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# Fouling in Membrane Filtration and Remediation Methods

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## 1. Introduction

The growth of the membrane technologies has fell far behind the initial anticipation, one of the major obstacles, which hinders more widespread of its application, is that the filtration performance inevitably decreases with filtration time. This phenomenon is commonly termed as membrane fouling, which refers to the blockage of membrane pores during filtration by the combination of sieving and adsorption of particulates and compounds onto the membrane surface or within the membrane pores. Pore blockage reduces the permeate production rate and increases the complexity of the membrane filtration operation. This is the most challenging issue for further membrane development and applications.

Permeate flux and transmembrane pressure (TMP) are the best indicators of membrane fouling. Membrane fouling leads to a significant increase in hydraulic resistance, manifested as permeate flux decline or TMP increase when the process is operated under constant-TMP or constant-flux conditions. In a system where the permeate flux is maintained by increasing TMP, the energy required to achieve filtration increases. Over a long period of operation, membrane fouling is not totally reversible by backwashing. As the number of filtration cycles increases, the irreversible fraction of membrane fouling also increases. In order to obtain the desired production rate, chemical cleaning is required for membrane to regain most of its permeability. The resultant elevated cost makes membranes economically less feasible for many separation processes. There are also concerns that repeated chemical cleaning might affect the membrane life.

Fouling can be broadly classified into backwashable or non-backwashable, and reversible or irreversible based on the attachment strength of particles to the membrane surface. Backwashable fouling can be removed by reversing the direction of permeate flow through the pores of the membrane at the end of each filtration cycle. Non-backwashable

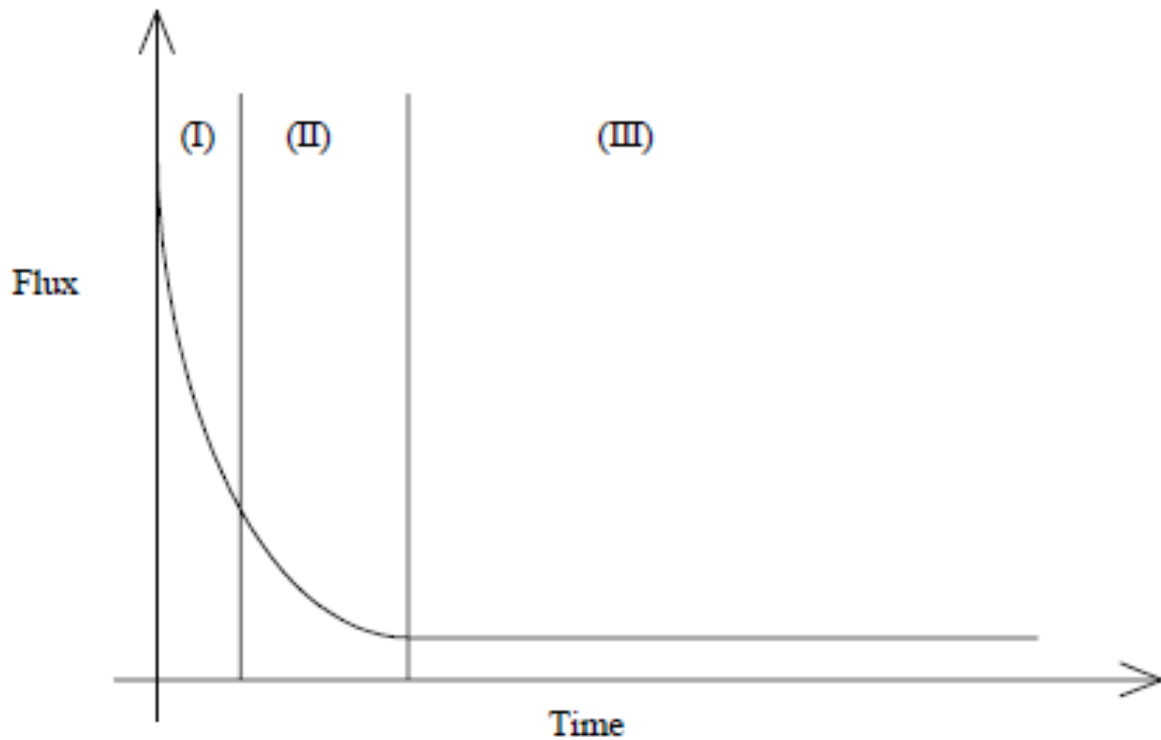
fouling is the fouling that cannot be removed by normal hydraulic backwashing in between filtration cycles. However, non-backwashable fouling of the membrane can be handled by chemical cleaning. On the other hand, irreversible fouling cannot be removed with flushing, backwashing, chemical cleaning, or any other means, and the membrane cannot be restored to its original flux. Fouling also can be classified, based on the type of fouling material, into four categories: inorganic fouling/scaling, particle/colloidal fouling, microbial/biological fouling, and organic fouling. Inorganic fouling or scaling is caused by the accumulation of particles when the concentration of the chemical species exceeds its saturation concentration. Several studies have shown that increased concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  caused more fouling [1-3]. On the other hand, organic fouling occurs due to the clogging of the membrane by organic substances, and organic carbons generally concentrate on the internal surface of the membrane [4]. Based on the analysis of the extracted solution during chemical cleaning, it was found that most soluble organic foulants were of low molecular weights, and calcium was the major inorganic foulant [5].

Natural organic matter (NOM) is the organic material present in surface or ground water and contains various high molecular weight organic compounds. NOM includes both humic and non-humic fractions. The humic fraction consists of high molecular weight organic molecules. Common non-humic NOM foulants are proteins, amino sugars, polysaccharides, and polyoxyaromatics [6]. Several studies have shown that NOM is the major ultrafiltration membrane foulant, and different components of NOM cause different forms of fouling [7-9]. According to Makdissy *et al.*, the organic colloidal fraction causes significant fouling [10]. However, polysaccharides are identified as the dominant foulant [11]. Other studies reported that most fouling was caused by hydrophobic NOM components [12]. Nevertheless, neutral hydrophilic NOM components were found the major foulants by some researchers [13]. The NOM components, as the major foulants, can be ranked in the order neutral hydrophilics > hydrophobic acids > transphilic acids > charged hydrophilics. Due to conflicting results from different researchers and many facets of membrane fouling, there would be no universal solution for membrane fouling remediation, but it has to be dealt with and designed specifically for a certain type of foulant and membrane in use, as presented later in this paper.

## 2. Membrane fouling mechanism

A typical flux-time curve of ultrafiltration (UF), as shown in Figure 1, starts with (I) a rapid initial drop of the permeate flux, (II) followed by a long period of gradual flux decrease, and (III) ended with a steady-state flux.

Flux decline in membrane filtration is a result of the increase in the membrane resistance by the membrane pore blockage and the formation of a cake layer on the membrane surface. The pore blocking increases the membrane resistance while the cake formation creates an additional layer of resistance to the permeate flow. Pore blocking and cake formation can be considered as two essential mechanisms for membrane fouling.



