# CHAPTER 2

# LITERATURE REVIEWS

## 2.1 Background on nanofiltration membrane and nanofiltration process

### *2.1.1 Nanofiltration membranes*

Nanofiltration (NF) membranes are a relatively new class of membrane, they have two remarkable features in applications from scientific and engineering standpoints as well: one is the molecular weight cut-offs of NF membranes ranging from few hundreds to few thousands Dalton, which is intermediate between conventional ultrafiltration membranes and reverse-osmosis membranes; the other is the rejection to inorganic electrode less than that of reverse-osmosis membranes. Their separation mechanisms involve both steric (sieving) effects and electrical (Donnan) effects. This combination allows NF membranes to be effective for a range of separations of mixtures of organic molecules (neutral or charged) and salt. In addition, NF membranes can be operated at low pressure, which will be very attractive in reducing capital and operation costs and will provide easier system maintenance (Ratanatamskul and Yamamoto, 1998). This can be confirmed by report of Comb in 1991 that NF process resulted lower energy consumption of 21% to compare with reverse osmosis.

The separation performance of NF membranes is strongly dependent on the operation modes, such as diafiltration and the properties of the solutes and solution treated such as the polarity and charges of solutes and the pH value of solution.

Nanofitration is capable of concentrating sugars, divalent salt, proteins, particles, dyes and other constituents that have molecular weight greater than 1000 daltons. NF, like reverse osmosis, is affected by the charge of particles being rejected. Thus, particles with larger charges are more likely to be rejected than others. Nanofiltration is not effective on small molecular weight organics, such as methanol. In the dairy industry the nanofitration process is used to concentrate and partially demineralize liquid whey or desalinate water.

### *2.1.2 Diafiltration*

Diafiltration is one of conventional process techniques to achieve high purification rates of macro–microsolutes with an economically acceptable permeation flux, which was first introduced by Blatt *et al.* in 1968. and summarized by Dutre and Tragardh in 1994 for the ultrafiltration applications in many different fields such as food processing, biotechnology, pulp and paper industry.

The overall process of diafiltration may involve the three steps, there are pre-concentration step, diafiltration step and post-concentration step (Dutre and Tragardh), and in the diafiltration step there is a continuous or discontinuous addition of pure solvent to the retentate feed to keep feed volume at constant. Diafiltration processes by using NF membranes make it to be effective for a range of separations of mixtures of salts and small organic solutes (either neutral or charged).

## 2.2 Nanofiltration membrane applications for desalinization

The NF membrane was found to have many applications not only in food processing, waste water treatment, drinking water. In order to separate mixtures of organic/inorganic salt, the nanofiltration membrane seems to be more preferable and has been successfully applied in many fields.

In 1998, Eert Vellenga and Gun Trägådh studied the separation of combined salt and sucrose solution using DS5 NF membrane. They concluded that this membrane has excellent properties for separating sodium chloride from combined sucrose and sodium chloride solutions. The retention of sugar was more than 99.6% and independent of salt concentration. The salt retention was found to depend on both the salt and sugar amount. The salt retention decreased with increase of salt and sugar amount. These results could be confirmed by a report Xiao-Lin Wang *et al.* in 2002 that the NF 45 membrane was to be able for separating sucrose or glucose from sodium chloride solution in diafiltration mode. These could be promising processes for separation of saccharides from solution of soybean waste water.

In 1999, Vandanjon *et al.* studied the effective of membrane processes on concentration and desalinization of natural pigment produced by the marine diatom *Haslea ostrearia* Simonsen. The membranes used were flat ultrafiltration membrane Iris 3028; spiral reverse osmosis membrane R 45P and two tubular NF membranes

MPT 20 and MPT 31. The results showed that NF membranes seemed to be the best performing technique for desalinization of the blue colored solution with a low salt rejection rate (less than 10% at transmembrane pressure of 14 bar) and a high pigment rejection (more than 95% for NF membrane MPT 20); also the use of NF membrane in diafiltration mode allowed to obtain an acceptable speed of desalting.

In pharmaceutical, the purification of heterocyclic drug derivatives from concentrated saline solution (containing ammonium salts, sodium acetate and sodium chloride) by spiral-wound nanofiltration was reported (Capelle *et al.*, 2002). The process consisted of a diafiltration step until the minerals salts were almost completely eliminated followed by a concentration step. The results showed that more than 99% of both sodium acetate and chloride could be eliminated from an initial solution containing more than 10% w/v of salts and the retention of ammonium salts was higher than 99.5%. In addition, the data of flux and rejection showed that it was not necessary to increase transmembrane pressure to obtain the faster salt elimination. This could be interesting in order to save energy consumption.

