BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS

Faculty of Chemical Technology and Biotechnology

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Development and examination of high-performance membranes for pervaporative alcohol dehydration and water desalination

Theses summary

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Budapest, Hungary, 2020

1. Introduction

Pervaporation (PV), a non-porous membrane separation process, is gaining considerable attention for solvent separation in a variety of industries ranging from chemical to water, food, pharmaceutical and petrochemicals. Dehydration of organic liquids is one of its most successful applications. Most recently, pervaporation has been also used as an alternative technique for water desalination. For both applications, hydrophilic membranes are used. Hence, in both processes, the membrane will be in direct contact with water, the high affinity of the hydrophilic membrane towards water affects the membrane swelling and mechanical properties and therefore the separation performance. To control swelling and improve the mechanical properties, often hydrophilic membranes are modified by cross-linking, physical blending with other polymers or combine with inorganic particles in the same membrane, these membranes are often called hybrid membrane or mixed matrix membrane. Hydrophilic polymers are the most used for both application due to their high hydrophilicity, easy to fabrication, organic pollution resistance, and chemical and thermal stability. However, the high crystallinity of the these polymers results in instability and low mechanical strength of the membranes in water because of the swelling phenomena and as a result the water selectivity of the membrane is decreasing and accordingly the pervaporation performance.

2. Literature review and motivation

In recent years, clean and green energy has received wide attention. Bio-fuel is considered one of the promising sources of renewable energy. Bio-ethanol is considered to have huge potential as a green renewable energy source owing to its environmental benefits and its high efficiency. Ethanol was originally dehydrated by distillation separation process at a concentration lower than the azeotrope (95.4 wt. % ethanol). However, high costs, low productivity, and extensive energy consumption resulted in that distillation became unsuitable for commercial and practical production of highly concentrated bioethanol especially for biofuel, ethanol has to be more concentrated than the azeotrope. Therefore, sustainable, efficient and economic production of bioethanol has turned to be the challenge. Membrane separation has been used as a convenient, economical, practical and green alternative of the bioethanol purification field. Among membrane separation processes; pervaporation technology (PV) has received much attention especially in the case of azeotropic mixtures[1,2,3]. Pervaporation is an essential alternative separation process due to the advantages attributed to its simple operation condition, low energy consumption, low cost, eco-friendly and higher separation efficiency. Comparing to the conventional distillation, 50% of energy could be saved using pervaporation with relatively higher separation efficiency[4,5,6].

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On the other hand, Freshwater scarcity has materialized a serious threat to human livings and social developments. Due to the spectacular increase in the population and water pollution, it is necessary to find engineering solutions to provide fresh water in many water-limited areas[7,8]. One of the most effective methods to produce freshwater from saltwater such as brackish water and seawater is desalination technology[9]. Nowadays, membrane technology is considered as an attractive desalination way, counting on of their high efficiency, potential energy savings, high operational stability, low chemical costs, ease of integration and scale-up compared with traditional distillation techniques[10,11].

PV is a promising membrane process that has been reported as a prospective process for treating high salinity water and brine treatment due to its potential in energy efficiency and feasibility in handling high salinity water[12,13,14]. Poly (vinyl alcohol), PVA is the most used polymer for both applications. However, during pervaporation process, excessive affinity of water towards hydrophilic membranes leads to undesirable swelling (water absorption) of the membrane matrix.

The main objectives of this work is to fabricate different modified PVA membranes has been fabricated to control swelling and enhance the pervaporation performance for both applications (alcohols dehydration and water desalination).

3. Approach and applied methodology

Two major modification has been applied (1) Crosslinking by physical crosslinking (heat treatment) and Chemical crosslinking (Glutaraldehyde) (2) Hybridization (combine with inorganic particles either chemical generation of the inorganic nanoparticles in the PVA matrix producing nanocomposite membranes or physical blending of synthesized nanofiller producing mixed matrix membranes).

In the case of crosslinking this was approached by developing a double-network PVA membrane using the sequential method and study the effect of interpenetrating a second network of the same polymer by thermal crosslinking on the chemical structure, crystallinity, thermal stability and hydrophilicity of the polymeric membrane. Consequently, investigate the effect of the second network on the pervaporation performance of dehydrating aqueous ethanol solution at different conditions.

