Membrane Science and Technology for Water

Treatment

Chapter 5: Membrane Filtration Technologies

5.1. Introduction

Over the past 2 decades, the technology of membrane has become the most useful technology of separation. New technologies are driving the water quality to the community by continuously advancing in the esthetic criteria and constraints. The technology of Membrane is one of those advanced technologies. Membranes are used in this advanced technology for the separation. It provides the alternative to the ion exchangers, adsorption, etc. This technology is mainly used for the filtration of water and purification and in industries of beverages and food. (Kurt et al., 2012; Ozgun et al., 2012). In dialysis It is also used.

A barrier that is selectively used between two homogenous phases is called a membrane. The membrane provides an alternative to the processes like distillation, adsorption, etc., its advantages are that it consumes low energy and the possibility of the process of separation is continuous. (Baker, 2004).

This process cannot be used with every fluid as the product, the content of the input and nature of the procedure of the membrane will be different. For water treatment mainly four processes are used with the difference in pore size of the used membrane. These procedures are as follows (Abdelrasoul et al., 2013; Akar et al., 2013):

- nanofiltration (NF);
- microfiltration (MF);
- reverse osmosis (RO); and
- ultrafiltration.

Reverse osmosis (RO) is not in the scope of this chapter. In Figure 5.1, the schematic separation spectrum given for membrane procedures is shown (Baker, 2004; Abetz et al., 2006).

Figure 5.1. A schematic spectrum for conventional filtration and membrane processes. Source: https://www.wiley.com/en-us/Membrane+Technology+and+Applications%2C+2nd+Editionp-9780470020388.

There are various applications of membrane technology and for selecting proper membrane process there are various guidelines like if the size of the particles removed is greater than 0.2 nm, then the process will be MF and of the contaminations are to be coagulated or precipitated then the process will be the UF or the MF. If the organic and inorganic ions are to be removed, then the process will be NF, while if monovalent ions occur or the dissolved solids' total elimination is 3000 mg/L, then the RO process will be essential. (Antelmi et al., 2001; AWWA, 2007).

5.2. Microfiltration (MF) Process

For the water treatment process, we usually use MF and UF process. MF can be applied to water that is on the surface or groundwater after the sand or cartridge filter. MF is used in the section on pretreatment in RO systems (Bérube et al., 2002; Buonomenna, 2013).

From 0.1 to 10 nm, the MF pore size usually varies. In the mechanism of separation, the large particles are rejected while the parties with the small size will flow freely from the pore.

By the Darcy's law the volume flow via MF membranes can be defined, where flux J from the membrane is directly proportional to the applied pressure (DP):

$J = A \Delta P$

where; A (permeability constant) contains structural features like pore size distribution and the porosity (Mulder, 1996).

Macrofiltration is a mostly used process in applications where particles having a size greater than 0.1 nm are to be reserved from the suspension. The very significant applications are of using cartridges on filtration that are dead-end. On the macro level, this filtration is replaced with cross-flow filtration. Its main application is in the beverage and pharmaceutical industry of sterilization and clarification. Further applications are listed below (Eykamp, 1995; Mir et al., 1992; Mulder, 1996):

- In the semiconductor ultrapure water;
- Drinking water treatment;
- Clarification of beer, wine, and fruit juice;
- Wastewater treatment:
- Pretreatment.

5.3. Ultrafiltration (UF) Process

In this process, the pore size usually ranges from 0.01 to 0.05 nm. The membranes used in UF blocks the large molecules. Instead of pore size, they are characterized via the MWCO. (Membrane Filtration Guidance Manual, 2005). UF and MF membranes are measured porous membranes in which particles are rejected based on the shape of solute and size related to the pore size of the membrane. MF and UF have alike separation membrane principle. The main difference lies in the structure of the membrane of UF which has the asymmetric structure of which the top layer is dense and greater hydrodynamic resistance (Mulder, 1996; Carroll et al., 2000).

The operating modes of both systems are two. Figure 5.2 of cross-flow showing that the input water is being pumped in the tangential direction to the membrane. The cleaned water will pass from the membrane while rejected water is recirculated and is combined with the input water again. Infiltration process which is dead-end or direct the whole water in the input flows from the membrane. So, in this process, the recovery is 100% while a minor amount is applied for the backwash of the system (2–15%) (Jacangelo et al., 1997).