**Figure 1.** A Schematic presentation of the three stages in flux decline [14]

The rapid initial drop of the permeate flux can be attributed to quick blocking of membrane pores. The maximal permeate flux always occurs at the beginning of filtration because membrane pores are clean and opened at that moment. Flux declines as membrane pores are being blocked by retained particles. Pores are more likely to be blocked partially and the degree of pore blockage depends on the shape and relative size of particles and pores. The blockage is generally more complete when the particles and pores are similar in both shape and size [15-17]. Pore blocking is a quick process compared with cake formation since less than one layer of particles is sufficient to achieve the full blocking [16, 18].

Further flux decline after pore blockage is due to the formation and growth of a cake layer on the membrane surface. The cake layer is formed on the membrane surface as the amount of retained particles increases. The cake layer creates an additional resistance to the permeate flow and the resistance of the cake layer increases with the growth of cake layer thickness. Consequently, the permeate flux continues decreasing with time.

### 3. Mathematical models for membrane fouling

Pursuant to the understanding of different roles of aquatic components in membrane fouling, different mathematical models have been developed to describe the membrane fouling. The

most widely used empirical model is the cake filtration model that focuses on the role of particles larger than membrane pore sizes. In this model, the hydrodynamic resistance of cake layer [ $R_c$ ,  $m^{-1}$ ] is defined as:

$$R_c = \hat{R}_c \cdot m_d \quad (1)$$

where  $\hat{R}_c$  [ $m/kg$ ] is the specific cake resistance of the cake layer on the membrane surface and  $m_d$  [ $kg/m^2$ ] is the mass of deposit per unit surface area of membrane. The corresponding permeate flux ( $J$ ,  $m^3/m^2 \cdot s$ ) is expressed using Darcy's law and a resistance-in-series model (RIS) as below:

$$J = \frac{\Delta P}{\mu (R_m + R_c)} \quad (2)$$

where  $\Delta P$  (Pa) is transmembrane pressure,  $\mu$  (Pa-s) is the solution viscosity and  $R_m$  ( $1/m$ ) is the hydrodynamic resistance of clean membrane. Additional work has been done to relate  $\hat{R}_c$  to the structure of the cake layer formed by particles or aggregates [19, 20]. The cake filtration model has been used to fit filtration data and reasonable results have been obtained [21]. However, the model does not explain the mechanisms of fouling, but only indicates the proportionality between the increase in hydrodynamic resistance and the mass of deposit on the membrane as filtration proceeds under some conditions. The values of  $\hat{R}_c$  vary from  $10^{10}$  to  $10^{16}$   $m/kg$  for different aquatic substances [22]. Babel *et al.* [23] found that  $\hat{R}_c$  for a *Chlorella* algae culture changed from  $10^{11}$  to  $10^{12}$   $m/kg$  when the growth condition became inhibitive. Foley [24] reviewed different factors affecting the permeability of the cake layer formed in dead-end microfiltration of microbial suspensions. It was found that  $\hat{R}_c$  is dependent on cell morphology, surface properties, operating pressure, and time. The resistance-in-series model has been used frequently to analyze membrane fouling phenomenon. Although it is easy to apply, one should be cautious in the use of this model as it doesn't consider pore blocking mechanism.

Kosvintsev *et al.* [25] developed another model to describe fouling by physical sieving of low pressure membranes by particles larger than membrane pore sizes. According to their analysis, membrane fouling by cake filtration does not start right after the onset of filtration, and the fouling is rather dominated by pore blocking until the membrane surface is covered by particles. This model describes the permeate volume as a function of permeate time, dominated by pore blocking at constant pressure as follows:

$$V = \frac{1}{\gamma n \beta} \ln (1 + \beta t^*) \quad (3)$$

where  $V$  is the permeate volume ( $\text{cm}^3$ ),  $\beta$  is the ratio of the membrane area fouled with particles to the area of clean pores. This constant must be identified from experimental measurement for a given membrane and it should be slightly greater than unity.  $n$  the number of particles per unit volume of the feed,  $\gamma$  is the ratio of the pores area to the total membrane area and  $t^*$  is the dimensionless filtration time  $= \gamma n \int_0^t \frac{dV}{dt}$ . More details of the model are presented in the authors' recent work [26]. This model was limited to pore blocking fouling and the effect of cake layer on the permeate volume was not considered.

Zydney *et al.* combined two fouling mechanisms, pore blockage and cake formation, to describe fouling of low pressure membranes by proteins and humic acids [27, 28]. Again, this model is established by assuming that the fouling is caused primarily by large particles, aggregates of proteins and humic acids. The mathematical development is based on constant pressure operation and varying flux, and it can be written as below:

$$\frac{J}{J_0} = \exp\left(-\frac{K_b \Delta P C_b}{\mu R_m} t\right) + \frac{R_m}{R_m + R_c} \left[1 - \exp\left(-\frac{K_b \Delta P C_b}{\mu R_m} t\right)\right] \quad (4)$$

where  $J$  and  $J_0$  ( $\text{m}^3/\text{s}$ ) are the permeate flux at a given time and the initial flux through the unfouled membrane respectively,  $K_b$  ( $\text{m}^2/\text{kg}$ ), a pore blockage parameter, is equal to the blocked membrane area per unit mass of aggregates convected to the membrane. This parameter can be measured experimentally.  $C_b$  ( $\text{kg}/\text{m}^3$ ) is the bulk concentration of large aggregates,  $R_m$  ( $1/\text{m}$ ) is the clean membrane resistance,  $R_c$  is cake layer resistance ( $1/\text{m}$ ),  $\mu$  is the solution viscosity and  $\Delta P$  is the transmembrane pressure (Pa). Both resistances can be measured experimentally. The right-hand side of the equation has two terms that are related to pore blocking and cake formation, respectively. The first term (pore blocking) dominates the early stage of fouling, and the second term (cake filtration) governs fouling at longer times. The impact of solution chemistry on membrane fouling is, however, not included in the model, but was rather considered as a prerequisite for the aggregation of proteins or humic acids.

In comparison to the aforementioned models, adsorptive fouling of membranes by particles smaller than membrane pore sizes is incorporated in the following model. The impact of the adsorption layer on the permeability of membranes can be estimated using a modified form of Hagen-Poiseuille capillary filtration model [29] as below:

$$\frac{J}{J_0} = \left[1 - \frac{\delta'}{r_p}\right]^4 \quad (5)$$

where  $J$  and  $J_0$  ( $\text{m}^3/\text{m}^2 \cdot \text{s}$ ) are the permeate flux after the formation of the adsorptive fouling layer and the initial flux, respectively, under a given transmembrane pressure,  $\delta'$  (m) is the thickness of the adsorption layer that can be measured experimentally and  $r_p$  (m) is the membrane pore radius. The major difficulty in applying the adsorptive fouling model to

filtration of natural surface waters lies in the complex nature of aquatic NOM. In other words, the value of  $\delta'$  is not easy to obtain either theoretically or experimentally. This problem is further complicated by the heterogeneity of membrane surface properties.

