



## Nanofiltration membranes review: Recent advances and future prospects



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### HIGHLIGHTS

- State-of-the-art overview of NF membranes and its approach on membrane fabrication and modification
- The trend and progress in the development and application of NF membranes over the past 5 years
- Fouling and fouling mitigation in the application of NF membrane
- Future direction in NF membrane development

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### ABSTRACT

Nanofiltration (NF) membranes have come a long way since it was first introduced during the late 80's. With properties in between those of ultrafiltration (UF) and reverse osmosis (RO), NF membranes have been used in many interesting applications especially in water and wastewater treatment and desalination. Other applications include those in pharmaceutical and biotechnology, food and non-aqueous types of application. This review will comprehensively look at the recent advances in NF membranes research. Significant development has taken place in terms of the fundamental understanding of the transport mechanism in NF membranes. This has been translated into predictive modeling based on the modified extended Nernst–Planck equation. Similarly various methods have been used to fabricate improved NF membranes especially through interfacial polymerization incorporating nanoparticles and other additives, UV grafting/photografting, electron beam irradiation, plasma treatment and layer-by-layer modification. New applications were also explored in many industries. However fouling is still a prevalent issue that may hinder successful application of NF membranes. Efforts towards NF fouling prevention and mitigation have also been reported. The review ends with several recommendations on the future prospect of NF membranes research and development.

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## 1. Introduction

Nanofiltration (NF) membranes have come a long way since it was first recognized in the late 80's. With properties in between ultrafiltration (UF) and reverse osmosis (RO), NF membranes possess pore size typically of 1 nm which corresponds to molecular weight cut-off (MWCO) of 300–500 Da. NF membranes in contact with aqueous solution are also slightly charged due to the dissociation of surface functional groups or adsorption of charge solute. For example, polymeric NF membranes contain ionizable groups such as carboxylic groups and sulfonic acid groups which result in charged surface in the presence of

a feed solution. Similar to RO membranes, NF membranes are potent in the separation of inorganic salts and small organic molecules. Key distinguishing characteristics of NF membranes are low rejection of monovalent ions, high rejection of divalent ions and higher flux compared to RO membranes. These properties have allowed NF to be used in niche applications in many areas especially for water and wastewater treatment, pharmaceutical and biotechnology, and food engineering. Some commercial membranes, together with their properties and top layer composition as specified by the manufacturer are given in Table 1. Various aspects of NF membranes have been covered in a few review papers [1,2] while Schäfer et al. [3] have written a comprehensive

**Table 1**  
Commercial nanofiltration membranes with specification of the manufacturers.

Membrane	Manufacturer	MWCO (Da)	Maximum temperature (°C)	pH range	Stabilized salt rejection (%)	Composition on top layer
NF270	Dow Filmtec <sup>a</sup>	200–400	45	2–11	>97%	Polyamide thin-film composite
NF200	Dow Filmtec <sup>a</sup>	200–400	45	3–10	50–65% CaCl <sub>2</sub> 3% MgSO <sub>4</sub> 5% Altrazine	Polyamide thin-film composite
NF90	Dow Filmtec <sup>a</sup>	200–400	45	3–10	85–95% NaCl >97% CaCl <sub>2</sub>	Polyamide thin-film composite
TS80	TriSep <sup>b</sup>	150	45	2–11	99%	Polyamide
TS40	TriSep <sup>b</sup>	200	50	3–10	99%	Polypiperazineamide
XN45	TriSep <sup>b</sup>	500	45	2–11	95%	Polyamide
UTC20	Toray <sup>c</sup>	180	35	3–10	60%	Polypiperazineamide
TR60	Toray <sup>c</sup>	400	35	3–8	55%	Cross-linked polyamide composite
CK	GE Osmonics <sup>d</sup>	2000	30	5–6.5	94% MgSO <sub>4</sub>	Cellulose acetate
DK	GE Osmonics <sup>d</sup>	200	50	3–9	98% MgSO <sub>4</sub>	Polyamide
DL	GE Osmonics <sup>d</sup>	150–300	90	1–11	96% MgSO <sub>4</sub>	Cross-linked aromatic polyamide
HL	GE Osmonics <sup>d</sup>	150–300	50	3–9	98% MgSO <sub>4</sub>	Cross-linked aromatic polyamide
NFX	Synder <sup>e</sup>	150–300	50	3–10.5	99% MgSO <sub>4</sub> 40% NaCl	Proprietary polyamide thin-film composite
NFW	Synder <sup>e</sup>	300–500	50	3–10.5	97% MgSO <sub>4</sub> 40% NaCl 20% NaCl	Proprietary polyamide thin-film composite
NFG	Synder <sup>e</sup>	600–800	50	4–10	50% MgSO <sub>4</sub> 10% NaCl	Proprietary polyamide thin-film composite
TFC SR100	Koch <sup>f</sup>	200	50	4–10	>99%	Proprietary thin-film composite polyamide
SR3D	Koch <sup>f</sup>	200	50	4–10	>99%	Proprietary thin-film composite polyamide
SPIRAPRO	Koch <sup>f</sup>	200	50	3–10	99%	Proprietary thin-film composite polyamide
ESNA1	Nitto-Denko <sup>g</sup>	100–300	45	2–10	89%	Composite polyamide
NTR7450	Nitto-Denko <sup>g</sup>	600–800	40	2–14	50%	Sulfonated polyethersulfone

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reference book on NF. Other recent reviews covered the chemical modification of NF membranes [4], fouling [5,6], effect of pH and salt on NF [7], NF for textile dye wastewater treatment [8], and NF modeling [9].

Advances over the last 6 years have shown a significant growth of papers published on NF membranes in many different areas. Based on a quick search using Scopus database, a total of 1642 papers have been published on NF membranes from 2008 to present. As shown in Fig. 1, the main areas of focus in these published papers on NF membranes were in environmental applications (25%), membrane fabrication (19%), miscellaneous topics (11%), fouling (10.68%), desalination (8.95%), pharmaceutical and biotechnology (7.49%), modeling (7.12%), fundamental studies (4%), non-water applications (3.65%), food applications (2.83%) and economics and design (0.55%). Such classifications may assist in understanding the overall view of current research efforts on NF membranes, thereby providing indicators and evidence of new applications and research direction.

The purpose of this paper is to critically review the advances in NF membrane research based on the important focus areas as shown in Fig. 1. The review will start by looking at the fundamental of NF membranes which include membrane characterization and modeling, followed by other important aspects such as membrane fabrication and modifications, applications of NF for environment, desalination, pharmaceutical and biotechnology, food and finally NF membrane fouling and fouling mitigations. The wide scope of the review signified the huge potential of NF for future research and development. The review will then look at the prospective recommendations for future works that should be addressed in order to make significant improvement in NF membrane processes.

## 2. Fundamental of NF

### 2.1. Separation mechanisms

NF is an extremely complex process and is dependent on the micro-hydrodynamic and interfacial events occurring at the membrane surface and within the membrane nanopores. Rejection from NF membranes may be attributed to a combination of steric, Donnan, dielectric and transport effects. The transport of neutral solutes is via the steric mechanism (size based exclusion) and has been well established through numerous studies of UF membranes [10]. The classical Donnan effect describes the equilibria and membrane potential interactions between a charged species and the interface of the charged membrane

[11]. The membrane charge originates from the dissociation of ionizable groups at the membrane surface and from within the membrane pore structure [12–14]. These groups may be acidic or basic in nature or indeed a combination of both depending on the specific materials used during the fabrication process. The dissociation of these surface groups is strongly influenced by the pH of the contacting solution and where the membrane surface chemistry is amphoteric in nature, the membrane may exhibit an isoelectric point at a specific pH [15]. In addition to the ionizable surface groups, NF membranes have a weak ion-exchange capacity and in some cases ions from the contacting solution may adsorb to the membrane surface causing a slight modification of the membrane charge [16,17]. Electrostatic repulsion or attraction takes place according to the ion valence and the fixed charge of the membrane that may vary depending on the localized ionic environment as a result of the aforementioned phenomena. The phenomena of dielectric exclusion are much less understood and there are two main competing hypotheses as to the exact nature of the interaction. These are the so called ‘image forces’ phenomenon [18] and the ‘solvation energy barrier’ mechanism [19]. Both exclusion mechanisms arise as a result of the extreme spatial confinement and nano-length scales that are present in NF membrane separations and are effectively charge based exclusion phenomena. These interactions have been reviewed in detail [20]. Solutes moving in free solution experience drag forces exerted by the solvent flowing through the confined pore structure. The movement of solutes in this confined space is greatly affected by the local environment and the transport of the solute is considered as hindered. Hindered transport can be expressed in terms of both a convective and diffusive element which contributes to the overall transport effect. The fact that the dimensions of the NF active layer are at near atomic length scales, coupled with limitations in current measurement technologies, has delayed a detailed knowledge of the physical structure and electrical properties of real NF membranes and has resulted in uncertainty and significant debate over the true nature of the separation mechanisms [3] and the role of dielectric exclusion is particularly contested [20].

### 2.2. Characterization of NF membranes

There is sufficient evidence now available to conclude that a porous active layer is indeed present in most NF membranes [20] and characterization of these nanopores in terms of pore size and distribution is key to understanding the steric partitioning that may be achieved by a given membrane. This characterization can be achieved using a variety of methodologies, namely;

- Gas adsorption–desorption technique, also known as the Brunauer–Emmett–Teller (BET) method, allows the direct measurement of a pore size distribution [21–23].
- Atomic force microscopy (AFM), allows the direct measurement of pore size and distribution, surface roughness, topography and force interactions between membrane and colloids [24–27].
- Use of neutral solute rejection studies and models, allows the indirect measurement of pore size (and distribution if coupled with other techniques) [28–30].
- Reverse surface impregnation coupled with Transmission Electron Microscopy (TEM), allows the direct measurement of pore size and distribution [31].

Each of the above mentioned methodologies can provide useful information if employed correctly. However, due to the length scales involved and the various imperfections associated with each method, a combination of methodologies is always recommended as well as the application of logical rationale. Measurement of the charge properties of NF membranes is the other key variable required for process understanding and these vary depending on the nature of the contact solution, the concentration and pH. Often these charge properties are

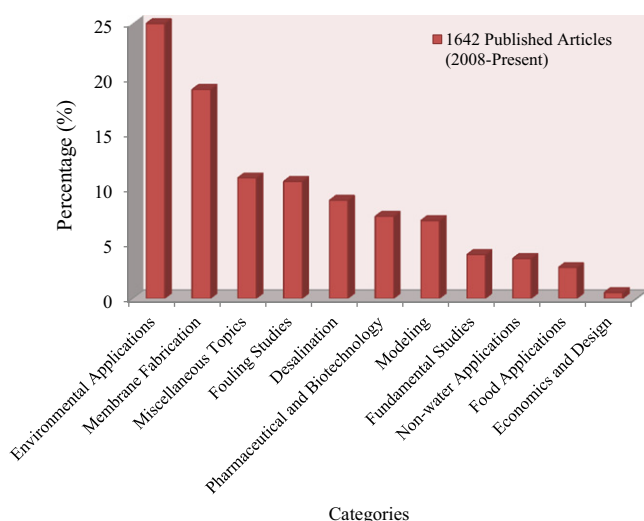


Fig. 1. Categorization of NF membrane process articles published from 2008 to present.

characterized across a range of process conditions using a variety of methodologies, namely;

- Streaming potential allows for the determination of the membrane surface zeta ( $\zeta$ ) potential which is a pseudo measurement of the Donnan potential [32–35].
- Streaming current, analogous to the measurement of streaming potential [36–38].
- Electro-osmosis allows for the determination of the zeta ( $\zeta$ ) potential through the membrane pore, i.e. perpendicular to the membrane surface [39].
- Use of charged solute rejection studies and models allows the indirect measurement of the effective membrane charge density (requires other characterization techniques in-situ) [32,40–42].

Other useful characterization measurements of NF membranes can be performed and the most useful of these being scanning electron microscopy (SEM) for imaging of the membrane surface, membrane cross-section and fouling layers [43–45]. Other techniques include simple methods with relatively low cost equipment such as contact angle for hydrophilicity/hydrophobicity [46–48] to more advanced and increased cost techniques for membrane morphology and structural analysis such as spectroscopy methods [49–52]. In essence there is a plethora of possible characterization techniques available for NF membranes and the key to success is choosing the right technique, with the right resolution for the desired end purpose.

### 2.3. Predictive modeling

The prediction of membrane performance has been an active area of research over the last two decades. During that time, the emphasis has shifted from empirical black box models based on irreversible thermodynamics [53] to models based on the extended Nernst–Planck equation [54] due to the ability of the latter to provide information related to properties of both the membrane and the process stream. The main purpose of such models is to incorporate as much physical realism of the membrane process as possible in order to better match measurable quantities to adjustable model parameters. One should always be mindful that the major limitation of NF modeling is the requirement for characteristic model parameters, such as pore radius and membrane charge, that are not readily measured at the near atomic length scales encountered. The nano-scale phenomena involved in neutral solute and charged electrolyte separations by NF membranes are extremely complex and, as such, are likely to be a rigorous test of any macroscopic continuum description of ion transport and partitioning. Similarly, the development of rigorous physical descriptions (such as molecular dynamics simulations) has been limited due to the lack of detailed knowledge of the physical structure and electrical properties of real NF membranes and process streams. As a direct consequence, developments in modeling have moved in parallel with improvements in the measurement techniques employed for the characterization of NF membranes and process streams, as only then will a check of the appropriateness of model parameters be possible.

The application of the extended Nernst–Planck equation was originally proposed by Schlogl [55] for the description of transport of electrolytes in RO through ion-exchange membranes and is arguably the most commonly used model of modern times. The equation is particularly useful for NF as consideration is given to the mechanisms of transport and the adjustable fitting parameters required are based upon real measurable membrane properties.

The transport of ions is typically described using the extended Nernst–Planck equation

$$j_i = -\frac{c_i K_{i,d} D_{i,\infty}}{RT} \frac{d\mu}{dx} + K_{i,c} c_i V \tag{1}$$

where  $j_i$  is the ionic flux,  $c$  is the concentration,  $V$  is the solvent velocity and  $K_{i,c}$  and  $K_{i,d}$  are hindrance factors to account for the convection and

diffusion inside a confined space. This equation can subsequently be manipulated to derive the full extended Nernst–Planck equation.

$$j_i = -D_{i,p} \frac{dc_i}{dx} - \frac{c_i D_{i,p}}{\gamma_i} \frac{d\gamma_i}{dx} - \frac{c_i D_{i,p}}{RT} V_{si} \frac{dP}{dx} - \frac{c_i D_{i,p}}{RT} z_i F \frac{d\psi}{dx} + K_{i,c} c_i V \tag{2}$$

Eq. (2) represents the full extended Nernst–Planck equation and governs the transport of an ion in solution. In this case the equation has been specifically developed to describe the transport of an ion through a membrane pore, typical of that found in NF and loose RO membranes. In order to solve the transport equation, the solute concentration at the feed side and permeate side,  $c_i(0)$  and  $c_i(\Delta x)$ , of the membrane must be known. The entrance and exit of an ion from such a pore are an equilibrium process and this relationship is expressed as

$$\frac{\gamma_i c_i}{\gamma_i^0 c_i^0} = \Phi_i \exp\left(-\frac{z_i F}{RT} \Delta\psi_D\right) \exp\left(-\frac{\Delta W_i}{k_B T}\right). \tag{3}$$

The first two terms on the right hand side of Eq. (3) are the classic expressions for both steric and Donnan effects respectively [10,11,56] and are generally well accepted throughout the literature [20]. The third term on the right hand side of Eq. (3) represents partitioning as a result of dielectric exclusion. There has been much debate over the nature of this effect and this has been summarized in a recent review [20].

A detailed description of the theory outlined above is reported by Bowen and Welfoot [19]. The theory was then further expanded to consider the pore size distribution of the membrane [57] and then simplified by the consideration of an average pore concentration which allows for the linearization of the transport model and avoids the computationally intense numerical integral required [58]. The solution to the transport equations then becomes a simple arithmetic matrix of equations. The application of this modeling approach to prediction of NF performance was first introduced to a separation of real industrial importance by considering the isolation of N-acetyl-D-neuraminic acid (Neu5Ac) [59], an example of an equilibrium-controlled biotransformation reaction and precursor for the antiviral agent 4-guanidino-Neu5Ac-2-en (zanamivir, Relenza™). In this work, a comparison was made between the full model and the linearized model and the agreement was found to be satisfactory for engineering purposes and the linearized model was then used for prediction of the diafiltration process to remove pyruvate from the reaction mixture. A further example of an industrial separation was provided by considering the recovery of sodium cefuroxime, an important cephalosporin antibiotic having activity against most gram-positive cocci, from spent crystallization liquors [60]. The full-scale recovery process was modeled theoretically and demonstrated that NF was more than adequate for the separation required. An estimate of the industrial scale process operating conditions was made and the addition of the NF process as a hybrid technology to the crystallizer was suggested as a favorable modification to existing plants.

