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Fouling of Reverse Osmosis and Ultrafiltration Membranes: A Critical Review

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ABSTRACT

Desalination by using reverse osmosis (RO) membranes has become very popular for producing freshwater from brackish water and seawater. Membrane lifetime and permeate flux, however, are primarily affected by the phenomena of concentration polarization and fouling at the membrane surface. The scope of the current paper was to critically review the literature on the fouling phenomena in RO and ultrafiltration (UF) membrane systems, the analytical techniques used to quantify fouling, preventive methods, and membrane cleaning strategies. The paper also makes

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specific recommendations on how scientists, engineers, and technical staff can assist in improving the performance of these systems through fundamental and applied research.

Key Words: Fouling; Desalination; Reverse osmosis; Ultrafiltration membranes.

INTRODUCTION

A large proportion of the world's population is experiencing water stress.[1] Arid regions in particular suffer from the constraining effects of limited water resources.[2–4] There is a growing awareness by scientists, political leaders, and the general public that the best way to approach this problem lies in a coordinated approach involving water management, water purification, and water conservation.[5]

The two most successful commercial water purification techniques involve thermal and membrane systems. Desalination by using reverse osmosis (RO) membranes, in particular, has become very popular for producing freshwater from brackish water and seawater. The technique has low capital and operating costs compared with other alternative processes such as multistage flash.[6] Ultrafiltration (UF) may be used before RO for feedwater pretreatment.[7] Membrane separation processes also are widely used in biochemical processing, in industrial wastewater treatment, in food and beverage production, and in pharmaceutical applications.[8]

Membrane lifetime and permeate (i.e., pure water) fluxes are primarily affected by the phenomena of concentration polarization (i.e., solute buildup) and fouling (e.g., microbial adhesion, gel-layer formation, and solute adhesion) at the membrane surface (Fig. 1).[9] Koltuniewicz and Noworyta,[10] in a highly recommended paper, summarized the phenomena responsible for limiting the permeate flux during cyclic operation (i.e., permeation followed by cleaning). Concentration polarization, during the initial period of operation within a cycle, is one of the primary reasons for flux decline, J_a, (Fig. 2). Large-scale membrane systems operate in a cyclic mode, where a clean-in-place operation alternates with the normal run. The figure shows a decrease in the flux for pure water from cycle to cycle, $J_o(t)$, due to fouling, the flux decline within a cycle due to concentration polarization, $J(t_p)$, and the average flux under steady-state concentration, J_a. The latter also decreasing from cycle to cycle, suggests irreversible solute adsorption or fouling. Accumulation of the solute retained on a membrane surface leads to increasing permeate flow resistance at the membrane wall region.

One of the most serious forms of membrane fouling is bacterial adhesion and growth.[11] Once they form, biofilms can be very difficult to remove, either

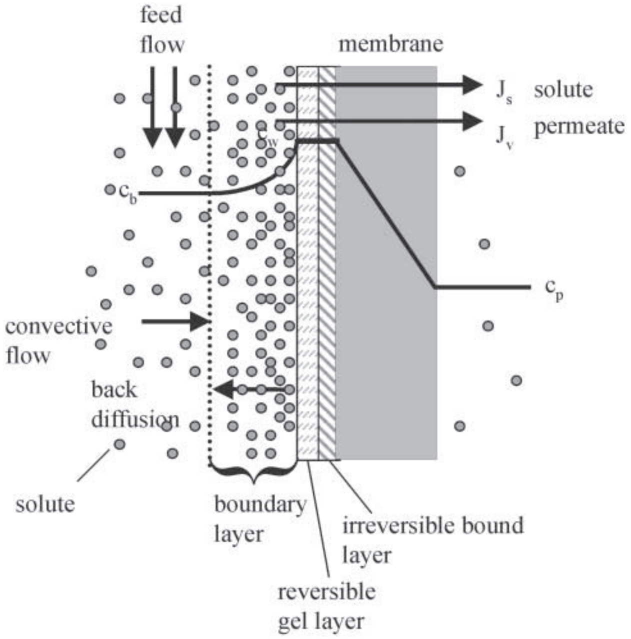

Figure 1. A schematic representation of concentration polarization and fouling at the membrane surface.

through disinfection or chemical cleaning. This wastes energy, degrades salt rejection, and leads to shortened membrane life. This is one area, for example, where further research is required.

Liquids to be Treated

RO and UF membranes have been used for the treatment of a variety of liquids, ranging from seawater, to waste water, to milk, and to yeast suspensions (Table 1). Each liquid varies in composition and in the type and the fraction of the solute(s) to be retained by the membrane. Complicating factors include the presence of substances, such as, for example, oil in seawater and in wastewater.[12–15] The presence of the oil normally necessitates an additional pretreatment step, as well as further complicating the fouling process. The presence of humic acids in surface water and wastewater also needs special attention.[16,17] The fouling phenomena, the preventive means (i.e., pretreatment), and the frequency and the type of membrane cleaning cycle are all dependent on the type of liquid being treated.

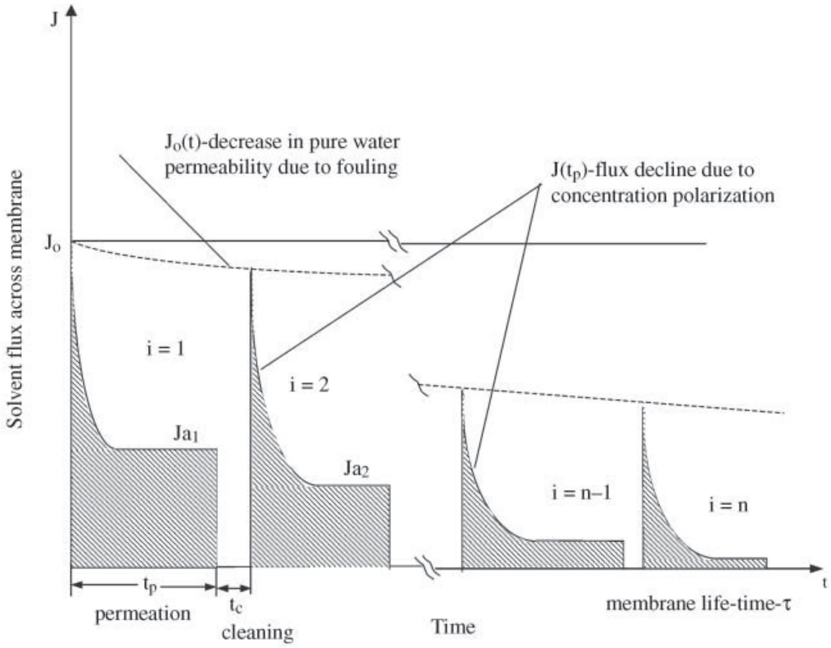

Figure 2. Diagram of typical flux-time dependency during cyclic operation in large-scale UF systems. Adapted from Koltuniewicz and Noworyta.[10]

Membrane Materials

Numerous polymer membranes have been developed for RO and UF applications (Table 2). The membrane materials range from polysulfone (PS) and polyethersulfone (PES) to cellulose acetate and cellulose diacetate.[12,18–23] Commercially available polyamide composite membranes for desalination of seawater, for example, are available from a variety of companies in the United States, Europe, and Japan.[24] The exact chemical composition and physical morphology of the membranes may vary from manufacturer to manufacturer. Since the liquids to be treated and the operating conditions also vary from application to application, it becomes difficult to draw general conclusions on which materials are the best to use to inhibit membrane fouling. The specific choice of which membrane material to use will depend on the process (e.g., type of liquid to be treated, operating conditions) and economic factors (e.g., cost of replacement membranes, cost of cleaning chemicals).

The scope of the current paper was to critically review the literature on the fouling phenomena in RO and UF membrane systems, the analytical

Table 1. Examples of liquids treated by RO and UF.

