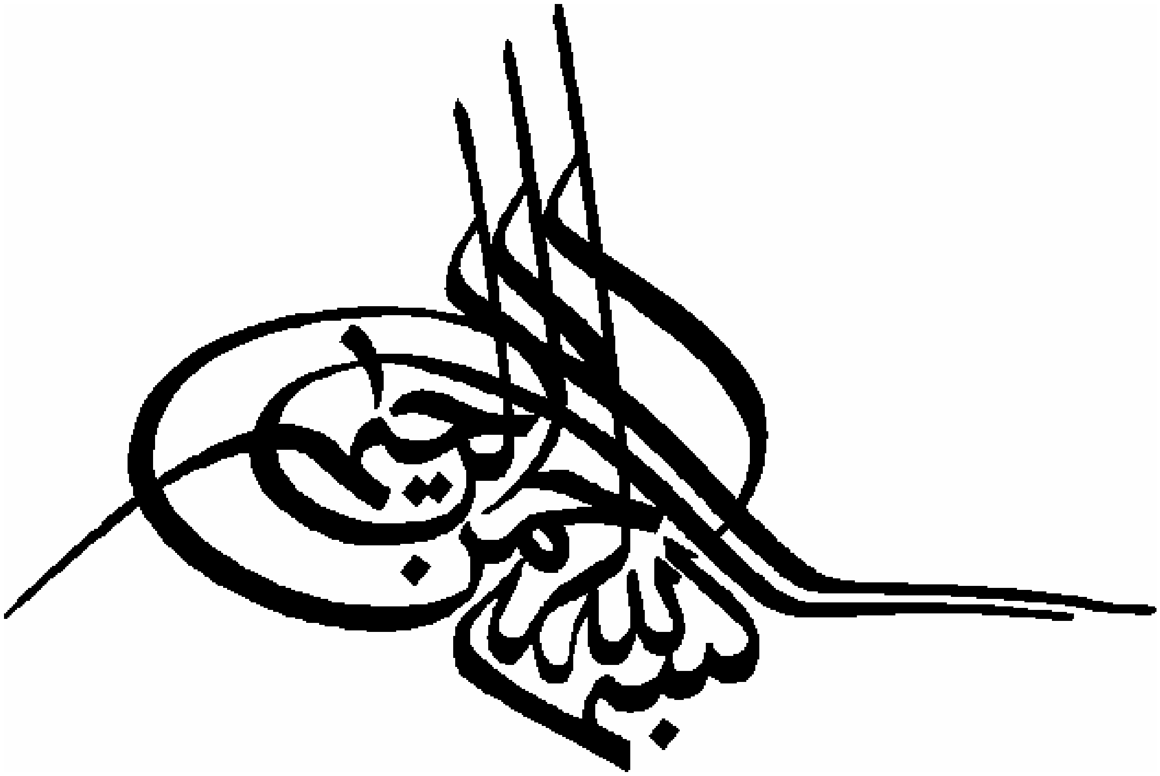

الهی!
بنده را از سه آفت نگاهدار:
از وساوس شیطانی،
از هوای نفسانی،
از غرور نادانی

Razi University

Faculty of Science

Department of Chemistry

PhD Thesis

Title of the Thesis:

Preparation of Polymeric Nanofilter Membranes for Water Treatment

Supervisor:
Prof. Sayed Siavosh Madaeni

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September 2009

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September 2009

To my wife,

a major driving force

Acknowledgment

I would especially like to thank Prof. Madaeni for his valuable guidance, utmost help, encouragement and advice through out the research. I want to sincerely thank my committee members, Dr. Rahimi, Dr. Joshagani, Prof. Giasvand and Dr. Yari for spending time and effort to review this thesis. I gratefully acknowledge my colleague and classmate Dr. Rahimpour, Amirinejad, Kocheki, Zereshki and Daneshvar for helpful suggestions and advice in conducting experiments, especially in our meetings. I express my profound gratitude to my wife for her strong encouragement and inspiration given to me.

Finally, I would like to acknowledge New Technologies Centre - Ministry of Industry of Iran for financial support.

Abstract

In the first work, the effect of microwave irradiation on morphology and performance of polyethersulfone (PES) membranes was investigated. The membranes were prepared with 20 wt.% of PES by phase inversion method. N,N- dimethylformamide (DMF) and a mixture of water and ethyl alcohol (90/10 vol%) were employed as solvent and coagulant, respectively. The effects of irradiation time (10, 30, 60, 90, 120 s) and microwave power (180, 360, 720 and 900 W) on structure and performance of membranes were studied. Increasing the irradiation time and power caused variation in permeate flux and ion rejection. Moreover, the effects of annealing processes (60, 70, 80 ^{o}C) were studied. The membrane exhibited moderate rejection (47%) and low permeate flux (4.5 kg/m^2.h) at 80 ^{o}C for NaCl solution. The SEM images indicate that the dense skin layer is formed at 80 ^{o}C annealing.

