CHAPTER 2

EXPERIMENTAL METHODS

2.1 MATERIALS

2.1.1 Polymers

Commercial grade cellulose acetate MYCEL cellulose acetate CDA 5770 (Acetyl content 39.99 wt%) procured from Mysore Acetate and Chemicals Company Limited., India, was used without any further treatment. PVA (molecular weight 125000) was obtained from SD Fine Chemicals Ltd., Mumbai, India. Gelatin (for bacteriological purposes) is obtained from Loba-Chemie Indoaustranal Co. Mumbai.

2.1.2 Solvents and other chemicals

Analar grade N,N-Dimethylformamide (DMF) as solvent from M/s.Qualigens Fine Chemicals, Glaxo India Limited was procured, sieved through molecular sieves (Type-4Å) for removing moisture and stored in dried condition prior to use. Other solvents of analar grade such as acetone, 1,2-dichloromethane and methanol from Qualigens Fine Chemicals Ltd., India were used. Sodium lauryl sulphate (SLS) of AR grade was obtained from Qualigens Fine Chemicals Ltd., India and used as surfactant. Sulfuric acid (97-99%), was obtained from Qualigens Fine Chemicals, Glaxo India and hydrochloric acid 35% pure was obtained from Merck Ltd. (India). Double-distilled water was used throughout the study.
2.1.3 Proteins

Proteins such as Bovine Serum Albumin (BSA), $M_w = 69$ kDa, trypsin $M_w = 20$ kDa and pepsin $M_w = 35$ kDa were purchased from Sisco research laboratories (SRL), India. Egg albumin (EA) $M_w = 45$ kDa is purchased from central drug house, India. These proteins were used for the protein rejection studies, fouling studies and determination pore statistics. Sodium dihydrogen ortho phosphate and disodium hydrogen ortho phosphate were obtained from CDH Chemicals Ltd., India and used for the preparation of phosphate buffer solutions in protein analysis. Proteins like BSA, Trypsin, Pepsin and Egg albumin were chosen for MWCO studies because the size and shape of the proteins are normally spherical and regular due to this, during filtration it can easily pass through the pores of the membrane and also the proteins are available in wide range of molecular weight ranging from 19 kDa to 150 kDa.

2.2 MEMBRANE FORMULATIONS

The polymers of blending materials cellulose acetate (CA) as base polymer, and PVA/gelatin (17.5 wt%) were prepared individually and blending the two polymers with different compositions (Table 2.1) of various levels of PVA/gelatin pair by using polar solvent DMF, under constant mechanical stirring in a round bottom flask for 3h at 65°C. The homogeneous solution was allowed to stand for 1 h in an airtight condition to get rid off the air bubbles.
2.3 PREPARATION OF MODIFIED MEMBRANES

2.3.1 Solution blending of polymers

Cellulose acetate (100 wt%) and CA with PVA/gelatin pair of different wt% with solvent DMF were prepared by mechanically stirring at 65°C for 3 h (Table 2.1) to get homogenous and well mixed solution for casting.

PVA/gelatin hydrogels was made by esterification of the hydroxyl group of PVA with the carboxyl group of gelatin. The hydrogel developed was found to have film forming ability with more void formation. Hence, it could be tried to prepare ultrafiltration membrane with CA as base polymer for various separation applications, such as protein and other ions. The DSC thermogram studied by Pal et al (2006) indicated that the both a glass transition temperature of 92°C and a melting isotherm at 292°C. The thermogram of gelatin indicated a glass transition temperature of 60°C. The glass transition temperature of the membrane was found to be 145°C, indicating the formation of a new product with homogeneity. The similar study for cellulose acetate with gelatin has been reported by (Peppas et al 1977; Oakenfull et al 2003; Bigi et al 2004; Babin et al 2001).

2.3.2 Preparation of membranes

All membranes were prepared by the “diffusion induced phase inversion” method, namely, casting a thin film of the polymeric solution on a glass plate and, after allowing the solvent to evaporate for a predetermined period at the desired humidity and temperature conditions, immersing it into a bath of non-solvent (water, solvent, and surfactant) for final precipitation.
Prior to membrane casting, a gelation bath of 2 lit of distilled water (non-solvent), containing 2% DMF (Solvent) and 0.2% SLS (Surfactant) was prepared and cooled to 10°C. The schematic flow diagram of membrane preparation is shown in Figure 2.1.