Liquid	References
Waste water (e.g., paper-mill effluent, municipal water, water containing polysaccharides, and amino sugars)	Chapman et al.,[60] Li et al.,[23] Dal-Cin et al.,[52] Ghayeni et al.,[25] Jarusutthirak et al.[41]
Surface water (humic acids)	Nystrom et al.,[16] Domany et al.[34]
Water-in-oil emulsions	Scott et al.,[15] Pope et al.,[14] Benito et al.,[13] Lindau and Jonsson[12]
Skimmed milk	Rabiller-Baudry et al.,[22] Mohammadi et al.[81]
Seawater	Glueckestern et al.,[58] Sablani et al.,[7] Wilf and Klinko[56]
Drinking water	Han et al.[62]
Yeast suspensions	Mores and Davis[82]
Water-containing proteins	Schafer et al.[35]
Water-containing organic colloids	Kabsch-Korbutowicz et al.[17]

techniques used to quantify fouling, preventive means, and membrane cleaning methods. The paper also makes specific recommendations on how scientists, engineers, and technical staff can assist in improving the performance of RO and UF systems through fundamental and applied research.

MEMBRANE FOULING PHENOMENA

Attempts to analyze membrane fouling have shown that the main mechanisms are adsorption of feed components, clogging of pores, chemical interaction between solutes and membrane material, gel formation, and bacterial growth. Let us first consider bacterial growth on membranes. Microbiological fouling of RO membranes is one of the main factors in flux decline and loss of salt rejection[25–29] (Table 3).

Microbiological Fouling

Understanding the mechanism of bacterial attachment may assist in the development of antifouling technologies for membrane systems. Bacterial fouling of a surface (i.e., formation of a biofilm) can be divided into three

Table 2. Examples of commercially available membrane materials.

Membrane material	References
Polyamide	Flemming and Schaule,[20] Belfer et al.,[24] Jenkins and Tanner,[72]
Polyamide–urea	Belfer et al.[24]
Polysulfone	Flemming and Schaule,[20] Rabiller-Baudry et al.,[22] Li et al.,[23] Lindau and Jonsson,[12] Tran-Ha and Wiley,[80] Mohammadi et al.[81]
Polyethersulfone	Flemming and Schaule,[20] Mohammadi et al.[81]
Polyetherurea	Flemming and Schaule[20]
Cellulose acetate/diacetate	Ridgway et al., [18,19] Amerlaan et al.[21]
Regenerated cellulose	Kabsch-Korbutowicz et al.[17]
Polyvinyl alcohol derivative	Ghayeni et al.[25]

phases: transport of the organisms to the surface, attachment to the substratum, and growth at the surface. Fleming et al.[30] have shown that it takes about 3 days to completely cover a RO membrane with a biofilm. Ghayeni et al.[25,26] studied initial adhesion of sewage bacteria belonging to the genus *Pseudomonas* to RO membranes. It was found that bacteria would sometimes aggregate upon adhering. While minimal bacterial attachment occurred in a very low ionic-strength solution, significantly higher numbers of attached microbes occurred when using salt concentrations corresponding to waste water.

In work similar to that of Ghayeni et al.,[25,26] Flemming and Schaule[20] demonstrated that after a few minutes of contact between a membrane and raw water, the first irreversible attachment of cells occurs. *Pseudomonas* was identified as a fast adhering species out of a tap water microflora. If nonstarving cells were used (i.e., sufficient nutrients and dissolved oxygen in the raw water), the adhesion process improved with an increase in the number of cells in suspension. When starving cells were used, incomplete coverage of the surface occurred. This is similar to the surface aggregate formations observed for membranes by Ghayeni et al.[25,26] Flemming and Schaule[20] also detected a biological affinity of different membrane materials toward bacteria. Polyetherurea, for example, had a significantly lower biological affinity than polyamide, PS, and PES. These results suggest that membrane manufacturers should stay away from polyamide and PS materials, at least for wastewater treatment applications.

Table 3. Summary of membrane fouling studies reported in the literature.

Fouling studies	References
Membrane fouling phenomena	
Microbial cell attachment	Flemming et al.,[30] Ghayeni et al.,[25] Flemming and Schaule,[20] ••Ridgway et al.,[28,31] Ridgway[33]
Humic acids and morphology of fouling layer	Nystrom et al.,[16] Schafer et al.,[35] Khatib et al.,[36] Kabsch-Korbutowicz et al.,[17] •Tu et al.,[37] Domany et al.,[34] ••Ridgway[31]
Inorganics	Sahachaiyunta et al.[38]
Proteins and colloids	Yiantsios and Karabelas,[39] Jarusutthirak et al.,[41] Schafer et al.,[35] Bacchin et al.[40]
Reversible adsorbed layer	••Nikolova and Islam,[29] ••Koltuniewicz and Noworyta[10]
Transition from reversible to irreversible fouling	••Chen et al.[42]
Variation in gel-layer thickness	••Denisov[54]
Pore blockage and cake formation	Zydney and Ho[27]
Analytical descriptions	
Fouling-layer morphology and growth	Riedl et al.,[43] Scott et al.[15]
Adhesion kinetics	Ridgway et al.[18,19]
Hydrodynamics	Altena and Belfort,[44] •Drew et al.,[45] Cherkasov et al.[32]
Passage of bacteria through membrane	•Ghayeni et al.[46]
Analysis of deposits: ATR, FTIR, measuring fouling in real time	Lindau and Jonsson,[12] Howe et al.,[47] Rabiller-Baudry et al.,[22] Chan et al.,[48] Bowen et al.,[49] ••Li et al.[23]
Measuring concentration polarization	•Gownan and Ethier,[50,51] Pope et al.[14]
Mathematical modeling of flux decline	Dal-Cin et al.,[52] •• Koltuniewicz and Noworyta[10]
Preventive means and cleaning methods	
Feedwater pretreatment	Wilf and Klinko,[56] Glueckstern and Priel,[58]
Microfiltration and ultrafiltration	Ghayeni et al.,[25] •Ghayeni et al.,[46] Karakulski et al.,[59] Chapman et al.[60]

(*continued*)

Table 3. Continued.

Fouling studies	References
Coagulation and flocculation	Nguyen and Ripperger,[61] Han et al.,[62] Choksuchart et al.,[63] Park et al.,[64] Guigui et al.,[65] ●●Lopez-Ramirez et al.,[66] Benito et al.,[13] Shaalan[67]
Spacers	●●Schwinge et al.,[69] Geraldes et al.,[68] Sablani et al.,[7] Li et al.,[23,69] Lipnizki and Jonsson[71]
Corrugated membranes	Lindau and Jonsson,[12] Scott et al.[15]
Surface chemistry	●Jenkins and Tanner,[72] Flemming and Schaule,[20] Ridgway et al.,[19] Belfer et al.[24]
Hydrophobic and hydrophilic membranes	Kabsch-Korbutowicz et al.,[17] ●Tu et al.,[37] Cherkasov et al.[32]
Control of operating parameters (Critical flux)	●Song,[79] ●●Chen et al.,[42] ●●Koltuniewicz and Noworyta,[10] Madireddi et al.,[74] Mallubhotla and Belfort,[77] Avlonitis et al.,[75] Goosen et al.,[3] Jackson et al.[78]
Rinsing water quality	Tran-Ha and Wiley,[80] ●Lindau and Jonsson[12]
Cleaning agents	Mohammadi et al.[81]
Back pulsing	Mores and Davis[82]
Membrane wear and degradation	Roth et al.,[83] ●Amerlaan et al.,[21] Ridgway et al.[19]
Economic aspects	Glueckstern et al.,[57] Brehant et al.[84]

Note: Specific papers are (●) recommended and (●●) highly recommended.

