Chapter 3

Experiment

In the present study, a permeation cell was built for the pervaporation setup. Chitosan membranes crosslinked by sulfuric acid were prepared and used for separation of ethanol-water mixture by pervaporation process. The conditions for membrane preparation and the operating conditions for pervaporation were investigated using RSM for experimental design to optimize membrane properties and pervaporation performance.

3.1 Materials

- Chitosan (94% DD, $\overline{M}_v$ = 1,383,566, Seafresh)
- Acetic acid (analytical reagent grade, Fluka)
- Sodium hydroxide (analytical reagent grade, Merck)
- Sulfuric acid (analytical reagent grade, Rhone Poulene Chemistry)
- Ethanol (HPLC grade, Merck)

3.2 Equipments

- Analytical balance, Precision:0.01g (PB 3002-L, Mettler Toledo)
- Analytical balance, Precision:0.00001g (CP225D, Sartorius)
- Aspirator pump (2012A, Alcatel)
- Circulation pump (IP31, Watson Marlow)
- Desiccator
- Diginatic thickness gage (l547, Mitutoyo)
- Digital timer (HS-3, Casio)
- Magnetic stirrer (MR 3001, Heidolph)
- Oven (ULM 500, Memmert)
- Pirani vacuum gauge (VAP 5, Vacuubrand)

- Refractometer (3T, Atago)
- Universal testing machine (LRX-Plus, Lloyd)
- Vacuum oven (282A, Fisher Scientific) with Vacuum pump (RV5, Edward)
- Vacuum pump (RZ 2.5, Vacuubrand)
- Viscometer (531-03, Schott)

3.3 Method

3.3.1 Membrane Preparation

RSM was used to design the experiment for membranes preparation in order to optimize membrane characteristics and membrane performance including swelling ratio, sorption selectivity, tensile strength, permeation flux and separation factor. In this study, three variables which influence membrane properties including concentration of crosslinking agent (sulfuric acid), crosslinking time and membrane formation temperature were of interest. Maximum and minimum values of these variables, presented in Table 3.1, were assigned base on preliminary study and literature survey. From Table 2.1, coded variables of each independent variable for membrane preparation were -1.682, -1, 0, +1 and +1.682. The natural variables of each independent variable were calculated from equation (2-9), and are shown in Table 3.2. The values of these natural variables were experimental conditions used for membrane preparation.

Table 3.1 Maximum and minimum values of each variable

Variables	Maximum value	Minimum value
Concentration of sulfuric acid, (M)	1.0	0.1
Crosslinking time, (min)	120	30
Membrane formation temperature, (°C)	70	50

Table 3.2 Coded and Natural variables of each independent variable for membrane preparation

Coded Variables			Natural Variables		
Concentration of sulfuric acid	Crosslinking time	Temperature	Concentration of sulfuric acid (M)	Crosslinking time (min)	Temperature (°C)
-1	-1	-1	0.28	48	54
1	-1	-1	0.82	48	54
-1	1	-1	0.28	102	54
1	1	-1	0.82	102	54
-1	-1	1	0.28	48	66
1	-1	1	0.82	48	66
-1	1	1	0.28	102	66
1	1	1	0.82	102	66
-1.682	0	0	1.00	75	60
1.682	0	0	1.00	75	60
0	-1.682	0	0.55	30	60
0	1.682	0	0.55	120	60
0	0	-1.682	0.55	75	50
0	0	1.682	0.55	75	70
0	0	0	0.55	75	60
0	0	0	0.55	75	60
0	0	0	0.55	75	60
0	0	0	0.55	75	60
0	0	0	0.55	75	60
0	0	0	0.55	75	60

Chitosan membranes were prepared by dissolving 1%w/v chitosan in 1 %v/v acetic acid aqueous solution. After stiring at room temperature for 48 h, the solution was filtered using aspirator pump to remove any non-dissolved residue particles. This solution 80 mL was poured on glass plate (18 cm × 18 cm) and dried at various temperatures as shown in Table 3.2. The dried membranes were neutralized in 1M NaOH solution for 4 h, washed, rinsed respectively with distilled water and then dried at room temperature for 24 h. Finally, the membranes were crosslinked with sulfuric acid. The concentrations of sulfuric acid and crosslinking time are shown in Table 3.2. The crosslinked chitosan membranes were washed with distilled water to remove excess sulfuric acid and dried at room temperature. Thickness of the obtained membranes was determined using diginatic thickness gage.

3.3.2 Membrane Characterization

The physical properties including swelling ratio, sorption selectivity and tensile strength of membranes prepared in 3.3.1 were studied.