Figure 5.2. (a) Cross-flow outline microfiltration; and (b) for microfiltration dead-end filtration. Source:

Mostly MF and UF plants work on the dead-end filtration mode nowadays. The reason is that deadend requires lower energy. In a cross-flow system, high velocity is essential to avoid fouling in enhanced energy usage and head loss (Chen et al., 2010; Chakrabortty et al., 2013).

5.4. Nanofiltration (NF) Process

Nanofiltration (NF) finds its usage in many areas (Koyuncu and Cakmakci, 2010). Its key application is the treatment of water for drinking purposes and also the treatment of wastewater (Debik et al., 2010). NF can be employed to treat all types of water like pretreatment, wastewater, and groundwater or for the process of purification (Cakmakci et al., 2009; Koyuncu et al., 2008; Uyak et al., 2008). By using NF we can remove microorganisms, hardness, or the dissolved salts. Comparing with RO this provides a process that operates at lower pressure and energy-efficient (Hilal et al., 2004).

The membranes which lie in a region among the RO membranes which are clean and ultrafiltration (UF) membranes which are pure are known as loose RO or low-pressure RO or usually NF membranes. NF membranes usually reject NaCl ranging from 20% to 80%. Among the RO membranes, these properties are in-between with a rejection of salt of over 90% and molecular weight (MW) cutoff of ≤ 50 and UF membranes with a salt rejection of $\leq 5\%$. The NF membrane rejects the salts depending upon the molecular size and the order is $Na₂SO₄ > CaCl₂ > NaCl$ (Baker, 2004).

For the softening of groundwater, NF has been used, according to many researchers. Schaep et al. (1998) have applied NF membranes and their results were 60 to 70% removal of ions. Sombekke et al., 1997) compared NF membranes by stimulated carbon adsorption. From the outcomes, both the processes showed great performance. Though, NF membranes have the benefit of cost. (Hilal et al., 2004; Schaep et al., 1998; Sombekke et al., 1997).

Ion selectivity is done by using the NF membranes. The valency of anions will determine the retention of the salt. That's why ions with monovalent can pass easily while multivalent are reserved. In Figure 5.3 the separation spectrum for NF membranes is being shown.

Some factors are to be considered while operating the NF units are solvent permeability/flux via the membrane, rejection of solutes, and yield/recovery. Similarly, the flux, permeability of membranes is also a vital factor. NF membranes are mostly hydrophilic excluding those applied for solvent.

Molecular size, charge, and hydrophobicity are the main factors that determine the rejection of the NF. Statistically the pore/void sizes are distributed and can be defined via a log-normal distribution (Bowen and Welfoot, 2005).

Figure 5.3. Separation penetrability spectrum of NF and other processes. Source: https://www.sciencedirect.com/science/article/pii/B9781782421214000034.

The even transition can be observed by varying the molecular size in an S-shaped curve. The value of MCWO indicates the molecular limit which can be retained. MCWO values between 150 and 1000 the NF membranes should need care while using: for example, molecules which are hydrophobic and have a greater size than MCWO experiences low rejection. The solution's pH may disturb the charge on the surface of the membrane and charge on the solute, so rejection can be greater or lesser (Chong et al., 2010).

Another property recovery which is used for designing industrial application rather than the characteristic of the membrane. It is the ratio of pervade stream to feed stream and its value lies around 40 to 90% (Chou and Yang, 2005; Corry, 2008).

5.4.1. Applications of NF Membranes

Ionic strength can be affected by NF membranes. NF membranes can be used to remove the hardness, organics, and contaminants. NF has been used by many researchers to achieve these objectives.

NF has been used for softening groundwater and all results of the researchers were good. Retention of multivalent ions was above 90% and monovalent was 60 to 70%. (Hilal et al., 2004; Scheap et al., 1998). For softening of water pellet and granular stimulated carbon of NF membranes were compared. NF membranes have shown good potential from a health point to lower installment cost. NF's advantage is that a slighter stream can be softened since it removes all actions that cause hardness. NF membranes allow side-stream treatment as in public water, it is not needed to bring hardness to very lower values. The membranes are fed with a part of the flow that needs to be softened and after that is mixed with the substance stream to get the amount value of blended. By using precipitated lime softening the hardness cannot decrease underneath around 50 mg/L CaCO₃, that's why side stream treatment is not applied (Cote et al., 2006; Crock et al., 2013).

There are three separate subsystems of a distinctive NF which are given: pretreatment, membrane processes, and posttreatment. Primarily NF membranes are used for desalting surface, saline, or groundwater. The chemistry of surface water changes with the season or due to dilution with rain. NF is used for treatment, yet the emphasis is to remove organics instead of softening them. (Hilal et al., 2004; Van der Bruggen and Vandecasteele, 2003).

