Nanofiltration Membranes as a Suitable Alternative to Reverse Osmosis/ Ultrafiltration Membranes in Separation Processes

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The paper reviews on thin-film composite membranes covering membranes, nanofiltration membranes, their advantages over other separation techniques and utility. Focuses on a limited area comprising nanofiltration (NF) membranes which appear as a suitable alternative to reverse osmosis (RO) and ultrafiltration (UF) membrane processes. Nanofiltration (NF) has emerged as a promising area which has extended membrane applications. NF membranes are generally polyamide membranes and are charged. They have higher flux and lower salt rejection facilitating a diverse cut-off based on molecular weight of a specie with more than 92 per cent rejection. NF membranes are considered to be best alternative of purification.

Introduction

Semipermeable membranes useful for desalination and separation processes are prepared by forming a polymeric ultrathin film having semipermeable properties on a microporous support. These are thin-film composite membranes having bilayer film which comprises an ultrathin film (0.3 to 3 um) deposited on a porous support. The two layers have different composition and diverse functions. The top barrier layer is selective for solutes, while maintaining a good flux, whereas the porous layer gives support and resists compression thus providing unhindered flow. Membrane process is a low energy process and can operate at mild temperatures and is a compact process in terms of space. It can achieve similar performance at lower power and at a lower capital cost. It does not involve any energy intensive phase change as required in other purification processes. It is a clean process and economical compared to other separation techniques. Membranes which can be “tailor-made” to meet specific separation properties may be non-porous, microporous, or macroporous.

Nanofiltration Membranes

NF is a relatively new membrane process which falls between RO and UF in its separation characteristics (Figure 1). NF membrane is termed as “Loose” reverse osmosis membrane. It operates at low pressures, whereas RO membrane requires pressure of about >600 psi. Many industrial processes require separation of large molecules from small molecules. UF membranes are not able to discriminate efficiently between low molecular weight molecules, whereas reverse-osmosis membranes reject both low molecular-weight organics and salt. NF is a membrane process which retains organics >300 g/mol based on cut-off of the solute with rejection above 92 per cent, and certain multivalent salts (in case of negatively charged NF membranes) but passes substantial amounts of monovalent salts. The retention characteristics are based on free volume.

The utility of these membranes is that the membranes can be used for dewatering large molecules in the molecular weight range 300 to 1000 g/mol, separating salts and organic acids from other organic compounds such as sugars and proteins, concentration, liquid phase separation, desalting of higher organics and passing solutions with high osmotic pressure at low pressures. Rejection
of ions is based on size and valency, whereas the rejection of organics is based on size and involves sieving effect\(^1\). On the other hand, R O membranes do not exhibit ion selectivity. Because of its ability to reject high percentage of many dissolved components N F membranes offer a single treatment alternative\(^7\).

R O membranes are considered to be homogeneous, whereas it has been established using Atomic Force Microscopy (AFM) that N F membranes have discrete pores of nm dimensions\(^6\). They have an average pore-size diam of \(-2 \) nm. N F membranes are more porous compared to R O membranes. Being more porous might result in concentration polarization and fouling. It can be overcome by better design and selecting materials possessing desirable properties. N F membrane's low salt rejection and high water flux at low pressures, its ability to separate low molecular weight organics from high molecular weight organics, and also ability to pass solutions with high osmotic pressure at low pressure make it ideal for water softening, desalting, food processing, waste-water treatment and for various separation processes in industry. N F membranes can also be used for cleaning contaminated ground water and for producing ultrapure water required in electronics & semiconductor industry. Another related advantage of N,F, membranes is the reduction in dissolved organics based on cut-off of the membrane. When used as a pre-treatment instead of conventional chlorination, the consumption of disinfectant can be reduced significantly. Also, N,F, membranes giving high salt rejection can be used for desalination at a relatively low pressure or a pre-treatment for desalination. Thus N F membranes which operate at low pressure have tremendous applications.