Figure 2.1 Flow diagram for preparation method of UF membrane
### Table 2.1 Composition and casting conditions of CA and PVA/gelatinblend membranes

<table>
<thead>
<tr>
<th>S.No</th>
<th>Blend polymer composition</th>
<th>Total Polymer (gm)</th>
<th>Solvent (DMF) (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CA wt%</td>
<td>PVA/ gelatin wt%</td>
<td>CA (gm)</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>4.375</td>
</tr>
<tr>
<td>2</td>
<td>98</td>
<td>2</td>
<td>4.287</td>
</tr>
<tr>
<td>3</td>
<td>96</td>
<td>4</td>
<td>4.200</td>
</tr>
<tr>
<td>4</td>
<td>94</td>
<td>6</td>
<td>4.112</td>
</tr>
<tr>
<td>5</td>
<td>92</td>
<td>8</td>
<td>4.025</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>10</td>
<td>3.937</td>
</tr>
<tr>
<td>7</td>
<td>88</td>
<td>12</td>
<td>3.850</td>
</tr>
<tr>
<td>8</td>
<td>86</td>
<td>14</td>
<td>3.762</td>
</tr>
<tr>
<td>9</td>
<td>84</td>
<td>16</td>
<td>3.675</td>
</tr>
<tr>
<td>10</td>
<td>82</td>
<td>18</td>
<td>3.587</td>
</tr>
</tbody>
</table>

10 gm of gelatin dissolved in 100 ml of aqueous solution of 10% PVA; from the mixture various weight percentages were taken to blend with CA.

Quantity of casting solution = 25 ml.

Total weight percentage of polymer = 17.5 wt%.

Total weight percentage of solvent = 82.5 wt%

Casting solution temperature = 24 ± 1°C, Casting temperature = 24 ± 1°C

Casting relative humidity = 50 ± 2 %, Solvent evaporation time = 30 sec.

10 gm of pure gelatin was dissolved in 100 ml of 10% aqueous PVA solution and 0.05 ml concentrated hydrochloric acid was added and stirred for half an hour by overhead stirrer (100 ± 5 rpm) at 65°C to carry out the esterification reaction between PVA and gelatin (Pal et al 2007). The thick dispersion becomes thick solution and rigid, from the mixture so obtained was taken according to required composition as per Table 2.1 and added to cellulose acetate and solvent DMF, to get homogenous solution, the resulting
dispersion was stirred again by using an overhead stirrer at 65°C for about 3-4 hrs. From the resultant solution the membrane was casted over a glass plate.

The prepared homogeneous polymer solution of cellulose acetate with mixer of PVA/gelatin pair (Pal et al 2006) were placed in the controlled casting room at a temperature of 24 ± 1°C. The relative humidity of the casting room was maintained at 50 ± 2%. The membrane casting conditions are shown in Table 2.2.

Table 2.2 Membrane casting conditions

<table>
<thead>
<tr>
<th>Membrane casting conditions</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of casting solution (°C)</td>
<td>24 ± 1</td>
</tr>
<tr>
<td>Temperature of casting atmosphere (°C)</td>
<td>24 ± 1</td>
</tr>
<tr>
<td>Humidity of casting atmosphere (%)</td>
<td>50 ± 2</td>
</tr>
<tr>
<td>Period of casting (sec)</td>
<td>5 -10</td>
</tr>
<tr>
<td>Solvent evaporation time (sec)</td>
<td>30 ± 5</td>
</tr>
<tr>
<td>Temperature of gelation bath (°C)</td>
<td>12 ± 2</td>
</tr>
<tr>
<td>Period of solvent diffusion in gelation bath (h)</td>
<td>1- 3</td>
</tr>
<tr>
<td>Thickness of membrane on glass plate (mm)</td>
<td>0.22 ± 0.02</td>
</tr>
</tbody>
</table>