In the case of chemical generation of the inorganic nanoparticles, silver nanoparticles were in-situ generated in the PVA matrix using thermal reduction without any additional reducing agent and the effect of silver nanoparticles on the thermal, chemical, and physical stability of the PVA membrane studied. In addition to, evaluating the pervaporation dehydration performance of ethanol/water mixture using the fabricated

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nanocomposite membrane on an experimental basis, at different silver content, ethanol concentration in the feed and operating temperature.

The fabrication of mixed matrix membranes by the physical blending of synthesized nanofiller was aiming to two types of membranes (1) chemically crosslinked mixed matrix membranes and (2) uncross-linked mixed matrix membranes. The chemical method was used to develop novel pervaporation membranes for water desalination consisting of laponite XLG/PVA and demonstrate the effect of the nanoclay dispersion on PVA chemical, thermal, mechanical and hydrophilicity. The pervaporation desalination performance was demonstrated when desalinating high-salinity water with different clay content at range of temperatures and detection of the salt transport properties (permeability, diffusivity, solubility) in the membrane. While on the other hand, the uncross-linked approach was for evaluating dehydration performance of C1-C3 alcohols solution via pervaporation using uncross-linked laponite XLG/PVA mixed matrix membrane with different clay concentration in the casting solution and a range of temperature and detecting the membrane intrinsic properties (permeability, selectivity).

All the experiments were carried out with a multi-purpose P-28 membrane unit provided by CM-Celfa Membrantechnik AG with a membrane area of 28 cm2.

4. Results

a. Thermal crosslinked double network (DN-PVAs)

The thermal crosslinking DN-PVAs showed that the two PVA matrices are compatible with no phase separation. The analysis shows that hydrophilicity of the membrane decreases because of the collaboration of the second thermal crosslinked PVA matrix. Contact angles measurements support the increasing trend of hydrophobicity for the obtained membranes. The reduction in the swelling degree of the DN-PVAs confirms the increase in the crystallinity character of the PVA membranes. The pervaporation dehydration of the water-ethanol mixture was investigated at three different feed compositions and temperatures. The separation selectivity showed significant improvement while the permeation flux declines due to the incorporation of the second PVA network compared to the PVA membrane under 85% & 95% ethanol and at 40 °C. Additionally, increasing the feed temperature enhances the permeability of the membrane, while decreasing the water content in the feed results in increasing the selectivity. Arrhenius equation has been used to investigate the influence of operating temperature on the pervaporation performance. Concluding that, the collaboration of the second thermal crosslinked PVA matrix led to approximately doubling the selectivity of the membrane while slightly declined the permeation flux and at a higher temperature and higher ethanol concentration in the feed, the prepared membranes are highly selective towards the water with reasonable fluxes values.

b. Nanocomposite membranes with silver NPs

With in-situ generation of silver nanoparticles in a crosslinked PVA matrix at five different concentrations, the silver nanoparticles prove to act as a hydrophilic filler agent facilitating the ethanol dehydration pervaporation process. The permeation fluxes show a simultaneous increase with the higher silver nanoparticle loading level. While the separation selectivity slightly decreased. Below 90 wt% ethanol and at 40 °C the measured flux and separation factor values of M2.5 are 12.67 $*10^{-2}$ $Kg/m^2.h$ and 43.6, respectively, showing better performance than those of the pristine PVA. On the other hand, the higher water content in the feed solution results in higher fluxes than other membrane types; nevertheless, the separation factor values show stable values at higher AgPNs concentration. Operating temperature shows a significant effect on the permeation flux and membrane selectivity, hence it directly proportional to the flux and inversely proportional to the selectivity. The significantly lower activation energy values obtained for water permeation as compared to ethanol prove that the membranes developed in this work demonstrate excellent separation efficiency towards the water. Based on my work it can be concluded as well that at a higher temperature and higher ethanol concentration in the feed that the prepared membranes show improved selectivity values towards the water.

c. Mixed Matrix Membranes with laponite nanoclay

i. Water desalination via pervaporation (crosslinked)