From the very start, the drinking water industry has been the major application area for nanofiltration (Bart Van der Bruggen *et al.* 2003). In this field NF was used for softening, removal of organic compounds, removal of individual organic micropollutants, desalting process. For desalinization, Hassan *et al.* (1998) reported the use of NF in an integrated desalination system NF-SWRO (Sea Water Reverse Osmosis) and NF-MSF (Multi Stage Flash). The NF plant received non-coagulated filtered seawater and reduced turbidity and microorganisms and hardness. The concentration of monovalent salts was reduced by 40%, and the overall concentration of total dissolved salts was reduced by 57.7%. The permeate thus obtained was far superior to seawater as a feed to SWRO or MSF. This made it possible to operate a SWRO and MSF pilot plant at a high recovery (resp. 70 and 80%). The MSF could be operated at a top brine temperature of 120°C without any scaling problem (Al-Sofi *et al.* 1998). The high water output in both integrated desalination systems, combined with a reduction of chemicals and energy (by about 25-30%) allows producing fresh water from seawater at a 30% lower cost compared to conventional SWRO (Al-Sofi *et al.* 2001). Recently, a demonstration plant was built at Umm Lujj, Saudi Arabia, consisting of six spiral wound NF modules (840 inches) followed by three SWRO elements (Hassan *et al.*, 2000).

The dyes are usually produced by chemical synthesis, so there is problem that salt and small molecular weight intermediates and residual compounds reduce the purity of product. Thus the removal of impurities is required before the dyes are dried for sale as powder. Conventionally, the dyes are purified by 2 steps containing precipitation of dyes from aqueous solution using salt and filtration of slurry. However, this method results low impurity of product (about 30% salt content) and inconsistency in the production quality. Yu S. *et al.*, 2001 reported that the use of NF membrane could solve these problems. They used a NF plant designed and built by the Development Center of Water Treatment Technology, SOA, Hangzhou, with 12 NF elements (style 4040), the operating conditions were at flow rate of 3.5 $m^3/h$ and at pressure of 2-3 MPa. The results showed that the retention of dyes were approximately 100% and the membrane system produced dye solution having more than 25% dye and about less than 1% salt content. Thus the use of NF membrane promises a higher purity of dyes and it is easy for continuous operation which required less intensive labor.

Recently, Koyuncu *et al.* in 2004 successfully applied flat sheet NF membrane DS5 to treat dye waste water from textile process. The dye water contained sodium chloride and other components such as acidic acid, mollan and slipper. The results showed that as expected, both water and salt recovery were about 80 % and the permeate was colorless. Thus it is possible to reuse of waste water for better environment protection; also the high concentration of sodium chloride in permeate allowed less supplement of salt in the reactive dyeing recipe.

## 2.3 *A. ebracteatus* Vahl.

The bioactive components of this plant as well as its activities have been reported.

The organic extracts were found to have anti-mutagenic (Rojanapo *et al.* 1991) and anti-tumor promoting properties (Murakami *et al.* 1993). Recently, Laupattarakasem *et al.*, 2003 studied on inflammation activity of whole plant of *A. ebracteatus* Vahl. extracted by boiled water and by 95% ethanol. The results showed that the aqueous extract inhibited eicosanoid synthesis.

The roots and leaves of *Acanthus sp.* were found to contain abundant of alkaloids, flavonoids, fatty acids, tritepenoids and saponins. Immune potential effects of *A. ebracteatus* Vahl. roots on human lymphocytes was observed in *vitro* study ( Masathien *et al.*,1991). Inhibition of diethylnitrosamine (DEN)-induced hepatic foci by pre and post treatment with *A. ebracteatus* Vahl. in rats was reported by Tiwawech *et al.* in 1993.

In 2001, Kanchanapoom *et al.* isolated megastigmane glycoside (ebracteatoside A), three aliphatic alcohol glycosides (ebracteatosides B–D), as well as 7-chloro-(2R)-2-O-b-d-glucopyranosyl-4-hydroxy-2H-1,4-benzoxazin-3(4H)-one (7-Cl-DIBOAGlc) along with 22 known components, from the aerial part of *A. ebracteatus* Vahl. The benzoxazinoids and phenylpropanoids were the major constituents accounted for the anti-inflammatory effects. Furthermore, the toxicological and pharmacological properties of benzoxazinoids have been reported as the chemical resistance factors against insects, fungi, bacteria and viruses in many crop plants of the family Gramineae.

The stems of this plant were found to have polysaccharides isolated into neutral and acid polysaccharides by Hokputsa *et al.* 2004. The neutral polysaccharide was rich in galactose, 3-O-methylgalactose and arabinose, whereas the acidic polysaccharide (A1002) consisted mainly of galacturonic acid along with rhamnose, arabinose and galactose as minor components indicating a pectin-type polysaccharide with rhamnogalacturonan type I (RG-1) backbone. 3-O-Methylgalactose is also present in the acidic fraction. Both neutral and acidic fractions showed potent effects on the complement system using pectic polysaccharide PM II from *Plantago major* as a positive control. A small amount of 3-O-methylgalactose present in the pectin seemed to be of importance for activity enhancement in addition to the amount of neutral sugar side chains attached to RG-1. The relationship between chemical structure and effect on the complement system of the isolated polysaccharides is considered in the light of these data. The presence of the rare monosaccharide 3-O-methylgalactose may indicate that it can be used as a chemotaxonomic marker. This confirms that the traditional way of using this plant as a medical remedy appears to have a scientific basis.