Preparation and Characterization of Modified Poly Vinyl Chloride for Water Treatment Applications

A THESIS

Submitted

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BY

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Introduction

1.1.Historical Introduction

Membranes are an intimate part of being alive. Several examples are simple to cite:
- The skin in all mammals is a very efficient and highly selective type of membrane controlling release of sweat to cool off the bodies through evaporation of tinny water droplets during hot weather. Skin selectivity as apparent, when it's cut the fine blood cells and vessels that run under neath the skin are broken and releases its blood content. A healthy and intact skin does not release blood. The lungs are also a good example of effective membranes, where fine cells within the lungs allow passage of oxygen from the inhaled air and release carbon dioxide into the same stream. The lungs as a membrane prevent permeation of the nitrogen in the inhaled air, irrespective of its high content. The kidney membranes regulate the water, salt ions, proteins, and other nutrient within the body. The kidneys are extremely efficient that a healthy body can survive with a quarter of both kidneys **(Hisham T. El-Dessouky 2002)**. On a much smaller scale, membrane walls in single cells within mammals, bacteria, and other microorganisms maintains the cell contents intact and regulate the input/ output rates of nutrients or products. Since the early days of civilization mankind have adopted simple forms of membranes. In early agriculture communities, household sieves were invented and developed to separate fin grain ground from coarse grain particles and shells. Similarly, cheesecloth was made from cotton fibers and used to manufacture cheese. Both forms of separation are based on differences in particle size. However, developments in membrane technology have focused on adoption of other separation mechanisms, such differences in solution and diffusion rates of various species across the membrane material. Other than the sieve type membrane use of artificial membranes is rather new **(Hisham T. El-Dessouky 2002)**.Major land marks in use of artificial membranes are summarized in the following points:

In 1823, Dutrochet gave correct explanation of osmosis (passage of solvent across a membrane from low to high concentration) and dialysis (passage of solute across a membrane from high to low concentration) **(Hisham T. El-Dessouky 2002)**.In 1867, Traube and Pfeffer performed one of the first quantitative studies on performance of artificial membranes **(Hisham T. El-Dessouky 2002)**.

- Moritz Taube, 1867, prepared the first synthetic membrane **(Hisham T. El-Dessouky 2002)**.In the late 1800's Graham discovered that arranging a membrane between a reservoir of pressurized air and another reservoir of unpressurized air could produce oxygen-enriched air **(Hisham T. El-Dessouky 2002)**.Early use of membranes was applied to recovery of NaOH by dialysis from wastewater containing hemicellulose from the viscose-rayon industry **(Hisham T. El-Dessouky 2002)**.Also, uranium isotopes (235 and 238) are separated in the vapor phase through porous membranes **(Hisham T. El-Dessouky 2002)**.As for the RO membranes, their history started with the following two studies .Reid and Breton, 1959, at the University of Florida developed cellulose acetate RO membranes **(Hisham T. El-Dessouky 2002)**.
- Loeb and Sourirajan, 1963, from the University of California, Los Angeles developed the first asymmetric cellulose acetate membrane, with higher salt rejection and water flux. Subsequently, a huge amount of research studies were conducted with focus on development of new membrane materials and performance evaluation of these membranes **(Hisham T. El-Dessouky 2002)**.As for commercialization of the RO membranes it is summarized in the following points:
- In the late 1960s, the Gulf General Atomics and Aerojet General used Loeb-Sourirajan cellulose acetate membranes for constructing spiral wound modules.
- In 1971, Dupont introduced the Permasep B-9 permeator for brackish water desalination. The permeator contains millions of asymmetric aromatic poly amide (aramid) hollow fine fibers **(Hisham T. El-Dessouky 2002)**. In late 1973, DuPont introduced the Permasep B-10 permeator, also using asymmetric aramid fibers, capable of producing potable water from sea water in a single pass. In the mid-1970s, cellulose triacetate hollow fiber permeators were introduced by Dow Chemical Company, followed by Toyobo of Japan **(Hisham T. El-Dessouky 2002)**.During the same period. Fluid Systems and Film Tec introduced the spiral wound polyamide thin film composite membranes **(Hisham T. El-Dessouky 2002)**.Throughout the 1980s, improvements were made to these membranes to increase water flux and salt rejection with both brackish water and sea water **(Hisham T. El-Dessouky 2002)**.Today the predominate membrane materials are still aramids, polyamides, and cellulose acetate and triacetate in spiral wound and hollow fiber configurations.

