PERVAPORATION OF ETHANOL/WATER MIXTURES BY ZEOLITE A MEMBRANES SYNTHESIZED IN BATCH AND FLOW SYSTEMS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

BERNA (ARICAN) YÜKSEL

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

JANUARY 2011

Approval of the thesis:

"PERVAPORATION OF ETHANOL/WATER MIXTURES BY ZEOLITE A MEMBRANES SYNTHESIZED IN BATCH AND FLOW SYSTEMS"

submitted by **BERNA (ARICAN) YÜKSEL** in partial fulfillment of the requirements for the degree of **Master of Science in Chemical Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen ____________________
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Deniz Üner ____________________
Head of Department, **Chemical Engineering**

Prof. Dr. Ali Çulfaz ____________________
Supervisor, **Chemical Engineering Dept., METU**

Assoc. Prof. Dr. Halil Kalıpçılar ____________________
Co-Supervisor, **Chemical Engineering Dept., METU**

Examining Committee Members:

Prof. Dr. Levent Yılmaz ____________________
Chemical Engineering Dept., METU

Prof. Dr. Ali Çulfaz ____________________
Chemical Engineering Dept., METU

Assoc. Prof. Dr. Halil Kalıpçılar ____________________
Chemical Engineering Dept., METU

Prof. Dr. Çigdem Güldür ____________________
Chemical Engineering Dept., Gazi University

Assoc. Prof. Dr. Meltem Doğan ____________________
Chemical Engineering Dept., Gazi University

Date: **24.01.2011**

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name: Berna (ARICAN) YÜKSEL

Signature :

ABSTRACT

PERVAPORATION OF ETHANOL/WATER MIXTURES BY ZEOLITE A MEMBRANES SYNTHESIZED IN BATCH AND FLOW SYSTEMS

(Arıcan) Yüksel, Berna
M. S., Department of Chemical Engineering
Supervisor: Prof. Dr. Ali Çulfaz
Co-supervisor: Assoc. Prof. Dr. Halil Kalıpçılar
January 2011, 157 pages

Zeolite A membranes have great potential in pervaporation separation of ethanol/water mixtures with high flux and selectivity. Zeolite membranes usually synthesized from hydrogels in batch systems. In recent years, zeolite membranes are prepared in semicontinuous, continuous and recirculating flow systems to allow the synthesis of zeolite membranes with enlarged surface areas and to overcome the limitations of batch system at industrial level production.

The purpose of this study is to develop a synthesis method for the preparation of good quality zeolite A membranes in a recirculated flow system from hydrogels and to test the separation performance of the synthesized membranes by pervaporation of ethanol/water mixture. In this context, three different experimental synthesis parameters were investigated with zeolite A membranes synthesized in batch system. These parameters were the composition of the starting synthesis hydrogel, silica source and the seeding technique. Syntheses were carried out using hydrogels at atmospheric pressure and at 95 °C. The membranes were characterized by X-ray diffraction, scanning electron microscopy and pervaporation of 90 wt% ethanol-10 wt% water mixtures.

Pure zeolite A membranes were synthesized both in batch and flow systems. The membranes synthesized in batch system have fluxes around 0.2-0.3 kg/m^{2}h and selectivities in the range of 10-100. Membranes with higher selectivities were obtained in batch system by using *waterglass* as silica source, seeding by *dip-coating wiping* method, and with a batch composition of $3.4Na_2O:Al_2O_3:2SiO_2:155H_2O$. The membranes prepared in flow system have higher pervaporation performances than the ones prepared in batch system in considering both flux and the selectivity. Fluxes were around 0.3-3.7 kg/m^{2}h and selectivities were in the range of 10^2-10^4 for the membranes prepared in flow system which are comparable with the data reported in literature for batch and flow systems.

A high quality zeolite A membrane was also synthesized from $3.4Na_2O:Al_2O_3:2SiO_2:200H_2O$ hydrogel at 95 °C for 17 hours in flow system. Pervaporation flux of this membrane was 1.2 kg/m^{2}h with a selectivity >25,000 at 50°C. Although the synthesis method is resulted with high quality membrane, reproducibility of the synthesis method is poor and it should be improved.

Key words: Zeolite A, zeolite membrane, hydrogel, flow system, pervaporation

ÖZ

KESİKLİ VE AKIŞLI SİSTEMLERDE SENTEZ EDİLMİŞ ZEOLİT A MEMBRANLARIYLA ETANOL/SU KARIŞIMLARININ PERVAPORASYONU

(Arıcan) Yüksel, Berna
Yüksek Lisans, Kimya Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Ali Çulfaz
Ortak Tez Yöneticisi: Doç. Dr. Halil Kalıpçılar
Ocak 2011, 157 sayfa

Zeolit A membranlar etanol/su karışımlarının pervaporasyonla ayırımında yüksek akı ve seçicilikle büyük potansiyele sahiptir. Zeolit membranlar genellikle kesikli sistemlerde hidrojellerden sentez edilmektedir. Son yıllarda zeolit membranlar, genişletilmiş yüzeylerle zeolit membran sentezine olanak sağlamak ve endüstriyel seviyedeki üretimde kesikli sistemin sınırlamalarının üstesinden gelmek için yarı-sürekli, sürekli ve döngülü akış sistemlerinde hazırlanmıştır.

Bu çalışmanın amacı döngülü akış sisteminde, hidrojellerden kaliteli membran üretmek için bir sentez yöntemi geliştirilmesi ve üretilen membranların ayırma performansının etanol-su karışımlarının pervaporasyonu ile test edilmesidir. Bu bağlamda, kesikli sistemde üretilmiş zeolit A membranlarıyla üç farklı deneysel sentez değişkenleri araştırılmıştır. Bu değişkenler başlangıç sentez çözeltisinin bileşimi, silika kaynağı ve tohumlama tekniğidir. Sentez, hidrojeller kullanılarak, atmosfer basıncında ve 95 °C' de yapılmıştır. Üretilen membranlar X-ışını kırınımı, taramalı elektron mikroskobu ve ağ% 90 etanol- ağ% 10 su karışımlarının pervaporasyonu ile karakterize edilmiştir.

Gerek kesikli gerekse akışlı sistemlerde, saf zeolit A membranları sentez edilmiştir. Kesikli sistemde üretilen membranlar yaklaşık 0.2-0.3 kg/m^{2}h akıya ve 10-100 aralığında seçiciliğe sahiptir. Kesikli sistemde, en yüksek ayırma seçiciliğine sahip membranlar silika kaynağı olarak *cam suyu* kullanıldığında, *daldırma ve silme* yöntemiyle tohumlandığında ve $3.4Na_2O:Al_2O_3:2SiO_2:155H_2O$ başlangıç bileşimiyle elde edilmiştir. Akışlı sistemde hazırlanan membranlar hem akı hem de seçicilik göz önünde bulundurulduğunda kesikli sistemde hazırlanan membranlardan daha yüksek pervaporasyon performansına sahiptir. Akışlı sistemde hazırlanan membranlar için akılar yaklaşık 0.3-3.7 kg/m^{2}h ve seçicilikler 10^2-10^4 aralığındadır ki kesikli ve akışlı sistemler için literatürde rapor edilen verilerle karşılaştırılabilir.

Ayrıca yüksek kalitede bir zeolit A membranı akışlı sistemde $3.4Na_2O:Al_2O_3:2SiO_2:200H_2O$ bileşimli hidrojelden 95 °C' de 17 saatte sentez edilmiştir. Bu membranın 50 °C' deki pervaporasyon akısı 1.2 kg/m^{2}h ve seçiciliği >25,000' dir. Sentez yöntemi yüksek kalitede membran ile sonuçlansa da sentez yönteminin tekrarlanabilirliği düşüktür ve geliştirilmesi gerekir.

Anahtar kelimeler: Zeolit A, zeolit membran, hidrojel, akışlı sistem, pervaporasyon

To my parents,
Nurten and Celal ARICAN
and my brother,
Cemal ARICAN
and my husband,
Berat YÜKSEL

ACKNOWLEDGEMENT

I would like to express my gratitude to my supervisor Prof. Dr. Ali ÇULFAZ and my co-supervisor Assoc. Prof. Dr. Halil KALIPÇILAR for their valuable supports, encouragements, supervisions and useful suggestions throughout this study. I am especially thankful to Prof. Dr. Ali ÇULFAZ for giving me the opportunity to make individual decisions throughout the study and also for being me a second father.

I would like to thank both the Central Laboratory and the Machine Shop technicians of the Chemical Engineering Department especially to İsa ÇAĞLAR for their help during the study.

I want to thank to my friend Derya Baran for her endless friendship and for being me a sister. She is the most valuable thing that I had.

I want to thank to my friend Belma Soydaş for her profound friendship and her endless patience to my questions and helpful comments during the thesis studies. She will have a very important place in my heart during all my life.

I want to thank to my friend Edibe Eda ORAL for valuable friendship and the moral supports enabled me during my study. Whenever I need her, she was sitting next to me.

I would like to thank to my dear friend Elif KARATAY, I always feel her support regardless of the distances.

I would also like to show my appreciation to my lab mates Canan GÜCÜYENER, Emre BÜKÜŞOĞLU, and my colleagues Hasan Zerze, Berk BALTACI, Sena YÜZBAŞI, Emre YILMAZ, Gamzenur ÖZSİN and Merve BAŞDEMİR for turning this experience into an enjoyable one with their friendship.

I am as ever, especially indebted to my parents Nurten ARICAN and Celal ARICAN for their love and support throughout my life. My sincere thanks go to my brother Cemal ARICAN for being my best friend at every stage of my life. Also I would like to thank my second mother Mine YÜKSEL and my other brother Burak YÜKSEL for their moral supports during this study.

Finally, I would like to show my special thanks to my husband, Berat YÜKSEL, for his endless support and patience to me, for making me happy, for making me feel comfortable and secure. I will always love him.

TABLE OF CONTENTS

CHAPTERS

APPENDICES

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

NOMENCLATURE

N : Soda, Na_2O

A : Alumina, Al_2O_3

S : Silica, SiO_2

H : Water, H_2O

LTA : Linde Type A

ZSM-5 : Zeolite Socony Mobile-5

MFI : Mobile Five

FAU : Faujasite group

XRD : X-Ray Diffraction

SEM : Scanning Electron Microscopy

IPA : Isopropanol

m_i : mass of species i

A : Area of membrane

t : Time

J_i : Partial molar flux of species i

J_{total}, J : Total molar flux

j_i : Partial mass flux of species i

j_{total}, j : Total mass flux

y_i : mass fraction of species i at permeate side

x_i : mass fraction of species i at feed side

SF, $\alpha_{A/B}$: Separation factor (selectivity)

$\alpha_{A/B(ideal)}$: Ideal selectivity

P_T, P : Total pressure

P_i : Partial pressure of species i

P_i^{sat} : Saturation (vapor) pressure of species i

P_i^G : Permeance of component i

ℓ : Membrane thickness

f_i^L : Fugacity of component i in liquid phase

γ_i^L : Activity coefficient of component i in liquid phase

CHAPTER 1

INTRODUCTION

Zeolites are crystalline, hydrated and microporous aluminosilicates of alkali or alkaline earth elements and they have a framework structure in which there are uniform molecular sized pores, channels and cavities [1]. The chemical composition, the pore size and the structure differ depending on the type of zeolite. Zeolites are attractive membrane materials due to their uniform molecular sized pores and their sorption properties. Hence, zeolites are able to selectively sieve components of a mixture. This is a unique property that results in much attention focused on zeolites as selective membrane layers and selective adsorbents for separating mixtures and as shape-selective catalysts.

Zeolite membranes are thin and selective zeolite layers on a thick macroporous support to obtain mechanical strength. Separation of gaseous and liquid mixtures is achieved by zeolite membranes due to their attractive sorption properties (hydrophilic/ hydrophobic) and their well defined pore sizes.

Zeolite A, also called Linde Type A (LTA), is a hydrophilic zeolite with a Si/Al ratio of one which is the lowest among all zeolites. Zeolite A is commonly used in membrane studies because it has high affinity for water and polar molecules and its pore dimensions are appropriate for the separation of mixtures of commercial importance, such as organic/water mixtures and azeotropic mixtures. Indeed, it is well known that zeolite A membranes have great potential in pervaporation separation of organic/water mixtures with high flux and selectivity [2-5].

Zeolite membranes are commonly prepared by hydrothermal synthesis. In hydrothermal synthesis the porous support (with or without a previous seeding step) is immersed in an autoclave which is filled with synthesis gel or clear solution. Then the autoclave is heated up to the synthesis temperature in an oven where the temperature is kept constant during the synthesis. Zeolite membranes usually prepared in batch systems. Zeolite A membranes are synthesized from either a gel or a clear solution and at temperatures between 80 °C and 100 °C [2, 5, 12, 13]. Membrane thicknesses are in the range of 3 to 30 μm [2-5, 13].

Zeolite A membrane is commercialized by Mitsui Engineering and Shipbuilding Co. Ltd.. Morigami et al. [6] reported the synthesis of commercialized zeolite A membranes which are synthesized on seeded tubular α-alumina supports having 80 cm length and 300 cm^2 area. Zeolite A membranes were prepared at 100°C for 3-4 h and thickness of the membranes were 20-30 μm. Performance of the synthesized membranes were tested both in pervaporation and vapor permeation to dehydrate different organic/water mixtures and excellent water-permselective performance was obtained. Using zeolite A membranes in the pervaporation systems can be a good choice for dehydrating of organic/water mixtures since zeolite A membranes have both high selectivity and high flux together. Hence, many researchers focused on the zeolite A, its preparation and pervaporation performance for separating organic/water mixtures.

The batch synthesis method may cause problems such as high production cost, non-uniform synthesis conditions and low reproducibility for industrial level production of zeolite membranes. Although there are few studies carried out for the production of large-area membranes to solve these problems, they still exist as the handicaps of batch systems. In industrial scale, the use of various membrane geometries and large area membranes such as capillary or multi-channel supports is needed according to the different purposes. But operating with these different types of supports in batch systems is difficult. Hence, as an alternative to preparation of membranes in batch system recent studies have focused on the synthesis of zeolite membranes in dynamic (continuous or recirculating flow) systems to improve the economical feasibility and reproducibility at industrial level production. Some pioneering studies were reported to improve a continuous system for the synthesis of zeolite membranes. Richter at al. [7] reported the synthesis of MFI type membranes at 150 °C by supplying the fresh synthesis solution continuously in the lumen of the supports. Pina et al. [3] synthesized zeolite A membranes on the outer surface of tubular alumina supports in a semi-continuous system by renewing the synthesis solution periodically. Yamazaki and Tsutsumi [8] reported the preparation of flat LTA membranes in a flow system by heating only the substrate to be coated and by flowing the synthesis solution over the substrate. Çulfaz et al. [9] and Soydaş et al. [10] prepared good quality MFI-type zeolite membranes on α-alumina tubular supports in a system in which the synthesis solution was recirculated through the support by a peristaltic pump. High performance of membranes in both studies is attributed to the more uniform synthesis conditions due to flow of synthesis mixture. Pera-Titus et al. [11] prepared zeolite A membranes on the inner side of tubular titania supports in a continuous system in which synthesis solution was flown in the lumen of the support by the action of gravity. Also, synthesis of zeolite A membranes on α-alumina supports from a clear solution in a recirculating flow system using the same system as Çulfaz and Soydaş is reported by Akbay [12]. Recently, Aguado et al. [13] have also prepared zeolite A membranes on the inner side of the tubular α-alumina supports in a continuous recirculating flow system from a clear solution.

Several attempts have been performed for the synthesis of zeolite A membranes both in batch and flow systems. Researchers preferred to use clear solutions especially in flow systems due to the high fluidity of the synthesis solution but clear solutions may result in formation of different zeolites or low quality zeolite A membranes. Only Pera-Titus preferred to use a hydrogel in a continuous system (with no recirculation) and in their study zeolite A membranes synthesized on titania supports.

The difference of this study from literature is that zeolite A membranes are synthesized from a hydrogel on α-alumina supports in a recirculated flow system. The purpose of this study is to develop a synthesis method for the preparation of good quality zeolite A membranes in a recirculated flow system from hydrogels and to show the dehydrating ability of the synthesized membranes by pervaporation separation of ethanol/water mixture. In this context, three different experimental synthesis parameters were investigated with zeolite A membranes synthesized in batch system. These parameters were the composition of the starting synthesis hydrogel, silica source and the seeding technique. The method developed for the synthesis of good quality membranes was adapted to recirculated flow system. It has the flexibility with various membrane supports and more uniform thickness was expected throughout the large membranes due to the less contribution of material deposition to the zeolite layer formation since flow prevents the deposition from synthesis solution. More uniform synthesis conditions can be provided in the flow system with more economical use of the raw materials. Since the method has the practical advantages it may be used in large-scale synthesis and it may overcome the problems of batch synthesis method at industrial level production.

CHAPTER 2

LITERATURE SURVEY

2.1 Zeolite Membranes

Membrane is a semipermeable barrier between two phases. Components of a mixture are separated by selective permeation of molecules through the membrane according to the sorption and diffusion properties of the components [14].

Organic membranes (polymer membranes) and the inorganic membranes are the different types of membranes that are used in pervaporation separation [15]. Polymeric type pervaporation membranes are mostly used in industrial applications [16]. Polymeric membranes have limited solvent and temperature stability which are major drawbacks of these membranes. In general, inorganic membranes have both high separation factor and permeability, are solvent and temperature stable and can be used in a wide pH range [15, 16]. A higher product quality can be obtained with the industrial use of ceramic membranes. Also application range of pervaporation can be extended. In pervaporation the separation depends only on the relative affinity of the components for the membrane, it is not based on the relative volatility of the components in the mixture. Zeolite membranes show attractive sorption properties (hydrophilic/hydrophobic) with their well defined pore sizes among both the organic and ceramic membranes [15, 17].

Zeolite membranes are generally composed of a thin and selective zeolite layer and a thick macroporous support to obtain mechanical strength. Membranes are prepared from many different support materials such as alumina, stainless steel and titania and with different geometries such as disc, tube or monolith [11, 18, 19, 20].

Zeolite membranes usually show randomly oriented polycrystalline structures on porous supports. The polycrystalline nature of membranes often led to the presence of non-zeolitic pores among adjacent crystals or grain boundaries in the zeolite layer. There are two ways of flow through the zeolite membrane (Figure 2.1). One of them is the flow through zeolite pores so that separation is achieved by molecular sieving based on the difference in size and shape of molecules and by preferential adsorption (hydrophilic/hydrophobic). When adsorption is less controlling, diffusion rate of molecules makes contribution to the separation achieved by zeolite membranes [17]. The other way is the flow through non-zeolitic pores and by that way the degree of separation is likely to be low, in other words, the feed permeates through the zeolite layer with a slight change or without any change in composition. Hence the formation of non-zeolitic pores should be minimized during the synthesis to obtain high quality zeolite membranes.

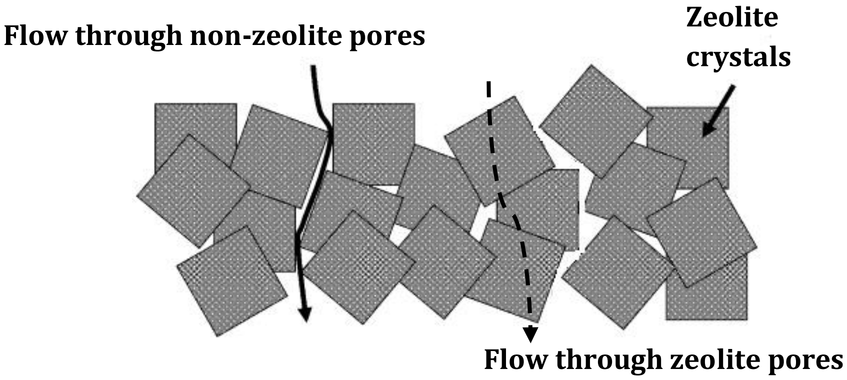


Figure 2.1 Schematic representation of flow through a zeolite layer

Membrane performance is reported in terms of flux, permeance and separation selectivity and ideal selectivity. Flux of a component through a membrane is defined as the amount of permeated component through the membrane per unit time per unit area and usually expressed in terms of kg/m^2 h or mole/m^2 h (Equation 2.1). Permeance of a component through a membrane is related to the molar flux by driving force for permeation and calculated as shown in Equation 2.2, where driving force is

$$\text{Flux } (j_i) = \frac{\Delta m_{\mathrm{i}}}{A \times \Delta t} \tag{2.1}$$

$$\text{Permeance } \left(P_i^G\right) = \frac{\text{Molar flux}}{\text{Driving force}} = \frac{\left(\frac{\Delta J_i}{A \times \Delta t}\right)}{\Delta \mathrm{P}} \tag{2.2}$$

usually the pressure difference between the upstream and downstream side of the membrane. The ideal selectivity (Eq. 2.3) is defined as the ratio of pure component permeances and for the mixtures separation selectivity (factor) (Eq. 2.4) is defined as the ratio of the mass component fractions in the fluids either side of the membrane and calculated as given in Equation 2.4; where y_A and y_B are the mass fractions of components A and B in the mixture at the permeate side and x_A and x_B are the mass fractions of these components at the feed side of the membrane.

$$\text{Ideal Selectivity}_{\mathrm{A/B}} \left(\alpha_{A/B_{ideal}}\right) = \frac{\text{Permeance of component A } \left(P_A^G\right)}{\text{Permeance of component B } \left(P_B^G\right)} \tag{2.3}$$

$$\text{Separation Selectivity}_{\mathrm{A/B}} \left(\alpha_{A/B}\right) = \frac{(y_A/y_B)_{permeate}}{(x_A/x_B)_{feed}} \tag{2.4}$$

If a membrane is prepared with two layers in same quality selectivity will remain constant. But selectivity may increase with an increase in membrane thickness due to the additional resistance to transport, if the second layer has higher quality (has less non-zeolitic pores) than the first one. Also a decrease in flux is observed at the same time. A high quality industrial membrane is expected to have high separation selectivity and high flux at the same time in spite of the trade-off between these two properties and also the synthesis method of this membrane is expected to be feasible in terms of cost.

2.2 Description of Zeolite A

The term zeolite designates a variety of crystalline, hydrated and microporous aluminosilicates of alkali or alkaline earth elements with a framework structure based on a well-defined system of channels and cavities [1].

The zeolite structures differ in chemical composition and also in the size of their pore apertures. So zeolites can be sorted as: small pore, medium pore and large pore. Zeolite A (LTA) (0.42 nm) can be listed as small pore zeolites, zeolite ZSM-5 (MFI) (0.55 nm) as medium pore, and zeolites X, Y (FAU) (0.74 nm) as large pore [1]. Zeolites behave as molecular sieves, since their pore size are of the same order of magnitude as the kinetic diameters of molecules. This is a unique property that gives zeolites their value as selective membrane layers and selective adsorbents for separating mixtures and as shape-selective catalysts. According to the type of the zeolite and its pore system, the molecules can penetrate into the cavity system or can be rejected from it.

Zeolite A also called Linde Type A (LTA) is a hydrophilic zeolite with a Si/Al ratio of one which is the lowest among all zeolites. Depending on the type of zeolite Si/Al ratio of a zeolite is changed from one to infinity. The framework of zeolite A comprised of secondary building units (SBU) of double four ring (D4R) and truncated octahedron (β-cage) as shown in Figure 2.2. These units make a large cavity called α-cage. For zeolite NaA, 0.42 nm and 0.22 nm are the pore openings of α-cage and β-cage, respectively. The pore size of zeolite A can be modified by ion exchange. Alkali or earth alkaline metals balance the negatively charged framework occurs due to the charge difference between silicon (+4) and aluminum (+3) atoms. These cations are mobile and exchangeable. For instance, when potassium is exchanged with sodium, 0.3 nm is the new pore size [1].

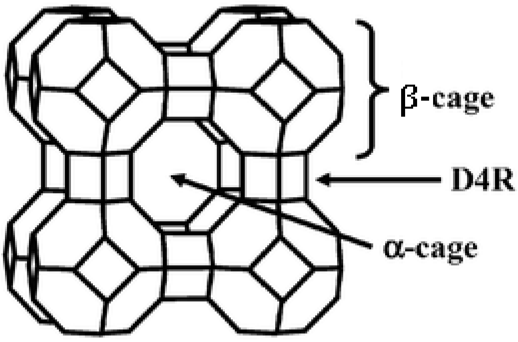


Figure 2.2 Framework structure of zeolite A

Zeolite A is commonly used in membrane studies because it has high affinity for water and polar molecules and its pore dimensions are appropriate for the separation of mixtures of commercial importance, such as organic/water mixtures and azeotropic mixtures. Indeed, it is well-known that zeolite A membranes have great potential in pervaporation separation of organic/water mixtures with high flux and selectivity [2-5].

2.3 Pervaporation

Pervaporation is a membrane process to achieve the separation of liquid mixtures (Figure 2.3). In pervaporation process driving force is provided by keeping the feed side at atmospheric or higher pressure whereas the permeate side is evacuated. The low pressure at the permeate side is provided with a vacuum pump. The feed is a liquid and permeate is a vapor since the vapor pressures of components in the mixture are higher than the low permeate pressure (evacuated) at the operation temperature.

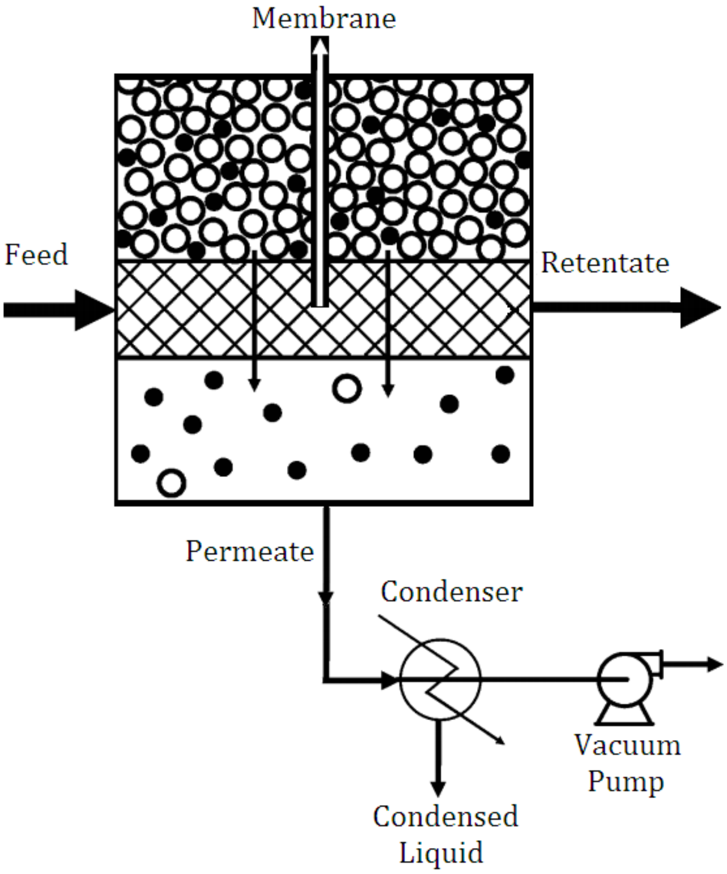


Figure 2.3 Schematic representation of pervaporation process

The vapor (permeate) is enriched in the preferentially permeating component and is condensed for future processing. At the same time, the retentate is rich in non-preferentially permeating component and is either recycled for further separation or used in another process.

Organic solvents are commonly used in different industrial applications. In general, these solvents constitute azeotropes with water. Azeotropes cannot be separated with standard distillation, they can be separated with pressure-swing, extractive or azeotropic distillation. But these processes add extra cost to the separation process and also these processes are very energy-intensive processes. For these kinds of cases (e.g. organic-water mixtures, etc.), pervaporation is an attractive separation process, since lower temperatures than those required in distillation are applicable and only a fraction of a mixture is vaporized and required energy for separation is reduced. Removing components present in low concentrations by pervaporation is preferred to complete separation by pervaporation in practice. Instead of making complete separation by pervaporation, using a combination of distillation and pervaporation (a hybrid system) will be energy reducing and economically attractive [16, 31].

Pervaporation has very widespread application areas. Some of these are dehydration of solvents, removal of volatile organic compounds from water, separation of polar/non-polar components, separation of aromatics/aliphatics and separation of isomers. The azeotropic mixtures like ethanol and water can be separated by pervaporation more effectively with usage of less energy with respect to conventional separation methods (distillation etc.). So zeolite A membranes synthesized in this study were used to separate ethanol/water mixture by pervaporation.

Permeation behavior of hydrophobic silicalite membrane is discussed using a Maxwell-Stefan Model [21-24], an adsorption-diffusion model [25] and a parallel diffusion model [26, 27]. The transport mechanism of pervaporation through hydrophilic zeolite A membranes was tested by gas transport model [28] and adsorption-diffusion model [29]. In very recent study of Kondo et al. [30] permeation mechanism through zeolite A and T membranes for pervaporation and vapor permeation was discussed. The mechanism is described as that there are very fine and narrow non-zeolitic pores opened to the support through the zeolite layer. At the feed side water molecules are selectively adsorbed in the hydrophilic zeolitic pores in the top surface layer. These water molecules transported to the non-zeolitic pores through the zeolitic pores by surface diffusion. After that, at narrower space in the non-zeolitic pore, the capillary condensation occurs non-zeolitic pore is filled with the condensate. Then condensate is transported to the downstream side by hydrostatic pressure difference and it evaporates and diffuses into the permeation side. Partial vapor pressure difference of water across the membrane and water flux is correlated in the light of the discussed mechanism.

Organic (polymeric) membranes are currently available for various pervaporation applications. Concentration polarization on the feed side and membrane swelling are the difficulties that reduce the effectiveness of pervaporation with organic membranes.

A major drawback of using polymeric membranes is their limited thermal, chemical and mechanical stability. On the other hand, zeolite membranes are also used for pervaporation and they do not swell, they are more chemically stable than organic membranes and they are stable at high temperatures. These properties make zeolite membranes attractive for pervaporation separation of molecular mixtures [16, 31].

Currently, in clear majority of pervaporation studies, pervaporation performances of membranes reported in terms of mass flux and separation factors, even though the reporting method leads to comparison difficulty for different operation conditions. A good quality membrane should have high selectivity and high flux at the same time for the pervaporation separation of the target liquid mixture.

2.4 Preparation of zeolite membranes by hydrothermal synthesis in different systems

Hydrothermal synthesis constitutes the commonly used preparation method of zeolite membranes. In hydrothermal synthesis the porous support (with or without a previous seeding step) is inserted in an autoclave and synthesis gel or clear solution is poured into the autoclave. Then the autoclave is placed in an oven and heated up to the synthesis temperature. The temperature is kept constant during the synthesis. In the synthesis of zeolite A membranes, either a gel or a clear solution is used as starting synthesis solution and temperatures between 80 °C and 100 °C are preferred [2, 5, 12, 13]. Thicknesses of the membranes are in the range of 3 to 30 μm [2-5, 13].

Zeolite crystals grow both on the porous support and in the bulk of synthesis solution and both of these growing steps can promote the formation of zeolite layer. Seeding is a crucial factor for better quality membranes and it enhance the reproducibility in the synthesis of zeolite membranes [32]. But seeding includes other mini factors that could affect the overall synthesis process and the performance of the membrane. These are size of seed crystals, the concentration of crystals in slurry, embedding method of seed crystals on the support and pre or post treatments to the support material. In the scope of finding a proper preparing method for obtaining reproducible zeolite A membranes, several attempts are made in the field of finding a promising seeding technique. Rubbing [2], dip-coating [5] and vacuum seeding [36] constitute the most widely preferred seeding techniques and several studies used these methods to prepare a good quality zeolite A membrane. Among these seeding methods, dip-coating is reported as resulting more uniform seeding with high reproducibility and in the same study, seed crystals composition in the aqueous solution is reported as a crucial factor [5]. It is indicated that sparse distribution of seed crystals on the support surface is preferred rather than a seed layer on the support to make high quality zeolite A membranes and using concentrated seed solutions led to some cracks in the membrane layer [5]. A seeding post treatment, wiping, is recently reported by Wang et al. [37] and it is mentioned that using dip-coating wiping seeding method improves the uniformity of seeding and hence high performance membranes have been synthesized reproducibly. In another study, it has been indicated that an UV irradiation of titania supports can help the growth of zeolite NaA layers with a good pervaporation performance [38].

It is also reported that good quality zeolite A layers can be obtained under a centrifugal field by rotation of horizontally or vertically, which promotes to set crystal nuclei of suitable size from the bulk of the solution on the support, thereby contributing intergrowth [39, 40].

Kita et al. [34] prepared zeolite A membranes from hydrogels of $N_2A_1S_2H_{60-120}$ on seeded alumina supports at 100°C for 3.5 h. The thicknesses of the membranes were about 30 µm. The dehydrating performance of the membranes was tested with pervaporation by using 10:90 (wt.%) water/ethanol mixture at 75°C. Membranes showed high selectivity and flux in pervaporation separation of ethanol/water mixture. The flux and selectivity of the membrane were 2 kg/m^2h and 10000, respectively.

In general zeolite membrane synthesis is conducted in conditions similar to the zeolite powder synthesis. Experimental conditions such as composition of the synthesis solution or gel, support material, contact position of support with synthesis solution or gel, and hydrothermal synthesis conditions should be carefully controlled in order to obtain a continuous film on the support. Zeolite membrane synthesis is sensitive to these experimental conditions, preparing a synthesis mixture from different reagent sources cause various results, even for almost same compositions. Masuda et al. [35]

studied the effect of alumina and silica sources on preparation of A type zeolite membranes and they reported that the morphology and thickness of the zeolite film were dependent on the reaction time and temperature, and especially on the types of silica and alumina sources and the preferred silica and alumina sources were Na_2SiO_3 and $Al(OH)_3$, respectively.

Several researchers investigated the effect of multi-stage synthesis [33, 41, 42]. In multi stage synthesis, gel or solution in the autoclave is renewed after each synthesis. Preparation of zeolite membranes by multi stage synthesis generally resulted with membranes having fewer defects. Kumakiri et al. [33] tested zeolite A membranes prepared by different synthesis steps and reported that ethanol permeability decreased on repeating the synthesis, while total flux showed a smaller decrease and as a result, PV selectivities increased on repeating the synthesis. Also they reported that after several sets of syntheses, the zeolite A membrane showed a good dehydration ability with a separation factor of more than 10000.

Zeolite A membranes are produced commercially by Mitsui Engineering and Shipbuilding Co. Ltd.. Synthesis of this zeolite A membranes is reported by Morigami et al. [6]. Membranes are synthesized on tubular α-alumina supports having 80 cm length and 300 cm^2 area. Zeolite A membranes are prepared on seeded supports at 100°C for 3-4 h and thickness of the membranes were about 20-30 μm. Synthesized membranes are used to dehydrate different organic/water mixtures and showed excellent water-permselective performance both in pervaporation and vapor permeation.

In recent years, Sato et al. [5] reported a reproducible preparation method to prepare high-flux zeolite A membranes for the industrial mass production. Zeolite A membranes were prepared on tubular α-alumina supports from $N_2A_1S_2H_{150}$ hydrogel by seeding with dip-coating wiping. Membranes are treated hydrothermally at 373 K for 4 hours. The membranes are used in pervaporation separation of a mixture of water (10wt.%)/ethanol (90wt.%) at 348K and showed high water permeating flux up to 5.6 kg/m^2h and high water/ethanol selectivity over 5000.

Although there are a few studies carried out for the production of large-area membranes to assist to the industrial level production of zeolite membranes, high production cost, non-uniform synthesis conditions and low reproducibility still exist as the handicaps of static systems. Also adapting these static systems to operate with various membrane geometries and with large area membranes such as capillary or multi-channel supports is laborious. Hence, recent studies have focused on the synthesis of zeolite A membranes in dynamic (continuous or re-circulating flow) systems to improve the economical feasibility and reproducibility at industrial level production. There are some pioneering studies to improve a continuous system for the synthesis of zeolite membranes. Richter at al. [7] reported the synthesis of MFI type membranes on the inner side of tubes and capillaries. The synthesis is conducted by supplying the fresh synthesis solution continuously in the lumen of the supports with a flow rate of 25 cm/min. Synthesis is done at 423 K for 72 hours. As a result of this synthesis method, the depletion of precursor solution is prevented and more homogenous membranes of 30 μm thickness are obtained with H_2/SF_6 ideal selectivity above the Knudsen selectivity.

Regarding to obtain zeolite A membrane by a non-static synthesis, Pina et al. [3] synthesized zeolite A membranes on the outer surface of tubular alumina supports in a semi-continuous system by supplying the fresh synthesis solution periodically from a vessel pressurized with dry nitrogen at a pressure of 10 bar and solution in the autoclave is removed by pneumatic valves. In this way the gel is replaced at different renewal rates from once in every 13 minutes to once in every 75 minutes. Synthesis is done at 363 K for 5 hours. This semi-continuous synthesis method is resulted with membranes of 10 μm thickness with fluxes of 2.2-3.8 kg/m^2 h and selectivities of 94-3603 for the pervaporation separation of a mixture of water (10wt.%)/ethanol (90wt.%).

Pera-Titus et al. [4] is also reported the synthesis of zeolite A membranes on the inner side of the seeded tubular supports by using the same semi-continuous system. Synthesis is done at 363-373 K for 5 hours. The gel is replaced at a renewal rate of once in every 10 minutes. Membranes synthesized with two batches of cycles showed good dehydration ability by having 0.5 kg/m^2 h flux and 16000 selectivity for pervaporation separation of 90:10 (wt%) ethanol/water mixture.

So far, the used synthesis systems are either a continuous or semi-continuous synthesis system which is related by renewing the synthesis solution. On the other hand, in the study of the Yamazaki and Tsutsumi [8], the synthesis solution is circulated through the support continuously like the system used in this study. In this study, liquid phase solution, which was separated from the gel, is circulated over the PTFE supports and zeolite A layers are synthesized by the aid of this circulation. To prevent the zeolite formation in the bulk solution, only the PTFE supports are heated. The static synthesis runs resulted with the formation of by-products such as gmelinite, chabazite and faujasite in addition to zeolite A but circulated synthesis runs resulted with formation of pure zeolite A.

Çulfaz et al. [9] prepared good quality MFI-type zeolite membranes on α-alumina tubular supports at 355–368K for 72–76h in one to three cycles in a system in which the synthesis solution recirculated through the support by the action of a peristaltic pump at a flow rate of 6–48 mL/min. The membranes had a thickness of 1-2 μm with a separation selectivity of 7.6 at 473K for separation of n-C_4H_{10}/ i-C_4H_{10} (50:50). Soydaş et al. [10] have also prepared good quality MFI-type zeolite membranes on α-alumina tubular supports at 368K for 72h in same recirculated flow system. Thin membranes with reasonable separation performances both in gas and liquid separations are obtained by the used recirculated flow system. High performance of membranes in both studies is attributed to the more uniform synthesis conditions due to flow of synthesis mixture.

In the course of making zeolite A membrane by a dynamic synthesis, Pera-Titus et al. [11] reported the synthesis of zeolite A membranes on the inner side of the titania tubular supports in a continuous system with a flow rate of 1.5-4 mL/min. The synthesis solution was flown in the lumen of the support by the action of gravity from a reservoir. Synthesis is carried out at 353-363 K for 3-7 hours. The membranes (10–20 μm in thickness) showed ability to dehydrate ethanol/water mixtures (92:8, w/w) by pervaporation with selectivities and fluxes, respectively, in the range of 51-8500 and 0.7-1.2 kg/m^{2}h at 323 K.

Akbay [12] reported the synthesis of zeolite A membranes in a recirculating flow system using the same system as Çulfaz and Soydaş on α-alumina supports from a clear solution. Synthesis is carried out at 353 K for 8 hours. In this study, for a double layer membrane synthesized separation factor is reported as about 3700 for the separation of 92:8 (wt.%) ethanol/water mixture at 318 K with a flux of 0.14 kg/m^{2}h. Poor stability of the membrane is explained by the high alkalinity of the synthesis solution and low reproducibility of the pervaporation tests especially at higher temperatures is attributed to the crack formation in the membrane.

Recently, Aguado et al. [13] have also prepared zeolite A membranes in a continuous recirculating flow system with a flow rate of 0.25-5 mL/min on inner side of the tubular α-alumina supports from a clear solution. And also some of the used supports modified with PDDA to promote the zeolite particle adhesion. Membranes which are prepared on modified support showed 17-21 kg/m^{2}h flux and 35-41 selectivity for the pervaporation separation of 65:35 (wt.%) isopropanol/water mixture at 90°C whereas membranes which are prepared on non-modified support showed 38 kg/m^{2}h flux and 17 selectivity for the pervaporation separation of same mixture at same temperature. For all the membranes, having low selectivity and high flux are attributed to the clear solution usage as synthesis solution.

Several attempts have been performed for the synthesis of zeolite A membranes both in static and dynamic systems. Researchers preferred to use clear solutions especially in dynamic systems due to the high fluidity of the synthesis solution but clear solutions may result with formation of different zeolites or low quality zeolite A membranes. Only Pera-Titus preferred to use a hydrogel in a continuous system (with no re-circulation) and in their study zeolite A membranes synthesized on titania supports. The difference of this study from literature is that zeolite A membranes are synthesized from a hydrogel on α-alumina supports in a recirculated flow system.

2.5 Use of zeolite membranes in pervaporation separations

In recent years, several researchers made a great effort for the development of inorganic microporous membranes. Many studies have reported the synthesis, pervaporation and vapor permeation properties of different membrane types, such as zeolite A [2], FAU-type zeolites X and Y [43-45], MFI-type zeolites ZSM-5 and silicalite-1 [20, 46, 47], MOR type zeolite [48], FER-type zeolite [49], MEL-type zeolite [50], and amorphous silica [51, 52]. These kinds of membranes are expected to have potential for separation and reaction applications due to their molecular sieving properties. Having good thermal, chemical and mechanical stability and molecular sieving properties give zeolites their value as unique membranes and pervaporation agents for separation of molecular mixtures.

2.5.1 Use of zeolite A membranes for pervaporation separations

In the application to industrial processes, zeolite A is the only reported commercial zeolite membrane that it utilized for dehydration. For the removal of water from its mixtures with organic components by pervaporation, zeolite A is the unique candidate with having both high selectivity and high flux together. Hence, many researchers focused on the zeolite A, its preparation and pervaporation performance for separating organic/water mixtures.

Table 2.1 shows the pervaporation performances of several zeolite A membranes for organic/water separation (especially for ethanol/water mixture) in literature. Different synthesis strategies were used to synthesize zeolite A membranes for pervaporation separation of organic/water mixtures.

Kita and co-workers [2, 18, 34] prepared zeolite A membranes from hydrogels of $N_2A_1S_2H_{60-120}$ on seeded alumina and mullite supports at 100°C for 3-3.5 h in batch system. The thicknesses of the membranes were about 10-30 μm. Membranes showed high selectivity and flux in pervaporation separation of ethanol/water mixture. The flux and selectivity of the membranes were in the range of 0.77-2.2 kg/m^{2}h and >10000, respectively.

Yang and co-workers [36, 53] prepared zeolite A membranes from clear solutions of $N_{50}A_1S_5H_{1000}$ on seeded alumina tubular supports at 60°C for 1- 24 h in batch system. The thicknesses of the membranes were about 6-14 μm. Membranes showed high selectivity and flux in pervaporation separation of isopropanol/water mixture. The flux and selectivity of the membranes were in the range of 1.12-1.67 kg/m^{2}h and 5300-10000, respectively.

Pera-Titus and co-workers [4, 11, 55] prepared zeolite A membranes from hydrogels of $N_{2.1\text{-}3.9}A_1S_{1.8\text{-}2}H_{120\text{-}400}$ on seeded alumina and titania supports at 80-100°C for 3-7 h in batch, semi-batch and continuous systems. The thicknesses of the membranes were about 30 µm. The flux and selectivity of the membranes were in the range of 0.5-0.9 kg/m^{2}h and 600-16000, respectively in pervaporation separation of ethanol/water mixture.

