Design, Fabrication Application and Advantages of Nanofiltration Unit

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Abstract- The term “membrane filtration” describes a family of separation methods. The basic principle is to use semi-permeable membranes to separate fluids, gases, particles and solutes. Membranes are usually shaped as a thin film, which allows transport of some materials, but not all. For separations from the water phase, the membrane is water-permeable, but less permeable to solutes and other particles depending on their size and to some degree other properties. All living organisms rely on natural membrane selective transport of solutes in and out of biological cells. Membranes are the active barriers in organs like kidneys and the stomach. Although membrane filtration is a relatively new family of methods for technical filtration, the principles of most methods have been known for some time.

Semi-permeable membranes have pores in the range 0.5 nm to 5 µm. Most filter membranes are produced with physical/chemical methods where the pores are formed by physical and chemical processes. An important property that characterizes the individual membrane methods is the driving force behind the separation. Some methods are summarized showing their driving force, membrane structure, and the approximate time of introduction for technical filtration. It can be seen that the driving force is different, and so is the design of the technical filter equipment. [C.J. Shirazi, S. Rao, P. Agarwal, Effects of operational parameters in nanofiltration. Water research (2006)]

Membranes are usually made from synthetic organic polymers and the thickness is in the order of 0.2 mm for sheet membranes. The physical shape of the membrane is designed to fit in suitable “modules”. A number of membrane module types are made, using sheet as well as hollow fibers, capillary or tubular membranes. Capillary membranes have achieved acertain foothold for drinking water, mainly because they can be backflushed to remove deposits. Hollow fine fibers are common in desalination of seawater. Spiral modules are popular for drinking water because of their low cost and moderate fouling tendency.

A prefilter is an essential part in a membrane plant in order to prevent that particles larger than the size of the narrow channels between the membranes, commonly 0.7–2 mm, enter the modules. Still some accumulation of matter on the membrane surface takes place and eventually reduces the flux and the capacity of the plant. This phenomenon is referred to as fouling. Avoiding and controlling fouling is the most important challenge for successful membrane filtration. The nanofiltration separation mechanism can be identified as a sum of convection and diffusion transport mechanisms, i.e., sieving effects, together with electromigration as a result of membrane charge. Desalination, by definition, refers to the process of removing salt from seawater or brackish water. In a broader sense of the definition, desalination can also be inferred as the removal of various inorganic ions from solution with the final target to produce clean and potable water. Nanofiltration as a subset of membrane processes has found wide application within this purview of desalination. Through the development of a good predictive modelling for nanofiltration membrane processes, it is possible to utilize the model for the purpose of membrane characterization, process modelling, optimization, membrane design and applications. [Nidal Hilal, Habis Al-Zoubi, Naif A. Darwish and Abdul Wahab Mohammad, Performance of Nanofiltration Membranes in the Treatment of Synthetic and Real Seawater, Separation Science and Technology (2007)]

Keywords- NF= Nanofiltration; MWCO= Molecular weight cut off; MF= Microfiltration; UF= Ultrafiltration; UV= Ultraviolet; TDS= Total Dissolved Solids; RO= Reverse Osmosis; ED= Electro dialysis; AFM= Atomic Force Microscope; SEM= Scanning Electron Microscope
I. INTRODUCTION

The nanofiltration (NF) membrane is a type of pressure-driven membrane with properties in between reverse osmosis (RO) and ultrafiltration (UF) membranes. NF offers several advantages such as low operation pressure, high flux, high retention of multivalent anion salts and an organic molecular above 300, relatively low investment and low operation and maintenance costs. Because of these advantages, the applications of NF worldwide have increased. [W.J., Conlon and S.A McClellan, Membrane softening: treatment process comes of age (2008)]

Desalination, by definition, refers to the process of removing salt from seawater or brackish water. In a broader sense of the definition, desalination can also be referred to as removal of various inorganic ions from solution with the final target to produce clean and potable water. Nanofiltration (NF) as a subset of membrane processes has found wide application within this purview of desalination. NF for example has been used in a desalination plant as pretreatment to both reverse osmosis (RO) and thermal processes, resulting in enhanced production of desalted seawater and reduced cost, yet remains an environmentally friendly process. Pre-treatment of seawater feed to RO using nanofiltration prevents scaling by removal of scale-forming hardness ions, prevents membrane fouling in RO processes by removal of turbidity and bacteria and is expected to lower the required pressure to operate RO plant by reducing seawater feed TDS.

