

CHAPTER II

LITERATURE SURVEY

2.1 Ultrafiltration

Filtration is defined as the separation of two or more components from a fluid stream. It usually refers to the separation of solid, particles from liquid or gaseous streams. Membrane filtrations are extended applications including the separation of dissolved solutes in liquid streams and the separation of gas mixtures. The membrane act as a selective barrier. It should allow passage of components and retain other components of a mixture (Cheryan, 1986).

Ultrafiltration (UF) is the pressure-driven membrane separation process to selectively separate water and microsolute from macromolecules and colloids (Baker, 2000). UF covers particles or molecules that range from molecular weight about 1,000 to 1,000,000 Daltons (10 to 200 Å in size) and retains only macromolecules or particles larger than about 10 to 200 Å. It deals with the separation of quite large molecule, such as natural polymers like proteins, starch and gums, and colloidal compounds such as clays, pigments, latex particles, etc. (Cheryan, 1986). The first commercial industrial ultrafiltration module used was to recover electrocoat paint from automobile paint shop rinse water in 1969 (Baker, 2000 and Nunes and Peinemann, 2001). Shortly afterwards, UF systems were used in the food industry for protein separation from cheese whey and for apple juice clarification. The separation of oil emulsions from wastewaters has become an important application especially in the chemical and refining industries (Baker, 2000). The useful ranges of common membranes separation processes are compared in Table 2.1.

A further advantage of ultrafiltration compared to conventional dewatering process is the absence of a change in phase or state of the solvent during the dewatering process. Ultrafiltration appears to be lower in energy consumption up to the feed concentration limits. It can be operated at ambient temperature. The fact is that no complicated heat transfer or heat-generating equipment is needed (Cheryan, 1986).

Table 2.1 Characteristics of common membrane separation processes (Cheryan, 1986)

Process	Driving force	Permeate	Retentate	Operating Pressure (kPa)	Fluxes (L/m ² x h)
Osmosis	Chemical potential	Water	Solutes	-	-
Dialysis	Concentration difference	Water + Small molecule	Large molecules	-	-
Ultrafiltration	Pressure	Water + Small molecule	Large molecules	100-500	10-200
Reverse osmosis	Pressure	Water	Solutes	700-20,000	1-20
Electrodialysis	E.M.F	Water + Ionic solutes	Nonionic solute	-	-
Microfiltration	Pressure	Water + Dissolved organic	Large suspended particles	-	-

However, there are some limitations to UF processes. The concentrated macromolecules which are retained cause low mass transfer rates and high viscosity that makes pumping of the retentate difficult. Other problems were the fouling of membranes, poor cleanability of some early modules and restricted operating conditions (Cheryan, 1986).

2.2 Polyelectrolytes

Polyelectrolyte (PEL) is polymer consisting of a macroion which is a macromolecule composing covalently bound anionic or cationic groups, and low molecular weight counterions for electroneutrality. Examples of anionic and cationic polyelectrolyte are presented in Figure 2.1 (Dautzenberg *et al.*, 1994).

Both sodium polystyrene sulfonate and poly(diallyldimethyl ammonium chloride) are dissociated into macroion and counterion in an aqueous solution in the total pH range between 0 and 14. Although polymers like poly(acrylic acid) or poly(ethylene imine) form a macroion-counterion system only in a limited pH range, they are usually classified as polyelectrolytes.

In principle, any macromolecular chemical structure can be changed into a polyelectrolyte structure by covalently attaching a number of ionic groups to the polymer backbone, arriving with linear or branched macromolecules soluble in an aqueous medium of appropriate pH after introducing a sufficient number of ionic groups (Dautzenberg *et al.*, 1994).

A vast number of polyelectrolyte classes are known today; a selection is listed in Table 2.2 demonstrating the variability of the polyelectrolyte chemical structure, resulting from the tremendous number of polymer backbone structures. Today's commercial polyelectrolytes are generally obtained by a polymerization, polycondensation, or polyaddition process, but numerous important polyelectrolytes also originate from nature, such as gelatin, as a representative of the widespread class of proteins or pectins belonging to the group of anionic polysaccharides (Dautzenberg *et al.*, 1994).

