

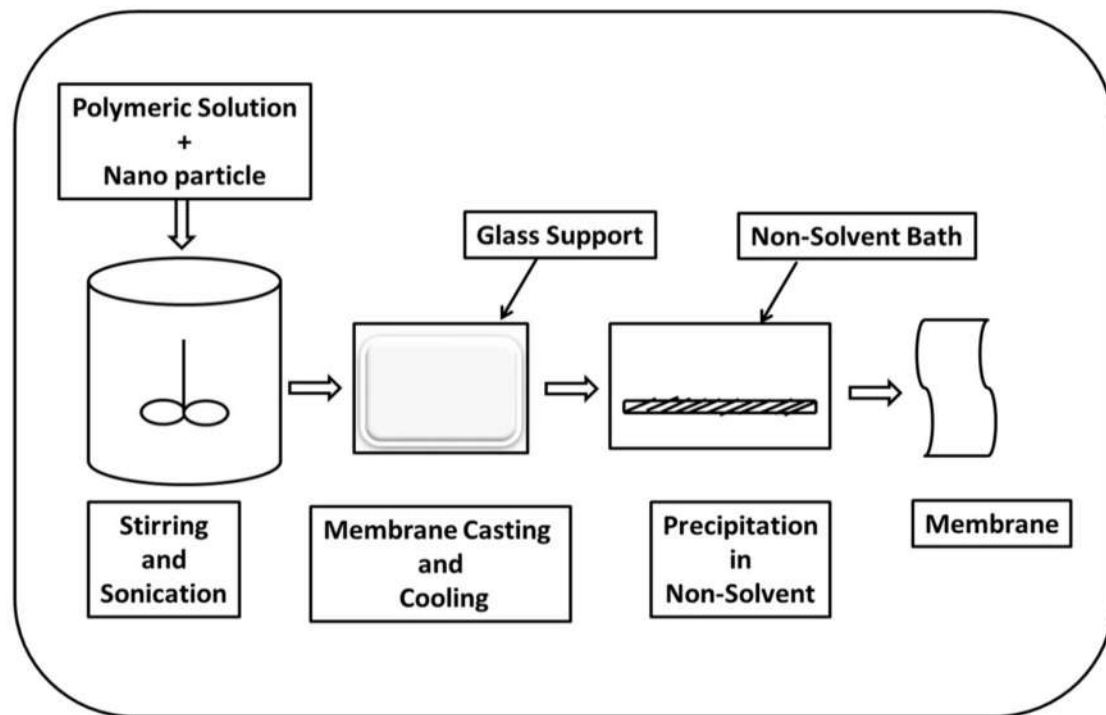
## **Chapter 3**

### **Materials and methods**

This chapter involves a brief description of the methodologies used for the synthesis, characterization and application of polyvinyl chloride based membranes in the present work. Polyvinyl chloride based composite membranes were prepared by non-solvent induced phase separation method and changes in physicochemical properties of membrane were observed by instrumental techniques. Membranes were further used for separation of humic acid solution. The techniques used to observe membrane performance and antifouling nature have also been discussed briefly in following sections.

#### **3.1 Membrane preparation**

In this study, non-solvent induced phase separation process was used for the fabrication of membranes. The major three constituents of this method are polymer, solvent and non-solvent. In our research work, polyvinyl chloride was used as base polymer, N, N-Dimethylacetamide (DMAc) as solvent, and deionized water was used as non-solvent for the preparation of polymeric membrane. A homogeneous polymer solution was prepared by dissolving known amount of PVC in the DMAc and a non-woven support was used for casting prepared solution on it. Then support was immersed in a non-solvent coagulation bath, which was deionized water. This resulted in penetration of solvent into non-solvent and penetration of non-solvent into the solution and this process continued until the equilibrium. Finally, two phases evolved, one polymer-rich phase and the other a liquid-rich phase. Polymer rich phase was PVC membranes that possess asymmetric structure. Membrane was then dried and stored for further



**Figure 3.1:** Schematic diagram of the membrane preparation process.

application. Composite membranes were prepared by same process and dispersing inorganic nanomaterials (alumina and bentonite) to polymeric dope solution before membrane casting. A simple representation of immersion precipitation method is briefly shown in figure 3.1.