## 4. Chemical attachment of foulants on membrane surfaces

An underlying question on membrane fouling is the origin of the attachment of foulants on the membrane surface. The major forces contribute to attachment are dispersion interaction force and polar interactions force [30]. These forces apply to material entities at different scales.

### 4.1. Chemical attachment by dispersion interaction

Foulants stay together on membrane surfaces most likely due to the presence of physiochemical interactions, such as the dispersion interaction between aqueous entities. This dispersion interaction is due to Van der Waals attractive force between molecules across water and is balanced by the electrostatic repulsion between particles and the membrane surface due to the presence of surface charges. As shown in energy curve figure (2) the height of the energy barrier depends not only on how strong the attractive interaction is, but also on the magnitude of the repulsive electrostatic interaction. Therefore, it is usually considered beneficial to increase the charge density of the similarly charged interacting entities to reduce attachment.

To represent the dispersion interaction, the Hamaker constant can be used. It is the property of a material, which represents the strength of van der Waals interactions forces between macroscopic bodies through a third medium as shown in Figure (3). Typical values of the Hamaker constant are in the range of  $10^{-19}$  -  $10^{-21}$  Joules. It can be estimated using the Lifshitz theory of macroscopic van der Waals interactions forces, which ignores the atomic structures of the interacting molecules, and calculates the forces between them in terms of their dielectric constants ( $\epsilon$ ) and refractive indices ( $n$ ) [31, 32]. The Hamaker constant,  $A$ , for two macroscopic phases 1 and 2 interacting across a medium 3 is approximated as:

$$A \approx \frac{3}{4}KT \frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \cdot \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \cdot \frac{3hv_e}{8\sqrt{2}} \cdot \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2} (n_2^2 + n_3^2)^{1/2} \left\{ (n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2} \right\}} \quad (6)$$

where "1" and "2" denote two interacting bodies inside medium "3",  $A$  is the Hamaker constant,  $ve$  is the medium absorption frequency (for  $H_2O$ ,  $ve = 3 \times 10^{15} s^{-1}$ ),  $\epsilon$  is the dielectric constant that indicates the extent to which a material concentrates electric flux,  $n$  is the refractive index,  $K$  is the Boltzmann constant,  $h$  is the Planck constant and  $T$  is the absolute temperature [33].

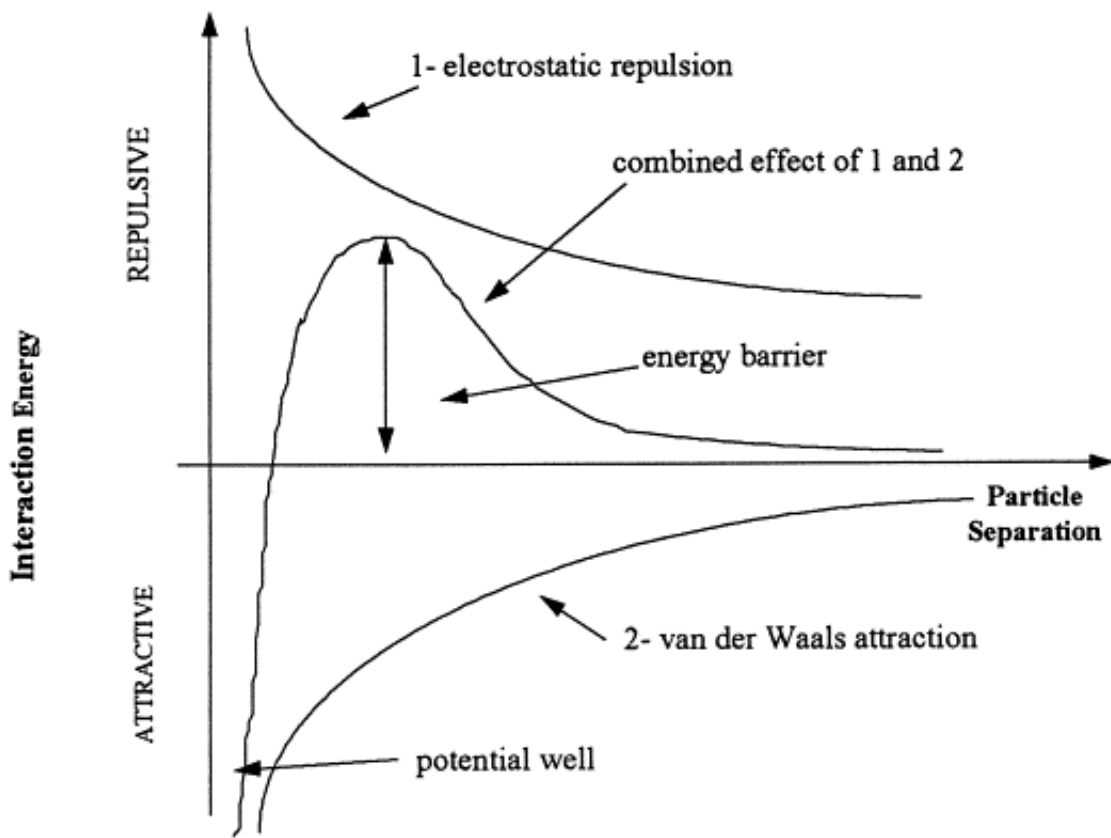


Figure 2. Energy curve of interaction forces [33]

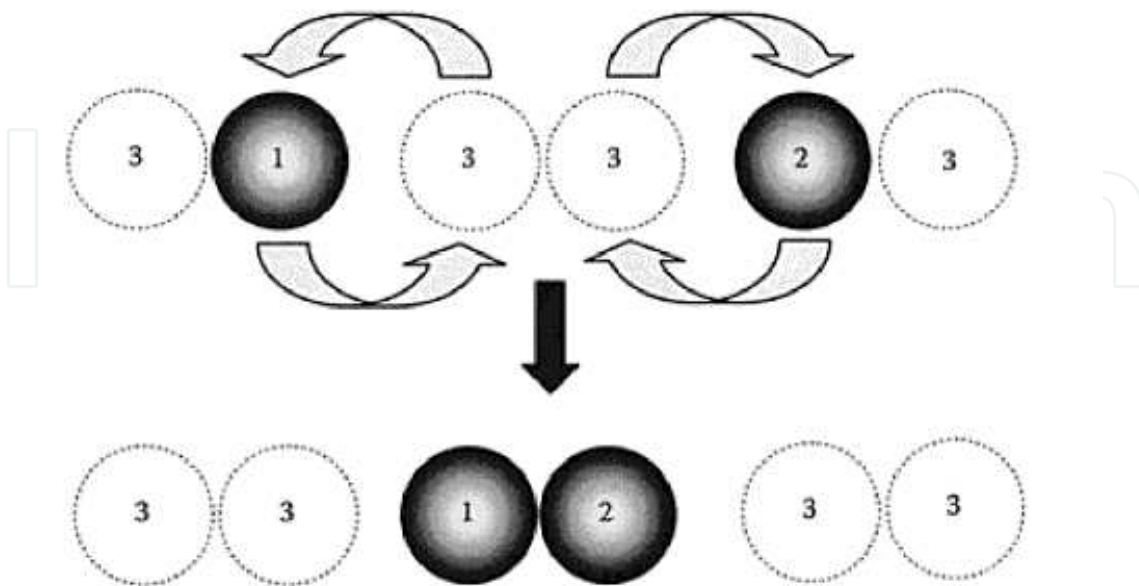


Figure 3. Interaction between 2 microscopic bodies 1 and 2 through medium 3 [33]