There are many variations on this basic modeling theme in existence, however, in essence they are all intrinsically related to the Nernst–Planck equation and are either variations in solution methodology, simplifications or mild extensions in particular parameters. For example, the model described above is an extension of the original Donnan–Steric–Pore–Model (DSPM) first proposed by Bowen et al. [61]. The version of the NF model described here is more rigorously derived from the extended Nernst–Planck equation by considering a Hagen–Poiseuille flow pattern through the nanopore. The model also includes dielectric exclusion by ion solvation phenomena by incorporation of the Born model into the equilibrium partitioning expression Eq. (3). The simplest description of dielectric exclusion by image forces phenomena (for slit-like pores) was first incorporated into NF models by Vezzani and Bandini [62]. This model was essentially an extension of the original DSPM model by inclusion of a description of dielectric exclusion by image forces derived from the theories of Yaroshchuk [63], aptly called

the DSPM & DE model. This model was further updated by Szymczyk and Fievet [64] to produce the Steric Electric and Dielectric (SEDE) model. This included descriptions of both image forces for cylindrical pores (although these are mathematically intense) and ion solvation via the Born term, i.e. both mechanisms of dielectric exclusion. Both the DSPM & DE and SEDE models suffer from inclusion of the fitting parameter thickness to porosity ratio ( $\Delta x/A_k$ ) which is irrelevant to membrane rejection. Some recent developments and applications of these NF models have been made. Saliha et al. [65] tested the ability of the SEDE model to describe the separation of multi-ionic solutions (3 and 4 ions) by NF and concluded that the experimental solute rejections were not well described when the two dielectric exclusion mechanisms were incorporated into the model. However, the model did work well when only one of the dielectric mechanisms was included, either ion solvation or image forces. This result shows that only one of the dielectric mechanisms is most likely apparent in NF membranes, but either model produces calculated values for the phenomena to the same order of magnitude. Thus, in earnest, either model could potentially be used to describe dielectric exclusion irrespective of which mechanism is fundamentally more appropriate. One concern raised by this work was the failure of the model to appropriately describe the effective membrane charge density. Estimates of the membrane charge density were made from measurements of the tangential streaming potential for the membrane across a range of pH. This methodology substitutes the measured zeta-potential for the Donnan potential at the membrane surface (pore interface) which has never been demonstrated to be truly representative and the authors state that this method provides only a rough estimate of the value. However, this does emphasize that the coupled effect of the membrane charge density and dielectric exclusion phenomenon remain the most elusive aspect in the complete understanding of the surface phenomenon occurring in NF processes.

Deon et al. [66] investigated a novel approach to modeling the membrane charge density by considering the membrane charge density to vary along the length of the pore. The authors named this the Pore Transport Model (PTM) and introduced this variation in charge by means of adsorption isotherms, which were determined beforehand from tangential streaming potential measurements. In some respects this model is a variation on the classic Space Charge Model (SCM) originally proposed by Gross and Osterle [67], which is a far more rigorous (and complex) model that takes into account a radial distribution of both concentration and electric potential within the nanopores. However, in this case the variation in charge is not in the radial direction but is in the axial direction. The authors concluded that the membrane charge evolution with concentration was successfully assessed from streaming potential measurements and Freundlich adsorption isotherms were found to be reliable to calculate the charge densities inside the pores. However, charge densities inside a nanopore have very little physical relevance to tangential streaming potential measurements across the surface of the membrane (as described previously) and adsorption of ions inside a nanopore is simply non-quantifiable. For these reasons, one would have to question the validity of the methodology employed without some form of reliable measurement or alternative verification of the charge density inside the nanopore. The authors also claim that charge distribution along the pores showed a strong influence on the applied pressure, as much as 70% reduction from inlet to outlet for high pressures with the inlet value of charge constant in all cases. This seems physically inconsistent as at higher pressures the rejection of the salt species will increase and cause an increase in the localized concentration at the membrane surface. When this is the case then one would expect that the charge adsorption will change accordingly and therefore the membrane charge density should change since this mechanism is claimed to be occurring inside of the pores. The authors move on to conclude that rejection curves were best described by the model when a constant charge was considered and the charge in question corresponded to the average value of the axial profile. This statement suggests that the best results were obtained from the model when using a constant value for the axial charge density distribution and

clearly contradicts the entire purpose of the work. Clearly there is some confusion, but the principle of a variation in effective membrane charge density in the axial direction is an area worth further investigation and there are some studies that claim deviations from electroneutrality can occur in nanopores [68] which this phenomenon may go some way to support.

Fadaei et al. [69] investigated the use of the DSPM & DE model for the prediction of NF performance in the separation of mono- and divalent ions. The authors concluded that the model was indeed capable of predicting the rejection of symmetric monovalent ions as a function of the membrane charge density when considering both ion solvation and image forces as a dielectric mechanism, which is in contrast to the findings of Saliha et al. [65] detailed above. Dey et al. [70] used the DSPM model to evaluate the separation of sugars and lactic acid from fermentation broths. The model worked well and was extremely accurate (relative error < 0.1 and  $R^2 > 0.98$ ) for the separation and recovery of sugar, lactate and lactic acid when accounting for the dissociation of the lactic acid in solution. Simultaneous recovery and recycle of the unconverted sugars was also demonstrated which significantly improved the process economics. The authors concluded that the model was very useful for the characterization of the membranes, defining the optimum process operating conditions and is now paving the way for scale-up and industrial design of a lactic acid production process using an integrated membrane system. Chakraborty et al. [71] conducted a modeling and simulation study (along with an economic evaluation) for the removal of fluoride from contaminated groundwater. The authors used a linearized approach and demonstrated that this simplification greatly reduced computation time. The effects of transmembrane pressure (TMP), cross-flow rate, pH and concentration on membrane charge density, solute rejection and solvent flux were investigated. The NF membrane process was found to be successful with a high pure water flux (158 LMH) and high rejection, removing more than 98% of the fluoride at a TMP of only 13.7 bar (pH = 10, cross flow rate = 750 L/h). The model compared well with the experimental findings (relative error < 0.1 and  $R^2 > 0.98$ ) and the economic analysis indicated that the membrane filtration system could be promising in purifying fluoride-contaminated groundwater at low cost.

### 3. NF membrane fabrication and modification

One of the keys to the development of NF membrane technology has been in terms of creating better filtration technologies to separate inorganic and organic substances from solution in a liquid. Great advances in NF generally occur due to the creation of better membranes through methods such as interfacial polymerization (IP), nanoparticles (NPs) incorporation, UV treatment and so forth. All these methods are aimed at developing membranes with higher selectivity, rejection tendency and also overcoming fouling issues.

In spite of the significant development of NF applications in various industries, there are still some drawbacks. Van der Bruggen et al. [2] identified several key improvements which are necessary such as reduction in membrane fouling, increase in separation and rejection efficiency, improvement in membrane lifetime and chemical resistance. Typical foulants can be organic solutes, inorganic solutes, colloids, or biological solids. Various studies have used innovative membrane fabrication and modification techniques in order to produce membranes that have significant improvement in terms of fouling propensity.

These techniques can be categorized into IP and grafting polymerization. IP method typically involved phase inversion followed by interfacial polymerization to produce thin-film composite (TFC) membranes. Recent progress included the incorporation of additives such as nanoparticles in the thin film layer which lead to thin-film nanocomposite (TFN) On the other hand, works on grafting polymerization focused more on UV/photo-grafting, electron beam (EB) irradiation, plasma treatment and layer-by-layer (LbL) methods.

### 3.1. Interfacial polymerization (IP)

IP has become a very practical and useful technique when it comes to the generation of thin active film layer for NF and RO membranes. The thin layer on the surface of the membranes is formed through the reaction and copolymerization of two reactive monomers. The development of thin-film composite (TFC) membrane through IP has received attention in recent decade due to significantly better improvement of membrane characteristics such as selectivity and fouling resistance. This technique is easy to apply and the reaction is self-inhibiting through the supply of reactants and an extremely thin film layer can be formed within the 50 nm range. This thin active layer will determine the overall permeability, solute retention and also the overall efficiency of the particular membranes.

There are several types of monomers that have been used in IP process such as bisphenol A (BPA), tannic acid, m-phenylenediamine (MPD), polyvinylamine reacting with trimesoyl chloride (TMC) or isophthaloyl chloride to form the thin active film layer. Based on the study of Tsuru et al. [72], the application of 2-step IP with TMC and MPD would increase the water permeability of the membranes. Abu Seman et al. [73] reported improvement on the antifouling properties and performance of membranes modified by IP where BPA and TMBPA had been used for the membrane development. Effect of varied concentration of monomer BPA in aqueous solution and also effect of IP time were investigated towards the NF polyester TFC membranes [73,74].

Other new types of monomers have also been studied. Among these are: diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and piperazine (PIP) [75]. Li et al. [76] reported a new material, namely polyhexamethylene guanidine hydrochloride (PHGH), which showed good bacteria inhibition properties, and was successfully used to prepare NF membrane by IP method. The medium of reaction was in aqueous phase and thus problems like NPs releasing from the interfacial layer could be solved. In addition, there were other modified monomers such as polyetherimide (PEI) which was modified with amine-functionalized silica NPs. The amino-functionalization of nanosilica was performed by using a silane coupling agent (APDEMS). This study reported that the PEI/modified SiO<sub>2</sub> support would improve the mechanical and thermal stability of the membranes polymer matrix. The high oil rejection performance also indicated that the produced PEI/modified SiO<sub>2</sub> membrane has high potential in application of the dewaxing solvent separation [77].

Recent study from Fan et al. [78] discussed the introduction of inorganic salt i.e. calcium chloride (CaCl<sub>2</sub>) dissolved in aqueous phase and used as an additive during the IP process. The calcium ions were believed to have complexation ability with carbonyl groups which would lead to the formation of loose polyamide layer. The finding showed significant increase in the pure water fluxes of the composite NF membranes with an increase in the concentrations of CaCl<sub>2</sub> added into the aqueous solution [78]. Other additives such as organic acids have also been reported. The effects of various types of organic acids with different structures such as ascorbic acid, citric acid and malic acid and acidic strengths were studied during the fabrication of polysulfone (PSf) NF membrane. The addition of organic acids would improve the retention performance in the separation of xenobiotics [4-dinitrophenol (DNP)] and p-nitrophenol (PNP) [79].

Recent strategy on metal-alkoxide-assisted IP was also reported for the synthesis of inorganic-polyamide nanocomposite membranes. The metal alkoxides applied were titanium tetraisopropoxide, bis (triethoxysilyl)ethane and phenyltriethoxysilane. These membranes exhibited great improvement in terms of membrane formation and permeability performance as the addition of greater amounts of metal alkoxide to the hexane solution increased both pore size and water flux [80].

Other methods that have been introduced to enhance membrane performance during interfacial polymerization included surface

fluorination of polyamide membrane [81], limiting the thickness of membranes [82], facile zwitterionization [83], hyper-branching of polyester [84], and hybridization via in-situ exfoliation of Mg/Al hydrotalcite [85].

#### 3.1.1. Nanomaterials

Nanoparticles (NPs) have received much attention recently due to their unique properties in terms of photoemission, antimicrobial and catalytic activity. NPs incorporated membranes have gained attention due to their ability to increase membrane permeability, mechanical properties, hydrophilicity, and selectivity in some cases. The NPs which are commonly reported in NF membrane fabrication are titanium dioxide (TiO<sub>2</sub>), silica, silver, and zinc oxide (ZnO).

For TiO<sub>2</sub>, recent study reported on the fabrication of NF composite membranes with polyethyleneimine-nanoparticle hybrid active layer through mineralization. Inorganic precursors such as tetraethoxysilane (TEOS) and tetra-n-butyl titanate (TBOT) were applied respectively in the preparation of PEI-silica and PEI-titania composite membranes [86]. The presence of both NPs resulted in an enhancement of the thermal and structural stabilities. As a result of the hybridization and cross-linkage, the membrane performances such as solvent resistant property and solvent flux were improved as well as prolonging the operational stability. It was suggested that hybrid nanomaterials were much better compared to the normal application of NPs. The functionalization of TiO<sub>2</sub> with immobilized laccase also gained attention due to its excellent bio-catalytic performance. The stability and activity of the laccase enzyme could be improved due to the covalent bonding between the immobilized enzyme and TiO<sub>2</sub> membranes. It was claimed that the membrane managed to enhance the BPA removal efficiency and thus providing an alternative to conventional wastewater treatment process [87]. Fig. 2 showed the structure of TiO<sub>2</sub> coated bio-catalytic membrane.

Recent study also demonstrated the use of Boehmite NPs as a new nanofiller for the fabrication of PES membranes [88]. As shown in Fig. 3, Boehmite is an aluminum oxide hydroxide ( $\gamma$ -AlOOH) particle which consists of extra hydroxyl groups on its surface. Boehmite can be considered as an advanced material possessing highest hydrated surface and hydrophilicity which would enhance membrane performance. Another new material being applied in thin-film nanocomposite (TFN) membrane was MCM-41 silica (as depicted in Fig. 4), a type of mesoporous silica developed recently [89]. The membrane performances such as water permeability, roughness and zeta potential were significantly improved due to its porous characteristics.

Apart from application of single type of NPs, the combination between two types of NPs may also lead to significant improvement of the membranes. For example, a novel PES nanocomposite membrane was produced using polyaniline and iron (II, III) oxide [PANI/Fe<sub>3</sub>O<sub>4</sub>] NPs prepared by in situ chemical oxidative polymerization. The essential properties of PANI and Fe<sub>3</sub>O<sub>4</sub> which could help in heavy metal removal and natural organic matter elimination, were shown to give great enhancement for Cu(II) removal from water [90]. Fig. 5 showed the core-shell structure of PANI/Fe<sub>3</sub>O<sub>4</sub> NPs. Other studies included the hydrophilic composite membrane for simultaneous separation and photocatalysis being fabricated by incorporating TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> NPs [91].

Stawikowska et al. [92] reported on the approach of nanoprobe imaging technique to improve the microscopic imaging of nanostructured NF membranes. The introduction of high electron contrast osmium dioxide (OsO<sub>2</sub>) NPs in the membrane pore structure was successful in assisting the electron microscopy technique to obtain a good magnification approaching macromolecule level [92].

Other interesting types of nanomaterials introduced during membrane fabrication included functionalized multi-walled carbon nanotubes [93], halloysite nanotubes [94], and electrospun nanofiber [95]. By applying all these new nanomaterials in membrane fabrication, the goal towards major improvement of NF membrane and other types of membranes can be achieved in the near future.

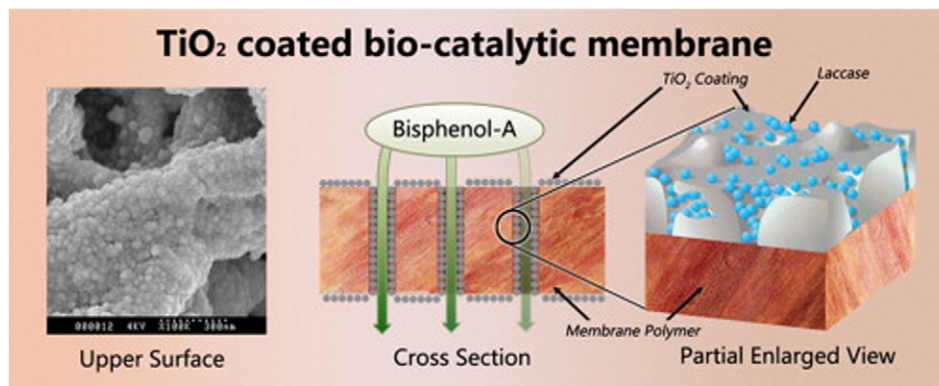


Fig. 2. Structure of  $\text{TiO}_2$  coated bio-catalytic membrane [87].

### 3.2. Grafting polymerization

#### 3.2.1. UV/photo-grafting

UV-assisted grafting polymerization is performed by the chemical bonding between membrane substrate and the active layer without affecting the bulk polymer. Therefore, it has been applied widely in various surface modification works. Recently high flux positively charged NF membranes prepared by UV-initiated graft polymerization with methacryloethyl trimethyl ammonium chloride (DMC) onto PSf UF membrane was reported [96]. Fig. 6 showed the chemical structure of DMC, PSf, and proposed mechanism for the grafting of PSf with DMC. In addition, the positively charged NF membranes via UV grafting on sulfonated polyphenylenesulfone (sPPSU) was shown to have high efficiency in removal of textile dyes from wastewater [97].

For photografting, the performance of NF membranes having a strong polyelectrolyte hydrogel as selective barrier layer prepared by photo-grafting methods was investigated at varied functionalization conditions such as MWCO of the base membrane, monomer concentration, crosslinker fraction, UV irradiation intensity and time [98]. Similarly surface modification of cardo polyetherketone UF membrane could be performed by photo-grafted copolymers in order to obtain NF membranes [99]. The method combined both UV irradiation followed by an in situ graft co-polymerization of water soluble monomers on cardo polyetherketone (PEK-C) membranes.

#### 3.2.2. Electron beam (EB) irradiation

High-energy EB irradiation is an easy and good approach in penetrating into polymer layer. Active sites on the polymer could be formed effectively and no special additives were required during the irradiation process. The mechanism of EB radiation could be visualized through the schematic diagram in Fig. 7 whereby the crosslinking reaction that forms a three dimensional network would result in the decrease of the membrane pore size [100].

Linggawati et al. [101] reported on nylon-66 membranes which act as a typical semicrystalline polymer and subsequently could be crosslinked by EB irradiation to form NF membranes. Nylon-66 contains functional groups which form hydrogen bonds with inorganic silica networks and allow the creation of hybrid membranes. With improvements in membrane pore size and the ratio of membrane thickness to porosity, nylon-66 membrane exhibited satisfactory permeability, excellent removal of neutral solutes and improved rejection of divalent ions [101].