The homogeneous solutions were spread over a smooth glass plate with the help of a knife-edge. The thickness of the membranes was controlled by varying the thickness of adhesive tapes at the sides of the glass plate. The glass plate was kept in an environment of controlled temperature and humidity during membrane casting as specified. Solvent present in the casting solution was allowed to evaporate for 30 seconds.
An evaporation step prior to immersion can lead to top layer formation. A point of interest is to investigate the conditions necessary to give rise to top layer formation. Besides toplayer formation, evaporation can also induce macrovoid formation (Zeman and Fraser 1993). The glass plate was subsequently immersed in a gelation bath, which is generally maintained at a known temperature of 10°C. Immediately phase inversion starts and after few minutes thin polymeric film separated out from the glass. After 1hr of gelation, the polymeric film (membrane) was removed from the gelation bath and thoroughly rinsed with demineralized water to remove all Hcl present in the film and also to remove all Solvent and surfactant (SLS). Then the actual thickness (approximately 0.22 mm) of the membranes was measured by using a micrometer. The membrane was always wet stored in 0.25% formaldehyde solution. In this research work, blends of CA and PVA/gelatin have been investigated for membrane formation to improve the performance of pure water flux of the membranes, especially hydrophilicity and permeation properties. It has been observed that the addition of PVA/gelatin pair beyond 0.788 gm (18 wt%) on the total polymer composition (4.375 gm) resulted in heterogeneous solution leading to phase separation during membrane formation (Sivakumar et al 2005). Hence, we chose a maximum CA/(PVA/gelatin) composition of 3.587/0.788 gm (82/18 wt%) prepared by 10 gm of gelatin dissolved in PVA solution and introduced PVA/gelatin pair as decrement by 2 wt% and by increasing the fraction of CA by 2 wt%. The prepared membranes have been characterized by ultrafiltration studies such as pure water flux and membrane hydraulic resistance. The molecular weight cut-off (MWCO) and pore statistics such as pore size, porosity and number of pores of the prepared membranes have been determined by using different molecular weight proteins. The morphology of the resulted membranes has also been studied by scanning electron microscopy (SEM).
The ultrafiltration (UF) experiments were carried out in a stirred type, dead end ultrafiltration cell fitted with Teflon coated magnetic paddle. This experimental setup was purchased from Millipore Ltd., USA (Model XUF 076 01). The schematic diagram of ultrafiltration test kit cell used for the present study is illustrated in Figure 2.2.

The specifications of the Ultrafiltration test cell used are as follows:

- Capacity of the test cell, ml : 300
- Membrane diameter, mm : 76.0
- Effective filtration area, cm$^2$ : 38.5
- Minimum volume of operation, ml : 10.0
- Height of the test cell, cm : 165.0
- Diameter of the test cell, cm : 11.0
- Maximum pressure, kPa : 483 (4.8 atm)

![Figure 2.2 Schematic diagram of ultrafiltration test cell](image)
2.5 MEMBRANE CHARACTERIZATION

The thicknesses of the prepared membranes were measured using a micrometer (Mityutoyo, Japan), at various parts of the membrane. The thickness of the membranes maintained in the present studies was 0.22 ± 0.02mm. The membranes prepared were cut into the desired size needed for fixing it up in the ultrafiltration cell. The characterization experiments were performed with prepared membranes in the stirred-cell ultrafiltration kit. The feed employed with agitation under pressure to minimize concentration polarization effect (Long and Anderson 1984). The membranes were initially pressurized with distilled water at 414 kPa for 5h and compacted to attain steady-state flux. These pre-pressurized membranes were subsequently characterized and utilized for further studies.

2.5.1 Pure water flux

After compaction, permeability of pure water through the membranes was measured using the experimental apparatus shown in Figure 2.2. The feed solution flowed at constant pressure (345 kPa) through the inside of the flat sheet membrane in UF cell. The filtrate from the UF cell was collected in measuring cylinders. The time required for permeation of a prescribed amount of water was measured (Chaudry et al 2002). After the permeation experiment, calculate the flux based on the inner surface area. From the measured values (Osada and Nakagawa 1992), the PWF was determined from the following equation (2.1).

\[ J_w = \frac{V}{A \Delta t} = \frac{Q}{A \Delta t} \]  \hspace{1cm} (2.1)

where, \( J_w \) the water flux (l m\(^{-2} \) h\(^{-1} \)); \( Q \) is the quantity of water permeated (l); \( \Delta t \) is the sampling time (h); and \( A \) is the membrane area (m\(^2\)).
2.5.2 Mechanical properties

Tensile stress and elongation at break of the membrane were measured by using tensile test machine (Instron 4500 model) at a crosshead speed of 10 mm/min. Cross-sectional area of the sample of known width and thickness was calculated. The membranes were then placed between the grips of the testing machine (Judith et al 1991). The tensile stress values and elongation at break values of the individual membranes are noted. Stress is defined as the force per unit area, normal to the direction of the applied force, and break elongation as the extension per gauge length at break.