In the other work, blends of polyethersulfone/polyimide (PES/PI) were prepared by dissolving in dimethylformamide/dioxane (DMF/DO) to manufacture nanofiltration membranes by using polyvinylpirrolidone (PVP) as a pore former. The membrane modification was carried out by adding ethylenediamine (EDA) to open the imide group ring of PI and by using polyethyleneglycol (PEG)-triazine, as a new modifier material, that was produced in the laboratory. After functionalizing the membranes, diethanolamine (DEA) was utilized as a hydrophilic modifier to change the membranes properties. The hydrophilicity of PES/PI membranes was improved by modification. By introducing PEG-triazine into the membrane recipe, salt rejection increased from 75 to 80%. Addition of DEA further enhances the salt rejection up to 93%.

Titanium dioxide (TiO_2) nanoparticles were assembled on the surface of nanofiltration blend membrane in the third work. To settle TiO_2 on the membrane surface, two membrane

categories were used: i) unmodified polyethersulfone (PES)/polyimide (PI) blend membrane, and ii) –OH functionalized PES/PI blend membrane with different concentrations of diethanolamine (DEA). These membranes were radiated by UV light (160 Waat) after TiO_2 depositing with different concentrations. The modification resulted in the formation of a photo-catalytic property with enhanced membrane hydrophilicity. A comparison between the UV irradiated TiO_2 deposited blend membrane and deposited-functionalized blend membranes showed that –OH groups originate excellent adhesion of TiO_2 nanoparticles on the membrane surface, increase reversible deposition, and diminish irreversible fouling. SEM images show that the presence of -OH groups on the DEA-modified membrane surface is the main parameter for extra uniformly settlement of TiO_2 nanoparticles on the membrane surface.

In the fourth work, the effect of microwave irradiation on preparation of composite nanofiltration membranes was investigated. Interfacial polymerization technique was employed by applying trimesoyl chloride (TMC) and piperazine (PIP) as the reagents for preparation of polyamide (PA) skin layer on a polyethersulfone (PES) support. The different times (0, 10, 30 and 60 s) and powers (540, 720 and 900 Watt) of microwave irradiation were applied. The results showed that under an operational pressure of 1.0 MPa, and 540 W for 0, 10, 30 and 60s irradiation, fluxes of 13, 8, 8, and 10 kg/m^2 h and 46, 63, 57, and 51% retention for NaCl and 82, 88, 87, and 88% rejection of Na_2SO_4 were obtained. Increasing the irradiation power resulted in a slight decline in the rejection.

Finally, the effects of addition of cationic (CTAB), non-ionic (Triton X-100) and anionic (SDS) surfactants in organic phase for preparing the composite nanofiltration membranes were investigated. The interfacial polymerization technique was employed by applying trimesoyl chloride (TMC) and piperazine (PIP) as the reagents for preparation of polyamide (PA) on a UF support. The prepared membranes containing SDS showed higher flux compared to the other membranes. SEM surface images demonstrate some defects and cracks on the thin layer surface of the membrane prepared with SDS. For the membrane containing CTAB, the salt rejection was increased in the order of Na_2SO_4 >NaCl >$MgCl_2$ with variation around 50 to 90%.

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Chapter 1

Membrane processes and nanofiltration (NF)

1.1. Introduction

Starting in the late sixties of 20 century, membrane processes gradually have found their way into industrial applications and serve as viable alternatives for more traditional processes like distillation, evaporation or extraction.

A membrane process requires two bulk phases physically separated by a third phase, the membrane. The membrane is an interphase between the two bulk phases. It is either a homogeneous phase or a heterogeneous collection of phase. The membrane phase may be any one or a combination of nonporous solid, microporous or macroporous solid with a fluid (liquid or gas) in the pores, a liquid phase with or without a second phase, or a gel. The membrane phase is almost thin when compared with the dimensions of the bulk phases. The membrane phase interposed between two bulk phases controls the exchange of mass between these phases. In membrane separation processes, the bulk phases are mixtures. One of the species in the mixture is allowed to be exchanged in preference to others. The membrane is selective to one of the species. One bulk phase is enriched in one of the species while the other is depleted of it. A membrane process then allows selective and controlled transfer of one species from one bulk phase to another bulk phase separated by the membrane [1].