Recent work on EB irradiation showed the fabrication of novel NF hollow fiber membranes by grafting of 2-acrylamido-2-methylpropanesulfonic acid (AMPS) onto a PSf support. The irradiation dose was varied from 20 to 100 kGy by controlling the number of passes. This membrane demonstrated high efficiency in removing hexavalent chromium,  $\text{Cr(VI)}$  ions which were mutagenic and carcinogenic. Besides, it was indicated that the degree of grafting which led to high

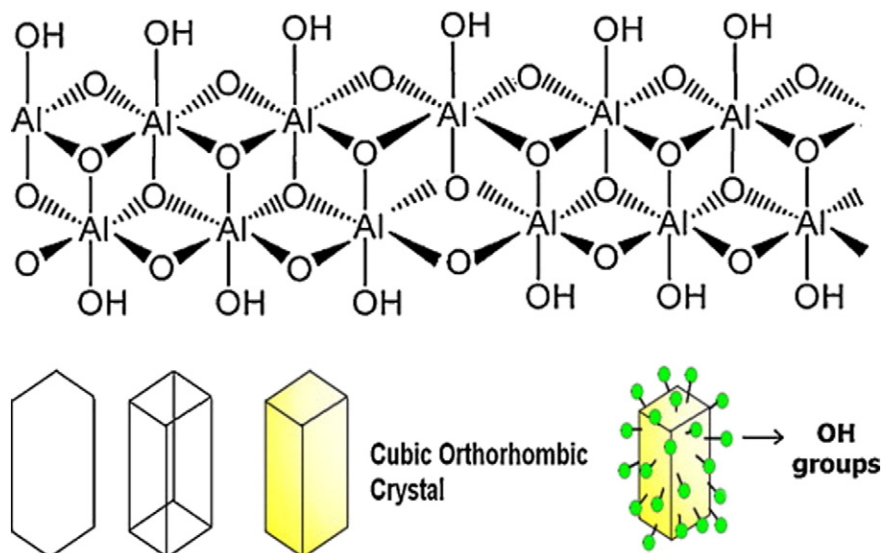


Fig. 3. Chemical structure of Boehmite nanoparticles [88].

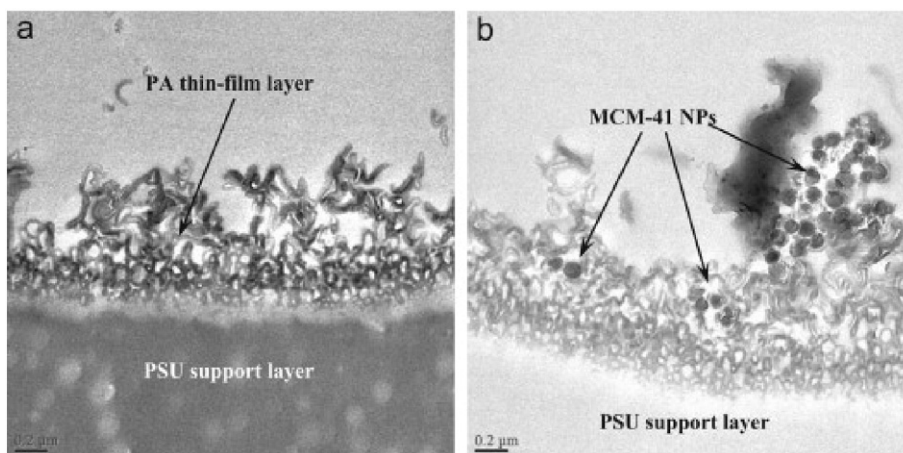


Fig. 4. TEM of PSU membrane with MCM-41 nanoparticles [89].

negative charge density would improve the NF performance at a relatively large pore size [102].

### 3.2.3. Plasma treatment

Plasma treatment is another effective way to increase the surface hydrophilicity and wettability as polar groups can be introduced on the surface. It is an advantageous method as only physical and chemical properties of polymeric surface will be altered without changing the bulk properties.

Plasma surface modification is a process whereby nitrogen-containing plasma can be applied to polymer membrane to generate nitrogen functional groups that may have increased hydrophilicity with decreased membrane fouling [103]. Other studies included the modification of polymeric membranes via plasma for NF of aqueous solution containing organic compounds [104]. Recently, a new negatively charged NF membrane has been prepared by grafting of AMPS on the PSf hollow fiber UF membrane using two-step plasma method. This plasma-induced graft polymerization can result in the permanent modification of polymer surfaces by grafting monomers onto a plasma-treated polymer [105]. Figs. 8 and 9 showed the simplified diagram for plasma treatment process and schematic diagram of plasma-induced graft polymerization respectively.

### 3.2.4. Layer-by layer (LbL)

The effects of LbL surface modification on characteristics and performances of cellulose acetate NF membranes prepared by modification

through adsorption of alternated layers of sodium alginate (ALG) and chitosan (CHI) was recently studied. From the result, it was reported that 15 bilayers were the optimal condition for the best performance of membranes [106]. Recent study by Ng et al. [107] demonstrated the development of NF membranes with high salt selectivity and performance stability by LbL method. Modification of 5 polyelectrolyte bilayers on the PES20 membranes could demonstrate similar performance with those with more than 50 bi-layers. Thus, the application of polyelectrolyte multilayers provides an alternative way in fine-tuning the membrane performance [107].

To date, two crosslinking methods, namely amine coupling and silane coupling, were introduced in LbL assembled NF membranes. Amine coupling was the crosslinkage between amino groups on cationic polyelectrolytes and carboxyl groups on anionic polyelectrolytes while silane coupling involved the reaction between oppositely charged polyelectrolytes on silane groups. By applying these two methods of crosslinkage, the stabilization on the LbL layer under the high ionic strength conditions and chlorine treatment could be improved. Fig. 10 showed the formation of LbL layer through amine coupling and silane coupling [108].

Apart from the normal multilayers method, novel dual-layer polybenzimidazole/polyethersulfone (PBI/PES) NF hollow fiber membranes were fabricated for heavy metals removal in wastewater. The outer layer was PBI which was chemical resistant and the inner layer would be PES/PVP. This membrane was developed by using a dry-jet wet phase inversion process and it exhibited superior rejections towards various types of heavy metal ions [109].

Other recent works showed the use of graphene oxide (GO) in membrane fabrication. Hu and Mi [110] reported on the development of a novel type of water purification membrane by LbL method. The electrostatic interaction would assist in the interconnection with positively charged poly(allylamine hydrochloride) (PAH) and the negatively charged GO nanosheets. The membrane exhibited high sucrose rejection and was considered suitable for water treatment process with low ionic strength.

### 3.2.5. Other grafting methods

Other novel grafting methods were also reported recently in the development of NF membrane. Based on a study from Mustafa et al. [111], Grignard grafting (GR) and phosphonic acid (PA) grafting or phosphorylation were introduced to overcome fouling problems in ceramic NF membranes. This study combined both NPs and grafting methods. TiO<sub>2</sub> membranes would undergo functionalization of alkyl or phenyl groups by organometallic Grignard reagents and alkyl PA by methyl phosphonic acid (MPA), phenyl phosphonic acid (PPA), and hexadecyl phosphonic acid (HDPa). The direct bond or complex bond functionalization through GR and PA grafting on the membrane surface would greatly

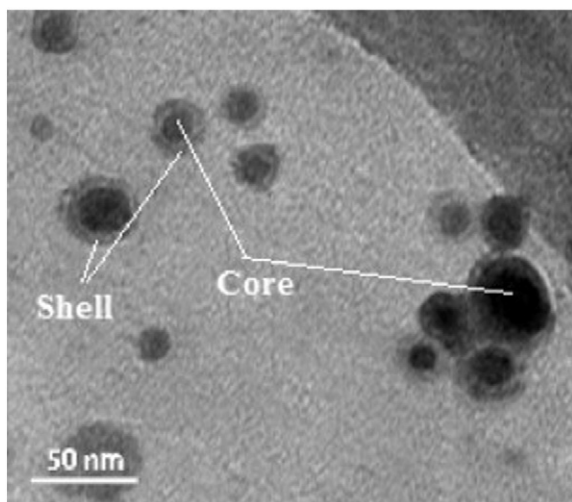


Fig. 5. Core-shell structure of PANI/Fe<sub>3</sub>O<sub>4</sub> nanoparticles [90].



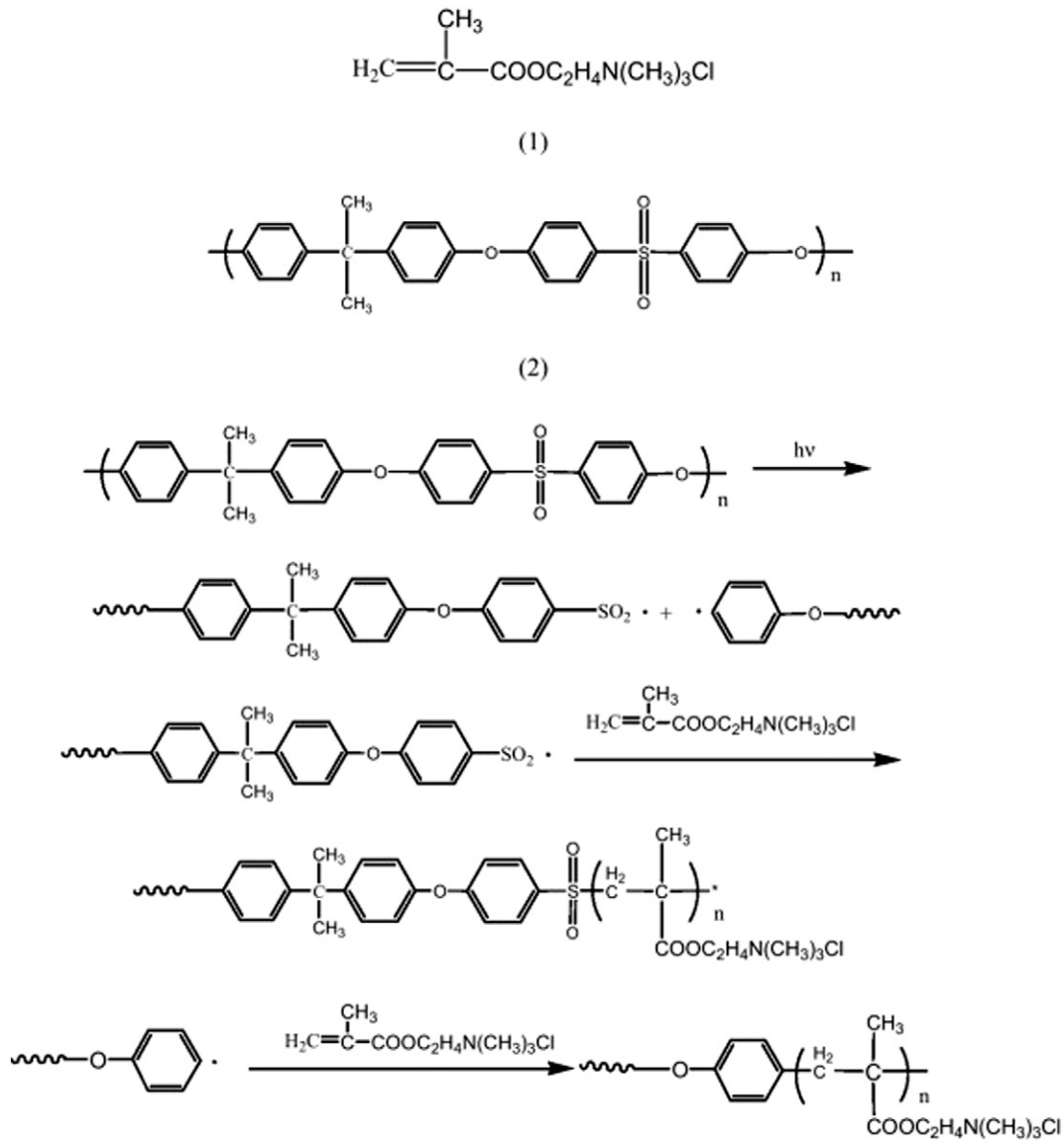


Fig. 6. Chemical reaction of UV-initiated graft polymerization [96].

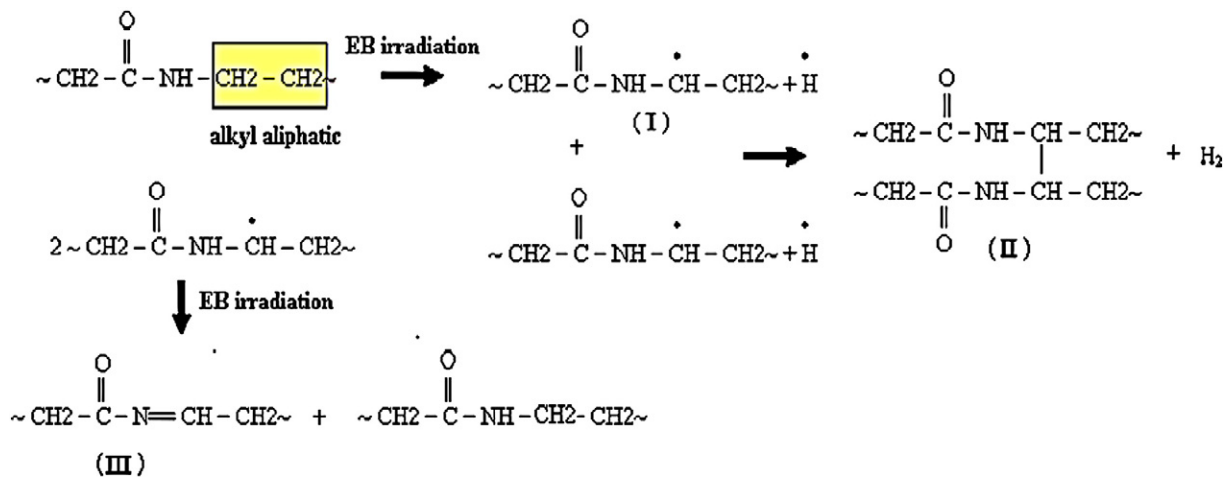


Fig. 7. Radicals of EB irradiated nylon-66 combine intramolecularly to form crosslink [100].

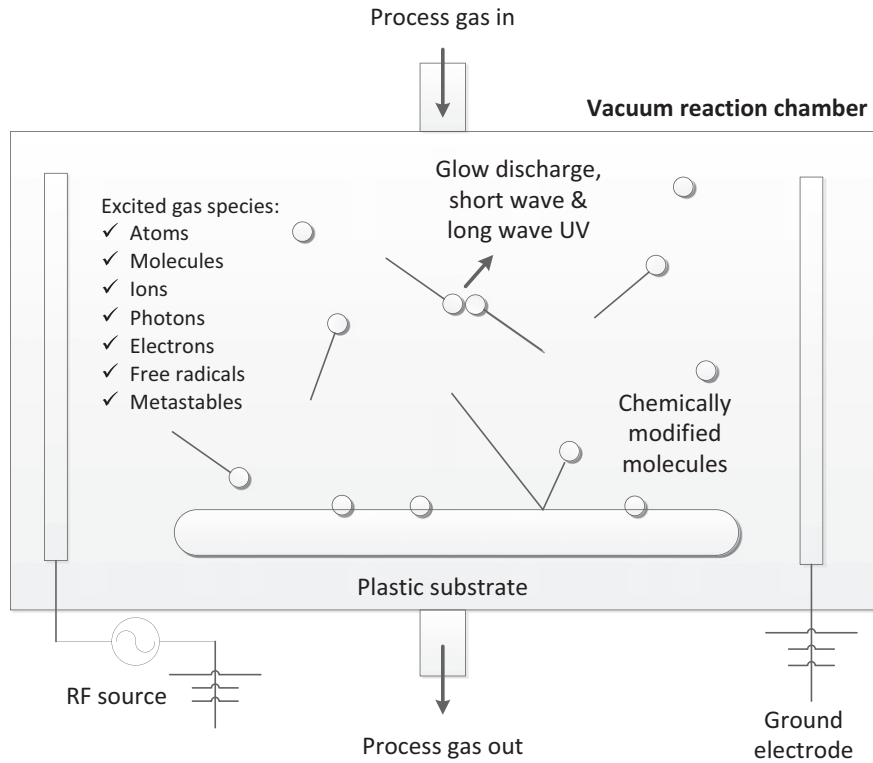


Fig. 8. Simplified diagram for plasma treatment process [274].

enhance antifouling properties. Thus, it would bring a remarkable effort to produce membranes with superb antifouling properties as well as contributing to some separation processes.

Recently, a type of novel positively charged composite NF membranes was prepared by using polydopamine (PDA) as a transition layer and also surface grafting by PEI on PES support [112]. PDA is an attractive material due to its powerful adhesion characteristic. The reaction between PEI and PDA on the membrane surface was mainly based on the Michael addition reaction with the quinone functional

groups of the PDA layer. The PEI/PDA membrane (Fig. 11) exhibited good rejection of the cationic dye. It was a controllable approach whereby several parameters could be altered in order to pursue desired membranes performance and thus it would be of great interest in the application of positively charged membranes on diverse substrates.

Diamine cross-linked polyimide membranes were known for the performance in solvent resistant NF. The recently developed in-situ crosslinking method eliminated the usage of methanol and subsequently was replaced by various diamine crosslinkers such as ethylenediamine

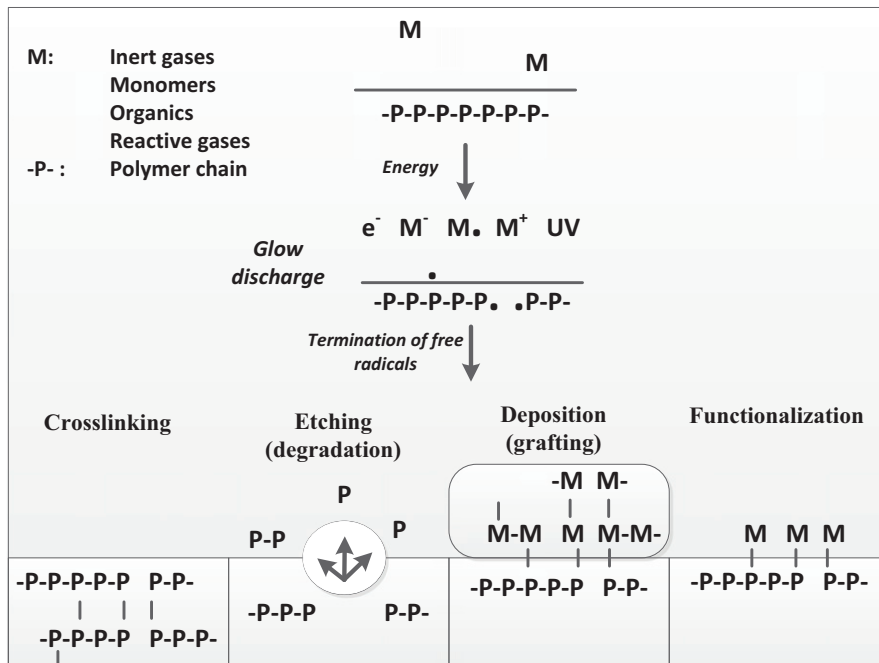


Fig. 9. Schematic diagram of plasma-induced graft polymerization [274].

