

## CHAPTER 3

### Experimental Methods

#### 3.1 Scope of Research

As mentioned, this research was a project for the modification of the chitosan film as the selective layer of composite nanofiltration membrane for a long application in the solvent recovery. This work focused on the properties of chitosan films as following topics a) study the crosslinking condition on the tensile strength b) determine the degree of crosslinking with glutaraldehyde solution by FT-IR analysis c) study the solvent resistance of uncrosslinked and crosslinked chitosan films by the tensile measurement.

For this study, The researcher started to apply crosslinking condition with highest tensile strength on the chitosan layer of the composite membrane. The membrane performances were determined by measuring the molecular weight cut off and the surface and cross-section morphology of the membranes.

#### 3.2 Materials

1. Poly(acrylonitrile) (PAN), molecular weight was 150 KDa was procured from Polysciences, USA.
2. Chitosan flakes were supplied by Polyscience, USA.
  - The molecular weight of chitosan was  $1.16 \times 10^5$  Da.
  - Degree of deacetylation (d.d.) was 86% (Musale and Kumar,1999).
3. Acetic acid was obtained from Aldrich Ltd., Canada.
4. Glutaraldehyde solution (50%w/w) was obtained from Aldrich Ltd., Canada.
5. The solvents : hexane, 95% ethanol (EtOH), methyl isobutyl ketone(MIBK), ethyl acetate (EtOAc) were procured from BDH, Canada.
6. Cyclohexylamine was obtained from Eastman Kodak Company, New York.

7. Polyethylene glycol and poly(ethylene oxide) of different molecular weights were obtained from Fluka and Aldrich Chemical Company Inc., USA.

8. All other reagents were obtained from Anachemia, Canada. Reverse osmosis-treated water with a conductivity of  $5 \times 10^{-4} \text{ S m}^{-1}$  was used throughout this study.

### 3.3. Preparation of Chitosan Films

Chitosan films making involved following two steps:

#### 3.3.1 Purification of chitosan

1. Chitosan flakes were mixed in 2% aq. acetic acid using mixing roller at 40 rpm. overnight at room temperature until the mixture was homogeneous. The chitosan solution (2%w/w) was left at room temperature for 24 hours.

2. Chitosan solution was filtered with polypropylene fabric that its pore size was 1 mm. and precipitated fully in 4 % aq. NaOH about 30 minutes. Precipitated chitosan was washed with distilled water many times to remove all NaOH traces.

3. The precipitated chitosan was dried in oven at 50 °C for 12 hours, then placed in a petridish and put in vacuum for 3 days to remove any residual water.

4. The purified chitosan was stored in a desiccator.

#### 3.3.2 Preparation of uncrosslinked chitosan film

1. The 2% purified chitosan in 2%(w/w) aq. acetic acid was stirred overnight at constant low speed and room temperature .

2. This chitosan solution (2%w/w) was filtered through the stainless tube (1.25×11.5 inch) packed with stainless steel fiber filter under air pressure as shown in Figure 3.1, then the chitosan solution was degassed to remove many bubbles with the water jet pump.

3. Before casting, the mirror mold was treated with small amount of sulfuric acid for about 10 min in fume hood. The mirror mold was washed with distilled water many times, wiped with paper, and then cleaned by blowing the air.

Chitosan solution (30 grams) was poured on the round mirror mold that its diameter was 13.2 cm., and put in the conventional oven to dry at 50°C for 2-3 hours.

4. The obtained chitosan film was peeled off, and then wrapped in aluminium foil. These films were dried in conventional oven at 50°C about 3 hours, and put into the vacuum oven at 40-41°C for 2 days

5. The chitosan films were kept in a desiccator.

6. The films were soaked in 4% aq. NaOH in 95% ethanol overnight (19 hours) to neutralize, and washed with water several times to remove all NaOH traces.



**Figure 3.1** Stainless filter tube.

### **3.4 Preparation of Crosslinked Chitosan Films.**

1. The uncrosslinked chitosan films obtained from 3.3 were soaked in 0.05%, 0.1% and 0.2% (w/w) aq. glutaraldehyde solution for 40 and 80 minutes, and 0.02%, 0.04% and 0.06% (w/w) aq. glutaraldehyde solution for 20 min and 40 minutes. and 0.01%(w/w) for 20 minutes under N<sub>2</sub> gas.

2. The films were then washed several times with the distilled water to get rid of all glutaraldehyde traces.

3. The wet films were dried via solvent exchange method by soaking in 95% ethanol for 1 hour followed by soaking in hexane for 1 hour.