Sato and co-workers [5, 58] prepared zeolite A membranes from hydrogels of $N_2A_1S_2H_{150}$ on seeded alumina tubular supports at 100°C for 4 h in batch system. The thicknesses of the membranes were about 2.5-4 µm. Membranes showed high selectivity and high flux in pervaporation separation of ethanol/water mixture. The flux and selectivity of the membranes were in the range of 5.6-8.4 kg/m^{2}h and 10000, respectively.

The membranes prepared from clear solutions have 1.7 – 14 µm thicknesses whereas the membranes prepared from hydrogels have 2.5 – 30 µm thicknesses. Typically pervaporation fluxes of the reported membranes are in the range of 0.5-1.5 kg/m^{2}h at 50 °C. However pervaporation fluxes of the reported membranes at 70-75 °C are 4-6 folds higher than the fluxes at 50 °C. Membranes synthesized on seeded supports and by multi-cycles showed better pervaporation performances due to the others and membranes synthesized in semi-continuous and continuous flow systems showed similar pervaporation performances with the membranes synthesized in batch system.

Table 2.1 Pervaporation performances of zeolite A membranes for organic/water separation (especially for ethanol/water mixture)

SYNTHESIS							PERVAPORATION				
Comp.	**Type**	**T (°C)**	**Duration (h)**	**Support**	**Seed**	**Membrane Thickness (μm)**	**Xwater (wt.%)**	**T (°C)**	**Flux kg/m²h**	**S.F.**	**Ref.**
$N_2A_1S_2H_{60}$	Batch	100	3.5	α-alumina cylindrical	<75 μm zeolite A	30	10	75	2	10000	34
$N_2A_1S_2H_{60}$	Batch	100	3.5	mullite tubular	<75 μm zeolite A	10	10	50	0.77	46000	18
$N_2A_1S_2H_{60}$	Batch	100	3.5	mullite tubular	<75 μm zeolite A	10	10	75	2.08	42000	18
$N_2A_1S_2H_{120}$	Batch	100	3	α-alumina tubular	<75 μm zeolite A	30	10	75	2.2	>10000	2
$N_{50}A_1S_5H_{1000}$	Batch	60	24	α-alumina tubular	1μm zeolite A	6	5*	70	1.67	>10000	36
$N_{50}A_1S_5H_{1000}$	Batch	60	1-24	α-alumina tubular	1μm zeolite A	14	5*	70	1.12	5289	53
$N_{41.9}A_1S_{4.4}H_{833.3}$	Batch	80	4	TiO_2 disc	-	3.5	5	45	0.86	54000	38

*The used mixture in pervaporation is isopropyl alcohol (IPA) - water; others are all ethanol-water mixture

Table 2.1 Pervaporation performances of zeolite A membranes for organic/water separation (especially for ethanol/water mixture)

SYNTHESIS							PERVAPORATION				
Comp.	**Type**	**T (°C)**	**Duration (h)**	**Support**	**Seed**	**Membrane Thickness (μm)**	**Xwater (wt.%)**	**T (°C)**	**Flux kg/m²h**	**S.F.**	**Ref.**
$N_{3.6}A_1S_{1.8}H_{270}$	Batch	100	3	α-alumina tubular	1μm zeolite A	7-10	9	93	2.5	130	40
$N_{3.9}A_1S_{1.8}H_{273}$	Semi-cont.	90	5	α-alumina tubular	1μm zeolite A	10	10	125	3.8	3600	3
$N_{3.16}A_1S_{1.93}H_{128}$	Batch 4 cycle	100	3	mullite tubular	1μm zeolite A	3.5	10	25	0.68	10000	54
$N_{2.1}A_1S_2H_{120-400}$	Batch	100	3	α-alumina tubular	2μm zeolite A	30	8	50	0.5	600	55
$N_{3.9}A_1S_{1.8}H_{270}$	Semi-cont.	90-100	5	α-alumina tubular	2μm zeolite A	30	10	50	0.5	16000	4
$N_{3.9}A_1S_{1.8}H_{270}$	Cont.	80-100	7	TiO_2 tubular	2μm zeolite A	30	8	50	0.9	8500	11
$N_2A_1S_4H_{120}$	Batch	80-100	4-24	α-alumina tubular	NA zeolite A	5	5	50	1.5	>10000	56
$N_{49}A_1S_5H_{980}$	Flow 2 cycle	80	8	α-alumina tubular	1- 2 μm zeolite A	3	8	45	0.14	3700	12

*The used mixture in pervaporation is isopropyl alcohol (IPA) - water; others are all ethanol-water mixture

Table 2.1 Pervaporation performances of zeolite A membranes for organic/water separation (especially for ethanol/water mixture)

SYNTHESIS							PERVAPORATION				
Comp.	**Type**	**T (°C)**	**Duration (h)**	**Support**	**Seed**	**Membrane Thickness (μm)**	**Xwater (wt.%)**	**T (°C)**	**Flux kg/m²h**	**S.F.**	**Ref.**
$N_{49}A_1S_5H_{980}$	Batch 2 cycle	85	3.5	α-alumina tubular	-	6	5	45	0.23	12500	57
$N_2A_1S_2H_{150}$	Batch	100	4	α-alumina tubular	<1μm zeolite A	4	10	75	5.6	10000	5
$N_2A_1S_2H_{150}$	Batch	100	4	α-alumina tubular	<1μm zeolite A	2.5	10	75	8.4	10000	58
$N_{3.16}A_1S_{1.93}H_{128}$	Batch 4 cycle	100	3	α-alumina disc	NA zeolite A	10	10*	25	1.3	5000	59
$N_{41.9}A_1S_{4.42}H_{833}$	Cont.	80	8	α-alumina tubular	-	1.7	35*	90	17	41	13
$N_{80}A_1S_9H_{5000}$	Batch 4 cycle	80	5	α-alumina disc	0.7μm zeolite A	7	10	30	0.86	54000	33
$N_{55}A_1S_5H_{1005}$	Batch	50	48	ceramesh sheet	-	4	10*	70	0.68	10000	60
$N_2A_1S_2H_{150}$	Batch	100	3.5	mullite cylindrical	<75 μm zeolite A	10	10	75	1.69	10000	30

*The used mixture in pervaporation is isopropyl alcohol (IPA) - water; others are all ethanol-water mixture

2.5.2 Factors affecting pervaporation performance of zeolite A membranes

Feed concentration and feed temperature are the main factors related with the operating conditions and that are affecting the pervaporation performance of membranes. Table 2.1 also shows the pervaporation performances of zeolite A membranes at different pervaporation conditions.

Effect of *feed concentration* to the pervaporation performance of zeolite A membranes is discussed in several studies [5, 11]. Sato et al. [5] and Pera-Titus at et al. [11] have seen that with an increase in water content of feed mixture, total flux is increased linearly and selectivity either stayed constant or increased. The increase in flux is explained by either the strong hydrophilic character of zeolite A or the water flux relation with difference of water partial pressure across the membrane. The driving force for permeation is indicated that the difference of water partial pressure across the membrane and hence it is stated that the permeation mechanism is controlled by only the water component and not affected by ethanol concentrations.

Effect of *feed temperature* on pervaporation performance of zeolite A membranes is a popular research area. Most of the studies are resulted with an Arrhenius trend for the feed temperature and flux relation. On the other hand in the case of selectivity, Sato et al. [5] reported that there is also a linear relation with temperature and selectivity and Pera-Titus at et al. [11] reported that selectivity either shows a little bit increase with an increase in feed temperature or reaches a maximum and then decreases with an increase in feed temperature. The trend is explained by that pervaporation favors high temperatures in the study of Sato et al. [5], whereas it is explained by the contribution of large defects for the linear relation case in the study of Pera-Titus at et al. [11].

Pressure difference across the membrane is the driving force for the permeation. Permeate pressure varies in the range of 0.1-0.3 kPa whereas feed pressure is usually atmospheric pressure in the literature. Thus, for this case, *permeate pressure* is practically not affecting the pervaporation performance of membranes.

For the case of *feed pressure*, pervaporation fluxes are independent of feed pressure and the pressure need only be high enough to maintain a liquid feed [31]. *Concentration polarization,* which is the feed concentration gradient occurred due to the depletion of preferentially permeating component at the membrane feed interface, may also be affecting factor for pervaporation. It can be prevented by mixing the feed solution or/and recirculating the feed solution over the membrane.

There may be some other factors such as *support material* and presence of *non-zeolitic pores* related with the intrinsic properties of the membranes. For membranes prepared on alumina supports if the alkalinity of the synthesis solution is very high, that high alkaline solution may dissolve the support and may result with membranes of low stability as happened in the study of Akbay [12]. Presence of non-zeolitic pores directly affects the permeation mechanism according to their sizes. As it is mentioned before Kondo et al. [30] proposed a new permeation mechanism for pervaporation and vapor permeation of the zeolite A membranes and this mechanism is based on very fine and narrow non-zeolitic pores. Also pure component pervaporation measurements can be a representative study to estimate the dimensions of non-zeolitic pores.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Materials for synthesis of zeolite A powders and membranes

In this study the following reactants were used in the synthesis of zeolite powder and membranes: sodium hydroxide (Carlo Erba Reagenti, NaOH %97 NaOH, 3%H_2O) as soda source, sodium aluminate (Riedel-de-Haen, 44% Na_2O, 55% Al_2O_3, 1%H_2O) or aluminum hydroxide (Merck, $Al(OH)_3$, pure) as alumina source, LUDOX AS- 40 (Aldrich, 40 wt% colloidal suspension of SiO_2 particles in water), sodium metasilicate pentahydrate (Sigma, $Na_2SO_35H_2O$) or waterglass (Merck, $0.287Na_2O:SiO_2:8.036H_2O$) as silica source, and deionized water.

3.2 Type of supports used for membrane synthesis

The membranes were prepared on two different types of porous alumina supports. These were commercial α-Al_2O_3 discs and commercial α-Al_2O_3 tubes.

Commercial α-Al_2O_3 discs, which were purchased from Inocermic, Germany had a diameter of 21 mm and a thickness of 1 mm. These discs had asymmetric structure composed of a thin ~20 μm top layer with pores 200-nm in size and a thick ~1mm macroporous body.

Commercial α-Al_2O_3 tubes, which were purchased from Inocermic, Germany had a length of 25 cm originally were cut into 4.7 cm pieces. They had an inner diameter of 0.7 cm with a wall thickness of 0.15 cm. The top layer on the inner surface has an average pore size of 200 nm. Before membrane synthesis, the tubes were cleaned by keeping in an ultrasonic bath for 10 min, washing in 0.1 M HNO_3 solution and rinsing with deionized water. The tubes were then dried at 80 °C. Both ends of the tubes were glazed with Duncan IN1001 Envision Glaze to create non-porous tips of about 1 cm. For glazing, tubes were dipped into the glaze suspension two or three times. Tubes were then dried at room temperature for a few minutes and put into the furnace to mature the glaze. The furnace was heated to 900°C with a heating rate of 1.5°C/min, kept at 900°C for one hour and then cooled with an average cooling rate of 1.5°C/min. After glazing, a tube had an effective membrane length and area of 2.7 cm and 5.9 cm^2, respectively.

3.3 Preparation of synthesis solution

There are two main steps in preparation of synthesis solution which are preparation of silicate solution and preparation of aluminate solution. Silica solution was prepared by mixing required amount of silica source and deionized water. For aluminate solution, firstly sodium hydroxide was dissolved in deionized water. After dissolving sodium hydroxide, required amount of alumina source was added and solution was heated and stirred until the alumina was totally dissolved in aqueous sodium hydroxide. Then lost amount of water because of evaporation was added. Finally aluminate solution was added to the silicate solution and they were mixed to obtain synthesis gel. According to the synthesis purpose synthesis gel was mixed by stirring vigorously at room temperature for an hour to 24 hours.

Throughout this study different reactants were used as silica and alumina sources in the synthesis of zeolite powder and membranes. Amount of reagents used for the preparation of 100 g batch with all compositions used in this study are listed in Table 3.1.

Table 3.1 Amount of reagents used for the preparation of 100 g batch with all compositions used in this study

Composition	REAGENTS						
	Aluminum hydroxide	**Sodium Aluminate**	**Sodium Metasilicate pentahydrate**	**LUDOX (AS 40)**	**Waterglass**	**Sodium hydroxide**	**Deionized water**
$N_{2.5}A_1S_{1.7}H_{150}$	-	5.69	-	8.34	-	3.68	82.29
$N_{2.5}A_1S_{1.7}H_{150}$	5.20	-	-	-	12.50	5.30	77.00
$N_{3.4}A_1S_2H_{155}$	4.84	-	-	-	13.80	7.23	74.13
$N_{3.4}A_1S_2H_{155}$	4.84	-	13.15	-	-	3.58	78.43
$N_{3.4}A_1S_2H_{155}$	5.07	-	-	4.88	-	9.13	80.92
$N_{3.4}A_1S_2H_{200}$	3.87	-	-	-	11.03	5.78	79.32

N: Na_2O, A: Al_2O_3, S: SiO_2, H: H_2O

3.4 Seed synthesis

In the synthesis of seed crystals LUDOX as silica source, sodium aluminate as alumina source, sodium hydroxide as soda source and deionized water were used. Amount of reagents used for the preparation of 100 g batch are given in Table 3.1. The solution was prepared according to the procedure given in Section 3.3. Synthesis gel was aged by stirring vigorously at room temperature for 24 hours.

3.4.1 Synthesis procedure and product recovery

Synthesis was carried out in flow system where solution was recirculated into 250 ml glass flask at 95°C for 3 hours. The schematic drawing of the system is given in Figure 3.1.

The product in the glass flask was filtered and washed with water until pH became less than 8. Then the powder was dried at 80 °C overnight. The dried powder was analyzed with XRD for phase identification. Then the powder was used to prepare seed suspension in which zeolite A powder was mixed with deionized water (0.5 wt% zeolite A suspension). To increase dispersion and homogeneity and to prevent the settling of the seed crystals in the seed suspension, it was stirred for overnight, kept in ultrasonic bath for 10 min and then stirred again for 30 min.

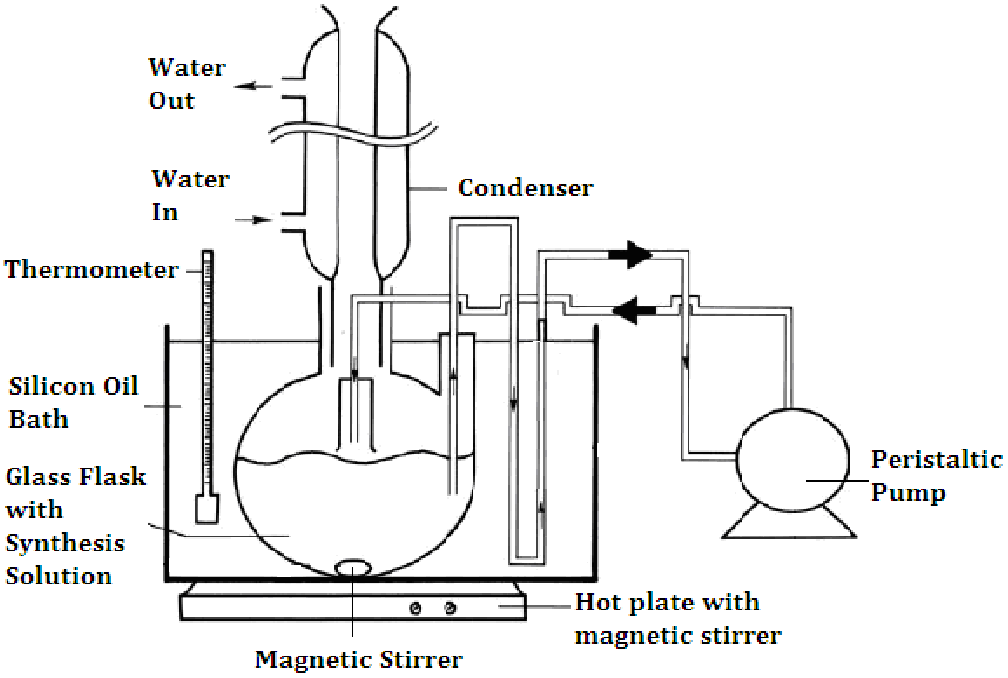


Figure 3.1 Schematic drawing of flow system (for powder synthesis) used in seed synthesis

3.4.2 Determination of percent crystallinity for powder

The dried products were weighed to determine percent yield. Maximum yield was defined as the amount which would be obtained if all silica in the synthesis solution was precipitated as product. The calculation of maximum yield is given in more detail in Appendix C.

Percent crystallinity of the samples was defined based on the twelve characteristic peaks of zeolite A at Bragg angles that shown with asterisks in Figure 3.2.

Among all the samples obtained, the one in which the sum of the diffraction intensities of these twelve peaks was highest was determined as the reference with 100% crystallinity and the crystallinity of others were obtained accordingly. The determined reference sample has higher crystallinity than the commercial zeolite A powder.

Thus, percent crystallinity was calculated as follows;

$$\% \, Crystallinity = \frac{\sum_{i=1}^{12} I_i}{\left(\sum_{i=1}^{12} I_i\right)_{ref}} \times 100 \qquad 3.1$$

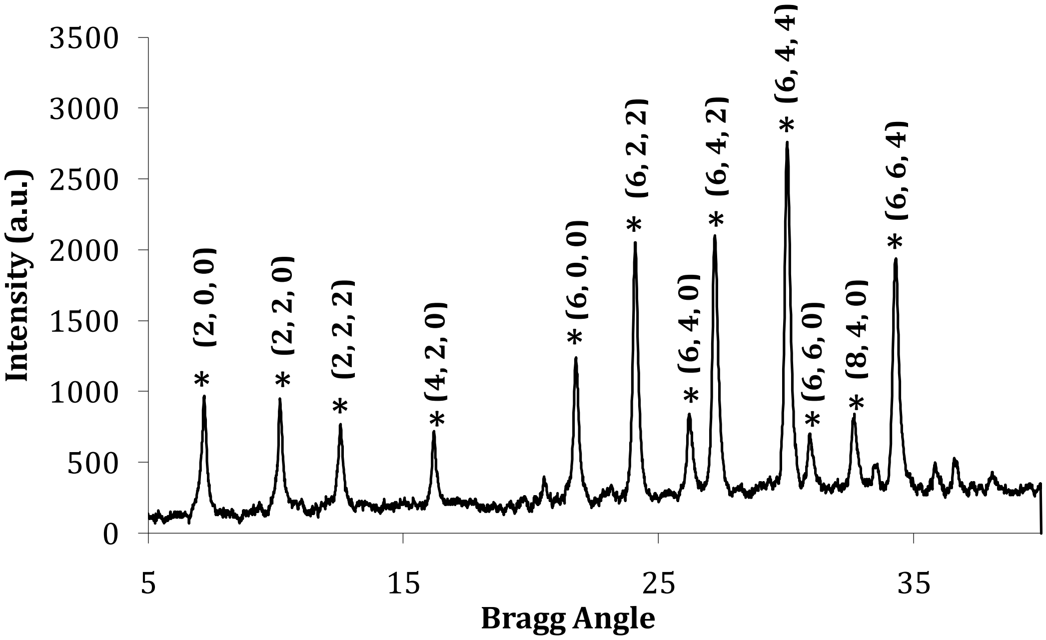


Figure 3.2 The XRD pattern of zeolite A and the twelve characteristic peaks used in percent crystallinity calculation ((h,k,l) index are also given in ICDD PDF card (39-0222) of zeolite A in Appendix D)

3.5 Seeding of the supports

Three different seeding methods were used to investigate the effect of seeding technique on membrane performance and morphology in batch system. The seeding techniques used were rubbing wiping, dip-coating wiping and vacuum seeding wiping. Also pore-filling seeding method was used for the membranes prepared in modified flow system.

In the rubbing method, zeolite A powder was rubbed to the surface of the discs by the help of a brush.

In the dip-coating method, alumina discs were immersed in and withdrawn from seed suspension in about 10 seconds and the procedure was repeated twice for each disc. The seed suspension was a 0.5 wt% aqueous suspension of zeolite A, which was synthesized as explained in Section 3.3.

In the vacuum seeding method, disc was sealed inside the rubber gasket and then placed between two polyamide dies and screws were used to hold disc. Then 0.4 mL seed suspension was poured on the disc and vacuum pump is used to get water in the suspension. Since the size of the seed crystals were larger than the pore sizes of disc, they could not penetrate into pores of disc. They coated the support surface. The seed suspension was a 0.25 wt% aqueous suspension of zeolite A, which was synthesized as explained in Section 3.3.

The seed coated discs were kept at 60 °C for overnight to adhere the seed crystals on the support and then wiped by hand with a Latex glove to improve the uniformity of the coating.

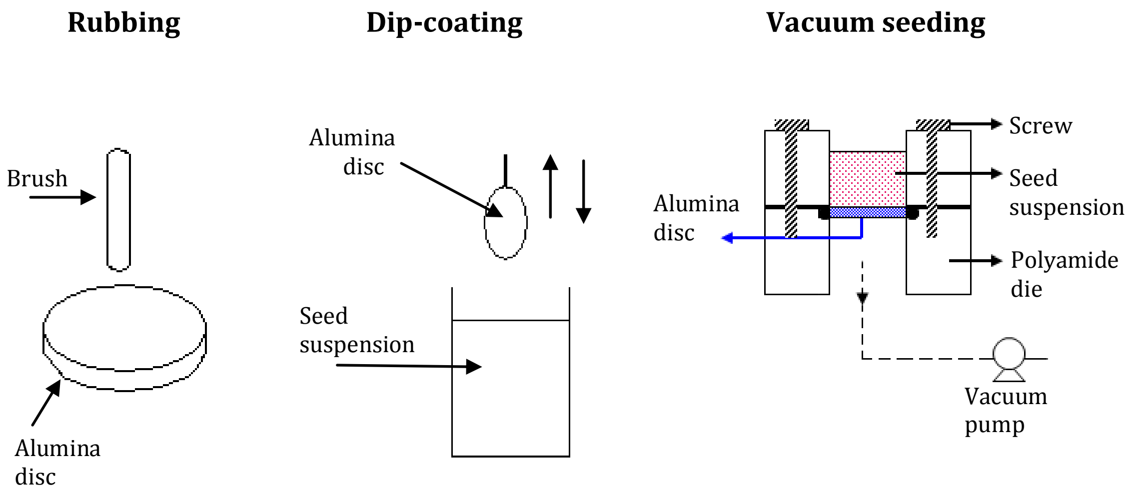


Figure 3.3 Schematic drawing of the seeding setups that were used in batch system in this study

The α-alumina tubular supports were also seeded with pore-filling method. In this method, the lumen of the tubular support was filled with seed suspension. Then the seed suspension was sucked by the alumina support and the water passed from support's pores. The passed water was flown out from the lumen to the outside. When the solution in the lumen was finished, the support was dried firstly at 80 °C for 1 hour and secondly at 130 °C for 2 hours. After drying, the support was cooled to room temperature and the tubular support's position is changed in the vertical direction and the filling with seed suspension and the other procedures are repeated for this side. The seed suspension was a 0.56 wt% aqueous suspension of zeolite A, which was synthesized as explained in Section 3.3.

3.6 Synthesis of zeolite A membranes

3.6.1 Synthesis in batch system

Zeolite A membranes were synthesized in autoclaves on alumina supports from two different gel compositions and three different silica sources to see the effect of composition and silica source on membrane performance and morphology. These compositions were, $2.5Na_2O:1Al_2O_3:1.7SiO_2:150H_2O$ and $3.4Na_2O:1Al_2O_3:2SiO_2:155H_2O$ and these silica sources were sodium metasilicate pentahydrate, silica sol (LUDOX) and waterglass. Amount of reagents used for the preparation of 100 g batch from every compositions are listed in Table 3.1. The synthesis solutions were prepared according to the procedure given in Section 3.3. Synthesis gel was aged by stirring vigorously at room temperature for one hour.

3.6.1.1 Synthesis procedure and product recovery

Zeolite A membranes were synthesized in stainless steel autoclaves with 30 mL Teflon flasks in it. The supports were placed vertically inside the flasks with a Teflon holder. Synthesis solution was poured into autoclaves for the synthesis. The synthesis was carried out at 95 °C for 4 hours. Synthesized membranes were washed with distilled water until pH was around 7 and they were dried at room temperature for one day. Also powder synthesized during membrane formation was centrifuged and washed with distilled water.

3.6.1.2 Determination of peak ratio of a membrane

A peak ratio was calculated using the strongest zeolite A peak at 30° Bragg angle together with the strongest alumina peak at 35.2° Bragg angle as shown in Equation 3.3 to compare the membranes quantitatively.

$$\text{Peak ratio}=\frac{I_{\text{LTA strongest}}}{I_{\text{alumina strongest}}+I_{\text{LTA strongest}}} \qquad 3.2$$

where, I=intensity

Peak ratio is proportional to the crystallinity of the membrane layer and amount of zeolite forming the membrane. If the support surface is covered with a thick, highly crystalline zeolite A layer, the peaks corresponding to zeolite A would be stronger than the peaks corresponding to alumina hence the peak ratio will be high. So peak ratio varies between 0, indicating amorphous layer or very thin zeolite A layer on the support, and infinity, indicating very thick zeolite A layer which hinders the alumina peaks. Therefore the peak ratio indicates quantitative information about thickness of the membrane which helps us to compare the membranes.

3.6.2 Synthesis in flow system

Zeolite A membranes were synthesized on alumina supports from the gel with a molar composition of $3.4Na_2O$:1 Al_2O_3:$2SiO_2$:$155H_2O$. Amount of reagents used for the preparation of 100 g batch are given in Table 3.1. The synthesis solution was prepared according to the procedure given in Section 3.3. Synthesis gel was aged by stirring vigorously at room temperature for one hour. Synthesis of membranes was carried out in a flow system where the synthesis solution was recirculated with a flow rate of 4 mL/s through the supports. The schematic drawing of the system is given in Figure 3.4.

The synthesis solution was kept in the reactor, which is a 30 mL glass flask, with three entries for the condenser, for the entering stream and for the exiting stream. The membrane was held vertically inside the glass flask with a Teflon holder as shown in Figure 3.4.

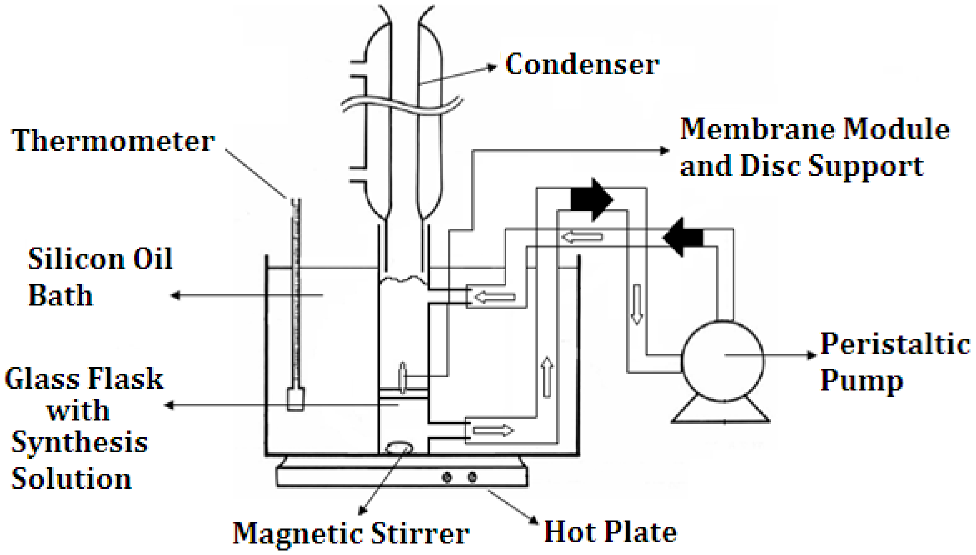


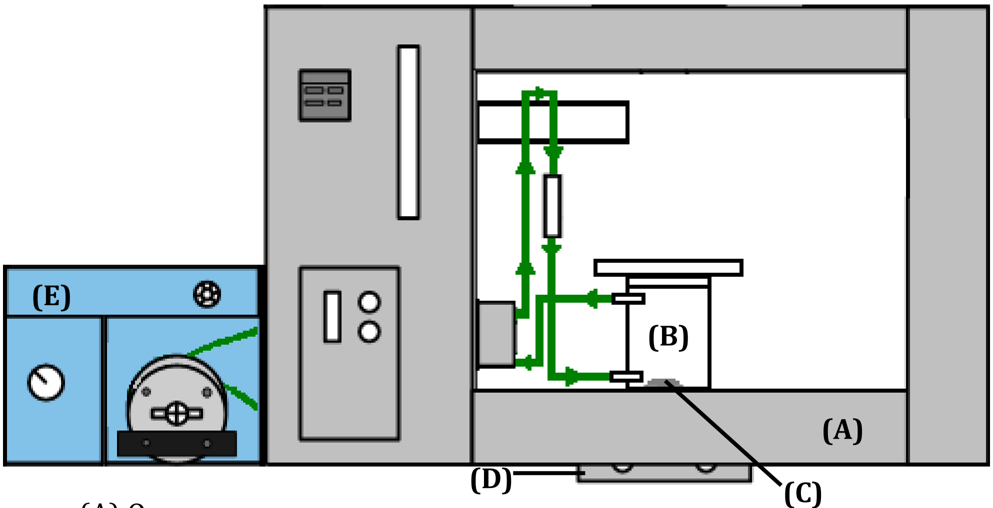
Figure 3.4 Schematic drawing of flow system setup

The lines between the reactor and the peristaltic pump were Platinum-cured silicon tubings (Cole-Parmer). The Platinum-cured silicon tubings were used because they are resistant to high temperature (230 °C) and to high alkalinity. Recirculation with a flow rate of 4 mL/s was provided by means of a peristaltic pump, which was placed between the entering stream and the exiting stream of the reactor. The reactor and the line in between the entering stream and the exiting stream were kept in a silicone oil bath kept at the synthesis temperature (Figure 3.4). During the synthesis, the temperature was measured from inside the oil bath. The oil bath was heated with the magnetic stirrer-heater that it was placed on. The synthesis solution in the reactor was stirred mildly. The detailed information for the flow system has been reported in the study of Çulfaz et al. [9, 61]. The synthesis was carried out at 95 °C for 4 hours. Synthesized membranes were washed with distilled water until pH was around 7 and they were dried at room temperature for one day. Also powder synthesized during membrane formation was centrifuged and washed with distilled water.

3.6.3 Synthesis in modified flow system

Zeolite A membranes were synthesized on the inner side of the tubular α-alumina supports from the gel with a molar composition of $3.4Na_2O:1\ Al_2O_3:2SiO_2:200H_2O$ in recirculating flow system. The schematic drawing of the system is given in Figure 3.5. The α-alumina tubular supports seeded with pore-filling method. Amount of reagents used for the preparation of 100 g batch are given in Table 3.1. The synthesis solution was prepared according to the procedure given in Section 3.3. Synthesis gel was aged by stirring vigorously at room temperature for one hour.

The synthesis solution was kept in the reactor, which is a 100 mL teflon flask, with two entries for the entering stream and for the exiting stream. The membrane was held vertically inside the silicon tubings as shown in Figure 3.5.



(A) Oven
(B) Teflon flask containing synthesis solution
(C) Magnetic stirrer
(D) Hot plate with magnetic stirrer
(E) Peristaltic pump

Figure 3.5 Schematic drawing of modified flow system setup

The lines between the reactor and the peristaltic pump were Platinum-cured silicon tubings (Cole-Parmer). The Platinum-cured silicon tubings were used because they are resistant to high temperature (230°C) and to high alkalinity. Circulation with a flow rate of 4 mL/s was provided by means of a peristaltic pump, which was placed between the entering stream and the exiting stream of the reactor. The reactor and the line in between the entering stream and the exiting stream were kept in an oven kept at the synthesis temperature (Figure 3.5). During the synthesis, the temperature was controlled by the oven controller. A magnetic stirrer-heater was installed below the oven. The synthesis solution in the reactor was stirred mildly. The detailed information for the flow system has been reported in the study of Çulfaz et al. [9, 61]. The synthesis was carried out at 95 °C for different hours. Synthesized membranes were washed with distilled water until pH was around 7 and they were dried at room temperature for one day. Also powder synthesized during membrane formation was centrifuged and washed with distilled water.

3.6 Characterization of the zeolite powders and membranes

3.6.1 Phase identification

Phase identification was done by Philips PW 1729 X-Ray Diffractometer. The powder samples were analyzed by using depression mounts. However when the powder amount was not enough to fill the depression mount, powders were analyzed by preparing smear slides. Membrane surface of the discs were analyzed by mounting the membranes on glass slides without breaking. Membrane surface of the tubes were analyzed by cracking the tubes to pieces and then mounting them on glass slides. Operating conditions of the X-ray diffractometer was given in Table 3.2.

Table 3.2 Operating conditions of X-ray diffractometer

	For powder	For membranes
Tube	Cu	Cu
Filter	Ni	Ni
Radiation	CuKα	CuKα
Voltage (kV)	30	40
Current (mA)	24	30
Speed (°2Θ/s)	0.1	0.1
Time constant (s)	1	1
Slit (mm)	0.2	0.2

In the analysis of membranes, in order to strengthen the signals, the operating voltage and the current were increased to 40 kV and 30 mA, respectively.

3.6.2 Determination of membrane morphology

Morphology of the membranes was determined by JEOL JSM-6400 Scanning Electron Microscope. The accelerating voltage was 30 kV. The samples were coated with palladium-gold before analysis.

3.6.3 Determination of particle size

Particle size of the powder samples was determined by Malvern MasterSizer 2000 Particle Size Analyzer. Specifications for this equipment were given in Table 3.3. For particle size analysis, approximately 2-3 ml of sample withdrawn from the autoclave or glass reactor was put in a glass flask and diluted with water. The diluted mixture was ultrasonicated for 10 minutes to break down the agglomerates and to distribute the crystals uniformly. The particle size analyzer has also an ultrasonication unit, which aims to prevent any agglomeration of the crystals during the analysis.

Table 3.3 Specifications for the particle size analyzer

Equipment	Malvern MasterSizer 2000
Size Range	0.02 to 2000 microns (depending on material properties)
Measurement principle	Mie scattering
Detection system	Red light: Forward scattering, side scattering and back scattering. Blue light: Wide angle forward and back scattering.
Light sources	Red light: Helium neon laser. Blue light: Solid state light source.

3.6.4 Pervaporation measurements

Pervaporation measurements were carried out with a small, simple and flexible system as shown in Figure 3.6. The system consists two parts, feed and permeate side. Feed tank, membrane and heater/stirrer with a thermocouple form the feed side of the system. One collector placed in nitrogen filled flask, pressure gauge, vacuum trap and vacuum pump form the permeate side of the system. The collector was used to accumulate the permeating samples, vacuum pump was used to provide driving force for permeation and vacuum trap was used to capture the permeating vapor escaped from the collector. Samples were condensed by liquid nitrogen filled flasks. Permeate side was kept at 0.37 kPa absolute in all measurements. The pressure at the permeate side was measured with a pressure gauge placed after the collector. Feed side was at 1 bar. Ethanol-water mixture of 10 wt% organic was separated by this pervaporation system.

All piping in feed and permeate sides were stainless steel. Glass containers were connected to each other with stainless steel ultra-torr Cajon fittings which are resistant to high vacuum.

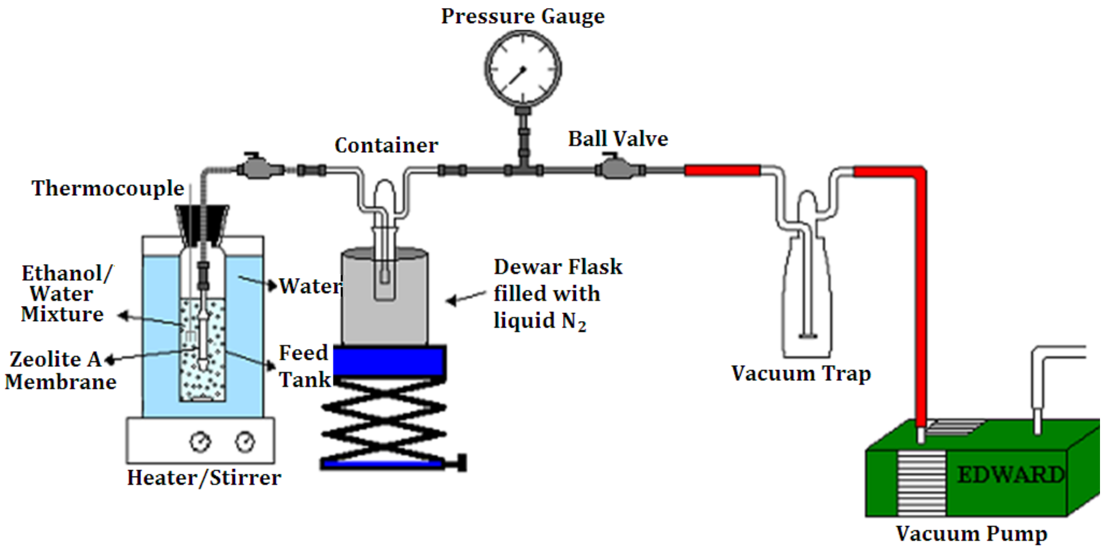


Figure 3.6 Schematic drawing of pervaporation setup

The membranes were stuck to glass tube with silicone and then put into a glass container which was filled with feed mixture. By this way system allows to mount membranes with different geometries and dimensions to the system only by modifying the dimensions of the glass connection tubes. The glass container has a volume of 600 mL and its diameter was 3.5 cm. The feed container was kept at constant temperature by a water bath and it was also put on a magnetic heater/stirrer with a thermocouple to keep temperature and concentration of the feed mixture uniform.

For the membranes prepared in modified flow system pervaporation set-up was also modified. A tubular module was installed just before the container and feed mixture was circulated around the membrane module by means of a peristaltic pump with a flow rate of 141 mL/min; other parts were the same and the modified pervaporation system is shown in Figure 3.7.

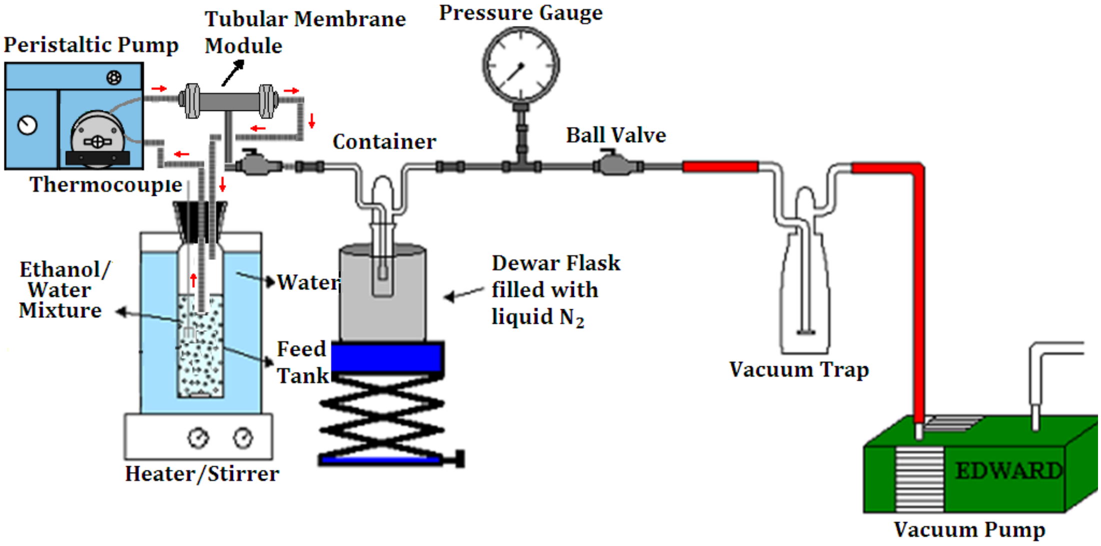


Figure 3.7 Schematic drawing of modified pervaporation setup that were used for the membranes prepared in modified flow system

To start the pervaporation measurements, first membrane was connected to the system and put in the feed container. Then vacuum was established at the permeate side. When the pressure gauge reads 0.37 kPa absolute and when the water bath at the specified operation temperature liquid N_2 was poured to the flask. Then sample collection was started by opening the valve which was placed before the collector. The time required for collecting the permeate sample depended on membranes flux. Six or seven hours of operation for each sample was usually enough to collect an appreciable amount. When the sample was collected, permeate side was opened to atmosphere.

Leak tests were performed under vacuum before beginning the pervaporation experiments and repeated once in every week to make sure that the system works properly. In these tests, the first valve was closed and then the vacuum pump was operated for 1-2 hours, the last valve was closed, and the pump was closed. Therefore all the permeate side was kept under vacuum. Any leak in the system could be detected by an increase in the permeate pressure. The system was left under vacuum overnight to make sure that no leak was present in the system.

The permeate samples were weighted and analyzed with HP 5890 Series II Gas Chromatograph with a Porapak T Column and a thermal conductivity detector and analyzed with a refractometer. Nitrogen gas was used as the carrier gas when analyzing in GC. The operating parameters of the gas chromatograph are given in Table 3.4. For all the membranes flux and selectivity was determined to compare the performances.

Table 3.4 Operating conditions for the gas chromatograph

Column	Porapak T
Column Temperature	150 °C
Detector	TCD
Detector Temperature	180 °C
Injector Temperature	170 °C
Column Head Pressure	30 psi
Reference flow rate	30 mL/min

In this analysis calibration curve was plotted. Manual injections of 1 μl sample were performed and calculated peak areas were compared with the areas in the calibration curve to determine percentage of ethanol and water in the sample.

There are refractive index values for ethanol-water mixtures of different compositions at 20 °C that taken from literature which are given in Appendix E. In the refractometer measurements 3-5 drops of permeate sample were put on the refractometer and the refractive index value was read. For this reading ethanol-water composition was determined with the help of data available.

The flux of the membranes were calculated by simply measuring the amount of permeate collected in a certain time. The calculation of separation factor and flux is given in literature survey part.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthesis of zeolite A seed crystals

Seed crystals were synthesized from $2.5Na_2O$: $1Al_2O_3$: $1.7SiO_2$: $150H_2O$ hydrogel at 95°C in a recirculated flow system. Before the synthesis, the hydrogel was aged for 24 hours at room temperature. During the synthesis 10 mL samples were taken from 250 mL glass flask at different times to observe crystallinity change versus time. The samples were centrifuged, washed, dried and analyzed by XRD to identify the phase and determine percent crystallinity.

The solid product obtained after 3 hours were pure zeolite A. The product synthesized at 95 °C in a recirculated flow system for 3 hours was used as seed. XRD pattern of the seed powder synthesized in flow system at 3 hours is given in Figure 4.1.

Figure 4.2 shows the percent crystallinity with respect to time for the products obtained in flow system. Percent crystallinity increases in an S-shaped curve and crystallization ends at nearly 3 hours at a maximum percent crystallinity of 98%.

Figure 4.3 shows the SEM micrographs of zeolite A seed crystals. The cubic zeolite A crystals are seen and their sizes are in the range of 0.2-0.5 μm. Figure 4.4 also shows the particle size distribution of zeolite A seed crystals. Because of the agglomerates, particle sizes of seed crystals are in the range of 0.15-2 μm.