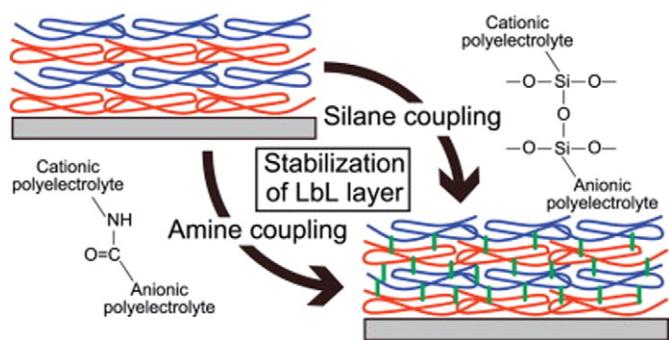


Fig. 10. Layer-by-layer through amine coupling and silane coupling [108].

(EDA), 1,6-hexanediamine (HDA) and p-xylylenediamine (XDA). The membranes obtained were excellent in terms of permeability as it showed 10 times higher fluxes when compared with commercial membranes [113]. Another study reported on the crosslinkage between sulfated CHI crosslinked with hexamethylene diisocyanate to develop amphoteric composite membranes for NF [114].

#### 4. NF membrane applications

##### 4.1. Environmental application

High pressure driven NF membrane process is capable in generating large amounts of high quality water. The excellent removal capacity of contaminants, decreasing prices for the membranes, lower energy consumption and enhanced membrane lifetimes as compared to RO have led to the wide acceptance and popularity of NF worldwide [115]. NF is applied by many researchers in environmental application for the treatment of ground water, surface water and wastewater reclamation. Apart from the typical purpose to remove divalent salts and small organics, recent studies have shown that NF has increasingly being used for many new interesting applications such as for removal of arsenic (As), persistent organic pollutants (POPs), pharmaceutical active compounds (PhACs) and hormones.

##### 4.1.1. Groundwater

The problem of As in groundwater has received increasing attention worldwide. For NF, different studies targeted towards As removal can be found [116–122]. However, most of these studies were performed at

laboratory or bench scale, using synthetic water contaminated with As as model solution. Recently, Sen et al. [121] studied As removal from groundwater naturally contaminated at laboratory scale. Nevertheless, there are few studies performed at pilot-plant scale; however, all of them performed in artificially contaminated waters [116–120,122]. Saitua et al. [123] studied the As (V) removal by TFC polyamide NF membrane (NF-300) pilot-plant from naturally contaminated groundwater. The membrane showed the same selectivity for both artificially contaminated groundwater and naturally contaminated groundwater.

Effective groundwater As (both in oxidation states of 3+ and 5+) separation by NF membrane was studied by Sen et al. [121] through pre-oxidation in membrane-integrated hybrid treatment system converting As (III) into As (V). However, the issue of As rejects disposal was not addressed. Attempts have been made by Pal et al. [124] in evolving a continuous treatment scheme with a sustainable solution to fill this technology gap. As revealed in Fig. 12, this novel approach integrates a largely fouling-free and highly selective NF membrane module with an upstream pre-oxidation unit for conversion of As (III) into As (V) and a downstream stabilization unit for effective stabilization of As rejects. This membrane-integrated hybrid system resulted in continuous removal of >98% As from water that contained around 190 mg/L of total suspended solid (TSS), 205 mg/L of total dissolved solid (TDS), 0.18 mg/L of As and 4.8 mg/L of iron at pH 7.2. The used flat sheet cross-flow NF membrane module yielded a high flux of 144–145 L/m<sup>2</sup> h at TMP of 16 kgf/cm<sup>2</sup> without frequent membrane replacement.

NF membrane has also been assessed as a novel approach integrated into fertilizer drawn forward osmosis (FDFO) desalination by Phuntsho et al. [125], either as a pre-treatment or post-treatment, to reduce the nutrient concentrations in final product water and thereby allow the direct use of the product water for fertigation without further dilution. NF as pre-treatment or post-treatment was found effective in reducing the nutrient concentrations in the final product water from the FDFO desalination process using brackish groundwater (BGW) sources with relatively low TDS. At higher TDS concentrations, the product water still requires further dilution or post-treatment before fertigation. A comparative study indicates that NF post-treatment could be more advantageous in terms of process efficiency and energy consumption.

The research on pesticide removal is extensive [126–131]. The main body of research on pesticide removal with membranes has looked at pesticides used for pest control. However, new compounds called pesticide transformation products (PTPs) have been found in real groundwater during percolation from surface to groundwater aquifer, and

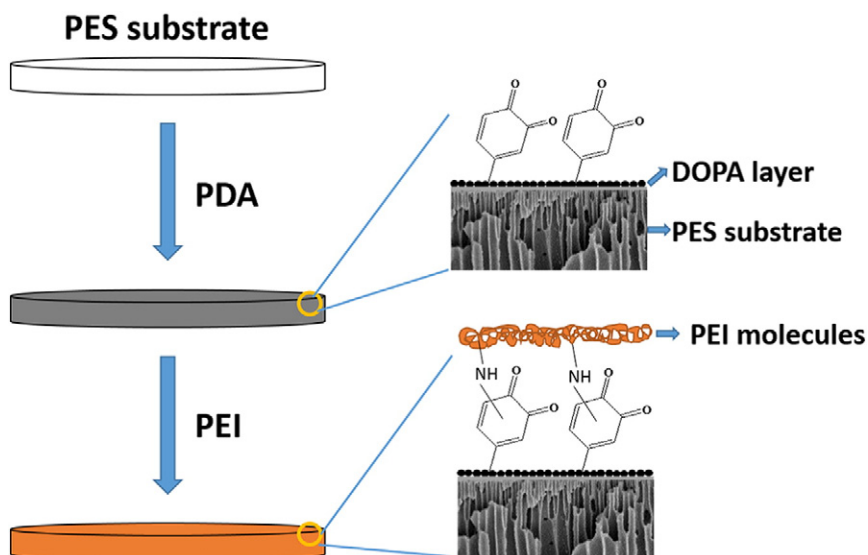


Fig. 11. PEI/PDA membrane [112].

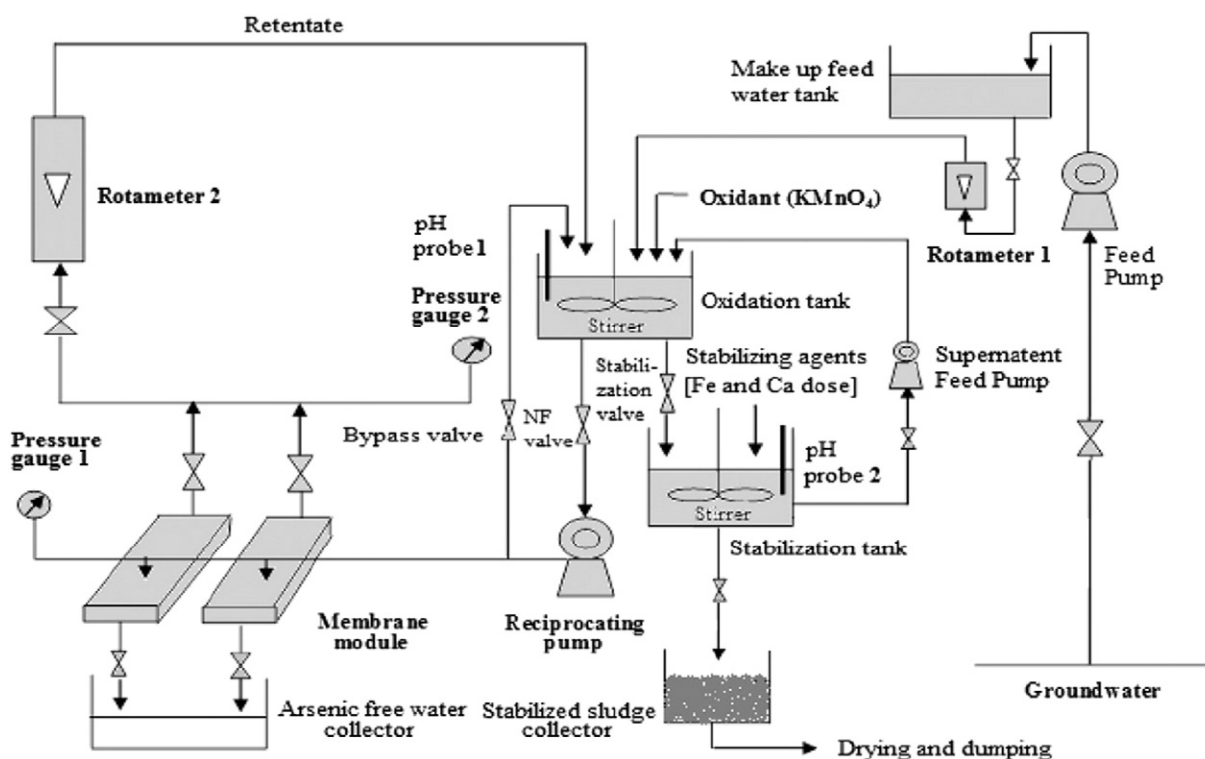


Fig. 12. Schematic diagram of the membrane-integrated hybrid process for removal of As from water and its stabilization in solid matrix [124].

therefore different from the pesticides that dominate literature. The applicability of NF/low pressure reverse osmosis (LPRO)/RO membrane filtration for the treatment of groundwater polluted with pesticides and PTPs has been studied by Madsen and Søgaard [132]. It was found that NF99HF membrane was capable on rejecting the regular pesticides >90% but did not give satisfactory PTPs' rejection, due to the smaller size. Therefore, it was necessary to employ LPRO membrane to obtain sufficient removal of these compounds [132].

The softening of ground water has also been widely studied by many investigators [133–135]. Galanakis et al. [136] investigated the NF of BGW using commercial polypiperazine membrane (NF99), in which the studies reporting NF of BGW using polypiperazine materials are very limited. High hardness retention coefficients (70–76%) and satisfactory permeate fluxes (15–47 L/m<sup>2</sup> h) were found at low TMP (6–10 bar) with high mineral fouling resistance (flux recovery values between 93 and 98%). However, due to low salinity removal (44–66% for BGW), this application is restricted for samples possessing salinity less than 1100 mg NaCl/L.

Chakraborty et al. [71] studied the removal of fluoride from some fluoride-affected areas in groundwater of Eastern India (Asanjola village, Rampurhat block 1, Birbhum, West Bengal, India). In addition to the membrane performance under varying operating condition, modeling and simulation study along with economic evaluation was also carried out by Chakraborty et al. [71]. This has enabled more confidence in the implementation of membrane-based technology in removing fluoride from contaminated groundwater in the vast affected areas of the world [71]. The removal of radium, Ra<sup>2+</sup><sub>226, 228</sub>, uranium, as uranyl cation, UO<sub>2</sub><sup>2+</sup>, or carbonate complexes, UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> and UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup>, and radon, Rn<sub>222</sub>, from contaminated groundwater was investigated by Gamal Khedr using RO (AD4040F) and NF (HL4040F) in comparison with the most common conventional methods of ion exchange resins (IERS), chemical precipitation/softening, coagulation, and adsorption on surface active media [137]. Only NF, parallel to RO, showed steady, high rejection of all isotopes which attained 99% without interference of similar ions, regeneration, or subsequent filtration but with lower water desalination than RO.

#### 4.1.2. Surface water

The focus for NF in surface water application has been on water softening and increasingly for removal of POPs such as pesticide, disinfection by-products, and hormones. Fang et al. [138] developed novel composite NF hollow fiber membranes under low operating pressure, which were desirable for water softening. The resultant membrane possesses a positively charged thin-film selective layer with pure water permeability (PWP) of about 17.1 L/m<sup>2</sup> h bar and a MWCO of 500 Da. With combined separation mechanisms of Donnan exclusion and steric hindrance, it was able to achieve MgCl<sub>2</sub> (1000 ppm) and MgSO<sub>4</sub> (1000 ppm) rejection of 96.7% and 80.6%, respectively, under 2 bar operating pressure. In addition, for 3000 ppm total dissolved salt (TDS) feed stream containing salt mixtures, the membrane rejections for Mg<sup>2+</sup> and Ca<sup>2+</sup> ions were found to be around 90% while the water flux was about 20 L/m<sup>2</sup> h at 2 bar pressure, suggesting the potential of the newly developed composite hollow fibers for effective water softening application. As an extension of these composite NF hollow fiber membranes, mixed polyamide-based composite NF hollow fiber membranes were fabricated and investigated by Fang et al. [139]. The resultant hollow fiber membrane was found to exhibit improved low-pressure water softening performance comparing to composite NF hollow fibers membranes with PWP of 18.2 L/m<sup>2</sup> h bar and a MWCO of 380 Da. Besides, under the operating pressure of 2 bar, the membrane was able to achieve rejection of 96.3% and 93.8% for MgCl<sub>2</sub> (1000 ppm) and MgSO<sub>4</sub> (1000 ppm) feed solutions, respectively.

The removal of natural organic matter (NOM) and disinfection by-products' (DBPs) precursors produced in chlorinated water has been studied by many investigators as chlorine is the most widely used disinfectant in the world [140]. However, studies on the evaluation of ceramic NF membranes are relatively scarce. Sentana et al. [141] studied the effects of pressure, conductivity and pH on the reduction of flow and the formation of the DBPs of two ceramic NF membranes with a MWCO of 450 Da (NF450) and 1000 Da (NF1000) in removing the dissolved organic carbon (DOC) from natural water. The results of the study indicated that NF450 membrane displayed greater elimination efficient than NF1000 with greater flux reduction. An increase in operating pressure improved the efficiency of DOC removal and reduced the

formation of DPBs. Alternatively, as the conductivity increased, the flow through the membranes decreased slightly. At low pH values, the loss of flow increased slightly and the efficiency of the elimination of DOC decreased. The values of trihalomethanes' (THMs) rejections at pH 8.3 were 79% and 58% for NF450 and NF1000 respectively, and these values decreased to 65% and 40% at pH 4.5.

PhACs are persistent throughout the process used to treat drinking water [142]. However, drinking water treatment plants are not specifically designed to remove PhACs and there are very few NF studies on PhACs removal from drinking water and surface water [143,144]. Vergili [145] study was designed to investigate the performance of a flat sheet NF membrane (FM NP010, Microdyn-Nadir, GmbH, Germany) in cross-flow filtration equipment for the removal of three PhACs, namely carbamazepine (CBZ), diclofenac (DIC) and ibuprofen (IBU) spiked in water taken from a drinking water treatment plant using surface water. The laboratory results of this study showed that the overall rejection was approximately 31–39% and 55–61% for neutral CBZ and ionic DIC and IBU PhACs, respectively. High organic matter removal in combination with a moderate PhACs removal thus makes the FM NP010 membrane particularly attractive for surface water treatment.

Nowadays xenobiotic production and disposition considerably increase in the environment, and many of them become contaminants in surface water [146]. Among them, there are herbicides based in glyphosate (N-phosphonomethyl glycine), which are the most used in the world, and at the time, main rivers and superficial water contaminants [147]. Among the alternative processes studied for active glyphosate removal, however, none of the studies have considered the removal of adjuvants (surfactants) present in commercial formulations, which can be as much or even more toxic than glyphosate [148]. Saitúa et al. [149] studied the treatment of synthetic and river water contaminated with glyphosate commercial formulations, using a NF pilot-plant. Process efficiency was evaluated by permeate analysis with acute toxicity tests with fish. The results showed that, distilled water permeates with concentrations five times above the lethal doses (48 mg/L) did not present toxicity and glyphosate removal was >80%, despite its molecular weight (MW) is lower than membrane MWCO (168 and 180 g/mol). This could be predominantly associated with Donnan exclusion and dielectric exclusion mechanisms due to the solute high charge density. Studies with river water matrix showed the same membrane behavior with a slight decrease in permeate flow and rejection. This turns NF into

a viable alternative for potable water treatment for surface water contaminated with glyphosate commercial formulation.

In recent years, attention has been focused on the effective removal of hormones from drinking water sources [150,151]. Different studies showed the possibility of using NF in the removal of hormones, and demonstrated that the rejections achieved for these compounds are largely controlled by adsorption of the compounds to the membrane [152–154]. A study focused on the validation and comparison of integrated NF and low pressure direct and indirect UV photolysis was conducted by Pereira et al. [155] for drinking water treatment in order to guarantee effective removal of different hormones with endocrine disruption capabilities (mestranol, octylphenol, nonylphenol, progesterone, estrone, estriol, 17 $\alpha$ -ethynylestradiol, and  $\beta$ -estradiol) from real water sources as shown in Fig. 13. The integration of NF to low pressure ultraviolet direct or indirect photolysis had good results in reducing the level of turbidity as well as the micropollutant contamination levels in drinking water supplies. The use of NF in the treatment of surface waters spiked with different hormones allowed the rejection with efficiencies higher than 71% (except estriol 38%). Low pressure indirect photolysis with the addition of 100 mg/L hydrogen peroxide was also found to be profoundly degraded the selected hormones, achieving 74% for all hormones, except nonylphenol (55%). This integrated process (NF followed by direct photolysis or indirect photolysis) extremely efficient to remove all the target hormones from a real surface water matrix and thus, guarantees the production of water with high chemical quality. Extensive study has been done by Lopes et al. [156], in introducing this combined process with NF and low pressure UV irradiation at pilot scale, in operational surface water treatment plant allocated in Vale da Pedra, Portuguese and treats surface water abstracted from Tagus River in Valada Tejo. It was found that the integrated system was also efficient in delivering high quality water from natural surface water with recovery rate as high as 91%.