In a similar but more thorough study than that performed by Ghayeni et al.,[25] and Ridgway et al.[28,31] in two excellent papers reported on the biofouling of RO membranes with wastewater. Cellulose diacetate membranes became uniformly coated with a fouling layer that was primarily organic in composition. Calcium, phosphorous, sulfur, and chlorine were the major inorganic constituents detected. Protein and carbohydrate represented as much as 30% and 17%, respectively, of the dry weight of the biofilm. Electronmicroscopy revealed that the biofilm on the feed-water side surface of the membrane was 10 to 20-μm thick and was composed of several layers of compacted bacterial cells, many of which were partially or completely autolyzed. The bacteria were firmly attached to the membrane surface by an extensive network of extracellular polymeric fibrils. They showed that mycobacteria adhered to the cellulose acetate membrane surface 25-fold more effectively than a wild-type strain of *Escherichia coli.* In a key finding, the ability of *Mycobacterium* and *E. coli* to adhere to the membrane was correlated with their relative surface hydrophobicities, as determined by their affinities for *n*-hexadecane.[31] The results suggested that hydrophobic interaction between bacterial cell-surface components and the cellulose membrane surface plays an important role in the initial stages of bacterial adhesion and biofilm formation. A key question that arises is whether the importance of this hydrophobic interaction between the cell and the membrane also holds true for other polymers. This work is similar to that reported by Cherkasov et al.[32] on fouling resistance of hydrophilic and hydrophobic membranes (Fig. 3). A later research study carried out by Ridgway[33] confirmed that bacterial adhesion is regulated by the physicochemical nature of both the bacterial cell and the polymer membrane surface. The chemical composition of the feed water also was found to be critical.

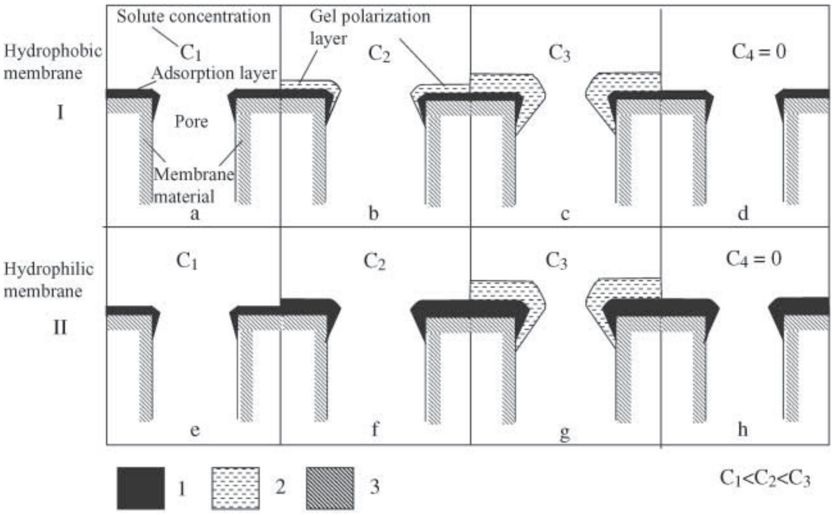

Figure 3. Gel-layer formation on surface of an UF membrane made from (I) hydrophobic and (II) hydrophilic material. *C*, solute concentration; $C_1 < C_2 < C_3$, 1 adsorption layer, 2 gel-polarization layer, 3 membrane material. Adapted from Cherkasov et al.[32]

Effect of Humic Acids

As organic matter, such as plants, degrades in the soil, a mixture of complex macromolecules, called humic acids, is produced. These complex molecules have polymeric phenolic structures with the ability to chelate metals, especially iron. They give surface water a yellowish to brownish color and often cause fouling problems in membrane filtration.[16,34] The fouling tendency of humic acids appears to be due to their ability to bind to multivalent salts. Nystrom et al.,[16] for example, showed that humic acids were most harmful in membranes that were positively charged (i.e., containing alumina—Al, and silica—Si). Humic acids formed chelates with the metals (i.e., multivalent ions) and could be seen as a gel-like layer on the filter surface. It was recommended that humic acids be removed from the process water before filtration by complexation (i.e., flocculation/coagulation; see section "Feed Water Pretreatment").

Morphology of Humic Acid Fouling Layer

Schafer et al.[35] studied the role of concentration polarization and solution chemistry on the morphology of the humic acid fouling layer. Irreversible fouling occurred with all membranes at high calcium concentrations. Interestingly, it was found that the hydrophobic fraction of the humic acids was deposited preferentially on the membrane surface. This result is similar to the work of Ridgway et al.[31] who showed that the hydrophobic interaction between a bacterial cell surface and a membrane surface plays a key role in biofilm formation. Schafer et al.[35] demonstrated that calcium-humate complexes caused the highest flux decline due to their highly compactable floc-like structures. Deposition increased with pH due to precipitation of calcite and adsorption of humic acid complexes on top of this layer. Humic acids had the highest concentration in the boundary layer. They also had the largest molecular weight and, therefore, the smallest back-diffusion rate and the greatest tendency toward precipitation. The formation of two layers, one on top of the other, also was observed by Khatib et al.[36] The formation of a Fe–Si gel layer directly on the membrane surface was mainly responsible for the fouling. Reducing the electrostatic repulsion between the ferric gel and the membrane surface encouraged adhesion.

Fouling Resistance of Hydrophilic Membranes

Kabsch-Korbutowicz et al.[17] demonstrated that the most hydrophilic of the membranes tested (i.e., regenerated cellulose) had the lowest proneness to fouling by organic colloids (i.e., humic acids). This is similar to the results of Schafer et al.[35] who showed that hydrophobic humic acid compounds had the greatest tendency toward membrane fouling. In the work of Kabsch-Korbutowicz et al.,[17] the best membrane displayed the highest permeability to humic acid solutions. The presence of mineral salts intensified the fouling process.

What these studies tell us is that to reduce fouling due to humic acids, it is best to use hydrophilic membranes, to have feed water with a low mineral salts content (e.g., calcium), and to work at low pH. These conclusions are supported by the excellent work of Tu et al.[37] who showed that membranes with a higher negative surface charge and greater hydrophilicity were less prone to fouling due to fewer interactions between the chemical groups in the organic solute and the polar groups on the membrane surface.

Effect of Inorganics

Dynamic tests were conducted by Sahachaiyunta et al.[38] to investigate the effect of silica fouling of RO membranes in the presence of minute amounts of various inorganic cations such as iron, manganese, nickel, and barium that are present in industrial and mineral processing wastewaters. Experimental results showed that the presence of iron greatly affected the scale structure on the membrane surface when compared with the other metal species.

Effect of Proteins and Colloid Stability

A dual-mode fouling process, similar to that observed for humic acids,[35] was found for protein [(i.e., bovine serum albumin (BSA)] fouling of microfiltration (MF) membranes. Protein aggregates first formed on the membrane surface, followed by native (i.e., nonaggregated) protein. The native protein attached to an existing protein via the formation of intermolecular disulfide linkages. The researchers successfully developed a mathematical model to describe this dual-mode process.

Yiantsios and Karabelas,[39] in a very interesting paper, found that apart from particle size and concentration, colloid stability plays a major role in RO and UF membrane fouling. Stable colloidal suspensions caused less fouling. They demonstrated that standard fouling tests as well as most well-known fouling models are inadequate. A key finding was that the use of acid, which is a common practice to avoid scaling in desalination, might promote colloidal fouling. Lowering the pH reduces the negative charge on particles, causing aggregate formation that deposits on the membrane surface. Colloidal fouling of membranes also has been modeled.[40]

Wastewater effluent organic matter was isolated into different fractions by Jarusutthirak et al.[41] Each isolate exhibited different characteristics in fouling of nanofiltration (NF) and UF membranes. For example, the colloidal fractions gave a high flux decline due to pore blockage, and hydrophobic interactions were very important for hydrophobic membranes, causing a reduction in permeate flux. In particular, polysaccharides and amino sugars were found to play an important role in fouling.

Reversible Adsorbed Layer Resistance

Nikolova and Islam[29] reported concentration polarization in the absence of gel-layer formation by using a laboratory scale UF unit equipped with a tubular membrane (Table 1). In a key study, they found that the decisive factor in flux decline was the adsorption resistance. With the development of a concentration polarization layer, the adsorbed layer resistance at the membrane wall increased linearly as a function of the solute concentration at the wall. They described the flux by the following relationship:

$$J = \frac{\Delta P - \Delta\pi(w)}{\mu(R_\mathrm{m} + kC_\mathrm{w})} \tag{1}$$

where ΔP is the hydraulic pressure difference across membrane, C_w is the concentration at the membrane surface, $\Delta\pi(w)$ is the corresponding osmotic pressure, R_m is the membrane resistance, kC_w is the adsorbed layer resistance, and μ is the fluid viscosity. In a key finding, they showed that the adsorption resistance was of the same order of magnitude as the membrane resistance. Surprisingly, the osmotic pressure was negligible in comparison with the applied transmembrane pressure. The significance of this study is that it showed that the reversible adsorbed solute layer at the membrane surface is the primary cause of flux decline and not the higher osmotic pressure at the membrane surface. This is supported by the work of Koltuniewicz and Noworyta[10] (Fig. 2).