### 3.2 Membrane characterization techniques

With the advancement of technology in recent decades, various material characterization technologies have been developed. Researchers are using automated instrumental techniques to characterize nanocomposite material. These analytical techniques provide specific information about the nature and structure of the materials. According to the type of the material, particular instruments are used to extract information about the material. In this research, Scanning Electron Microscope (SEM), Energy-dispersive X-ray spectroscopy (EDS), X-Ray Diffraction (XRD), Thermo

gravimetric analysis (TGA) and Universal Testing Machine were used to characterize membranes.

### **3.2.1 Scanning electron microscope**

Scanning electron microscopy is used to study the surface morphology of the prepared membranes and compare the morphology of different membranes. This comparison is done between pure polymer membrane and composite membranes of varying composition of modifiers and the effect of membrane modification on membrane morphology is investigated by this technique. Sometimes it can be used for comparing neat and fouled membranes. Surface morphology provides information regarding the structure, size, and distribution of pores.

### **3.2.2 Energy-dispersive x-ray spectroscopy**

Energy-dispersive X-ray spectroscopy is an elemental analysis instrument, which is equipped with SEM and provides information regarding the elemental composition at any particular position on the membrane surface.

### **3.2.3 X-Ray diffraction**

XRD is a very important characterization tool, used to check the crystallinity of nanocomposites. The structure of polymeric membranes is semi-crystalline; therefore, XRD analysis of membranes sample is mostly done to compare the effect of modifiers on the crystallinity of membrane material. It is also used to verify presence of inorganic nanoparticle within the bulk structure of polymeric membranes.

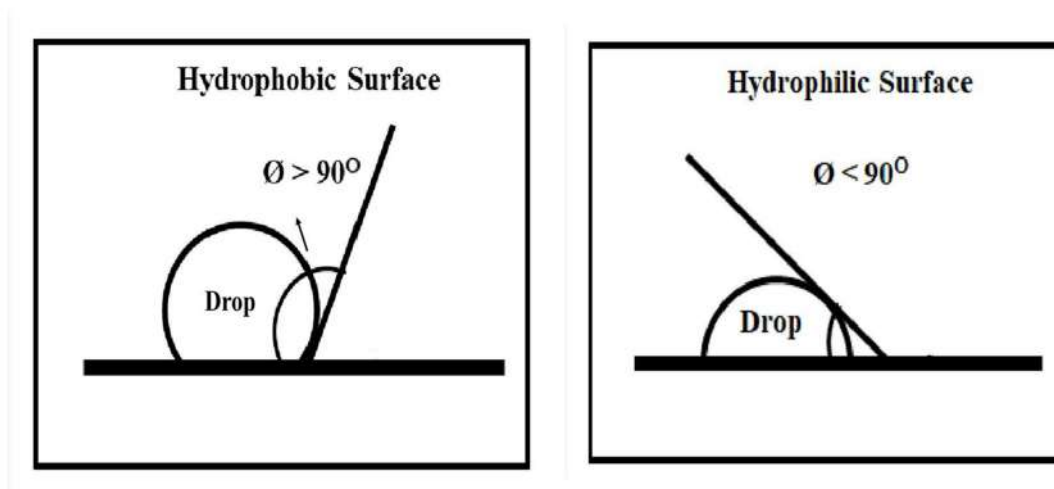
### **3.2.4 Thermo gravimetric analysis**

Thermo gravimetric analysis is done to investigate the thermal stability of the membrane for high-temperature applications. A membrane need to be highly thermal

stable so that it should not deteriorate at elevated temperatures. TGA analysis is also utilized to understand the change in thermal stability of polymeric composite membranes due to additives. In this research, membrane samples of different compositions were analyzed by TGA and were compared to observe changes due to membrane modification.

### 3.2.5 Contact angle analysis

Contact angle analysis is done to measure the wettability of the membrane surface. A water droplet spreads on the membrane surface due to surface tension between the water droplet and the membrane surface. If the contact angle between the surface and water drop is above  $90^{\circ}$  i.e. water droplets do not spread on the surface of membrane then the membrane is said to be hydrophobic. Lower contact angle below  $90^{\circ}$  represents the hydrophilic nature of surface. A simple illustration of hydrophobic and hydrophilic surfaces is illustrated in figure 3.2. The highly preferred property of membrane, required for separation process of aqueous solutions is hydrophilicity. If the membrane surface is highly hydrophilic then during the filtration process, water hydration layer forms on the surface and keeps the foulant away, thereby imparting the anti-fouling effect.