Laponite XLG nanoclay was dispersed in water and exfoliated in PVA matrix to produce dense MMMs with different clay concentrations for desalination by pervaporation. The MMMs surface hydrophilicity is increased by increasing the laponite content. The mechanical properties of the membrane were outstandingly enhanced by reaching 65.7 MPa and 3.3 GPa for the yield stress and young's modulus, respectively. In the beginning, the MMMs water flux increased followed by a decrease with a maximum value at 2 wt% laponite content. The salt rejection of the pristine PVA membranes preserved over 99.5% while the incorporation of the laponite clay led to improving the salt rejection to over 99.9%. The 2 wt.% laponite content PV membrane had fluxes of 58.6 $kg/m^2.h$ and 39.9 $Kg/m^2.h$ when desalinating 3 wt% and 10 wt% aqueous NaCl solution at 70 °C, respectively. However, the salt rejection still remained over 99.9% irrespective of the feed concentrations and temperatures. Additionally, for RO waste desalination, increasing the operating temperature from 30°C to 70 °C led to remarkably increase in the water flux by approximately 30 %, while the salt rejection remained > 99.9 %. It can be concluded that PVA-Lap MMMs is a promising and competitive candidate as far as pervaporation desalination is concerned either for high-salinity water or for RO waste desalination.

ii. Alcohol dehydration (uncross-linked membranes)

MMMs were produced and tested for the separation of alcohol-water mixtures via pervaporation. The pervaporation dehydration performance of the developed MMMs shows a promising prospective for C1-C3 alcohol dehydration. The low concentration of laponite nanoclay at 1 mg/ml up to 2.5 mg/ml can disperse uniformly in the PVA matrix without any voids or crack and agglomeration. Increasing the laponite concentration in the starting solution to 3.5 mg/ml results in agglomeration of the nanoclay and forming a separated layer for 5 mg/ml. This layer acts as a second selective layer. Furthermore, the hydrophilic nanodiscs provided higher water affinity to the PVA membrane and lower the alcohol affinity, subsequently increased the selectivity of the membranes. The fractional free volume initially followed the same trend as the water uptake, clearly initially increased due to the well-dispersed nanofiller with high surface area and then decrease due to agglomeration and the separated layer formation. The MMMs with all concentrations exhibit higher pervaporation performance for the dehydration of C1-C3 alcohols compared to the thermally crosslinked PVA membranes. PVA-5 discloses the highest separation factor for alcohol separation with an order of isopropanol > ethanol > methanol/water, while the higher fluxes achieved by PVA-3.5 complied with the reverse order.

5. Theses

Thesis 1 [I, VIII, XIII]

I developed and produced a new double-network poly (vinyl alcohol) membrane on the basis of the sequential method and I proved to what extent the interpenetrating of a second network of the same polymer by thermal crosslinking affects the chemical structure, crystallinity, thermal stability and hydrophilicity of this polymeric membrane. This membrane has higher thermal stability compared to the common PVA membranes. The swelling degree of the developed membrane has decreased by approx. 30 % using 85% aqueous ethanol solution. Additionally, I determined the effect of the second network of my double-network PVA (DN-PVAs) membrane on the pervaporation performance of dehydrating aqueous ethanol solution. On the basis of my measurements I proved that 85% ethanol solution could be dehydrated with 82% higher separation factor than that of the common PVA membrane using DN-PVAs membrane of my development at 40 °C by pervaporation.

Thesis 2 [IX,X]

I successfully in-situ generated silver nanoparticles in PVA matrix using thermal reduction in a novel way without any additional reducing agent that is a novel solution. I studied the effect of in-situ generation of silver nanoparticles on the thermal, chemical, and physical properties of PVA membrane. I proved with measurements that the incorporation of silver nanoparticles could improve the stability of the PVA polymeric membranes in both water and aqueous solutions.

Thesis 3 [II,III,XI]

I proved the successful and highly efficient pervaporative dehydration of the ethanol/water mixture using my novel Ag/PVA nanocomposite membrane on an experimental basis at different operating temperature and with different feed water concentrations. I also proved that my membranes can be more successfully assigned to separate water from ethanol even at the azeotropic point than common PVA membranes. I derived on the basis of dehydration experiments of the binary ethanol/water mixtures and on the basis of the estimated Arrhenius activation energy that in the case of my novel membranes (Ag/PVA) the heat of sorption (ΔH_s) values were all negative indicating that the sorption process was controlled by Langmuir's mode.

Thesis 4 [IV, V, VII, XII, XIV]

I developed a novel crosslinked laponite XLG/PVA pervaporation membrane for water desalination and I demonstrated the improving effect of the nanoclay dispersion on PVA chemical, thermal and mechanical stabilities and hydrophilicity. I proved with measurements that this novel crosslinked Laponite/PVA membrane could produce pure water from high-saline water with rejection of 99.9 % at 40°C. Additionally, I demonstrated experimentally that the improved desalination performance of the crosslinked Laponite/PVA membranes could be used to treat the reverse osmosis process high salinity waste with approximately 100 % rejection using membrane containing 7 wt% laponite. Consequently, I detected that the salt permeability in the membrane was lower by two orders of magnitude than that of water indicating that water improved preferential permeation through this novel membrane.