The mechanical properties of the modified CA membrane (Meenakshi et al 2002) with PVA/gelatin pair are given by the maximum load, elongation at the break and tensile stress. The elongation at break and the tensile stress of the membranes were reported.

2.5.3 Morphological studies

The top surface and cross-sectional morphology of the CA and (PVA/gelatin) pair membranes were studied using Scanning Electron Microscopy (LEICA Stereoscan, Cambridge, UK). The membrane samples were air dried to remove the surface water and fractured under cryogenic conditions using liquid nitrogen and were dried at 21±1°C. The sample was dipped into the water bath for 1sec before freeze fracturing. Water dipping allowed facile fracturing of the membrane (Han and Bhattacharyya 1995). The membranes were cut into pieces of varied sizes, mopped with filter paper and immersed in liquid nitrogen for few seconds to fracture the membranes. The dried bits of membranes were stored in desiccators and used for SEM studies.
The sample were mounted on Gold-sputtered sample called ‘studs’ to provide electrical conductivity to very thin layers of polymeric membranes and photomicrographs were taken in very high vacuum conditions operating at 15-25 kV depending upon the physical nature of the sample (Brink et al 1993). Scanning Electron Micrographs (SEM) at various magnifications were recorded to study the surface and cross-sectional view of the membrane samples.

2.5.4 Protein rejection studies

The characterized membranes were mounted in the ultrafiltration cell, the feed reservoir was filled with the individual protein solution and pressurized to 345 kPa and maintained constant throughout the run. Different molecular weight of proteins such as bovine serum albumin, trypsin, pepsin and egg albumin were dissolved (0.1 wt%) in phosphate buffer (0.5 m, pH 7.2) and used as standard solutions (Vilker 1981). The concentration of the feed solution was maintained constantly for all experiments. The % protein rejections were evaluated from the concentration of the feed and permeate using equation (2.2). On completion of an each run, the membranes were removed from the UF kit and washed with distilled water to remove adhering proteins and then subjected to pure water flux measurement. The percentage rejection was calculated by using the equation (2.2).

2.5.4.1 Molecular weight cut-off

Molecular weight cut-off is an attribute of pore size of the membranes and is related to the rejection of a spherical solute of given molecular weight. The molecular weight cut-off has a linear relationship with the pore size of the membrane (Mahendran et al 2004). In general, the molecular weight cut-off of the membrane is determined by identifying an inert solute of lowest molecular weight that has a solute rejection of 80-100 %
in steady state UF experiments (Mahendran et al 2004) Thus, the proteins of
different molecular weights such as, bovine serum albumin (69 kDa), egg
albumin (45 kDa), pepsin (35 kDa) and trypsin (20 kDa) were taken for
rejection studies of the CA membrane and CA/(PVA/gelatin) membranes. In
general, the molecular weight cut-off of the membrane is determined by
identifying an inert solute of different molecular weights that have a solute
rejection of 80-100% in steady state UF experiments. Linear polymers such as
PEG or poly (vinylpyrrolidone) or natural bio macromolecules such as bovine
serum albumin, trypsin, pepsin, etc or various molecular weight dextrans are
generally selected for the determination of MWCO of membranes. In this
study, proteins were selected since they are available in a wide molecular
weight range; On the other hand, proteins were readily available in a wide
molecular weight ranging from 19 to 150 kDa and inexpensive, which were
suitable in estimating the MWCO of different blend membranes of varying
porosity. The UF cell was filled with protein solution and pressurized at a
constant pressure of 345 kPa. The permeate from the cell was collected over
measured time intervals in graduated tubes and the tube contents were
analyzed to determine the protein concentration by spectrophotometry at
$\lambda_{\text{max}}$ of 280 nm using Hitachi U-2000 Spectrophotometer. From the feed and
permeate concentrations, the percentage rejection was calculated using the
equation (2.2).