Transition from Reversible Adsorption to Irreversible Fouling

The solute adsorption described by Nikolova and Islam[29] is reversible. The transition between this type of adsorption and irreversible fouling is crucial to determining the strategy for improved membrane performance and for understanding the threshold values for which optimal flux and rejection can be maintained. In a very thorough study, Chen et al.[42] reported on the dynamic transition from concentration polarization to cake (i.e., gel layer) formation for membrane filtration of colloidal silica. Once a critical flux, J_{crit}, was exceeded, the colloids in the polarized layer formed a consolidated cake structure that was slow to depolarize and in which reduced the flux. This study showed that by controlling the flux below J_{crit}, a polarization layer may form and solute adsorption may occur, but it is reversible and responds quickly to any changes in convection. This paper is a very valuable source of information for membrane plant operators. By operating just below J_{crit}, they can maximize the flux while at the same time reduce the frequency of membrane cleaning.

ANALYTICAL DESCRIPTIONS

Measuring Fouling-Layer Morphology and Growth

The physical structure of the membrane surface (i.e., surface roughness) can influence the morphology of the fouling layer. Riedl et al.[43] used an atomic force microscopy (AFM) technique to measure membrane surface roughness and scanning electron microscopy (SEM) to assess the fouling layer. It was shown that smooth membranes produced a dense surface fouling layer, whereas, this same layer or biofilm on rough membranes was much more open. The primary conclusion of a study by Riedl et al. was that fluxes through rough membranes are less affected by fouling formation than fluxes through smooth membranes. In a related study with a water-in-oil emulsion, Scott et al.[15] found that the use of corrugated membranes enhanced the flux in a more efficient way by promoting turbulence near the wall region, resulting in mixing of the boundary layer and, hence, reducing fouling.

Cell Adhesion Kinetics

The kinetics of adhesion of *Mycobacterium* to cellulose diacetate RO membranes have been described.[19] Adhesion of the cells to the membrane surface occurred within 1–2 hr and exhibited saturation-type kinetics that conformed closely to the Langmuir adsorption isotherm, a mathematical expression describing the partitioning of substances between a solution and a solid–liquid interface. This suggested that cellulose diacetate membrane surfaces may possess a finite number of available binding sites to which the mycobacteria can adhere. Treatment of the attached mycobacteria with different enzymes suggested that cell-surface polypeptides, 4- or α-1.6 linked glucan polymers, and carboxyl ester bond-containing substances (possibly peptiglycolipids) may be involved in the adhesion process. The exact molecular mechanisms of adhesion, however, have not as yet been clearly defined. Nor have all the specific macromolecular cell-surface ligands that mediate the attachment been identified. This is one area where further research is needed.

Hydrodynamic Studies of Microbial Adhesion

Fundamental studies of the membrane fouling process based on the movement of rigid neutrally buoyant spherical particles (i.e., a model bacterial foulant) toward a membrane surface were performed by Altena and Belfort[44] and Drew et al.[45] Their studies were an attempt to give clearer insight into the hydrodynamics behind the mechanism of microbial adhesion in RO systems. Under typical laminar flow conditions, particles with a radius smaller than 1 μm were captured by a porous membrane surface (i.e., the microbial adhesion step), resulting in cake formation. Due to convective flow into the membrane wall, particles moved laterally toward the membrane. The particle concentration near the membrane surface increased significantly over that in the bulk solution and resulted in a fouling layer. In their cross-flow membrane filtration experiments there appeared to be two major causes for lateral migration: a drag force exerted by the fluid on the particle due to the convective flow into the membrane wall (i.e., wall suction effect or permeation drag force) that carried particles toward the membrane and an inertial lift force that carried particles near the membrane away from the porous wall. For small particles (<1 μm) the permeation drag force dominated. An expression was developed from first principles to predict conditions under which a membrane module exposed to dilute suspensions of spherical particles will not foul. While these researchers did not work directly with microbial cells, their hydrodynamic studies do provide useful information on how the particle size and fluid flow affects microbial adhesion.

Passage of Bacteria Through MF Membranes

In a recommended paper, Ghayeni et al.[46] studied the passage of bacteria (0.5-μ diameter) through MF membranes in wastewater applications. Total and viable cell counts were measured microscopically by using two stains consisting of a bright blue DNA fluorochrome 4,6-diamidino-2-phenylindole (DAPI) and a red fluorescent flourochrome 5-cyano-2,3-ditolyl tetrazolium chloride (CTC), respectively. Membranes with pore sizes smaller than

0.2 μm still transmitted secondary effluent cells. This is an interesting study which showed that based on total cell counts (DAPI) up to 1% of the bacteria in the feed can pass to the permeate side. While a significant portion of the cells (e.g., 50%) in the permeate showed biological (CTC) activity, none of the cells were able to reproduce (i.e., culture on agar or in suspension). This is a good quantitative method for measuring cell injury. We can speculate that smaller cells, or membranes with larger pores, would allow for the passage of viable bacteria that would be able to reproduce. This could occur at some critical cell/pore ratio (Fig. 4).

Analysis of Deposits on Membrane Surface

Deposits on a membrane surface, before and after cleaning, can be analyzed by using SEM in combination with energy dispersive x-ray (EDX) combined with a microanalysis system permitting quantitative determination of elements.[12]

Attenuated Total Reflection and Fourier Transform Infrared Spectroscopy

Attenuated total reflection (ATR) and Fourier transform infrared (FTIR) spectroscopy can provide insight into the chemical nature of deposits on

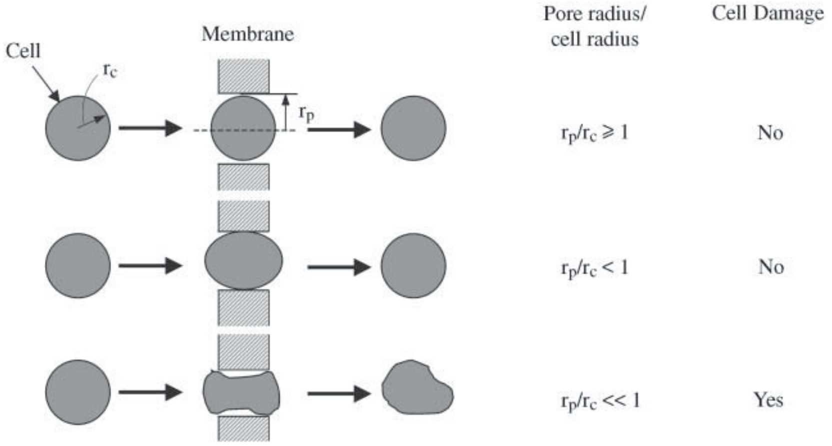

Figure 4. Passage of bacterial cells through membrane pores. Cell damage occurs at critical pore radius/cell radius ratio.

membranes.[47] The spectra of the foulants can be easily distinguished from the spectra of the membrane material. ATR–FTIR spectroscopy also can indicate the presence of inorganic foulants as well as the ratio of inorganic to organic foulants.

The surface deposits on UF PES membranes fouled by skimmed milk have been studied by using ATR–FTIR spectroscopy to detect the functional groups of the fouling species.[22] Two types of fouling conditions were assessed: static conditions as performed in a beaker and dynamic conditions as performed on a UF loop with applied pressure. For static conditions, all milk components adsorbed onto the PES surface. Some milk components (lactose and salts) were eliminated by water rinsing, whereas, proteins were only partially removed by chemical cleaning at basic pH. For dynamic conditions, the cleanliness of the membrane was evaluated through two criteria: hydraulic (i.e., recovery of initial flux) and chemical (i.e., no more contaminants detected). The hydraulic cleanliness of the membrane was achieved, whereas, the membrane initial surface state was not restored. Also, ATR–FTIR spectroscopy is a useful tool for evaluating other fouling species such as oil and humic acids.