Table 1 lists the Hamaker constants representing the van der Waals interaction between polystyrene latex particles and different membrane materials across water, calculated using the macroscopic approach [30]. The Hamaker constant at zero frequency,  $A_{v=0}$ , represents the static interaction and this term is always less than or closed to  $\frac{3}{4} KT$ . The Hamaker constant at zero frequency is less than the total strength of van der Waals interactions forces. Hamaker constants at frequencies above zero,  $A_{v>0}$ , is related to the three refractive indices, or fundamentally, the dispersion interaction between these surfaces. As shown in Table 1, the minimum and the maximum interaction force are observed in PTFE and alumina membranes with latex particles, respectively. The dispersion interaction between latex and PVDF is slightly less than half of that between two latex particles which indicates less irreversible fouling. [33]

Interaction System <sup>1</sup> (1-3-2)	Dielectric Constant (kHz) <sup>2</sup>			Refractive Index <sup>3</sup>			Hamaker Constant x 10 <sup>21</sup> (J)		
	$\epsilon_1$	$\epsilon_3$	$\epsilon_2$	n1	n3	n2	$A_{v=0}$	$A_{v>0}$	$A_{tot}$
Latex -Water- PTFE	2.55	80	2.1	1.557	1.333	1.359	2.75	1.55	4.3
Latex -Water- PVDF	2.55	80	6.4	1.557	1.333	1.42	2.47	5.12	7.59
Latex -Water- CA	2.55	80	4.5	1.557	1.333	1.475	2.59	8.27	10.9
Latex -Water- PP	2.55	80	1.5	1.557	1.333	1.49	2.79	9.12	11.9
Latex -Water- Cellulose nitrate	2.55	80	6.4	1.557	1.333	1.51	2.47	10.2	12.7
Latex -Water- PES	2.55	80	3.5	1.557	1.333	1.55	2.65	12.5	15.1
Latex -Water- Latex	2.55	80	2.55	1.557	1.333	1.557	2.72	12.8	15.6
Latex -Water- PC	2.55	80	2.95	1.557	1.333	1.586	2.69	14.4	17.1
Latex -Water- Alumina	2.55	80	11.6	1.557	1.333	1.75	2.16	22.9	25.1
Latex -Water- fused quartz	2.55	80	3.8	1.557	1.333	1.448	2.63	6.74	9.37

Note: 1 PTFE: Polytetrafluoroethylene, PVDF: Polyvinylidene fluoride, CA: Cellulose acetate, PP: Polypropylene, PES: Polyethersulfone, PC: Polycarbonate; dielectric constant [31], Refractive index [32];  $A_{tot} = A_{v>0} + A_{v=0}$

**Table 1.** Hamaker constants calculated using the Lifshitz equation for representative particle-membrane interaction systems [30]

#### 4.2. Physiochemical attachment by “polar” interactions

The Derjaguin and Landau, Verwey and Overbeek ( DLVO) theory has been extended, including different types of interactions, to applications with aqueous phase. Van Oss postulated the concepts of apolar and polar interactions to classify and predict these interactions [30]. The apolar interaction mainly consists of dispersion interaction. On the other hand, the polar (or Lewis acid-base) interaction is comprised of the interactions between Lewis acid-base pairs in the system, including the two interacting entities and surrounding water molecules. These interactions are useful in explaining the advantage of hydrophilizing the membrane surface to reduce the irreversible attachment of particles and other fouling materials

on membrane surface. According to the concept of apolar/polar interactions, the strength of chemical attachment depends not only on the dispersion interaction (apolar), but also, or even more dominantly, on the polar interactions. The latter can be either attractive or repulsive based on the hydrophilicity of the two interacting surfaces.

For two hydrophilic surfaces, the polar interaction is repulsive and counteracts the attractive dispersion interaction. Therefore, the total interaction becomes either weakly attractive or repulsive even in the absence of electrostatic repulsion which leads to reduce fouling. In comparison, the polar interactions would be fairly attractive between hydrophobic surfaces, which are additive to the attractive dispersion interactions. Consequently, electrostatic repulsion becomes the dominant factor in balancing the attractive and repulsive interaction which enhances fouling. Therefore, there are in principle at least two possible approaches to make the membrane less vulnerable to the attachment of aquatic contaminants: hydrophilization of membrane surfaces (to enhance thermodynamic stability) and ionization of membrane surfaces (to achieve kinetic stability). Both approaches have been investigated by several researchers [34, 35-39]. The presence of polar interaction has also been used to explain different affinities of silica and latex particles on hydrophilic membranes [40]. Hydrophobic polystyrene latex particles showed less affinity to three commercial hydrophilic membranes than silica particles, as measured using atomic force microscopy (AFM). The hydrogen bonding attraction between silica particles and membrane surfaces was speculated to be the primary reason for the greater attachment. Regardless of the true mechanisms, such results suggest that the molecular structure of membranes and aquatic particles can be important to their interactions. Another complicated problem is the presence of NOM in natural water. The sorption or deposition of NOM moieties on particle and membrane surfaces can form an additional polymeric layer at solid/water interfaces.

#### **4.3. Chemical attachments between heterogeneous surfaces**

All previous chemical attachment mechanisms are based on the assumption that the interacting surfaces have homogeneous surface properties, and thus can be characterized using some global parameters, such as: charge density, hydrophobicity, and the Hamaker constant. However, this may not be realistic because particles could have heterogeneous surfaces. Different parts of the surface have different affinities to the membrane. In addition, the membrane surface, especially that modified, also likely has heterogeneous surface properties relevant to foulant attachment. This heterogeneity can be attributed to different physical and/or chemical origins. For instance, the attachment of particles to membrane pores of various shapes was investigated. It was found that membrane pores with round corners are the least affinitive to colloidal fouling compared to those with sharp and spiky corners due to enhanced electrostatic repulsion [41]. In another investigation, the surface heterogeneity of nanofiltration and reverse osmosis membranes was studied using chemical force microscopy, a modified technique based on AFM to obtain the lateral distribution of surface energies/stickiness. It was found that the surfaces of the two membranes used were chemically heterogeneous, and that the heterogeneity became more significant below micron-sized dimensions [42]. This implies

that the stickiness of membrane surfaces to foulants can be heterogeneous, rather than uniformly homogenous as considered previously.