Applications of the RO membranes include potable water production, waste recovery, food applications, kidney dialysis, high-purity water for boiler feed, and ultrapure water electronics applications **(Hisham T. El-Dessouky 2002)**.

- In 2000, the RO technology was used to treat more than two billion gallons of water per day, and this market is expected to continue growing during the first half of the 21ST century **(Hisham T. El-Dessouky 2002)**.

1.2. Elements of Membrane Separation

A number of membrane-based desalination processes are used on industrial scale. As is shown in Fig.1.1, the membrane-based processes include reverse osmosis, nano-filtration, ultrafiltration, and microfiltration. Differences among these processes is shown in Fig.1.1 where,

- Microfiltration operates on a particle size range of 15 µm to 0.15 µm.
- Ultrafiltration operates on a particle size range of 0.15 µm to $5xl0^{-2}$ µm
- Nanofiltration operates on a particle size range of $5xl0^{-2}$ µm to $5x10^{-3}$ µm
- Reverse osmosis operates on a particle size range of $5x10^{-3}$ µm to 10^{-4} µm

There is an inherent difference in the separation mechanism in all filtration processes and the reverse osmosis process. In filtration, separation is made by a sieving mechanism, where the membrane passes smaller particles and retains larger ones.

In osmosis or reverse osmosis processes the membrane permeates only the solvent and retains the solute. Further distinction of the four membrane processes is shown in Fig. 1.1. The microfiltration, ultrafiltration, and nanofiltration processes are used to separate the suspended material.

On the other hand, the reverse osmosis process is used to separate dissolved solids. Nano-filtration is used for partial softening of brackish water **(Hisham T. El-Dessouky 2002)**.