Identification of specific species deposited onto membrane surfaces also can be carried out by using matrix assisted laser desorption ionization mass spectroscopy (MALDI-MS). Chan et al.[48] used this technique to differentiate between desorption of proteins from the membrane surface, from inside pores and from the membrane substrate. It was shown that the technique is a powerful tool for distinguishing between different proteins in fouling deposits. It has the potential for quantitative measurement of protein fouling on membrane surfaces.

Measuring Fouling in Real Time

AFM has proved to be a rapid method for assessing membrane–solute interactions (fouling) of membranes under process conditions.[49] Given the good agreement between the correlations when using AFM and the operating performance, it should be possible, in the future, to use these techniques to allow prior assessment of the fouling propensity of process streams.

Nondestructive, real-time observation techniques to detect and to monitor fouling during liquid separation processes are of great importance in the development of strategies to improve operating conditions. In a recommended paper by Li et al.,[23] ultrasonic time-domain reflectometry (UTDR) was used to measure organic fouling, in real time, during UF with PS membranes. The feed solution was a paper-mill effluent, which contained breakdown products of lignin or lignosulphonate, from a wastewater treatment plant. Experimental results showed that the ultrasonic signal response can be used to monitor fouling-layer formation and growth on the membrane in real time. Traditional flux measurements and analysis of the membrane surface by microscopy corroborated the UTDR results. Furthermore, the differential signal developed indicated the state and progress of the fouling layer and gave warning of advanced fouling during operation. This is a useful paper.

Measurement of Concentration Polarization

In other recommended papers, Gowman and Ethier[50,51] developed an automated laser-based refractometric technique to measure the solute concentration gradient during dead-end filtration of a biopolymer solution. This is a good paper that attempts to reconcile theory with experimental data. The refractometric technique may be useful to other researchers working on quantification of membrane fouling.

A nuclear magnetic resonance technique was used by Pope et al.[14] to quantitatively measure the concentration polarization layer thickness during cross-flow filtration of an oil–water emulsion. The technique, which measured layer thickness by using chemical shift selective microimaging, may be useful in studying other membrane fouling situations that occur in food processing and desalination. This method will help to clarify the relative quantitative contributions to flux decline of the adsorbed layer resistance and the concentration polarization layer gradient and thickness. It can help to explain the flux declines due to different resistances, as shown in Fig. 2.

Mathematical Models for Flux Decline and Relative Contributions

Dal-Cin et al.[52] developed a series resistance model to quantify the relative contributions of adsorption, pore plugging, and concentration polarization to flux decline during UF of a pulp mill effluent. They proposed a relative flux loss ratio as an alternative measure to the conventional resistance model that was found to be a misleading indicator of the flux loss. By using experimental and simulated flux data, the series resistance model was shown to underpredict fouling due to adsorption and to overpredict concentration polarization. This appears to be a disadvantage and would make the model of limited use in its current form. As mentioned in the Introduction, Koltuniewicz and Noworyta[10] modeled the flux decline as a result of the development of a concentration polarization layer based on the surface renewal theory developed by Danckwerts.[53] This is a highly recommended paper. The surface renewal model is more realistic than the commonly used film model, because mass transfer at the membrane boundary layer is random in nature due to membrane roughness. Specifically, the membrane is not covered by a uniform concentration polarization layer, as was assumed in the film model, but rather by a mosaic of small surface elements with different ages and, therefore, different permeate flow resistance. Any element can be swept away randomly by a hydrodynamic impulse and then a new element starts building up a layer of retained solute at the same place on the membrane surface. They showed that the decrease in flux with respect to time, $J(t_p)$, due to the development of the concentration polarization layer is given by the following equation, which also takes into account the rate of membrane surface renewal, s (area/unit time):

$$\bar{J}(t_p) = (J_o - J^*)\frac{s}{s+A}\frac{1 - e^{-(s+A)t_p}}{1 - e^{-st_p}} + J^* \tag{2}$$

where A is rate of loss of membrane surface area as a function of time, J_o is the initial value of the flux, J^* is the flux observed after infinite time, and t_p is the time of permeation.

$$s = A\frac{J_{lim} - J^*}{J_o - J_{lim}} \tag{3}$$

where J_{lim} is the limiting flux, which is similar to critical flux, J_{crit}. The former can be obtained from literature data. The average flux under steady-state conditions, J_a, can be calculated directly from Eq. (6) as a limit:

$$\bar{J}_a = \lim_{t_p \to \infty} \bar{J}(t_p) = (J_o - J^*)\frac{s}{A+s} + J^* \tag{4}$$

In support of this model, calculated values of flux by using Eqs. (2) and (3) agreed well with experimental data. The two equations describe a permeation cycle of duration, t_p, as shown in Fig. 2. This is a highly recommended paper for those who are operating large-scale continuous UF plants and to a certain extent RO plants. The model developed describes not only the dynamic behavior of a plant but it also allows for optimization of operating conditions (i.e., permeation time, cleaning time, cleaning strategy).

Variation in Gel-Layer Thickness along Flow Channel

It often is assumed that the thickness of the gel layer and the concentration of the solute are uniform over the membrane surface. However, these assumptions are only valid for systems where the hydrodynamic conditions of the solution flow near the membrane provide equal accessibility of solute to the entire membrane surface.[54] This is not true in the case of cross-flow filtration. One can, thus, expect that the gel-layer thickness and/or the surface concentration of the solute will vary with distance from the channel entrance. As a consequence, the local permeate flux will also vary with longitudinal position. In a highly recommended article, Denisov[54] presented a mathematically rigorous theory of concentration polarization in cross-flow UF, which takes into account the nonuniformity of the local permeate membrane flux. He derived equations describing the pressure/flux curve.

In the case of the gel-layer model, the theory led to a simple analytical formula for a limiting or critical flux, J_{lim}. The flux turned out to be proportional to the cube root of the ratio of the gel concentration to the feed solution concentration, rather than to the logarithm of this ratio, as the simplified Michaels–Blatt theory predicted:

$$J_{\text{lim}} = \left(\frac{3}{2}\right)^{2/3} KP_{\text{g}} = 1.31\left(\frac{C_{\text{g}}}{C_{\text{o}}}\right)\frac{m^{1/3}D^{2/3}U_{\text{o}}^{1/3}}{L^{1/3}h^{1/3}} \tag{5}$$

where

$$P_{\text{g}} = \left(\frac{C_g mD^2 U_{\text{o}}}{C_{\text{o}}K^3 Lh}\right) \tag{6}$$

where K is hydraulic permeability of membrane to pure solvent ($\text{m}^3/\text{N sec}$), C_{g} is the gel concentration (kmol/m^3), C_{o} is the solute concentration in feed solution (kmol/m^3), m is the channel parameter, D is the solute diffusion coefficient (m^2/sec), U_{o} is the longitudal component of fluid velocity averaged over the channel cross section (m/sec), L is the channel length (m), h is the transversal dimension of the channel (m).

In the case of the osmotic pressure model, the rigorous theory allowed the conclusion that at high applied transmembrane pressure, the permeate flux increased as a cube root of the pressure, so that the limiting flux was never reached:

$$\overline{J} \approx \left(\frac{3}{2}\right)^{2/3} K\overline{P}^{1/3}P_{\text{o}}^{2/3} \approx 1.31\left(\frac{\overline{P}}{RTC_{\text{o}}}\right)^{1/3}\frac{m^{1/3}D^{2/3}U_{\text{o}}^{1/3}}{L^{1/3}h^{1/3}} \tag{7}$$

where

$$P_{\text{o}} = \left(\frac{mD^2 U_{\text{o}}}{RTC_{\text{o}}K^3 Lh}\right) \tag{8}$$

where J is the average flux over the channel (m/sec), P is the transmembrane pressure (N/m^2), R is the gas constant (J/kmol K), T is the temperature (K). However, one minor weakness of the study was that the analysis ignored the concentration dependence of the viscosity and the partial transmission of the solute through the membrane.