Taste and odour is a special case for membranes in that the chemical nature of such compounds is highly variable, from relatively large organic molecules to low-molecular compounds. Often the source of taste and odour is volatile compounds that are typically low-molecular, and in these cases RO may be benevolent. In that case the use of activated carbon or ozone as a secondary treatment may be the best solution. [M.M. VanPaassen, J.M., Jong, Nanofiltration concentrate disposal experiences in the Netherlands. Desalination (2005)]

Table 1: Membrane Separation Processes and Membrane Characteristics

<table>
<thead>
<tr>
<th>Membrane Process</th>
<th>Separation Mechanism</th>
<th>Nominal pore size or Intermolecular Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
<td>Size exclusion</td>
<td>500-50000</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>Size exclusion</td>
<td>10-1000</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>Size exclusion, Electrical exclusion</td>
<td>5-20</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Size exclusion, Solution/diffusion</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

Similarly, the application of the models and membranes in areas such as wastewater treatment and seawater desalination has been successful and resulted in the development of inherent principles for the selection of membranes, process conditions and economic assessment for NF system. The applications studied include removal of divalent ions from seawater, heavy metals from leachate and electrolysis plating solutions. Another important work is in creating a value added product as a result of desalination application in a palm oil mill effluent treatment. The retentate and permeate of such processes were utilized successfully to produce enzymes and itaconic acids respectively through biotechnological means. This finding will augur well in the effort to balance environmental concerns with cost-effective treatment and value-added usage of the resulting waste. [Petersen RJ (2006) Composite reverse osmosis and nanofiltration membranes.]

II. PROCESS APPLICATIONS

III. MEMBRANE PROCESS
Membranes have the ability to differentiate and selectively separate salts and water. Using this ability but differently in each case, three membrane desalination processes have been developed for desalting water: Electro dialysis (ED), reverse osmosis (RO), and nanofiltration (NF). The RO represents the fastest growing segment of the desalination market [Blank et al., 2007].

Membrane technologies can be used for desalination of both seawater and brackishwater, but they are more commonly used to desalinate brackish water because energy consumption is proportional to the salt content in the source water. Although thermal technologies dominated from the 1950s until recently, membrane processes now approximately equal thermal processes in global desalination capacity. Compared to thermal distillation processes, membrane technologies generally have lower capital costs and require less energy, contributing to lower operating costs. In fact, the most important progress in the area of membrane systems is the reduction of membrane cost by a factor of approximately 10 over the last 30 years making the pretreatment and seawater intake as the most expensive items of a membrane system [Khawaji et al., 2008]. However, the product water salinity tends to be higher for membrane desalination (< 500 ppm TDS) than that produced by thermal technologies (< 25 ppm), but when making use of a second RO pass the same quality can be obtained.

IV. CHARACTERIZATION OF THE ULTRAFILTRATION OR NANOFILTRATION MEMBRANES

Most porous ultrafiltration or nanofiltration membranes, either polymeric or inorganic, have a complex porous structure, with a set of pores with various sizes ranging from a few nanometers to several tens of nanometers which determines mass transport through the membrane. There are several well-established techniques for the determination of pore size and pore size distribution. They include the bubble point technique, mercury porosimetry, the microscopic approach, solute transport method, permeametry and thermoporometry [Cuperus, 2012].

AFM (atomic force microscope) can image the non-conducting sample without damaging the membrane. While SEM (scanning electron microscope) requires heavy metal coating for non-conducting sample and high beam energy which may damage polymeric membranes. However, average pore sizes obtained from SEM were smaller than those obtained by AFM due to the sample preparation. In addition, AFM images are distorted by convolution between pore shape and cantilever tip shape. Moreover, from SEM and AFM, the images can only give structure information on the membrane outer layersurface without pore inside morphology. This can be verified from the experimental results in which the mean pore sizes measured by AFM were about 3.5 times larger than those calculated based on the data from solute transport technique [Singh et al. 1998].

V. DIFFERENT MEMBRANE OPERATIONS

A. Driving Forces-

Membrane processes can be divided according to their driving forces. As driving forces, gradients in pressure, concentration, temperature and electrical potential are used.

B. Electrically Driven Processes-

The electrically driven processes are electro dialysis and membrane electrolysis. The driving force for (ionic) transport in these processes is supplied by an electrical potential difference. Electrically driven processes can be employed only when charged molecules are present, using ionic or charged membranes.