## 5. Factors affecting fouling

- Membrane properties: pore size, hydrophobicity, pore size distribution and membrane material.
- Solution properties: solid (particle) concentration, particle size and nature of components.
- Operating conditions: pH, temperature, flow rate and pressure.

### 5.1. Membrane properties

In an aqueous environment a membrane can be attractive or repulsive to water. The composition of the membrane and its corresponding surface chemistry determine its interaction with water, thus affecting its wettability. The wettability of the membrane can be determined by measuring the contact angle between the membrane surface and a droplet of liquid, as shown in Figure (4). Hydrophilic membranes are characterized by the presence of active groups that have the ability to form hydrogen-bonds with water and so these membranes have wettability as can be seen in Figure (4.b). Hydrophobic membranes have the opposite interaction to water compared to hydrophilic membranes as they have little or no tendency to adsorb water and water tends to bead on their surfaces (i.e. discrete droplets) as shown in Figure (4.a). This tends to enhance fouling. Hydrophobic membranes possess low wettability due to the lack of active groups in their surface for the formation of hydrogen-bonds with water. Particles, which foul membranes in aqueous media, tend to be hydrophobic. They tend to cluster or group together to form colloidal particles because this process lowers the interfacial free energy. Usually, greater charge density on a membrane surface is associated with greater membrane hydrophilicity. Polysulfone, cellulose acetate, ceramic and thin-film composite membranes used for water treatment and wastewater recovery typically carry some degree of negative surface charge and hydrophilic. Thus, fouling can be reduced with use of membranes with surface chemistry which have been modified to render them hydrophilic.



**Figure 4.** a) Hydrophobic membrane, (b) Hydrophilic membrane [14]

Membrane morphology also has a considerable effect on fouling as pore size, pore size distribution and pore geometry especially at the surface of the membrane. These determines

the predominant fouling mechanisms such as pore blocking and cake formation as previously discussed in section 2.

## 5.2. Solution properties

The properties of the feed solution also significantly influence membrane fouling. Some of the important feed properties are solid (particle) concentration, particle properties, pH and ionic strength. Generally, an increase in the feed concentration results in a decline in the permeate flux. This is due to the increase in membrane fouling by the presence of a higher foulant concentration. Particles may be present in the feed because of the nature of the feed or through precipitation of soluble feed component(s). The particles can cause fouling by pore blocking, pore narrowing or cake formation, dependent on the particle sizes. Higher permeate fluxes and cake thicknesses are usually obtained with larger particles [43]. Large particle size is one of the factors that inhibit deposition. In a filtration process, the particle sizes in the feed often cover a wide range. The presence of fine as well as coarse particles results in a lower cake porosity as the fine particles can slide between the large ones, filling the interstices. The range of the particle size distribution plays a major role in the selective deposition at high crossflow. In addition to the particle size, the particle shape affects the porosity of the cake formed on the membrane surface. In general, the lower the particle sphericity, the greater is the porosity [43].

Some other factors, such as: pH, ionic strength, and electric charges of particles, are also important. The pH and ionic strength of the feed affect the charge on the membrane, the charge on the particles, conformation and stability of, and thereby adhesiveness of particles/molecules and the size of the cake. For example, a study of the impact of pH of the latex emulsion on membrane fouling showed that the latex emulsion pH should be high enough to prevent the coagulation of latex particles, and hence, to increase the antifouling properties of the latex emulsion. Also, it has been showed that a reduction in pH could decrease the molecular size of NOM and thus enhances adsorption onto membrane, resulting in a significant fouling.

## 5.3. Operating conditions

The effect of temperature on the permeate flux was investigated and found that at higher temperatures, the permeate flux increased, indicating a lower degree of fouling. Changing the feed temperature from 20°C to 40°C lead to an increase in the permeate flux up to 60% [44]. This might be due to the fact that changes in the feed water temperature resulted in changes in the permeate diffusion rate through the membrane.

The cross-flow velocity is defined as the superficial velocity of the feed stream travelling parallel to the membrane surface. The effect of the cross-flow velocity on permeate flux has been studied for a wide variety of feed solutions. It is believed that increasing the cross-flow velocity positively affects the mass transfer coefficient of the solute and the extent of mixing near the membrane surface [45]. Consequently, the permeate flux is increased with cross-flow velocity. Higher mixing experienced with larger cross-flow velocity leads to a reduction of aggregation of the feed solids in the gel layer, essentially due to increasing diffusion of these

components back towards the bulk, leading to an overall reduction in the effect of concentration polarization.

The control of the transmembrane pressure (TMP) which is the pressure difference between the feed and permeate stream is essential as it greatly affects the permeation rate. At a higher TMP, the force of the fluid flowing towards the membrane is increased, leading to a higher permeate flux. Increasing the applied pressure influence the permeate flux as illustrated in Figure (5). At very low pressure  $p_1$ , the flux is close to pure water flux at the same pressure. As the applied pressure is increased to pressure  $p_2$ , the higher flux causes increased concentration polarization of the retained material at the membrane surface increases. If the pressure is increased further to  $p_3$  which considered the critical pressure, concentration polarization becomes enough for the retained solutes at the membrane surface to reach the gel concentration,  $c_{gel}$ . Once a gel layer has formed, further increase in the applied pressure does not lead to further increase in the permeate flux above this critical value. The gel layer thickness and the density of the retained material at the membrane surface layer, however, increase. This limits the permeate flux through the membrane, and hence, the flux reaches a steady state level. It was reported that no fouling was experimentally observed when the process was operated under this critical flux [14].