Thesis 5 [VI]

I determined that the addition of laponite nanoclay improved the dehydration performance of the uncross-linked PVA membranes. I proved with measurements that PVA-5 which contains the highest laponite concentration (5 mg/ml) discloses the highest separation factor for alcohol-water separation for isopropanol > ethanol > methanol/water in this order, while the higher fluxes obtained by PVA-3.5 complied with reverse order. I determined that my membranes with the highest laponite concentration achieved the highest water permeability for all the three alcohol solutions compared to the up to date literature data.

6. Application

Bio-ethanol is considered to have huge potential as a green renewable energy source owing to its environmental benefits and its high efficiency and widely investigated in research laboratories and increasingly applied in the industry. The aqueous products of the producing procedures are usually dilute, often forming several azeotropes. Pervaporation is a promising alternative to some conventional techniques, especially for dehydration of azeotrope mixtures. It offers highly selective separation with a significantly lower energy demand than the conventional methods. The fabricated membranes (DN-PVAs, Ag-PVA and uncross-linked PVA-Laponite MMMs) in the present work prove and demonstrate excellent separation efficiency towards the water. Consequently, they provide higher purity of the produced bio-ethanol.

On the other hand, with a deep look to the fresh water scarcity which has materialized a serious threat to human livings and social developments. Due to the spectacular increase in the population and water pollution. Our novel produced chemically crosslinked PVA/laponite nanocaly mixed matrix membranes offering a promising solutions to provide fresh water in many water-limited areas from different high-salinity sources. With these membranes, literally fresh clean water can be produced from any water source and with almost 100% rejection and zero waste.

7. Publication

a. Related to thesis

I. **Selim, A**.; Valentínyi, N.; Mizsey, P., Influence of double-network interpenetration on ethanol dehydration performance of PVA-based pervaporation membranes. Chemical Papers 2019, 73 (5), 1069 (IF_{2018}=1.246, Q3,I=1)

II. **Selim, A**.; Valentínyi, N.; Nagy, T.; Toth, A. J.; Fozer, D.; Haaz, E.; Mizsey, P., Effect of silver-nanoparticles generated in poly (vinyl alcohol) membranes on ethanol dehydration via pervaporation. Chin. J. Chem. Eng. 2018, 27 (7), 1595-1607. (IF_{2018}=1.911, Q2)

III. **Selim, A**.; Toth, A. J.; Fozer, D.; Haaz, E.; Mizsey, P., Pervaporation performance of Ag-PVA nanocomposite membranes: Effect of operating temperature ,Periodica Polytechnica Chemical Engineering. 2019. (IF_{2018}=1.382, Q3)

IV. **Selim, A**.; Toth, A. J.; Fozer, D.; Haaz, E.; Szanyi, A.; Hegyesid, N.; Mizsey, P., Preparation and characterization of PVA/GA/Laponite membranes to enhance pervaporation desalination performance , *Separation and purification Technology*. 2019. (IF_{2018}=5.107, D1, I=4)

V. **Selim, A**.; Toth, A. J.; Fozer, D.; Haaz, E.; Nagy, T.; Mizsey, P., Laponite/PVA pervaporation membrane for desalinating simulated RO high-salinity by-product, *Desalination and Water Treatment Journal*. 2019. (IF_{2018}=1.234, Q2)

VI. **Selim, A**.; Haaz, E.; Toth, A. J.; Fozer, D.; Süvegh, K.; Szanyi, A.; Mizsey, P., High pervaporative dehydration performance of C1-C3 alcohols employing Laponite-PVA mixed matrix membranes, (under major revision *Journal of Membrane* Science)

VII. **Selim, A**.; Toth, A. J.; Fozer, D.; Haaz, E.; Mizsey, P., Pervaporative desalination of concentrated brine solution employing crosslinked PVA/Silicate nanoclay Membranes, *Chemical Engineering Research and Design 2020* . (IF_{2018}=3.073, Q1)

VIII. **Selim, A**.; Toth, A. J.; Fozer, D.; Haaz, E.; Mizsey, P., Comparison of single and double-network PVA pervaporation performance: Effect of operating temperature, *Periodica Polytechnica Chemical Engineering2020.* (IF_{2018}=1.382, Q3)

b. Oral presentation

IX. **Selim, A**.; Toth, A. J.; Fozer, D.; Haaz, E.; Mizsey, P., Swelling studies of in-situ reduced Ag-NPs/ PVA nanocomposite films , World Colloid Conference, Vienna-Austria.