4. The crosslinked chitosan films were put in a vacuum oven at 40-41°C for 24 hours to remove all solvent and stored in a desiccator.

### 3.5 Characterization of Uncrosslinked and Crosslinked Chitosan Films.

#### 3.5.1 Determination of degree of crosslinking

Fourier Transform Infrared (FT-IR) spectroscopy, model M Series from MIDAC Corp. as shown in Figure 3.2 was used in this study. The degree of crosslinking was determined the imine concentration of chitosan films for each of the crosslinking conditions at 0.02%, 0.04%, 0.06% w/w, 20 min and 40 min by using Beer's law or Bouguer-Beer-Lambert law as shown in equation 2.1 (Griffiths and de Haseth, 1986).



**Figure 3.2** FT-IR spectroscopy model M series

#### 3.5.2 Swelling in water

1. The crosslinked chitosan films with 0, 0.02%, 0.04% and 0.06%(w/w) glutaraldehyde solution, 20 minutes of crosslinking time were weighed before soaked the films in the distilled water.
2. The chitosan films were soaked in the distilled water for 24 hours at the room temperature.
3. After gently blotting with tissue paper, the wet films were weighed after soaked films in the distilled water.

The percentage of swelling in water (%S) was calculated in equation 3.1

$$\%S = (W_w - W_d / W_d)100 \quad (3.1)$$

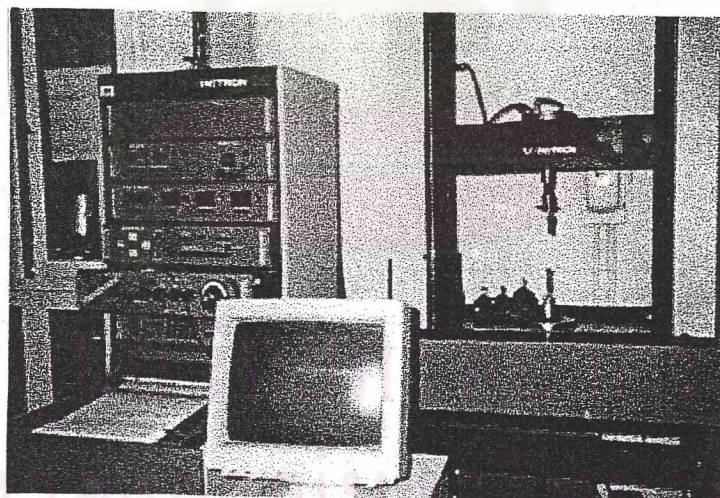
Where, % S = the percentage of swelling in water

$W_w$  = the weight of the dry film before soaked in water (grams)

$W_d$  = the weight of the wet film after soaked in water (grams)

### 3.5.3 Tensile strength measurement

The tensile strength of the uncrosslinked and crosslinked chitosan films were determined at 25°C using an Instron Universal Testing Instrument (Instron Model No.1123 ) as shown in Figure 3.3 from Instron Canada Inc. Films were cut into strip (2×40 mm.) and tested at crosshead speed of 10 mm/min, gauge length 10 mm., load factor 5 and tension load cell of 500 gram.



**Figure 3.3** Instron Model No.1123

### 3.5.4 Investigation of solvent resistance of uncrosslinked chitosan and crosslinked chitosan films

The solvent resistance of crosslinked chitosan and uncrosslinked chitosan films was determined by the tensile measurement after soaked films in each solvents: hexane, 95% aq. EtOH, MIBK, EtOAc for 24 hours. The tensile strength was determined at 25°C with an Instron universal testing instrument (Instron Model No.1123 ) from Instron Canada Inc. Films were cut into strip (2×40 mm.) and tested at a crosshead speed of 10 mm/min, the gauge length 10 mm., load factor 5 and tension load cell of 500 gram.

## **3.6 Preparation of the Chitosan/ Poly(acrylonitrile) (PAN) Composite Membrane**

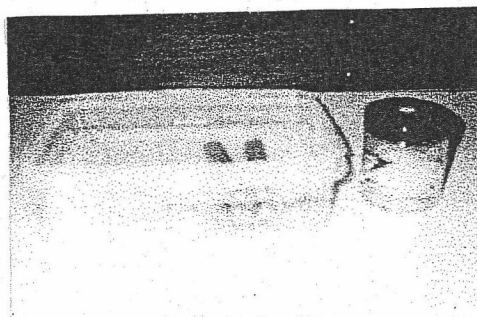
### 3.6.1 Preparation of poly(acrylonitrile) membrane

1. The 14% poly(acrylonitrile) powder was mixed in N,N- dimethyl formamide using mixing roller for 2 weeks ,and put in the oven at 60°C until the mixture was homogeneous.
2. The glass plate and casting bar were cleaned and dried in the conventional oven to remove the moisture.
3. The poly(acrylonitrile) solution (14%w/w) was cast on the non-woven porous polyester backing, and soaked in the distilled water at 22°C for 20 minutes.
4. The obtained membranes were washed with the distilled water several times to remove the solvent traces.
5. The poly(acrylonitrile) membranes were cut into 6.6 cm. of coupon diameter stored in the distilled water as shown in Figure 3.4

The thickness of two sheets of polyacrylonitrile membranes was measured by a micrometer:

Sheet 1: 0.28 – 0.30 mm.