## 6. Remediation of membrane fouling

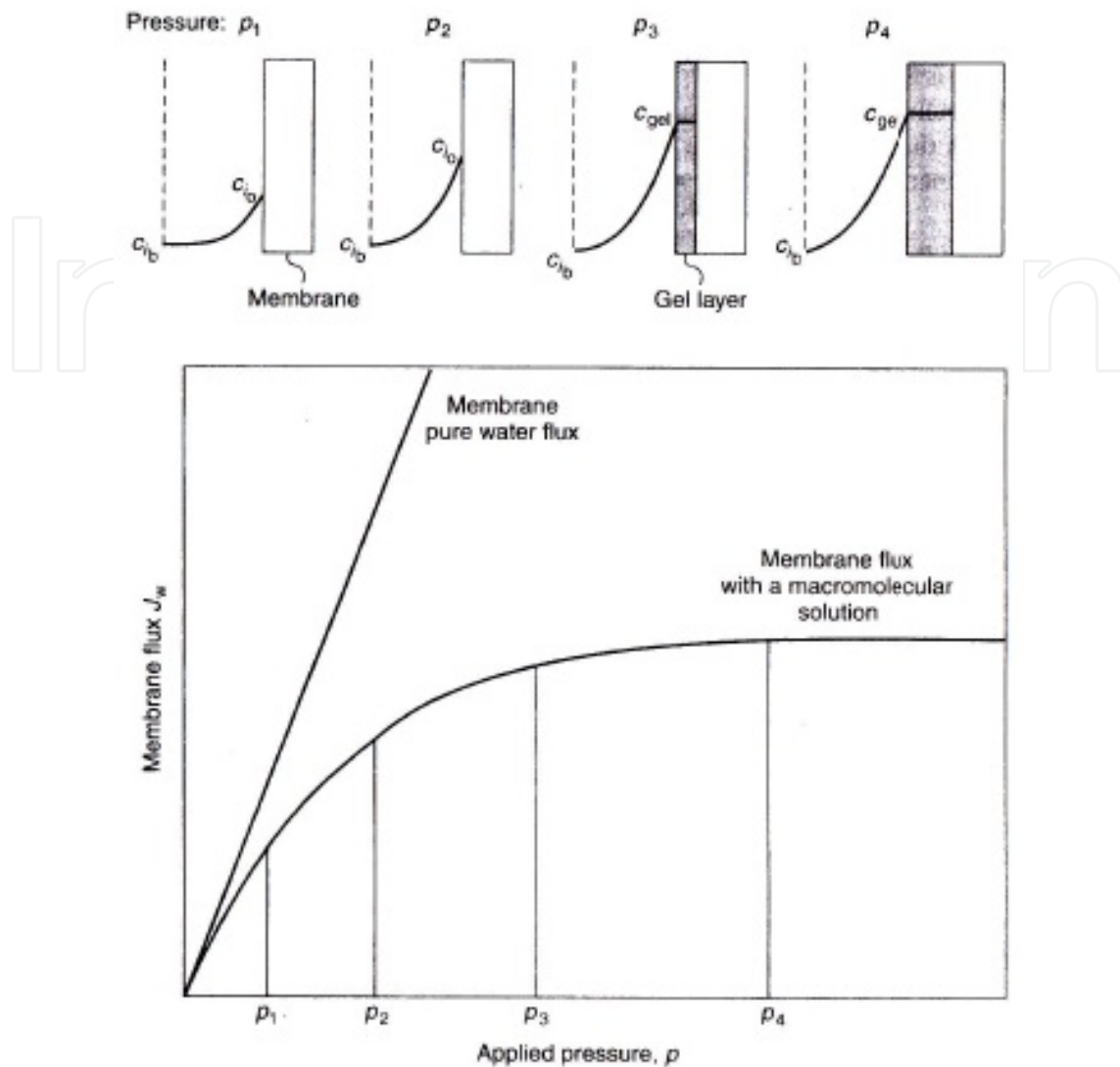
Fouling remediation can be done through pre-treatment the feed to limit its fouling propensity, improving the antifouling properties of the membrane, membrane cleaning and backwash conditions and optimization of the operating conditions already discussed previously.

### 6.1. Feed pre-treatment

Membranes are susceptible to fouling; therefore, pretreatment of the feed is required to control colloidal, organic, and biological fouling as well as scaling. The pretreatment scheme must be capable of controlling membrane fouling to such an extent that a practical cleaning frequency can be achieved. For low-pressure membranes, a number of pretreatment methods are currently used.

#### 6.1.1. Coagulation

Coagulation involves the addition of chemicals coagulants, such as:  $\text{FeCl}_3$ ,  $\text{FeSO}_4$ , alum, polyaluminum chloride, etc., to increase the size of suspended and colloidal particles in the feed prior to filtration. It was found that reversible fouling was reduced with coagulation pretreatment, but the extent of irreversible fouling was unchanged. This can be attributed to the fact that large particles are formed from small particles, and hence, reversible fouling decreases with the use of coagulation. However, smaller particles, which are not coagulated, still remain in the feed and causes irreversible fouling. Factors affecting membrane fouling includes coagulant dosage, pH, nature of dissolved organic matters as well as  $\text{Ca}^{2+}$  content of the feed water [14]. Moreover it was found that following coagulation pretreatment, most membrane



**Figure 5.** The effect of pressure on membrane flux [14]

fouling was due to the smaller hydrophilic NOM particles [13]. This finding is consistent with the fact that most metal-based coagulants are known to preferentially remove hydrophobic rather than hydrophilic substances. Coagulation reduced the rate of membrane fouling by minimizing pore plugging and increasing the efficiency of membrane backwashing.

Coagulation can be done by In-line coagulation process (IC), which refers to the dosing of coagulant into the feed stream. Rapid mixing in the feed stream allows the flocs to form (but not to settle) and finally enter the filtration unit (e.g., UF). Therefore, In-line coagulation doesn't require the sedimentation or prefiltration step prior to UF. Despite a larger fouling load in terms of suspended matter, IC may improve membrane performance due to the change in the fouling mechanism to cake formation rather than pore blocking. Once a cake is built up, it can be removed by backwashing easily. For in-line coagulation, the influence of membrane polymer nature and structure on fouling is alleviated. Cleaning frequency is also reduced and

cleaning aggressiveness could be lowered. Consequently, the permeate flux increases, and the effect of seasonal water quality variations on filtration can be better controlled [46].

Sedimentation process can be used following the coagulation process. In this combined pretreatment method, a coagulant is applied and the formed flocs are settled out by sedimentation. The supernatant is then fed to the membrane filtration unit. In one study at East St. Louis, when UF was used after coagulation-sedimentation (CS) for 400 h, no membrane fouling was observed [47]. The coagulation or CS pretreatment process was very effective in increasing UF membrane life because this process removed the primary foulants such as high molecular weight humics [48].

Alternative process is coagulation-adsorption, which refers to adsorption of foulants using an adsorbent such as powdered activated carbon (PAC) between the coagulation step and UF. In one study, wastewater with the initial COD of 165 mg/L and turbidity of 90 NTU was treated with 120 mg FeCl<sub>3</sub>/L at pH of 5.5. The COD and turbidity of the treated water were reduced to 23 mg/L and 12 NTU, respectively. When a further treatment step by adsorption with PAC was used, the COD dropped further to 7 mg/L [49]. The use of adsorption (PAC) and coagulation (alum and polyaluminum chloride) as pretreatment steps prior to membrane filtration was also investigated to remove organics. Significant improvement in the removal of organic materials and trihalomethane precursors were obtained [50].

Flocculation is another pretreatment method that can remove particles and colloids and hence improve the permeate flux. It is used to achieve three objectives: eliminating the penetration of colloidal particles into the membrane pores, increasing the critical flux, and modifying the characteristics of the deposits. The use of flocculation prior to membrane filtration reduced clogging of the membrane by aggregating smaller particles, thereby retaining them on the surface of the membrane. The larger flocs on the membrane surface are washed off by the retentate due to the tangential force (cross-flow) of the incoming solution, thus preventing membrane clogging. Flocculation can be used in combination with coagulation. Flocculation enhances the formation of larger flocs from particle aggregates generated by coagulation. In addition, flocculants induce floc formation from smaller particles that would not form particle clusters by coagulants.