NF technologies are attracting great interest for their potential to solve water shortage and water quality problems. From an environmental point of view, however, NF is an energy intensive process. The use of NF powered by renewable energy (RE) is an increasing trend, especially in arid and semiarid areas due to the potential of these areas for RE production [157]. It is also an interesting alternative for those remote locations far away of electricity grids. García-Vaquero et al. [158] compared the removal of trace organic compounds in municipal drinking water

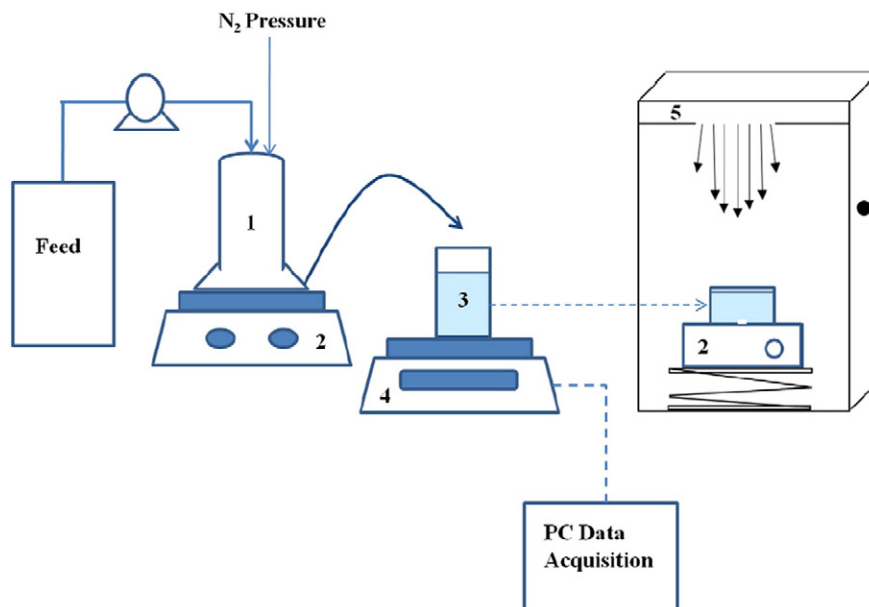
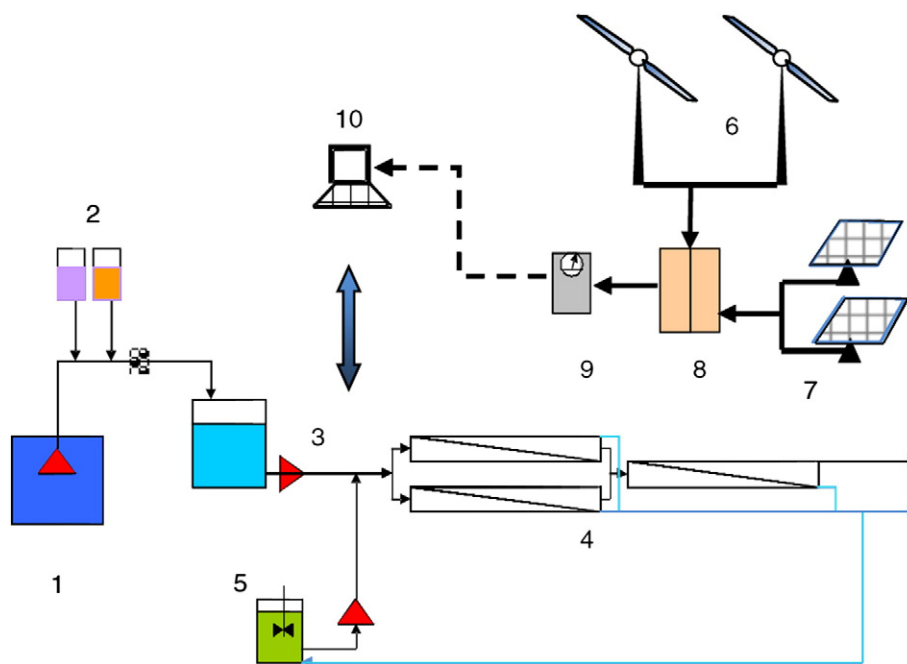


Fig. 13. NF and low pressure UV batch systems used; 1. NF module (metcell); 2. Mixers; 3. NF permeate; 4. Scale; and 5. Low pressure UV lamp housing [155].



**Fig. 14.** Scheme of the pilot-plant showing RE and NF units. 1: treated drinking water tank; 2: antiscaling and sodium bisulfite tanks; 3: high pressure pumps; 4: pressure vessels; 5: flushing system; 6: windmills; 7: PV field; 8: battery; 9: CC/DC inverter; and 10: control [158].

treatment plant (MDWTP) and in a NF pilot-plant powered by RE (wind mills and photovoltaic (PV)) resources abundant in Andalusia as shown in Fig. 14. Results obtained from the experiments show that the applicability of this kind of containerized pilot-plant, powered exclusively by a hybrid RE system through efficient removal of color and turbidity (100%), DOC (93%), ions (97%), metals and metalloids (ranging from 80%–100%), THMs (53%), boron (17%) and pharmaceuticals (varied from 15%–100%) beyond the conventional treatment.

#### 4.1.3. Wastewater

NF has been proven to eliminate pharmaceuticals and personal care products (PPCPs) that are often hardly removed in most conventional wastewater treatment plants [159,160]. Zaviska et al. [159] developed a new type of ceramic NF membrane bioreactor (NF-MBR) for the treatment of acclimated activated sludge artificially doped by two pharmaceutical compounds (cyclophosphamide and ciprofloxacin). The results showed a high chemical oxygen demand (COD), TSS and color removal confirming the potential of NF-MBR. Lin et al. [160] compared one RO (XLE) and two NF (NF90 and NF270) membranes for the removal of six PPCPs including CBZ, triclosan (TRI), IBU, sulfadiazine (DIA), sulfamethoxazole (SMX) and sulfamethazine (SMZ). The high PPCPs' rejection (90–100%) by XLE without the influence of solution pH implied that size exclusion was the dominating mechanism. For NF90, size exclusion and electrostatic repulsion worked synergistically so that PPCPs' rejection increased with the increase of pH. As for the loose NF270, electrostatic repulsion was the dominant mechanism, which was validated by the increased rejection of TRI when pH increased from 8 to 10.

However, a real wastewater always contains complex matters which are difficult to be separated. Röhrich et al. [161] studied the use of submerged NF flat sheet module which can be run at comparable low pressures (0.7 bar) to remove pharmaceuticals from the municipal wastewater treatment plant (MWTP) in Giessen, Germany. CBZ was retained slightly by the NF membranes, whereas DIC was retained by approximately 65% and the permeate reached the level of quantification (LOQ). Recent studies have focused on the use of advanced oxidation processes (AOPs) as tertiary treatments for eliminating such micropollutants in MWTPs. Klamerth et al. [162] have shown that it was

possible to degrade pharmaceuticals in MWTP effluents using photo-Fenton with low starting concentrations of iron (5 mg/L) and  $H_2O_2$  (50 mg/L) with complexing agents (humic acid, HA and ethylenediamine- $N,N'$ -disuccinic acid, EDDS) at pH 3 or neutral pH. Miralles-Cuevas et al. [163] compared three different advanced tertiary treatments of NF concentrate, solar photo-Fenton, solar photo-Fenton-like Fe(III)–EDDS complex and ozonation, for removing five pharmaceuticals (CBZ, flumequine, IBU, ofloxacin, and SMX) typically found in natural waters. It was demonstrated that mild solar photo-Fenton combined with EDDS (low starting concentration of iron, no pH modification and low consumption of  $H_2O_2$ , <25 mg/L) could be a good option for tertiary treatment of NF concentrates from MWTPs containing low concentrations of pharmaceuticals. The photo-Fenton-like Fe(III)–EDDS complex makes it possible to work at pH > 6. Whereas, ozone consumption was lowered by combining ozonation with NF instead of using direct ozonation. Extension of this work was done by Miralles-Cuevas et al. [164] using solar photo-Fenton to treat a real MWTP effluent (initial iron < 0.2 mM and  $H_2O_2$  < 2 mM) and the concentrate stream generated by NF. Promising results were also shown in both effluents, in which pharmaceuticals were efficiently removed (>90%).

Treatment of a model dairy wastewater (diluted skim milk) by NF with a rotating disk membrane (RDM) module (Fig. 15) was investigated by Luo et al. [165] using NF270 (Dow-Filmtec). NF270 membrane showed high permeate flux, thus permits one to fully exploit the potential of the RDM filtration system. Under extreme hydraulic conditions of highest TMP (40 bar) with high shear rate, the RDM filtration system could produce better quality permeate and save energy, because of its very high permeate flux. A real dairy wastewater was also treated by NF270 under the same hydraulic conditions, and results were similar to those of model solution. Therefore, the RDM module appeared to be a suitable technology to treat dairy waste without any biological and chemical treatments. Andrade et al. [166] evaluated the application of membrane bioreactor (MBR) as secondary treatment and NF as tertiary treatment of real effluents from large dairy industries. MBR alone showed high removal efficiency of COD (mean of 98%) and nutrients (86% total nitrogen and 89% phosphorus). However, the concentration of dissolved solids in the permeate still prevented its reuse. In order to remove these solids, the MBR permeate was nanofiltrated. The proposed treatment

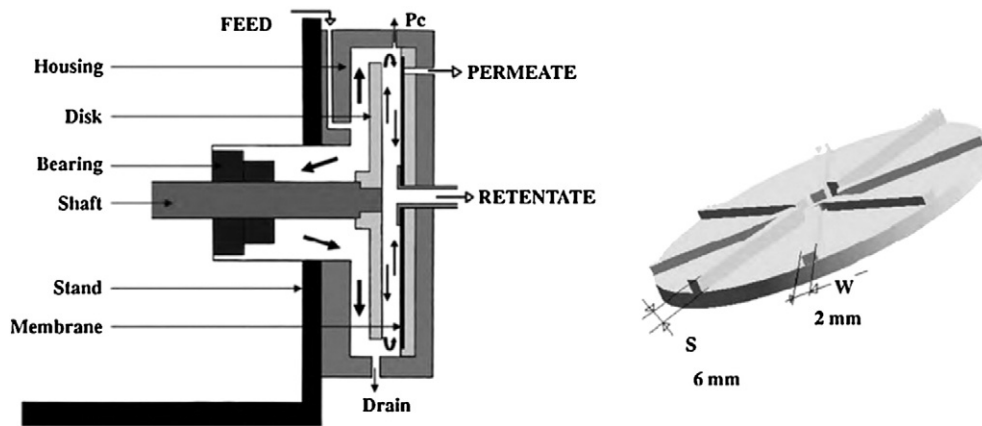


Fig. 15. Schematic of the rotating disk module (RDM) and of the disk with vanes [165].

system (MBR + NF) showed overall efficiencies of 99.9% for COD and 93.1% for total solids, thereby allowing the treated water to be reused in cooling or heating systems and for good manufacturing practices.

Ren et al. [167] investigated the feasibility of employing a novel asymmetrical poly (*m*-phenylene isophthalamide) (PMIA) NF membrane for the removal of Cr(VI) from simulated wastewater at different operating conditions. The PMIA NF membranes exhibited different rejection to electrolytes in a sequence of  $\text{Na}_2\text{SO}_4 > \text{MgSO}_4 > \text{NaCl} > \text{MgCl}_2$ , which seems to correspond to the Donnan exclusion mechanism of the negatively charged NF membranes. Separation experiments on Cr(VI) salt solution indicated that PMIA NF membranes can be effectively employed in the treatment of Cr(VI) contaminated water under alkaline condition while maintaining their pollution resistance based on the interaction between the negatively charged membrane and Cr(VI) ions. However, studies on NF hollow fiber membranes on heavy metal removal are still lacking. Zhu et al. [109] developed dual-layer NF hollow fiber membrane for the removal of heavy metal ions ( $\text{Cd}^{2+}$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Pb}^{2+}$ ) with various molecular sizes and charge properties from model wastewater. The membrane has shown superior rejections to  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , achieving 95% and 93%, respectively. Whereas, rejection to  $\text{Cr}_2\text{O}_7^{2-}$  can reach 98% when the salt solution is at pH 12.

Out of numerous applications, the retention and concentration of dyes are still one of the largest applications for NF [168]. Zhong et al. [97] used novel positively charged sulfonated polyphenylenesulfone (sPPSU) NF membrane to treat two model dye solutions, i.e. with positive (Safranin O) and negative charges (Orange II). In view of salt rejections, the resultant NF membranes follow the order  $R(\text{MgCl}_2) > R(\text{NaCl}) > R(\text{MgSO}_4) > R(\text{Na}_2\text{SO}_4)$  with high  $\text{MgCl}_2$  rejection up to 95.20%. Besides, a superior Safranin O rejection up to 99.98% was achieved by the newly developed membranes, which was due to their positive surface charges and thus demonstrated an impressive prospect for the application on textile dye wastewater treatment. On the other hand, comparative study on the treatment of biologically treated textile effluent by NF and RO for water reuse has been carried out by Liu et al. [169] through the use of NF90 and BW30. The experimental results showed that, both the membrane adopted in this study could effectively remove color completely and reduce COD and BOD to desirable level of less than 25.0 mg/L and 2.0 mg/L, respectively. However, the COD removal efficiency of NF90 was better compared to BW30, while the BW30 reduced salinity to a greater extent than NF90. The treated water with good quality could be recycled back to the process, thereby offering economical benefits by reducing the water consumption and wastewater treatment cost.

#### 4.2. Desalination

Desalination technology, especially membrane based process has been widely recognized as one of the best candidate to resolve water

scarcity. However, there are several issues that still require attention in the operation of large scale desalination plant. Two of the major impediments are membrane fouling and energy consumption. Membrane fouling will affect and reduce the productivity of the plant. High energy consumption due to high operating pressure hinders the acceptance of membrane desalination process as it accounts for around 44% of the cost of the water produce [170]. Hence, few suggestions have been proposed to tackle the problems of membrane fouling and energy consumption with researches relevant to these obstacles has been carried out. NF membrane has shown high potential to be one of the options to reduce those obstacles in desalination process. In this section, the studies about the application of NF in desalination process will be discussed. Basically, NF has shown its usefulness as pre-treatment for seawater (SW) desalination, replacement for RO in water treatment process and it can be integrated with other processes for better overall performance.

Starting in the late 90s, NF had been tried out as one of the pre-treatment processes in SW membrane based and thermal based desalination plant [171]. This resulted in the reduction of TDS or salts in the feed water to RO and multistage flash distiller (MSF) unit. The reduction in TDS enabled the MSF plant to operate at higher temperature and higher distillate recovery rate [172]. The integration of NF as part of the pre-treatment process also led to a higher water production (around 60%) and resulted in about 30% cost reduction for RO and MSF plants [173]. These findings have encouraged further studies about the application of NF as pre-treatment in desalination process. Studies about the effect of various pre-treatments for particulates and inorganic fouling in SWRO desalination plant was carried out by [174]. It was reported that the highest RO flux production was achieved with NF as pre-treatment due to the removal of colloidal particles and inorganic scales. Besides that, the capability of UF–NF integrated membrane process as pre-treatment for SWRO had also been carried out [175]. This UF–NF pre-treatment process managed to produce a good grade of filtrate with 96.3% of total organic carbon (TOC) removal for long term operation. However, the problem of membrane fouling has been observed even though after chemical cleaning was carried out. Thus, further study should be carried out to improve this system and to reduce the fouling propensity of the membranes. For example, the scaling potential of NF and SWRO in an integrated UF–NF–SWRO desalination system was investigated [176]. It was discovered that the scaling potential of NF stage was different from traditional SWRO and thermal desalination processes. Such study could provide some useful understanding about the fouling mechanism in membrane process and fouling problem can be tackle accordingly.

To date, few predicting studies about the benefits of incorporating NF as pre-treatment prior to RO desalination process have been carried out. Energy and exergy analyses are useful in predicting the energy requirements of a system. This analysis has been used to simulate and

determine the optimum operating condition for integrated NF–SWRO desalination plant for energy minimization purpose [177,178]. From the comparison done between NF–SWRO and standalone RO processes, the integrated process yielded higher recovery (higher production rate) and lesser loss in energy. Thus, this analysis provided useful guidelines in determining the operating conditions of an integrated process.

Recently, few studies have been carried out to investigate the possibility of NF to replace or as an alternative approach to RO in SW and brackish water desalination. This is due to the lower operating pressure and higher production rate of NF compared to RO unit. One of the interesting findings is from the bench scale test of NF for SW desalination done by the Long Beach Water Department [179]. They proposed a dual-stage NF process to replace the RO unit with the primary goal of reducing the energy consumption without sacrificing the recovery rate of potable water produced. The bench and pilot scale testing were proven successful with the cut-down in desalting cost. Eventually, a 300,000 gallon-per-day (gpd) SW desalination prototype facility was constructed and operated from the year of 2006 to 2010 [180]. The TDS of the SW was around 30,000 to 35,000 ppm. Based on the performance of the dual-stage NF process, it was concluded that this process is efficient and reliable with the quality of water produced met the drinking water guidelines. Besides that, it was shown that dual-stage NF process resulted in lower cost of product water compared to RO–NF system. These findings show that NF has the capability to be utilized in SW desalination process. Another alternative design to dual-stage NF has been tested by AlTae and Sharif [181] to investigate its applicability for brackish water desalination. They used simulation software (ROSA–RO system analysis by Dow Chemical Co.) to determine the specific power consumption and permeate TDS for NF–NF and NF–BW processes. The simulation range of feed TDS was from 35,000 to 43,000 ppm. The simulation results showed that the overall cost of NF–NF was slightly lower than NF–BW process but with higher permeate TDS. These simulation results might differ from real plant process but it can provide a guideline for further investigations about the benefits of dual-stage NF desalination process.