Pore Blockage and Cake Formation

To understand the effect of membrane fouling on system capacity, the $V_{\max}$ test is often used to accelerate testing. This test assumes that fouling occurs by uniform constriction of the cylindrical membrane pores. This does not happen in practice. Zydney and Ho[27] examined the validity of the $V_{\max}$ model and compared the results with predictions from a new model that accounts for fouling due to both pore blockage and cake formation. It was found that the $V_{\max}$ analysis significantly overestimates the system capacity for proteins that foul primarily by pore blockage, but it underestimates the capacity for compounds that foul primarily by cake formation. In contrast, the pore blockage–cake filtration model provides a much better description of membrane fouling, leading to more accurate sizing and scale-up of normal flow filtration devices. Cake formation, shear forces, and other mathematical aspects, and the kinetics of the boundary layer are also described in an early study by Hermia.[55]

PREVENTIVE MEANS AND CLEANING METHODS

Feed Water Pretreatment

MF and UF

RO seawater systems that operate on surface feed water normally require an extensive pretreatment process to control membrane fouling. In recent years, new effective water microfiltration technologies have been introduced commercially. Wilf and Klinko[56] and Glueckstern et al.[57] noted that these developments can improve the quality of surface seawater feed to a level comparable with or better than the water quality from well-water sources. The utilization of capillary UF as a pretreatment step enabled operation of the RO system at a high recovery (15%) and permeate flux rate. In a similar study using MF and UF as seawater pretreatment steps for RO, Glueckstern and Priel[58] showed that such technology can dramatically improve the quality of the feed water. This is especially important if cooling water from existing power stations is used as feed water for desalination plants.

Municipal wastewater is one of the most reliable sources of water since its volume varies little through the year. The reuse of such water requires treatment to an acceptable quality level that satisfies regulatory guidelines. Ghayani et al.[25] used hollow fiber MF as a pretreatment for wastewater for RO in the production of high-quality water. Organisms present in MF-treated secondary effluent were able to attach to RO membranes and proliferate to form a biofilm. Total cell counts in this treated effluent (i.e., permeate from the MF unit) were several orders of magnitude higher than viable cell counts. This was confirmed in a later study.[46] What these results indicate is that MF membranes will not be totally effective in removal of bacteria from the feed water stream. The result showed that most cells were severely damaged by passage through the membrane (Fig. 4). However, we can speculate that this damaging effect may be cell-strain specific and/or dependent on the cell/pore diameter. Other types of microbial cells may survive the passage through the MF polymer membrane, resulting in possible fouling of the RO membrane farther upstream.

Ultrafiltration membranes also may be used to improve the quality of treated, potable water by removing suspended solids and colloids.[59]

Coagulation and Flocculation

Studies have looked at flocculation and its effects on membrane fouling from a range of different angles. In a study by Chapman et al.,[60] a flocculator was used to remove suspended solids, organics, and phosphorus from wastewater. The flocculator produced uniform microflocs, which were removed by cross-flow MF. Flocculated particles can form a highly porous filtration cake on a membrane surface. This will help inhibit fouling on the membrane by preventing the deposition of particles and, therefore, reducing the number of membrane cleaning cycles.[61]

Arsenic removal from drinking water is a major problem in many parts of the world. Han et al.[62] investigated arsenic removal by flocculation and MF. Ferric chloride and ferric sulfate were used as flocculents. The results showed that flocculation before MF led to significant arsenic removal in the permeate. Furthermore, the addition of small amounts of cationic polymeric flocculants resulted in significantly improved permeate fluxes during MF.

Coagulation, to remove turbidity from water by the addition of cationic compounds, is another commonly used method. The usefulness of coagulation as a pretreatment to remove microparticles in aqueous suspension before a membrane filtration was shown by Choksuchart et al.[63] There are several types of coagulation systems. Comparisons were made by Park et al.[64] between coagulation with only rapid mixing in a separate tank (i.e., ordinary coagulation) and coagulation with no mixing tank (i.e., in-line coagulation) before a UF process. The former was superior. An in-line coagulation (without settling) UF process also was ussed by Guigui et al.[65] Floc cake resistance was found to be lower than resistance due to the unsettled floc and the uncoagulated organics. A reduction in coagulant dose induced an increase in the mass transfer resistance. This study supported the results of Nguyen and Ripperger[61] who found that the flocculant cake was very porous.

Combining flocculation and coagulation in a pretreatment process also has been studied. In an key paper by Lopez-Ramirez et al.,[66] the secondary effluent from an activated sludge unit was pretreated, before RO, with three levels: intense (coagulation–flocculation with ferric chloride and polyelectrolite and high pH sedimentation), moderate (coagulation–flocculation with ferric chloride and polyelectrolite and sedimentation), and minimum (only sedimentation). The optimum for membrane protection, in terms of calcium, conductivity, and bicarbonates reduction, was the intense treatment. Membrane performance varied with pretreatment but not reclaimed water quality. The study recommended intense pretreatment to protect the membrane.

A modular pilot-size plant involving coagulation/flocculation, centrifugation, UF, and sorption processes was designed and constructed by Benito et al.[13] for the treatment of oily wastewaters. Different treatments were considered, depending on the nature of the oily waste emulsion. The main advantage of the plant was its versatility by allowing combinations of different treatments to be used for the most economic and safest treatment scheme for a given wastewater.

Empirical equations developed by Shaalan[67] predict the impact of water contaminants on flux decline. These formulas enable decision making concerning a suitable water pretreatment scheme and also selection of the most appropriate cleaning cycle.

Effects of Spacers on Permeate Flux and Fouling

Influence of Spacer Geometry on Boundary Layer Disruption

Sablani et al.[7] studied the influence of spacer thickness in spiral-wound membrane units on permeate flow and its salinity. Membrane parameters also were estimated by using an analytical osmotic pressure model for high salinity applications. The effects of spacer thickness on permeate flux showed that the observed flux decreases by up to 50% in going from a spacer thickness of 0.1168–0.0508 cm. The authors commented that the different geometry/configuration of the spacer influenced turbulence at the membrane surface and that, in turn, affected concentration polarization. This suggested less turbulence with the smaller spacer thickness and is opposite to what is normally expected. A membrane module with an intermediate spacer thickness of 0.0711 cm was found to be the best economically since it gave the highest water production rate (L/h).

Geraldes et al.[68] assessed the effect of a ladder-type spacer configuration in NF spiral-wound modules on concentration boundary layer disruption. The results showed that the average concentration polarization for the membrane wall was independent of the distance to the channel inlet, while for the membrane wall without adjacent filaments, the average concentration polarization increased with the channel length. This was due to the fact that in the first case the transverse filaments periodically disrupted the concentration boundary layer, while, in the second case, the concentration boundary layer grew continuously along the channel length. The experimental results of the apparent rejection coefficients were compared with model predictions, the agreement being good. Their results clearly established how crucial the spacers configuration is in the optimization of the spiral-wound module efficiency.

Computational Fluid Dynamics of Flow in Spacer-Filled Channels

The unexpected results of Sablani et al.[7] (i.e., less turbulence with smaller spacer thickness) may be best explained by an excellent paper by Schwinge et al.[69] The latter used computational fluid dynamics (CFD) in a study of unsteady flow in narrow spacer-filled channels for spiral-wound membrane modules. The flow patterns were visualized for different filament configurations incorporating variations in mesh length and filament diameter, and for channel Reynolds numbers, Re_{ch}, up to 1000. The simulated flow patterns revealed the dependence of the formation of recirculation regions on the filament configuration, mesh length, filament diameter, and the Reynolds number. When the channel Reynolds number was increased above 300, the flow became super critical, showing time-dependent movements for a filament located in the center of a narrow channel; and, when the channel Reynolds number was increased above 500, the flow became supercritical for a filament adjacent to the membrane wall. For multiple filament configurations, flow transition can occur at channel Reynolds numbers as low as 80 for the submerged spacer at a very small mesh length [mesh length/channel height $(L_{\mathrm{m}}/h_{\mathrm{ch}}) = 1$] and at a slightly larger Reynolds number at a larger mesh length ($L_{\mathrm{m}}/h_{\mathrm{ch}} = 4$). The transition occurred above Re_{ch} of 300 for a cavity spacer and above Re_{ch} of 400 for a zigzag spacer. We can speculate that the conclusions of Sablani et al.,[7] less turbulence with smaller spacer thickness, was due to fewer recirculating regions as a result of smaller mesh length and filament diameter.