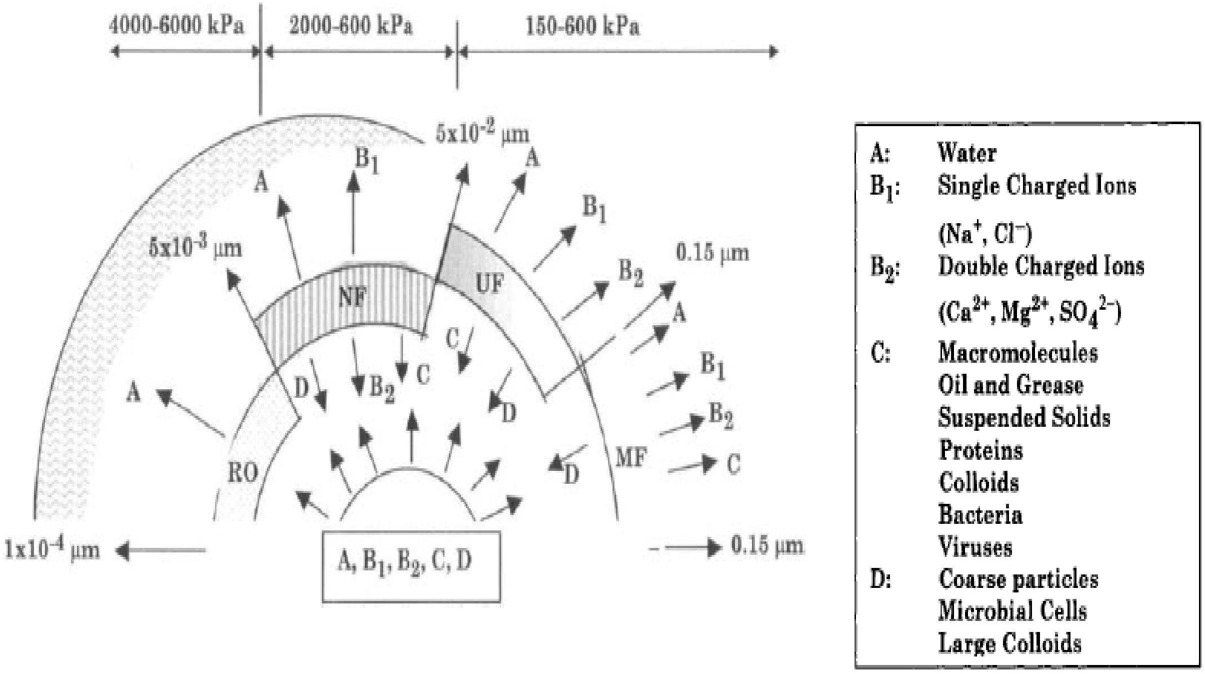

Fig. 1.1 Membrane separation processes and corresponding particle sizes **(Hisham T. El-Dessouky 2002)**.

A schematic for the osmosis and reverse osmosis phenomenon are shown in Fig. 1.2. In this configuration, the direction of solvent flow is determined by its chemical potential, which is a function of pressure, temperature, and concentration of dissolved solids. Pure water in contact with both sides of an ideal semi-permeable membrane at equal pressure and temperature has no net flow across the membrane because the chemical potential is equal on both sides. If a soluble salt is added on one side, the chemical potential of this salt solution is reduced. Osmotic flow from the pure water side across the membrane to the salt solution side will occur until the equilibrium of chemical potential is restored. Equilibrium occurs when the hydrostatic pressure differential resulting from the volume changes on both sides is equal to the osmotic pressure **(Hisham T. El-Dessouky 2002)**.

This is a solution property independent of the membrane. Application of an external pressure to the salt solution side equal to the osmotic pressure will also cause equilibrium. Additional pressure will raise the chemical potential of the water in the salt solution and cause a solvent flow to the pure water side, because it now has a lower chemical potential **(Hisham T. El-Dessouky 2002)**.

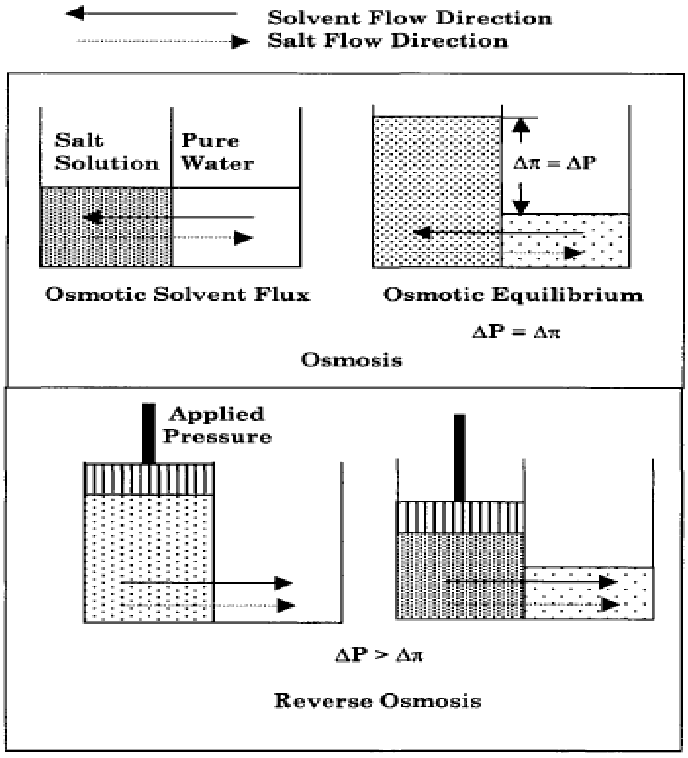

Fig.1.2. Osmosis and reverse osmosis processes **(Hisham T. El-Dessouky 2002)**.

1.3 Performance Parameters

The RO process is defined in terms of a number of variables, which Includes Osmotic and operating pressure, Salt rejection, and Permeate recovery.

Membrane manufacturing companies define system specifications in terms of the feed quality, which includes salinity and temperature.

1.3.1 Osmotic and Operating Pressure

The osmotic pressure, π, of a solution can be determined experimentally by measuring the concentration of dissolved salts in the solution. The osmotic pressure is obtained from the following equation

$$\pi = R\ T \sum X\ i \qquad (1)$$

where

π is the osmotic pressure (kPa).