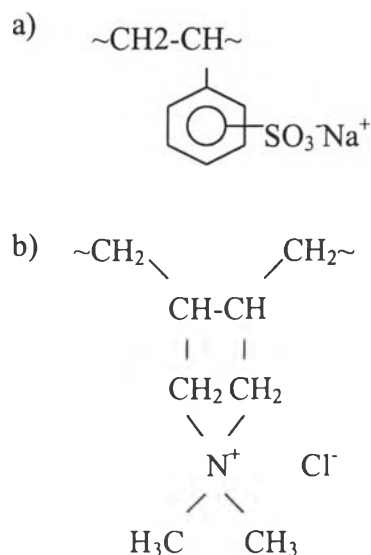


Figure 2.1 Chemical structure of (a) sodium polystyrene sulfonate and (b) poly (diallyldimethylammonium chloride) (Dautzenberg *et al.*, 1994).

In contrast to the wide variability of the polymer backbone structure, the number of different chemical structures of anionic or cationic sites responsible for the special behavior of polyelectrolytes in solution is rather small (Table 2.3).

Moreover, the nature of the low molecular weight counterions has a strong influence on the properties of the whole system in solution, especially on solubility and structure formation. For example, the chloride of the poly(diallyldimethyl ammonium) polycation is easily soluble in water, but the iodide is quite insoluble (Dautzenberg *et al.*, 1994).

Generally, low molecular weight substances can be bound to macromolecules by intermolecular forces which are mainly ionic or complex bond or the combination of ionic and complex bond. An ion exchange is a common technique related to the ionic interactions such as the removal of arsenate anions by using soluble polycation polymer. Whereas, complex bonding is significantly more selective than ionic interaction, the formation of complexes with water-soluble polymers takes place in the same manner as in the case of chelating resins containing amino and imino groups forming stable chelates with copper, nickel, and other transition metal ions (Geckeler *et al.*, 1996). The separation methods should have

high selectivity owing to the use of selective binding of target ions (Juang and Chen, 1996).

Table 2.2 Selected Classes of Polyelectrolytes (Dautzenberg *et al.*, 1994)

Anionic and cationic polysaccharides of polysaccharidic derivatives

Nucleic acids

Gelatin

Lignosulfonic acids

Polyacrylic and polymethacrylic acid and its copolymers

Maleic acid anhydride copolymers

Polystyrene sulfonic acid

Polyethylene imine

Polyamines and polyamidamines

Ionenes

Poly(diallyldimethylammonium chloride)

Homo- and copolymers of cationic acrylic acid esters

Table 2.3 Structures of ionic sites of polyelectrolytes (Dautzenberg *et al.*, 1994)

-COO ⁻	-NH ₃ ⁺
-CSS ⁻	=NH ₂ ⁺
-OSO ₃ ⁻	≡NH ⁺
-SO ₃ ⁻	-NR ₃ ⁺
-OPO ₃ ²⁻	

2.3 Gel Polarization

When a solute is rejected at an ultrafiltration membrane, the solute concentration becomes higher in a region of the retentate solution near the membrane surface than in the bulk solution. This phenomena is called “concentration polarization”. The development of concentration polarization in the retentate solution decreases the flux passed through the membrane due to the increase in resistance to

flow caused by the higher viscous solution formed near the membrane surface or the gel layer. Concentration polarization can be described by the gel polarization theory, which assumes the solute concentration at or near the membrane surface is C_g , and the flux(J_w) varies with the bulk concentration of solute (C_b) as follows:

$$J_w = K_T \ln (C_g/C_b) \quad (2.1)$$

Where K_T is mass transfer coefficient for back diffusion from the membrane surface. This expresses that the bulk concentration is equal to the gel concentration (C_g) when the corresponding flux is zero.

2.4 Chromium

Chromium is heavy metal toxic in the Cr(VI) form contained in some wastes from pigment production, steel production and finishing, and electroplating. Chromium metal is used to produce alloys, especially stainless steel, and as a decorative, corrosion-resistant plating on other metal (Manahan, 1990 and Sittig, 1973).

Chromium, transition metal, exists in the oxidation states from +2 through +6. The +3 and +6 oxidation numbers are predominant. Chromium(III) sulfate is used for some leather tanning processes. Chromium(VI) or hexavalent chromium, often called chromate, exists in acidic aqueous solution as dichromate, $Cr_2O_7^{2-}$, and in more basic solutions as chromate ion, CrO_4^{2-} . Chromium(VI) is used in plating baths and in some cooling tower systems for its corrosion resistance (Manahan, 1990).

Chromium(VI) can cause health effects such as lung cancer, skin ulcers, and lung irritation when it exceeds the environmental exposure limit (Sax, 1979).