#### 6.1.2. Magnetic ion exchange

Magnetic ion exchange (MIEX) is a chemical process in which dissolved ions and charged species in water are adsorbed to polymer beads. Once they are saturated, the beads can be recovered and regenerated using a brine solution to desorb the charged species and ions. As a large percentage of the dissolved organic carbon (DOC) is polar, so it can be removed by MIEX, by exchanging chloride ions on the resin surface for polar dissolved and colloidal organic materials. Numerous studies have shown that ion exchange preferentially removes high charge density, medium-to-low molecular weight organic materials, which can consist of hydrophobic, transphilic and hydrophilic organic fractions. Ion exchange can therefore be synergistic with coagulation in reducing DOC loading entering the membrane unit, where coagulation removes the lower charge density, higher molecular weight hydrophobic fractions. A number of DOC removal methods were compared: alum coagulation (without pH

control), alum coagulation (with pH controlled at 6), ion exchange using MIEX resin, and combined treatment of alum coagulation and MIEX. The relative effectiveness of those pretreatment methods for DOC removal was ranked in the order: alum/MIEX > MIEX > alum pH 6 > alum (no pH control) [51]. Also, it was found that MIEX could remove more NOM than coagulation process could, even at very high coagulant concentrations [52]. When it is used as a pretreatment step, up to 80% of NOM can be removed prior to UF. Moreover, combining coagulation with MIEX was found to be able to remove 90 % of trihalomethane and haloacetic acid precursors from water [53].

### 6.1.3 Micellar-Enhanced filtration

Micellar enhanced ultrafiltration is an emerging technique that it is used to improve the performance of a filtration process by adding a surfactant to the feed in order to promote the entrapment of foulants in the micelles formed by the surfactant. Surfactants are molecules that contain a hydrophobic tail (usually long chain hydrocarbon) and a hydrophilic head. Above a specific concentration, surfactant molecules come together to form clusters or micelles. This concentration is termed the critical micelle concentration (CMC) and differs depending on the type of surfactant.

There are numerous types of surfactants used in industry today, categorized by the charge of the hydrophilic portion of the molecule: anionic (negatively charged), cationic (positively charged), non anionic (neither positively nor negatively charged), and zwitterionic (both negatively and positively charged). The formation of micelles increases the particle size, allowing the use of membranes with larger pore sizes for the same feed. Some surfactants also interfere with hydrophobic interactions between bacteria and membranes. In addition, surfactants can disrupt functions of bacterial cell walls. Therefore, they reduce fouling dominated by the biofilm formation. The choice of a surfactant is based on its compatibility with the solid for the solid recovery and reuse and its effect on the filtration system. A study has been conducted to compare the use of dodecylbenzenesulfonic acid, as an anionic surfactant, and dodecylamine, as a cationic surfactant, to improve the removal of lead and arsenic from municipal wastewater [54]. It was concluded that while both surfactants enhanced separation of the heavy metals, the cationic surfactant was more effective than the anionic one. In another study, sodium dodecyl sulphate (SDS), as an anionic surfactant, and trimethylammonium bromide (CTAB), as cationic surfactant, were used to improve ultrafiltration of latex paint wastewater [55]. With SDS at twice its CMC, a reduction of 58% of permeate flux was observed. In contrast, using CTAB at twice its CMC, the permeate flux increased up to 134%. The effectiveness of surfactant also depends on the membrane material and its surface charge. One study indicated that for hydrophilic membranes, the permeate flux was reduced when ethoxylated alkyl phenol alcohol (Triton X-100), a non-ionic surfactant, was used above its CMC. However, for hydrophobic membranes, no significant flux reduction was observed with the same surfactant [56].



## 6.2. Membrane properties modification

Membrane properties affect the solute-membrane interaction and, consequently, the extent of adsorption and fouling. For filtration of proteins, since proteins adsorb more strongly to hydrophobic surfaces than hydrophilic ones, the use of hydrophilic membranes (cellulose esters, aliphatic polyamides) can help reducing membrane fouling. Chemical modification of a membrane (for example, sulfonation of polysulfone) or blending a hydrophobic polymer (polyetherimide, polyvinylidene fluoride) with a hydrophilic one (polyvinylpyrrolidone) can enhance the anti-fouling property of membranes. Another way to influence the solute-membrane interaction can be achieved by the pretreatment of the membrane with hydrophilic surfactants or enzymes. Conventional ultrafiltration membranes, such as: polysulfone, polyethersulfone or polyvinylidene fluoride, can be made more hydrophilic by surface modification using various methods [57, 58]:

- Plasma treatment of the membrane surface;
- Polymerization or grafting of the membrane surface initiated by UV, heat or chemicals;
- Interfacial polymerization;
- Introduction of polar or ionic groups to the membrane surface by reaction with bromine, fluorine, strong bases and strong acids.

Hydrophilization of the membrane surface also can be done by pre-coating the membrane with a nonionic surfactant. This method is very attractive for practical application because of it is simple. With this treatment, ultrafiltration of antifoam rejection was improved significantly, and hence, the permeate flux was almost doubled [59]. Alternatively, ozone can be used to modify the membrane surface and its hydrophobicity. This treatment introduces peroxide groups to the polymer surface, which can initiate graft polymerization of monomers with hydrophilic groups, and thus improves the hydrophilicity of the polymer surface. The concentration of peroxide groups formed can be used to determine the effectiveness of the ozonation process. The effect of ozonation on the permeate flux was studied using a polysulfone UF membrane. It was found that ozonation increased the permeate flux by 10%, and membrane surface oxidation by the mixture of ozone and hydrogen peroxide was even more effective. Ozone prolonged the period required to reach appreciable fouling rather than eliminated it [57]. The applied ozone dose and ozonation time determine the amount of peroxide groups generated and thus the degree of hydrophilicity enhancement of the membrane surface.

## 6.3. Membrane fouling cleaning

Membrane cleaning is an integral part of a membrane system operation and has a significant impact on the process operation. Fouling materials can be removed by hydraulic means such as backwashing or by chemical means such as enhanced backwash (EBW). Cleaning operation can be classified as cleaning in-place (CIP) or off-line chemical cleaning (or soaking). In CIP the membrane module is cleaned without removing it from the installation while in off-line cleaning the module is removed from the system and soaked in a chemical.

Backwashing is done by reversing the flow across the membrane, using the permeate to remove foulants accumulated on the membrane surface and/or clogged the membrane pores.

In EBW a cleaning chemical is added to the backwash water and the water is recirculated for a short period of time (10-15 min). Chemical cleaning is an integral part of a membrane process operation, which has a profound impact on the performance and economics of the process. Currently, types of cleaning chemicals used are recommended by membrane manufacturers. Some of them are proprietary cleaners while others are commercial chemicals. Chemical cleaning is required for the membrane to regain most of its permeability. Chemical cleaning is performed when flushing and/ or backwashing cannot restore the permeate flux. In chemical cleaning, the chemical dose is usual higher than that for the enhanced backwashing and the frequency of chemical cleaning is usual lower (approximately 1 per week). Moreover, the enhanced backwashing can be fully automated while the chemical cleaning involves manual labor due to its off-line operation. Proper selection of chemical cleaning agents, conditions for their application and understanding their performance are important. A cleaning agent is usually selected based on the types of foulants. The effectiveness of various operating strategies for different fouling types is summarized in Table 2. As indicated in Table 2, the chemical cleaning is an effective control strategy for a majority of membrane fouling types.