T is the temperature (K).

R is the universal gas constant, 8.314 kPa m^3/kgmol K

$\sum Xi$ is the concentration of all constituents in a solution (kg mol/m^3).

An approximation for π may be made by assuming that 1000 ppm of Total Dissolved Solids (TDS) equals to 75.84 kPa of osmotic pressure.

Operating pressure is adjusted to overcome the adverse effects of the Following: Osmotic pressure, Friction losses, Membrane resistance, and Permeate pressure.

If the operating pressure is set equal to the sum of the above resistances the net permeate flow rate across the membrane would be minimal or equal to zero; therefore, the operating pressure is set at higher value in order to maintain economical permeate flow rate.

1.3.2 Salt Rejection

Salt rejection is defined by

$$SR = 100\% \, (1 - (Xp/Xf)) \qquad (2)$$

Where SR is the salt rejection, Xp and Xf are salts concentrations of the product and feed.

1.3.3 Permeate Recovery

Permeate recovery is another important parameter in the design and operation of RO systems. Recovery or conversion rate of feed water to product (permeate) is defined by

$$R = 100\% \, (Mp/Mf) \qquad (3)$$

Where R is recovery rate (in %), Mp is the permeate water flow rate, and M_f is the feed water flow rate. The recovery rate affects salt passage and product flow. As the recovery rate increases, the salt concentration on the feed-brine side of the membrane increases, which causes an increase in salt flow rate across the membrane. Also, a higher salt concentration in the feed-brine solution increases the osmotic pressure, reducing the (ΔP-$\Delta\pi$) and consequently reducing the product water flow rate. Membrane recovery for RO systems have increased over the years from lower values of 10-20% to current higher values up to 50%. This is achieved in part by proper system design and use of multiple modules of spiral wound membranes within the same pressure vessel. As for the hollow fiber membranes it common to use a single module within the same pressure vessel **(Hisham T. El-Dessouky 2002)**.

1.4.Membranes, Membrane Classifications and Membrane Configurations

For a better understanding of the development of membrane technology, the fundamentals of membranes and membrane processes will be briefly reviewed. The word “membrane” is derived from the Latin word “membrana” and was first used in popular English media sometime before 1321 (Webster’s Online Dictionary, “Membrane” has different meanings in different domains. In association with separation, concentration or purification processes, a membrane can be essentially defined as a barrier to separate two phases and be able to restrict the transport of various components in a selective manner, as shown schematically in Fig.1.3.

A conventional filter also meets the definition of a membrane; however, the term “filter” is usually limited to structures that separate particulate suspensions larger than 1–10 µm. There are many ways to classify synthetic membranes.

They can be classified by the nature of the membrane material, the membrane morphology, geometry, preparation methods, separation regime and processes, etc.

For instance, synthetic membranes can be organic (polymeric) or inorganic (ceramic/metal), solid or liquid, electrically charged or neutral in nature; they can be homogeneous or heterogeneous, symmetric or asymmetric in structure. Grouped by membrane geometric shapes, synthetic membranes can be flat, tubular or hollow fiber membranes. There are separation membranes to change the composition of mixtures, packaging membranes to prevent permeation, ion-exchange and biofunctional membranes to physically/chemically modify the permeating components, proton conducting membranes to conduct electric current or non-selective membranes to control the permeation rate **(Mulder M.,1996)** .