The CFD simulations were used by Li et al.[70] to determine mass transfer coefficients and power consumption in channels filled with nonwoven net spacers. The geometric parameters of a nonwoven spacer were found to have a great influence on the performance of a spacer in terms of mass transfer enhancement and power consumption. The results from the CFD simulations indicated that an optimal spacer geometry exists. Lipnizki and Jonsson[71] also studied mass transfer in membrane modules. Their experiments were used to calculate the energy consumption vs. the mass transfer coefficient for different spacers.

MF by Using Corrugated Membranes

In a study with an oil-in-water emulsion Scott et al.[15] compared fluxes and fouling between flat membranes and corrugated membranes. Membrane fouling was found to consist of two distinct stages: initial pore blocking followed by cake layer formation. They found that the use of corrugated membranes enhanced the flux in a more efficient way by promoting turbulence near the wall region, similar to spacers, resulting in mixing of the boundary layer and, hence, reducing the concentration polarization.

Membrane Surface Modification

A fouling-resistant RO membrane that reduces microbial adhesion was reported by Jenkins and Tanner.[72] In this interesting study that confirmed the results of Flemming and Schaule,[20] they compared two types of thin-film composite membranes with different chemistries. One type was classified as a polyamide, the other used a new chemistry that formed a polyamide–urea barrier (i.e., surface) layer. The latter composite membrane proved superior in RO operation similar to that of the polyetherurea membrane of Flemming and Schaule,[20] including rejection of certain dissolved species and fouling resistance. These results suggest that the presence of urea groups in the membrane reduces microbial adhesion, perhaps through charge repulsion. The results of work by Ridgway[19] on the kinetics of adhesion of *Mycobacterium* to cellulose diacetate RO membranes has similar implications. Scientists should, therefore, be able to minimize microbial adhesion by controlling the surface chemistry of polymer membranes through, for example, the inclusion of urea groups.

Belfer[24] described a simple method for surface modification of commercial composite polyamide RO membranes. The procedure involved radial grafting with a redox system consisting of potassium persulfate/sodium metabisulfite. The ATR–FTIR spectroscopy provided valuable information about the degree of grafting and the microstructure of the grafted chain on the membrane surface. Both acrylic and sulfo-acidic monomers and neutral monomers such as polyethylene glycol methacrylate were used to demonstrate the wide possibilities of the method in terms of grafting of different monomers and initiators. It was shown that some of the modified membranes conserved their previous operating characteristics, flux, or rejection, but exhibited a higher resistance to humic acid. Additional work needs to be done to find out what happens to the fouling resistance of such membranes over the long term (i.e., after initial biofilm formation).

Chemical modification of a membrane surface can be used in combination with spacers and periodic applications of bioacids.[73] The paper by Redondo, however, is short on specifics (e.g., details of chemical modification of aromatic polyamides membrane surface) and, therefore, is not very useful to those looking for insights into membrane fouling

Fouling Resistance of Hydrophilic and Hydrophobic Membranes

Kabsch-Korbutowicz et al.[17] demonstrated that the most hydrophilic of the membranes tested (i.e., regenerated cellulose) had the lowest proneness to fouling by organic colloids (i.e., humic acids). These conclusions were further supported by the thorough work of Tu et al.[37] who showed that membranes with a higher negative surface charge and greater hydrophilicity were less prone to fouling due to fewer interactions between the chemical groups in the organic solute and the polar groups on the membrane surface. Cherkasov et al.[32] presented an analysis of membrane selectivity from the standpoint of concentration polarization and adsorption phenomena. The results of their study also showed that hydrophobic membranes attracted a thicker irreversible adsorption layer than hydrophilic membranes. The layer thickness was determined by the intensity of concentration polarization (Fig. 3). This may be due to the stronger attraction of water to hydrophilic membranes.

System Design and Control of Operating Parameters

Predicting Membrane Performance

A comprehensive difference model was developed by Madireddi et al.[74] to predict membrane fouling in commercial spiral-wound membranes with various spacers. This is a useful paper for experimental studies on the effect of flow-channel thickness on flux and fouling.

Avlonitis et al.[75] presented an analytical solution for the performance of spiral-wound modules with seawater as the feed. In a key finding, they showed that it was necessary to incorporate the concentration and pressure of the feed into the correlation for the mass transfer coefficient. In a similar study, Boudinar et al.[76] developed the following relationship for calculating mass transfer coefficients in channels equipped with a spacer:

$$k = 0.753\left(\frac{K}{2-K}\right)^{1/2}\frac{D_{\mathrm{S}}}{h_{\mathrm{B}}}Sc^{-1/6}\left(\frac{Peh_{\mathrm{B}}}{M}\right) \tag{9}$$

where Pe is Peclet number, $K = 0.5$ and $M = 0.6$ (cm).

Controlled centrifugal instabilities (called Dean vortices), resulting from flow around a curved channel, were used by Mallubhotla and Belfort[77] to reduce both concentration polarization and the tendency toward membrane fouling. These vortices enhanced back-migration through convective flow away from the membrane–solution interface and allowed for increased membrane permeation rates.

Temperature Effects

Goosen et al.[3] showed that the polymer membrane can be very sensitive to changes in the feed temperature. There was up to a 100% difference in the permeate flux between feed temperatures of 30°C and 40°C. A more recent study showed that the improved flux was due primarily, though not completely, to viscosity effects on the water. Reversible physical changes in the membrane also may have occurred.[78]

Critical Flux

A key phase in membrane separation processes is the transition from concentration polarization to fouling. This occurs at a critical flux. Song[79] indicated that in most theories developed, the limiting or critical flux is based on semi-empirical knowledge rather than being predicted from fundamental principles. To overcome this shortcoming, he developed a mechanistic model, based on first principles, for predicting the limiting flux. Similar to the critical flux results of Chen et al.[42] and the limiting flux of Koltuniewicz and Noworyta,[10] Song showed that there is a critical pressure for a given suspension. When the applied pressure is below the critical pressure, only a concentration polarization layer exists over the membrane surface. A fouling layer, however, will form between the polarization and the membrane surface when the applied pressure exceeds the critical pressure. The limiting or critical flux values predicted by the mechanistic model compared well with the integral model for a low concentration feed. Operators of RO/UF plants/units should, therefore, operate their systems just below the critical flux to maximize productivity while minimizing membrane fouling.

Membrane Cleaning

Since feed water pretreatment helps to prevent biofouling, once a membrane surface has been fouled, it must be cleaned. This will result in wear and tear and eventual loss of membrane properties.

Rinsing Water Quality

Membranes used in the food industry for UF of milk or whey are cleaned on a regular basis with water and various aqueous solutions to ensure hygienic operation and to maintain membrane performance. Water quality, therefore, is of special importance in the rinsing and cleaning process, because impurities present in the water could affect cleaning efficiency and, in the long term, could contribute to a reduction in performance and life of the membrane.[80] Membrane manufacturers generally recommend the use of high-quality water such as filtered and demineralized water. Installing and running water-purification systems, however, is expensive. Alternatively, water-treatment chemicals such as sequestering agents (e.g., ethylene diamine tetra-acetic acid (EDTA), polyphosphates) can be added to low-quality water to increase the solubility of metal ions such as calcium, magnesium manganese, and iron. RO permeate also may be of suitable quality for use in cleaning.