Type of Fouling	Effects of Operating Strategy			
	Hydraulic Cleaning / Backwashing	Feed Chlorination	Feed Acidification	Chemical Cleaning
Inorganic	-	-	++	++
Particulate	++	-	-	++
Microbial	+	++	+*	++
Organic	-	+	-	++

Notes: “-”: No effect/ negative effects; “+”: some positive affects; “++”: positive effects; “\*”: together with feed chlorination.

**Table 2.** Effects of operating strategies on membrane fouling [14]

Calcium, magnesium and silica scaling, often a serious problem in reverse osmosis operation, is generally not a concern in ultrafiltration because these ions permeate through the membrane. Ultrafiltration of cheese whey, in which high calcium levels can lead to calcium scaling, is an exception. Because many feed waters contain small amount of soluble ferrous salts, hydrate iron oxide scaling is a problem. In ultrafiltration, these salts are oxidized to ferric iron by entrained air. Ferric iron is insoluble in water; hence, an insoluble iron hydroxide gel forms and accumulates on the membrane surface. Such deposits are usually removed with citric or hydrochloric acid wash. Chemicals commonly used for cleaning UF and MF membranes in water industry fall into five categories, as summarized in Table 3

Category	Major Functions	Typical Chemicals
Caustic	Hydrolysis, solubilisation	NaOH
Oxidants / disinfectants	Oxidation, disinfection	NaOCl, H <sub>2</sub> O <sub>2</sub> , peroxyacetic acid
Acids	Solubilization	Citric, nitric, hydrochloric acid
Chelating agents	Chelation	Citric acid, EDTA
Surfactants	Emulsifying, dispersion, surface conditioning	Surfactants, detergents

**Table 3.** Major categories of membrane cleaning chemicals [14]

Regardless of the membrane system used, chemical cleaning is cumbersome and requires shutdown of the unit. This results in a reduction of the overall plant capacity and produces a waste that may be difficult to dispose of. There are also concerns that repeated chemical cleaning might affect the membrane life. Chemical cleaning should thus be limited. Because membrane cleaning is essentially conducted through chemical reactions between cleaning chemicals and fouling materials, factors that affect the cleaning efficiency are concentration, temperature, length of the cleaning period and hydrodynamic conditions. The cleaning chemical concentration can affect both the equilibrium and the rate of the reaction. The cleaning chemical concentration plays a key role not only to maintain a reasonable reaction rate but also to overcome mass transfer barriers imposed by the fouling layer. In practice, the cleaning chemical concentration is usually high enough to ensure a desirable reaction rate. It is mass transfer, which dictates the limiting chemical concentration that is adequate for cleaning purpose.

Temperature can affect membrane cleaning by (1) changing the equilibrium of a chemical reaction, (2) changing the reaction kinetics, and (3) changing the solubility of fouling materials and/or reaction products during the cleaning. Generally, membrane cleaning is more efficient at elevated temperatures. However, compatibility of the membrane and other filter components regarding temperature should also be checked.

Membrane cleaning involves mass transfer of chemicals to the fouling layer and the reaction products back to the bulk liquid phase. Therefore, hydrodynamic conditions that promote contact between cleaning chemicals and fouling materials during cleaning are required. From a mass transfer point of view, dynamic cleaning involving circulating cleaning solutions through the system can be more effective than static cleaning such as soaking.

Moreover, mechanical cleaning can be used if chemical cleaning does not restore the permeate flux. Tubular membrane modules could be effectively cleaned by forcing sponge balls of a slightly larger diameter. The balls gently scrape the membrane surface, removing deposited materials. Sponge-ball cleaning is an effective but relatively time-consuming process, so it is performed rather infrequently.

## 7. Conclusion

Membrane fouling is a critical problem that reduces the permeate flux, requires periodic cleanings, and limits further membrane development due to the hindrance of wider application to various processes by fouling. Fouling is caused by the deposition of suspended or dissolved solids in the feed on the external membrane surface, on the membrane pores, or within the membrane pores. One of the two main factors, which has a significant effect on membrane fouling, is the membrane properties, such as: pore size and distribution, hydrophobicity and membrane material. Membrane fouling is a phenomenon involving the interaction between the membrane and the solution. Therefore, another important factor governing fouling is the solution properties, such as: concentration and nature of components and the particle size distribution. In addition, operational conditions such as pH, temperature, flow rate and pressure also greatly affect fouling.

Even though membrane fouling is inevitable during the filtration process, it can be controlled and alleviated. Current approaches to deal with membrane fouling include mathematical model prediction of membrane fouling and membrane fouling reduction using different techniques such as pre-treatment of the feed water, membrane modification, improving the operational conditions and cleaning. In order to determine the proper pre-treatment, a complete and accurate analysis of the feedwater should be made. In addition, the interaction of a particular membrane and a specific foulant needs to be understood so that an appropriate method can be selected. Finally the fouling behaviour and autopsy protocol for membrane fouling can be concluded in four basic aspects: identification of fouling components, development of conceptual or phenomenological models for membrane fouling, establishment of mathematical models to describe or predict fouling, and development of fouling control strategies.

## Nomenclature

Symbol	Unit	Physical Meaning
$\beta$	dimensionless	Ratio of membrane area influenced with the particles suspension to open area of the membrane pores
$C_b$	kg/m <sup>3</sup>	Bulk concentration of large aggregates
$J$	m <sup>3</sup> /m <sup>2</sup> .s	Permeate flux at any time
$J_0$	m <sup>3</sup> /m <sup>2</sup> .s	Initial permeate flux
$K_b$	m <sup>2</sup> /kg	Pore blockage parameter
$m_d$	kg/m <sup>2</sup>	Mass of deposits accumulated on unit surface area of membranes
$m_p$	kg	Total mass of aggregates retained by the membrane
$\mu$	Pa-s	Solution viscosity

Symbol	Unit	Physical Meaning
$n$	dimensionless	Number of particles per unit volume
$\Delta P$	Pa	Transmembrane pressure (TMP)
$r_p$	m	Pore radius of membranes
$R_c$	$m^{-1}$	Hydrodynamic resistance of cake layers
$\hat{R}_c$	m/kg	Specific resistance of cake layer on the membrane surface
$R_m$	$m^{-1}$	Hydrodynamic resistance of clean membranes
$t^*$	dimensionless	Filtration time
$V$	$cm^3$	Permeate volume
$\delta'$	m	Thickness of the adsorption layer
$\gamma$	dimensionless	Ratio of the pores area to the total membrane area
$\epsilon$	dimensionless	Dielectric Constant

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