N F membranes are charged which is utilized in separating salts based on charge and valency. They are mostly negatively charged and selectively reject divalent anions. Bipolar membranes can be used for separating both divalent cations and anions from monovalent salts\(^9\). In bipolar membranes, positively charged layers are formed on negatively charged N F membranes, such as NTR-7410

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Figure 1 — Separation characteristics of different types of membranes
and 7450, by using adsorption method using polyethyleneimine or quarternary ammonium polyelectrolyte. Negative charge on membrane cause strong Donnan repulsion to divalent anions and not monovalent and divalent cations. Whereas, bipolar membranes showed good ion selectivity for both divalent cations and anions.

Although the mechanism of transport through NF membranes is yet not well understood, its applications are increasing rapidly. Various models have been developed to describe performance of NF membranes. The salt transport through a membrane is governed by different mechanisms such as diffusive flow, convective flow coupled to solvent flow, and convective flow through membrane defects. Performance of membrane systems is governed by fluid dynamics at the interface and chemical potential gradient. These factors can be varied by chemical modification of the membranes.

The composite membranes NTR-729HF and NTR-739HF, having significant chlorine resistance, have been commercialized by Nitto-Denko. It is a poly(vinylalcohol) membrane also having a polyamide composition. NF-40 and NF-70 membranes have a barrier layer which is fully aromatic polyamide and crosslinked. They are anionic in nature which is reflected by their high MgSO4 rejection compared to NaCl rejection. They are low pressure membranes which are used for textile effluents, dye salts and pigments, water softening or purification, and pulp and paper industry. It also has great potential in food and pharmaceutical industries, removal of sulphate from sea water and colour removal from caustic bleach effluents. NF-40 is the tightest membrane and is free from defects. It can be used for the concentration of organics in the molecular weight range of 300 - 1000 g/mol with simultaneous removal of sodium chloride and has high flux due to the presence of relatively charged hydrophilic groups attached to a hydrophobic group. Due to surface active groups, they have improved fouling resistance against hydrophobic organics.

Other NF membranes reported are hydroxyalkyl cellulose crosslinked with a diaidehyde and coated on an asymmetric polyetheramide support with operating at >70°C, useful for separating compounds with molecular weight 300-2000. Interpenetrating polymeric NF membranes developed by polycondensation reaction between trimesoyl chloride and different amines in a dense layer of poly(ethyleneoxide-b-amide). Amines containing ethylene glycol blocks resulted in best performance hydrophobic membranes with a cut-off as low as 600 g/mol and a reasonable water flux. Reinforced dry NF membranes were synthesized from acrylonitrile grafted on cellulose acetate.

Reverse Osmosis (RO) membranes may be transformed into NF membranes useful for separation of dissolved substances from solvents by incorporating inorganic ammonium cation salts before the membrane is cured. Ammonium salt of gluconic acid (2.0 per cent) was used in an aqueous solution of polyamine to impart desirable rejection characteristics. Flux of a composite reverse osmosis or nanofiltration membranes having a polyamide discriminating layer is enhanced by using alkyl amines such as butylamine, cyclohexylamine, and 1,6-hexanediamine, N,N-dimethylethanalamine or benzylamine. By incorporating additives solute rejections can also change leading to conversion of RO to NF membranes.

Most of the nanofiltration membranes are polyamide based containing -NH groups which are susceptible to chlorine attack. The major requirement for a membrane is that its separation characteristics should not change due to oxidative degradation. Membranes should be tolerant to attack by oxidising species and chemical attack. This can be achieved with polyester membranes which are known to be more resistant to oxidative degradation. Also, fouling problem can be reduced by increasing hydrophilicity. Polysulphone backed polyetheramide based resorcinol membranes were synthesized by in-situ interfacial condensation reaction. Such membranes can be used for separation of solutes having molecular weight >300 g/mol. The resultant membranes can be used for dewatering large molecules, separating salts and organic acids from other organic compounds such as sugars and proteins and for desalting. Negatively charged phthalalene based NF membranes based on polyester/polyetheramide with cut-off of higher molecular weight species were also synthesized (Razdan U & Kulkarni S S, applied for Indian Patent, 1999). They can be used for separating higher organics and multivalent anions from monovalent salts. New membranes are being developed which have improved performance, separation characteristics, and higher flux.

NF membranes have introduced a new perspective for applications in the processing of foods, pharmaceuticals, demineralising water, for downstream processes, treatment of industrial effluents, and separation processes.

References