C. Concentration Driven Processes-

Concentration driven membrane processes are dialysis and osmosis. In dialysis process, the transfer of the solute across the membrane occurs by diffusion and separation is obtained through differences in diffusion rates because of differences in molecular weight [Pontié, 2003]. Osmosis is the transport of water across a selectively permeable membrane from a compartment of higher water chemical potential to a compartment of lower water chemical potential until the osmotic pressures of both compartments are equal. It is driven by a difference in solute concentrations across the membrane that allows passage of water, but rejects most solute molecules or ions. Osmotic pressure (σ) is the pressure which, if applied to the more concentrated solution, would prevent transport of water across the membrane [Cath et al. 2006].
**D. Heat Driven Process**

Membrane distillation is a separation process for aqueous solutions, based on the use of hydrophobic micro porous membranes. The membranes are not wetted by the aqueous phase, until the operating pressure remains lower than the minimum penetration pressure of the membrane, so that the entrance of the pores acts as the physical support for a liquid vapour interface which can originate the separation of components of different volatility. The driving force for mass transfer across the membrane is a difference in the partial pressure between the two ends of the membrane pores. That can be maintained by acting on the temperature difference across the membrane, as in direct contact MD, by using a sweeping gas on the permeate side, by introducing an air gap or by applying vacuum in the permeate side [Cabassud et al. 2003].

**E. Pressure Driven Processes**

Pressure driven membrane processes use the pressure difference between the feed and permeate side as the driving force to transport the solvent through the membrane. Particles and dissolved components are (partially) retained based on properties such as size, shape and charge. Four membrane processes can be distinguished when the driving force is a pressure difference across the membrane, separating two liquid solutions. These processes are Microfiltration (MF), Ultrafiltration (UF), nanofiltration (NF) and reverse osmosis. Going from MF through UF and NF to RO, the hydrodynamic resistance increases and consequently higher driving forces are needed. On the other hand the product flux through the membrane and the size of the molecules being retained decreases. The product flux obtained is determined by the applied pressure and the membrane resistance (Shih et al 2005).

<table>
<thead>
<tr>
<th>METHOD</th>
<th>DRIVING FORCE</th>
<th>MEMBRANE</th>
<th>PERMEATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dialysis</td>
<td>Concentration</td>
<td>Porous</td>
<td>Solute</td>
</tr>
<tr>
<td>Electro dialysis</td>
<td>Electrical</td>
<td>Porous</td>
<td>Ions</td>
</tr>
<tr>
<td>Cross flow filtration</td>
<td>Pressure/concentration</td>
<td>Porous</td>
<td>Water</td>
</tr>
<tr>
<td>Pervaporation</td>
<td>Partial pressure</td>
<td>Dense</td>
<td>Liquid</td>
</tr>
<tr>
<td>Membrane distillation</td>
<td>Partial pressure</td>
<td>Porous</td>
<td>Liquid</td>
</tr>
</tbody>
</table>

Table 2. Properties of various methods for membrane filtration

**V. GROUNDWATER AND SOFTENING APPLICATIONS**

Nanofiltration processes are capable of removing hardness, heavy metals,NOM, particles and a number of other organic and inorganic substances in one single treatment step. NF membranes have a reasonable high rejection of bivalent ions whereas the rejection of monovalent ions is moderate to low. Operating pressure is typically in the range of 5-30 bar. The process will be adequate for surface and ground waters with high concentrations of total dissolved solids (TDS), i.e. more than 500 mg/L, but with low NaCl concentrations,[Thorsen, T., Krogh, T. and Bergan. E.: "Removal of humic substances with Membranes. System, use and experiences", AWWA Proceedings, 2011 Membrane technology conference, Baltimore 2011]

Nanofiltration membranes have properties in between RO and UF Membranes. In Table the rejection of RO, loose RO, NF and UF membranes is compared for a number of substances. The most distinctive features of typical NF membranes are:

- The rejection of bivalent or higher charged anions, like sulphate (SO42-) and phosphate (PO43-) is practically total. Multivalent cations are retained to a higher extent than monovalent cations.
- The rejection of sodium chloride (NaCl) varies from about 70 % down to 0 %.
- The rejection of uncharged dissolved materials in solution depends mostly on the size and shape of the molecule.
Table 3. Comparative rejection values for RO, loose RO, NF and UF.

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>RO (%)</th>
<th>LOOSE RO (%)</th>
<th>NF (%)</th>
<th>UF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>99</td>
<td>70-95</td>
<td>0-70</td>
<td>0</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>99</td>
<td>80-95</td>
<td>99</td>
<td>0</td>
</tr>
<tr>
<td>Calcium sulphate</td>
<td>99</td>
<td>80-95</td>
<td>0-90</td>
<td>0</td>
</tr>
<tr>
<td>Magnesium sulphate</td>
<td>&gt;99</td>
<td>95-98</td>
<td>&gt;99</td>
<td>0</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>98</td>
<td>80-90</td>
<td>0-5</td>
<td>0</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>90</td>
<td>70-85</td>
<td>0-5</td>
<td>0</td>
</tr>
<tr>
<td>Fructose</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>20-99</td>
<td>0</td>
</tr>
<tr>
<td>Sucrose</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>0</td>
</tr>
<tr>
<td>Humic acid</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 3. Comparative rejection values for RO, loose RO, NF and UF.