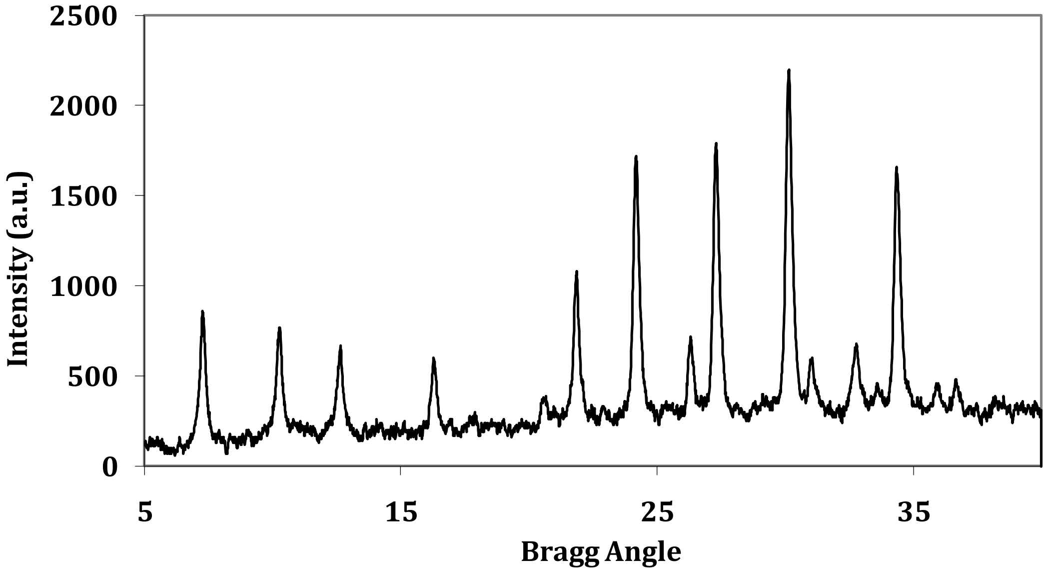


Figure 4.1 The XRD pattern of the zeolite A seed crystals synthesized in the flow system from a batch composition of $2.5Na_2O$: $1Al_2O_3$: $1.7SiO_2$: $150H_2O$ at 95 °C for 3h (BA-33)

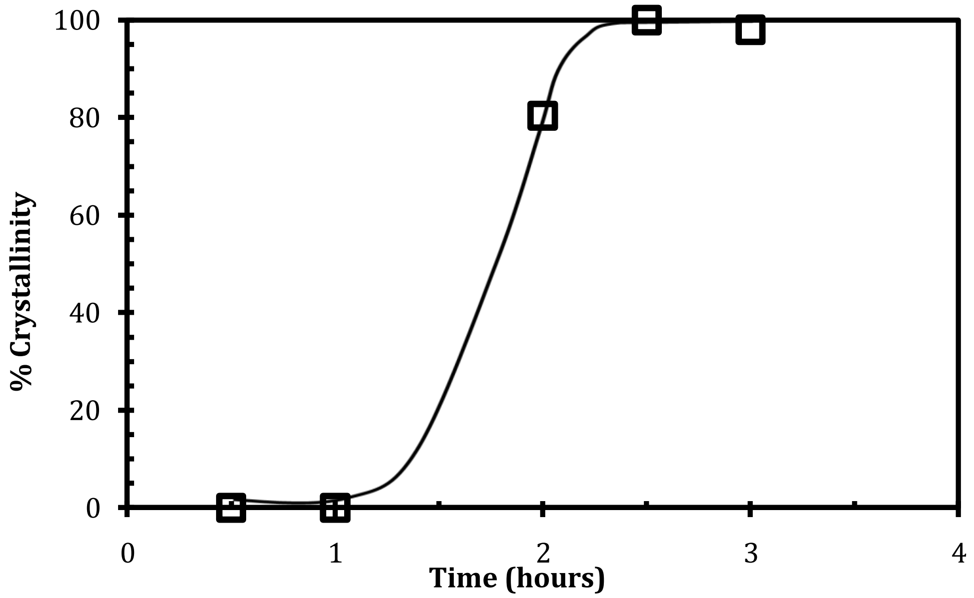


Figure 4.2 Percent crystallinity (□) with respect to time for the products obtained in flow system from a batch composition of $2.5Na_2O$: $1Al_2O_3$: $1.7SiO_2$: $150H_2O$ at 95 °C

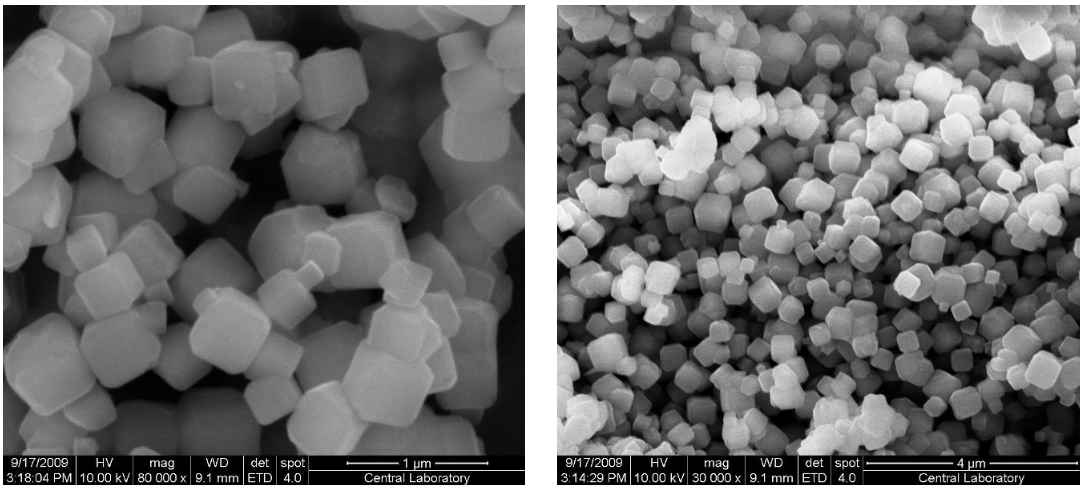


Figure 4.3 SEM micrograph of zeolite A seed crystals synthesized in the flow system from a batch composition of $2.5Na_2O: 1Al_2O_3: 1.7SiO_2: 150H_2O$ at 95 °C for 3h (BA33)

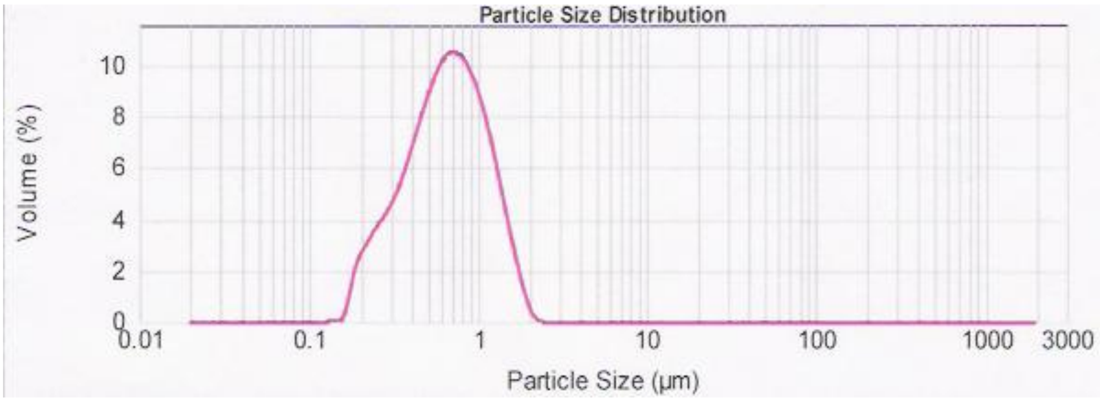


Figure 4.4 Particle size distribution of zeolite A seed crystals synthesized in the flow system from a batch composition of $2.5Na_2O: 1Al_2O_3: 1.7SiO_2: 150H_2O$ at 95 °C for 3h (BA33)

4.2 Seeding of support surfaces

Zeolite NaA membranes have been traditionally synthesized in autoclaves by using either a milky-like gel or a clear solution onto the surface of a porous support with or without a previous seeding step [2, 5, 41, 62, 63]. The seeding of the support has been indicated to enhance the reproducibility in the synthesis of zeolite membranes [32, 33, 64-67] by decoupling the nucleation and crystal growth steps.

Rubbing, dip-coating and vacuum seeding are the most widely used seeding techniques. These three different seeding methods were used to investigate the effect of seeding technique on membrane performance and morphology. The only added step was wiping the membranes after seeding. In a recent study wiping has been reported to improve the uniformity of seeding and hence high performance membranes have been synthesized reproducibly [37]. The seeding techniques used were rubbing wiping, dip-coating wiping and vacuum seeding wiping.

The SEM micrographs of the seeded supports are shown in Figure 4.5. The SEM micrographs of the supports seeded with dip-coating wiping and the supports seeded with vacuum seeding wiping are very similar to each other. The surfaces of the supports are nearly completely covered by cubic, 0.2-0.5 μm sized zeolite A crystals. As the top layer on the asymmetric support has an average pore size of 200 nm, the 0.2-0.5 μm sized seeds coated the top layer mostly by deposition on the surface.

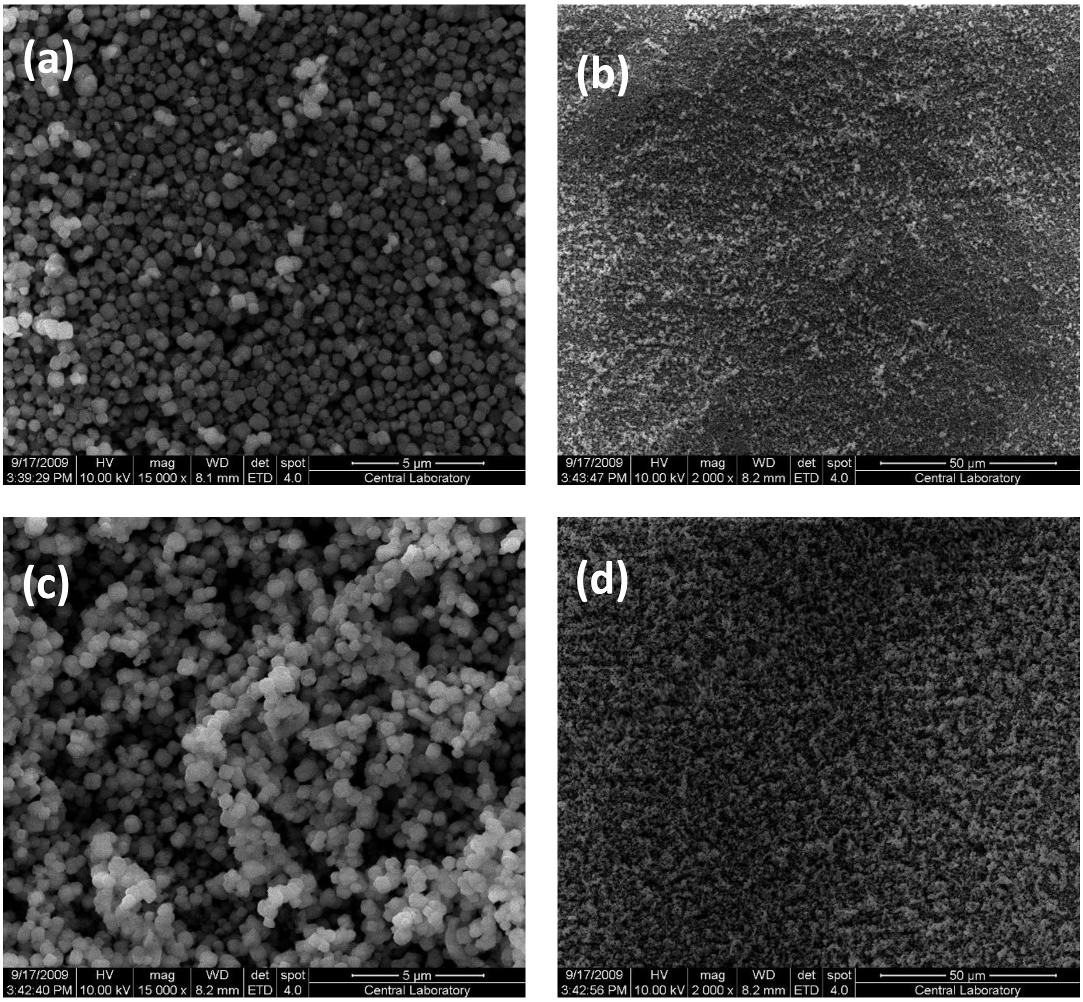


Figure 4.5 Surface SEM images of the seeded alumina supports with different methods (a), (b): dip-coating wiping; (c), (d): vacuum seeding wiping

4.3 Synthesis of zeolite A membranes in batch system

Three different experimental synthesis parameters were investigated with zeolite A membranes synthesized in batch system. These parameters were starting synthesis solution composition, silica source and seeding technique. The pervaporation performances of the synthesized membranes were also determined and used as a criterion to decide the better synthesis conditions. The aim for the different types of batch synthesis was to adapt the better synthesis conditions to be used in flow system.

After determination of better conditions for flow system in terms of these three parameters, zeolite A membranes were synthesized at these obtained conditions in flow system. The effects of these parameters on the membrane properties are explained in the following sections.

Some preliminary studies were done in order to choose a starting synthesis composition. Zeolite A membranes were synthesized in autoclaves from two different gel compositions. These compositions are, $2.5Na_2O:1Al_2O_3:1.7SiO_2:150H_2O$ (BA44-BA67, BA88-BA91) and $3.4Na_2O:1Al_2O_3:2SiO_2:155H_2O$ (BA68-BA87, BA92-95). The membranes were synthesized at 95 °C for 3-8 hours in autoclaves. The synthesis conditions of all membranes are given in Appendix L. Most of the membrane synthesis trials with the $2.5Na_2O:1Al_2O_3:1.7SiO_2:150H_2O$ composition were resulted either not selective membranes or low performance membranes. Slightly selective membranes (BA64, etc.) were compared with the membranes prepared from $3.4Na_2O:1Al_2O_3:2SiO_2:155H_2O$ (BA84, BA92) and the results were given in Appendix A.

As a conclusion with both the starting compositions, as evaluated with the XRD patterns (Figure A.1, Figure A.2) and SEM images (Figure A.3, Figure A.4), a continuous and uniform zeolite A membranes were synthesized whereas only the membranes synthesized from $N_{3.4}A_1S_2H_{155}$ composition have high selectivities in terms of pervaporation measurements (Table A.1). So it was decided to use $N_{3.4}A_1S_2H_{155}$ composition to synthesize zeolite A membranes from now on.

4.3.1 Effect of silica source and seeding technique on membrane properties

Zeolite A membranes were synthesized in autoclaves on alumina supports from the hydrogel with a molar composition of $3.4Na_2O:1Al_2O_3:2SiO_2:155H_2O$. The synthesis solution was prepared from three different silica sources and α-alumina supports were seeded with three different techniques to see the effect of silica source and seeding technique on membrane performance and morphology. The used silica sources were sodium metasilicate pentahydrate, silica sol (LUDOX) and waterglass. The seeding techniques used were rubbing wiping, dip-coating wiping and vacuum seeding wiping. Zeolite A membranes were also prepared on blank α-alumina supports to see the effect of seeding on membrane properties. All membranes were synthesized at 95 °C for 4 hours in autoclaves. The synthesis conditions of all membranes are given in Appendix L.

Many researchers indicated that the crystal phase observed in the remaining powder is recognized as the proof of the phase that forms the membrane layer [68-70]. XRD patterns of zeolite A membranes synthesized from different silica sources and seeded with different techniques are shown in Figure 4.6a. XRD patterns of the membranes synthesized from sodium metasilicate and waterglass showed that the crystal phase formed on the supports was highly crystalline zeolite A. All zeolite A peaks at Bragg angles of 7°, 10°, 12.5°, 16.1°, 21.5°, 24°, 26.1°, 27.2°, 30°, 30.8°, 32.5° and 34.3° are clearly observable in these XRD patterns of the membranes. However in the XRD patterns of the membranes synthesized from silica sol. (LUDOX) zeolite A peaks are very weak compared to alumina support peaks which is the indication of that there is no zeolite A layer on the support or there is very thin layer on the alumina support. Also peak ratios for the membranes synthesized from different silica sources are different (Table 4.1). Membranes synthesized sodium metasilicate have highest peak ratios and membranes synthesized from LUDOX have lowest peak ratios. Ordering is same for the membrane thicknesses since peak ratio and membrane thickness are proportional to each other. And in the case of the remaining powders from the synthesis of membranes XRD patterns showed that the crystal phase of the powders in all synthesis including LUDOX was highly crystalline zeolite A (Figure 4.7).

XRD patterns of zeolite A membranes prepared on blank α-alumina supports and remaining powders of those membranes are shown in Figure 4.6b. Patterns of the membranes prepared on blank α-alumina supports showed that zeolite A peaks even the stronger ones were not visible which means that there is no zeolite layer on the support or there is very thin layer on the support. Peak ratios (Table 4.1) of these membranes are also very low (0.036-0.042) due to the lack of a continuous zeolite A membrane. The SEM cross-section and surface images of the membranes prepared on blank α-alumina supports are shown in Figure 4.8. Cross-section images show that there is no continuous zeolite A layer on the support and surface images also show that there are very few zeolite crystals on the support which are partly covered the support surface.

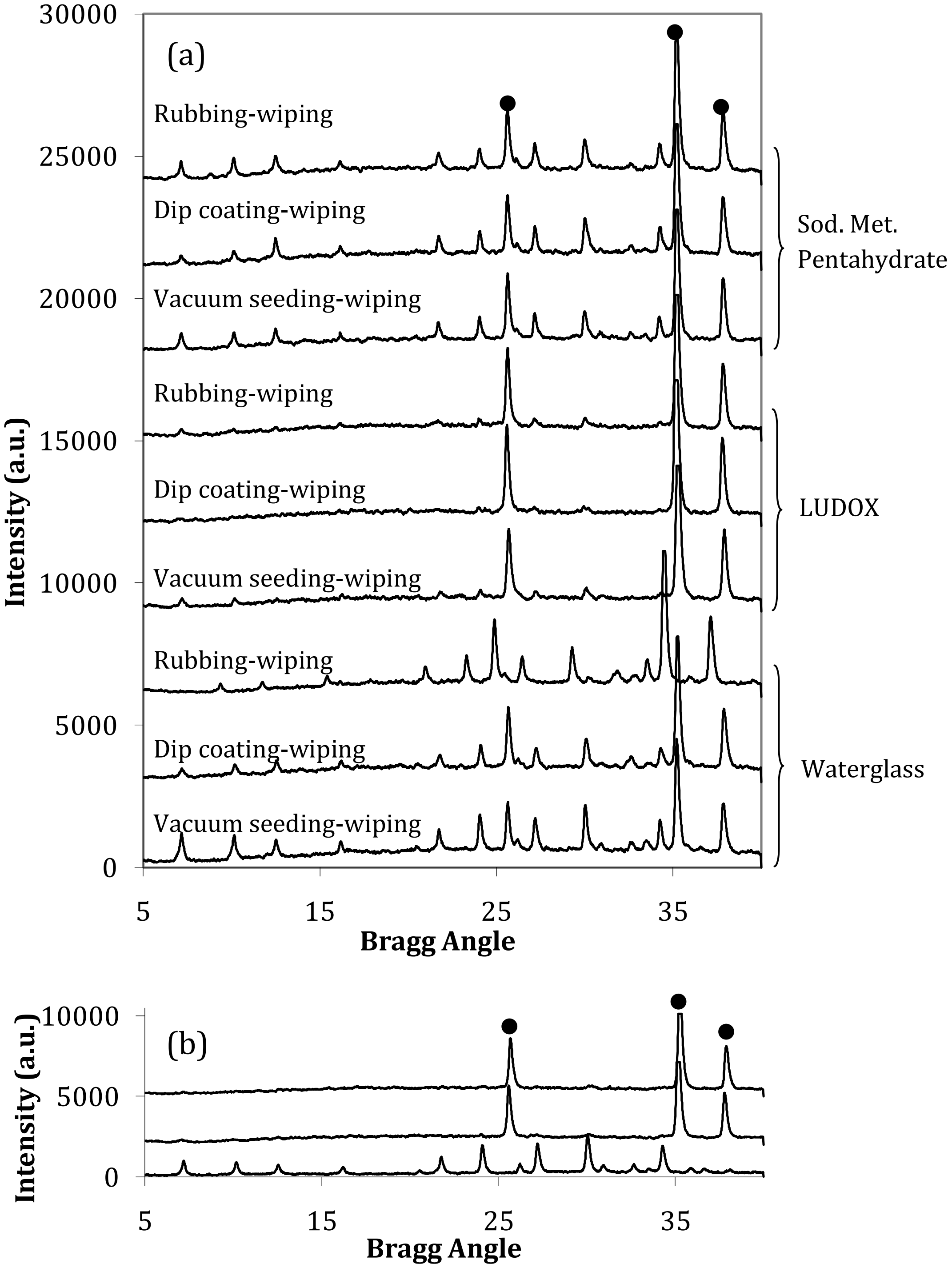


Figure 4.6 XRD patterns of (a) zeolite A membranes synthesized from three different silica sources and seeded with three different techniques (b) zeolite A membranes (BA128-BA129) prepared on blank α-alumina supports and remaining powders of those membranes (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, 95 °C, 4h). Dots represent the α-alumina peaks and other peaks belong to zeolite A

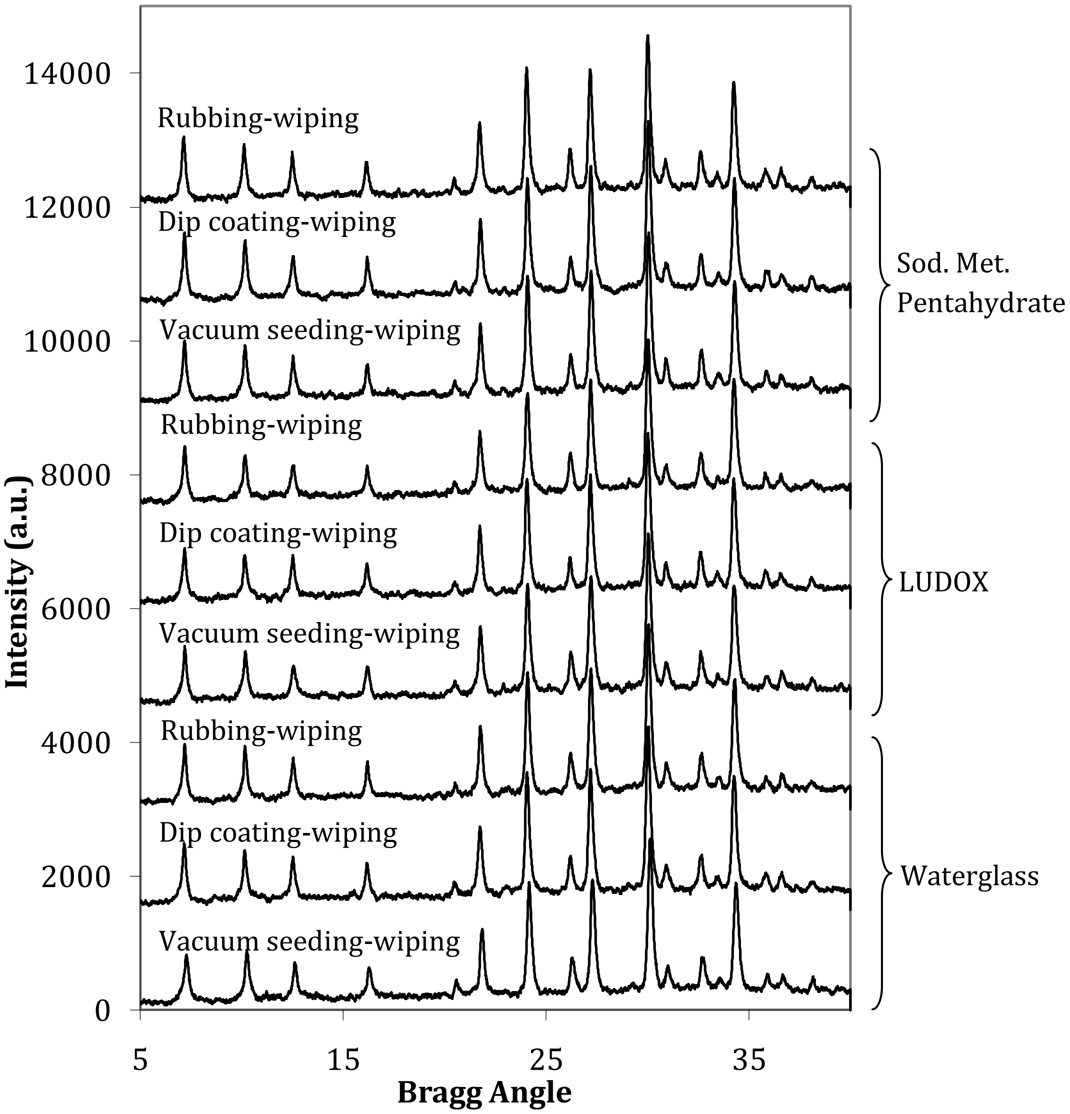


Figure 4.7 XRD patterns of the remaning powders from the synthesis of membranes prepared from three different silica sources and seeded with three different techniques (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, 95 °C, 4h).

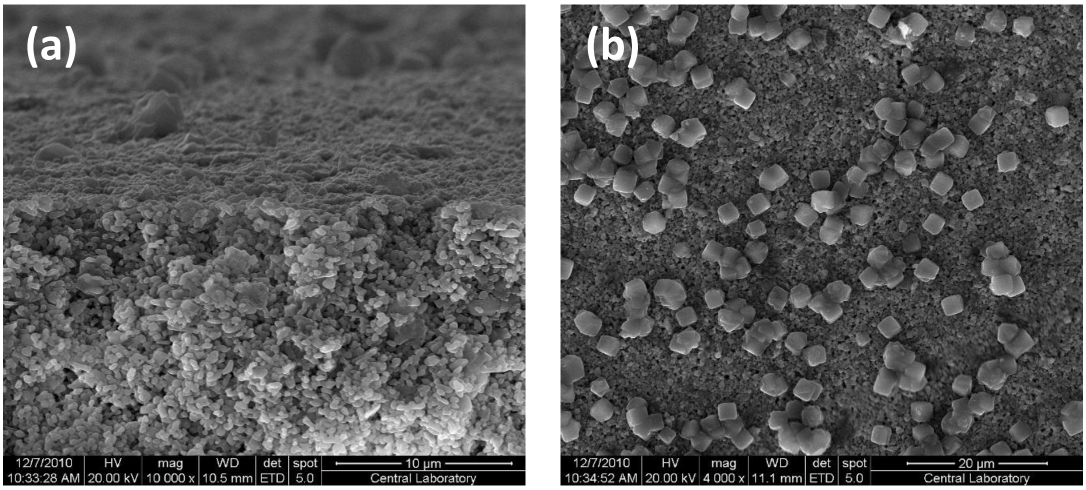


Figure 4.8 Cross-section and surface micrographs of the membrane (BA128) synthesized in batch system on blank α- alumina support. Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, 95 °C, 4h, no seeding, waterglass

The SEM cross-section images of the membranes synthesized from different silica sources are shown in Figure 4.9. The membrane thicknesses differ from one silica source to another. For instance, BA68 which was synthesized from sodium metasilicate pentahydrate has the thickness of 8.3 µm and for BA92, waterglass was used as silica source and it has the thickness of 3 µm (Figure 4.9) whereas BA78 which was synthesized from silica sol. (LUDOX) has the thickness of 1.5 µm and the thicknesses are uniform through the membranes. The SEM images show continuous zeolite A layers for the sodium metasilicate (BA68) and waterglass (BA92) cases. And in these cases the crystals forming the membrane layers show good intergrowth hence the layers seen very dense from the cross-section micrographs. But for the LUDOX (BA78) case it is suspicious that the layer is continuous or not.

The SEM surface images of the membranes synthesized from different silica sources are shown in Figure 4.10. For all of the membranes except BA78, support surfaces are totally covered with zeolite A crystals with no voids and the intergrowth in all membranes are clearly observed from surface micrographs. For BA78, the surface is covered with zeolite A crystals but the crystals are not intergrown they seem as separate from each other and this may lead some voids in the membrane. The particle size of crystals is about 1 μm for this membrane. For BA68, cabbage-like agglomerates are seen very commonly. The particle size of crystals forming the BA92 is about 2-3 μm.

The SEM cross-section images of the membranes synthesized from different seeding techniques are shown in Figure 4.11. According to the used seeding technique the membrane thicknesses differ for both one layer and two layer membranes. For instance, BA83-2 which was synthesized by seeding with rubbing wiping method has the thickness of 6 μm and for BA85-2, the seeding technique was dip-coating wiping and it has the thickness of 3 μm (Figure 4.11) whereas BA87-2 which was synthesized by seeding with vacuum seeding wiping method has the thickness of 9.5 μm and the thicknesses are uniform through the membranes. In a same manner one layer membranes BA92 (dip-coating wiping) and BA95 (vacuum seeding wiping) have the thicknesses 3 μm and 9 μm, respectively. The SEM images show continuous zeolite A layers for all the membranes and the crystals forming the membrane layers show good intergrowth hence the layers seen very dense from the cross-section micrographs. The SEM surface images of the membranes synthesized from different seeding techniques are shown in Figure 4.12. For all of the membranes, support surfaces are totally covered with zeolite A crystals with no voids and the intergrowth in all membranes are clearly observed from surface micrographs. The particle sizes of crystals are about 3-4.5 μm, 2-3 μm and 3 μm for the BA83-2, BA85-2 - BA92 and BA87-2 - BA95 membranes, respectively. (The membranes BA83-2, BA85-2 and BA87-2 prepared in a same way with BA82, BA84 and BA86, respectively. The only difference is BA83-2, BA85-2 and BA87-2 has two consecutive syntheses)

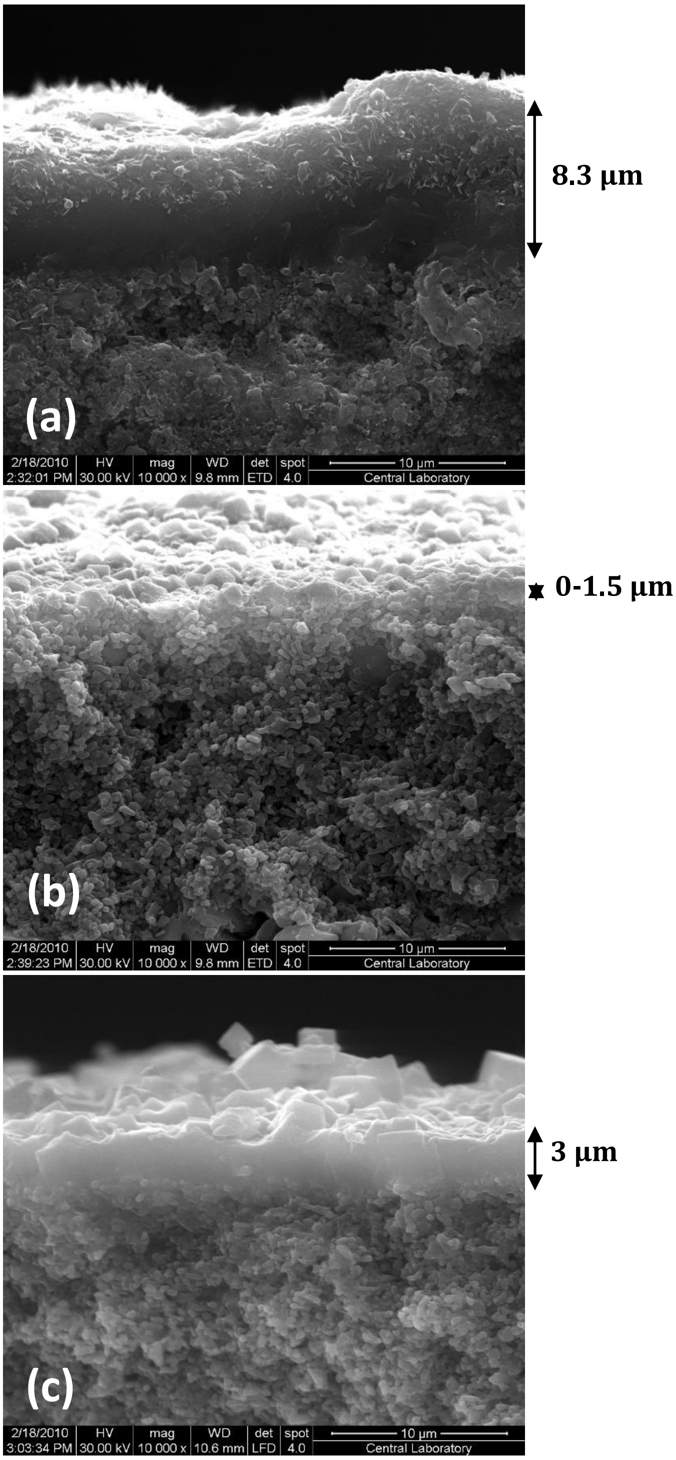


Figure 4.9 Cross-section micrographs of zeolite A membranes synthesized from different silica sources (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, dip coating-wiping, 95 °C, 4h); (a) BA68 (sodium metasilicate pentahydrate), (b) BA78 (silica sol (LUDOX)) and (c) BA92 (waterglass)

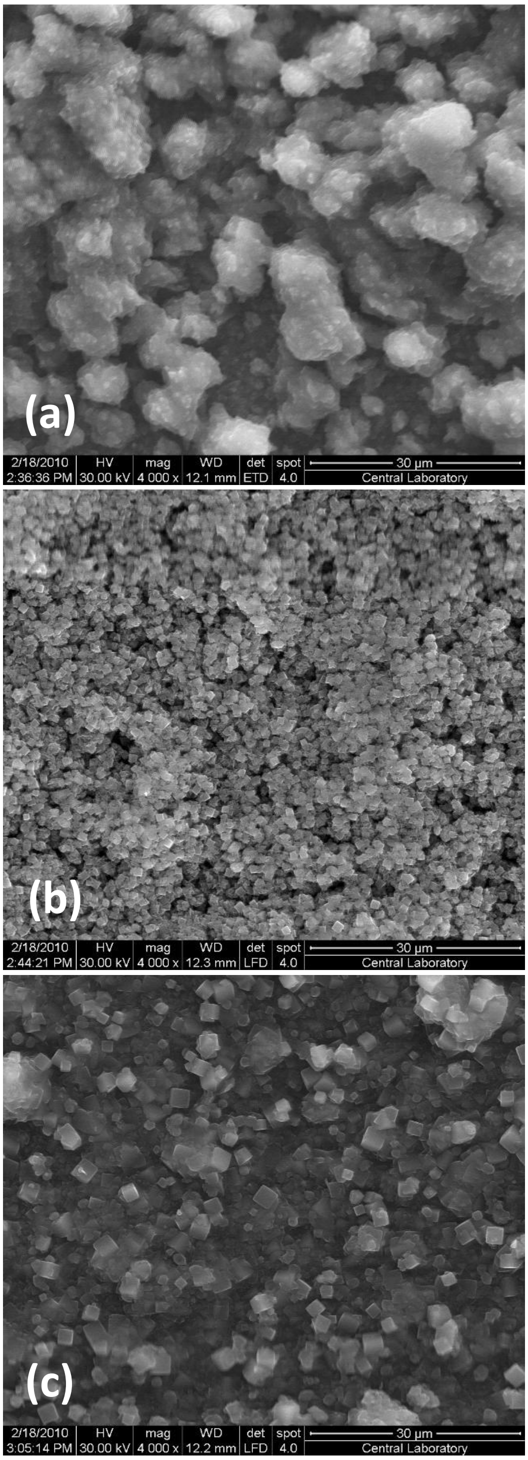


Figure 4.10 Surface micrographs of zeolite A membranes synthesized from different silica sources (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, dip coating-wiping, 95 °C, 4h); (a) BA68 (sodium metasilicate pentahydrate), (b) BA78 (silica sol (LUDOX)) and (c) BA92 (waterglass)

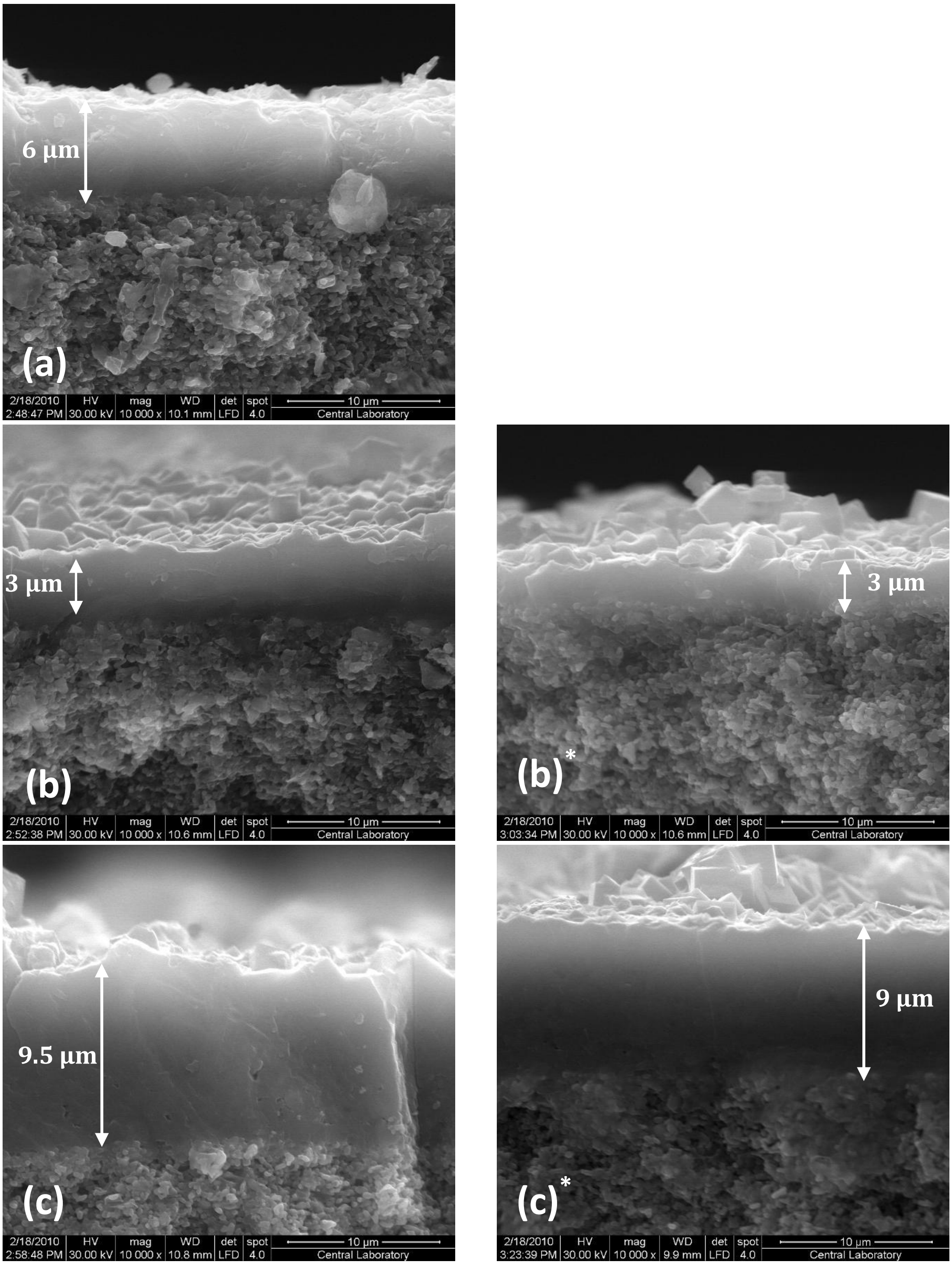


Figure 4.11 Cross-section micrographs of zeolite A membranes synthesized from different seeding techniques (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, waterglass, 95 °C, 4h); (a) BA83-2 (rubbing-wiping), (b) BA85-2 and (b)* BA92 (dip coating-wiping), (c) BA87-2 and (c)* BA95 (vacuum seeding-wiping)

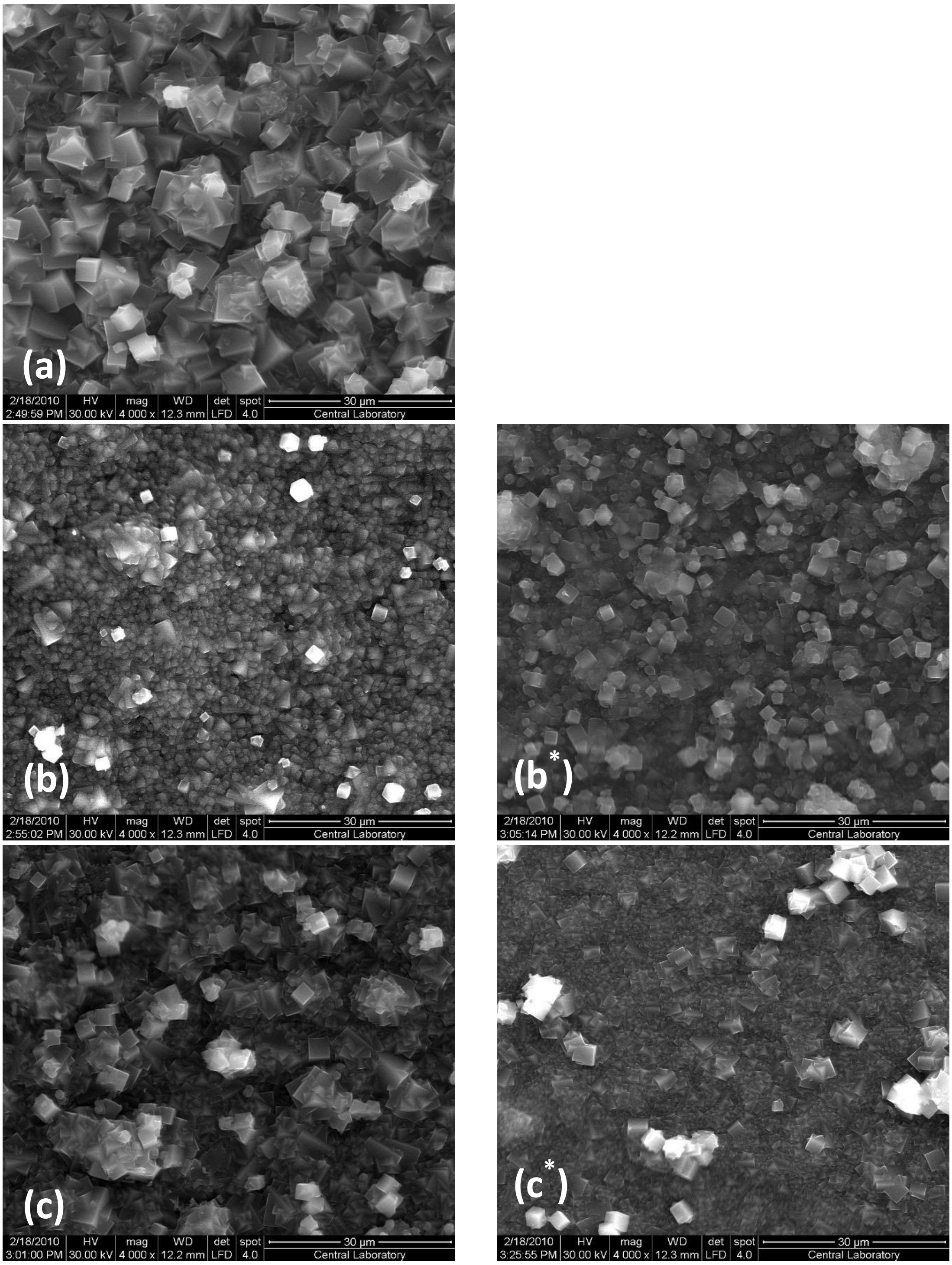


Figure 4.12 Surface micrographs of zeolite A membranes synthesized from different seeding techniques (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, waterglass, 95 °C, 4h); (a) BA83-2 (rubbing-wiping), (b) BA85-2 and (b)* BA92 (dip coating-wiping), (c) BA87-2 and (c)* BA95 (vacuum seeding-wiping)

Pervaporation results of the membranes synthesized from different silica sources and the membranes seeded with different techniques are summarized in Table 4.1. The results show that the membranes (BA82, BA84, BA92 and BA86) prepared by using waterglass as silica source have higher selectivities than the membranes prepared by sodium metasilicate and silica sol (LUDOX). Among these highly selective membranes better pervaporation performances obtained with the membranes (BA84 and BA92) seeded by dip-coating wiping method. But in the case of LUDOX as silica source, the layers did not show membrane characteristics in pervaporation tests. Pervaporation performances of the membranes were very poor for every type of seeding method. The fluxes were very high and the layers were not selective, the feed solution coming from the permeate side was directly passing through the layer without any change in the composition of feed solution. When we compare the membranes BA72 and BA92, the flux of BA72 is 10 times as high as flux of BA92 although BA72 is thicker than BA92. However selectivity of BA92 is 10 times as high as the selectivity of BA72. This may indicate the existence of more non-zeolitic pores in the membrane layer of BA72 than BA92. Membranes fluxes are in the range of 2.5-0.2 kg/m^{2}h whereas selectivities are in the range of 1-171. According to the data in Table 4.1, the highest selectivities are obtained by using waterglass as silica source and by seeding dip-coating wiping method.