DBPs (Disinfection by-products) precursors are being removed by using NF membranes like natural organic matter (NOM), which can form carcinogens after reacting with the disinfectants in the process of water treatment. NF is used in many cases for the total reduction of organic carbon to < 0.5 mg/L.(AWWA, 2007).

NF is more operative for lime softening than RO, eradicating color and the DBPs precursors. NF membranes which are semipermeable are non-porous; they can screen microbes and the matter present in the input water. This capability of NF membranes has been proved by many researchers such as one who has reported that it can remove virus between 4 and 5 logs (Di Zio et al., 2005; Dahe et al., 2012).

5.4.2. Integrated Membrane Systems

To meet the standards of the consumption water NF and RO with low-pressure processes are being used though their sensitivity is high to ensnarling and requires pretreatment processes such as productivity is enhanced by using UF and MF. These systems are known as integrated membrane systems, and they are used for reducing and controlling fouling (Elimelech and Phillip, 2011; Fane et al., 2011).

5.5. Pretreatment Requirements

Pretreatment is usually done on the water earlier it enters the membrane system to reduce fouling. Though, it can be applied to address other concerns related to water. Pretreatment is usually done to remove foulants, enhance productivity and recovery of the system, and increase membrane life. Physical damage to the membrane can be avoided by doing pretreatment (Galanakis et al., 2012).

Many pretreatments can be done with a given membrane type. Pilot testing is applied in comparing pretreatment options, optimizing, and demonstrating the performance of pretreatment (Membrane Filtration Guidance Manual, 2005). Feedwater consists of dissolved matter and solids dependent on the source. Suspended solids can be inorganic particles, colloids, and microorganisms, and algae. Dissolved matter consists of chlorides, soluble salts, and carbonates or sulfates. Reliant on the freshwater quality, the pretreatment procedure may follow steps such as:

By using a rough strainer exclusion of large particles;

- With chlorine disinfection of water;
- Clarification without or with flocculation;
- Clarification and hardness decrease by using lime treatment;
- Media filtration:
- By pH adjustment reduction of alkalinity;
- Addition of scale inhibitor;
- By using sodium bisulfite or stimulated carbon filters decrease of free chlorine;
- Water sterilization using UV (ultraviolet) radiation;
- The final elimination of suspended particles by using container filters.

5.6. Applications of Water Treatment by NF, UF, and MF

For clean and drinking water supply naturally, there are four main water bases: rainwater, groundwater, surface water, and seawater. Due to their physical and chemical features, diverse membrane methods are valid to these sources. Graphic describing water sources and probable membrane stages to safe water is being shown in Figure 5.4. For example, the surface water can be transformed into safe water by applying a UF, MF, MF $+$ UF plus a supporting, or NF membrane. Due to the high metal concentrations and hardness of groundwater UF and MF alone will not be effective. They require a supporting system.

5.6.1. Applications for Surface Water Treatment

NF, UF, and macrofiltration membranes can be applied in surface water treatment unaided or along with a supporting system. Due to their high efficiency, they are fetching useful in the treatment of surface water. In the removal of cysts, particles, turbidity, and bacteria macro filtration and UF process are active. Macrofiltration and UF might not be applied to acquire high water value if a high organic content of water occurs. In contrast, to treat many water impurities like synthetic organic compounds (SOCs) and DBPs, the NF process would be applied in this case (Glucina et al., 2000).

5.6.2. Membranes for Groundwater Treatment

Due to inadequate rainfall, in few places, surface water is rare. For these places, sources of groundwater become significant. Though in nature they are adjustable, groundwater sources usually comprise carbonate/alkalinity, magnesium, silica, and calcium. If the concentrations of these ions reach a high level of concentrations that surpass limits of mineral solubility, rainfall initiates. In the end, this precipitation makes deposits and scales. The formation of scale can be difficult. To resolve this challenge, membrane methods are operative (Kinsela et al., 2012).

Figure 5.4. Water sources and appropriate membrane steps to attain drinking water. Source: https://www.sciencedirect.com/science/article/pii/B9781782421214000034.

