Jiraratananon R, and Fane AG. Humic acid fouling in the membrane distillation process. *Desalination*. 2005. 174:63–72.

Suryani and Y.-L. Liu. Preparation and properties of nanocomposite membranes of polybenzimidazole/sulfonated silica nanoparticles for proton exchange membranes. *Journal of Membrane Science*. 2009. 332. 121-128.

Sotto A, Martı A, Teli SB, and Abajo J De. Influence of the type, size, and distribution of metal oxide particles on the properties of nanocomposite ultrafiltration membranes. Journal of membrane science. 2013. 428.131–141.

Tang C. Y., Kwon, Y. N., and Leckie, J. O. Fouling of reverse osmosis and Nan filtration membranes by humic acid-Effects of solution composition and hydrodynamic. *Journal Environment Health Science Engineering*. 2008, Vol. 5, . 11-18 18.

Tebbutt, T.H.Y., *Principles of water quality control*: ButterWorth-Heinemann page 107-118.1998.

Vatanpour V., S.S. Madaeni, R. Moradian, S. Zinadini, and B. Astinchap, Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite. *Journal of Membrane Science*. 2011. 375. 284-294.

Wang J, Wang X. Ultrafiltration with in-line coagulation for the removal of natural humic acid and membrane fouling mechanism. *Journal Environment Science.* 2006. 18-5

Wang, Y., Combe, C., & Clark, M.M. The effect of pH and calcium on the diffusion coefficient of humic acid. *Journal of membrane science.* 2001.183 (49-60).

Winfield B.A. A study of the factors affecting the rate of fouling of reverse osmosis membranes treating secondary sewage effluents. *Water Research*. 1979.13(7), 565-569.

Wu H, Mansouri J, and Chen V. Silica nanoparticles as carriers of antifouling ligands for PVDF ultrafiltration membranes. *Journal Membrane Science.* 2013.433.135-151.

Wu H, Tang B, and Wu P. Development of novel SiO_2–GO nanohybrid/polysulfone membrane with enhanced performance. *Journal Membrane. Science.* 2014. 451.94–102.

Xie M, Nghiem LD, Price WE, and Elimelech M. Impact of humic acid fouling on membrane performance and transport of pharmaceutically active compounds in forward osmosis. *Water Research.* 2013.47.4567–75.

Yan L., Y. Li, C. Xiang, and S. Xianda. Effect of nano-sized Al_2O_3-particle addition on PVDF ultrafiltration membrane performance. *Journal of Membrane Science*. 2006. 276.162-167.

Yanlei Su, chao Li, Wei Zhao, Qiang Shi, Haijing Wang, Zhongyi Jiang, *Shiping Zhu.* Modification of polyethersulfone ultrafiltration membranes with phosphorylcholine copolymer can remarkably improve the antifouling and permeation properties. *Journal of Membrane Science. 2008. 322*.1771-177.

Yuliwati E. and A.F Ismail. Effect of additives concentration on the surface properties and performance of PVDF ultrafiltration membranes for refinery produced wastewater treatment. *Desalination*. 2011. 273.226–234.

Yuliwati E, Ismail a. F, and Lau WJ, et al. Effects of process conditions in submerged ultrafiltration for refinery wastewater treatment: Optimization of operating process by response surface methodology. *Desalination*. 2012. 287.350–361.

Yuliwati E, Ismail a. F, Matsuura T, Kassim M a., Abdullah MS. Characterization of surface-modified porous PVDF hollow fibers for refinery wastewater treatment using microscopic observation. *Desalination*. 2011. 283.206–213.

Yu L-Y, Xu Z-L, Shen H-M, and Yang H. Preparation and characterization of PVDF–SiO_2 composite hollow fiber UF membrane by sol–gel method. *Journal Membrane Science.* 2009. 337.257–265.

Yunos MZ, Wang D, Basri H, and Ismail AF. Effects of Water as Non-Solvent Additive on Performance of Polysulfone Ultrafiltration Membrane. *Advance. Material Research.* 2012.488-489:46–50.

Yunos M. Z, Harun Z, Basri H, and Ismail AF. Studies on fouling by natural organic matter (NOM) on polysulfone membranes: Effect of polyethylene glycol (PEG). *Desalination*. 2014. 333.36–44.

Zhao, C., Nie, S., Tang, M., and Sun, S., Polymeric pH-sensitive membranes. A review. Progress in Polymer Science, 2011. 36.1499-1520

Zhang Z-H, An Q-F, Liu T, et al. Fabrication and characterization of novel SiO_2-PAMPS/PSF hybrid ultrafiltration membrane with high water flux. *Desalination*. 2012.297.59–71.

Zularisam A. W, Ismail a. F, Salim MR, Sakinah M, Matsuura T. Application of coagulation–ultrafiltration hybrid process for drinking water treatment: Optimization of operating conditions using experimental design. *Separation. Purification Technology*. 2009.65.193–210.

Zuo D, Xu Y, Xu W and Zou H. The influence of peg molecular weight on morphologies and properties of PVDF asymmetric membrane. *Journal of polymer science*. 2008.26.405–414.