As a conclusion for different silica sources and different seeding techniques, as evaluated with the XRD patterns and SEM images, a continuous and uniform zeolite A membranes were synthesized by using both the sodium metasilicate pentahydrate and waterglass as silica sources whereas the membranes synthesized using waterglass as silica source and seeded with dip-coating wiping method have the highest selectivities in terms of pervaporation measurements. The membranes synthesized by using LUDOX as silica source did not show zeolite A XRD patterns clearly and SEM pictures were suspicious that there is a membrane layer or not. These results were supported with the poor pervaporation results. So it was decided that to synthesize good quality zeolite A membranes in a flow system to separate organic/water mixtures by pervaporation, membranes will be prepared from $N_{3.4}A_1S_2H_{155}$ hydrogel by using waterglass as silica source and by seeding with dip-coating wiping method.

Table 4.1 Effect of silica source and seeding technique to PV performance of the membranes prepared in batch system (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, 95 °C, 4 h)

					PV Results [a]		
Code	**Seeding Method**	**Silica Source**	**SEM thickness (μm)**	**Peak Ratio**	**Flux (kg/m^2h)**	**SF**	**Permeate Water wt %**
BA68	Dip-coating wiping	Sod. Met. Penta.	8.3	0.214	0.24	10.5	54
					0.23	7.4	46
BA70	Rubbing wiping	Sod. Met. Penta.	3.5	0.323	0.15	23	72
					0.27	10	52
BA72	Vacuum seeding wiping	Sod. Met. Penta.	9.5	0.338	2.35	15.3	63
					2.45	12.4	58
BA74	Vacuum seeding	Sod. Met. Penta.	14.5	0.395	1.16	13.5	60
					0.45	12.4	58
BA76	Rubbing wiping	LUDOX	0-2	0.072	very large	1	10
BA78	Dip-coating wiping	LUDOX	0-1.5**	0.052	very large	1	10
BA80	Vacuum seeding wiping	LUDOX	4.5	0.085	very large	1	10
BA82	Rubbing wiping	Waterglass	-	0.143	0.42	6.8	43
					0.24	6.8	43
BA84	Dip-coating wiping	Waterglass	-	0.196	0.25	**120**	**93**
					0.28	**171**	**95**
BA92	Dip-coating wiping	Waterglass	3	0.196	0.23	**129.5**	**93.5**
					0.20	**73**	**89**
BA86	Vacuum seeding wiping	Waterglass	-	0.291	0.22	**44**	**83**
					0.18	**66**	**88**
BA128	-	Waterglass	no layer	0.042	-	-	-
BA129			-	0.036	-	-	-

[a] PV conditions: feed water fraction, 10 wt. %; T, 50°C; permeate pressure, 0.37kPa. Permeate samples are analyzed by RI.

** not a continuous layer

Note: Selectivities determined according to GC analysis results of permeate samples are shown in Appendix L in detail. All membranes tested at least two runs to see the reproducibility of the PV measurements.

There are some studies [35, 73-78] in which effect of silica source on crystallization process of zeolites were investigated. Mohamed et al. [73] synthesized zeolite 4A from different silica and aluminum sources using sol-gel method. Twu et al. [74] examined the effect of two common commercial silica sources, LUDOX and waterglass (N-Brand) on the formation of faujasite zeolites. These studies showed that the initial reactant sources affect the type of intermediate species formed in the crystallization medium. They also showed the complexity of the zeolite nucleation/crystallization process, which is dependent on the overall composition of hydrogel and silica and alumina sources used [75].

These results on the synthesis of zeolites can give an idea about the effect of silica source on membrane properties. In the case of zeolite A membrane synthesis from different silica sources, LUDOX was not an effective silica source compared to waterglass and sodium metasilicate. This may be due to that LUDOX is colloidal silica, which means the silica is not dissolved in water; it exists as colloidal particles; whereas waterglass and sodium metasilicate are solutions of silicate. This difference in silica sources may also affect the type and concentration of intermediate species that can be observed during crystallization and formation of membranes.

4.3.2 Effect of consecutive synthesis on membrane properties

Multiple synthesis steps are commonly used to prepare defect-free zeolite membranes [33, 41, 79, 80]. After first synthesis, a second synthesis was carried out on the same membrane by using a new synthesis solution without seeding the membrane second time. These consecutive syntheses are continued until the membrane has the desired separation properties. In literature, the morphology and PV performance of membranes after intermediate synthesis steps were usually not reported; but the data are given for the final product.

Zeolite A membranes were prepared from the $N_{3.4}A_1S_2H_{155}$ hydrogel by using waterglass as silica source and seeded with different techniques and two consecutive syntheses were performed. All membranes were synthesized at 95 °C for 4 hours in autoclaves. The synthesis conditions of all membranes are given in Appendix L and for the membranes used in this section, synthesis conditions are also summarized in Table 4.2.

The XRD patterns of the synthesized membranes are shown in Figure 4.13. XRD patterns of the two consecutive syntheses membranes showed that the crystal phase formed on the supports in all synthesis was highly crystalline zeolite A. All zeolite A peaks are clearly observable in all XRD patterns of the membranes.

Cross-section micrographs of both one and two consecutive synthesis membranes are shown in Figure 4.14. BA92 and BA85-2 were synthesized under the same conditions, only the difference is BA92 was synthesized with single step whereas BA85-2 was synthesized with two consecutive steps. Both of the cross-sections of BA92 and BA85-2 showed continuous films of thickness about 3 μm. In a same way BA95 and BA87-2 were synthesized under the same conditions, only the difference is BA95 was synthesized with single step whereas BA87-2 was synthesized with two consecutive steps. Both of the cross-sections of BA95 and BA87-2 showed continuous films of thickness about 9 μm. No indication of multilayer is seen in the layers. From the surface micrographs, the films of dip-coating wiping membranes (BA92 and BA85-2) differ with different consecutive steps. BA92 has sharp edged cubic zeolite A crystals on the surface whereas BA87-2 has chamfered edged zeolite A crystals on the surface. The surface micrographs showed that the films of vacuum seeding wiping membranes (BA95 and BA87-2) look similar, but BA87-2 has some crystal agglomerates on its surface. From the micrographs, in all membranes the support is covered fully and the film is well-intergrown (Figure 4.15).

The quality of the consecutively synthesized membranes was evaluated by pervaporation tests. The used feed composition was 10 % water and 90 % ethanol by weight. Pervaporation results of the synthesized membranes are summarized in Table 4.2.

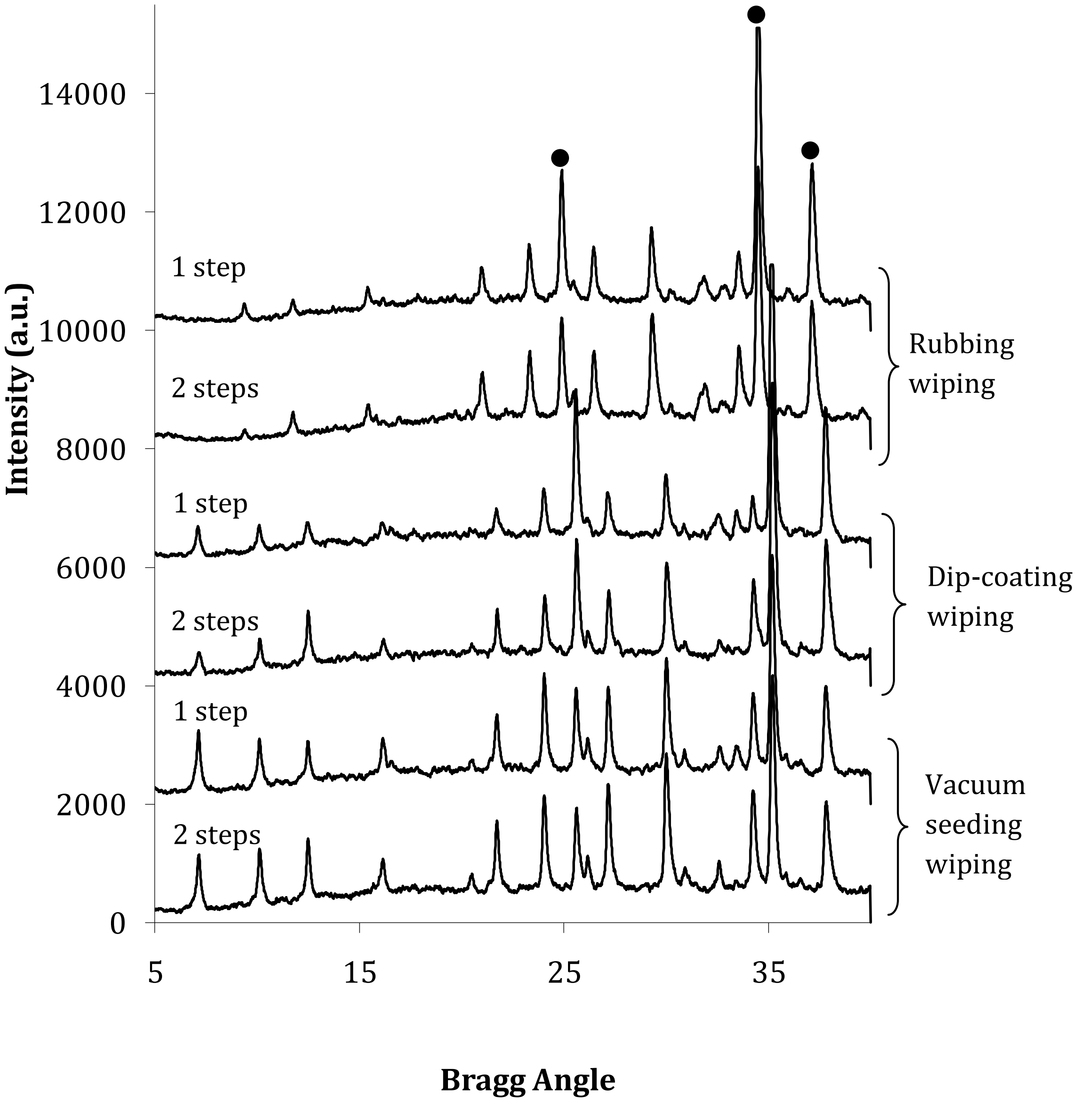


Figure 4.13 XRD patterns of zeolite A membranes synthesized from two different consecutive steps and three different seeding techniques (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, waterglass, 95 °C, 4h); BA82 (one step, rubbing wiping), BA92 (one step, dip-coating wiping), BA95 (one step, vacuum seeding wiping), BA83-2 (two steps, rubbing wiping), BA85-2 (two steps, dip-coating wiping) and BA87-2 (two steps, vacuum seeding wiping). Dots represent the α-alumina peaks and other peaks belong to zeolite A

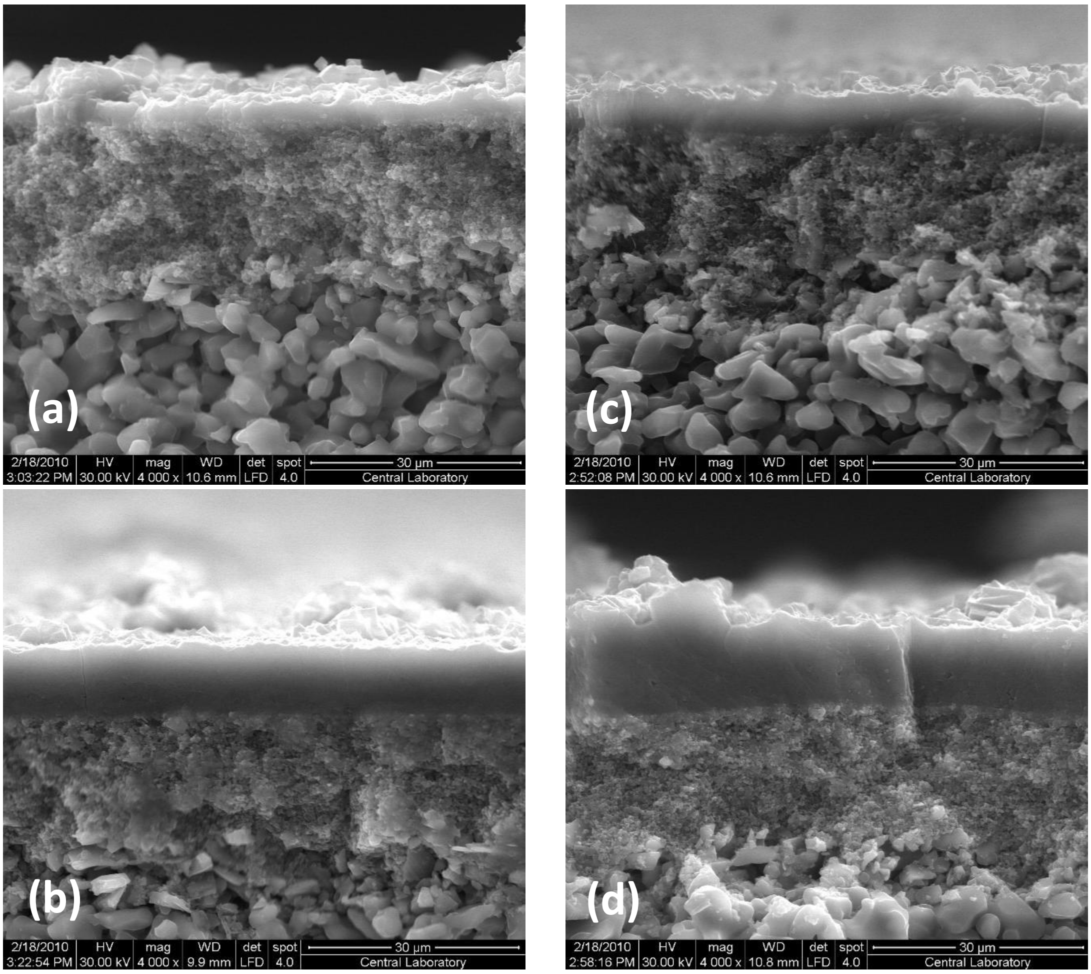


Figure 4.14 Cross-section micrographs of zeolite A membranes synthesized from two different consecutive steps and two different seeding techniques (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, waterglass, 95 °C, 4h); (a) BA92 (one step, dip-coating wiping), (b) BA95 (one step, vacuum seeding wiping), (c) BA85-2 (two steps, dip-coating wiping) and (d) BA87-2 (two steps, vacuum seeding wiping)

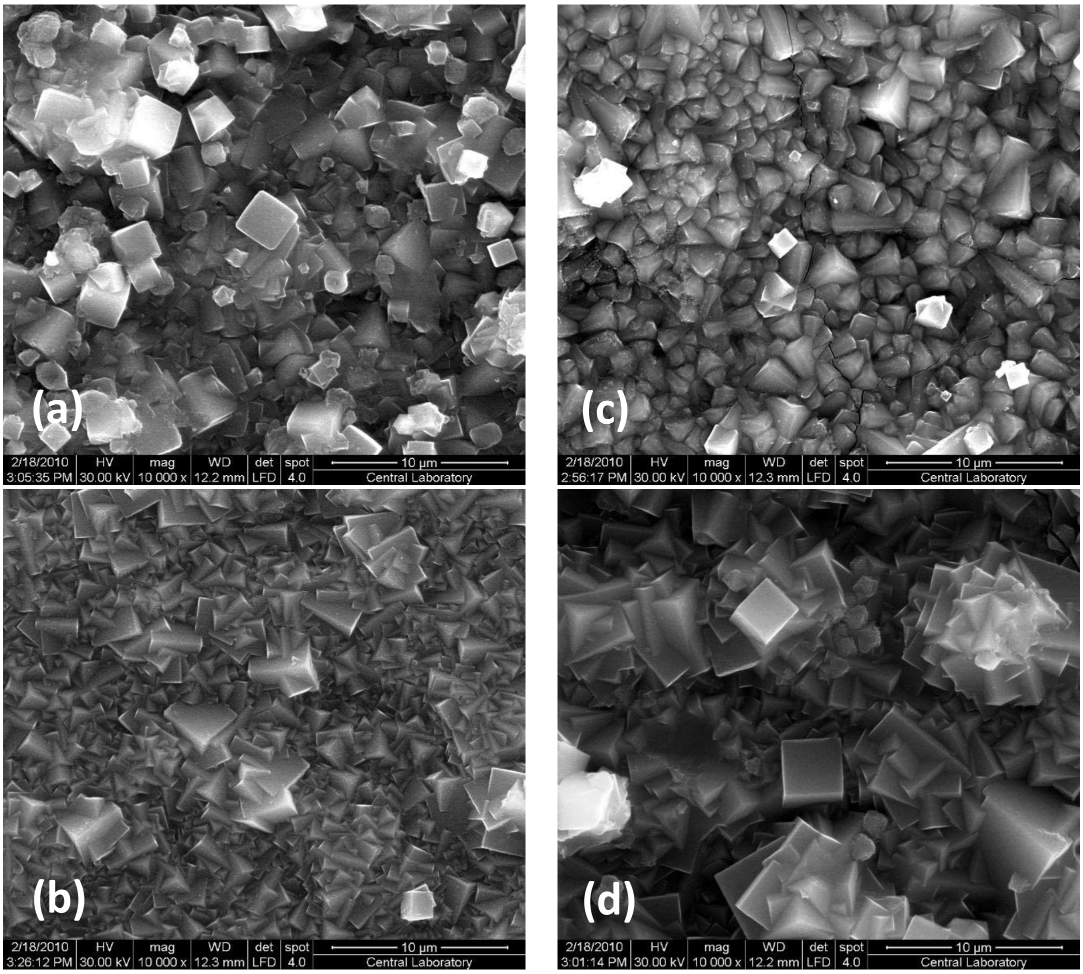


Figure 4.15 Surface micrographs of zeolite A membranes synthesized from two different consecutive steps and two different seeding techniques (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, waterglass, 95 °C, 4h); (a) BA92 (one step, dip-coating wiping), (b) BA95 (one step, vacuum seeding wiping), (c) BA85-2 (two steps, dip-coating wiping) and (d) BA87-2 (two steps, vacuum seeding wiping)

Table 4.2 Effect of consecutive synthesis to PV performance of the membranes prepared in batch system (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, 95 °C, 4 h or 4+4 h, waterglass)

					PV Results [a]		
Code	**Seeding Method**	**# of layer**	**SEM thickness (μm)**	**Peak Ratio**	**Flux (kg/m^2h)**	**SF**	**Permeate Water wt %**
BA82	Rubbing wiping	1	-	0.143	0.42	6.8	43
					0.24	6.8	43
BA83-2	Rubbing wiping	2	6	0.268	0.20	120	93
					0.20	104	92
BA84	Dip-coating wiping	1	-	0.196	0.25	120	93
					0.28	171	95
BA92	Dip-coating wiping	1	3	0.196	0.23	130	93.5
					0.20	73	89
BA85-2	Dip-coating wiping	2	3	0.250	0.22	120	93
					0.21	171	95
BA86	Vacuum seeding wiping	1	-	0.291	0.22	44	83
					0.18	66	88
BA95	Vacuum seeding wiping	1	9	0.345	0.21	32	78
					0.21	44	83
BA87-2	Vacuum seeding wiping	2	9.5	0.385	0.21	38	81
					0.19	32	78

[a] PV conditions: feed water fraction, 10 wt. %; T, 50°C; permeate pressure, 0.37kPa. Permeate samples are analyzed by RI.

Note: Selectivities determined according to GC analysis results of permeate samples are shown in Appendix L in detail. All membranes were tested twice to see the reproducibility of the PV measurements.

Considering the membranes BA82 (single synthesis) and BA83-2 (two consecutive synthesis steps), after two consecutive synthesis steps peak ratio of the membrane was doubled. On the other hand in terms of pervaporation after the second synthesis, flux was decreased slightly whereas selectivity increased nearly twenty times (Figure 4.16). This implies that there was a zeolite A layer containing some defects after the single synthesis step. But the defects were patched through the second synthesis step. The membrane after the second synthesis contains much less defects since selectivity increased dramatically.

Pervaporation performances of other single and double synthesis membranes (BA92, BA95 and BA85-2, BA87-2) were not affected much from the second synthesis step (Figure 16) whereas peak ratios of those membranes increased slightly with two consecutive steps. This may be due to there were no non-zeolitic pores or much less non-zeolitic pores and they were not patched since the flux and selectivities remained nearly constant (Figure 4.16).

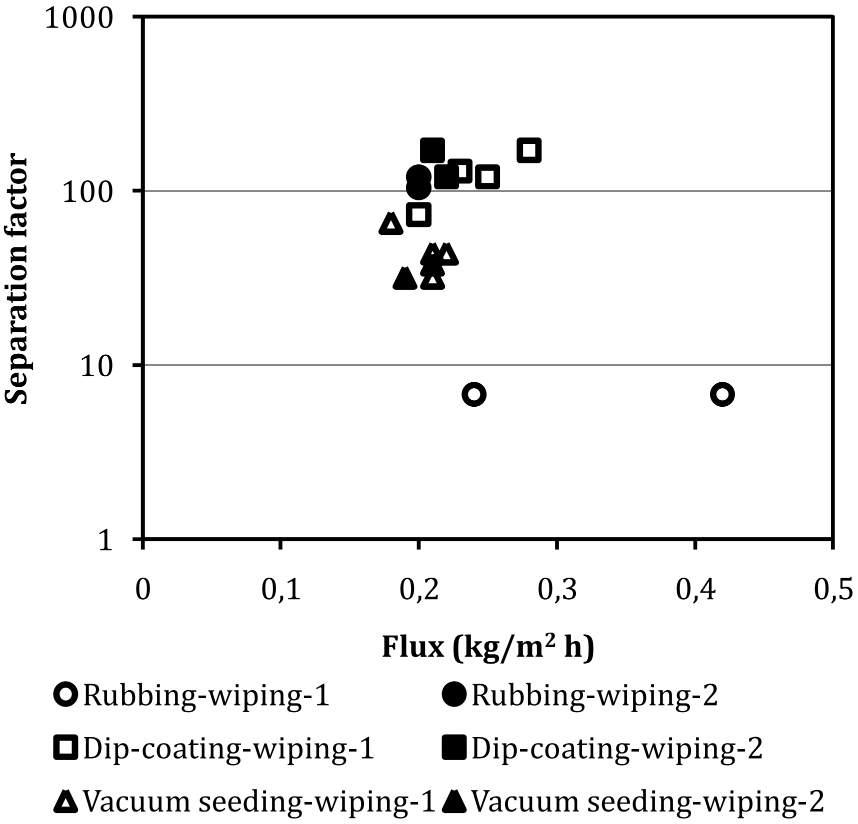


Figure 4.16 Effect of consecutive synthesis to PV performance of the membranes prepared in batch system from three different seeding techniques. Open symbols show one step membranes and closed ones show two step membranes (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, 95 °C, 4h, waterglass)

4.4 Synthesis of zeolite A membranes in flow system

Three different experimental synthesis parameters were investigated with zeolite A membranes synthesized in batch system. These parameters were starting synthesis solution composition, silica source and seeding technique. And the better synthesis conditions were adapted to be used in flow system. It was decided to prepare zeolite A membranes from $N_{3.4}A_1S_2H_{155}$ hydrogel by using waterglass as silica source and by seeding with dip-coating wiping method. Membranes were synthesized at 95 °C for 4 hours in flow system with a flow rate of 4 mL/s. The synthesis conditions of all membranes are given in Appendix L. The method developed for the synthesis of good quality membranes was adapted to flow system since flow system has some possible advantages to be used. It has the flexibility with various membrane supports and more homogeneous thickness is observed throughout the large membranes. The raw materials are used more economically. The flow system may offer improvement in reproducibility.

Zeolite A membranes were synthesized on α-alumina discs from $N_{3.4}A_1S_2H_{155}$ hydrogel both in batch and in re-circulating flow systems. Membranes were analyzed by XRD and SEM for phase identification and determination of morphology as it was done before for the batch membranes.

XRD patterns of zeolite A membranes synthesized both in batch and in re-circulating flow systems are shown in Figure 4.17. XRD patterns of the membranes synthesized in flow system showed that the crystal phase formed on the supports was highly crystalline zeolite A. XRD patterns of the membranes are very similar. All zeolite A peaks at Bragg angles of 7°, 10°, 12.5°, 16.1°, 21.5°, 24°, 26.1°, 27.2°, 30°, 30.8°, 32.5° and 34.3° are clearly observable in these XRD patterns of the membranes. And in the case of the remaining powders from the synthesis of membranes XRD patterns showed that the crystal phase of the powders was highly crystalline zeolite A (Figure 4.18).

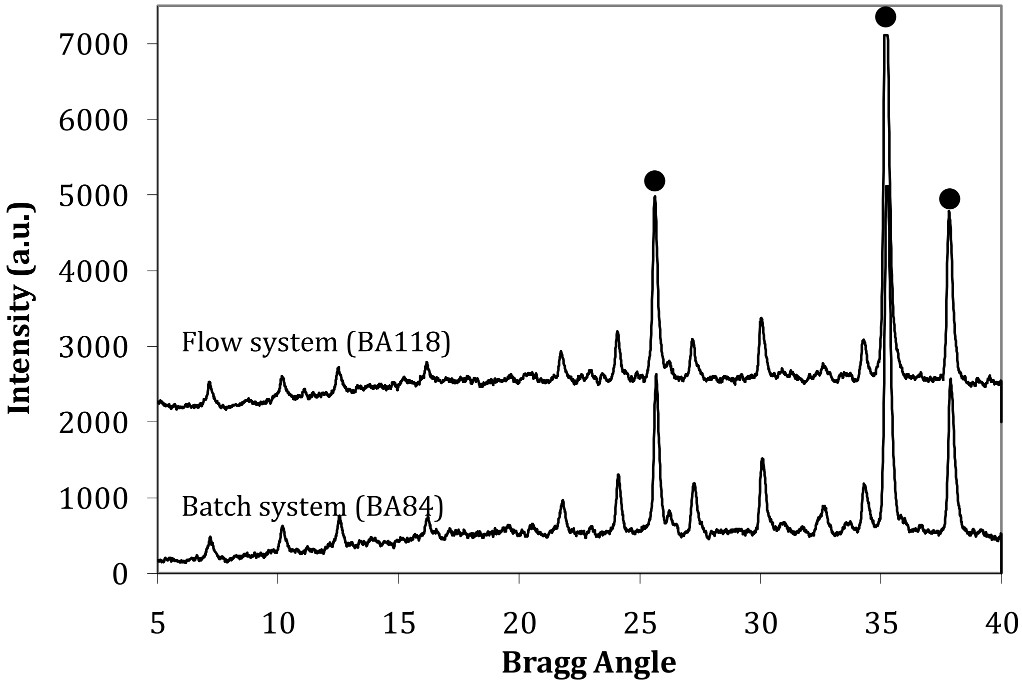


Figure 4.17 XRD patterns of zeolite A membranes synthesized both in batch (BA84) and in recirculating flow systems (4 mL/s) (BA118) (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, waterglass, 95 °C, 4h, dip-coating wiping). Dots represent the α-alumina peaks and other peaks belong to zeolite A

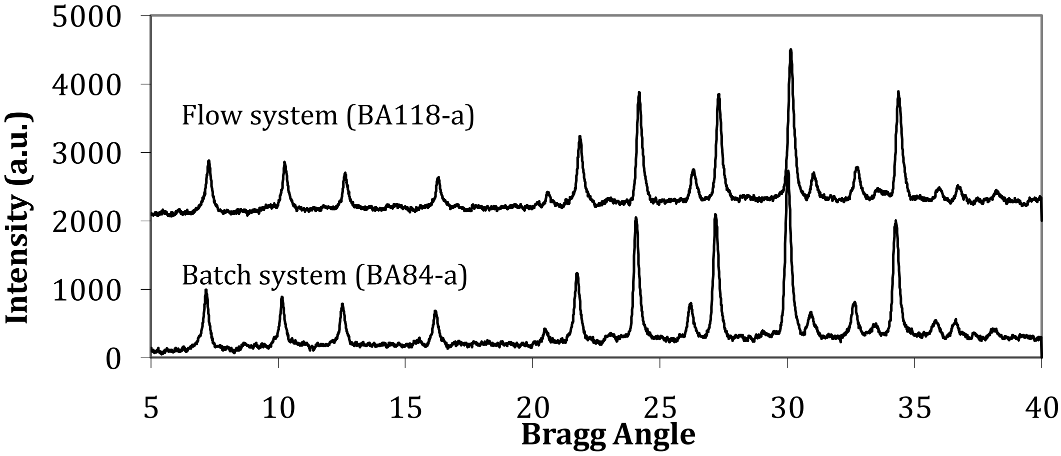


Figure 4.18 XRD patterns of the remaning powders from the synthesis of membranes prepared both in batch (BA84-a) and in recirculating flow systems (4 mL/s) (BA118-a) (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, waterglass, 95 °C, 4h, dip-coating wiping)

The SEM cross-section and surface images of the membranes synthesized both in batch and flow systems are shown in Figure 4.19. According to the cross-section images the membrane thickness of BA118, the membrane synthesized in flow system, is 1.5 µm and it is half of the membrane thickness of BA92 (batch membrane, and also synthesis repetition of BA84). The SEM images show continuous and uniform zeolite A layers for both of the membranes. From the SEM surface images of the membranes it is seen that both of the membranes support surfaces are totally covered with zeolite A crystals with no voids and the intergrowth in the membranes are clearly observed from surface micrographs. In addition to that surface of BA118 is seen more uniform than BA92. The particle sizes of crystals are 2-3 µm and 1-1.5 µm for the batch and flow systems, respectively. The membrane synthesized in flow system (BA118) has more uniform and intergrown appearance and also the smaller crystals form the membrane synthesized in flow system.

In the course of zeolite membrane synthesis zeolite crystals can grow either on the surface of the support or they can grow in the bulk solution. Both of these growing steps can promote the formation of the zeolite layer. Zeolite crystals or precursors to zeolite crystal formation form in the bulk solution. They may deposit on the growing layer and in this manner they form a part of the zeolite layer or zeolite layer grows directly on the support or on the seeded support [2, 62, 81, 82]. In a batch system, both growing steps can contribute equally to the zeolite layer formation whereas, in a flow system where the synthesis solution is re-circulated over the support, material deposition has no contribution or very little contribution to the zeolite layer formation since flow prevents the material deposition [61]. Hence the more homogeneous and intergrown appearance and the smaller crystals forming the membrane synthesized in flow system can be caused by the existing of flow over the support.

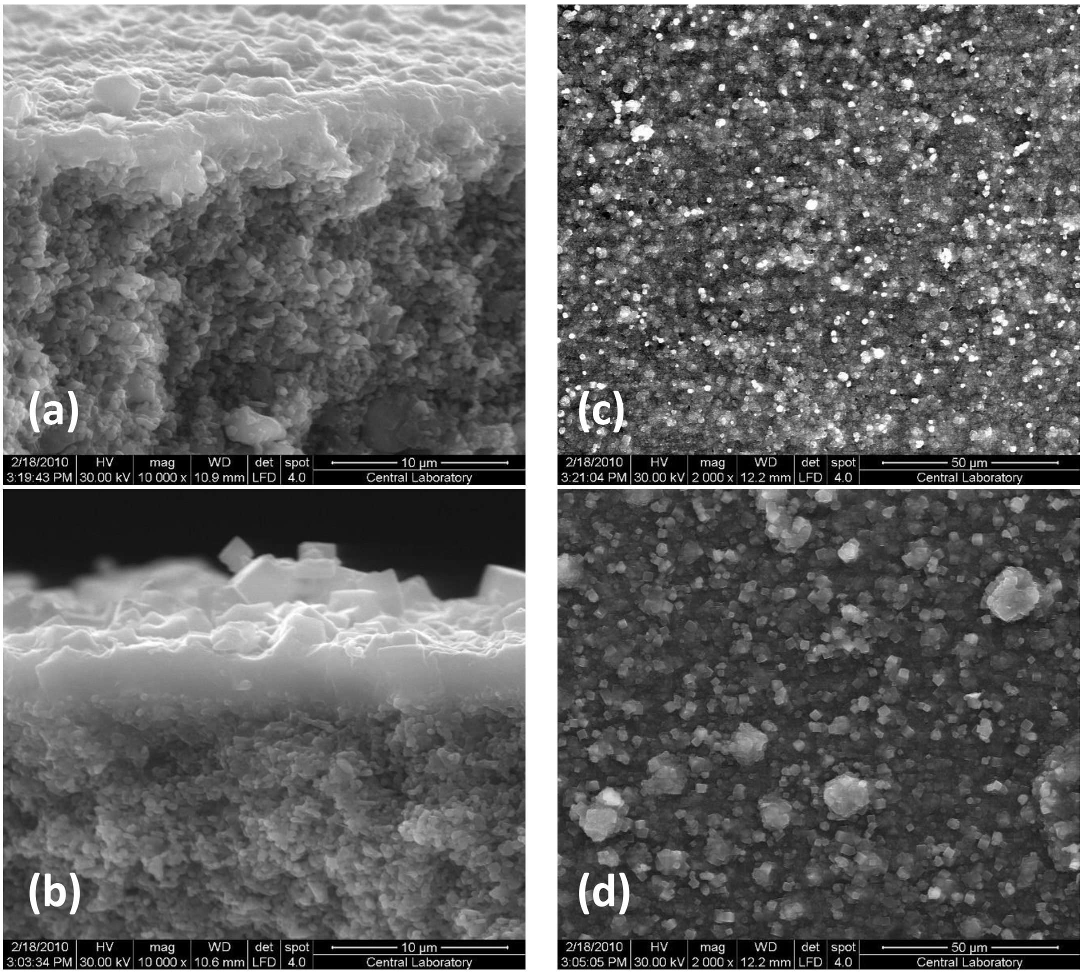


Figure 4.19 Cross-section and surface micrographs of zeolite A membranes synthesized both in batch (BA92) and in recirculating flow systems (BA118) (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, waterglass, 95 °C, 4h, dip-coating wiping); (a), (c) BA118 (flow system, 4 mL/s) and (b), (d) BA92 (batch system)

4.5 Comparison of pervaporation performances of batch and flow system membranes

The quality of the membranes synthesized both in batch and flow systems were evaluated by pervaporation tests. The used feed composition was 10 % water and 90 % ethanol by weight. Pervaporation results of the synthesized membranes are summarized in Table 4.3.

Table 4.3 PV performance of the membranes prepared both in batch and flow systems (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, 95 °C, 4 h, dip-coating wiping, waterglass)

				PV Results [a]		
Code	**Synthesis Type**	**SEM thickness (μm)**	**Peak Ratio**	**Flux (kg/m^2h)**	**Selectivity**	**Permeate Water wt %**
BA84	Batch	-	0.196	0.25	120	93
				0.28	171	95
BA92	Batch	3	0.196	0.23	130	93.5
				0.20	73	89
BA118	Flow	1.5	0.151	0.29	**130**	**93.5**
				0.28	**130**	**93.5**

[a] PV conditions: feed water fraction, 10 wt. %; T, 50°C; permeate pressure, 0.37kPa. Permeate samples are analyzed by RI.

Note: Selectivities determined according to GC analysis results of permeate samples are shown in Appendix L in detail. All membranes tested at least two runs to see the reproducibility of the PV measurements.

The membrane (BA118) prepared in flow system showed similar pervaporation performance with the one (BA84 and BA92) prepared in batch system. The membranes prepared in batch system are thicker, have slightly lower fluxes (in average) than the membrane prepared in flow system and the membranes prepared in batch system have similar selectivities (in average) with the membrane prepared in flow system. So selective zeolite A membranes were also synthesized in recirculating flow system on α-alumina supports from hydrogels.

Many researches were conducted on synthesis of zeolite A membranes in batch system due to its high potential application at industrial level [5, 6, 83, 84]. Zeolite A membranes have high selectivity and flux values in pervaporation separation of alcohol-water mixtures. For instance, Sato et al. [5] who studied the synthesis of high flux zeolite A membranes reproducibly for the industrial production, reported high pervaporation performances. The pervaporation results reported at their study showed higher water permeating flux up to 5.6 kg/m^2h and high water/ethanol selectivity over 5000 in a mixture of water (10wt.%)/ethanol (90wt.%) at 75 °C. These membranes were also synthesized in batch system hydrothermally which is similar to the method used in this study. Although the used methods are similar, the pervaporation results are significantly different. Flux of the membrane prepared in batch system in this study was around 0.2-0.3 kg/m^{2}h which is very low compared to the results reported by Sato et al. [5]. Also selectivity of the membranes synthesized in batch system in this study was around 130 whereas Sato et al. [5] reported selectivities in the range of 10^3-10^4. Therefore selectivities are also low compared to their results. The lower fluxes of the membranes can be due to the higher effective membrane thickness and mass-flow resistance of the support due to permeation of the synthesis solution to be crystallized inside the support. This may affect the selectivity as well. The performance difference can also be with the existence of non-zeolitic pores. On the contrary the flux was expected to be higher with the existence of non-zeolitic pores.

Recent studies are focused on the synthesis of zeolite A membranes in dynamic (continuous or re-circulating flow) systems because of the handicaps in static systems in terms of economical feasibility and reproducibility at industrial level production. A few studies are reported on the synthesis of zeolite A membranes in dynamic systems [11-13]. Zeolite A membranes were synthesized in a recirculating flow system on α-alumina supports from a clear solution of $N_{49}A_1S_5H_{980}$ by Akbay [12]. The membrane was prepared in the flow system at 80°C for 8h with two consecutive synthesis had a separation factor of about 3700 in the separation of 92:8 (wt.%) ethanol/water mixture at 45°C. The membrane had a flux of 0.14 kg/m^{2}h [12]. However, because of the high alkalinity of the synthesis solution, stability of the membranes was poor. And also the reproducibility of the pervaporation tests was poor especially at higher temperatures due to the crack formation in the membrane.

Pera-Titus et al. [11] also reported the synthesis of zeolite A membranes on the inner side of the titania tubular supports in a continuous system with a flow rate of 1.5-4 mL/min. The synthesis solution is flown in the lumen of the support by the action of gravity from a reservoir. Synthesis is carried out at 80-90 °C for 3-7 hours. The membranes (10–20 μm in thickness) showed ability to dehydrate ethanol/water mixtures (92:8, w/w) by pervaporation with selectivities and fluxes, respectively, in the range of 51-8500 and 0.7-1.2 kg/m^{2}h at 50 °C. Lastly Zeolite NaA membranes were prepared in a flow system on α-alumina supports from a clear solution and for the synthesized membranes fluxes and separation factors, respectively, were reported as in the range of 17-38 kg/m^{2}h and 17-41 for the separation of 65:35 (wt.%) isopropanol/water mixture at 90°C in the study of Aguado et al. [13]. The selectivities of the membranes were not too high but the fluxes of the membranes were very high compared to the other studies reported in the literature.

In the light of these studies, it was concluded that membranes synthesized in flow system in this study are comparable with the membranes, which were synthesized in dynamic systems, reported in literature. However it was known that zeolite A has really high potential in dehydrating organic/water mixtures. So for all the developed methods to synthesize high quality zeolite A membranes in a dynamic system, further improvements can be done. In this context it was decided to make further modifications to improve the developed synthesis method in this study.

4.6 The modification of the flow system synthesis method to make good quality zeolite A membranes

Selective zeolite A membranes were synthesized in re-circulating flow system on α-alumina supports from $N_{3.4}A_1S_2H_{155}$ hydrogel. In order to improve the dehydrating performance of the synthesized membranes, some further modifications were done in the synthesis process. The first one was addition of extra water to the gel composition to increase the fluidity of the synthesis solution for effective pumping. The second one was changing the set-up configuration of the seeded support. The support was immersed in a reservoir filled with synthesis solution and the synthesis solution was circulated through the support in the earlier experiments. By the modification of configuration, the support was placed in the silicon tubings to provide a flow in the lumen of the tubular support. Zeolite A membranes were synthesized from $N_{3.4}A_1S_2H_{200}$ hydrogel by using waterglass as silica source and by seeding with pore-filling method and by placing seeded support in silicon tubings in flow system. The synthesis was done at 95 °C for 17 hours in flow system. The synthesis conditions of all membranes are given in Appendix L and also synthesis conditions of the membranes (BA132-BA138) discussed in this section are summarized in Table 4.4.

4.6.1 Phase identification and determination of morphology for the membranes prepared with the modified synthesis method in flow system

The tubular membranes prepared with the modified synthesis method were analyzed by XRD and SEM for phase identification and determination of morphology.

Figure 4.20 shows the XRD patterns of zeolite A membranes synthesized in recirculating flow systems and the XRD pattern of remaining powder. XRD patterns of the disc and the tube membranes synthesized in flow system showed that the crystal phase formed on the supports was highly crystalline zeolite A. The peaks on the pattern of disc membranes are stronger than those of tubular membranes. Since disk membranes have flat surfaces and tube membranes have concave surfaces, scattering of X-rays from concave surfaces cause this difference. Though major peaks of zeolite A at Bragg angles of 24°, 27.2°, 30° and 34.3° were observed in both patterns. And in the case of the remaining powder from the synthesis of membrane XRD patterns showed that the crystal phase of the powders was highly crystalline zeolite A (Figure 4.20). This is also recognized as the proof of the zeolite A phase that forms the membrane layer.

The SEM cross-section and surface images of the membrane prepared in flow system by modified synthesis method are shown in Figure 4.21. According to the cross-section image, the membrane thickness of BA136 is 10 μm and it is tenfold of the membrane thickness of BA118 (Figure 4.19) (flow disc membrane). The SEM image shows continuous and uniform zeolite A layer for the tube membrane. From the SEM surface image of the membrane it is seen that the membrane support surface is totally covered with zeolite A crystals with no voids and the intergrowth in the membrane is clearly observed. The particle size of crystals is 2.5-3.5 μm for the membranes prepared in flow system by modified synthesis method.