$$\% SR = \left[1 - \left( \frac{C_p}{C_f} \right) \right] \times 100$$  \hspace{1cm} (2.2)

where $C_p$ and $C_f$ are the concentrations of the permeate and feed, respectively.
2.5.4.2 Pore statistics

The average pore radius \((R)\), surface porosity or porosity percentage \((\varepsilon)\), and number of pores \((n)\) of modified CA membranes were determined by using the proteins such as bovine serum albumin (69 kDa), trypsin (20 kDa), pepsin (35 kDa) and EA (45 kDa).

The average pore size, surface porosity and number of pores per unit membrane surface area were determined by the ultrafiltration of protein solutions of different molecular weights. The molecular weight of the solute that has a solute rejection (SR) above 80% was used to evaluate the average pore size, \(R\) of the membranes by using equation (2.3) the same study has been reported by Malaisamy et al (2002).

\[
R = 100 \left( \frac{\alpha}{\%SR} \right)
\]

(2.3)

where \(R\) is the average pore radius of the membrane (Å), and \(\alpha\) is the average solute radius (Å). The average solute radii also known as the Stoke radii was obtained from the plot of solute molecular weight versus solute radius in aqueous solution, which was developed by Sarbolouki (1982). The average solute radii also known as the Stoke radii was obtained from the plot of solute molecular weight versus solute radius in aqueous solution, which was developed by Sarbolouki. The mathematical correlation used to calculate the average solute radii of proteins was the product of 52.79 and \(M^{0.3915}\) divided by \(%R\). Where \(M\) is molecular weight cutoff, \(%R\) is percentage recovery of solute and the numerals are constants. The solute sizes of BSA, Trypsin, Pepsin and Egg albumin used for this study were 45.0, 21.5, 28.5 and 33.0 Å respectively.
The surface porosity $\varepsilon$, of the membrane was calculated by the orifice model given below assuming that only the skin layer of the membrane is effective in separation (Sarbolouki 1982; Velicangil 1980)

$$\varepsilon = \frac{3\pi \mu J}{\Delta P R}$$  \hspace{1cm} (2.4)

where, $\mu$ is the viscosity of the permeate water in (Pa.s); $J$ is the pure water flux of the membrane in (m$^3$/m$^2$.s); $R$ is the average pore radius in (m) and $\Delta P$ is the transmembrane pressure in (Pa).

From the values of $\varepsilon$ and $R$ the number of pores per unit area, $n$ can be calculated from the equation (2.5) Malaisamy et al (2002).

$$n = \frac{\varepsilon}{\pi R^2}$$  \hspace{1cm} (2.5)

### 2.5.5 Fouling studies

After 4h of ultrafiltration, the membranes were washed with deionized water for 20 min and the water flux of the cleaned membranes was measured ($J_{w2}$) at 414 kPa. In order to evaluate the fouling-resistant ability of the blend membranes, flux recovery ratio (FRR) was introduced by Wang et al (2006) and calculated using the following expression:

$$\% \text{FRR} = \frac{J_{w2}}{J_{w1}} \times 100$$  \hspace{1cm} (2.6)

To analyze the fouling process in details, we defined several ratios to describe the fouling-resistant ability of the blend membrane. The first ratio was $r_t$ as in equation
\[ r_t = 1 - \frac{J_p}{J_{W1}} \]  

(2.7)

Here, \( r_t \) was the degree of total flux loss caused by total fouling. \( r_r \) and \( r_{ir} \) were also defined to distinguish reversible fouling and irreversible fouling (Pradanos et al 1996). Reversible fouling ratio (\( r_r \)) describes the fouling caused by concentration polarization and irreversible fouling ratio (\( r_{ir} \)) describes the fouling caused by adsorption or deposition of protein molecules on the membrane surface (Elimelech et al 1997). They are defined by equations (Xinghua et al 2008).

\[ r_r = \frac{(J_{w2} - J_p)}{J_{W1}} \]  