In order to understand how efficient the dual-stage NF process is, energy and exergy analysis using ROSA simulation program was carried out by [182]. In this simulation, the dual-stage NF process was combined with energy recovery device (ERD) to reduce the specific energy consumption and enhance the exergetic efficiency and recovery ratio. From the simulation, it was reported that the specific energy consumption can be reduced to 2.09 kWh/m<sup>3</sup> and the system recovery ratio can be increased to 42.78% under the condition specified in the paper. Such simulation study suggested that the development of a novel energy-saving membrane module and the incorporation of energy recovery device can further reduce the energy consumption of the dual-stage NF SW desalination.

There are several interesting studies about the integration of NF with other processes such as ion exchange and forward osmosis (FO) in the application of desalination. The concept of hybrid ion exchange–NF process is to specifically convert the monovalent chloride into divalent sulfate through a reversible anion-exchange process [183]. Laboratory studies indicated that the hybrid process required two times lesser energy compared to RO process for the same feed water. The existent of ion exchange process enable the osmotic pressure of the feed water to be lowered and divalent salts can be rejected by NF. Besides that, NF also being combined with FO using divalent draw solute to desalinate brackish water. According to the study done by Mehdizadeh [178], this hybrid FO–NF process was tested to have several advantages over standalone RO process, such as lower hydraulic pressure, lower membrane fouling propensity, lesser flux decline and higher flux recovery after cleaning. These results indicated that FO–NF can be a useful alternative to RO process in brackish water desalination. However, prototype study should be carried out to verify the applicability of hybrid ion exchange–NF and FO–NF processes in real case.

As can be seen from the examples above, more and more studies on integrated/hybrid membrane processes have been carried out since the combination of different processes with membranes showed promising outcomes. The specificity of each process makes their integration more efficient and the shortcoming of each process can be resolved by other processes. These promising results can be obtained from [184] where the application of integrated/hybrid membrane processes in desalination had been discussed in detail.

#### 4.3. Pharmaceutical and biotechnological application

Recently, many researches have focused on the development of membrane purification of active pharmaceutical ingredient (API) from common classes of genotoxic impurities (GTIs) [185–189]. Martinez et al. [189] studied the potential of self-made NF membranes with 25% and 27% PES and the commercial NF membrane NF270 (FilmTec, Dow) for the recovery of API, 1-(5-bromo-fur-2-yl)-2-bromo-2-nitroethane (or G-1) using a cross-flow configuration. The application of cross-flow NF has been observed to be feasible, achieving retentions higher than 80% for all the studied membranes.

Organic solvent NF (OSN), also known as organophilic NF (ONF) or solvent resistant NF (SRNF), is an emerging technology for performing membrane separation/purification processes in organic solvents and has been successfully applied for API, albeit mainly at laboratory scale [188,190–193]. Székely et al. [188] discussed the use of OSN as general platform for the removal of GTI from a total of nine API model compounds from four different chemical families namely N-heterocycles, steroids, macrolides and amides to be representative for the diversity of chemical reactions and compound structures produced by the pharmaceutical industry as schematically illustrated in Fig. 16. The proposed OSN for GTI removal from API post-treatment solution can be applied to replace the phase extraction in conventional purification processes, where typically the API recovery yield is 80%.

Székely et al. [185] evaluate the adequacy of different approaches for the removal of 1,3-diisopropylurea (IPU), a potentially GTI from APIs. The use of OSN at diafiltration (DF) dilution ratio of 3 was found as optimum to achieve 90% removal of IPU with a 2.5% loss of the model API. A novel IPU-selective molecularly imprinted polymer (MIP) was then used for final polishing to remove the remaining IPU. Below 100 ppm IPU, IPU removal of 83% was achieved in one single stage. The combination of OSN with DF dilution ratio of 3 and a single MIP polishing stage (Fig. 17) developed by Székely et al. [185] allows the reduction of IPU contamination from 100 mg IPU/g API to 2 mg IPU/g API with an API loss, mostly at the OSN stage, of about 3%.

However, in the relatively young area of OSN, there are only a few reports on membrane cascades. Siew et al. [186] recently demonstrated successful API enrichment and organic solvent recovery in an automated multistage cascade. They were able to concentrate a dilute API product solution with concurrent solvent recovery downstream of a chromatographic process. The 3-stage cascade (Fig. 18) was able to achieve an effective rejection of 80% compared to a single pass rejection of 55%. Kim et al. [187] presented a simplified-control cascade process that operates using a single high pressure pump as primary pressure source, and has no need for a buffer tank between membrane stages. The proposed two-stage cascade configuration was validated on batch purification of API (roxithromycin macrolide antibiotic) from potential GTIs (4-dimethylaminopyridine and ethyltosylate). By implementing the two-stage cascade configuration for membrane DF, process yield was increased from 58% to 95% while maintaining less than 5 ppm GTI in the final solution.

#### 4.4. Non-water application

Polymers of intrinsic microporosity (PIMs) which are only soluble in a few solvents, are expected to have high stability in many solvents thus feasible for the OSN application. However, to date, there is only very



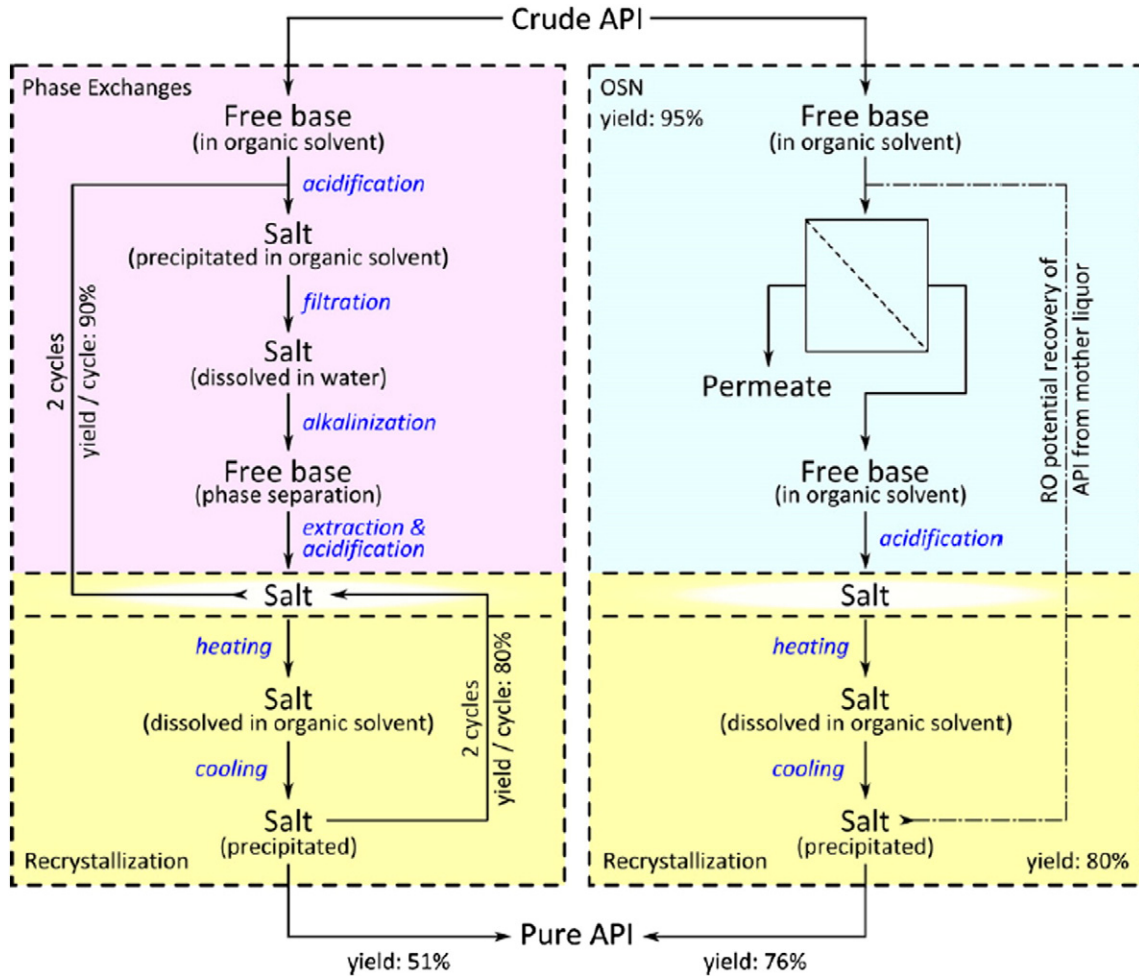


Fig. 16. Schematic comparison of API purification by a conventional and OSN-based process [188].

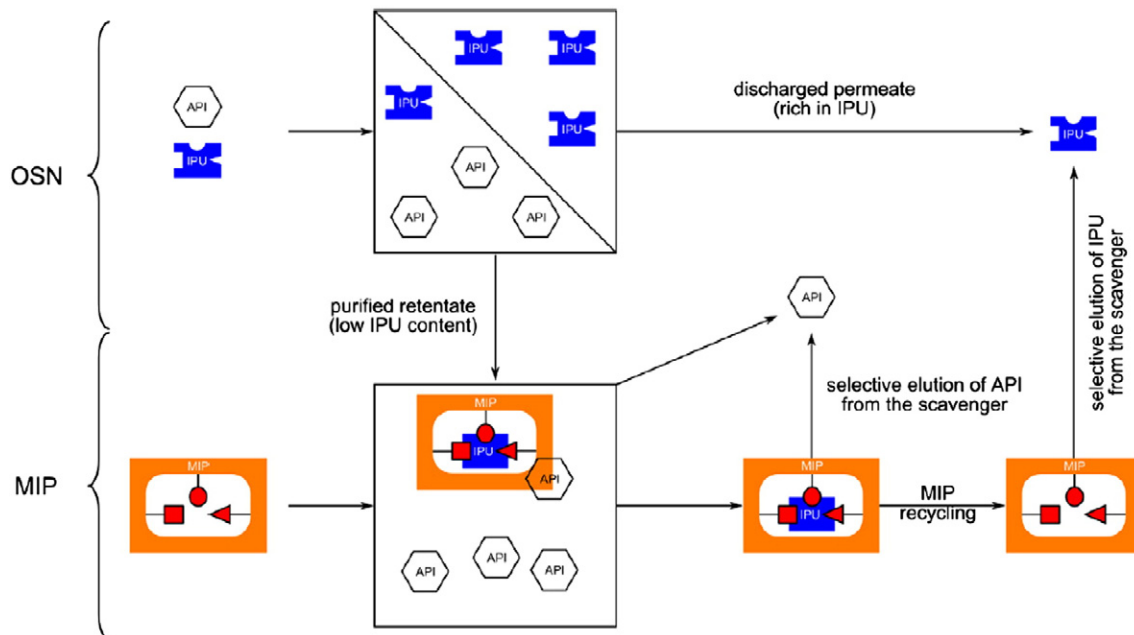


Fig. 17. Schematic principles of using OSN (stage 1) and MIP (stage 2) to remove GTI from API solutions [185].

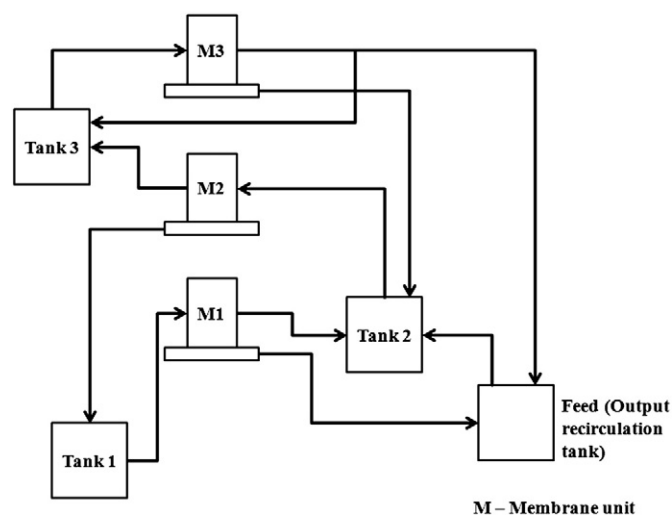


Fig. 18. Process flow diagram of the 3-stage membrane cascade for API enrichment and organic solvent recovery [186].

little work that has been done to test on this approach. TFC membranes of PIM-1 and PIM copolymers were developed by Fritsch et al. [194] on a polyacrylonitrile (PAN) porous support. The TFCs were tested in OSN with various solvents: n-heptane, toluene, chloroform, tetrahydrofuran, and alcohols, and compared to similarly crosslinked poly(trimethylsilyl propyne) TFCs. Better retention, a steeper retention curve and much higher fluxes were detected for the newly developed PIM TFC membranes.

Even though industrial applications typically include multi-component mixtures with non-ideal mixture properties, most experimental studies on OSN membrane are only conducted with single solvents and/or single dissolved solutes [195–197]. The few experimental reports on solvent mixtures have been mostly restricted to binary systems. Darvishmanesh et al. [198] conducted experiments to characterize multiple types of membranes, ranging from RO to UF, using binary mixtures of ethanol and n-hexane. They highlighted the role of viscosity, surface tension, coupled diffusion and the solubility parameter difference between the membranes and the solvents. Recently, Zeidler et al. [199] investigated the retentions of two, three and four ring-type core substances with different functional groups dissolved in ethanol, n-heptane and tetrahydrofuran using a GMT-oNF-2 membrane (PDMS/PAN). A strong dependence of the retention on the used solvent was observed while even negative retentions were measured using ethanol as solvent. Schmidt et al. [200] expanded the experimental studies available in the literature using five different solutes (n-hexadecane, 2,2,4,4,6,8,8-heptamethylnonane, phenyldodecane, 2,6-diisopropyl-naphthalene and triphenylphosphine) in binary and ternary solvent mixtures of toluene, isopropanol and n-hexane. They observed a strong influence of the used solvent on the retention with two commercial polyimide-based membranes, namely STARMEM™ 122 (polyimide based) and PURAMEM™ 280 (silicone coated polyimide). Using the binary mixtures of n-hexane and isopropanol for example, a maximum of retentions was observed at 25 wt.% isopropanol. But only a small difference was measured regarding the retention of the five dissolved compounds using the same solvent or solvent mixtures.

A few polymeric membranes have been reported in literature which can withstand either acids or bases in aqueous feed streams [201,202]. However, these membranes are not able to withstand many organic solvents. Valtcheva et al. [203] reported a new class of OSN fabricated from crosslinked PBI. To critically assess their chemical stability, these membranes were tested in realistic chemical process conditions that employ different types of acids and bases, e.g. concentrated dichloroacetic acid in acetonitrile, piperidine in N,N-dimethylformamide (DMF) and monoethanolamine in water. The filtration experiments showed

that membranes fabricated from crosslinked PBI were stable and could lead to wider implementation in chemically harsh conditions found in processes ranging from pharmaceutical to petrochemical industries.

Despite the rapid development of research on OSN, the application of OSN in industry is still at laboratory scale, mainly hindered by a limited choice of OSN membranes and configurations. The performance of OSN was studied by Silva et al. [204] in a pilot-plant apparatus using a spiral-wound (STARMEM™ 1221) membrane element, which is the most effective way for scaling up the flat sheet membrane area over extended periods [205], with 0–20 wt.% of tetraoctylammonium bromide (TOABr) in toluene and comparing with flat sheet cross-flow NF results investigated by Peeva et al. [206] earlier. Comparisons between the experimental and calculated results suggested that the membrane transport parameters obtained from cross-flow experiments using flat sheet membranes could be used for reasonably good estimation of flux and rejection in an OSN spiral-wound element, which might provide a useful design tool for OSN processes up-scaling.

In Sairam et al. [207] study, spiral-wound modules of solvent stable integrally skinned asymmetric NF membranes made from polyaniline (PANI) through both thermal and chemical methods of crosslinking were attempted. Filtrations carried out in a spiral-wound module filtration for acetone, tetrahydrofuran (THF) and DMF gave stable permeate fluxes and good separation performances in the NF range at elevated temperatures up to 65 °C. The reusability of the PANI spiral-wound membrane modules with low MWCO and full rejection in NF range showed its potential to be further scale-up for commercial applications.

Despite spiral-wound module, there are also neither OSN hollow fibers nor capillary membranes commercially available and literature reports that this is very limited. Dutczak et al. [208] prepared and studied the novel OSN composite capillary membranes, comprising of a commercial Hyflux InoCep M20  $\alpha$ -alumina capillary support and selective tailor made poly (dimethylsiloxane) (PDMS) top layer. As reported, the best composite membrane M20/55 prepared by coating PDMS on the inside of the  $\alpha$ -alumina support showed stable performance for over 40 h in toluene, toluene permeance of 1.6 L/m<sup>2</sup> h bar and MWCO of ~500 Da.

In contrast to well-established design approaches for conventional unit operations such as distillation, design methods for integrating OSN in chemical production processes are very limited. Schmidt et al. [209] demonstrated the utilization of targeted solvent modifications to enhance OSN membrane properties, such as permeability and rejection in the recycling of homogeneous rhodium based catalysts during hydroformylation of 1-pentene. The developed four-step design work flow was based on the analysis of membrane rejection maps (MRM) and membrane modeling maps (MMM). According to Schmidt et al. [209] analysis, promising solvent modifications using small addition of toluene before the OSN membrane separation unit were performed for polyimide-based Puramem™280 membranes and PDMS-based GMT-oNF-2 membranes. The results showed that targeted solvent additions can be utilized to enhance process economics and to attain processes with fewer stages, improving process operability and control and reducing overall membrane area demand. Similar effort has been done by Schmidt et al. [200] in developing MRM and membrane selectivity maps (MSM) to facilitate conceptual process design by selecting either pure solvents or solvent mixtures that enhance the downstream processing in OSN and thus can replace costly and time-consuming membrane screening or OSN membrane modification.