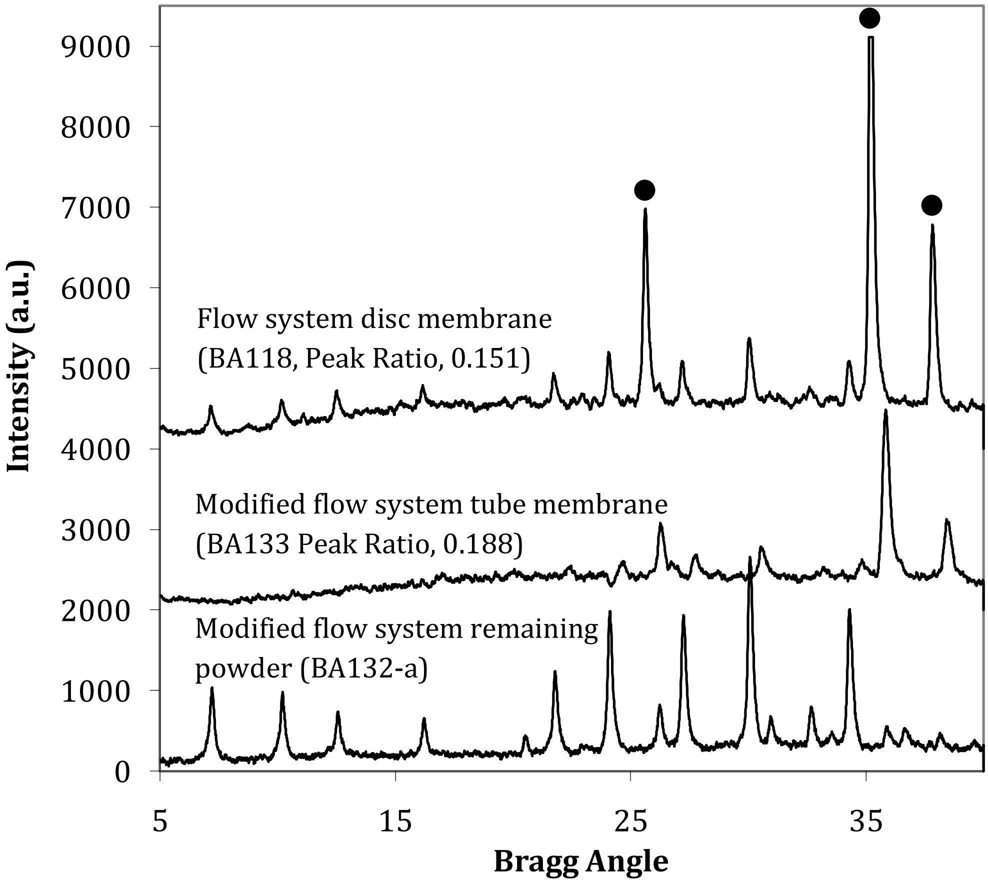


Figure 4.20 XRD patterns of zeolite A membranes synthesized in recirculating flow systems and the remaining powders. BA118, Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, 95 °C, 4h, dip-coating wiping, waterglass, 4 mL/s; BA133 and BA132-a, Synthesis conditions: $N_{3.4}A_1S_2H_{200}$, 95 °C, 17h, pore-filling, waterglass, 4 mL/s. Dots represent the α-alumina peaks and other peaks belong to zeolite A

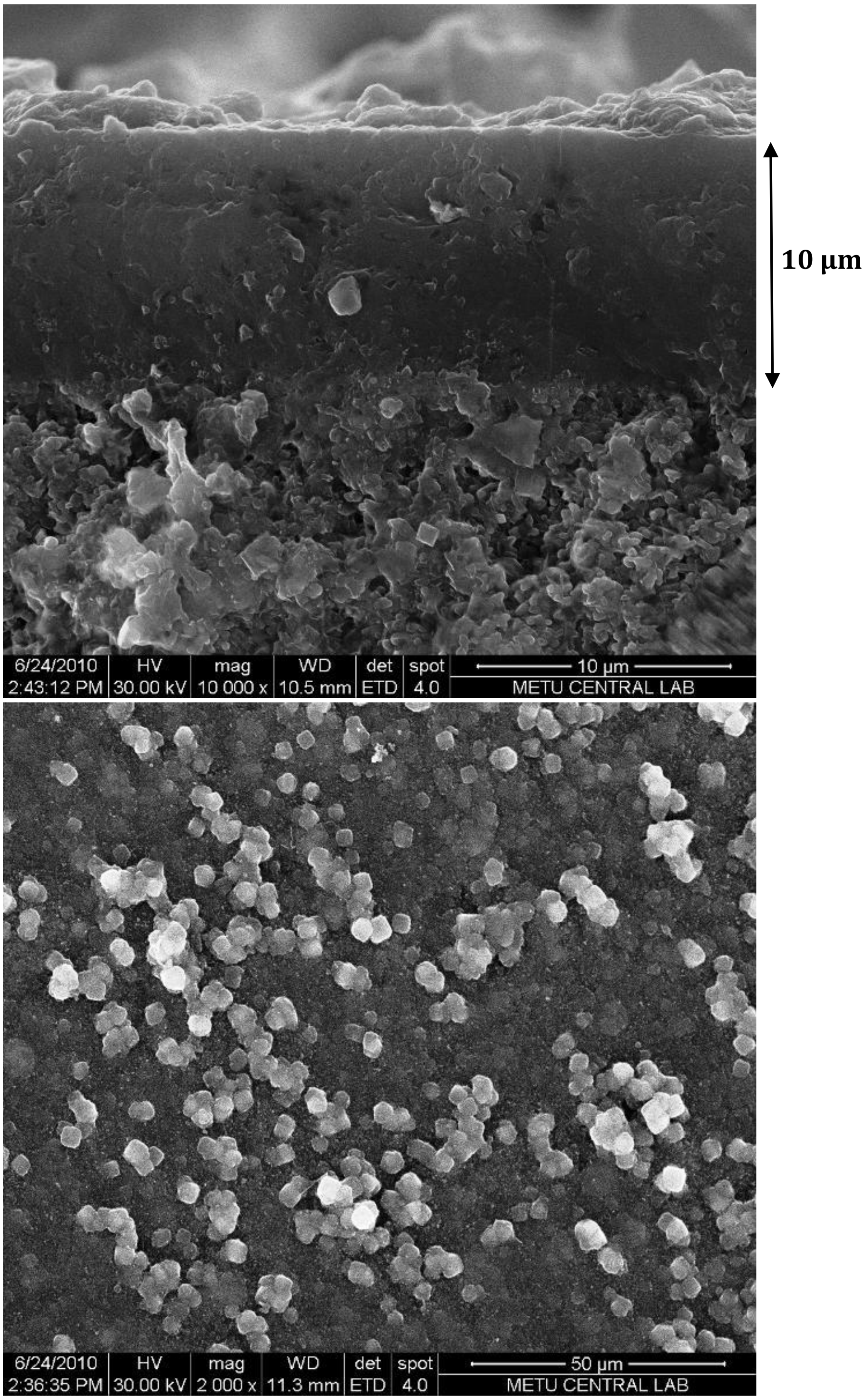


Figure 4.21 Cross-section and surface micrographs of the membranes synthesized in flow system (BA136) by modified synthesis method (Synthesis conditions: $N_{3.4}A_1S_2H_{200}$, 95 °C, 17h, pore-filling, waterglass)

4.6.2 Pervaporation performance of the membranes prepared with the modified synthesis method in flow system

The dehydration ability of the membranes prepared in flow system by modified synthesis method was evaluated by pervaporation tests. The used feed composition was 10 % water and 90 % ethanol by weight. Pervaporation results of the synthesized membranes are summarized in Table 4.4. Among these membranes BA132 has the highest dehydrating performance. The membrane showed ability to dehydrate ethanol/water mixtures (90:10, w/w) by pervaporation with selectivities and fluxes, respectively, >25,000 and 1.2 kg/m^{2}h at 50 °C. So high quality zeolite A membrane is prepared in flow system with the modified synthesis method. Membranes (BA133-138) were also prepared to check the reproducibility of the synthesis method. The synthesis conditions and PV performance of those membranes are also shown in Table 4.4. Although the synthesis method was very similar for the other membranes, their dehydrating performances were not high as BA132. Hence the synthesis method is resulted with high quality membranes but reproducibility of the synthesis method is poor and it should be improved.

Table 4.4 PV performance of the membranes prepared in flow system by modified synthesis method (Synthesis conditions: $N_{3.4}A_1S_2H_{200}$, 95 °C, pore-filling, waterglass)

					PV Results [a]		
Code	**# of steps**	**Synthesis Time (h)**	**SEM thickness (μm)**	**Peak Ratio**	**Flux (kg/m^{2}h)**	**SF**	**Permeate Water wt %**
BA132*	1	17	-	-	1.2	**>25,000**[b]	**>99.96**
BA133	1	17	-	-	1.2	30	77
BA133-2	2	17+3	16	0.188	2.7	104	92
BA134	1	6	8.5	0.195	2.0	15	65
BA136	1	17	10	0.160	2.2	30	77
BA137	1	17	-	-	3.65	15	63
BA137-2*	2	17+17	-	-	2.1	81	90
BA138	1	17	-	-	2.9	12	58

[a] PV conditions: feed water fraction, 10 wt. %; T, 50°C; permeate pressure, 0.37kPa. Permeate samples are analyzed by RI.

[b] Selectivities determined according to GC analysis results of permeate samples.

*These membranes were not broken for SEM and XRD since they are in use for different pervaporation tests in our research laboratory.

Note: All membranes tested at least two runs to see the reproducibility of the PV measurements. The reported results are the average values of repeated PV measurements and the details of the results are shown in Appendix L.

Considering these membranes except BA132, two layer membranes has higher pervaporation performances compared to one layer ones. For the two layer membranes, selectivities increased nearly 5-6 folds whereas fluxes are not decreased so much.

Table 4.5 shows the pervaporation performance of BA132 at different temperatures. The data in the table are summarized from a set of data which is available in Appendix I. Variation of flux, selectivity and permeate water content with temperature for pervaporation of 10 wt % ethanol/water mixtures are shown in Figure 4.22. As expected, an Arrhenius trend of flux with temperature is seen for the tested membrane (Figure 4.22a), with an effective activation energy is being equal to 20 kJ/mol. This value is similar with the literature but slightly smaller than the reported values [11].

Zeolite A membranes preferentially permeate water over ethanol since water is adsorbed more strongly with high coverage. Because of the strong adsorption of water, ethanol may also be blocked by water and permeate much slowly through zeolite pores. Selectivities were seemed to pass a maximum at 50 °C. However the permeate concentration are between 99-100 % water for all temperatures, therefore the large appeared range of selectivity can be interpreted as nearly the same. These observations are consistent with the results previously reported for zeolite A membranes [11]. Pera-Titus et al. [11] reported high quality zeolite A membranes synthesized in a continuous system which shows good dehydrating performance with 8-9 wt% ethanol /water pervaporation selectivities around 8500. The selectivity decreased to around 80 with increasing temperature in their study. Sato et al. [5] reported that both flux and selectivity increased with temperature. The reason can be transport through very fine and narrow non-zeolitic pores in their study. The variation of separation factors and fluxes in our case indicates that the transport is through zeolite pores dominantly.

Table 4.5 PV performance of the membrane (BA132) prepared in flow system by modified synthesis method at different temperatures (Synthesis conditions: $N_{3.4}A_1S_2H_{200}$, 95 °C, 17 h, pore-filling, waterglass)

PV Results [a]			
T (°C)	Flux (kg/m^2 h)	Selectivity	Permeate Water wt %
30	0.12	1,300	99.40
40	0.86	5,550	99.85
50	1.20	>25,000	>99.96
70	3.83	13,000	99.92

[a] PV conditions: feed water fraction, 10 wt. %; permeate pressure, 0.37kPa. Permeate samples are analyzed by GC.

Note: All membranes tested at least two runs to see the reproducibility of the PV measurements. The reported results are the average values of repeated PV measurements and the details of the results are shown in Appendix I.

From a point of that selectivity is being 1000 or larger it is not useful to report it alone. Instead; reporting of permeate composition with selectivity is more useful. Because even 10 folds increase happen in selectivity, permeate composition changes very little. For instance, for a feed mixture of 90 % wt. ethanol – 10 % wt. water; when selectivity is 1000, permeate water content is 99.108 %; when selectivity increased to 10000 permeate water content is 99.910 which can be considered nearly same for many application fields. However in literature generally this situation was not considered when reporting PV data. Recently Cho et al. [85] reported a study on improvement in thermal stability of NaA zeolite composite membrane by control of intermediate layer structure. They have reported flux and separation factor data of their membranes at different temperatures with a feed mixture of 50 % wt. ethanol – 50 % wt. water. The selectivities were reported in the range of 30,000-670,000 and this change was interpreted as the effect of temperature on PV performance. However these separation factors correspond to 99.996 – 99.999 % wt. water in permeate concentrations, suggesting that the temperature has not significant effect for this very selective membrane. On the other hand, the fluxes increased from 1.1 kg/m^2 h at 50 °C to 8.6 kg/m^2 h at 130 °C indicates that temperature has much more pronounced effect on the flux rather than selectivity.

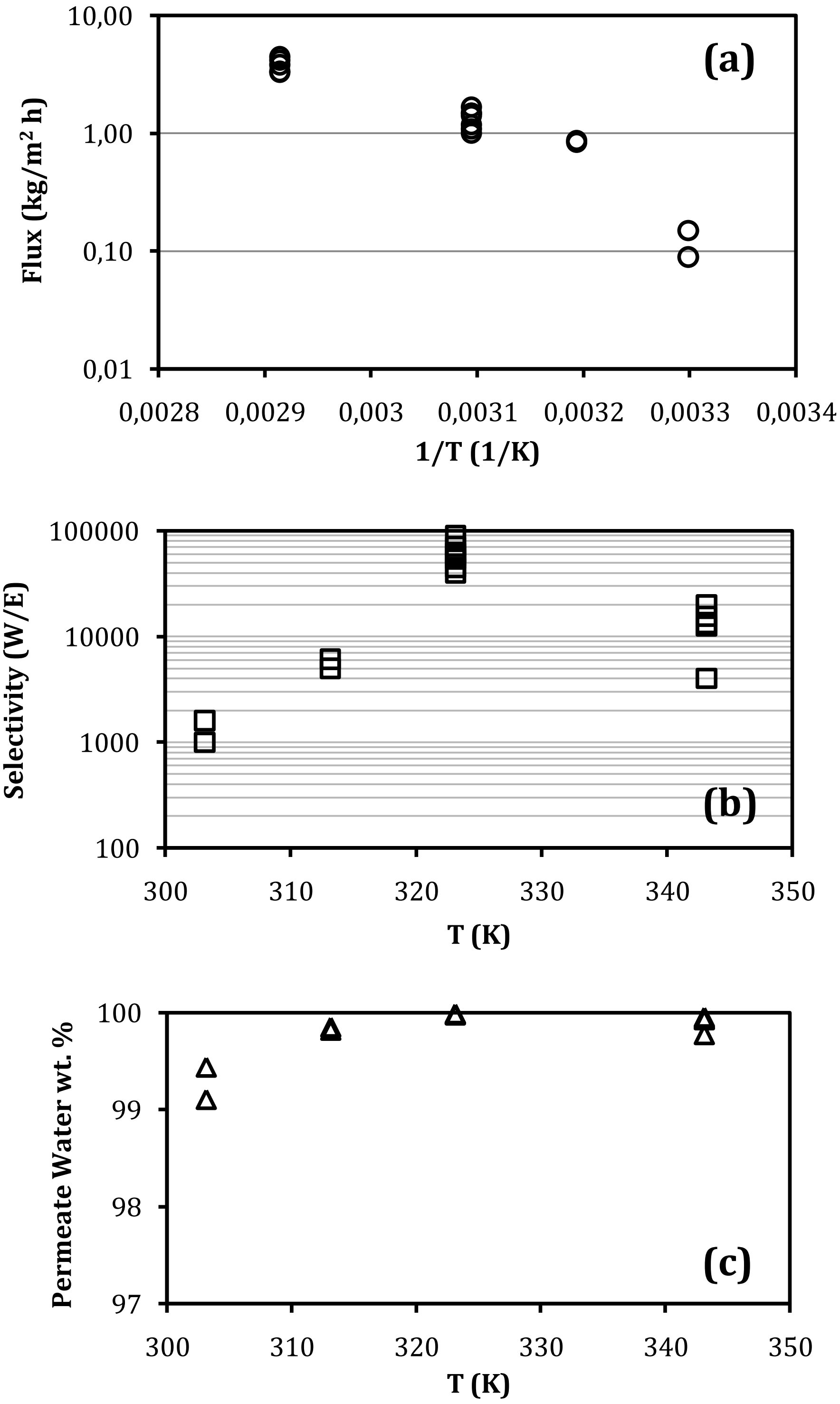


Figure 4.22 Variation of (a) flux (○), (b) selectivity (□) and (c) permeate water wt. % (Δ) with temperature for the membrane (BA132) prepared in flow system by modified synthesis method (Synthesis conditions: $N_{3.4}A_1S_2H_{200}$, 95 °C, 17 h, pore-filling, waterglass)

4.6.3 Comparison of pervaporation performances of the membranes prepared in the batch system and in the modified flow system

Zeolite A membranes prepared both in batch and modified flow systems were characterized by pervaporation separation of 10 % water – 90 % ethanol mixtures. The pervaporation results of the prepared membranes are shown in Figure 4.23.

The zeolite A membranes synthesized in batch system have 3-15 μm thickness whereas the membranes synthesized in modified flow system have 8.5-16 μm thickness. On the other hand at pervaporation temperature of 50 °C, fluxes of the membranes prepared in flow system are 4-10 times higher than the membranes prepared in batch system. Although the membranes prepared in the flow system are thicker, they have higher fluxes than the membranes prepared in batch system. This may be due to the positive effect of narrow non-zeolitic pores, existing in the zeolite layer, to the permeation flux. It is clearly seen that the membranes prepared in modified flow system have higher pervaporation performances in considering both flux and the selectivity (Figure 4.23). This high performance of the membranes synthesized in flow system can be attributed to the more uniform synthesis conditions which are provided with flow system.

The main product of pervaporation of ethanol-water mixture by using zeolite A membranes is the retentate, which is purified ethanol. The commercial tubular zeolite A membranes have typically 25-50 cm^2 membrane area per tube. For instance, for a pilot pervaporation plant that with 1 m^2 effective membrane area requires 200 - 400 tubes with an area of 25-50 cm^2 per tube in order to obtain the ethanol with desired purity. Such as membrane system introduces substantial mechanical difficulties and high instrumentation cost. Therefore, from the industrial point of view for operate with same capacity membranes with high fluxes are essential to decrease needed effective membrane area. Thus, the number of tubes required will also decrease and plant will operate more effectively. Figure 4.24 shows the variation of feed water content with time for membranes having a constant pervaporation flux and different separation factors. It is clearly seen that for the both of the fluxes of 1 kg/m^{2}h (Figure 4.24(a)) and 5 kg/m^{2}h (Figure 4.24(b)) time needed to purify the feed mixture is nearly the same for membranes having separation factors larger than 100. For instance, a membrane having a flux of 1 kg/m^{2}h and selectivity of 100 is purified the feed mixture (90 wt %

ethanol – 10 wt % water) in 30 hours PV operation whereas a membrane having same flux and selectivity of 20,000 is purified the same feed mixture in 28 hours PV operation.

On the other hand with an increase in flux, time needed to purify the feed mixture is decreased. For instance, a membrane having a flux of 1 kg/m^{2}h and selectivity of 100 is purified the feed mixture (90 wt % ethanol – 10 wt % water) in 30 hours PV operation whereas a membrane having a flux of 5 kg/m^{2}h and selectivity of 100 is purified the same feed mixture in 6 hours PV operation. Therefore, at a point of that a membrane having a selectivity of 100 or larger, flux of the membrane is more important quality criteria.

When purifying ethanol-water feed mixture by pervaporation with zeolite A membranes, some ethanol (organic) is lost with permeate. From an economical point of view if the desired organic solvent is very valuable and if it has high price, membranes having high selectivities are required to use in pervaporation in order to minimize the lost amount of valuable organic solvent. But if the desired organic solvent has not very high price, using the membranes having high fluxes is more effective. Table 4.6 shows the lost ethanol wt % for membranes having different fluxes and separation factors with the assumption of left water content in the feed mixture <0.001 wt %. It is also assumed that flux and selectivity remain constant and retentate recycled to feed mixture during the pervaporation operation. For all fluxes, by using the membranes having selectivity of 10, nearly 10 wt % of the initial feed ethanol is lost. But by using the membranes having selectivity of 100, 1000 and 20000, the lost ethanol wt % is became 1 wt %, 0.1 wt% and 0.005 wt %, respectively. Since ethanol price is not very high, the use of high flux membranes having selectivity of 100 or larger will be more efficient.

The fluxes of membranes synthesized in modified flow system are in the range of 1.2-3.7 kg/m^{2}h and selectivities are in the range of 12-25,000 at 50 °C. As it is mentioned before, fluxes of the membranes prepared in modified flow system are 4-10 times higher than the membranes prepared in batch system with reasonable selectivities at pervaporation temperature of 50 °C, this high flux of membranes prepared in modified flow system can also be attributed to the more uniform synthesis conditions which are provided with flow system.

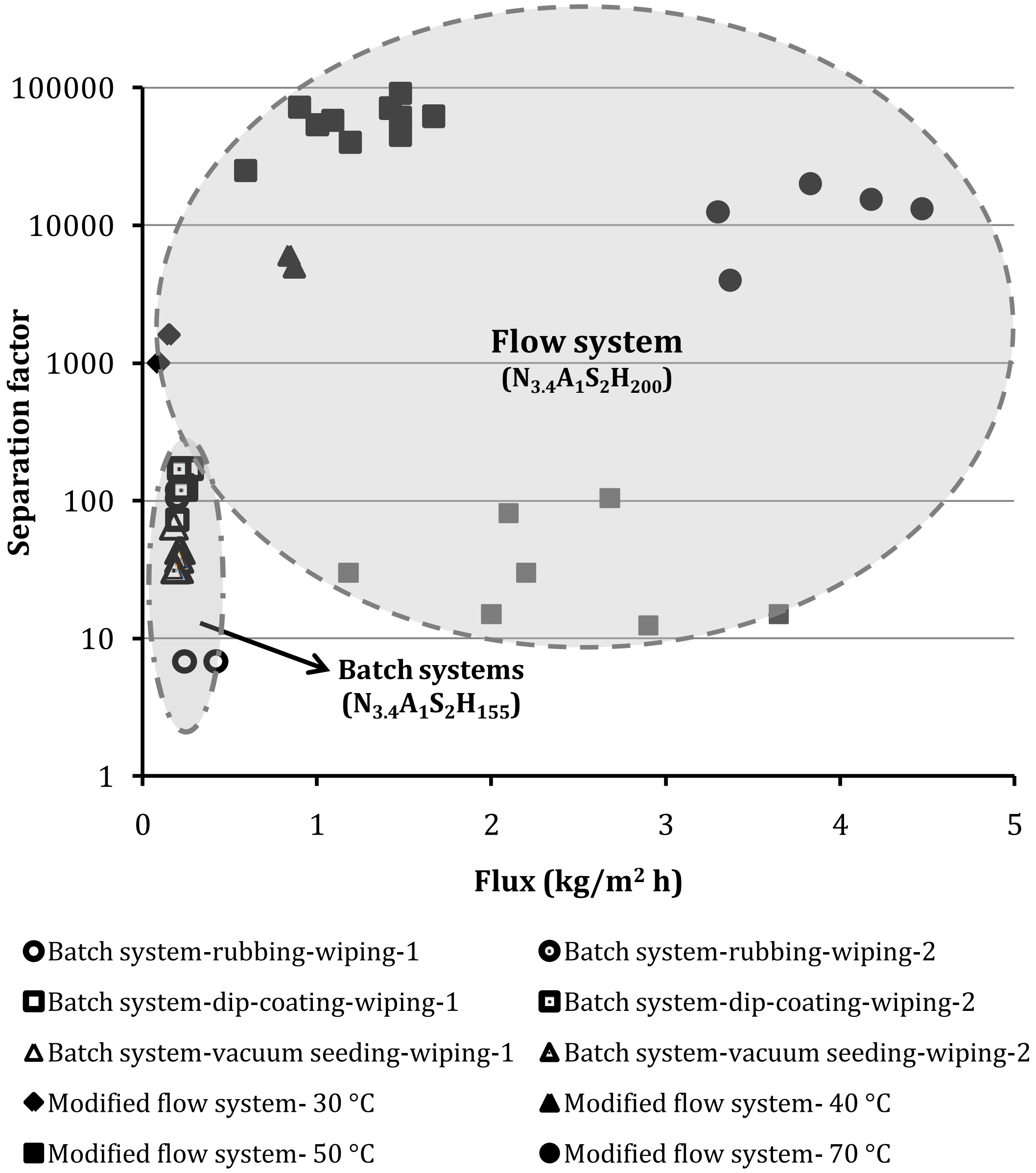


Figure 4.23 Comparison of separation factors and fluxes at different temperatures (25-75 °C) obtained from pervaporation separations of ethanol-water mixture (wt% 90-10) with zeolite A membranes prepared in the batch (open symbols) and modified flow (filled symbols) systems (Synthesis conditions: waterglass, 95 °C, 4 h (for batch system), 17 h (for modified flow system))

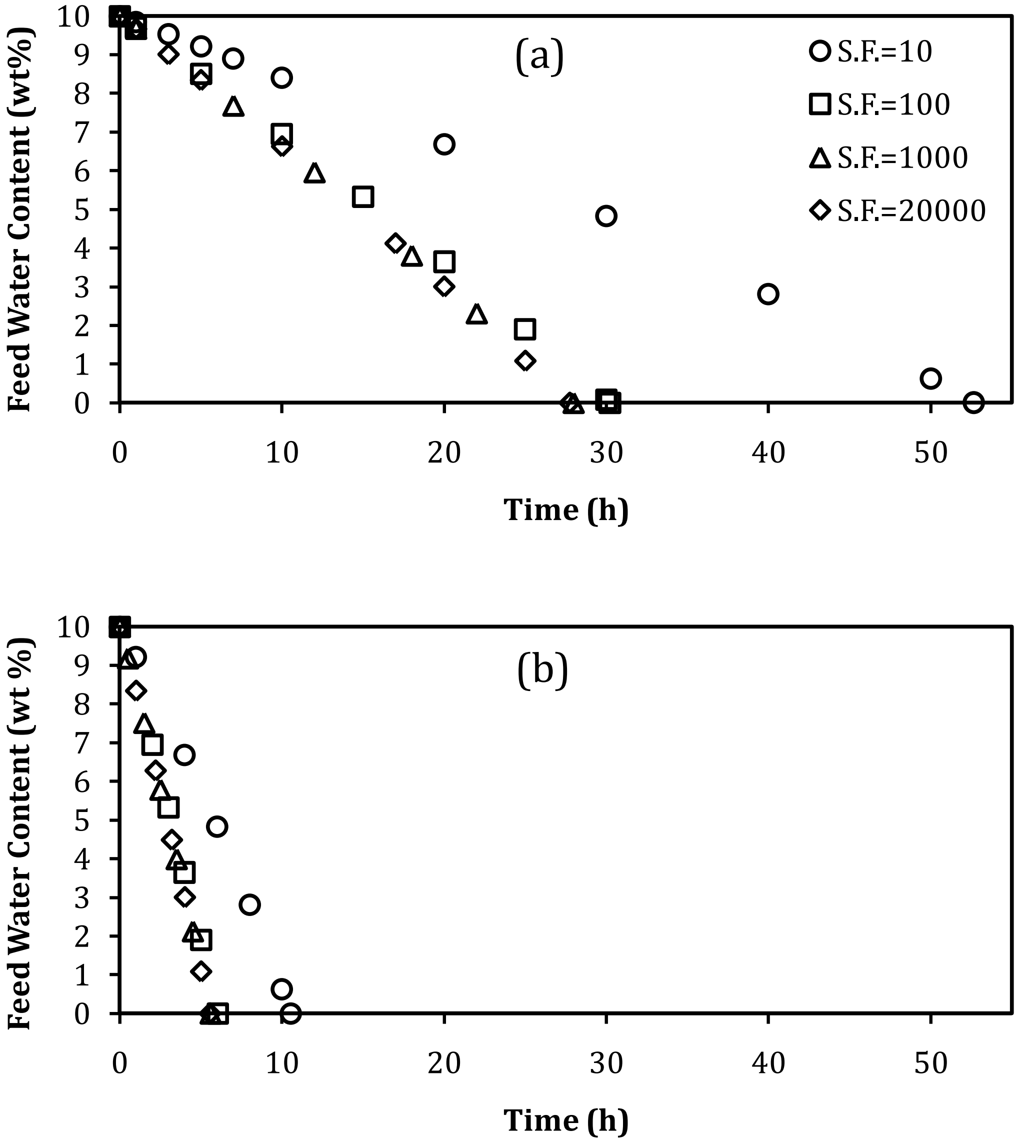


Figure 4.24 Variation of feed water content with time for membranes having a constant pervaporation flux of (a) 1 kg/m^{2}h, (b) 5 kg/m^{2}h and different separation factors (Feed Composition = 90 wt % ethanol – 10 wt % water at time=0)

Table 4.6 Lost ethanol wt % for membranes having different fluxes and separation factors with the assumption of left water content in the feed mixture < 0.001 wt %

S.F.	Flux (kg/m^{2}h)	Time (h)	Lost ethanol wt %*
10	1	53	10.000
10	5	11	10.000
10	20	2.6	10.000
100	1	30	1.000
100	5	6.1	1.000
100	20	1.5	1.000
1000	1	28	0.100
1000	5	5.6	0.100
1000	20	1.4	0.100
20000	1	28	0.005
20000	5	5.6	0.005
20000	20	1.4	0.005

*Lost ethanol wt % = Lost ethanol (g)/ Initial feed ethanol content (g) *100

4.7 Comparison of the membranes synthesized in this study and the membranes reported in literature

Figure 4.25 shows the separation factors and fluxes at different temperatures (25- 75 °C) for pervaporation separation of ethanol-water mixture with zeolite A membranes prepared in this study and in literature.

The zeolite A membranes synthesized in this study, in flow system have comparable pervaporation performances with the membranes synthesized both in flow and batch systems reported in literature. The fluxes of the membranes prepared in this study are as good as the high quality membranes reported in literature and the selectivities are in the range of (10^2-10^6) highly selective membranes. In literature, included in this plot, zeolite A membranes mainly synthesized in batch system. The only membranes synthesized in a continuous system to separate ethanol/water mixtures are reported by Pera-Titus et al. [11]. The membranes (10–20 μm in thickness) showed ability to dehydrate ethanol/water mixtures (92:8, w/w) by pervaporation with selectivities and fluxes, respectively, in the range of 51-8500 and 0.7-1.2 kg/m^{2}h at 50 °C. The only the difference with these membranes and the membranes prepared in this study was the support material. Our membranes prepared on α-alumina supports whereas the Pera-Titus et al. prepared membranes on porous titania (rutile) asymmetric supports. Our dehydrating results are slightly better than their results at 50 °C. Also our membranes (10 μm) prepared in flow system are slightly thinner than their membranes (15 μm).

The pervaporation separation performance of the membranes synthesized in this study, in batch system are slightly low separation performances compared to the membranes synthesized in batch systems reported in literature. The membranes synthesized in batch system in this study have low fluxes and low separation factors compared to literature [2, 4-6, 33, 38, 54, 55, 57, 84]. Although low separation factor can be due to the existence of non-zeolitic pores, the flux is expected to be higher with the existence of non-zeolitic pores. There is a recent study in which NaA zeolite membranes with narrow non-zeolitic pores were prepared by the secondary growth process using a nanometer-size seed, after which their ethanol dehydration behaviors were evaluated [86]. In that study, the water flux sharply decreased in an existing of alcohol and the phenomenon explained by the ethanol blockage in the α-cage with window of 4.2Å, being activated by the hydrogen bond between the adsorbed water and ethanol. This interaction may be also the reason of the low flux of the membranes prepared in our study.

Figure 4.26 (a) shows the separation factors and fluxes for pervaporation separation of ethanol/water mixtures reported in literature and in this study. Currently, in clear majority of pervaporation studies, pervaporation performances of membranes reported in terms of mass flux and separation factors. The problem with reporting data in this way is that these values are not only a function of the intrinsic properties of the membranes used, but also depend on the operating conditions of the experiments (feed concentration, permeate pressure, feed temperature). When the operating conditions change all the reported results change. Therefore, using flux and separation factors makes comparison of pervaporation data sets obtained under different operating conditions difficult [87, 88]. In order to prevent this comparison difficulty, permeation and permeability data of the pervaporation separation results of ethanol/water mixtures reported in literature and in this study are given respectively, in Figure 4.26 (b) and in Figure 4.26 (c). To see the effect of reporting (in this way) clearly, a point is marked with dashed circle in Figure 4.26 (a) and also in Figure 4.26 (b) and in Figure 4.26 (c). The location of the marked point in comparison to the other points changed in different figures due to the normalization of driving forces. The full set of data used for the preparation of Figure 4.26 is given in Appendix J.

The calculation methodology of permeance and permeability from conventional pervaporation data (total mass flux and separation factor) are listed below;

1. Calculation of partial fluxes of species i in $\frac{cm^3 STP}{cm^2 \cdot s}$ from total flux by using the permeate content of i which can be calculated from separation factor.

$$J_i = J_{total} \times x_{i,permeate} \qquad 4.1$$

2. Mole fraction of species i at the permeate side can be calculated from mass fraction at the permeate side which is known. Partial pressure of species i at the permeate side can be calculated from the total pressure of permeate side, $P_{T,permeate}$ and mole fraction of species i at the permeate side.

$$P_{i,permeate} = P_{T,permeate}\, y_{i,permeate} \qquad 4.2$$

3. Temperature and composition of the feed mixture is known. Activity coefficient of species i, γ_i^L (from UNIFAC computer program) and vapor pressure of species i, P_i^{sat} can be evaluated. By using γ_i^L and P_i^{sat}, fugacity of species i at the feed side can be obtained from the relation below;

$$f_{i,feed}^L = \gamma_i^L \times x_{i,feed} \times P_i^{sat} \qquad 4.3$$

4. Finally, permeance of species i is partial flux of species i over the partial pressure difference of species i from both feed and permeate sides; permeability is permeance times the membrane thickness.

$$\text{Permeance} = \frac{J_i}{\left(f_{i,feed}^L - P_{i,permeate}\right)} \qquad 4.4$$

$$\text{Permeability} = J_i \frac{l(thickness)}{\left(f^{L}_{i,feed} - P_{i,permeate}\right)} \qquad 4.5$$

In the light of this information, looking at the separation performance data for ethanol/water mixtures, the membranes synthesized in this study, in flow system, are again comparable to the membranes synthesized in batch systems reported in literature. But this time the performance of the membranes prepared in flow system are same as or slightly higher than the membranes synthesized in flow systems reported in literature. This may be due to normalization of driving forces when reporting the data in terms of permeance and permeability.

In a same manner, looking at the separation performance data for ethanol/water mixtures, the membranes synthesized in this study, in batch system, have again slightly low separation performances compared to the membranes synthesized in batch systems reported in literature. The membranes synthesized in batch system in this study have low permeances/permeabilities and low selectivities compared to literature.

The membranes synthesized in modified flow system have higher fluxes than the membranes prepared in batch system. The membranes synthesized in modified flow system generally have higher separation factors than the membranes prepared in batch system. But reproducibility of the synthesis of zeolite A membranes in modified flow system is lower than the reproducibility of the synthesis of zeolite A membranes in batch system. Considering these results, the method used in this study is promising for the synthesis of zeolite A membranes in the case of improved synthesis reproducibility. Since the method has the practical advantages it will possibly have in large-scale synthesis and it will overcome the handicaps in static systems at industrial level production.

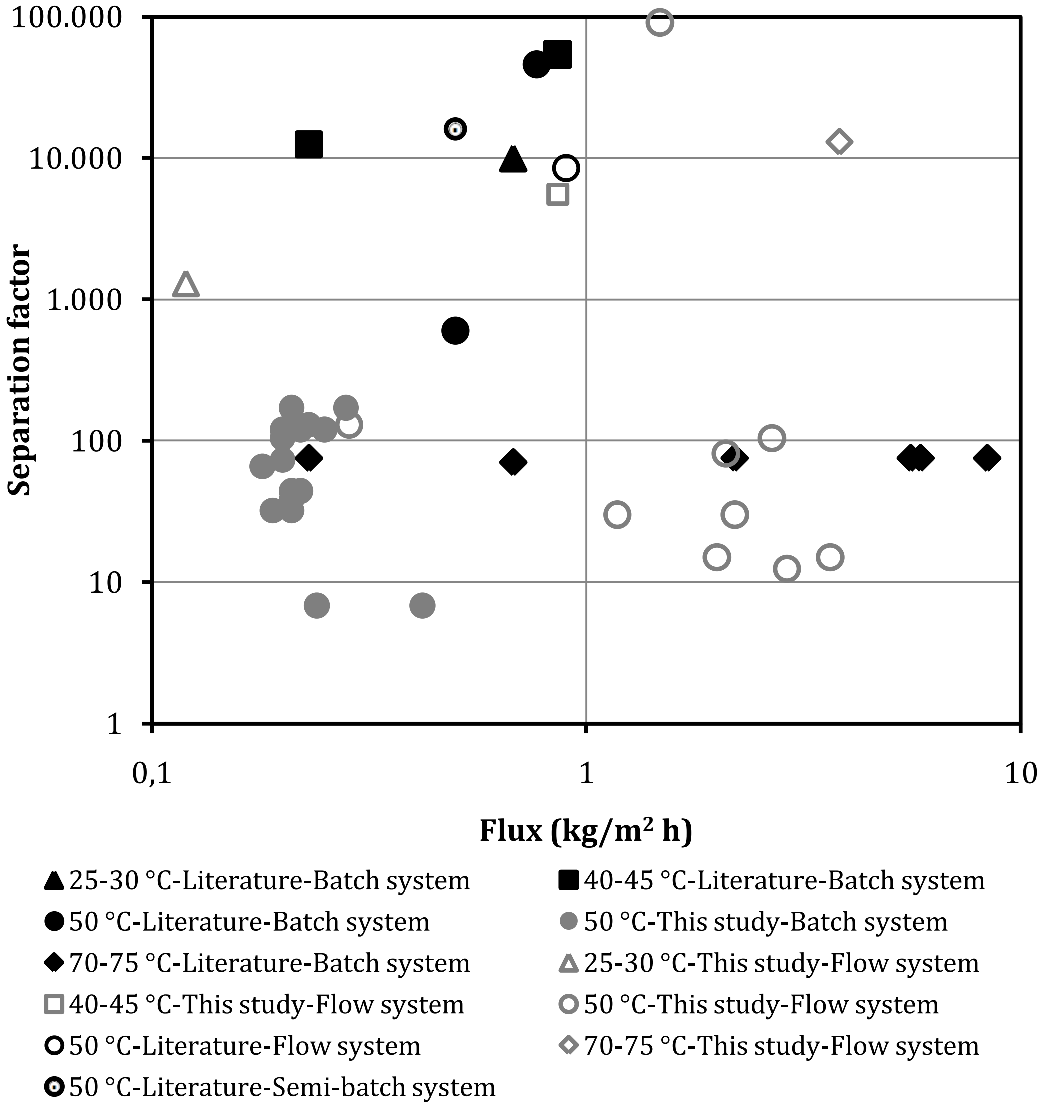


Figure 4.25 Comparison of separation factors and fluxes at different temperatures (25 - 75 °C) for pervaporation separation of ethanol-water mixture with zeolite A membranes prepared in this study and in literature [2-6, 11, 18, 33, 38, 40, 54, 55, 57, 58, 60, 84]

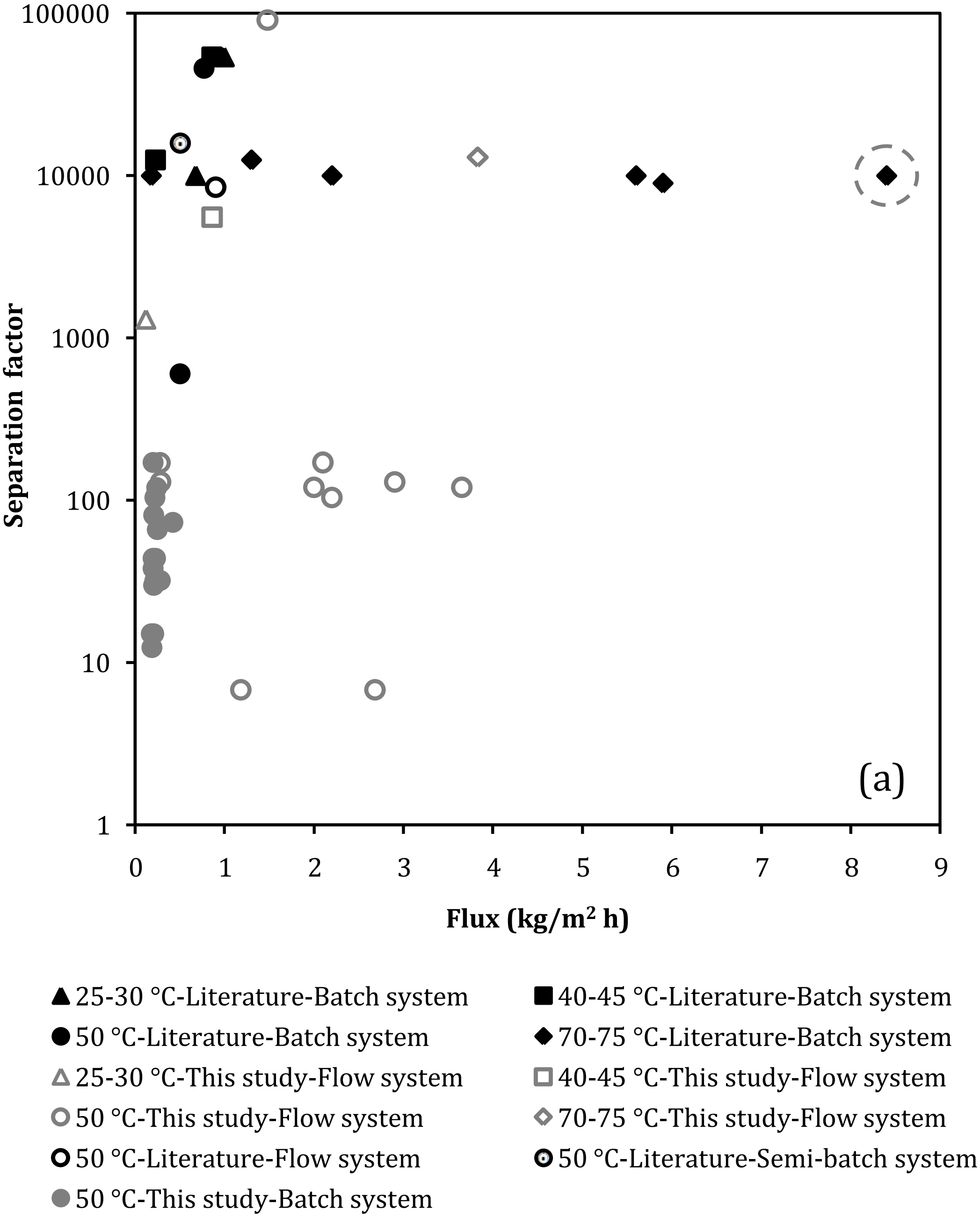


Figure 4.26 Comparison of separation factors and fluxes for ethanol/water mixture separations with literature (a), the permeance data of a (b), the permeability data of a (c). Filled symbols represent flow system results and open symbols represent batch system results

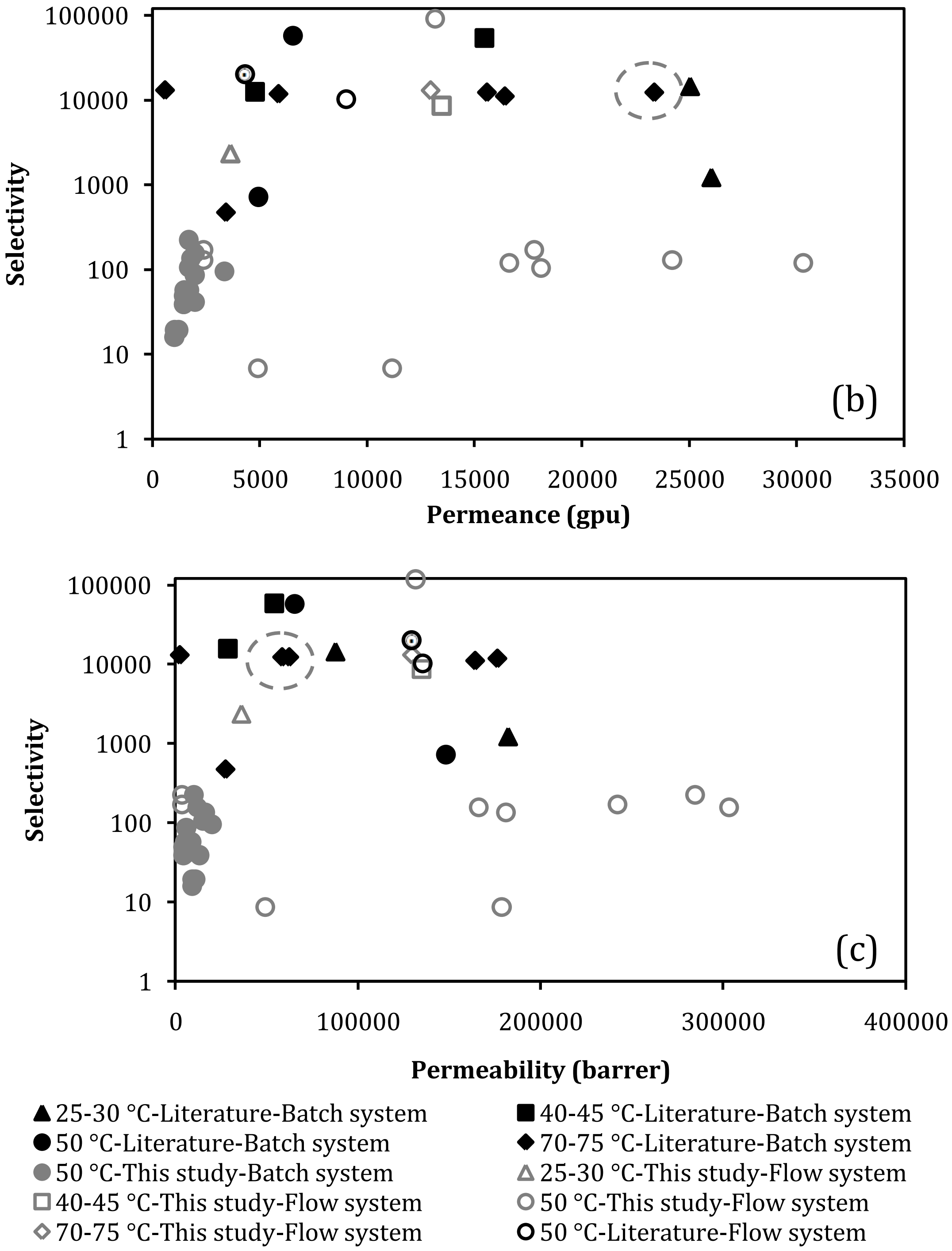


Figure 4.26 Comparison of separation factors and fluxes for ethanol/water mixture separations with literature (a), the permeance data of a (b), the permeability data of a (c). Filled symbols represent flow system results and open symbols represent batch system results

4.8 Difficulties to prepare zeolite A membranes reproducibly

Zeolite A membrane is traditionally synthesized in autoclaves by using either a milky-like gel or a clear solution without organic templates, onto the surface of a porous support with or without a previous seeding step. No calcination step is required due to the absence of organic templates, so it is expected that there are less non-zeolitic pores in the zeolite A membrane than other membranes prepared with organic templates, like MFI membrane. But some researchers reported that there are many non-zeolitic pores in the zeolite A layer [5, 31]. The existence of these pores caused difficulties to prepare shape-selective zeolite A membranes for gas separation [2, 41, 89]. Caro et al. [90] discussed two possible reasons for this difficulty to prepare zeolite A membranes for gas separations. One mentioned reason is the strongly negative surface charge of Al-rich zeolites like zeolite A in aqueous media, that is expected to prevent the negatively charged silica species to enter the narrow openings between the crystallites in zeolite layer. The other reason is the extreme mismatches in the expansion coefficients between the zeolite layer and support material upon drying the membrane. They also indicated that non-zeolitic pores in the zeolite A layer contribute to the total flux in pervaporation or vapor permeation separation of short-chain alcohols.