5.6.3. Nanofiltration (NF) for Seawater Desalination

The NF membrane's MW cutoff values are around 200 to 2000 Da. The rejection rate of monovalent ions and divalent ions is 85% and 98%respectively. NF membranes have greater penetrability than RO membranes, which in energy consumption gives them a benefit. In Figure 5.5, a figure of dualstep NF is being shown. There is a discrepancy about whether it is probable to purify seawater by applying dual-step NF at a lesser price than RO. In the dual-step NF method, seawater is poured into the $1st$ NF membrane, and then the gathered pervade is fed to the $2nd$ NF membrane. Lastly, clean water is attained. Optionally concentrates are thrust into the NF feed tank. For seawater purification, the requirement of energy by using dual-stage NF is comparative to the saltiness of the pervade. For lower permeate salinity more energy is desired (Altaee and Sharif, 2011).

Source: http://epubs.surrey.ac.uk/833655/.

5.6.4. Membranes for Harvesting Rainwater

For irrigation purposes reaped rainwater is ideal. Conversely, for indoor and other drinking uses there is rising attention in harvesting rainwater. Through NF, UF, and MF rainwater can be filtered as per the required quality. For gray water production, the MF treatment is appropriate. For the consumption water supply, NF, and UF treatment can be applied. In consumption water production home size water treatment parts can be applied. For cleansing to eradicate bacteria and viruses, UF gives a great choice. Several companies provide UV, membrane filtration systems, and granulated activated carbon for rainwater cleansing.

5.6.5. Applications of Membranes for Specific Contaminant Removal

In both organic and inorganic forms, As (arsenic) occurs in natural water sources. Cancer could be caused if exposure (As) is long-term. The recommended amount of arsenic in water is 0.01 mg/L as per the World Health Organization (WHO). Nowadays the elimination of arsenic with membranes is effective and is common. In the literature, there is both lab-scale and pilot research (Nguyen et al., 2009) applied both macro filtration and NF. For the elimination of arsenic, NF membranes are more effective than macro filtration membranes, which have larger pores. Sato et al. (2002) also estimated elimination productivity by using NF and a system of quicksand filtration inter-chlorination. NF membranes having 99.6% sodium chloride denial capacity detached 75% of As(III) and 95% of As(V) with no chemical addition below low pressure. Floch and Hideg (2004) directed a research with 200e300 mg/L as comprising deep well water. They accomplished a concentration ≤ 10 mg/L by using membranes of Zenon ZW 1000 hollow-fiber.

To control pests like insects and weeds, pesticides are used. They are useful in avoiding sickness and are applied to food manufacturing. On water quality, unfortunately, they have a hostile consequence and may have bad impacts on aquatic and human life. Chen et al. (2004) shown that NF membranes can discard insecticides from 46% to 100%. According to them, the denial rate is directly related to the MW of the insecticide. When the MW is enlarged, the rejection rate also enlarged. By regulating the functioning flux and recovery, they also discovered rejection could be enlarged. Van der Bruggen et al. (1998) studied the elimination of insecticides along with the systems of membrane filtration that displayed great efficacy of membranes in insecticide elimination. They tried NF membranes and attained around 95% rejection of Ar through an NF-70 membrane.

In the last step of the treatment of consumption water, cleansing is used to neutralize biological agents. Though, NOM in water counters with disinfectants and origins DBPs to produce, like Hans (haloacetonitriles), HAAs (halogenated acetic acids), THMs, and HKs (halo ketones), which are damaging to the health of human. Lee and Lee (2007) used NF membranes to eradicate NOMs from surface water and investigated the outcome of membrane pretreatment and membrane material. They came to know that monitoring NOM in surface water membranes having a MW cutoff < 200 Da was useful. Positively charged and hydrophobic membranes contaminated more than negatively charged and hydrophilic membranes. They also discovered that for avoiding NF fouling ozone pretreatment was ineffective, but PAC (powdered activated carbon) or UF pretreatment was effective.

Because of their impacts on biological activities the pharmaceuticals have just gained attention. Pharmaceutical releases to the atmosphere should be stopped. Radjenovic et al. (2008) by using groundwater studied the elimination of medicines in full-scale NF and RO plant of drinking water treatment. By applying RO and NF the 85% rejection rate was attained. Boleda et al. (2011) studied medicines in a full-scale plant of treatment of drinking water; treatment contained sand filtration, flocculation/coagulation, and oxychlorination parts. The system was torn apart into two equivalent lines after the sand filtration, advanced (RO and UF), and conventional (carbon and ozonation) treatment. In Figure 5.6, a diagram of the plant is being shown. A progressive system was more operative than an orthodox system to eradicate pharmaceuticals.

Figure 5.6. Water treatment plant of drinking. Source: https://pubmed.ncbi.nlm.nih.gov/21459501/.

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