In a study by Tran-Ha and Wiley,[80] it was shown that impurities, such as particulate and dissolved salts present in the water, can affect the cleaning efficiency of a PS UF membrane. The water used for cleaning was doped with a known amount of specific ions (i.e., calcium, sodium, chloride, nitrate, and sulfate). The presence of calcium in water, at the usual concentrations found in tap water, did not greatly affect cleaning efficiency, chloride was found to reduce it. Sodium, nitrate, and sulfate appeared to improve the flux recovery during membrane cleaning. The cleaning efficiency also was improved at higher ionic strengths. For further reading, a similar study by Lindau and Jonsson[12] is recommended. They assessed the influence of different types of cleaning agents on a polysulfone UF membrane after treatment of oily wastewater.

Cleaning Agents

The effect of different cleaning agents on the recovery of the fouled membrane was studied by Mohammadi et al.[81] Results showed that a combination of sodium dodecyl sulfate and sodium hydroxide can be used as a cleaning material to reach the optimum recovery of the PS membranes used in milk concentration industries. Also, a mixture of sodium hypocholorite and sodium hydroxide showed acceptable results, whereas washing with acidic solutions was not effective.

Backpulsing

Mores and Davis,[82] to view membrane surfaces at different times in cross-flow MF, used direct visual observation (DVO) of yeast suspensions with rapid backpulsing at varied backpulsing duration and pressure. The DVO photograph showed that the membranes were more effectively cleaned by longer backpulse durations and higher backpulse pressures. However, trade-offs existed between longer and stronger backpulses and permeate loss during the backpulse. Shorter, stronger backpulses resulted in higher net fluxes than longer, weaker backpulses.

Membrane Wear and Degradation

Roth et al.[83] proposed a method to determine the state of membrane wear by analyzing sodium chloride stimulus–response experiments. The shape of the distribution of sodium chloride in the permeate flow of the membrane revealed the solute permeation mechanisms for used membranes. For new membranes, the distribution of sodium chloride collected in the permeate side, as well in the rejection side, was unimodal. For fouled membranes, they noted the presence of several modes. The existence of a salt leakage peak, as well as an earlier detection of salt for all the fouled membranes, gave evidence of membrane structure modification. The intensive use of the membranes might have created an enlargement of the pore sizes. Salt and solvent permeabilities increased as well. While this is a difficult paper to follow, it may be of use to those who want to develop new methods for measuring membrane degradation.

Amerlaan et al.[21] reported on membrane degradation resulting in a premature loss of salt rejection by cellulose acetate membranes. Tests were initiated to find a solution to the problem and to gain a better understanding of the mechanisms involved. It was found that removal of all free chlorine solved the problem. This was accomplished by injecting ammonia in the feed water, presumably resulting in formation of ammonium chloride. Membrane damage by chlorine was also reported by Ridgway et al.[18]

They studied membrane fouling at a wastewater treatment plant under low- and high-chlorine conditions. High chlorine residuals damaged the membrane structure and reduced mineral rejection capacity.

ECONOMIC ASPECTS

Scientists often forget that successful commercialization of a new technology is dependent on economic factors. Just because a novel separation technique works in the laboratory, for example, it does not mean that it will replace current methods. The new technique must, at minimum, be comparable in overall cost and, preferably, be lower in cost.

Field evaluation of a hybrid membrane system consisting of an UF membrane pretreatment unit and a RO seawater unit was conducted by Glueckstern et al.[57] For comparison, a second pilot system consisting of conventional pretreatment and an RO unit was operated in parallel. The conventional pretreatment unit included in-line flocculation followed by media filtration. The study showed that UF provided a very reliable pretreatment for the RO system, independent of the raw-water-quality fluctuations. However, the cost of membrane pretreatment was higher than conventional pretreatment. This suggested that membrane pretreatment for RO desalting systems is only economical for sites that require extensive conventional pretreatment or where wide fluctuations in the raw-water quality are expected.

The competitiveness of UF pretreatment in comparison with conventional pretreatment (i.e., coagulation and media filtration) was assessed by Brehant et al. [84] by looking at the impact on RO hydraulic performances. The study showed that UF provided permeate water with high and constant quality resulting in a higher reliability of the RO process than with a conventional pretreatment. The combination of UF with a precoagulation at low dose helped in controlling UF membrane fouling. The authors concluded that the combined effect of a higher recovery and a higher flux rate promised to significantly reduce the RO plant costs. The conclusions reached where opposite of those reported in the paper by Glueckstern et al.[57] above, and demonstrate the complexity of the overall economics of a membrane separation process.

CONCLUDING REMARKS

Experimental and modeling studies were assessed to give a more fundamental insight into the mechanism of the biofouling process, how to quantify it, and how to reduce it. This review has shown that the fouling process is a complex mechanism where the physicochemical properties of the membrane, the type of cells, the quality of the feed water, the type of solute molecules, and the operating conditions all play a role. The end result of most membrane processes is a fouled surface that the operator will not be able to clean to its original state. To reduce the tendency to irreversible fouling, it is essential to operate the plant/unit below the critical flux. This must go hand in hand with reliable feed water pretreatment schemes.

What areas need further research? Studies are required on effective removal of biofilms without damaging the membrane. Additional work needs to be done to find out what happens to the fouling resistance of chemically modified membranes over the long term (i.e., after initial biofilm formation). Membrane resistance to humic acids is another area for further study. It is also noteworthy that the molecular tools needed for exploring the biochemical details of the microbial adhesion process to membranes are now available.

In closing, consider for a moment the entire water resources issue on a global scale. Various aspects of the water problem need to be considered not only by developing nations but also by developed countries. Water is required for urban development, industrialization, and agriculture. An increase in the world population results in an increase in water usage. We can stipulate that in the future serious conflicts will arise not because of a lack of oil but because of water shortages. A three-pronged approach, therefore, needs to be taken by society; water needs to be effectively managed, it needs to be economically purified, and it needs to be conserved. As scientists and engineers continue to improve the technical and economic efficiency of membrane desalination systems, it is imperative that we do not lose sight of the bigger water resources picture. It is a challenge that we should be well able to meet.

NOMENCLATURE

A	Rate of loss of membrane surface area as function of time (m^2/sec)
AFM	Atomic force microscopy
ATR	Attenuated total reflection
c_b	Bulk solute concentration (mole/cm^3)
C_g	Gel concentration (kmol/m^3)
C_o	Solute concentration in feed solution (kmol/m^3)
c_p	Permeate solute concentration (mole/cm^3)
C_w	Concentration at membrane surface (mole/cm^3)
D	Solute diffusion coefficient (m^2/sec)
FTIR	Fourier transform infrared
h	Transversal dimension of channel (m)
i	Cycle number

J	Solvent flux across membrane (m^3/m^2 sec)
J^*	Flux at infinite time (m^3/m^2 sec)
J_a	Average flux under steady-state conditions (m^3/m^2 sec)
J_{ai}	Solvent flux at time a and in cycle i (m^3/m^2 sec)
J_{crit}	Limiting or critical flux (m^3/m^2sec)
J_{lim}	Limiting or critical flux (m^3/m^2 sec)
J_o	Solvent flux at beginning of cycle (m^3/m^2 sec)
J_s	Solute flux (mole/cm^2 sec)
$J(t_p)$	Solvent flux as function of permeation time (m^3/m^2 sec)
J_v	Permeate flux (mole/cm^2 sec)
K	Hydraulic permeability of membrane to pure solvent (m^3/N sec)
k	Mass transfer coefficient
kC_w	Adsorbed layer resistance
L	Channel length (m)
m	Channel parameter
ΔP	Hydraulic pressure difference across membrane (cm/sec)
P	Transmembrane pressure (N/m^2)
Pe	Peclet number
RO	Reverse osmosis
R_m	Membrane resistance
R	Gas constant (J/kmol K)
Sc	Schmidt number
T	Temperature (K)
t_p	Permeation time (hr)
t_c	Cleaning time (hr)
UF	Ultrafiltration
UTDR	Ultrasonic time-domain reflectometry
U_o	Longitudal component of fluid velocity averaged over channel cross section (m/sec)

Greek Symbols

$\Delta(w)$	Osmotic pressure at membrane surface (cm/sec)
μ	Fluid viscosity
τ	Membrane lifetime (y)

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