Okamoto et al. [2] were also indicated that non-zeolitic pores which are smaller in number and size significantly contribute to the high total flux, but the issue about which kind of non-zeolitic pores contribute the total flux and which ones lead to low separation performance is still unknown.

Pera-Titus et al. [91] is also indicated that the main problem when preparing zeolite membranes either for gas separation or PV purposes is the presence of non-zeolitic pores. It is said that these non-zeolitic pores usually consist of mesopores and grain boundaries, but might also include *pin holes* and *cracks* generated during the *synthesis* or *operation*. But the issue about what mean diameters of non-zeolitic pores may be a function of is also unknown.

Lastly in a recent study of Cho et al. [86], they indicated that there is a mismatch of thermal expansion coefficients of zeolite A layer and the alumina support. This mismatch caused crack formation and low separation performance even in PV operations. They also stated that by a simple thermal stress calculation, the zeolite membranes with a clear phase boundary between LTA layer and α-alumina support is highly vulnerable to thermal crack formation during heating.

Although there are some difficulties to prepare high performance zeolite A membranes reproducibly, there are also some studies in literature, in which high performance zeolite A membranes synthesized with high reproducibility [2, 5]. Table 4.7 show the reproducibility analysis for the membranes prepared in literature and in this study. Kita et al. [2], prepared nine high quality membranes from $N_2A_1S_2H_{120}$ hydrogel at 100 °C in 3 hours on seeded tubular supports with a high reproducibility. Those nine membranes have fluxes and selectivities in the range of 1.62-2.15 kg/m^{2}h and 8000-30000, respectively at 45 °C. Sato et al. [5], also prepared four high quality membranes from $N_2A_1S_2H_{150}$ hydrogel at 100 °C in 4 hours on seeded tubular supports with reproducibly. Three of those membranes have fluxes and selectivities in the range of 4.2-24.6 kg/m^{2}h and 6600-13000, respectively at 75 °C. Pera-Titus et al. [11], synthesized six zeolite A membranes from $N_{3.9}A_1S_{1.8}H_{270}$ hydrogel at 80-90 °C in 3-7 hours on seeded tubular supports. Four of those membranes have fluxes and selectivities in the range of 0.72-1.16 kg/m^{2}h and 160-8538, respectively at 50 °C. Cho et al. [86], synthesized fourteen membranes from $N_{4.5}A_1S_2H_{600}$ hydrogel at 100 °C in 24 hours on seeded tubular supports. These membranes showed two kinds of PV performances at 70 °C. Nine of those membranes have high fluxes (1-10 kg/m^{2}h) with low selectivities (30-300). However five of those membranes have low fluxes (< 0.1 kg/m^{2}h) with high selectivity (~10000). In this study eight membranes prepared from $N_{3.4}A_1S_2H_{200}$ hydrogel at 95 °C in 6-17 hours on seeded tubular supports. Three of these membranes have fluxes and selectivities in the range of 1.2-2.7 kg/m^{2}h and 81->25000, respectively at 50 °C. Although the synthesis methods are very similar to each other, PV performances vary in a wide range. So there may be some unknown factors influencing the reproducibility of the synthesis method.

In this study, a synthesis method for the preparation of selective zeolite A membranes in a recirculated flow system is developed and dehydrating ability of the synthesized membranes by pervaporation separation of ethanol/water mixture is shown but reproducibility of the synthesis method should be improved. Mainly the fluxes of membranes synthesized in modified flow system are in the range of 1.2-3.7 kg/m^{2}h and selectivities are in the range of 12-25,000 at 50 °C even the same synthesis method was used. In the light of these discussions, this wide variation of selectivity can be attributed to presence of non-zeolitic pores having large mean diameters. For further improvements in this synthesis method; minimizing the number of non-zeolitic pores and their mean diameters can be the area that should be focused on.

Table 4.7 Reproducibility analysis for the membranes prepared in literature and in this study

Synthesis Conditions	# of synthesized membranes	# of membranes having similar PV performances/ Flux (kg/m² h), SF	# of membranes having different PV performances/ Flux (kg/m² h), SF	PV Temp. (°C)	Feed Water wt %	Ref.
Batch system, $N_2A_1S_2H_{120}$ 100 °C, 3 h Rubbing a slurry of 4A zeolite and water	9	9 Flux=1.62-2.15 SF=8000-30,000	-	45	10	2 Kita et al.
Batch system, $N_2A_1S_2H_{150}$ 100 °C, 4 h Dip-coating with 0.5 wt % zeolite A suspension	4	3 Flux=4.2-4.6 SF=6600-13,000	1 Flux=4.1 SF=1,900	75	10	5 Sato et al
Flow system, 1.5-4 mL/min $N_{3.9}A_1S_{1.8}H_{270}$ 80-90 °C, 3-7 h Brush seeding with powder zeolite A	6	4 Flux=0.72-1.16 SF=160-8,538	2 Flux=0.93-0.97 SF=51-76	50	8-9	11 Pera-Titus et al.
Batch system, $N_{4.5}A_1S_2H_{600}$ 100 °C, 24 h Nano-sized seeds were coated by vacuum assisted filtration method	14	9 Flux=1-10 SF=30-300	5 Flux<0.1 SF ~10,000	70	5	85 Cho et al.
Flow system, 4 mL/s $N_{3.4}A_1S_2H_{200}$, 95 °C, 6-17 h Dip-coating with 0.56 wt % zeolite A suspension	8	3 Flux=1.2-2.7 SF=81- >25,000	5 Flux=1.2-3.7 SF=12-30	50	10	This study

CHAPTER 5

CONCLUSIONS

In this study, pure, continuous and uniform zeolite A membranes were synthesized both in batch and recirculated flow systems. Membranes with higher selectivities were obtained by using $N_{3.4}A_1S_2H_{155}$ batch composition, using *waterglass* as silica source, and seeding by *dip-coating wiping* method in batch system.

Selective and thin (1.5 μm) zeolite A membranes were also synthesized in recirculating flow system on α-alumina supports from $N_{3.4}A_1S_2H_{150}$ hydrogels at 95 °C, with a flow rate of 4mL/s and atmospheric pressure. The membranes prepared by using recirculated flow system had comparable pervaporation performance with the membranes prepared in batch systems and with the membranes, which were synthesized in flow systems, reported in literature.

By making further modifications in the synthesis method; high quality zeolite A membranes (10 μm) were also synthesized on the inner side of the α-alumina tubular support from $N_{3.4}A_1S_2H_{200}$ hydrogel at 95 °C for 17 hours with a flow rate of 4mL/s in flow system. These membranes showed ability to dehydrate ethanol/water mixtures (90:10, w/w) by pervaporation with selectivities and fluxes, respectively, >25,000 and 1.2 kg/m^{2}h at 50 °C. Although the synthesis method is resulted with high quality membranes, reproducibility of the synthesis method is poor and it should be improved.

Flux of the membrane is also very important quality criteria in addition to selectivity from an industrial point of view. Hence making zeolite A membranes with high fluxes such as 10-20 kg/m^{2}h at 50 °C with reasonable selectivities can be one of the area that should be focused on.

Considering that selective zeolite A membranes synthesized in a flow system with recirculation of the synthesis solution, therefore, it is concluded that the method used in this study is promising for the synthesis of zeolite A membranes in the case of improved synthesis reproducibility. Since the method has the practical advantages it will possibly have in large-scale synthesis and it will overcome the handicaps in static systems at industrial level production.

CHAPTER 6

RECOMMENDATIONS

Continuous and high quality zeolite A membranes have been synthesized on the inner side of tubular alumina supports in a re-circulated flow system. In addition to what has been done in this study, recommendations on further work to be done are as follows:

- Investigations need to be made to improve the reproducibility of synthesis method. Investigations can be focused on position of the support material during the synthesis and minimizing the number of non-zeolitic pores and their mean diameters.
- Zeolite A membranes with high fluxes such as 10-20 kg/m^{2}h at 50 °C with reasonable selectivities can be synthesized from $N_{3.4}A_1S_2H_{200}$ hydrogel at 95 °C for 3-6 hours with a flow rate of 4mL/s in modified flow system since flux of the membrane is also very important quality criteria in addition to selectivity from an industrial point of view.
- Zeolite A membranes can be prepared on different supports by using same synthesis method to see if there is effect of support material on membrane performance and/or morphology or not.
- A commercial membrane should have a small volume with high membrane area for efficient industrial use. So zeolite A membranes can be synthesized on multi channeled monoliths, and hollow fibers to increase the area to volume ratio.

REFERENCES

[1] Breck, D.W., “Zeolite molecular sieves: Structure, chemistry, and use”, Wiley, New York, 1974.

[2] Okamoto, K., Kita, H., Horii, K., Tanaka K., “Zeolite NaA Membrane: Preparation, Single-Gas Permeation, and Pervaporation and Vapor Permeation of Water/Organic Liquid Mixtures” *Industrial and Engineering Chemistry Research,* 40 (2001) 163-175.

[3] Pina, M.P., Arruebo, M., Felipe, M., Fleta, F., Bernal, M.P., Coronas, J., Menendez, M., Santamaria J., “A semi-continuous method for the synthesis of NaA zeolite membranes on tubular supports”, *Journal of Membrane Science,* 244 (2004) 141–150.

[4] Pera-Titus, M., Mallada, R., Llorens, J., Cunill, F., Santamaria, J., “Preparation of inner-side tubular zeolite NaA membranes in a semi-continuous synthesis system”, *Journal of Membrane Science,* 278 (2006) 401–409.

[5] Sato, K., Nakane, T., “A high reproducible fabrication method for industrial production of high flux NaA zeolite membrane”, *Journal of Membrane Science,* 301 (2007) 151–161.

[6] Morigami, Y., Kondo, M., Abe J., Kita, H., Okamoto K., “The first large-scale pervaporation plant using tubular-type module with zeolite NaA membrane”, *Separation and Purification Technology*, 25 (2001) 251–260.

[7] Richter, H., Voigt, I., Fischer, G., Puhlfürß, “Preparation of zeolite membranes on the inner surface of ceramic tubes and capillaries”, *Separation and Purification Technology*, 32 (2003) 133-138.

[8] Yamazaki, S., Tsutsumi, K., “Synthesis of A-type zeolite membrane using a plate heater and its formation mechanism”, *Microporous and Mesoporous Materials*, 37 (2000) 67-80.

[9] Çulfaz, P.Z., Çulfaz,A., Kalıpçılar, H., “Preparation of MFI type zeolite membranes in a flow system with circulation of the synthesis solution”, *Microporous and Mesoporous Materials*, 92 (2006) 134-144.

[10] Soydaş, B., Dede, O., Çulfaz,A., Kalıpçılar, H., “Separation of gas and organic/water mixtures by MFI type zeolite membranes synthesized in a flow system”, *Microporous and Mesoporous Materials*, 127 (2010) 96-103.

[11] Pera-Titus, M., Bausach, M., Llorens, J., Cunill, F., “Preparation of inner-side tubular zeolite NaA membranes in a continuous flow system”, *Separation and Purification Technology*, 59 (2008) 141–150.

[12] Akbay, S., “Synthesis of Low Silica/Alumina Zeolite Membranes in a Flow System”, M.S. Thesis in Chemical Engineering Department. 2007, Middle East Technical University: Ankara.

[13] Aguado, S., Gascón, J., Jansen, J.C., Kapteijn F., “Continuous synthesis of NaA zeolite membranes”, *Microporous and Mesoporous Materials*, 120 (2009) 170–176.

[14] Mulder, M., “Basic Principles of Membrane Technology”, Kluwer Academic Publishers, Dordrecht, 1996.

[15] Van Hoof, V., Van den Abeele, L., Buekenhoudt, A., Dotremont, C., Leysen, R., “Economic comparison between azeotropic distillation and different hybrid systems combining distillation with pervaporation for the dehydration of isopropanol”, *Separation and Purification Technology*, 37 (2004) 33-49.

[16] Van Hoof, V., Dotremont, C., Buekenhoudt, A. , "Performance of Mitsui NaA type zeolite membranes for the dehydration of organic solvents in comparison with commercial polymeric pervaporation membranes", *Separation and Purification Technology*, 48 (2006) 304-309.

[17] Sommer, S., Melin, T., "Performance evaluation of microporous inorganic membranes in the dehydration of industrial solvents", *Chemical Engineering and Processing*, 44 (2005) 1138–1156.

[18] Kondo M., Komori, M., Kita, H., Okamoto, K., "Tubular-type pervaporation module with zeolite NaA membrane", *Journal of Membrane Science,* 133 (1997) 133-141.

[19] Soydaş, B., Çulfaz, A., Kalıpçılar, H., "Effect of Mid-synthesis Addition of Silica to the Synthesis Medium on the Properties of MFI-Type Zeolite Membranes", *Industrial and Engineering Chemistry Research*, 49 (2010) 5407-5414.

[20] Bowen, T.C., Kalıpçılar, H., Falconer, J.L., Noble, R.D., "Pervaporation of organic/water mixtures through B-ZSM-5 zeolite membranes on monolith supports", *Journal of Membrane Science*, 215 (2003) 235-247.

[21] Broeke, L.J.P., "Simulation of diffusion in zeolitic structures", *AIChE Journal*, 46 (1996) 2399.

[22] Krishna, R., Broeke, L.J.P., "The Maxwell–Stefan description of mass transport across zeolite membranes", *Chemical Engineering Journal*, 57 (1995) 155.

[23] Kapteijn, F,. Bakker, W.J.W., Zheng, G., Poppe, J., Moulijn, J.A., "Permeation and separation of light hydrocarbons through a silicalite-1 membrane. Application of the generalized Maxwell–Stefan equations", *Chemical Engineering Journal*, 57 (1995) 145.

[24] Graaf, J.M., Kapteijn, F., Moulijn, J.A., "Modeling permeation of binary mixtures through zeolite membranes", *AIChE Journal*, 45 (1999) 497.

[25] Nomura, N., Yamaguchi, T., Nakao, S., "Ethanol/water transport through silicalite membranes", *Industrial and Engineering Chemistry Research,* 36 (1997) 4217.

[26] Nishiyama, N., Ueyama, K., Matsukata, M., "Gas permeation through zeolite–alumina composite membranes", *AIChE Journal*, 43 (1997) 2724.

[27] Nomura, N., Yamaguchi, T., Nakao, S., "Transport phenomena through intercrystalline and intracrystalline pathways of silicalite zeolite membranes", *Journal of Membrane Science*, 187 (2001) 203.

[28] Shah, D., Kissick, K., Ghorpade, A., Hannah, R., Bhattacharyya, D., "Pervaporation of alcohol–water and dimethylformamide–water mixtures using zeolite NaA membranes: mechanism and experimental results", *Journal of Membrane Science*, 179 (2000) 185.

[29] Sommer, S., Melin, T., "Influence of operation parameters on the separation of mixtures by pervaporation and vapor permeation with inorganic membranes. Part 1: dehydration of solvents", *Chemical Engineering Science*, 60 (2005) 4500.

[30] Kondo, M., Kita H., "Permeation mechanism through zeolite NaA and T-type membranes for practical dehydration of organic solvents", *Journal of Membrane Science,* 361 (2010) 223–231.

[31] Bowen, T.C., Noble, R.D., Falconer, J.L., "Fundamentals and applications of pervaporation through zeolite membranes", *Journal of Membrane Science,* 245 (2004) 1–33.

[32] Chau, J.L.H., Téllez, C., Yeung, K.L., Ho, K., "The role of surface chemistry in zeolite membrane formation", *Journal of Membrane Science,* 164 (2000) 257.

[33] Kumakiri, I., Yamaguchi, T., Nakao, S., "Preparation of Zeolite A and Faujasite Membranes from a Clear Solution", *Industrial and Engineering Chemistry Research*, 38 (1999) 4682-4688.

[34] Kita, H., Horii, K., Ohtoshi, Y., Tanaka, K., Okamoto, K., “Synthesis of a zeolite NaA membrane for pervaporation of water/organic liquid mixtures”, *Journal of Materials Science Letters*, 14 (1995) 206-208.

[35] Masuda, T., Hara, H., Kouno, M., Kinoshita, H., Hashimoto, K., “Preparation of an A-type zeolite film on the surface of an alumina ceramic filter”, *Microporous Materials*, 3 (1995) 565-571.

[36] Huang, A., Lin L., Yang, W., “Synthesis and properties of A-type zeolite membranes by secondary growth method with vacuum seeding”, *Journal of Membrane Science*, 245 (2004) 41–51.

[37] Wang, Z., Ge, Q., Shao, J., Yan, Y., “High Performance Zeolite LTA Pervaporation Membranes on Ceramic Hollow Fibers by Dipcoating-Wiping Seed Deposition”, *Journal of American Chemical Society*, 131 (2009) 6910-6911.

[38] Van den Berg, A.W.C., Gora, L., Jansen, J.C., Makkee, M., Maschmeyer, Th., “Zeolite A membranes synthesized on a UV-irradiated TiO2 coated metal support: the high pervaporation performance”, *Journal of Membrane Science*, 224 (2003) 29–37.

[39] Salomón, M.A., Coronas, J., Menéndez, M., Santamaría, J., “Synthesis of MTBE in zeolite membrane reactors”, *Applied Catalysis A*, 200 (2000) 201-210.

[40] Tiscareño-Lechuga, F., Téllez, C., Menéndez, M., Santamaria, J. “A novel device for preparing zeolite—A membranes under a centrifugal force field”, *Journal of Membrane Science*, 212 (2003) 135–146.

[41] Xu, X., Yang, W., Liu, J., Lin L., “Synthesis of NaA zeolite membranes from clear solution”, *Microporous and Mesoporous Materials*, 43 (2001) 299–311.

[42] Xu, X., Yang, W., Liu, J., Lin L., “Synthesis and perfection evaluation of NaA zeolite membrane”, *Separation and Purification Technology*, 25 (2001) 475–485.

[43] Kita, H., Asamura, H., Tanaka, K., Okamoto, K.-I., Kondo, M., "Preparation of X- and Y-type zeolite membranes and pervaporation properties", *Abstracts* of *Papers* of the American *Chemical Society,* 214 (1997) 269.

[44] Kusakabe, K., Kuroda, T., Uchino, K., Hasegawa, Y., Morooka, S., "Gas permeation properties of ion-exchanged faujasite-type zeolite membranes", *AIChE Journal*, 45 (1999) 1220.

[45] Li, S., Tuan, V.A., Falconer, J.L., Noble, R.D., "X-type zeolite membranes: preparation, characterization, and pervaporation performance", *Microporous and Mesoporous Materials,* 53 (2002) 59.

[46] Sano, T., Yanagishita, H., Kiyozumi, Y., Mizukami, F., Haraya, K., "Separation of ethanol–water mixture by silicalite membrane on pervaporation", *Journal of Membrane Science*, 95 (1994) 221.

[47] Lovallo, M.C., Gouzinis, A., Tsapatsis, M., "Synthesis and characterization of oriented MFI membranes prepared by secondary growth", *AIChE Journal*, 44 (1998) 1903.

[48] Li, S., Tuan, V.A., Noble, R.D. and Falconer, J.L., "Pervaporation of water/THF mixtures using zeolite membranes", *Industrial and Engineering Chemistry Research*, 40 (2001) 4577–4585.

[49] Nishiyama, N., Ueyama, K., Matsukata, M., "Synthesis of FER membrane on an alumina support and its separation properties", *Studies in Surface Science and Catalysis*, 105 (1997) 2195.

[50] Tuan, V.A., Li, S., Noble, R.D., Falconer, J.L., "Preparation and pervaporation properties of a MEL-type zeolite membrane", *Journal of the Chemical Society - Chemical Communications*, (2001) 583.

[51] Kitao, S., Asaeda, M., "Separation of organic acid/water mixtures by thin porous silica membrane", *Journal of Chemical Engineering of Japan*, 23 (1990) 367.

[52] Asaeda, M., Okazaki, K., Nakatani, A., "Preparation of thin porous silica membrane for separation of nonaqueous organic solvent by pervaporation", *Ceramic Transactions*, 31 (1992) 411.

[53] Huang, A., Yang, W., Liu, J., "Synthesis and pervaporation properties of NaA zeolite membranes prepared with vacuum-assisted method", *Separation and Purification Technology*, 56 (2007) 158–167.

[54] Kazemimoghadam, M., Mohammadi T., "Preparation of NaA zeolite membranes for separation of water/UDMH mixtures", *Separation and Purification Technology*, 47 (2006) 173–178.

[55] Pera-Titus, M., Llorens, J., Cunill, F., Mallada, R., Santamaria, J., "Preparation of zeolite NaA membranes on the inner side of tubular supports by means of a controlled seeding technique", *Catalysis Today*, 104 (2005) 281–287.

[56] Ahn, H., Lee, H., Lee, S., Lee, Y., "Pervaporation of an aqueous ethanol solution through hydrophilic zeolite membranes", *Desalination*, 193 (2006) 244–251.

[57] Zah, J., Krieg, H. M., Breytenbach J. C., "Pervaporation and related properties of time-dependent growth layers of zeolite NaA on structured ceramic supports", *Journal of Membrane Science*, 284 (2006) 276–290.

[58] Sato, K., Sugimoto, K., Nakane, T., "Preparation of higher flux NaA zeolite membrane on asymmetric porous support and permeation behavior at higher temperatures up to 145 °C in vapor permeation", *Journal of Membrane Science*, 307 (2008) 181–195.

[59] Malekpour, A., Millani, M.R., Kheirkhah, M., "Synthesis and characterization of a NaA zeolite membrane and its applications for desalination of radioactive solutions", *Desalination*, 225 (2008) 199–208.

[60] Jafar, J.J., Budd, P. M., "Separation of alcohol/water mixtures by pervaporation through zeolite A membranes", *Microporous Materials*, 12 (1997) 305 311.

[61] Çulfaz, P.Z., "Synthesis of MFI type zeolite membranes in a continuous system", M.S. Thesis in Chemical Engineering Department. 2005, Middle East Technical University: Ankara.

[62] Zah, J., Krieg, H. M., Breytenbach J. C., "Layer development and growth history of polycrystalline zeolite A membranes synthesized from a clear solution", *Microporous and Mesoporous Materials,* 93 (2006) 141–150.

[63] Han, Y., Ma, H., Qiu, S., Xiao F., "Preparation of zeolite A membranes by microwave heating", *Microporous and Mesoporous Materials*, 30 (1999) 321–326.

[64] Lai, R., Gavalas, G.R., "Surface seeding in ZSM-5 membrane preparation", *Industrial and Engineering Chemistry Research*, 37 (1998) 4275.

[65] Hedlund, J., Sterte, J., Anthonis, M., Bons, A.J., Carstensen, B., Cororan, N., Cox, D., Deckman, H., Ginst, W.M., de Moor, P.P., Lai, F., McHenry, J., Mortier, W., Reinco, J., Peters, J., "High-flux MFI membranes", *Journal of Membrane Science,* 52 (2002) 179.

[66] Lai, Z., Bonilla, G., Diaz, I., Nery, J.G., Sujaoti, K., Amat, M.A., Kokkoli, E., Terasaki, O., Thompson, R.W., Tsapatis, M., Vlachos, D.G., Microstructure optimization of a zeolite membrane for organic vapor separation, *Science*, 300 (2003) 456.

[67] Boudreau, L.C., Tsapatsis, M., A highly oriented thin film of zeolite A, *Chemistry of Materials*, 9 (1997) 1705.

[68] Oonkhanond, B., Mullins, M.E., "The preparation and analysis of zeolite ZSM-5 membranes on porous alumina supports", *Journal of Membrane Science*, 194 (2001) 3-13.

[69] Coronas, J., Falconer, J.L., Noble, R.D., "Characterization and permeation properties of ZSM-5 tubular membranes", *AlChe Journal*, 43 (1997) 1797.

[70] Funke, H.H., Kovalchick, M.G., Falconer, J.L., Noble, R.D., "Separation of hyrdocarbon vapors with silicalite zeolite membranes", *Industrial and Engineering Chemistry Research*, 35 (1996) 1575-1582.

[71] Mitsui Engineering and Shipbuilding Co. Ltd., Enviroment- Related Recycling Bulletin, 2010 http://www.mes.co.jp/english/business/environ/; last accessed on 1st November 2010.

[72] Liu Q., Noble R.D., Falconer J.L., Funke, H.H., "Organics/water separation by pervaporation with a zeolite membrane" *Journal of Membrane Science*, 117 (1-2) (1996) 163-174.

[73] Mohamed, R.M., Ismail, A.A., Kini, G., Ibrahim, I.A., Koopman, B., "Synthesis of highly ordered cubic zeolite A and its ion-exchange behavior", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 348 (2009), 87-92.

[74] Twu, J., Dutta, P.K. and Kresge, C.T. "Raman spectroscopic studies of the synthesis of faujasitic zeolites: Comparison of two silica sources", *Zeolites*, 11 (1991) 672-679.

[75] Smaihi M., Barida, O., Valtchev, V., "Investigation of the Crystallization Stages of LTA-Type Zeolite by Complementary Characterization Techniques", *European Journal of Inorganic Chemistry*, 2003 (2003) 4370-4377.

[76] McCormick, A.V., Bell, A.T., "The Solution Chemistry of Zeolite Precursors", Catalysis Reviews, 31 (1989) 97-127.

[77] Antonic, T., Subotic, B., Stubicar, N., "Influence of gel properties on the crystallization of zeolites: Part 1: Influence of alkalinity during gel preparation on the kinetics of nucleation of zeolite A", Zeolites, 18 (1997) 291-300.

[78] Mintova, S., Valtchev, V., Bein, T., "Formation of colloidal molecular sieves: influence of silica precursor", Colloids and Surfaces A: Physicochemical and Engineering Aspects, 217 (2003), 153-157.

[79] Lin, H., Chao, Z., Chen, G., Wan, H., "Synthesis and gas separation performance of NaA zeolite composite membrane", *Chinese Journal of Catalysis*, 21 (5) (2000) 474.

[80] Vroon, Z.A.E.P., Keizer, K., Burggraaf, A.J., Verweij, H., "Preparation and characterization of thin zeolite MFI membranes on porous supports", *Journal of Membrane Science*, 144 (1998) 65-76.

[81] Lin, Y. S., Kumakiri, I., Nair, B. N., Alsyouri, H., "Microporous inorganic membranes", *Separation and Purification Methods*, 31 (2) (2002) 229–379.

[82] Cundy, C. S., Cox, P. A., "The hydrothermal synthesis of zeolites: Precursors, intermediates and reaction mechanism", *Microporous and Mesoporous Materials*, 82 (2005) 1–78.

[83] Richter, H., Voigt, I., Kühnert, J., "Dewatering of ethanol by pervaporation and vapour permeation with industrial scale NaA-membranes", *Desalination*, 199 (2006) 92–93.

[84] Sato, K., Aoki, K., Sugimoto, K., Izumi, K., Inoue, S., Saito, J., Ikeda, S., Nakane, T. "Dehydrating performance of commercial LTA zeolite membranes and application to fuel grade bio-ethanol production by hybrid distillation/vapor permeation process", *Microporous and Mesoporous Materials*, 115 (2008) 184-188.

[85] Cho, C.H., Oh, K.Y., Kim, S.K., Yeo, J.G., Lee, Y.M., "Improvement in thermal stability of NaA zeolite composite membrane by control of intermediate layer structure", *Journal of Membrane Science,* 366 (2011) 229-236.

[86] Cho, C.H., Oh, K.Y., Yeo, J.G., Kim, S.K., Lee, Y.M., "Synthesis, Ethanol Dehydration and Thermal Stability of NaA Zeolite/Alumina Composite Membranes with Narrow Non-zeolitic Pores and Thin Intermediate Layer", *Journal of Membrane Science,* 364 (2010) 138-148.

[87] Baker , R.W., Wijmans, J.G., Huang, Y., “Permeability, permeance and selectivity: A preferred way of reporting pervaporation performance data”, *Journal of Membrane Science*, 348 (2010) 346–352.

[88] Wijmans, J.G., “Letter to the editor”, *Journal of Membrane Science*, 220 (2003) 1–3.

[89] Zah, J., Krieg, H.M., Breytenbach, J.C., “Single gas permeation through compositionally different zeolite NaA membranes: Observations on the intercrystalline porosity in an unconventional, semicrystalline layer”, *Journal of Membrane Science*, 287 (2007) 300–310.

[90] Caro, J., Albrecht, D., Noack, M., “Why is it so extremely difficult to prepare shape-selective Al-rich zeolite membranes like LTA and FAU for gas separation?”, *Separation and Purification Technology*, 66 (2009) 143–147.

[91] Pera-Titus, M., Llorens, J., Cunill, F., “On a rapid method to characterize intercrystalline defects in zeolite membranes using pervaporation data”, *Chemical Engineering Science*, 63 (2008) 2367–2377.

APPENDIX A

PRELIMINARY STUDIES FOR SELECTION OF STARTING SYNTHESIS COMPOSITION

Some preliminary studies were done in order to choose a starting synthesis composition. Zeolite A membranes were synthesized in autoclaves on α-alumina supports from two different gel compositions to see the effect of composition on membrane performance and morphology. These compositions are, $2.5Na_2O:1Al_2O_3:1.7SiO_2:150H_2O$ (BA44-BA67, BA88-BA91) and $3.4Na_2O:1Al_2O_3:2SiO_2:155H_2O$ (BA68-BA87, BA92-95). The membranes were synthesized at 95 °C for 3-8 hours in autoclaves. The synthesis conditions of all membranes are given in Appendix L.

Most of the membrane synthesis trials with the $2.5Na_2O:1Al_2O_3:1.7SiO_2:150H_2O$ composition were resulted either not selective membranes or low performance membranes. Slightly selective membranes (BA64, etc.) were compared with the membranes prepared from $3.4Na_2O:1Al_2O_3:2SiO_2:155H_2O$ (BA84, BA92) and the results were given in the following sections.

XRD patterns of the membranes and the remaining powders from the synthesis of membranes showed that the crystal phase formed on the supports in all synthesis was highly crystalline zeolite A. The XRD patterns of the synthesized membranes are shown in Figure A.1. All zeolite A peaks at Bragg angles of 7°, 10°, 12.5°, 16.1°, 21.5°, 24°, 26.1°, 27.2°, 30°, 30.8°, 32.5° and 34.3° are clearly observable in all XRD patterns of the membranes.

Many researchers indicated that the crystal phase observed in the remaining powder is recognized as the proof of the phase that forms the membrane layer [68-70]. The XRD patterns of the remaining powders from the synthesis of membranes are shown in Figure A.2. All of the remaining powders obtained from the synthesis of membranes are highly crystalline zeolite A. XRD patterns of the membranes and the remaining powders represents that the support surface is covered with pure zeolite A crystals.

The SEM cross-section images of the membranes (Figure A.3) show thin and continuous zeolite A layers. BA64 and BA84-2 have thickness of 5.6 μm and 5.3 μm, respectively, whereas BA92 (the membrane prepared for synthesis repetition of BA84) has thickness of 3 μm and the thicknesses are uniform through the membranes. (BA84 prepared by one consecutive synthesis and BA84-2 prepared by two consecutive syntheses, SEM pictures belong to BA84-2 and PV results belong to BA84.) The crystals forming the membrane layers show good intergrowth hence the layers seen very dense from the cross-section micrographs. The SEM surface images of the membranes are shown in Figure A.4. For all of the membranes, support surfaces are totally covered with zeolite A crystals with no voids and the intergrowth in all membranes are clearly observed from surface micrographs. The particle size of crystals is about 3 μm for all membranes.

The feed composition was composed of 10 % water and 90 % ethanol by weight. The pervaporation performances of the synthesized membranes were measured and the results are summarized in Table A.1. BA64, BA84 and BA92 were all synthesized in same way experimentally. The only difference was the starting synthesis composition. Membranes fluxes are in the range of 0.2-0.4 kg/m^{2}h whereas selectivities are in the range of 12-171. According to the data in Table A.1, membranes synthesized from $N_{3.4}A_1S_2H_{155}$ composition have much better pervaporation performances with a flux of 0.20-0.28 and with a selectivity of 73-171.

As a conclusion with both the starting compositions, as evaluated with the XRD patterns and SEM images, a continuous and uniform zeolite A membranes were synthesized whereas only the membranes synthesized from $N_{3.4}A_1S_2H_{155}$ composition have high selectivities in terms of pervaporation measurements. So it was decided to use $N_{3.4}A_1S_2H_{155}$ composition to synthesize zeolite A membranes from now on.

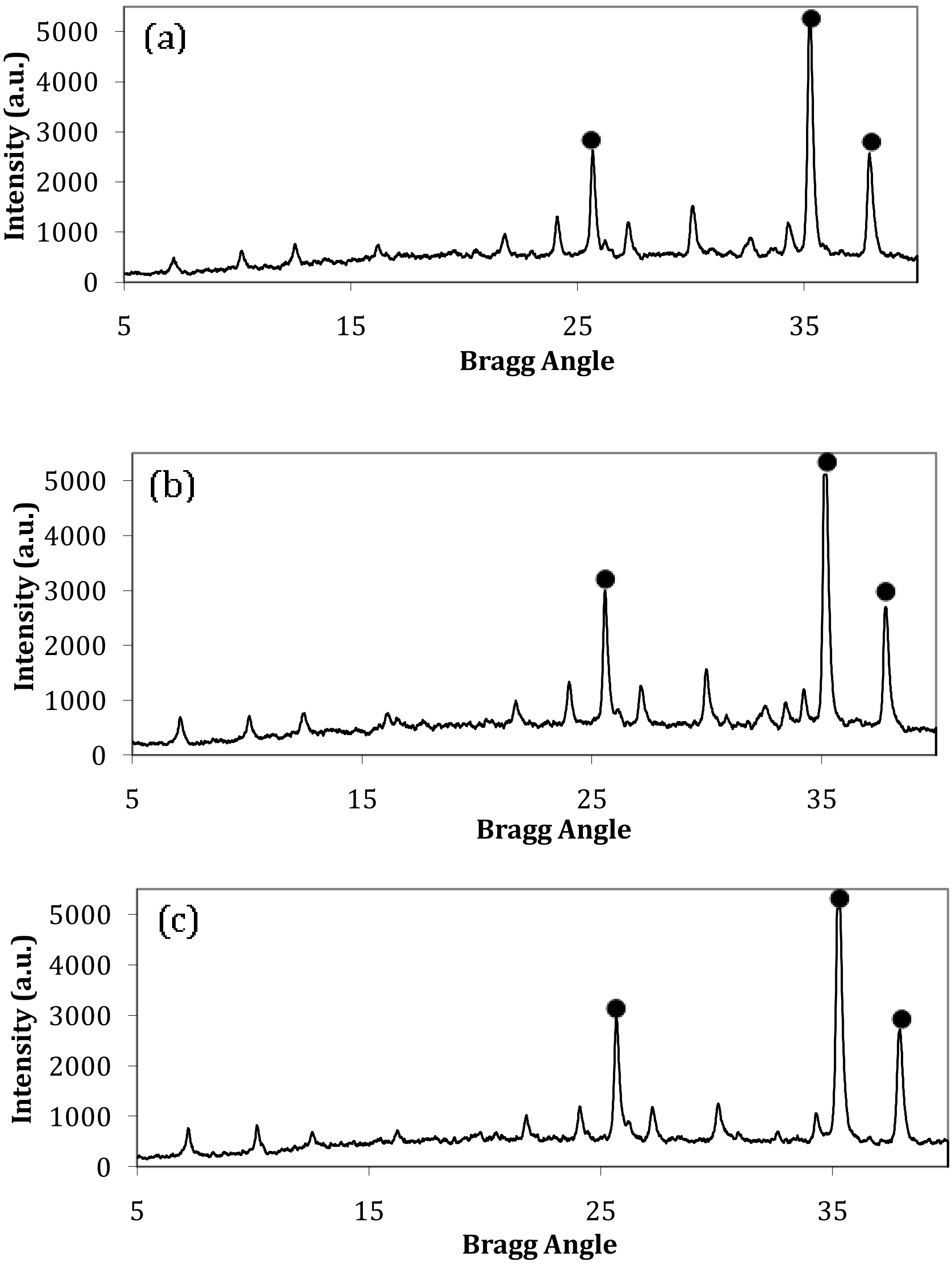


Figure A.1 XRD patterns of the zeolite A membranes prepared from different gel compositions at 95 °C for 4 hours in autoclaves; (a) BA64 ($N_{2.5}A_1S_{1.7}H_{150}$) , (b) BA84 ($N_{3.4}A_1S_2H_{155}$) and (c) BA92 ($N_{3.4}A_1S_2H_{155}$). Dots represent the α-alumina peaks and other peaks belong to zeolite A

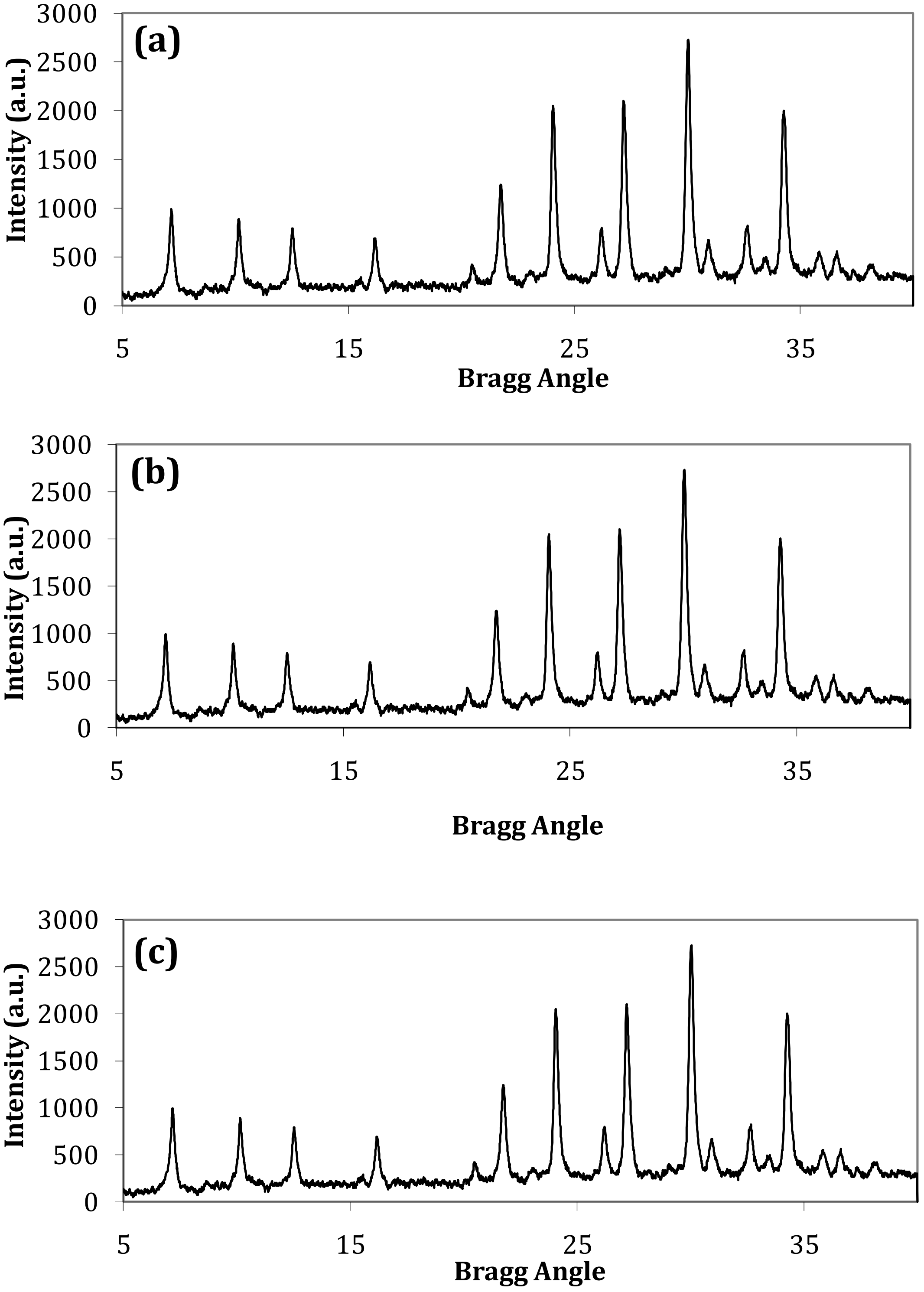


Figure A.2 XRD patterns of the remaning powders from the synthesis of membranes prepared from different gel compositions at 95 °C for 4 hours in autoclaves; (a) BA64-a ($N_{2.5}A_1S_{1.7}H_{150}$) , (b) BA84-a ($N_{3.4}A_1S_2H_{155}$) and (c) BA92-a ($N_{3.4}A_1S_2H_{155}$)