Sheet 2: 0.23-0.25 mm.



**Figure 3.4** Storage of membranes

### 3.6.2 Preparation the surface crosslinking of polyacrylonitrile (PAN) / chitosan (CTS) composite membrane.

The 2% purified chitosan was stirred in 2% aq. acetic acid overnight at room temperature. The chitosan solution (2% w/w) was coated on the poly(acrylonitrile) membrane by using the glass rod, and put in the oven at 50°C to evaporate the solvent for 20 minutes. The membranes were soaked in 4% aq. NaOH solution for converting chitosan salt to chitosan for 10 minutes and washed with distilled water several times. The membranes were soaked in 0.02% w/w glutaraldehyde solution for 20 minutes, the condition which gave the films with highest tensile strength under N<sub>2</sub> gas at the room temperature, and washed with the distilled water several times to remove all glutaraldehyde traces.

## 3.7 Characterization of PAN/CTS Composite Membrane

### 3.7.1 Morphology of membrane

The morphology of PAN/CTS composite membrane with and without crosslinking was studied by SEM (Scanning Electron Microscope) using JEOL JSM 5300. A piece of the membrane was mounted on carbon tape on an SEM stub at 45°, then sputter coated with gold.

### 3.7.2 Percentage of separation

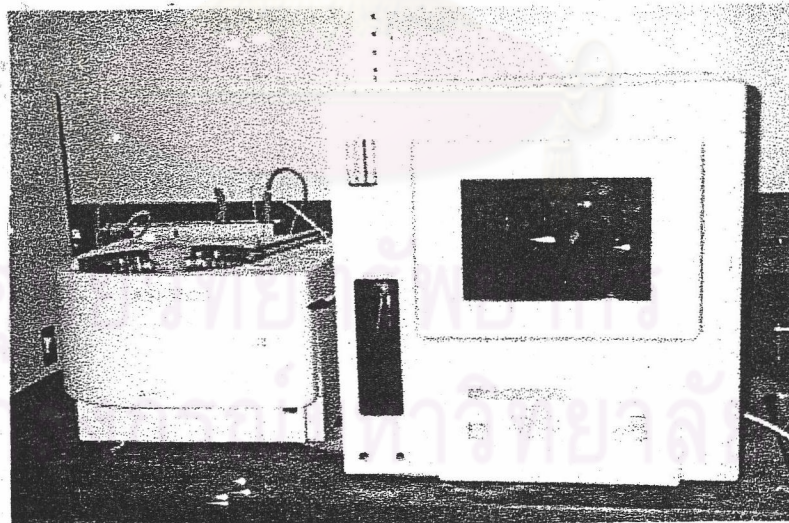
The concentration of permeate solute was determined by using a Shimadzu total organic carbon analyzer (TOC-5000) shown in Figure 3.5. The percentage of separation of PAN/CTS membrane, PAN/CTS membrane crosslinked with 0.02% (w/w) glutaraldehyde solution for 20 minutes and PAN membrane was calculated in equation 3.2. The feed solutes of various molecular weight were polyethylene glycol 0.6, 1.5, 6, 12, 35 KDa. and poly(ethylene oxide) 35, 100, 200, 300 and 600 KDa. The concentration of feed solutes was 200 ppm.

$$\% \text{ Separation} = \frac{(\text{feed} - \text{TC}_{\text{pure water}}) - (\text{permeate} - \text{TC}_{\text{pure water}})}{(\text{feed} - \text{TC}_{\text{pure water}})} \times 100\% \quad (3.2)$$

Where ; feed = concentration of feed solute (ppm.)  
= 200 ppm.

permeate = concentration of permeate solute obtained from  
TOC ( ppm.)

$\text{TC}_{\text{pure water}}$  = TC concentration of pure



**Figure 3.5** Total organic carbon analyzer

This TC value was used in the calculation of % separation of membrane, then lead to the molecular weight cut off (MWCO) of membrane.