VI. INDUSTRIAL DESALINATION PROCESSES

The choice of technology used for water desalination depends on a number of site specific factors, including source water quality, the intended use of the water produced, plant size, capital costs, energy costs and the potential for energy reuse [Al-Subaie et al. 2007].

Water desalination can be accomplished by different techniques that can be classified into two categories: thermal and membrane processes. The thermal processes can be subdivided into the following processes: (i) Multistage flash evaporation, (ii) Multiple effect distillation and (iii) Vapour compression. The membrane processes are subdivided into: (1) Reverse osmosis (2) Electrodialysis and (3) Nanofiltration. Some basic information on these processes

A. Thermal Processes-

This method mimics the hydrological cycle in that salty water is heated producing water vapor that in turn condensed to form fresh water free of salts. The fresh water is mineralized to make it suitable for human consumption. The important factors to be considered for this method of desalination are the proper temperature relative to its ambient pressure and enough energy for vaporization for energy minimization and the control of scale formation. The energy needed for vaporization is reduced usually by the use of multiple boiling points in successive vessels, each operating at a lower temperature and pressure, where the scale formation is controlled by controlling the top temperature of the process or by the addition of antiscalants to the seawater. The known thermal methods are the multi-stage flash process (MSF), multi effect distillation (MED) process and the vapor compression (VC) distillation process.

B. Multiple-Effect Distillation-

The multiple-effect distillation (MED) process is the oldest desalination method and is very efficient thermodynamically. The MED process takes place in a series of evaporator’s called effects, and uses the principle of
reducing the ambient pressure in the various effects. This process permits the seawater feed to undergo multiple boiling without supplying additional heat after the first effect. The seawater enters the first effect and is raised to the boiling point after being preheated in tubes. The seawater is sprayed onto the surface of evaporator tubes to promote rapid evaporation. The tubes are heated by externally supplied steam from anormally dual purpose power plant. The stream is condensed on the opposite side of the tubes, and the steam condensate is recycled to the power plant for its boiler feed water. The MED plant’s steam economy is proportional to the number of effects. The total number of effects is limited by the total temperature range available and the minimum allowable temperature difference between one effect and the next effect. Only a portion of the seawater applied to the tubes in the first effect is evaporated. The remaining feed water is fed to the second effect, where it is again applied to a tube bundle. These tubes are in turn heated by the vapors created in the first effect. This vapor is condensed to fresh water product, while giving up heat to evaporate a portion of the remaining seawater feed in the next effect. The process of evaporation and condensation is repeated from effect to affect each at a successively lower pressure and temperature.

C. Multi-Stage Flash Distillation (MFS)-

In flash distillation, the water is heated under pressure, which prevents it from vaporizing while being heated. It then passes into a separate chamber held at lower pressure, which allows it to vaporize, but well away from the heating pipes, thus preventing them from becoming scaled. Like MED, practical flash-distillation systems have compartments and each compartment is called stage, hence the term Multi-Stage Flash (MSF). When first introduced in the 1960’s, MSF offered slightly lower energy efficiency than MED, but this was outweighed by scaling considerations and MSF became the industry standard. The desalinated water produced by the MSF process contains typically 2-10 ppm dissolved solids. Therefore, it is remineralized through the potabilization (or post-treatment) process.

D. Vapour Compression-

Compressing water vapour raises its temperature, which allows it to be used at a heat source for the same tank of water that produced it. This allows heat recycling in a single effect distillation process. In Thermal Vapour Compression, the compressor is driven by steam, and such systems are popular for medium-scale desalination because they are simple, in comparison to MSF. In Mechanical Vapour Compression, the compressor is driven by a diesel engine or electric motor.

The water produced by the thermal process is very pure with almost no salts, where the feed water quality has almost negligible effect on energy consumption [Nicos, 2001]. Thermal processes are the primary desalination technologies used throughout the Middle East because these technologies can produce high purity water from seawater and because of lower fuel costs in the region.