**Figure 3.2:** Concept of contact angle measurement of hydrophobic surface and hydrophilic surface.

### 3.2.6 Porosity

The porosity of membranes was measured by a 24-hour water retention test. Membrane samples of known measurements were soaked in distilled water for one day and after that sample was taken out and gently wiped on both surfaces by tissue paper and weighed.

After that, samples were kept at 50° C in the oven to evaporate the moisture content and again weighed after drying.

Porosity is calculated as (Saini et al., 2019)

$$\phi (\%) = \frac{W_w - W_D}{\rho_w * V} * 100\% \quad (3.1)$$

where  $W_w$  and  $W_D$ : the weight of the sample in the wet and dry state,  $V$ : volume of membrane and  $\rho_w$ : density of water.

### 3.2.7 Mean pore radius

To calculate the mean pore radius of membranes, Guerout–Elford–Ferry (GEF) equation (Behboudi et al., 2016; Hamid et al., 2011; Li et al., 2009; Vatanpour et al., 2012) was used. GEF equation is stated as follows

$$r_m = \sqrt{\frac{8\eta l Q (2.9 - 1.75\epsilon)}{\epsilon A \Delta P}} \quad (3.2)$$

Where

$\eta$ : Viscosity of water;  $l$ : Thickness of membrane;  $Q$ : Volume of permeate;  $\epsilon$ : Porosity of membrane;  $\Delta P$ : Trans membrane pressure;  $A$ : membrane area.

## 3.3 Performance study and antifouling analysis

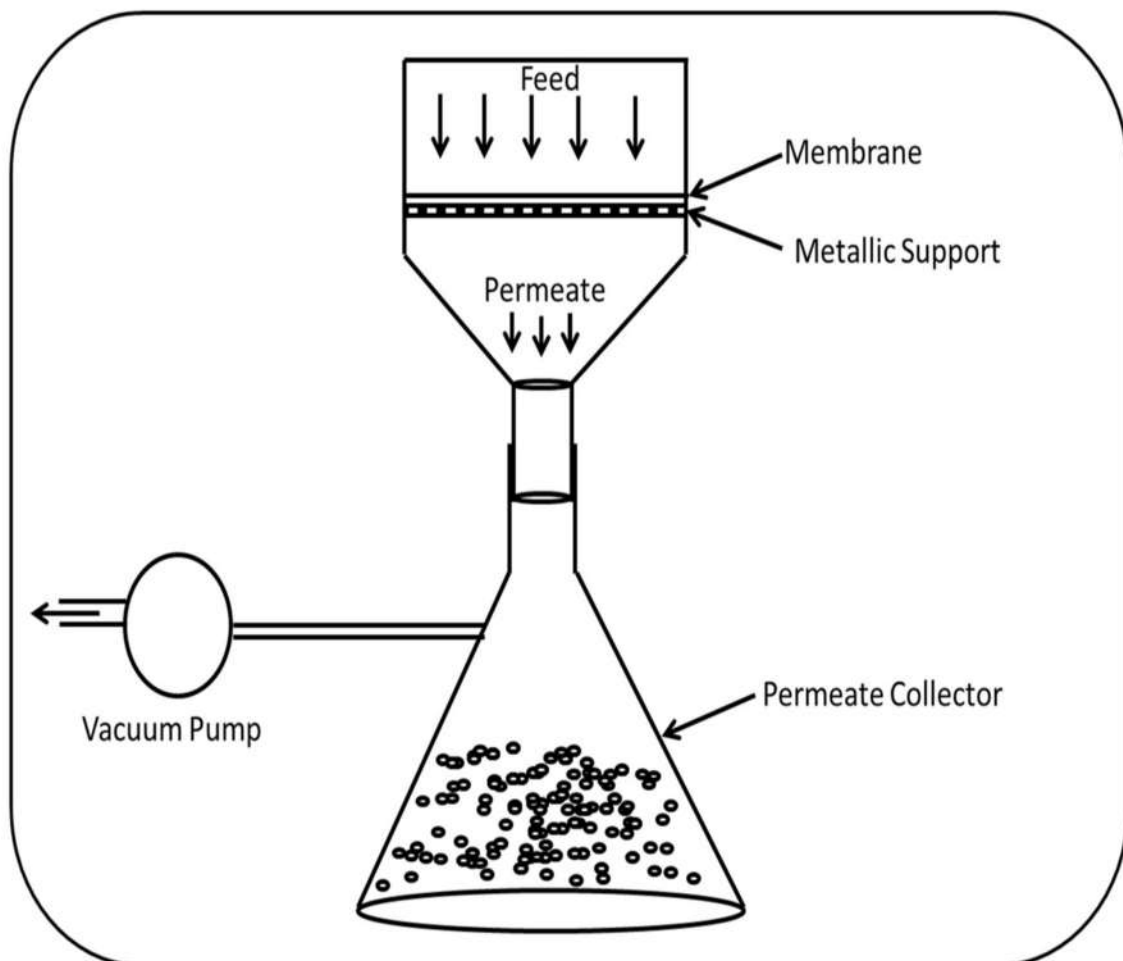
Performance of membranes was studied on a self-made dead end lab scale filtration setup as shown in figure 3.3. Membranes of different composition were prepared in the