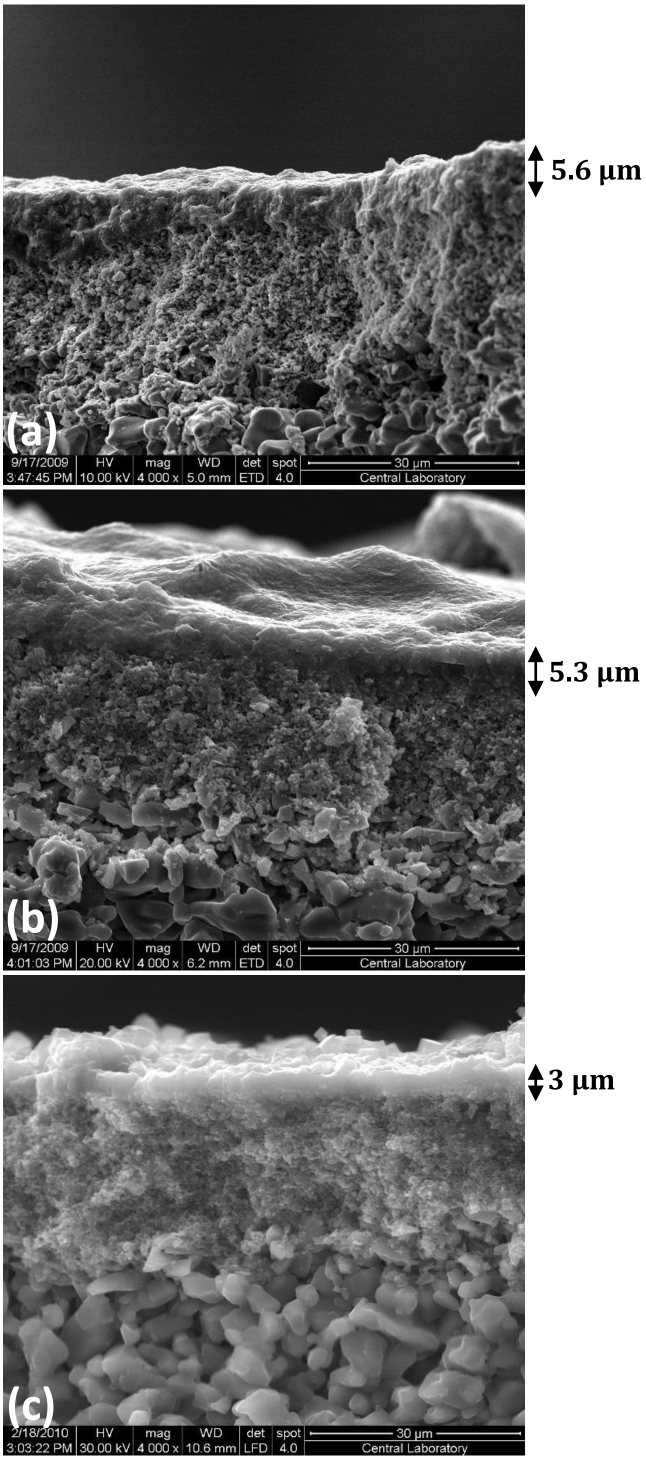
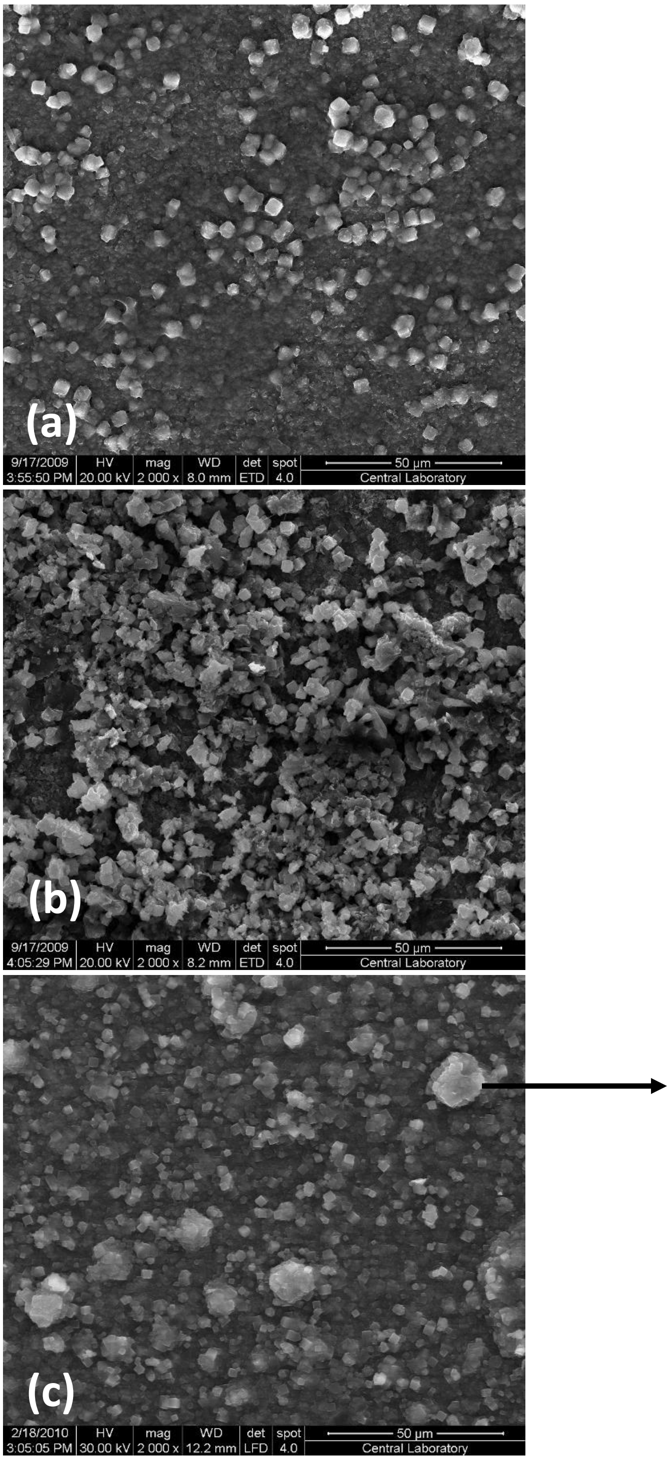


Figure A.3 Cross-section micrographs of the zeolite A membranes prepared from different gel compositions at 95 °C for 4 hours in autoclaves; (a) BA64 ($N_{2.5}A_1S_{1.7}H_{150}$) , (b) BA84-2 ($N_{3.4}A_1S_2H_{155}$) and (c) BA92 ($N_{3.4}A_1S_2H_{155}$)



Cabbage-like agglomerate

Figure A.4 Surface micrographs of the zeolite A membranes prepared from different gel compositions at 95 °C for 4 hours in autoclaves; (a) BA64 ($N_{2.5}A_1S_{1.7}H_{150}$) , (b) BA84-2 ($N_{3.4}A_1S_2H_{155}$) and (c) BA92 ($N_{3.4}A_1S_2H_{155}$)

Table A.1 Effect of synthesis composition to PV performance of the membranes prepared in batch system (Synthesis conditions: 95 °C, 4h, dip-coating wiping, waterglass)

				PV Results [a]		
Code	**Composition**	**Peak Ratio**	**SEM thickness (µm)**	**Flux (kg/m²h)**	**Selectivity**	**Permeate Water wt %**
BA64	$N_{2.5}A_1S_{1.7}H_{150}$	0.143	5.6	0.18	12.4	58
				0.38	17	65
BA84	$N_{3.4}A_1S_2H_{155}$	0.196	-	0.25	**120**	**93**
				0.28	**171**	**95**
BA92	$N_{3.4}A_1S_2H_{155}$	0.196	3	0.23	**130**	**93.5**
				0.20	**73**	**89**

[a] PV conditions: feed water fraction, 10 wt. %; T, 50°C; permeate pressure, 0.37kPa. Permeate samples are analyzed by RI. (N:Na_2O, A:Al_2O, S:SiO_2, H:H_2O)

Note: Selectivities determined according to GC analysis results of permeate samples are shown in Appendix L in detail. All membranes tested at least two runs to see the reproducibility of the PV measurements.

APPENDIX B

CALCULATION OF SYNTHESIS RECIPE FROM A BATCH COMPOSITION

A sample calculation for amounts of reagents to prepare 100 g synthesis solution for a molar batch composition $3.4Na_2O:1Al_2O_3:2SiO_2:155H_2O$ is given below. Waterglass (sodium silicate solution) as silica source, aluminum hydroxide as alumina source, sodium hydroxide pellets as sodium source and deionized water were used.

Table B.1 Composition of raw materials used in this study

Raw Material	Formula Weight (g/mol)	Reactant			
		Na_2O	Al_2O_3	SiO_2	H_2O
Aluminum hydroxide	156.01	-	1 (mole)	-	3 (mole)
Sodium Aluminate	174.17	1.136 (mole)	1 (mole)	-	0.103 (mole)
Sodium Metasilicate pentahydrate	212.14	1 (mole)	-	1 (mole)	5 (mole)
LUDOX (AS 40)	150.16	-	-	1 (mole)	5 (mole)
Waterglass	222.55	0.287 (mole)	-	1 (mole)	8.036 (mole)
Sodium hydroxide	82.52	1 (mole)	-	-	1.14 (mole)

Table B.2 Molecular weight of reactants

Reactant	Molecular Weight (g/mol)
Na_2O	61.979
Al_2O_3	101.961
SiO_2	60.084
H_2O	18.015

Molar composition of the batch: $3.4Na_2O{:}1Al_2O_3{:}2SiO_2{:}155H_2O$

Formula weight of the batch:

$$3.4 \times 61.979 + 1 \times 101.961 + 2 \times 60.084 + 155 \times 18.015 = 3225.183\ \mathrm{g/gmole}$$

Silica source: Waterglass ($0.287Na_2O{:}1SiO_2{:}8.036H_2O$)

Alumina Source: Aluminum hydroxide ($1Al_2O_3{:}3H_2O$)

Sodium source: Sodium hydroxide ($1Na_2O{:}\ 1.14H_2O$)

Basis: 100g batch

Calculation of amounts of raw materials required to prepare the batch:

Amount of Waterglass:

$$100\ g\ batch \times \frac{1\ mol\ batch}{3225.183\ g\ batch} \times \frac{2\ mol\ SiO_2}{1\ mol\ batch} \times \frac{1\ mol\ waterglass}{1\ mol\ SiO_2} \times \frac{222.55\ g\ waterglass}{1\ mol\ SiO_2} = 13.801\ g\ waterglass$$

Amount of Aluminum hydroxide:

$$100\ g\ batch \times \frac{1\ mol\ batch}{3225.183\ g\ batch} \times \frac{1\ mol\ Al_2O_3}{1\ mol\ batch} \times \frac{1\ mol\ aluminum\ hydroxide}{1\ mol\ Al_2O_3} \times \frac{156.01\ g\ aluminum\ hydroxide}{1\ mol\ Al_2O_3} = 4.838\ g\ aluminum\ hydroxide$$

Amount of Sodium hydroxide:

$$100\ g\ batch \times \frac{1\ mol\ batch}{3225.183\ g\ batch} \times \frac{3.4\ mol\ Na_2O}{1\ mol\ batch} \times \frac{1\ mol\ sodium\ hydroxide}{1\ mol\ Na_2O} \times \frac{82.52\ g\ sodium\ hydroxide}{1\ mol\ Na_2O} = 8.6993\ g\ sodium\ hydroxide$$

From waterglass,

$$100\ g\ batch \times \frac{1\ mol\ batch}{3225.183\ g\ batch} \times \frac{(0.287 \times 2 \times\ 82.52)}{1\ mol\ batch}$$
$$= 1.4686\ g\ sodium\ hydroxide$$

$$m_{sodium\ hydroxide,needed} = 8.6993 - 1.4686 = 7.231\ g\ sodium\ hydroxide$$

Amount of Deionized water:

$$100\ g\ batch \times \frac{1\ mol\ batch}{3225.183\ g\ batch} \times \frac{155\ mol\ H_2O}{1\ mol\ batch} \times \frac{18.015\ g\ H_2O}{1\ mol\ H_2O} = 86.5788\ g\ H_2O$$

From Waterglass,

$$100\ g\ batch \times \frac{1\ mol\ batch}{3225.183\ g\ batch} \times \frac{(8.036 \times 2 \times\ 18.015)}{1\ mol\ batch} = 8.9774\ g\ H_2O$$

From Aluminum hydroxide,

$$100\ g\ batch \times \frac{1\ mol\ batch}{3225.183\ g\ batch} \times \frac{(3 \times 1 \times\ 18.015)}{1\ mol\ batch} = 1.6757\ g\ H_2O$$

From Sodium hydroxide,

$$100\ g\ batch \times \frac{1\ mol\ batch}{3225.183\ g\ batch} \times \frac{(1.14 \times 2.826 \times\ 18.015)}{1\ mol\ batch} = 1.7995\ g\ H_2O$$

$$m_{H_2O,needed} = 86.5788 - (8.9774 + 1.6757 + 1.7995) = 74.13\ g\ H_2O$$

Amount of reactants were calculated as in Table B.3

Table B.3 Amount of reactants for 100 g batch preparation

Reactant	Amount (g)
Waterglass	13.801
Aluminum hydroxide	4.838
Sodium hydroxide	7.231
H_2O	74.130

Throughout this study different reactants were used as silica and alumina sources in the synthesis of zeolite powder and membranes. Amount of reagents used for the preparation of 100 g batch with all compositions used in this study are listed in Table 3.1.

APPENDIX C

SAMPLE CALCULATION OF MAXIMUM YIELD AND PERCENT CRYSTALLINITY

Calculation of maximum yield;

Composition: $N_{2.5}A_1S_{1.7}H_{150}$ Formula weight: 3061.27 g/mol

100 g basis

$$100\ g\ batch \times \frac{mol}{3061.27\ g} = 0.0327\ mol\ synthesis\ solution$$

Zeolite A is $N_1A_1S_2H_{4.5}$ Formula weight: 364.88 g/mol

Limiting reactant is S, so from 0.0327 mol synthesis solution;

$$0.0327\ mol\ synthesis\ solution \times \frac{1.7\ mol\ S}{1\ mol\ synthesis\ solution} \times \frac{1\ mol\ zeolite\ A}{2\ mol\ S} \times \frac{364.88g}{1\ mole\ zeolite\ A} = 10.13\ g\ zeolite\ A\ can\ be\ produced$$

So the maximum yield is 10.13%.

Calculation of percent crystallinity;

Percent crystallinity of the samples was defined based on the twelve characteristic peaks of zeolite A at Bragg angles that shown with asterisks in Figure 3.2. Reference sample is BA84-85-a which has a total intensity of 12,770.

For BA86-87-a sample from Figure C.1 crystallinity calculated as follows;

$$\% \, Crystallinity = \frac{\sum_{i=1}^{12} I_i}{\left(\sum_{i=1}^{12} I_i\right)_{ref}} \times 100$$

$$\% \, Crystallinity = \frac{(700 + 750 + 500 + 450 + 920 + 1700 + 520 + 1650 + 2250 + 360 + 500 + 1600)}{12{,}770} \times 100 = 97.7\%$$

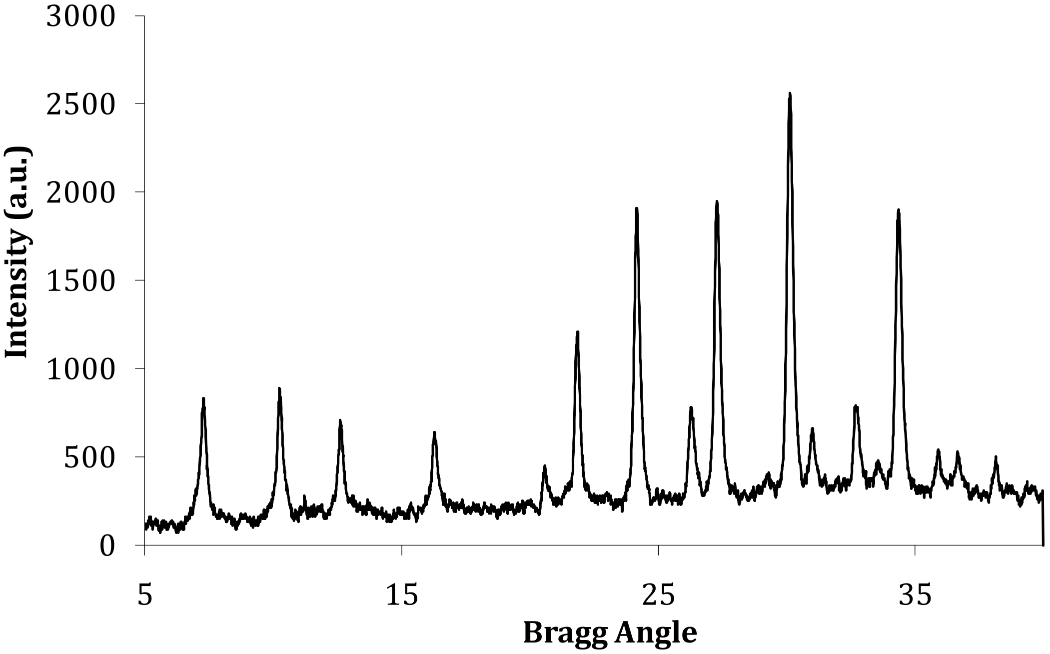
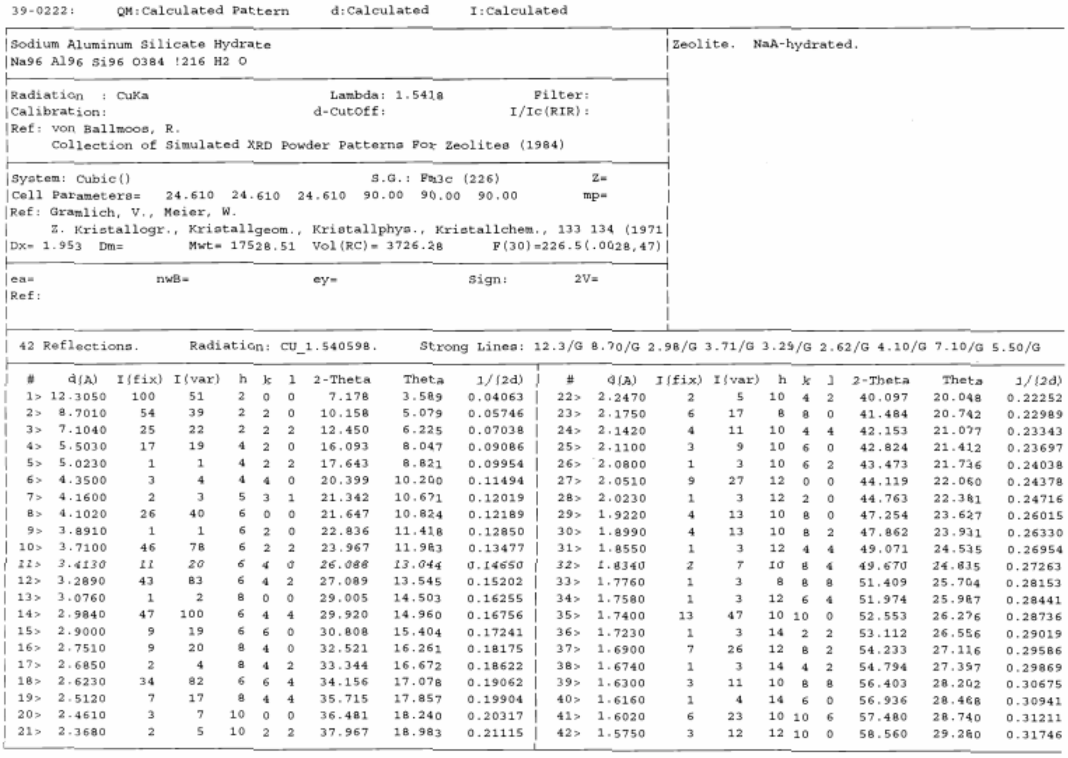


Figure C.1 XRD pattern of BA86-87-a

APPENDIX D

ICDD PDF CARD OF ZEOLITE A WITH (h, k, l) INDEX



```
39-0222:     QM:Calculated Pattern     d:Calculated     I:Calculated
 --------------------------------------------------------------------------------------------------
|Sodium Aluminum Silicate Hydrate                                          |Zeolite.  NaA-hydrated.
|Na96 Al96 Si96 O384 !216 H2 O                                             |
|--------------------------------------------------------------------------|
|Radiation  : CuKa                     Lambda: 1.5418          Filter:     |
|Calibration:                        d-CutOff:              I/Ic(RIR):     |
|Ref: von Ballmoos, R.                                                     |
|     Collection of Simulated XRD Powder Patterns For Zeolites (1984)      |
|--------------------------------------------------------------------------|
|System: Cubic()                             S.G.: Fm3c (226)          Z=  |
|Cell Parameters=   24.610  24.610  24.610  90.00  90.00  90.00        mp= |
|Ref: Gramlich, V., Meier, W.                                              |
|     Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem., 133 134 (1971|
|Dx= 1.953  Dm=        Mwt= 17528.51  Vol(RC)= 3726.28     F(30)=226.5(.0028,47)|
|--------------------------------------------------------------------------|
|ea=              nwB=              ey=              Sign:        2V=      |
|Ref:                                                                      |
|                                                                          |
 --------------------------------------------------------------------------------------------------
| 42 Reflections.     Radiation: CU_1.540598.     Strong Lines: 12.3/G 8.70/G 2.98/G 3.71/G 3.29/G 2.62/G 4.10/G 7.10/G 5.50/G
 --------------------------------------------------------------------------------------------------
|  #    d(A)  I(fix) I(var)  h  k  l  2-Theta   Theta   1/(2d) |  #    d(A)  I(fix) I(var)  h  k  l  2-Theta   Theta   1/(2d)
|  1> 12.3050   100    51    2  0  0    7.178   3.589  0.04063 | 22>  2.2470    2      5   10  4  2   40.097  20.048  0.22252
|  2>  8.7010    54    39    2  2  0   10.158   5.079  0.05746 | 23>  2.1750    6     17    8  8  0   41.484  20.742  0.22989
|  3>  7.1040    25    22    2  2  2   12.450   6.225  0.07038 | 24>  2.1420    4     11   10  4  4   42.153  21.077  0.23343
|  4>  5.5030    17    19    4  2  0   16.093   8.047  0.09086 | 25>  2.1100    3      9   10  6  0   42.824  21.412  0.23697
|  5>  5.0230     1     1    4  2  2   17.643   8.821  0.09954 | 26>  2.0800    1      3   10  6  2   43.473  21.736  0.24038
|  6>  4.3500     3     4    4  4  0   20.399  10.200  0.11494 | 27>  2.0510    9     27   12  0  0   44.119  22.060  0.24378
|  7>  4.1600     2     3    5  3  1   21.342  10.671  0.12019 | 28>  2.0230    1      3   12  2  0   44.763  22.381  0.24716
|  8>  4.1020    26    40    6  0  0   21.647  10.824  0.12189 | 29>  1.9220    4     13   10  8  0   47.254  23.627  0.26015
|  9>  3.8910     1     1    6  2  0   22.836  11.418  0.12850 | 30>  1.8990    4     13   10  8  2   47.862  23.931  0.26330
| 10>  3.7100    46    78    6  2  2   23.967  11.983  0.13477 | 31>  1.8550    1      3   12  4  4   49.071  24.535  0.26954
| 11>  3.4130    11    20    6  4  0   26.088  13.044  0.14650 | 32>  1.8340    2      7   10  8  4   49.670  24.835  0.27263
| 12>  3.2890    43    83    6  4  2   27.089  13.545  0.15202 | 33>  1.7760    1      3    8  8  8   51.409  25.704  0.28153
| 13>  3.0760     1     2    8  0  0   29.005  14.503  0.16255 | 34>  1.7580    1      3   12  6  4   51.974  25.987  0.28441
| 14>  2.9840    47   100    6  4  4   29.920  14.960  0.16756 | 35>  1.7400   13     47   10 10  0   52.553  26.276  0.28736
| 15>  2.9000     9    19    6  6  0   30.808  15.404  0.17241 | 36>  1.7230    1      3   14  2  2   53.112  26.556  0.29019
| 16>  2.7510     9    20    8  4  0   32.521  16.261  0.18175 | 37>  1.6900    7     26   12  8  2   54.233  27.116  0.29586
| 17>  2.6850     2     4    8  4  2   33.344  16.672  0.18622 | 38>  1.6740    1      3   14  4  2   54.794  27.397  0.29869
| 18>  2.6230    34    82    6  6  4   34.156  17.078  0.19062 | 39>  1.6300    3     11   10  8  8   56.403  28.202  0.30675
| 19>  2.5120     7    17    8  4  4   35.715  17.857  0.19904 | 40>  1.6160    1      4   14  6  0   56.936  28.468  0.30941
| 20>  2.4610     3     7   10  0  0   36.481  18.240  0.20317 | 41>  1.6020    6     23   10 10  6   57.480  28.740  0.31211
| 21>  2.3680     2     5   10  2  2   37.967  18.983  0.21115 | 42>  1.5750    3     12   12 10  0   58.560  29.280  0.31746
 --------------------------------------------------------------------------------------------------
```

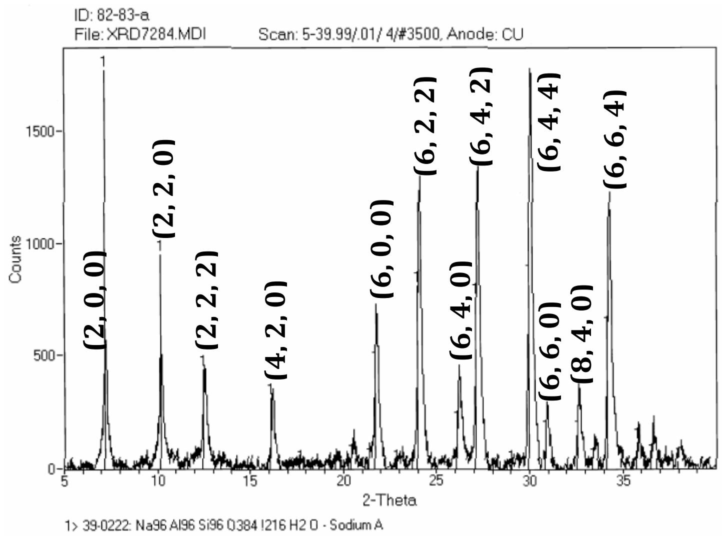


Figure D.1 XRD pattern of BA82-83-a with the reference no 39-0222 (zeolite A)

APPENDIX E

REFRACTIVE INDEX DATA OF ETHANOL-WATER MIXTURES

Table E.1 Refractive Index of Ethanol-Water mixture at 20 °C

Ethanol weight %	Refractive index by CRC handbook (at λ=589nm, 20°C)	Ethanol weight %	Refractive index by CRC handbook (at λ=589nm, 20°C)	Ethanol weight %	Refractive index by measurement (25°C)
0.5	1.3333	34	1.3557	0	1.3330
1	1.3336	36	1.3566	10	1.3390
2	1.3342	38	1.3575	20	1.3475
3	1.3348	40	1.3583	30	1.3530
4	1.3354	42	1.3590	40	1.3575
5	1.3360	44	1.3598	50	1.3615
6	1.3367	46	1.3604	55	1.3630
7	1.3374	48	1.3610	60	1.3640
8	1.3381	50	1.3616	65	1.3645
9	1.3388	60	1.3638	70	1.3650
10	1.3395	70	1.3652	75	1.3655
12	1.3410	80	1.3658	80	1.3660
14	1.3425	90	1.3650	85	1.3650
16	1.3440	92	1.3646	90	1.3640
18	1.3455	94	1.3642	95	1.3625
20	1.3469	96	1.3636	100	1.3600
22	1.3484	98	1.3630		
24	1.3498	100	1.3614		
26	1.3511				
28	1.3524				
30	1.3535				
32	1.3546				

Reference: Weast, R.C., Astle, M.J., Beyer, W.H., *"CRC Handbook of Chemistry and Physics", 53rd edition, D-189, Chemical Rubber Company Press, Inc., Cleveland, Ohio, 1972-1973.*

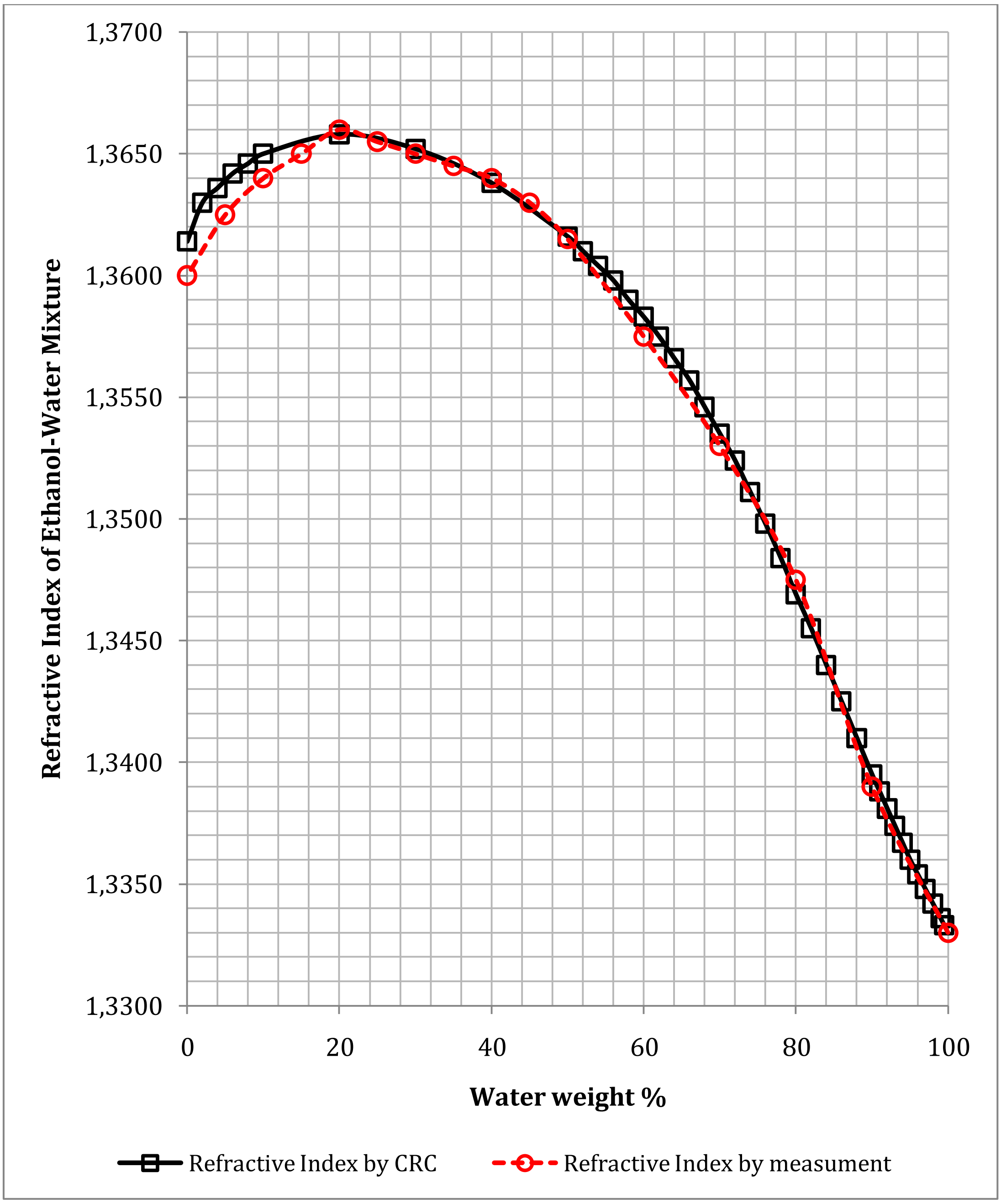


Figure E.1 Calibration curve of refractive index of ethanol-water mixture at 20 °C

APPENDIX F

SAMPLE CALCULATION FOR THE FLUX AND SELECTIVITY

Calculation of flux (kg/m² h);

For BA83-2;

M1 = 87.5502 g   M2 = 87.9529 g   Δt = 7.7333 h

Effective membrane area = $2.55\times\ 10^{-4}$ m²

$$Flux=\frac{(M2-M1)\times10^{-3}kg}{time(h)area\ (m^2)}=\frac{(87.5502-87.9529)\times10^{-3}kg}{7.7333(h)\ 2.55\times\ 10^{-4}(m^2)}=0.204\frac{kg}{m^2\ h}$$

Calculation of selectivity;

$$\alpha=\frac{\left(\frac{y_{water}}{y_{ethanol}}\right)_{permeate}}{\left(\frac{x_{water}}{x_{ethanol}}\right)_{feed}}$$

-From refractive index measurements

Feed composition of the ethanol - water mixture was known, it was 90 wt% ethanol - 10 wt% water. So x_{water}=10, $x_{ethanol}$=90 at the feed. In order to obtain mass composition of permeate side, refractive index of the liquid permeate sample was measured. By the help of the data available as water-ethanol compositions vs. refractive index, the ethanol weight % can be read according to the measured refractive index value. Then $y_{water,ethanol}$ are obtained and selectivity was calculated.

For BA83-2

Refractive index of permeate sample = 1.3380 from Table E.1;

y_{water}=92, $y_{ethanol}$=8 at the permeate side. So selectivity;

$$\alpha = \frac{\left(\frac{92}{8}\right)_{permeate}}{\left(\frac{10}{90}\right)_{feed}} = 103.5$$

-From gas chromatograph measurements

Calibration curves were obtained by relating the chromatographic peak area to the weight percent of each component under fixed operating conditions of GC. The amount of each component in the mixture was determined from these calibration curves. The GC calibration curves for water and ethanol is given in Appendix G. GC measurements were done at least two times to check the precision. For BA83-2;

Table F.1 Peak area values for the measured sample BA83-2

	Permeate		**Feed**	
Run No	**Water Area**	**Ethanol Area**	**Water Area**	**Ethanol Area**
1	377776.1	21993.0	37396.4	155447.8
2	389772.3	22525.9	35898.1	151177.2
3	383893.3	21139.0	-	-
Average	383813.9	21886.0	36647.3	153312.5

Table F.2 Weight percents of water and ethanol according to their peak area values

	Water Area	**Water wt%**	**Ethanol Area**	**Ethanol wt%**	**Total wt%**
Feed	36647.3	8.210	153312.5	92.294	100.504
Permeate	383813.9	85.974	21886.0	13.175	99.149

$$\alpha = \frac{\frac{\left(\frac{85.974}{13.175}\right)_{permeate}}{(0.99149)}}{\frac{\left(\frac{8.210}{92.294}\right)_{permeate}}{(1.00504)}} = 74.4$$

APPENDIX G

CALIBRATION OF GAS CHROMATOGRAPH FOR WATER AND ETHANOL

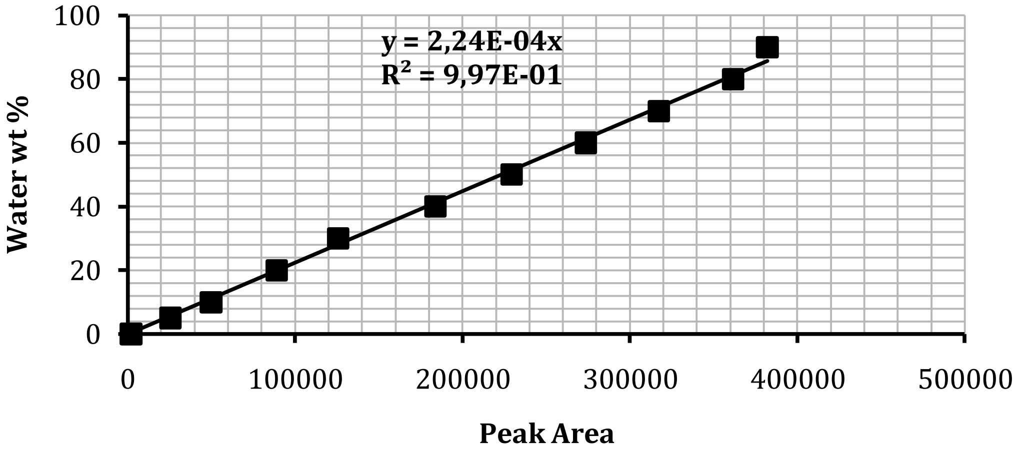


Figure G.1 Gas chromatograph calibration curve for water

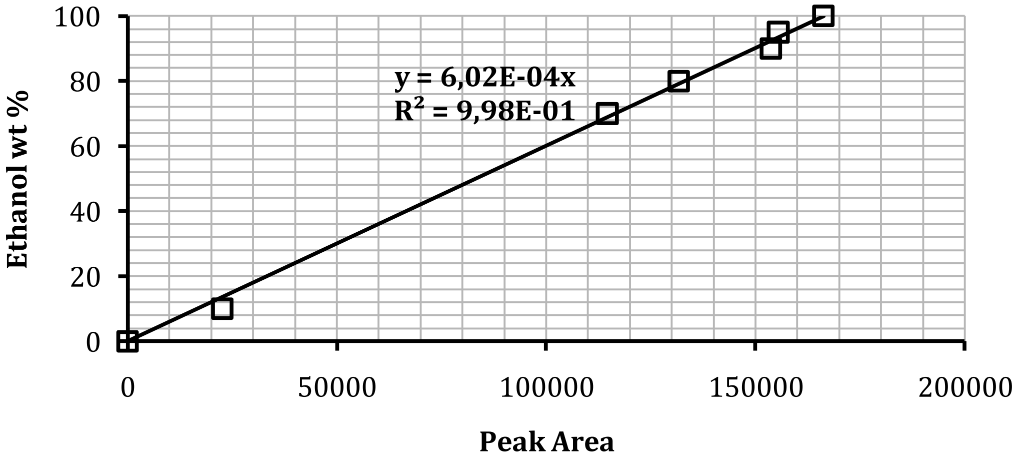


Figure G.2 Gas chromatograph calibration curve for ethanol

APPENDIX H

RELATION OF XRD PEAK RATIO WITH MEMBRANE THICKNESS

The relation of XRD peak ratio and SEM thickness of synthesized tube (a) and disc (b) membranes are shown in Figure H.1

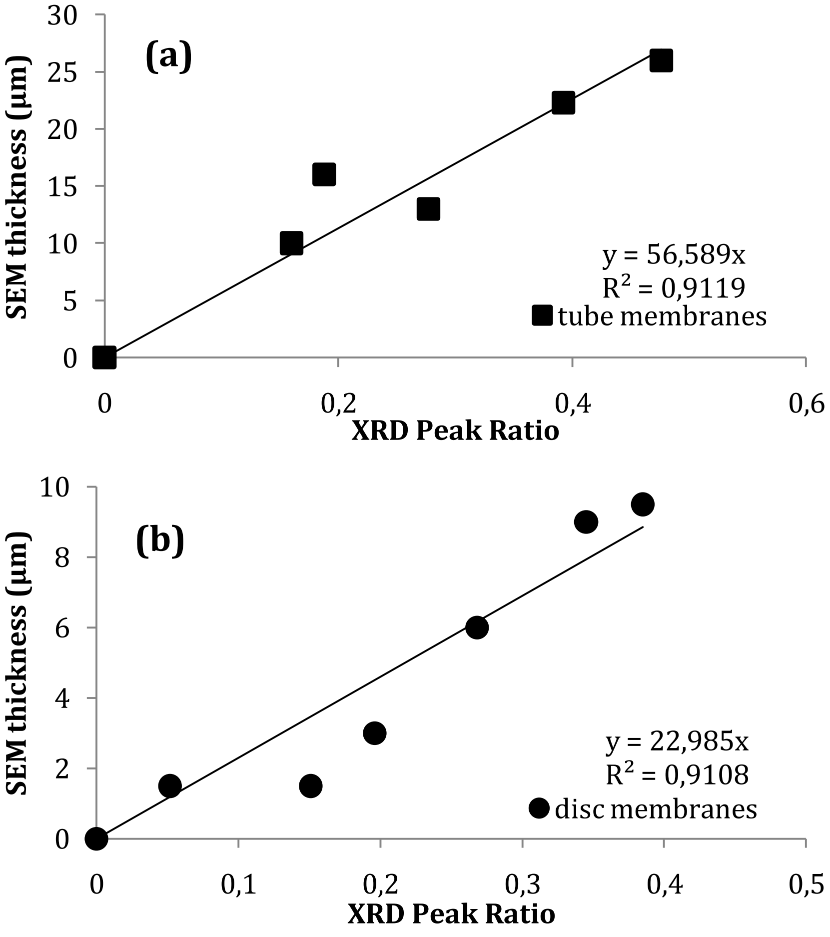


Figure H.1 The relation of XRD peak ratio and SEM thickness of synthesized tube (a) and disc (b) membranes

APPENDIX I

ALL PERVAPORATION RESULTS OF BA132

Pervaporation results of all runs for BA132 are shown in Table I.1

Table I.1 Pervaporation results of BA132

Flux	T (°C)	SF
0.09	30	1,000
0.15	30	1,600
0.87	40	5,000
0.84	40	6,100
1.19	50	40,000
0.59	50	25,000
1.67	50	62,000
0.90	50	72,000
1.00	50	54,000
1.48	50	45,000
1.48	50	61,000
1.42	50	71,000
1.48	50	91,000
1.09	50	58,000
3.37	70	4,000
3.30	70	12,500
3.83	70	20,000
4.18	70	15,500
4.47	70	13,200

APPENDIX J

REFERENCES FOR FIGURE 4.26 WITH WHOLE DATA

Table J.1 shows the references for figure 4.26 with the whole data that were used to prepare Figure 4.26.

Table J.1 The whole set of data for Figure 4.26 with references

			Permeance (gpu)				Permeability (barrer)				ΔP (cm Hg)		Conventional way of reporting			
Reference	X wt % of water	T (°C)	Ethanol	Water 10^{-3}	Total 10^{-3}	Membrane Thickness (μm)	Ethanol	Water 10^{-3}	Total 10^{-3}	Selectivity 10^{-3}	Ethanol	Water	Ethanol flux (kg/m^2 h)	Water flux (kg/m^2 h)	Total flux (kg/m^2 h)	SF 10^{-3}
TS	10	50	0.1	13.2	13.2	10	1.1	131.6	131.6	117.8	17.90	3.88	0.0001	1.4799	1.48	91.0
TS	10	30	1.5	3.6	3.6	10	15.4	36.2	36.2	2.4	6.37	1.14	0.0007	0.1193	0.12	1.3
TS	10	40	1.6	13.5	13.5	10	15.6	134.7	134.8	8.7	10.89	2.20	0.0013	0.8587	0.86	5.6
TS	10	70	1.0	13.0	13.0	10	9.9	129.5	129.6	13.0	43.71	10.20	0.0032	3.8268	3.83	13.0
TS	10	50	14.0	2.4	2.4	1.5	21.0	3.5	3.6	0.2	17.89	3.89	0.0185	0.2665	0.285	0.1
TS	10	50	10.6	2.4	2.4	1.5	15.8	3.5	3.6	0.2	17.90	3.89	0.0140	0.2660	0.28	0.2
5	10	75	1.3	15.6	15.6	4	5.1	62.3	62.3	12.3	53.61	12.40	0.0050	5.5950	5.6	10.0
58	10	75	1.9	23.4	23.4	2.5	4.8	58.4	58.4	12.3	53.61	12.40	0.0076	8.3924	8.4	10.0
84	10	75	1.5	16.4	16.4	10	14.8	164.1	164.1	11.1	53.61	12.40	0.0059	5.8941	5.9	9.0
55	8	50	6.8	4.9	4.9	30	205.0	147.9	15.0	0.7	18.58	3.44	0.0094	0.4906	0.5	0.6
4	10	50	0.2	4.3	4.3	30	6.4	129.1	129.1	20.3	17.90	4.01	0.0003	0.4997	0.5	16.0
11	8	50	0.9	9.0	9.0	15	13.3	135.5	135.5	10.2	18.58	3.44	0.0012	0.8988	0.9	8.5
3	10	125	0.4	1.8	1.8	10	4.3	18.1	18.1	4.2	296.83	72.45	0.0095	3.7905	3.8	3.6
40	9	93	21.1	3.4	3.4	5	105.6	16.8	16.9	0.2	107.69	23.95	0.1684	2.3316	2.5	0.1
18	10	50	0.1	6.5	6.5	10	1.1	65.5	65.5	57.6	17.90	4.06	0.0002	0.7698	0.77	46.0
2	10	75	0.5	5.9	5.9	30	15.0	176.3	176.3	11.8	53.61	12.92	0.0020	2.1980	2.2	10.0
6	10	105	0.1	4.0	4.0	30	3.4	120.1	120.1	34.8	159.72	39.08	0.0014	4.5286	4.53	30.0
57	5	45	0.3	4.8	4.8	6	1.8	28.7	28.7	15.7	15.47	1.66	0.0003	0.2297	0.23	12.5
38	5	45	0.3	15.5	15.5	3.5	0.9	54.1	54.1	58.5	15.47	1.92	0.0003	0.8597	0.86	54.0
54	10	25	1.7	25.0	25.0	3.5	6.0	87.7	87.7	14.5	4.80	0.94	0.0006	0.6794	0.68	10.0
54	10	75	7.2	3.4	3.4	8	57.6	27.4	27.4	0.5	53.61	12.83	0.0051	0.2249	0.23	12.5
33	10	30	21.2	26.0	26.0	7	148.4	182.0	182.1	1.2	6.37	1.31	0.0086	0.8514	0.86	54.0
60	10	70	0.1	0.6	0.6	4	0.2	2.4	2.4	13.0	43.71	10.47	0.0006	0.6794	0.68	10.0

APPENDIX K

LIST OF SAMPLES SYNTHESIZED IN POWDER FORM

Table K.1 List of the synthesized powders at different synthesis conditions and the remaining powders from membrane synthesis

Code	Composition	Synthesis Method	Aging (h)	Silica Source	Synthesis Temperature (°C)	Time (h)
BA1	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	-	Ludox	80	19.5
BA2	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	-	Ludox	80	24.5
BA3	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	-	Ludox	80	33.5
BA4	$N_2A_1S_2H_{150}$	Batch	-	Ludox	80	27.5
BA5	$N_2A_1S_2H_{150}$	Batch	-	Ludox	80	48
BA6	$N_{50}A_1S_5H_{1000}$	Batch	-	Ludox	80	164
BA7	$N_{50}A_1S_5H_{1000}$	Batch	-	Ludox	80	194
BA8	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	-	Ludox	80	6
BA9	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	-	Ludox	95	0.5
BA10	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	-	Ludox	95	1
BA11	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	-	Ludox	95	2
BA12	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	-	Ludox	95	3
BA13	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	-	Ludox	95	5
BA14	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	-	Ludox	80	72
BA15	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	-	Ludox	80	96
BA16	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	1
BA17	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	1.5
BA18	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	2
BA19	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	3
BA20	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	6.5
BA21	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	80	96
BA22	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	80	2
BA23	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	80	3.5
BA24	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	80	4.5
BA25	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	80	20
BA26	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	93	1.75
BA27	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	93	16
BA28	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	0.5
BA29	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	1

Table K.1 cont'd.