E. Membrane Processes-

Membranes have the ability to differentiate and selectively separate salts and water. Using this ability but differently in each case, three membrane desalination processes have been developed for desalting water: Electro dialysis (ED), reverse osmosis (RO) and nanofiltration (NF). The RO represents the fastest growing segment of the desalination market [J.S. Blank et al. 2007]. Membrane technologies can be used for desalination of both seawater and brackish water, but they are more commonly used to desalinate brackish water because energy consumption is proportional to the salt content in the source water. Although thermal technologies dominated from the 1950s until recently, membrane processes now approximately equal thermal processes in global desalination capacity. Compared to thermal distillation processes, membrane technologies generally have lower capital costs and require less energy, contributing to lower operating costs. In fact, the most important progress in the area of membrane systems is the reduction of membrane cost by a factor of approximately 10 over the last 30 years making the pretreatment and the seawater intake as the most expensive items of a membrane system [Khawaji et al., 2008]. However, the product water salinity tends to be higher for membrane desalination (< 500 ppm TDS) than that produced by thermal technologies (< 25 ppm), but when making use of a second RO pass the same quality can be obtained.
Figure 2. Ion rejection as a result of the IEP Tests. Tested feed solution: sodium chloride and sodium sulphate solutions. Tested membrane: NF 270 and TS 80.

<table>
<thead>
<tr>
<th>Method of desalination</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multi-effect desalination (MED)</td>
<td>High production capacity&lt;br&gt;Low capital cost&lt;br&gt;High purity (&lt;30ppm)&lt;br&gt;Energy input independent on salinity&lt;br&gt;Minimal skilled operator</td>
<td>Dependence of output on local power availability&lt;br&gt;Long construction period&lt;br&gt;Difficult to control water quality&lt;br&gt;Low conversion of feed water (30%-40%)&lt;br&gt;Labor-intensive&lt;br&gt;Large space and material requirements</td>
</tr>
<tr>
<td>Reverse osmosis (RO)</td>
<td>Suitable for both sea and brackish water&lt;br&gt;Flexibility in water quantity and quality&lt;br&gt;Low power requirement compared with MED and VC&lt;br&gt;Flexibility in site location&lt;br&gt;Flexibility in operation start-up and shut-off&lt;br&gt;Simple operation</td>
<td>Low quality (250-500 ppm)&lt;br&gt;Requires high quality feed water&lt;br&gt;Relatively high capital and operating costs&lt;br&gt;High pressure requirements&lt;br&gt;Long construction time for large scale plants</td>
</tr>
<tr>
<td>Vapor compression (VC)</td>
<td>High water quality (20 ppm)&lt;br&gt;High operational load&lt;br&gt;Short construction period&lt;br&gt;Operation and production flexibility</td>
<td>High operational costs&lt;br&gt;High energy consumption&lt;br&gt;Lack of water quality control</td>
</tr>
</tbody>
</table>
Electrodialysis (ED) & Low operating and capital costs
Flexible energy source
High conversion ratio (80%)
Low energy consumption
Low space and material requirements

Low to medium brackish water capability (3000ppm)
Requires careful pretreatment of feed water
Low production capacity
Purity affected by quality of feed water

Multi-stage flash & Flexibility in salinity of feed water
High purity production (< 30ppm)
High production capacity
Low skill requirement
Production of both water and electricity
High energy input

Labor intensive
Low conversion ratio (30%-40%)
High operating costs
High construction requirements
Limited potential for improvement

Table 4. Characteristics of desalination operations

VII. CONCLUSION

From this study the following conclusions can be drawn:

• Nanofiltration can be used for removal of a wide range of pollutants from groundwater and surface water in view of drinking water production. Softening and NOM-removal are major applications, but NF is frequently applied for the combined removal of NOM, micro pollutants, pesticides, arsenic, iron, heavy metals, sulphate, nitrate and bacteria and viruses. Reduced THM-formation potential can also be achieved. Full-scale installations have proven the reliability of NF in these areas.

• The main challenge in NF for water treatment is to control fouling of the membrane by scaling etc.
• Regardless of other conditions there will always be a maximum flux that can be applied in long term stable operation and therefore the flux should be limited and not exceed this value.
• This critical flux is almost always lower than the maximum flux capacity of the membrane and therefore there is a significant potential reduction in treatment costs to gain from better fouling control.
• There is a need for better understanding of the connection between source water characterization and proper plant design and operation, in particular the value of the critical flux.
• There is a clear need for a better and cost-efficient prefilter that is effective in the particle range 0.1 to 3 µm.
• More knowledge of the rejection of typical and specific and important water pollutants and groups of pollutants for various types of membrane material would be useful.
• For softening and groundwater applications criteria for anticipant or acid dosing should be developed.
• There is a need for evaluation of waste disposal options and to assess the environmental impact of discharge.

REFERENCES