3.3.2.1 Swelling measurement

Swelling ratio of the membranes was determined by immersing dried membrane strips (7 cm x 1.5 cm) in water at room temperature for at least 30 min to allow the strips to reach equilibrium sorption. The dimension of swollen strips was measured. The strips were dried at room temperature and the dimension of the strips was measured again. Swelling ratio was calculated using equation (2-4).

3.3.2.2 Sorption studies

Sorption property of the chitosan membranes was investigated using apparatus shown schematically in Figure 3.1. The dried membrane sheet (6 cm x 10 cm) was first immersed in a closed bottle containing 50/50 water-ethanol mixture. After swelling equilibrium state was reached (for at least 30 min), the membrane was removed from the bottle, surface liquid was quickly wiped off with tissue papers and the swollen membrane was weighed. Then the swollen membrane was put into the sample tube and cooled with liguid nitrogen for 10 minutes in order to freeze all substance in the membrane. The system was brought to a high vacuum while the sample tube was cooled. After the valve between sample tube and receiver tube was closed, the receiver tube was cooled with liquid nitrogen for 10 minutes, then the sample tube was heated by removing liquid nitrogen and this valve was opened. The substance released from the membrane was condensed in the receiver tube. Compositions of this condensate were analyzed by refractometer. At the end of each experiment which lasted for 1 h, sorption was calculated using equation (2-5).

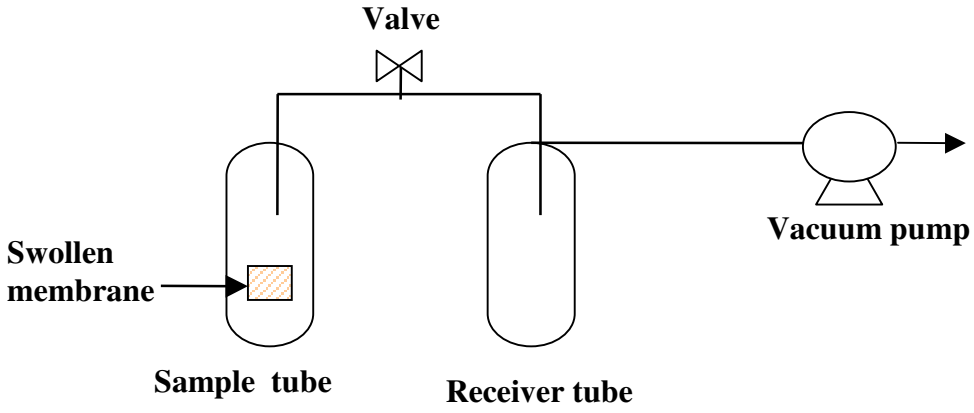

Figure 3.1 Schematic diagram of sorption apparatus.

3.3.2.3 Tensile strength

Tensile strength of the chitosan membranes was measured according to ASTM D882 using universal testing machine. The sample dimension was 6 inch x 1 inch, and the cross-head speed was 50 mm/min. Five specimens were used for each measurement.

3.3.3 Pervaporation Experiment

3.3.3.1 Pervaporation setup

Figure 3.2 shows schematic diagram of cross-section of permeation cell designed and built for using in this work. The membrane was housed between two detachable stainless steel parts. A porous stainless steel plate was imbedded in one side to support the membrane. Rubber o-ring was used to provide a pressure tight seal between the membrane and the permeation cell. Effective membrane area in contact with feed liquid was 13.35 cm^2. The pervaporation apparatus setup is shown schematically in Figure 3.3. Feed mixture with predetermined composition was circulated from a feed tank to the permeation cell using feed circulation pump, and retentate from the permeation cell was recycled to the feed tank. Volume of the feed

was 1L and flow rate was 500 mL/min. Downstream pressure was kept at 2.54 mm of Hg by vacuum pump. Permeate vapor was condensed and collected in cold trap immersed in liquid nitrogen. Compositions of permeate and feed were determined at 293 K using refractometer. At the end of each experiment which lasted for 3 h, flux, separation factor and separation index were calculated from equation (2-1), (2-2) and (2-3), respectively.

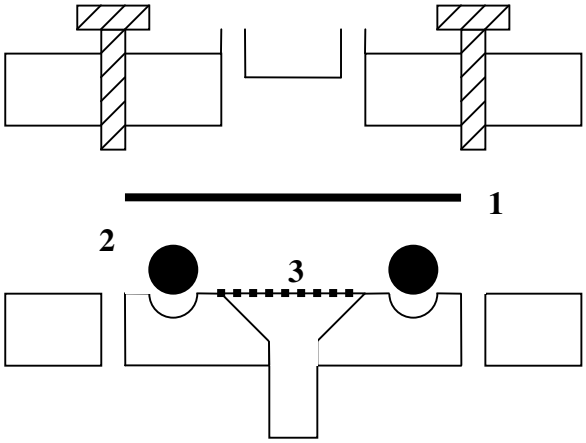

Figure 3.2 Schematic diagram of cross-section of permeation cell , 1: membrane, 2: o-ring and 3: porous steel plate.