Code	Composition	Synthesis Method	Aging (h)	Silica Source	Synthesis Temperature (°C)	Time (h)
BA30	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	1.5
BA31	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	2
BA32	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	2.5
BA33	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	3
BA33-a	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	3
BA34	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	0.5
BA35	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	1
BA36	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	1.5
BA37	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	2.5
BA38	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	3
BA39	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	1
BA40	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	1.5
BA41	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	2
BA42	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	2.5
BA43	$N_{2.5}A_1S_{1.7}H_{150}$	Flow	24	Ludox	95	3
BA45-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	4
BA46-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	4
BA47-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	4
BA45-b	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	3
BA46-b	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	3
BA47-b	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	3
BA48-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Ludox	95	5
BA49-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	5
BA48-b	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Ludox	95	5
BA46-c	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	5
BA50-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Ludox	95	2
BA51-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Ludox	95	2.25
BA50-b	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Ludox	95	2
BA52	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	24	Ludox	95	2.5
BA53-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Ludox	95	8
BA53-b	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Ludox	95	8
BA54-55-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Waterglass	95	6
BA54-55-b	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Waterglass	95	6
BA56-57-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Waterglass	95	6
BA58-59-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Waterglass	95	6
BA58-59-b	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Waterglass	95	6
BA60-61-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Sod. Met. Penta.	95	4
BA62-63-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Sod. Met. Penta	95	4
BA64-65-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Waterglass	95	4
BA66-67-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Waterglass	95	4
BA68-69-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Sod. Met. Penta	95	4
BA70-71-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Sod. Met. Penta	95	4

Table K.1 cont'd.

Code	Composition	Synthesis Method	Aging (h)	Silica Source	Synthesis Temp. (°C)	Time (h)
BA72-73-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Sod. Met. Penta	95	4
BA74-75-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Sod. Met. Penta	95	4
BA76-77-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Ludox	95	4
BA78-79-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Ludox	95	4
BA80-81-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Ludox	95	4
BA82-83-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Waterglass	95	4
BA84-85-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Waterglass	95	4
BA86-87-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Waterglass	95	4
BA82-83-b	$N_{3.4}A_1S_2H_{155}$	Batch	1	Waterglass	95	4
BA84-85-b	$N_{3.4}A_1S_2H_{155}$	Batch	1	Waterglass	95	4
BA86-87-b	$N_{3.4}A_1S_2H_{155}$	Batch	1	Waterglass	95	4
BA88-89-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Waterglass	95	4
BA88-89-b	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Waterglass	95	4
BA90-91-a	$N_{2.5}A_1S_{1.7}H_{150}$	Batch	1	Waterglass	95	6
BA92-93-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Waterglass	95	4
BA94-95-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Waterglass	95	4
BA96-97-a	$N_{3.4}A_1S_2H_{270}$	Batch	0.5	Waterglass	105	1
BA98-99-a	$N_{3.4}A_1S_2H_{270}$	Batch	1	Waterglass	95	6
BA102-107-a	$N_{3.4}A_1S_2H_{270}$	Batch	0.5	Waterglass	105	2
BA103	$N_{3.4}A_1S_2H_{270}$	Batch	1	Waterglass	95	8
BA104	$N_{3.4}A_1S_2H_{270}$	Batch	1	Waterglass	95	6
BA105	$N_{3.4}A_1S_2H_{270}$	Batch	1	Waterglass	95	4
BA106	$N_{3.4}A_1S_2H_{270}$	Batch	1	Waterglass	95	2
BA108-109-a	$N_{3.4}A_1S_2H_{270}$	Batch	0.5	Waterglass	105	4
BA110	$N_{11.82}A_1S_{1.82}H_{273}$	Batch	24	Waterglass	35	18
BA111	$N_{11.82}A_1S_{1.82}H_{273}$	Batch	24	Waterglass	35	138
BA112	$N_{11.82}A_1S_{1.82}H_{273}$	Batch	24	Waterglass	35	195
BA113-1	$N_{0.167}A_1S_{6.25}(TMA_2O)_{7.44}H_{389}$	Batch	24	Ludox	60	24
BA113-2	$N_{0.167}A_1S_{6.25}(TMA_2O)_{7.44}H_{389}$	Batch	24	Ludox	60	48
BA113-3	$N_{0.167}A_1S_{6.25}(TMA_2O)_{7.44}H_{389}$	Batch	24	Ludox	60	72
BA114-1	$N_{11.82}A_1S_{1.82}H_{273}$	Batch	1	Waterglass	35	18
BA114-2	$N_{11.82}A_1S_{1.82}H_{273}$	Batch	1	Waterglass	35	18
BA115-116-a	$N_{3.4}A_1S_2H_{270}$	Batch	1	Waterglass	95	6
BA117	$N_{3.4}A_1S_2H_{155}$	Flow	1	Waterglass	95	4
BA118-119-a	$N_{3.4}A_1S_2H_{155}$	Flow	1	Waterglass	95	4
BA119-b	$N_{3.4}A_1S_2H_{155}$	Flow	1	Waterglass	95	4
BA120-121-a	$N_{3.4}A_1S_2H_{155}$	Flow	1	Waterglass	95	4
BA122-123-a	$N_{3.4}A_1S_2H_{155}$	Flow	1	Waterglass	95	4

Table K.1 cont'd.

Code	**Composition**	**Synthesis Method**	**Aging (h)**	**Silica Source**	**Synthesis Temperature (°C)**	**Time (h)**
BA124-125-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Waterglass	95	4
BA126-127-a	$N_{3.4}A_1S_2H_{155}$	Flow	1	Waterglass	95	4
BA128-129-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Waterglass	95	4
BA130-131-a	$N_{3.4}A_1S_2H_{155}$	Batch	1	Waterglass	95	4
BA132-a	$N_{3.4}A_1S_2H_{200}$	Flow	5	Waterglass	95	17
BA133-a	$N_{3.4}A_1S_2H_{200}$	Flow	5	Waterglass	95	17
BA133-b	$N_{3.4}A_1S_2H_{200}$	Flow	5	Waterglass	95	3
BA134-a	$N_{3.4}A_1S_2H_{200}$	Flow	5	Waterglass	95	6
BA135-1	$N_{3.4}A_1S_2H_{200}$	Batch	5	Waterglass	95	1
BA135-2	$N_{3.4}A_1S_2H_{200}$	Batch	5	Waterglass	95	2
BA135-3	$N_{3.4}A_1S_2H_{200}$	Batch	5	Waterglass	95	3
BA135-4	$N_{3.4}A_1S_2H_{200}$	Batch	5	Waterglass	95	4
BA135-5	$N_{3.4}A_1S_2H_{200}$	Batch	5	Waterglass	95	4.5
BA135-6	$N_{3.4}A_1S_2H_{200}$	Batch	5	Waterglass	95	5
BA135-7	$N_{3.4}A_1S_2H_{200}$	Batch	5	Waterglass	95	5.5
BA135-8	$N_{3.4}A_1S_2H_{200}$	Batch	5	Waterglass	95	6
BA135-9	$N_{3.4}A_1S_2H_{200}$	Flow	5	Waterglass	95	6.5
BA135-10	$N_{3.4}A_1S_2H_{200}$	Flow	5	Waterglass	95	7
BA135-11	$N_{3.4}A_1S_2H_{200}$	Flow	5	Waterglass	95	21.25
BA136-a	$N_{3.4}A_1S_2H_{200}$	Flow	5	Waterglass	95	17
BA137-a	$N_{3.4}A_1S_2H_{200}$	Flow	5	Waterglass	95	17
BA137-b	$N_{3.4}A_1S_2H_{200}$	Flow	5	Waterglass	95	17
BA138-a	$N_{3.4}A_1S_2H_{200}$	Flow	5	Waterglass	95	17
BA139-a	$N_{3.4}A_1S_2H_{200}$	Batch	5	Waterglass	95	17

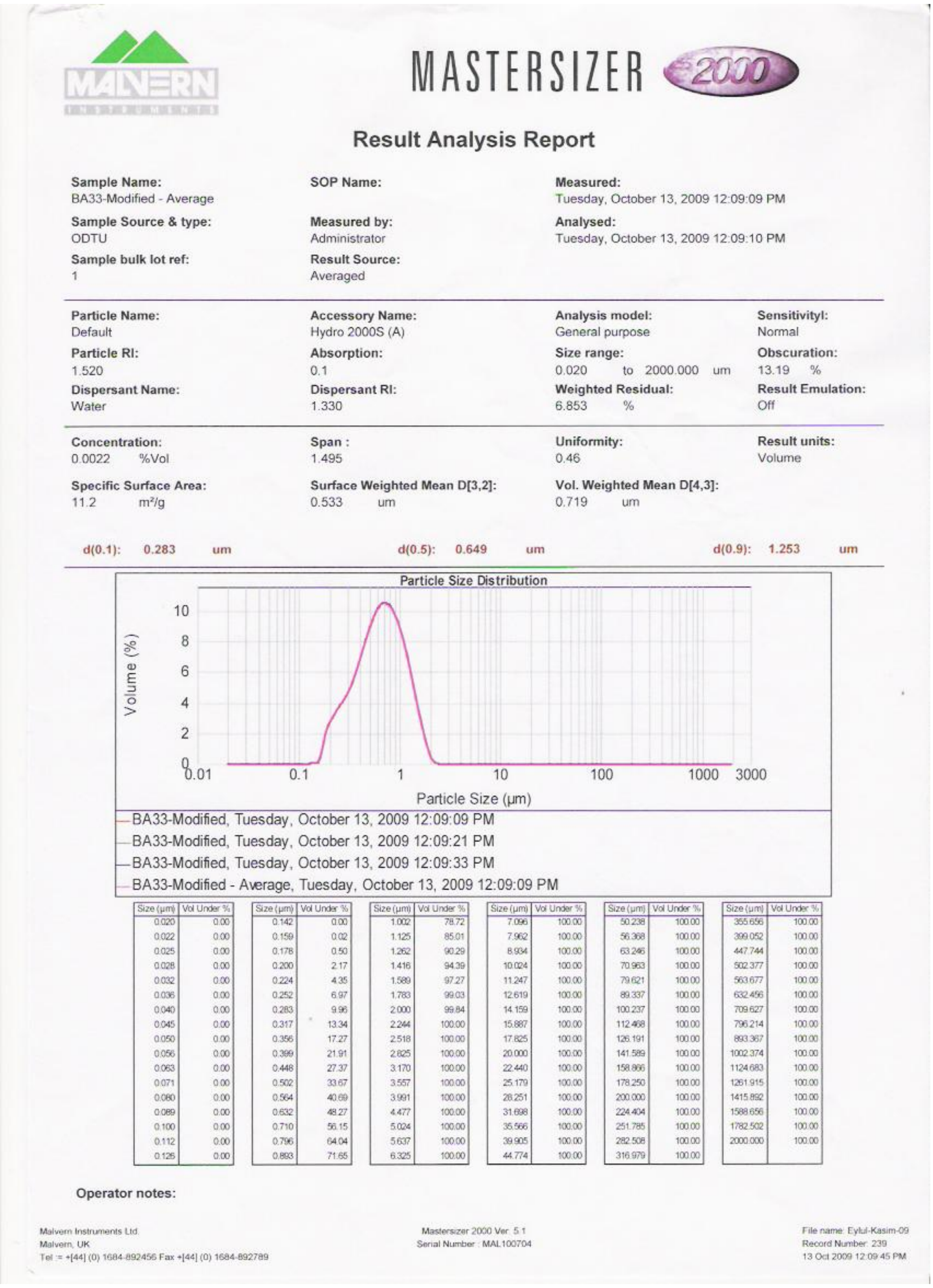
Note

First 43 sample and BA52, BA103, BA104, BA105, BA106, BA110, BA111, BA112, BA113, BA117 and BA135 are the synthesized powder samples only.

Membranes generally synthesized as couples in same synthesis flasks. There are also remaining powders from membrane synthesis which are named with this principle; "Code of membrane-Code of its couple-a, b, c … etc." a, b, c indicate the # of consecutive synthesis, for instance BA120-121-a means that BA120 and BA121 are synthesized in same synthesis flask and "a" means that one cycle synthesis was done or membrane has one layer.

If a powder has a group, then they named as "Code-number".

K1. Particle size distribution of powder to be used as seed



Result Analysis Report

Sample Name: BA33-Modified - Average

Sample Source & type: ODTU

Sample bulk lot ref: 1

SOP Name:

Measured by: Administrator

Result Source: Averaged

Measured: Tuesday, October 13, 2009 12:09:09 PM

Analysed: Tuesday, October 13, 2009 12:09:10 PM

Particle Name: Default

Particle RI: 1.520

Dispersant Name: Water

Accessory Name: Hydro 2000S (A)

Absorption: 0.1

Dispersant RI: 1.330

Analysis model: General purpose

Size range: 0.020 to 2000.000 um

Weighted Residual: 6.853 %

Sensitivityl: Normal

Obscuration: 13.19 %

Result Emulation: Off

Concentration: 0.0022 %Vol

Specific Surface Area: 11.2 m²/g

Span : 1.495

Surface Weighted Mean D[3,2]: 0.533 um

Uniformity: 0.46

Vol. Weighted Mean D[4,3]: 0.719 um

Result units: Volume

d(0.1): 0.283 um d(0.5): 0.649 um d(0.9): 1.253 um

BA33-Modified, Tuesday, October 13, 2009 12:09:09 PM
BA33-Modified, Tuesday, October 13, 2009 12:09:21 PM
BA33-Modified, Tuesday, October 13, 2009 12:09:33 PM
BA33-Modified - Average, Tuesday, October 13, 2009 12:09:09 PM

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.142	0.00	1.002	78.72	7.096	100.00	50.238	100.00	355.656	100.00
0.022	0.00	0.159	0.02	1.125	85.01	7.962	100.00	56.368	100.00	399.052	100.00
0.025	0.00	0.178	0.50	1.262	90.29	8.934	100.00	63.246	100.00	447.744	100.00
0.028	0.00	0.200	2.17	1.416	94.39	10.024	100.00	70.963	100.00	502.377	100.00
0.032	0.00	0.224	4.35	1.589	97.27	11.247	100.00	79.621	100.00	563.677	100.00
0.036	0.00	0.252	6.97	1.783	99.03	12.619	100.00	89.337	100.00	632.456	100.00
0.040	0.00	0.283	9.96	2.000	99.84	14.159	100.00	100.237	100.00	709.627	100.00
0.045	0.00	0.317	13.34	2.244	100.00	15.887	100.00	112.468	100.00	796.214	100.00
0.050	0.00	0.356	17.27	2.518	100.00	17.825	100.00	126.191	100.00	893.367	100.00
0.056	0.00	0.399	21.91	2.825	100.00	20.000	100.00	141.589	100.00	1002.374	100.00
0.063	0.00	0.448	27.37	3.170	100.00	22.440	100.00	158.866	100.00	1124.683	100.00
0.071	0.00	0.502	33.67	3.557	100.00	25.179	100.00	178.250	100.00	1261.915	100.00
0.080	0.00	0.564	40.69	3.991	100.00	28.251	100.00	200.000	100.00	1415.892	100.00
0.089	0.00	0.632	48.27	4.477	100.00	31.698	100.00	224.404	100.00	1588.656	100.00
0.100	0.00	0.710	56.15	5.024	100.00	35.566	100.00	251.785	100.00	1782.502	100.00
0.112	0.00	0.796	64.04	5.637	100.00	39.905	100.00	282.508	100.00	2000.000	100.00
0.126	0.00	0.893	71.65	6.325	100.00	44.774	100.00	316.979	100.00		

Operator notes:

Malvern Instruments Ltd.
Malvern, UK
Tel := +[44] (0) 1684-892456 Fax +[44] (0) 1684-892789

Mastersizer 2000 Ver. 5.1
Serial Number : MAL100704

File name: Eylul-Kasim-09
Record Number: 239
13 Oct 2009 12:09:45 PM

APPENDIX L

LIST OF MEMBRANES AND THEIR SYNTHESIS CONDITIONS

Table L.1 shows the membranes and their synthesis conditions with the XRD, SEM and pervaporation results.

Table L.1 Synthesis conditions and characterization summary of the prepared membranes (Synthesis Temp:95°C for all membranes, [a] PV conditions: feed water fraction, 10 wt. %; T, 50°C; permeate pressure, 0.37kPa. Permeate samples are analyzed by RI, [b] Selectivities are determined according to GC analysis results of permeate samples, [c] tube membranes, [d] PV Temp, 18°C, [e] Synthesis Temp:105°C)

Code	Synthesis Type	Synthesis Composition	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (μm)	XRD Peak Ratio	PV Results [a]		
									Flux (kg/m²h)	S.F.	Permeate Water wt %
BA44[c,d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	3	1	Rubbing	LUDOX	13	0.277	20	1	10
BA45[c,d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Rubbing	LUDOX	-	-	very large	1	10
BA45-2[c,d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4+3	2	Rubbing	LUDOX	22.3	0.393	very large	1	10
BA46[c,d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Rubbing	LUDOX	-	-	very large	1	10
BA46-2[c,d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4+3	2	Rubbing	LUDOX	-	-	3	1.6	~15
BA46-3[c]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4+3+5	3	Rubbing	LUDOX	-	-	1	1	10
BA47[c,d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Rubbing	LUDOX	-	-	very large	1	10
BA47-2	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4+3	2	Rubbing	LUDOX	26	0.476	4.5	1	10
BA48[c]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	5	1	Rubbing	LUDOX	-	-	1	1.3	~12
BA48-2[c,d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	5+5	2	Rubbing	LUDOX	-	0.261	0.48	1	10
BA49[c,d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	5	1	Rubbing	LUDOX	2.3	0.154	2	1.3	~12

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Comp.	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (µm)	XRD Peak Ratio	PV Results[a]		
									Flux (kg/m^{2}h)	S.F.	Permeate Water wt %
BA50[c]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	2	1	Rubbing	LUDOX	-	-	0.64	21	70
									0.63	17	65.4
BA50-2[c]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	2+2	2	Rubbing	LUDOX	-	-	0.8	6	40
BA51[c]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	2.25	1	Rubbing	LUDOX	-	-	0.52	1	10
BA53[c]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	8	1	Rubbing	LUDOX	-	-	0.24	4.8	34.8
BA53-2[c]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	8+8	2	Rubbing	LUDOX	-	-	0.22	5	35.7
BA54	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	6	1	Rubbing	Waterglass	-	-	0.11	12.4	57.9
BA54-2	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	6+6	2	Rubbing	Waterglass	-	-	cracked	-	-
BA55	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	6	1	Rubbing	Waterglass	-	0.233	-	-	-
BA55-2	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	6+6	2	Rubbing	Waterglass	-	0.286	0.15	66	88
									0.26	47 28[b]	84 75.7
BA56[d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	6	1	Rubbing	Waterglass	-	-	cracked	-	-
BA57	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	6	1	Rubbing	Waterglass	-	0.288	-	-	-
BA58[d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	6	1	Rubbing	Waterglass	-	-	very large	1	10
BA58-2[d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	6+6	2	Rubbing	Waterglass	-	-	very large	1	10
BA59	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	6	1	Rubbing	Waterglass	-	0.328	-	-	-

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Comp.	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (μm)	XRD Peak Ratio	PV Results[a]		
									Flux (kg/m²h)	S.F.	Permeate Water wt %
BA60	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Dip-coating	Sod. Met. Penta.	-	0.076	-	-	-
BA61[d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Dip-coating	Sod. Met. Penta.	-	-	very large	1	10
BA62[d]	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Dip-coating	Sod. Met. Penta.	-	-	very large	1	10
BA63	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Dip-coating	Sod. Met. Penta.	-	0.05	-	-	-
BA64	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Dip-coating wiping	Waterglass	5.6	0.143	0.18	12.4	58
									0.38	17 10[b]	65 52.6
BA65	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Dip-coating wiping	Waterglass	-	0.145	-	-	-
BA66	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Dip-coating wiping	Waterglass	-	0.182	-	-	-

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Composition	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (µm)	XRD Peak Ratio	PV Results [a]		
									Flux (kg/m²h)	S.F.	Permeate Water wt %
BA67	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Dip-coating wiping	Waterglass	-	0.156	very large	1	10
BA68	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Sod. Met. Penta.	8.3	0.214	0.24	10.5	54
									0.23	7.4	46
BA69	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Sod. Met. Penta.	-	0.216	-	-	-
BA70	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Rubbing wiping	Sod. Met. Penta.	-	0.323	0.15	23	72
									0.27	10	52
BA71	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Rubbing wiping	Sod. Met. Penta.	-	0.235	1.24	12.4	58
									0.44	6.5 3[b]	42 25
BA72	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Vacuum seeding wiping	Sod. Met. Penta.	-	0.338	2.35	15.3	63

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Composition	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (µm)	XRD Peak Ratio	PV Results [a]		
									Flux (kg/m²h)	S.F.	Permeate Water wt %
BA73	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Vacuum seeding wiping	Sod. Met. Penta.	-	0.340	-	-	-
BA74	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Vacuum seeding	Sod. Met. Penta.	-	0.395	1.16	13.5	60
									0.45	12.44[b]	58 30.8
BA75	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Vacuum seeding	Sod. Met. Penta.	-	0.364	-	-	-
BA76	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Rubbing wiping	LUDOX	-	0.072	very large	1	10
BA77	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Rubbing wiping	LUDOX	-	0.086	-	-	-
BA78	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	LUDOX	1.5	0.052	very large	1	10

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Composition	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (μm)	XRD Peak Ratio	PV Results ^{a}		
									Flux (kg/m^{2}h)	S.F.	Permeate Water wt %
BA79	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	LUDOX	-	0.072	-	-	-
BA80	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Vacuum seeding wiping	LUDOX	-	0.085	very large	1	10
BA81	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Vacuum seeding wiping	LUDOX	-	0.143	-	-	-
BA82	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Rubbing wiping	Waterglass	-	0.143	0.42	6.8 4^b	43 30.8
									0.24	6.8 2^b	43 18.2
BA83-2	Batch	$N_{3.4}A_1S_2H_{155}$	4+4	2	Rubbing wiping	Waterglass	6	0.268	0.20	120 89^b	93 90.8
									0.20	104 74^b	92 89.2

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Composition	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (µm)	XRD Peak Ratio	PV Results ^{a}		
									Flux (kg/m^{2}h)	S.F.	Permeate Water wt %
BA84	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	0.196	0.25	120 80^b	93 89.9
									0.28	171 81^b	95 90.0
BA84-2	Batch	$N_{3.4}A_1S_2H_{155}$	4+4	2	Dip-coating wiping	Waterglass	5.3	-	-	-	-
BA85-2	Batch	$N_{3.4}A_1S_2H_{155}$	4+4	2	Dip-coating wiping	Waterglass	3	0.250	0.22	120 78^b	93 89.7
									0.21	171 187^b	95 95.4
BA86	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Vacuum seeding wiping	Waterglass	-	0.291	0.22	44 29^b	83 76.3
									0.18	66 42^b	88 82.4

Table L.1 cont'd.

									PV Results ^{a}		
Code	**Synthesis Type**	**Synthesis Composition**	**time (h)**	**# of consecutive synthesis**	**Seeding method**	**Silica source**	**SEM thickness (μm)**	**XRD Peak Ratio**	**Flux (kg/m^{2}h)**	**S.F.**	**Permeate Water wt %**
BA87-2	Batch	$N_{3.4}A_1S_2H_{155}$	4+4	2	Vacuum seeding wiping	Waterglass	9.5	0.385	0.21	38 30^b	81 77
									0.19	32 25^b	78 73.5
BA88	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	6+6	2	Rubbing	Waterglass	-	0.260	0.21	86 78^2	90.5 89.7
									0.25	36 32^2	80 78
BA89	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	6+6	2	Rubbing	Waterglass	-	-	-	-	-
BA90	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Rubbing	Waterglass	-	-	0.34	20 14.4^2	69 61.5
									0.24	8 7^2	47.1 43.8
BA91	Batch	$N_{2.5}A_1S_{1.7}H_{150}$	4	1	Rubbing	Waterglass	-	0.490	-	-	-

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Composition	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (μm)	XRD Peak Ratio	PV Results[a]		
									Flux (kg/m²h)	S.F.	Permeate Water wt %
BA92	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	3	0.196	0.23	130 142[b]	93.5 94
									0.20	73 62[b]	89 87.3
BA93	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	0.196	0.19	51 49[b]	85 84.5
									0.22	34 22[b]	79 71
BA94	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Vacuum seeding wiping	Waterglass	-	0.302	0.42	12.4 10.4[b]	58 53.6
									0.08	35 28[b]	79.5 76.3

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Composition	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (µm)	XRD Peak Ratio	PV Results[a]		
									Flux (kg/m²h)	S.F.	Permeate Water wt %
BA95	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Vacuum seeding wiping	Waterglass	9	0.345	0.21	32 23[b]	78 72
									0.21	44 33[b]	83 78.6
BA96[e]	Batch	$N_{3.4}A_1S_2H_{270}$	1	1	Dip-coating wiping	Waterglass	-	0.042	-	-	-
BA97[e]	Batch	$N_{3.4}A_1S_2H_{270}$	1	1	Dip-coating wiping	Waterglass	-	0.082	-	-	-
BA98	Batch	$N_{3.4}A_1S_2H_{270}$	6	1	Vacuum seeding wiping	Waterglass	-	0.371	0.17	15	62.5
									0.17	17	65.4
BA99	Batch	$N_{3.4}A_1S_2H_{270}$	6	1	Vacuum seeding wiping	Waterglass	-	0.386	-	-	-

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Composition	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (µm)	XRD Peak Ratio	PV Results[a]		
									Flux (kg/m²h)	S.F.	Permeate Water wt %
BA100	-	-	-	-	Dip-coating wiping	-	-	0.	-	-	-
BA101	-	-	-	-	Vacuum seeding wiping	-	-	0.1	-	-	-
BA102[e]	Batch	$N_{3.4}A_1S_2H_{270}$	1	2	Dip-coating wiping	Waterglass	-	0.135	0.20	1 5.5[b]	10 38
BA107[e]	Batch	$N_{3.4}A_1S_2H_{270}$	1	2	Dip-coating wiping	Waterglass	-	0.143	-	-	-
BA108[e]	Batch	$N_{3.4}A_1S_2H_{270}$	1	4	Dip-coating wiping	Waterglass	-	0.224	0.43	1 2.2[b]	10 19.6
BA109[e]	Batch	$N_{3.4}A_1S_2H_{270}$	1	4	Dip-coating wiping	Waterglass	-	0.211	-	-	-

Table L.1 cont'd.

									PV Results[a]		
Code	**Synthesis Type**	**Synthesis Composition**	**time (h)**	**# of consecutive synthesis**	**Seeding method**	**Silica source**	**SEM thickness (μm)**	**XRD Peak Ratio**	**Flux (kg/m²h)**	**S.F.**	**Permeate Water wt %**
BA115	Batch	$N_{3.4}A_1S_2H_{270}$	6	1	Dip-coating wiping	Waterglass	-	0.237	0.22	1	10
BA116	Batch	$N_{3.4}A_1S_2H_{270}$	6	1	Dip-coating wiping	Waterglass	-	0.196	-	-	-
BA118	Flow	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	1.5	0.151	0.29	129.5 108[b]	93.5 92.3
									0.28	129.5 91.4[b]	93.5 91
BA119	Flow	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	0.151	-	-	-
BA119-2	Flow	$N_{3.4}A_1S_2H_{155}$	4+4	2	Dip-coating wiping	Waterglass	-	-	0.09	66	88
									0.39	8	47
BA120[c]	Flow	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	0.231	very large	1	10

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Composition	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (µm)	XRD Peak Ratio	PV Results [a]		
									Flux (kg/m²h)	S.F.	Permeate Water wt %
BA121[c]	Flow	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	-	very large	1	10
BA122	Flow	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	0.167	0.33	33	78.6
									0.37	7	43.8
BA123	Flow	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	0.151	0.23	28	75.7
									0.36	10	52.6
BA124[c]	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	-	0.79	8	47
BA125[c]	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	-	0.14	8	47
BA126	Flow	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	0.211	0.16	47	84
									0.20	36	80
BA127	Flow	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	0.167	-	-	-

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Composition	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (μm)	XRD Peak Ratio	PV Results[a]		
									Flux (kg/m^{2}h)	S.F.	Permeate Water wt %
BA128	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	-	Waterglass	-	0.042	-	-	-
BA129	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	-	Waterglass	-	0.036	-	-	-
BA130	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	0.151	2.45	1	10
BA131	Batch	$N_{3.4}A_1S_2H_{155}$	4	1	Dip-coating wiping	Waterglass	-	0.167	-	-	-
BA132[c]	Flow	$N_{3.4}A_1S_2H_{200}$	17	1	Pore filling	Waterglass	-	-	1.2	>25,000[b]	>99.96
BA133[c]	Flow	$N_{3.4}A_1S_2H_{200}$	17	1	Pore filling	Waterglass	-	-	1.2	30	77
BA133-2[c]	Flow	$N_{3.4}A_1S_2H_{200}$	17+3	2	Pore filling	Waterglass	16	0.188	2.7	104	92

Table L.1 cont'd.

Code	Synthesis Type	Synthesis Composition	time (h)	# of consecutive synthesis	Seeding method	Silica source	SEM thickness (μm)	XRD Peak Ratio	PV Results[a]		
									Flux (kg/m^{2}h)	S.F.	Permeate Water wt %
BA134[c]	Flow	$N_{3.4}A_1S_2H_{200}$	6	1	Pore filling	Waterglass	-	0.195	2.0	15	65
BA136[c]	Flow	$N_{3.4}A_1S_2H_{200}$	17	1	Pore filling	Waterglass	10	0.160	2.2	30	77
BA137[c]	Flow	$N_{3.4}A_1S_2H_{200}$	17	1	Pore filling	Waterglass	-	-	3.65	15	63
BA137-2[c]	Flow	$N_{3.4}A_1S_2H_{200}$	17+17	2	Pore filling	Waterglass	-	-	2.1	81	90
BA138[c]	Flow	$N_{3.4}A_1S_2H_{200}$	17	1	Pore filling	Waterglass	-	-	2.9	12	58
BA139[c]	Batch	$N_{3.4}A_1S_2H_{200}$	17	1	Pore filling	Waterglass	-	-	very large	1	10

Note: Membranes are named with this principle; "Code - # of consecutive synthesis", only "Code" means that the number of consecutive synthesis is one for that membrane. Membranes generally synthesized as couples in same synthesis flasks.

L1. SEM images of the synthesized membranes

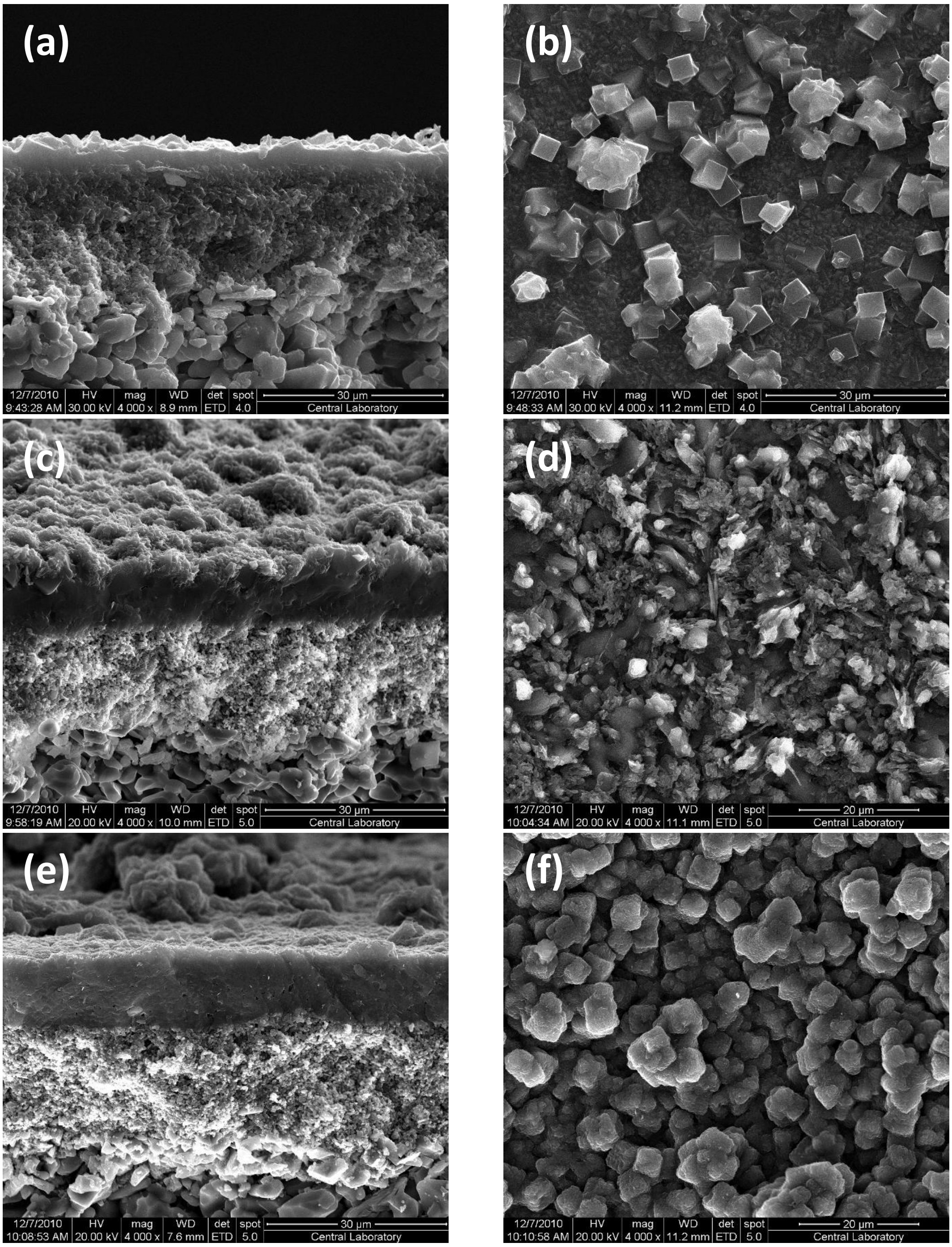


Figure L.1.1 Cross-section and surface micrographs of zeolite A membranes synthesized in batch system (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, Sod. Meta. Penta., 95°C, 4h,); (a), (b) BA70 (rubbing wiping); (c), (d) BA72 (vacuum seeding wiping) and (e), (f) BA74 (vacuum seeding)

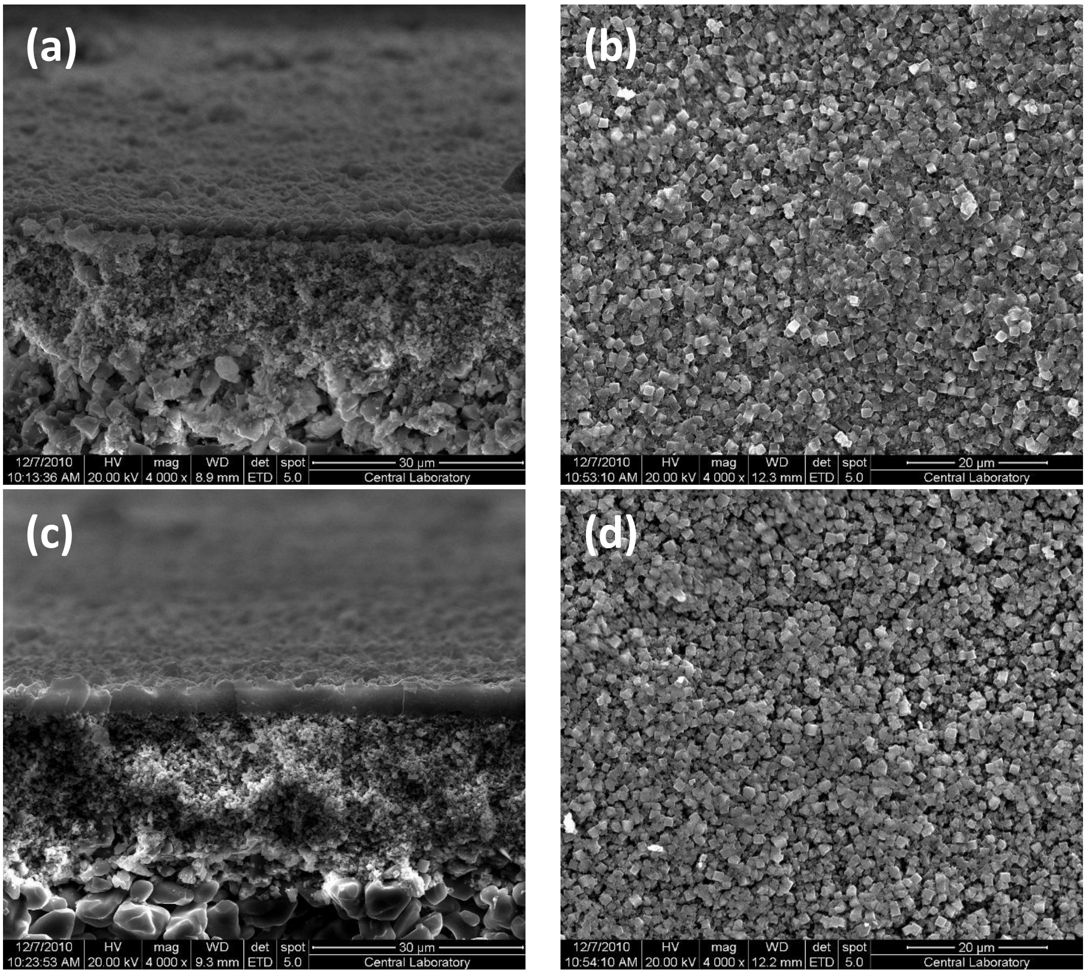


Figure L.1.2 Cross-section and surface micrographs of zeolite A membranes synthesized in batch system (Synthesis conditions: $N_{3.4}A_1S_2H_{155}$, LUDOX, 95°C, 4h,); (a), (b) BA76 (rubbing wiping) and (c), (d) BA80 (vacuum seeding wiping)

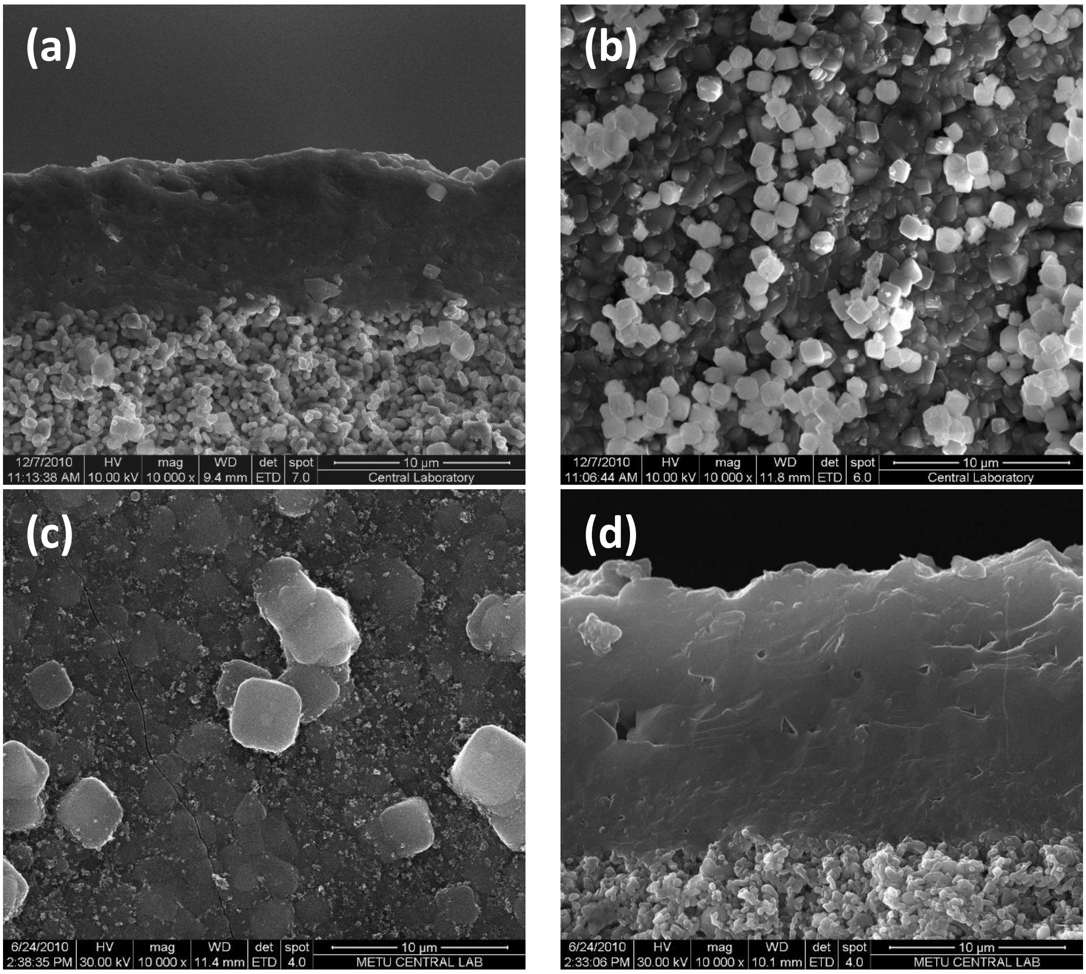


Figure L.1.3 Cross-section and surface micrographs of zeolite A membranes synthesized in modified flow system (Synthesis conditions: $N_{3.4}A_1S_2H_{200}$, waterglass, pore filling, 95°C,); (a), (b) BA134 (6h, one layer) and (c), (d) BA133-2 (17+3 h, two layer)