

Chapter 11

Fouling Mechanisms in Nanofiltration Membranes



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Abstract Nanofiltration (NF) membranes have been attaining research interest since the late 1980s, especially in water purification applications; they are very efficient and can selectively remove undesired ions and other organic substances. Various applications of nanofiltration such as treatment of surface and groundwater, removal of organic contaminants and pathogens from water for its reuse are discussed in this chapter. However, a significant disadvantage of any membrane separation process is the fouling phenomenon, adversely affecting membrane efficiency. The fouling phenomenon is majorly dependent on the properties of the membrane and interactions between the solutes and membranes. The present chapter discusses various fouling phenomena such as gel formation, adsorption, deposition, pore blocking, and cake formation in NF membranes. To better understand the fouling, mechanisms involved and various mathematical models to describe fouling are necessary. Therefore, Hermia's models to describe fouling, such as standard pore blocking, complete pore blocking, intermediate pore blocking, and cake filtration models, are discussed in detail. In addition, many researchers are working on fouling mitigation of nanofiltration membranes to avoid fouling. Consequently, this chapter described the various fouling mitigation methods.

Keywords Nanofiltration · Fouling mechanism · Fouling mitigation · Water purification

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11.1 Introduction

Nanofiltration (NF) is a pressure-driven membrane separation process used to separate nano-sized molecules. The pore size of the nanofiltration membrane ranges from 0.2 to 2 nm, which lies between ultrafiltration and reverse osmosis membranes. NF membranes can selectively reject different dissolved salts possessing low molecular weight. Therefore, they are being efficiently used in desalination applications. NF processes are usually operated between 5 and 30 bar trans membrane pressure to attain strong divalent ion rejection. Nanofiltration membranes are neither fully dense nor fully porous, so their retention mechanism can be defined by size exclusion, sorption, and diffusion. Usually, NF membranes have a high charge density and possess pore diameters in the nanometer range. The surface charge is generally negative and has the most significant impact on the membrane's selectivity. New investigations are being conducted, and new membranes with distinct properties such as a wide range of hardness rejection and fouling resistance are being developed (Broeckmann et al. 2005; Bartels et al. 2008).

However, the fouling phenomenon limits a large scale utilization of the nanofiltration membrane processes, which gradually reduces the permeate flux. Fouling can be caused by multiple reasons that are intricately related. First, it is a time-dependent phenomenon caused by membrane features and the interactions between solute and membrane, solute and solute, which results in an irreparable decrease in permeate flux. Process variables can also impact fouling, including feed concentration, flow rate, equipment design, temperature, and pressure. A few common types of fouling include particulate, biological, organic and inorganic fouling. Nevertheless, the membrane can regain its performance (permeability and selectivity) if fouling is removed by proper cleaning methods (Ogawa et al. 2010).

The present chapter discusses the applications of nanofiltration membranes. Furthermore, various kinds of fouling and mechanisms involved in the fouling phenomenon are discussed in detail. Consequently, this chapter highlights the different fouling mitigation methods.

11.2 Applications of Nanofiltration

Nanofiltration membranes were commonly utilized to partially soften potable water by permitting few minerals to flow through the membrane, boosting the water's steadiness and preventing them from becoming aggressive to the piping material. Furthermore, they are being widely used to cleanse industrial effluents and reduce waste disposal. The membrane material is generally designed/chosen according to the required application. Nanofiltration could be used in various ways in various industries. For example, membrane processing looks to be a viable alternative to traditional processing in a wide range of industrial processes. These membranes were also increasingly used to filter effluents at the industrial level and reduce waste

disposal. The ability to process waste, preserve essential substances derived from it, reduce energy consumption, and eliminate other additives are just a few of the main advantages of NF membranes (Silva 2018). A few promising applications of nanofiltration are elaborated as follows.