(2.8)

\[ r_{ir} = \frac{(J_{w1} - J_{w2})}{J_{W1}} \]  

(2.9)

Obviously, \( r_t \) was the sum of \( r_r \) and \( r_{ir} \):

\[ r_t = r_r + r_{ir} \]  

(2.10)

In order to test the recycling potential of CA/(PVA/gelatin) membranes, three repetitive UF operations were carried out using BSA solution at 414 kPa. The BSA solutions of 0.1 wt. % were prepared by dissolving in (0.5 M, pH 7.2) phosphate buffer that were used as standard feed solutions. This recycling process includes four times run of pure water flux and three times run of BSA solution flux using dead end UF experiment cell.
The water cleaning processes were carried out after every time of BSA solution flux, and again the pure water flux of cleaned membranes was measured. The process was stopped with four runs, because the BSA molecules foul on the membrane surface and the flux remained constant. The schematic diagram of fouling mechanism is shown in Figure 2.3.

Figure 2.3  Schematic diagram of fouling mechanisms: (a) complete blocking (b) standard blocking; (c) intermediate blocking; (d) cake filtration
2.6 MATHEMATICAL MODELING OF ULTRA FILTRATION MEMBRANE

To study the ultrafiltration of a solution by using modified CA membrane with PVA/gelatin pair, however some other resistances add to membrane resistance causes flux decline. There are several models developed to predict the performance of ultra filtration, but most of them developed to predict the effect of concentration only. In the present investigation, for predicting membrane resistance, pore blocking and concentration polarization the following models has been used.

2.6.1 Kinetic model representing pore blocking

The deposition mechanism on the membrane surface and into its porous structure was analyzed in terms of various kinetic models, viz., cake filtration, standard blocking and complete pore-blocking models. It was seen that an initial intense flux decline due to external blockage followed by the formation of a cake. The kinetic model by Hermia et al is given by

\[
\frac{d^2I}{dV^2} = K \left( \frac{dt}{dV} \right)^\beta
\]

(2.11)

The \( \beta \) value represents the nature of fouling, theoretically defined values and type of fouling is given by blocking filtration laws as Table 2.3.
Table 2.3  Blocking filtration laws

<table>
<thead>
<tr>
<th>Blocking filtration law</th>
<th>$\beta$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cake filtration with compression</td>
<td>$&lt; 0$</td>
</tr>
<tr>
<td>Cake filtration</td>
<td>0</td>
</tr>
<tr>
<td>Intermediate blocking</td>
<td>1</td>
</tr>
<tr>
<td>Complete blocking</td>
<td>2</td>
</tr>
</tbody>
</table>

Equation (2.11) is integrated to give it in general form by

$$\frac{t}{V} = \left[K(1 - \beta)\right]^{\frac{1}{1-\beta}} \cdot (V)^{\frac{1}{1-\beta}}$$  \hspace{1cm} (2.12)

From the above equation $t/V$ vs $v$ gives the $\beta$ value which represents the nature of filtration.

2.6.2 Resistance in series model considering cake layer

This is a mathematical model based on resistance in series model considering membrane resistance and concentration polarization resistance acting in series to the filtrate. Mathematical model equation for permeate flux and membrane resistance is given by

$$J = \frac{\Delta P}{\mu \left( R_m + \frac{z}{p_m} \right)}$$  \hspace{1cm} (2.13)

$$R_m = \frac{\Delta P}{\mu J_v}$$  \hspace{1cm} (2.14)

In above equation $Z$ is the thickness of the solute ($m$) is given by Bhattacharjee et al (1996).
\[ Z = \frac{V(c_v - c_p)}{A(c_g - c_p)} - \frac{K_b c_g \, wt}{A(c_g - c_b)} \]  
(2.15)

\[ c_g \text{ gel concentration can be calculated from concentration polarization model given by} \]

\[ J = K \ln \left( \frac{c_g - c_p}{c_b - c_p} \right) \]  
(2.16)

Substituting \( Z \) in equation (2.11) gives

\[ \frac{1}{J} = \frac{\mu R_m}{\Delta P} + \frac{\mu t}{P_m \Delta P} \times \left[ \frac{V(c_b - c_p)}{A(c_g - c_b)} - \frac{K_b c_g \, wt}{A(c_g - c_b)} \right] \]  
(2.17)