X. **Selim, A.;** Toth, A. J.; Fozer, D.; Haaz, E.; Mizsey, P., Effect of silver nanoparticles on chemical, thermal properties and stability of Poly (vinyl alcohol) nanocomposite membranes , Science in Practice, XXXIV. Kandó Conference 2018, Budapest, Hungary, 22 November 2018, pp. 26. ISBN 978-963-449-096-8

XI. **Selim, A**.; Toth, A. J.; Fozer, D.; Haaz, E.; Mizsey, P.,Influence of Silver Nanoparticles on Pervaporation Performance of PVA Membranes, 6th PVVPSGMD conference, Torun-Poland.

XII. **Selim, A**.; Toth, A. J.; Fozer, D.; Haaz, E.; Mizsey, P., Separation of aqueous salt solution using PVA based pervaporation membrane: Effect of nanofiller concentration, PERMEA2019 Membrane Conference of Visegrad Countries, Budapest-Hungary.

XIII. **<u>Selim, A</u>**.; Mizsey, P.Thermal cross-linked double network membrane for ethanol dehydration, PERMEA2019 Membrane Conference of Visegrad Countries, Budapest-Hungary.

XIV. **<u>Selim, A</u>**.; Toth, A. J.; Fozer, D.; Haaz, E.; Mizsey, P., Clean water production from high salinity water using pervaporation membranes, 11th Eastern European IWA Young Water Professionals Conference, Prague- Czech Republic.

c. Others

XV. Eniko Haaz, Nora Valentinyi, Ariella Janka Tarjani, Daniel Fozer, Anita Andre, Selim Asmaa, Fuad Rahimli , Tibor Nagy , Peter Mizsey, Csaba Deak, Andras Jozsef Toth, Platform Molecule Removal from Aqueous Mixture with Organophilic Pervaporation: Experiments and Modelling , Periodica Polytechnica Chemical Engineering (2019). https://doi.org/ 10.3311/PPch.12151

XVI. Andras Jozsef Toth, Eniko Haaz, Nora Valentinyi, Tibor Nagy, Ariella Janka Tarjani, Daniel Fozer, Anita Andre, Selim Asmaa Khaled Mohamed, Szabolcs Solti, and Peter Mizsey ,Selection between Separation Alternatives: Membrane Flash Index (MFLI) , Industrial & Engineering Chemistry Research (2018). https://doi.org/10.1021/acs.iecr.8b00430

XVII. Laszlo Racz,Daniel Fozer,Tibor Nagy,Andras Jozsef Toth,Eniko Haaz ,Janka Ariella Tarjani, Anita Andre, Asmaa Selim, Nora Valentinyi, Laszlo Tamas Mika, Csaba Deak, Peter Mizsey , Extensive comparison of biodiesel production alternatives with life cycle, PESTLE and multi-criteria decision analyses , Clean Technologies and Environmental Policy (2018). https://doi.org/10.1007/s10098-018-1527-1

XVIII. Andras Jozsef Toth, Botond Szilagyi, Daniel Fozer, Do Thi Huyen Trang, Asmaa Selim, Eniko Haaz, Separation of acetone-butanol-ethanol (ABE) fermentation products by pervaporation, Circular Economy and Environmental Protection, 3/3, 2019, pp. 5–19.

XIX. Andras Jozsef Toth, Eniko Haaz, Reka Ladanyi, Botond Szilagyi, Daniel Fozer, Asmaa Selim, Tibor Nagy, Peter Mizsey, Modelling of organophilic and hydrophilic pervaporations for separation of ethyl acetate – water mixture, Computer-Aided Chemical Engineering2020.

XX. Greta Sztancs, Lilla Juhasz, Balazs Jozsef Nagy, Aron Nemeth, Asmaa Selim, Anita Andre, Andras Jozsef Toth, Peter Mizsey, Daniel Fozer, Co-Hydrothermal gasification of Chlorella vulgaris and hydrochar: The effects of waste-to-solid biofuel production and blending concentration on biogas generation, Bioresources Technology 2020.