Heavy metals such as lead, copper, mercury, and chromium are dangerous in the environment because they do not naturally degrade and are toxic even at relatively low concentrations. Salts of heavy metals are generally not very soluble in water and can be removed by physical methods, such as settling or filtration. Removal requires pH adjustment to the appropriate condition to precipitate the metal

and then removal of the precipitated solid by coagulation and gravity settling and/or filtration. Some metals have special characteristics that make their removal more difficult. Hexavalent chromium is very toxic and does not precipitate at alkaline pH as chromic hydroxide (Corbitt, 1990). An appropriate method for treating hexavalent chromium is needed.

Reduction is the most common technique to separate toxic heavy metal ions from wastewater streams (Beszedits and Wei, 1980, Sittig, 1973). Ferrous sulfate and sulfur dioxide must be added into wastewater containing chromium(VI) to reduce chromate to trivalent form. Subsequently, alkaline treatment precipitates Cr(III) as chromic hydroxide (Morisset *et al.*, 1954). This process is expensive due to the addition of chemicals and the sludge removal (Morisset *et al.*, 1954).

2.5 Sulfate

Sulfate (SO_4^{2-}) occurs naturally in groundwater. As water moves through soil and rock formations that contain sulfate minerals, some of the sulfate dissolves into the groundwater. High sulfate levels may corrode plumbing, particularly copper piping. In areas with high sulfate levels, plumbing materials more resistant to corrosion, such as plastic pipe, are commonly used (Minnesota Department of Health, 2002).

Sulfate can be removed by several types of treatment systems such as reverse osmosis, ion exchange, or chemical precipitation, while water softeners, carbon filters, and sediment filters cannot remove sulfate. For example, water softeners simply change magnesium or calcium sulfate into sodium sulfate (Minnesota Department of Health, 2002).

2.6 Chromate and Sulfate Removal by PEUF

Sriratana *et al.* (1996) studied chromate rejection and flux of PEUF which can be used to remove chromate ions from water. The polyelectrolyte, poly(diallyldimethyl ammonium chloride) with an average molecular weight of 240,000 Daltons, was added to bind the target ion that has the opposite charge to the

polyelectrolyte. The results showed that chromate rejections up to 99.8% were obtained in the absence of other added electrolytes. The presence of added sodium chloride reduces the chromate rejection substantially. An extrapolation of the flux data yields a gel concentration of 0.55 M polyelectrolyte. This high gel concentration and high rejection mean that ultrafiltration can produce a concentrated, low-volume waste stream, and a purified stream containing low concentration of chromate.

Later, Dunaway and coworkers (1998) used equilibrium dialysis to investigate the binding of chromate anions to the cationic polyelectrolyte, poly(diallyldimethylammonium chloride) in the presence and in the absence of added sodium chloride. They found that the binding of chromate to the polyelectrolyte can be predicted by using a model which combines thermodynamic relations with the Oosawa two-state polyelectrolyte theory. The ion-binding model quite successfully accounts for the experimental data when the theoretical value of a potential parameter is utilized and when the fraction of the apparent volume containing the bound counterions is determined by considering the dimensions of the bound chromate ions.

Furthermore, Juang and Chiou (2001) studied the removal of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- and SO_4^{2-} from brackish water by using polymer-enhanced ultrafiltration. Three weakly basic cationic water-soluble polymers which are chitosan, poly(ethyleneimine) or PEI and poly(diallyldimethyl ammonium chloride) or QUAT were used. Experiments were carried out as a function of the solution pH. It was found that pH affects the degree of protonation of the amino groups in chitosan and PEI but QUAT which has quarternary ammonium groups can bind with ions via ion exchange rather than electrostatic attraction. Also, the removal of divalent Ca^{2+} and Mg^{2+} was more effective than the removal of monovalent Na^+ and K^+ . In addition, the rejection of anions were placed in the order $\text{NO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$. Membrane fouling is most serious with chitosan, evaluated via conventional cake filtration theory for considering incompressible (PEI, QUAT) and compressible (chitosan) deposited cakes.

Recently, Tangvijitsri and coworkers (2002) studied the efficiency of polyelectrolyte-enhanced ultrafiltration (PEUF) of chromate, sulfate, and nitrate by binding of water-soluble polyelectrolyte, poly(diallyldimethyl ammonium chloride)

or QUAT, with target anions. The results showed that the removal of chromate and sulfate have the same high rejection more than 98%. Whereas the rejection of monovalent nitrate ion is below that of divalent anions, but can be as high as 97% under proper operating conditions. The rejection of anions increases with increasing concentration ratio of QUAT to anion. A high QUAT concentration in the retentate decreases relative flux due to the accumulation of QUAT near the membrane surface which indicates concentration polarization. However, the concentration polarization is not a severe problem in PEUF when the retentate concentration of QUAT is lower than the gel polarization concentration.