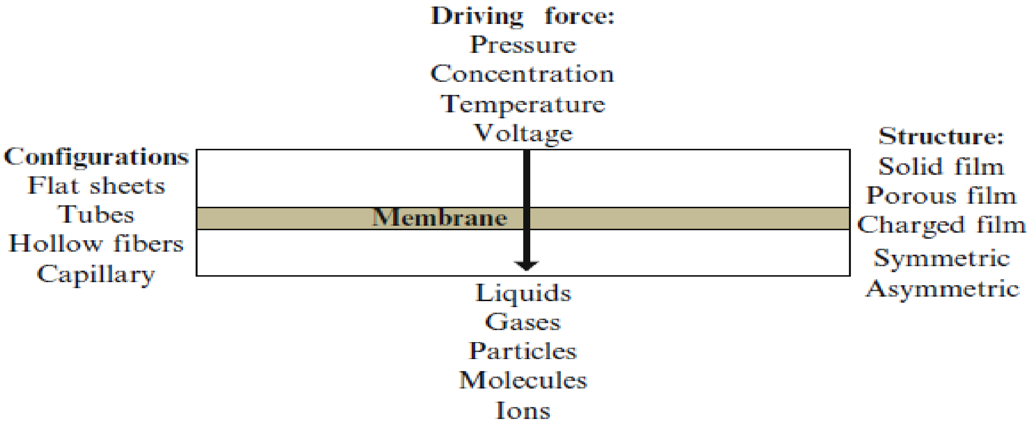

Fig.1.3. Fundamentals of membrane and membrane processes **(Mulder M., 1996)** .

1.5. **Membrane Processes, Operation Modes and Membrane Fouling**

Membrane-based processes enjoy numerous industrial applications as they potentially offer the advantages of highly selective separation, continuous, automatic and economical operation at ambient temperature, and simple integration into existing production processes, as well as appreciable energy savings **(Mulder M., 1996, Ferry JD., 1936)**.

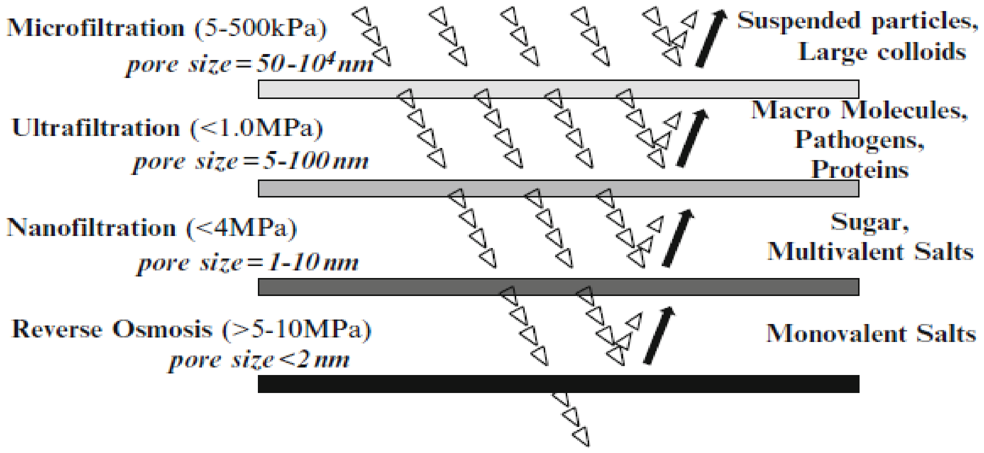

Fig.1.4. Pressure-driven membranes for water and wastewater treatments **(Ferry JD, 1936)**

According to the driving force applied, the membrane processes can be classified as:

●Pressure-driven processes, such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), or gas separation (GS); or partial-pressure-driven processes, such as pervaporation (PV).

●Concentration-gradient-driven processes, such as dialysis.

●Temperature-driven processes, such as membrane distillation (MD).

●Electrical-potential-driven processes, such as elctrodialysis (ED).

Figure 1.4 shows the ranges of applications, pore sizes and working pressures for the pressure driven membrane processes for water and wastewater treatments. There are other processes or hybrid processes such as membrane contactors, membrane reactors and membrane bioreactors (MBRs), in which the function of the membrane is integrated with conventional processes to provide highly efficient performance. Different membrane processes can also be combined together to overcome the limitations of individual systems, and to maximize the productivity of the target separation processes. Membrane filtration can be operated basically in two modes: dead-end and cross flow (Fig.1.5). In dead-end mode, the entire feed flow transports towards the membrane perpendicularly so that the retained particles and other components accumulate and deposit on the membrane surface. In a cross-flow operation, the feed stream moves parallel to the membrane surface and only a portion of the feed stream passes through the membranes under the driving pressure. Moving the feed flow tangentially to the membrane surface can result in much higher permeation fluxes as the stream continuously removes retained material.