lab, and then fabricated in circular shape with the effective diameter of 5 cm and fitted to the membrane cell. An aqueous solution of humic acid was fed from the feed side and water permeated from the permeate side.

Three different feeds of wastewater containing humic acid in concentration 10, 20 and 40 ppm were prepared and filtered through the membranes. The time taken for permeation was noted, and flux was calculated using the following equation (3.3)

$$J = \frac{V}{A * t} \quad (3.3)$$

Where J: Flux, V: volume of permeated water, A: membrane area, and t: time.



**Figure 3.3** Schematic diagram of the filtration experiment.

Fluxes obtained for distilled water and HA solution was denoted as  $J_0$  and  $J_p$ . After completion of the experiment, membrane was again subjected to distilled water to check the change in the performance of the membrane after fouling, and distilled water flux was measured. After this foulant layer that was deposited at membrane surface was scrapped and membrane was back washed. Later distilled water was again run on membrane system, and the flux was measured. Fluxes, calculated in those situations were denoted as  $J_1$  and  $J_2$ , respectively.

With the help of these three flux information, fouling parameters of the membrane such as total fouling ratio (TFR), reversible fouling ratio (RFR), irreversible fouling ratio (IFR) and flux recovery (FR) were calculated.

Following equations (3.4-3.7) were used to estimate the fouling parameters (Behboudi et al., 2016; Jafarzadeh et al., 2015):

$$\mathbf{TFR} = \frac{J_0 - J_1}{J_0} \quad (3.4)$$

$$\mathbf{RFR} = \frac{J_2 - J_1}{J_0} \quad (3.5)$$

$$\mathbf{IFR} = \frac{J_0 - J_2}{J_0} \quad (3.6)$$

$$\mathbf{FR} = \frac{J_2}{J_0} * 100\% \quad (3.7)$$

The total resistance of the membrane during filtration depends on three factors viz. intrinsic membrane resistance ( $R_m$ ), irreversible fouling resistance ( $R_{if}$ ), and resistance due to concentration polarization ( $R_{cp}$ ).

These resistances are calculated by following equations (3.8-3.11) (Younas et al., 2016):

$$\mathbf{R_{Total} = R_m + R_{if} + R_{cp} = \frac{\Delta P}{\mu J_P}} \quad (3.8)$$

$$\mathbf{R_m = \frac{\Delta P}{\mu J_0}} \quad (3.9)$$

$$\mathbf{R_{if} = \frac{\Delta P}{\mu J_2} - R_m} \quad (3.10)$$

$$\mathbf{R_{cp} = \frac{\Delta P}{\mu J_P} - R_m - R_{if}} \quad (3.11)$$

The concentration of humic acid in feed and permeate was calculated using spectrophotometric analysis and noted as  $C_F$  and  $C_P$ . These concentration values were used to measure percentage rejection through the membrane according to the equation 3.12 (Fan et al., 2014; Rana et al., 2010; Zhang et al., 2016).

$$\mathbf{Rejection = \left[ 1 - \frac{C_P}{C_F} \right] * 100\%} \quad (3.12)$$