1.2. Advantages of membrane technology

Membrane separation technology has many advantage compare to common processes and classic separation, some of them are mentioned here:

1. Consumption of energy is relatively low because phase change doesn't occur.
2. Membrane modules are flexible and have low volumes.
3. Because of low thickness of membrane (about 100 μm), mass transfer through it is high.
4. Pressure decrease and energy lost in this unit is negligible.
5. In this method the separation process is carried out at room temperature so can be used for separation of temperature sensitive material in food and pharmacutical industry and biotechnology.
6. Some of separations by membrane can not be done by other separation methods.
7. In this method the need for second chemical materials such as solvent, additive and etc., is very low.
8. Separation of very dilute solutions by membrane has higher efficiency.
9. There is no need to complex design for membrane application in separation process.
10. In many cases membrane process can be incorporated with other process to obtain high separation efficiency.
11. Membrane processes are cost effective compare to other processes based on the international figures.

1.3. Classification of membrane processes based on driving forces

One or more driving forces cause the movement of any species across the membrane. These driving forces arise from a gradient of chemical or electrical potentials. A gradient in chemical potential may be due to a concentration gradient, pressure gradient or both. The transmembrane flux of any species per unit driving force is proportional to the permeability of the species.

Based on the main driving force, which is applied to accomplish the separation, many membrane processes can be distinguished. An overview of the driving forces and the related membrane separation processes is given in Table (1-1).

Table (1-1). Classification of membrane processes based on driving forces [1]

Process	Driving Force	Materials Passed	Materials Retained
Microfiltration (MF)	ΔP	Solvent, dissolved solutes	Suspended solids, fine particulates
Ulterafiltration (UF)	ΔP	Solvent, low moleculare weight solutes	Macrosolutes, Colloids
Nanofiltration (NF)	ΔP	Solvent, Monovalence ions	Macrosolutes, Multivalence ions
Reverse Osmosis (RO)	ΔP	Solvent (water)	All dissolved & suspended solids
Gas Permeation (GP)	ΔP	Gases, vapours	Less permeable gases & vapours
Dialysis	ΔC	Solute, ion & low molecular weight organics	Dissolved & suspended solids with molecular weight > 1000
Liquid Membrane (LM)	ΔC	Cations / anions or low molecular weight organics or gases	Anions / cations or less permeable organic or gases
Gas Diffusion (GD)	ΔC	Gases, vapours	Less permeable gases & vapoure
Electrodialysis (ED)	ΔE	Solute, ions	Non-ionic & macro-molecular species
Membrane Distillation	ΔT	Volatile	Non volatile

1.4. Applications of separation processes by membrane

Membrane separation technology has considerable application in industry. Main applications of this technology are listed in Table (1-2).

Table (1-2). Some major applications of membrane technology [1]

Membrane process	Applications
Dialysis (D)	Hemodialysis (artificial kidney)
Electrodialysis (ED)	Water desalination Acidity reduction in citrus juices Deionisation of whey
Reverse osmosis (RO)	Water desalination Dairy industry
Nanofiltration (NF)	Water desalination Chemical industry Effluents
Ulterafilteration (UF)	Dairy (whey recovery, precheese Concentration) Electrocoat colloids Effluents (oil-water, pulp and paper, Dye-stuffs, tannery) Biological (enzyms, fermantations) Water purification
Microfilteration-Cross Flow Filteration (MF-CFF)	Sterile solution / water purification Beverage filteration Effluents Cell Harvesting
Liquid membrane (LM)	Hydrometallurgy Effluents Gas separations
Gas Permiation (GP)	Helium recovery Hydrogen recovery /removal CO_2 from hydrocarbons
Gas Diffusion (GD)	Uranium enrichment
Pervapioration (PV)	Ethanol / water separation
Membrane Distillation (MD)	Pure water

1.5. The ideal membrane characteristics

An ideal membrane should be resistant to chemical and microbial attack and the separation and mechanical characteristics should not change after long-term operation.

An ideal membrane has the following characteristics:

- High water flux
- High salt rejection
- Tolerant to chlorine and other oxidants
- Resistant to biological attack
- Resistant to fouling by colloidal and suspended material
- Inexpensive
- Mechanically strong, e.g., tolerates high pressures
- Chemically stable
- Able to withstand high temperatures

1.6. Types of membranes for water treatment

In the beginning, membrane processes for drinking water production were only applied in the US and the middle East. Nowadays the applications are rapidly expanding all over the world. World-wide, more than 9×10^6 m^3 of water is processed per day by reverse osmosis (RO) and 10^6 m^3 by NF and UF [2].

Water treatment processes employ several types of membranes. They include microfiltration (MF), ultrafiltration (UF), reverse osmosis, and nanofiltration membranes.