Equation (2.13) can be written as

\[ \frac{1}{J} = a_1 V - a_2 t + a_3 \]  
(2.18)

The above equation can be solved by least square method to find the constants \( a_1, a_2, a_3 \). Solving non-linear equation (2.14) by least square method (Madsen 2004) the equations can be given by

\[ a_1 \Sigma V^2 - a_2 \Sigma V \, t + a_3 \Sigma V = \Sigma (V \cdot \frac{1}{J}) \]  
(2.19)

\[ a_1 \Sigma V \, t - a_2 \Sigma t^2 + a_3 \Sigma t = \Sigma \frac{1}{J} \cdot t \]  
(2.20)

\[ a_1 \Sigma V - a_2 \Sigma t + n a_3 = \frac{1}{J} \Sigma \frac{1}{J} \]  
(2.21)

From Equations (2.13) and (2.12) \( a_1, a_2, a_3 \) can be given by
\[ a_1 = \frac{\mu l (c_b - c_p)}{P_m \Delta PA (c_g - c_b)} \]  

(2.22)

\[ a_2 = \frac{\mu K_b c_g w}{P_m \Delta PA (c_g - c_b)} \]  

(2.23)

\[ a_3 = \frac{\mu l R_m}{\Delta P} \]  

(2.24)

From the above equations, \( P_m, K_b, R_m \) can be calculated. They are given by

\[ P_m = \frac{\mu l (c_b - c_p)}{a_1 \Delta PA (c_g - c_b)} \]  

(2.25)

\[ K_b = \frac{a_2 P_m \Delta PA (c_g - c_b)}{\mu c_g \omega} \]  

(2.26)

\[ R_m = \frac{a_3 \Delta P}{\mu l} \]  

(2.27)

where \( P_m \) is permeability coefficient, \( K_b \) is back transport coefficient.

From the above three parameters the gel polarized layer resistance is given by

\[ R_{pca} = \frac{V}{P_m A} \left( \frac{c_b - c_p}{c_g - c_b} \right) - \frac{K_b}{P_m A} \left( \frac{c_g}{c_g - c_b} \right) wt = \frac{\Delta P}{P_m} \]  

(2.28)

The permeate flux may be determined by

\[ J_{calc} = \frac{\Delta P}{\mu l (R_m + R_{pca})} \]  

(2.29)
The constant $a_1$, $a_2$ and $a_3$ were found by this method for each experiment under different operating conditions from which concentration polarized resistance can be calculated at different operating conditions.

### 2.6.3 Gel-Polarized model

This model applies to concentration polarization (Redkar et al 1996) of non-interacting particles in cross-flow filtration system.

\[ J = k \ln \frac{C_g - C_p}{C_b - C_p} \]  
(2.30)

$C_g$ depends on the size, shape, chemical structure and degree of salvation of the solution and the $C_g$ is given by

\[ C_g = C_p + (C_b - C_p)e^{\frac{J}{K}} \]  
(2.31)

The mass transfer coefficient appearing in the previous equation can be computed from the well-known empirical correlation applicable for stirred cell given by

\[ K = \phi \left( \frac{D}{r} \right) \left( \frac{v}{D} \right)^{0.33} \left( \frac{wv^2}{v} \right)^{0.8} \]  
(2.32)

$\phi$ is a module geometry dependent constant and can be experimentally determined for a given stirred cell unit as described by Opong and Zyndey and the $\phi$ value was determined to be 0.343.
The diffusivity was calculated using the following expression:

\[
D = 8.34 \times 10^{-8} \left( \frac{T}{\mu W^{\frac{1}{3}}} \right)
\]  

(2.33)

Here \( D \) is in cm\(^2\) s\(^{-1}\) and \( \mu \) is in C\(_p\) based on a molecular weight of and ambient operating conditions using dilute aqueous solution.

From the above models Resistance in series model considering cake layer was predicted by bhattacharjee, and used for the calculation of polarized layer resistance and gel polarized model used for finding the gel concentration. The kinetic model representing pore blocking was used to find the pore blocking mechanism in the ultrafiltration membrane.