Micovic et al. [210] elaborated a four-step design method for the combination of OSN and distillation in a hybrid separation of heavy boilers (hexacosane, 5%) from a hydroformylation mixture containing a light boiler (solvent for the reaction, decane, 70%), a mid-boiler (product, dodecanal, 25%) and small amount of high-boiler (aldol condensation product, 5%) as illustrated in Fig. 19. This approach gives a deep process insight on the advantages of the integrated OSN-process that performs experimental investigations and process design simultaneously.

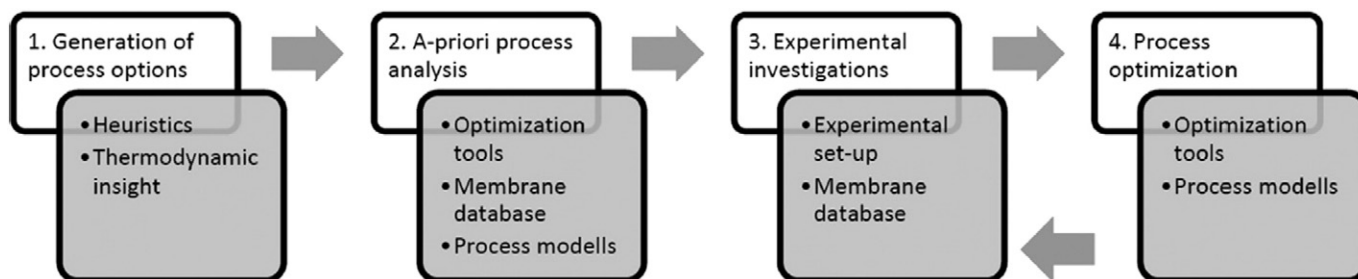


Fig. 19. The four steps of the design method for OSN-assisted processes [210].

#### 4.5. Food industry application

NF appears as an important alternative to conventional methods of food processing, including vegetable oil processing [211–213], beverage industry [214–219], dairy industry [35,165,166,220–227] and sugar industry [228–233].

Recent research on the application of membrane technology to vegetable oils is the separation of compounds present in trace amounts in the oil such as antioxidants [234] and deacidification [213]. Galanakis et al. [235] study the clarification of two high-added value products (pectin containing solution and phenol containing beverage) from olive mill wastewater with four types of UF (100, 25, 10 and 2 kDa) and one NF membranes under optimum TMP. The membranes possessing MWCO between 25 and 100 kDa (GR60PP and GR40PP, respectively) showed very satisfying results to recover pectin and separate it from smaller solutes like potassium, sodium and phenols. GR60PP membrane was also able to partially remove the heavier fragments of hydroxycinnamic acid derivatives and flavonols, and simultaneously to sustain the antioxidant properties of the phenol containing beverage in the permeate stream. Finally, NF clarified the beverage from potassium and sodium that passed in the permeate stream, but this process reduce the antioxidant ability of the product due to a loss of *o*-diphenols in the permeate stream.

In Sereewatthanawut et al. [234] study, the refining and  $\gamma$ -oryzanol enrichment of rice bran oil (RBO) was investigated through solvent extraction optimization and NF processing. Several solvent resistant NF membranes (Starmem™ and DuraMem™ membrane series, Evonik, Ltd., UK) were screened and successfully applied in a two step membrane cascade with fluxes between 39 and 53 L/m<sup>2</sup> h. Overall, the integrated process provided a RBO  $\gamma$ -oryzanol enrichment of 0.95–4.1 wt.% in oil, which corresponded to more than a two fold increase in the oil's antioxidant capacity. Their results demonstrate the potential of OSN as a technology to enrich and refine oil based products.

On the other hand, there are only a few works related to oil deacidification and disagreeable flavors removed by NF membrane technology. Firman et al. [213] evaluated four tailor-made flat composite membranes made of poly(vinylidene fluoride) (PVDF) as a support and polydimethylsiloxane (PDMS) or cellulose acetate (CA) as coating layer, and a commercially available composite membrane (Solsep 030306) for their ability to remove hexane and free fatty acid (FFA) from crude soy-bean oil–hexane mixture. PVDF-12% siloxane composite NF membrane being stable in commercial hexane and showed excellent deacidification and solvent recovery from soybean oil/hexane miscella, thus presented a high potential of application. Improved separation performance was obtained at  $C_f = 25\%$ ,  $\Delta P = 20$  bar, and  $T = 30$  °C, achieving a permeate flux of 20.3 L/m<sup>2</sup> h, 80% oil retention and 58% FFA removal.

A conceptual process design with the use of integrated membrane processes for blackcurrant juice concentrate production to replace the traditional multiple step evaporators and aroma recovery was studied by Sotoft et al. [217]. The annual production scale was 17,283 t of 66°Brix out of single strength juice. The operation cost was 0.40 €/kg blackcurrant juice concentrate, which was lower than the price of traditional operation by about 43%. Therefore, the economical potential of

this integrated membrane process is very promising and could supersede the conventional evaporators.

Attribute to the increasing demand of non-alcoholic drinks market, Catarino and Mendes [218] used membrane for producing wine with low alcohol content. Several membranes of RO (CA995PE, Alfa Laval) and NF (NF99 HF, NF99, NF97, Alfa Laval and YMHLS1905, Osmonics) were used for removing ethanol from a 12 vol.% red wine. YMHLS1905, NF99 and NF99 HF NF membranes showed higher effectiveness in alcohol removal from wine, due to their good ethanol permeability and high aroma compounds' rejection, resulting in dealcoholized wine samples with promising organoleptic properties. However, NF97 NF membrane showed low flux with high ethanol rejection, making it unsuitable for dealcoholization. The results of this study indicate that, NF is effective for dealcoholizing wine while preserving its original characteristics.

Development in NF technology has created the opportunity for an entirely new approach to whey utilization. Prudêncio et al. [227] reported that NF and NF followed by DF processes offer an opportunity for an entirely new approach regarding the utilization of whey in producing the ricotta cheeses with identical physicochemical, color, rheological and microstructural properties which bring economic and environmental advantages.

The production of highly colored salty effluents as main drawbacks of an ion-exchange resin decolorization process in the sugar industry has found an answer with the use of NF membrane process. Salehi et al. [232] used AFC80 PA NF membranes (PCI membrane) to investigate the effect of feed concentration (40, 60, 80 and 100 g/L), TMP (1.0, 1.25, 1.5, 1.75 and 2.0 MPa) and temperature (30, 40 and 50 °C) on the recovery of usable brine obtained from waste brine in order to save on both salt and water consumption for ion-exchange regeneration process. As high as 77% salt consumption reduction, 90% water consumption reduction and greater than 99% colorants removal were reported. The rejection of NaCl was found to be 15–37%. The rejection of NaCl declined with the increase of feed concentration and temperature, whereas increasing of TMP led to an increase in NaCl rejection. The permeate flux was decreased by increasing the feed concentration and increased with the increasing of temperature and pressure. The satisfactory qualitative performance and higher reduction in water and salt consumption was reported by Salehi and Razavi [231], (90% and 81%, respectively), using AFC40 PA NF membranes (PCI membrane). The average rejection of NaCl was found to be 9%.

#### 5. Fouling and fouling mitigation

Though the performances of membrane processes were found to be better or at least competitive to conventional processes, membrane fouling is still a great hindrance for membrane based applications including NF. Fouling limits the competitiveness of membrane operation and cost effectiveness. Fouling leads to several deleterious effects including flux decline (drop in productivity), increase in costs due to increased energy demand, maintenance, chemicals and frequency for cleaning, membrane degradation and replacement as well as shorter membrane lifespan. Hence, effective fouling control and mitigation are

very important to reduce the adverse effects of membrane fouling. In order to come out with an effective fouling control, the mechanism and type of fouling as well as factors that contribute to fouling phenomena should be understood.

### 5.1. Fouling mechanism and type of fouling

Fouling is a major obstacle for membrane to be used widely. It may exist in different forms [236]:

- Adsorption — Specific interaction between the membrane and solutes. It may occur on the membrane surface or in pores.
- Pore blocking — Solutes block and clog the pores of membrane. The size of particles will decide whether the pores of membrane will be partially or fully blocked.
- Cake layer formation — Deposition of particles which grows layer by layer on the membrane surface. Usually caused by particles with size larger than the pore size of membrane.
- Gel layer formation — Concentration polarization leads to the formation of gel layer in the immediate vicinity of the membrane surface.

Fouling mechanisms are closely related to another two phenomena, concentration polarization and osmotic pressure. Concentration polarization is a process of accumulation of retained solutes in the membrane boundary at the feed side. It results in the formation of a high solute concentration at the membrane surface compared to the bulk solution. Concentration polarization has the tendency to contribute to the more problematic fouling mechanisms mentioned above, that is adsorption, cake layer and gel layer formation [237]. Besides that, the accumulation of inorganic or organic solutes will increase the osmotic pressure of the solution and lead to the reduction of effective TMP and permeate flux. One should be aware that although the study of fouling mechanisms have been carried out but until now it still remains difficult to predict which mechanism involves in a membrane operation. Fouling mechanism might change from one to another after the membrane process being operated for some time or affected by feed properties. For instance, Koyuncu et al. [238] found that the main cause of flux decline of NF treating dye was cake layer formation at low salt concentration while adsorption was dominant at high salt concentration. Nghiem and Hawkes [239] revealed that permeate flux decline due to organic fouling would be more severe for membrane with larger pore size. The authors argued that during the first stage of fouling, pore blocking was the predominant fouling mechanism while the latter stage was governed by cake-enhanced mechanism.

Generally, fouling can be classified into 4 major categories: organic fouling, colloidal (particulate) fouling, scaling (inorganic fouling) and biofouling (biological fouling). Table 2 below briefly describes each fouling phenomena and the common foulants that contribute to these problems.

It should be noted that usually several types of fouling will be encountered in a membrane process. For instance, the existence of organic matter in feed solution will result in organic fouling and at the same time it will become the nutrient for microorganisms to grow and adhere to the membrane surface. But some observed that the presence of

certain foulants might suppress the other fouling propensity. Operating conditions such as recovery rate and flow velocity will affect fouling propensity of a membrane process. Thus, fouling is a complex phenomenon where it involves the interaction between the feed solution, membrane properties and operating conditions. As shown in Fig. 20, Tang et al. [6] had grouped the factors affecting colloidal fouling propensity into three categories, which is membrane properties, feed water composition and hydrodynamic conditions. It has been reported that membrane fouling can either improve or deteriorate the quality and efficiency of membrane separation. Several studies about the type of NF membrane fouling and the mechanisms involved will be discussed here.

A study about the scale formation in the presence of dissolved organic matter (DOM) for NF was carried out by [240]. It was observed that fouling due to scale (calcium sulfate) formation had been reduced with the presence of DOM. Although DOM is an organic foulant to membrane, in this case it acted like an antiscalant to suppress the formation of scale. This finding showed how complicated is the fouling phenomena in membrane process. At the same time, it provided a guideline for future research where the interaction between DOM and antiscalant (additive used to prevent scaling) should be studied for better and optimal membrane process.

Organic fouling is one of the major problems encountered during membrane operation. Several studies have been conducted to determine the change in membrane performance due to organic fouling in NF. Agenson and Urase [241] had conducted such study by fouling the NF membrane with activated sludge and landfill leachate to determine its trace organic contaminants rejection capability. It was reported that a marked decrease in large organics and higher retention of low MW solutes were observed compared to clean membrane. They correlated these findings with fouling and rejection mechanisms. The removal of large organics by virgin membrane was mainly due to size exclusion but for the fouled membrane, adsorption and diffusion played the role in the penetration of large organics through the fouled membrane. While for the low MW solutes, the increase in rejection might be attributed to the narrower pores resulting in more dominant size exclusion.

Lee et al. [242] reported that due to colloidal cake formation fouling, the NF membrane charge was reduced and led to a decrease in salt rejection. Tu et al. [243] conducted a study to investigate the effect of different model foulants on boron rejection by NF membrane. It was found that the boron rejection by the adsorption of HA on the membrane surface was improved may be due to the highly negatively charge of the humic substance.

Nghiem et al. [244] showed that the retention of hydrophobic triclosan (trace organic contaminant) by membrane pre-fouled with organic foulants was considerably improved but not for the case of three other hydrophilic compounds. This could be attributed to the cake-enhanced concentration polarization phenomena where the solutes were accumulated within the fouling layer and resulted in higher passage through the membrane [245]. Similar study was conducted by Chang et al. [246] to investigate the fouling effect of HA and calcium ion on the rejection of pharmaceutical and personal care product by NF membranes. It was concluded that fouling with HA was due to complete blocking and cake layer

**Table 2**  
Fouling phenomena and common foulants.

Type of fouling	Definition	Foulants
Organic fouling [242,275,276]	Deposition or adsorption of dissolved or colloidal organic material on the membrane surface [265].	NOM, effluent organic matter (EfOM), proteins, polysaccharides [277]
Colloidal fouling	Accumulation of retained colloidal and particulate matter on the membrane surface [278].	Clay minerals, colloidal silica, metal oxides (iron, aluminum and manganese), organic colloids, suspended matter and salt precipitates [279]
Scaling	Ionic product of a sparingly soluble salt exceeds its equilibrium solubility product and precipitates and forms a scaling layer on the membrane surface [280].	Calcium sulfate, calcium carbonate, barium sulfate, silica scale [259,281]
Biofouling [270,282]	Adhesion and growth of microorganisms (bacterial cells or microbial flocs) accompanied with agglomeration of extracellular materials on the membrane surface [283–285].	Bacteria, fungi

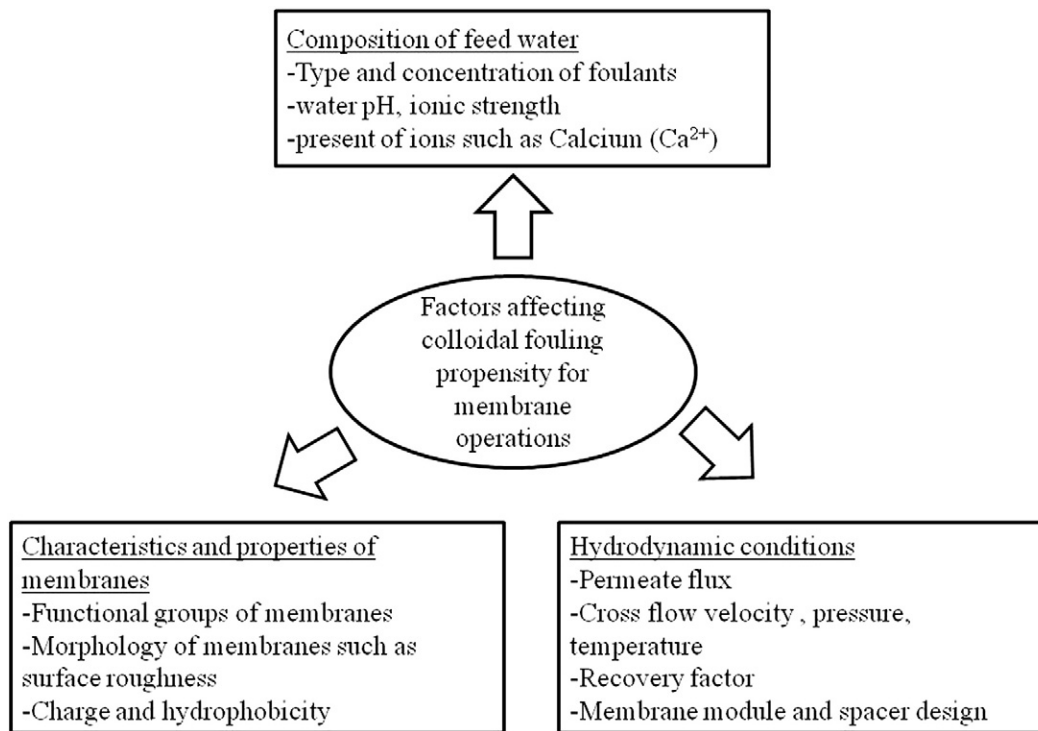


Fig. 20. Factors affecting colloidal fouling propensity in membrane operation (adapted from Tang et al. [6]).

formation while membranes fouled with HA and calcium ion were attributed to cake layer formation with elements of pore blocking. The presence of HA and calcium ion increased rejection of small and neutral-charged compound due to extra hindrance layer provided by the foulants. On the other hand, fouling of the membrane reduced the retention of larger compounds due to concentration polarization phenomena which was enhanced by the presence of HA and calcium ions.

The understanding of fouling phenomena is critical for the development of effective and successful membrane-based applications. Fouling studies provide useful information on what can be done to reduce fouling and offer valuable guides for membrane process design and development in industrial application.

## 5.2. Fouling prevention and mitigation

Fouling is a severe trouble for membrane processes and it must be prevented or controlled so that its negative impacts can be reduced and production loss can be cut down. Prevention and mitigation of fouling have been investigated actively. Basically, fouling can be controlled by taking preventive measures before the membrane unit (feed pre-treatment and early fouling prediction), membrane selection, module design and operation mode, and cleaning process when the performance of the membrane processes drop to a certain level [247].

The first barrier to fouling is fouling indices through feed water analysis [248]. Feed water analysis such as pH, ionic strength, turbidity, silt density index, TOC, COD, BOD, SUVA, salts' composition and concentration, MFI and biofilm formation rate can give some indication of likelihood of fouling and presence of contaminants [3]. It affects the design of the processes to be used for the treatment purpose. Such analysis also provides a guide on what membrane to be used, mode of operation and operating conditions as well as the appropriate processes to be involved in the treatment system. Parameters like pH and salt will affect the filtration performance and NF membrane properties as well as fouling mechanisms can be referred to the review done by Luo and Wan [7].

One of the most effective fouling control strategies is the feed pre-treatment before the NF membrane unit. Different types of pre-treatment have been used to reduce the foulants in the feed and thus

decreasing the chance of severe membrane fouling in many operation processes. Successful pre-treatments prior to membrane units have been reported; such as coagulation, flocculation, ozonation, adsorption, H<sub>2</sub>O<sub>2</sub>/UV oxidation, UF/MF [249]. However, it must be noted that those pre-treatment processes might not be able to eliminate all the foulants in the water, which means NF membrane process still requires some other fouling control strategies.