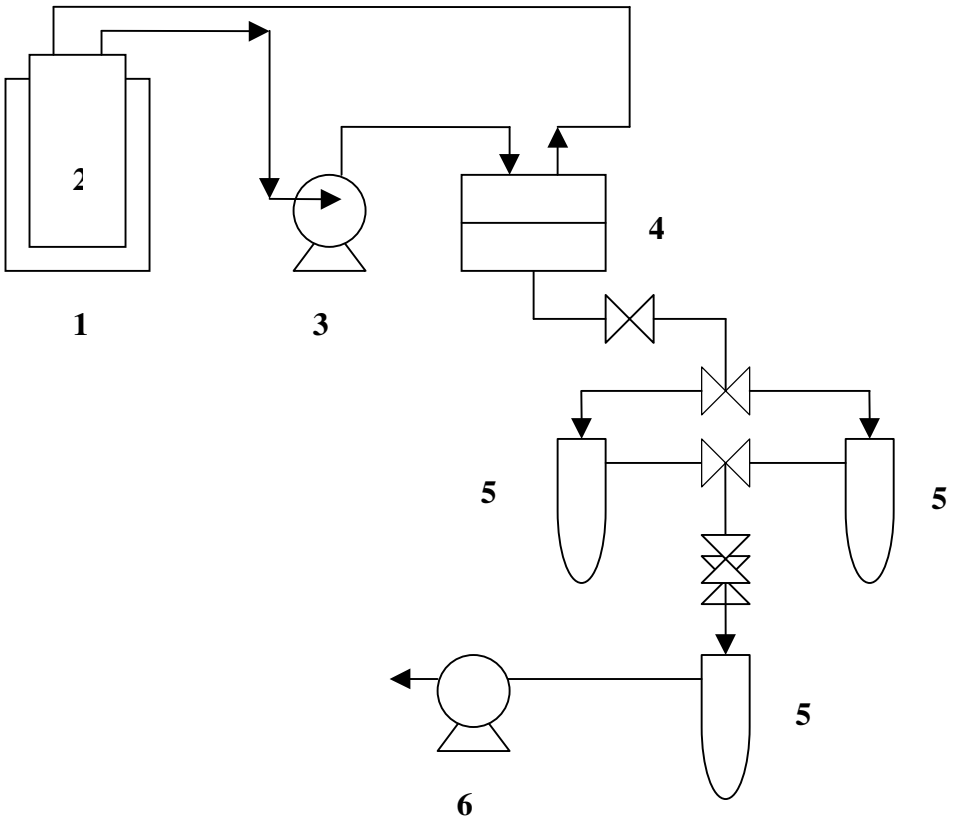

Figure 3.3 Schematic diagram of pervaporation setup, 1: heating mental, 2: feed tank, 3: feed circulation pump, 4: permeation cell, 5: cold trap and 6: vacuum pump.

3.3.3.2 Pervaporation studies

Pervaporation performance of the membranes from 3.3.1 was investigated in order to obtain the membranes which gave optimum permeation flux, separation factor and separation index. The method used for this study is described in 3.3.3.1 with feed concentration 87 %w/w ethanol and feed temperature 60 °C. Next step, the membrane which gave optimum permeation flux, separation factor and separation index were prepared and RSM was used to design the experiments for pervaporation study in order to optimize pervaporation performance. In this work, two variables which influence pervaporation including feed concentration and feed temperature were of interest. The range of feed concentration was 70-95 %w/w ethanol solution,

and of feed temperature was 50-70 °C. From Table 2.1, coded variables of each independent variable for pervaporation study were -1.414, -1, 0, +1 and +1.414. The natural variables of each independent variable were calculated from equation (2-9), and are shown in Table 3.3. The values of these natural variables were operating conditions used for pervaporation study. Pervaporation performance was investigated from permeation flux, separation factor and separation index using the method in 3.3.3.1.

Table 3.3 Coded and Natural variables of each independent variable for pervaporation study

Coded Variables		Natural Variables	
Concentration of feed	Temperature of feed	Concentration of feed (%w/w)	Temperature of feed (°C)
-1	-1	73	53
-1	1	73	67
1	-1	91	53
1	1	91	67
-1.414	0	70	60
1.414	0	95	60
0	-1.414	83	50
0	1.414	83	70
0	0	83	60
0	0	83	60
0	0	83	60
0	0	83	60
0	0	83	60