Hydrodynamic conditions such as crossflow velocity, permeate flux, TMP and operating temperature of the membrane process will strongly affect the membrane fouling. In the study of paper machine process waters treated by NF, based on the results from the Hermia's model, it was predicted that at higher TMP, the reversible cake filtration mechanism was dominant while at lower pressure, irreversible pore blocking fouling was present [250]. Wang et al. [251] discovered that membrane performance can be improved by decreasing the initial flux (lower operating pressure) and increasing the crossflow velocity, as illustrated in Figs. 21 and 22. With lower operating pressure, lesser accumulation of HA on the membrane can be achieved while higher crossflow velocity resulted in lower calcium ions acting as a bridge between the membrane surface and HA molecules. For RDM module, it was found that by increasing the rotational speed (higher shear), NF permeate flux and solutes' rejection were enhanced due to lower concentration polarization effect [252]. Besides that, membrane selection also will affect the performance of the membrane system. For instance, it was found that membrane properties such as zeta potential and contact angle strongly affect the fouling characteristics of the NF membranes for municipal wastewater reclamation [253]. Hence, by identifying the feed components then appropriate membrane with specific capability can be selected to reject the foulants.

Once the membrane process is started, some mitigation strategies can be taken to reduce fouling propensity of the process. As mentioned above, concentration polarization is a severe phenomenon that will contribute to other worse fouling. Hence, several approaches have been attempted by researchers to reduce the adverse effects of concentration polarization. These approaches include the use of pulsating flow induced by pulse pumps or valve sequences [254], air sparging [255], intermittent jets and use of novel type spacers [256], flow reversals

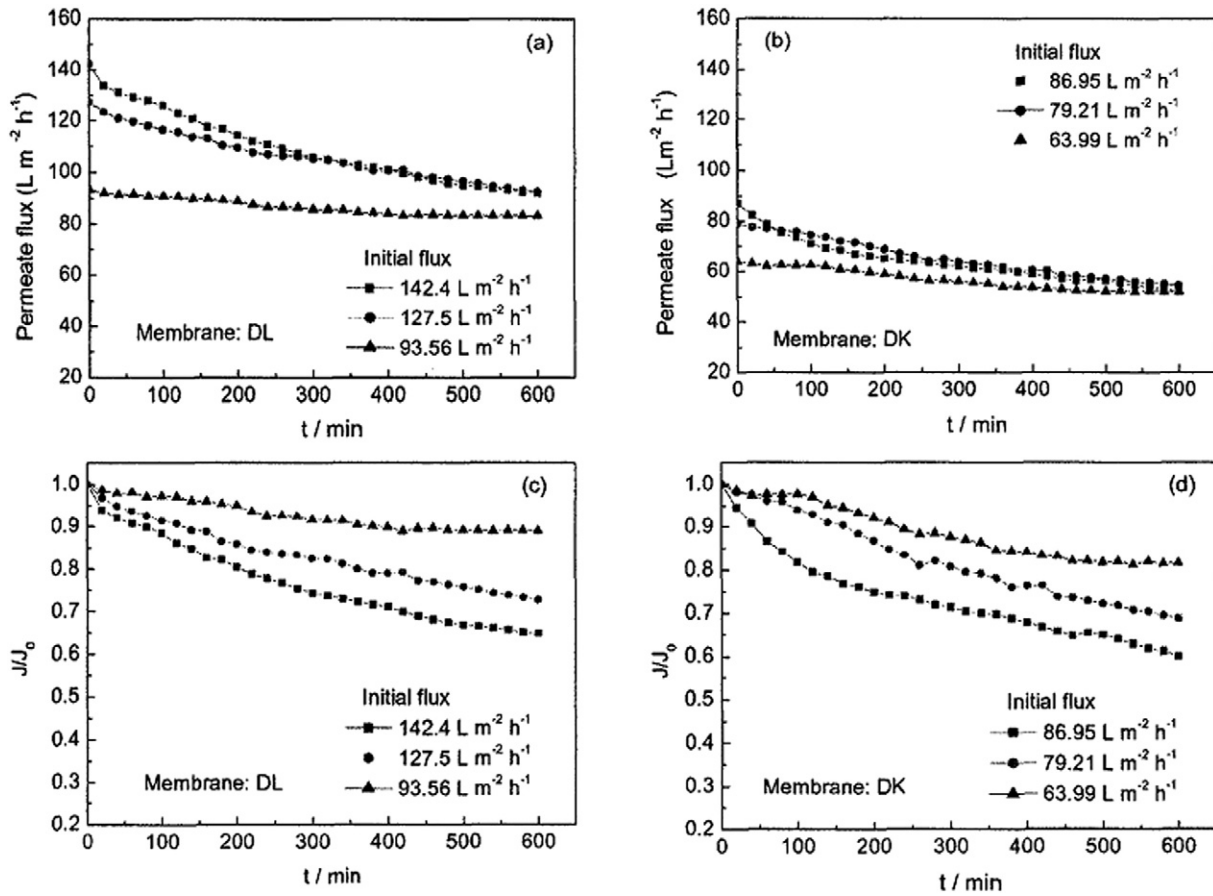


Fig. 21. Effect of initial permeate flux on the membrane performance [251].

[257] and low frequency ultrasonic irradiation [258]. Patel and Nath [258] applied low frequency ultrasonic irradiation on NF membrane for the treatment of dye-salt mixture solution. It was observed that the flux decline can be effectively mitigated but the rejection performance of the membrane showed no significant changes. Still, such study can be used as a guide for further application of ultrasonication in membrane operation. In addition, several chemicals might be added during the operation to reduce membrane fouling. Antiscalant can be added to prevent scaling [259] and oxidizing biocides such as chlorine can be injected into the solution to prevent biological fouling [260–262].

After some operating period, NF membrane will be inevitably fouled by contaminants in the feed solution. Hence, cleaning process has to be conducted from time to time to ensure its productivity can be regained.

However, inappropriate selection of cleaning agents may result in membrane damage or unsatisfactory performance. Thus, usually cleaning efficiency will be used to determine the suitability of particular cleaning agent. Cleaning efficiency depends on the ability of cleaning agent to break down the integrity of the fouling layer with the membrane. For example, in a study of NF for municipal wastewater treatment, amount of foulants extracted with alkaline solution (0.1 N NaOH) was significantly higher than acid solution (0.1 N HCl) [263]. Thus, it indicated that alkaline cleaning was a more effective cleaning process to remove the fouling layer on the membrane surface. Wei et al. [264] compared the effectiveness of NaOH, HCl, citric acid and EDTA cleaning agent for NF used to treat complex pharmaceutical wastewater. EDTA was found to be the most favorable cleaning agent as it managed to achieve

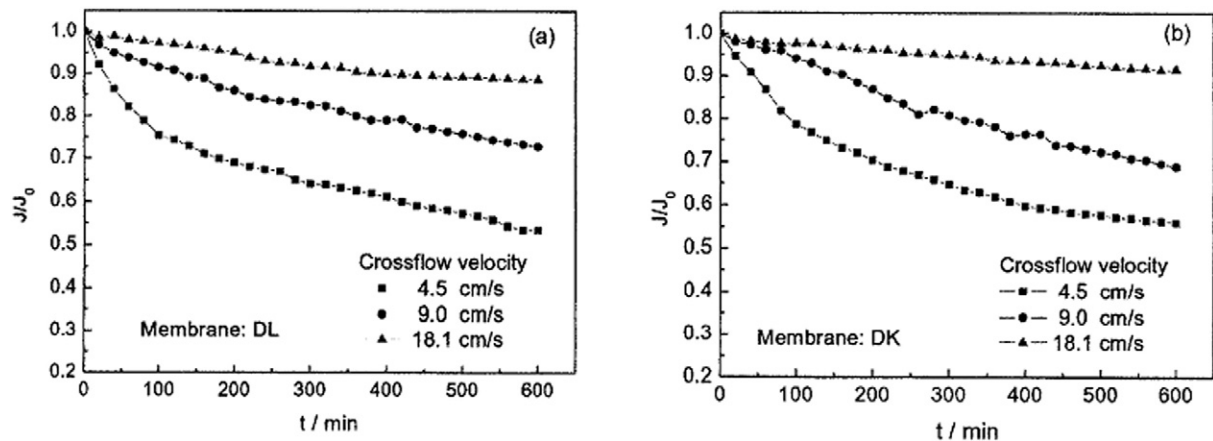


Fig. 22. Effect of crossflow velocity on the membrane performance [251].

about 99% of membrane flux recovery ratio. However, one should be cautioned about the effect of the cleaning on membrane surface properties. According to Simon et al. [265] and Simon et al. [266], caustic cleaning had resulted in notable changes in NF membrane surface properties and solute separation efficiency due to the enlargement of membrane pore size. Al-Amoudi et al. [267] also found that chemical cleaning will alter the zeta potential of the membrane. This should be taken into consideration especially for NF membrane where one of the main rejection mechanisms involves electrostatic repulsion. Thus, besides the ability to restore the flux, the effect of chemical cleaning on membrane properties should be studied as well. Due to the complexity in the nature of fouling, sometimes several cleaning processes have to be combined for an effective foulant removals and flux recoveries. From the study done by Liikanen et al. [268], alkaline chelating cleaning agents were most efficient in organic and biological fouling but not for inorganic foulants. So acidic cleaning has to be carried out periodically in order to ensure the removal of inorganic precipitants.

Even though fouling mitigation and control have been implemented, some membrane processes still encounter the problem of fouling. At this moment, membrane autopsy can provide valuable information about the nature of foulants on the membrane surface and give a guide on what can be improved for fouling mitigation and control. Those autopsy methods can be referred to Pontié et al. [269] and Xu et al. [270]. In addition, membrane autopsy can be used to assess the cleaning efficiency of a particular cleaning agent. Several new assessment methods have been introduced to provide a more accurate prediction. Positron annihilation spectroscopy has been used to measure the membrane pore size of NF membranes cleaned by various cleaning agents [271]. The changes in membrane pore size showed that the cleaning agents affected membrane surface properties and consequently the rejection of foulants and flux will be affected too. Characterization of membrane materials and foulant layers is crucial for an accurate understanding of fouling processes. AFM can be used to characterize the change in membrane surface after being used or cleaned. Another powerful usage of AFM is force spectroscopy, where it can be used to investigate the adhesion force between the foulant–foulant and foulant–membrane. This data gives an indication and prediction on how efficient the design and chemical agent used in the process [272].

## 6. Future prospects in NF membrane technology

The successful use of NF membranes thus far has been due to its uniqueness in having selectivity between the intended separation species. Depending on the application of interests, membrane with suitable selectivity should be selected in order to provide the most optimum separation. With this ability, NF membranes will continue to find new applications in various areas especially for water and wastewater treatment, desalination of brackish water, pretreatment in desalination of seawater, separation of small organics from other species in pharmaceutical, biotechnology and food applications. There will definitely be more interesting applications that will be explored in the future.

Based on the advances that have been reviewed so far, the following aspects would most likely be important in terms of research and development works on NF membranes:

- Predictive modeling of NF membrane processes: The extended Nernst–Planck equation can in essence be used to model the transport of infinite number ions and dissolved species through the NF membrane. However, the overwhelming majority of modeling studies to date have considered only very dilute and idealized solutions typically containing a maximum of only 2, 3 or sometimes 4 ions. If accurate modeling of concentrated multi-component electrolyte solutions realistic of industrial processing is to become common place then more effort needs to be placed into modeling systems of real industrial importance. Oatley-Radcliffe et al. [9] have critically reviewed the applicability of the current approaches of modeling with respect to

concentrated multi-component separations of industrial importance by considering seawater desalination. This study highlighted some of the key deficiencies in the current academic approach to modeling these complex separations and concluded that there is currently a lack of understanding of the physical properties and physicochemical phenomena inside nanopores. Most notably the lack of understanding in relation to activity coefficients, ordering of finite water layers at the solid–liquid interface and simple physical properties. For example, the study revealed that even simple physical property information such as osmotic pressure for high saline waters is not entirely accurate. Thus, in order for NF models to be successful in the true ab initio prediction of NF process performance new approaches need to be developed in order to understand the complex interactions and physical phenomena in such systems, such as membrane charge and particle–particle–membrane interactions. Similarly, fresh approaches need to be developed for solution of the intensive mathematics that will result from such systems. A recent model that illustrates the kind of approach needed is that of Yaroshchuk et al. [273]. Although focused on the solution–diffusion model, this paper looks at the separation of ions as a dominant salt among a series of trace ions. In principle, one could draw parallels to the short cut method known as the key component methodology for designing fractional distillation columns which are extremely complex in nature. The authors concluded that the approach taken could be useful for the optimization of NF for mixed electrolyte solutions in various applications. The challenge for the future of NF modeling must be to gain further understanding of the fundamental phenomena occurring during the NF process in order to find answers to the questions posed above, but also to develop accurate yet simplified models and design methodologies for concentrated multi-component feed streams that may be used by non-specialist scientists and engineers.

- Innovative methods in NF membrane fabrication: Advances in nanotechnology have pushed the boundary limit in terms of NF membrane fabrication. TFC and thin film TFN NF membranes obtained through interfacial polymerization method will continue to be the benchmark in development of NF membranes. Other methods such as UV or photografting, electron beam irradiation, plasma grafting and layer-by-layer methods will find their niche in terms of small scale development in labs. However these techniques will have their limitation and problems when large scale production of membranes is required. New nanomaterials and other types of additives will also be explored to determine the effect of these new materials on the membrane properties and performance. More research is required in elucidating the role of these new nanomaterials in NF membrane structure, morphology and effect on solute transport. It would also be interesting to further investigate the safety and environmental aspects of these new nanomaterials especially when the membranes are to be used for potable water treatment. Finally the ability to tailor made NF membranes with specific selectivity by controlling the various factors that are important in the fabrication process should also be considered. This will lead to significant breakthrough in optimizing the performance of NF membranes.
- Long term techno-economic studies of NF membrane processes: While various works have reported new and interesting applications of NF membranes in many areas, few works have reported on the large scale and long term operation of the processes. In order for the membrane operation to be industrially successful, techno-economic assessment of the process at least at the pilot scale is required. This will help to answer many issues especially on the viability and profitability of the process, fouling control and mitigation, and membrane susceptibility to complex feed materials as opposed to synthetic feed materials commonly used in many lab studies. Admittedly, this type of study will require more time and higher cost, but successful outcome will lead to more sustainable NF membrane operation. For desalination, based on the research trend, it can be seen that the integrated and hybrid process of NF in desalination application will play more prominent role in the future. Standalone NF process might not be able to produce

the water that meets the requirement but after coupling it with other processes or membranes, the overall process can perform well. So the future work should focus on the possibility of combining NF with different processes in order to solve the problems encountered by conventional system or standalone process. Besides that, reliable simulation and modeling can be used to predict the performance of the integrated/hybrid process such that it can give a guideline on the operating conditions and productivity of the proposed process. This avoids the time taken for carrying out the experimental study.

- New applications of NF membranes: Due to its wide range of salt selectivity as well as organic solutes selectivity, NF membranes will continue to be explored for various other applications. New applications are expected in the removal of emerging pollutants such as pharmaceuticals, personal care products (PPCPs), perfluorinated compounds and hormones. For water treatment, the use of NF membranes has been well established. However since the water resources are slowly depleting, NF membranes are expected to be used more for water recycle and reused. Studies have shown that water recycling will incur much less cost as compared to desalination. New strategies in optimizing the use of NF membranes in such scenario are required. There should also be more studies in energy integration from renewable resources with the NF processes. This will lead to more sustainable applications that will minimize the use of energy.
- Fouling prevention and mitigation: Fouling study has long been carried out but it still remains a problem for membrane application due to its complexity nature. Effort has been taken to understand the fouling mechanisms involved in the membrane processes. For better prediction of fouling, it should be studied together with rejection mechanism and modeling prediction. From the discussion in the text, it can be seen that rejection of solutes may change for different types of fouling mechanisms. Modeling for solutes' rejection can provide valuable prediction for the mechanisms involve in fouling. Such a combination study may give a better perspective about fouling and rejection mechanism for NF membrane. Optimizations of cleaning efficiency and development of cost-effective cleaning procedures have always been a challenge in membrane operation, especially various types of foulants encountered in different fields of membrane application. This is also true for fouling mitigation and control strategies such as pretreatment and operating conditions. Overall, from the view of bigger picture, fouling mitigation and control strategies require a more extensive research to come out with a fouling mitigation plan that covers from the start until the end of the membrane process. Early fouling detection strategy can play a role in preventing the problem of membrane fouling. When fouling starts to take place, early detection can identify it and appropriate measures can be taken to prevent it from developing into worse fouling. Currently, most of the fouling monitoring assessments were done on permeates fluxes. This technique provides a gap of times where by the time obvious fouling is observed, the fouling is already fully established. Such study can provide valuable information about fast detection of early fouling so that appropriate action can be taken before the fouling develops into irreversible state.

## 7. Conclusions

NF membranes, as a subset of pressure-driven liquid membrane processes, have had successful applications in various industries. The solute transport in NF membranes is generally controlled by steric, Donnan, dielectric and transport effects and this has led to the development of predictive modeling based on the extended Nernst–Planck equation. The model has been successfully used in many studies. Methods for NF membranes fabrication have also been quite successful in producing membranes with better selectivity, and improved flux and fouling propensity. The main method is still based on interfacial polymerization to produce thin-film composite or nanocomposite membranes. Introduction of nanomaterials in the thin film has had a significant effect on membrane performance. Due to its varied selectivity, NF membranes

have also been successful in water and wastewater treatment, desalination, pharmaceutical, biotechnology and food applications. However problems still persist in fouling control and mitigation. Future works should focus on developing better membranes and new innovative applications while improving the ability to control, reduce and mitigate fouling.

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