11.2.1 Surface-Water Treatment

Surface water is the primary source of drinking water. It is available in various forms, including streams, rivers, lakes, and reservoirs. Generally, the surface water offers superior quality with the TDS (total dissolved solids) less than 1000 mg/L. Nevertheless, surface water properties vary from one season to another in terms of its composition. Moreover, the composition of surface water may also change when rainwater dilutes it. The traditional method involving coagulation-sedimentation followed by filtration and disinfection exists to treat surface water. But, disinfectants in this process may react with precursors and form undesired disinfection byproducts.

On the other hand, nanofiltration membranes can efficiently reject most organic matter. Hence, it is becoming an efficient option for treating surface water (Al-Qadami et al. 2020). A study developed a hollow-fibre membrane that operates at relatively low pressures to soften the surface water. This particular membrane has a thin film layer, and positive charges have permeability and molecular weight cut off of 17.1 L/m² h bar and 500 Da, respectively. While operating at a pressure of about 2 bar, Donnan exclusion and steric hindrance's separation mechanisms showed rejection of magnesium chloride and magnesium sulphate around 96.7% and 80.6%, respectively. In addition, at a water flow of 20 L/m² h with 3000 ppm of total dissolved solids and salt mixtures, membrane rejection was around 90% of Mg²⁺ and Ca²⁺ ions (Fang et al. 2013).

11.2.2 Groundwater Treatment

Groundwater is majorly used for drinking water supply and agriculture irrigation. In most cases, groundwater possesses ions such as Ca and Mg, which leads to the hardness of the water. These hardness ions should be removed to get safe drinking water. In addition, the water is being continuously polluted by the disposal of industrial wastes. These pollutants may cause adverse health effects in humans. Therefore, efficient technologies such as NF must treat polluted groundwater into potable water. NF is gaining priority over RO as it can be operated under less pressure comparatively. In addition, the permeate obtained from NF does not require remineralization.

Arsenic (As) is one of the toxic pollutants that can be identified in groundwater. It can cause severe health hazards such as skin cancer and lung cancer. As is usually occur in its trivalent (As (III)) and pentavalent (As (V)) forms. A study has used the pre-oxidation step before nanofiltration to convert trivalent arsenic into a pentavalent

format for better removal. A 97–100% rejection percentage was obtained by size exclusion and electrostatic repulsion (Sen et al. 2010).

11.2.3 Removal of Organic Contaminants and Pathogens for Water Reuse

The effluents produced from the wastewater treatment plants are generally used as feed water for membrane-based separation processes to get water ready for reuse. The effluents contain a more complex composition when compared to surface and groundwater. This complexity will remain even after necessary treatments have been carried out. This will pose a difficulty in the separation performance of nanofiltration membranes. Removal of organic contaminants from the effluent of wastewater treatment plants is one of the main challenges associated with health and water safety (Guo et al. 2022).

The removal of organic contaminants by NF membrane may occur by several mechanisms, including size exclusion, electrostatic interactions, polar effects, and hydrophobic interactions. NF membranes can easily remove hydrophilic organic contaminants and possess higher molecular weight due to the size exclusion effect. Besides, NF is negatively charged at the pH range of 6–9, which is advantageous for rejecting contaminants with a negative charge because of electrostatic repulsion. At the same time, organic contaminants with positive charges might not be entirely removed because of the Donnan effect. Furthermore, organic pollutants that are highly hydrophobic and polar are also poorly permeated through the membrane. Accelerating the water transport is one of the ways to increase the rejection of organic contaminants due to dilution effects on the side of permeate. Other than this, strategies like porous nanofillers, preparation of selective nanochannels and introduction of interlayers can improve the water permeance through a membrane, thereby increasing the rejection of contaminants.

Removal of pathogens has utmost priority in the membrane-based water reuse and wastewater treatment chain. It has become severe after the pandemic of covid-19. In general, the average size of pathogens ranges from 220 to 300 nm, which is appreciably larger than that of the effective pore size of NF membranes. Hence, there is a scope for completely removing pathogens by NF membranes. But several studies have reported incomplete removal of the virus and bacteria by reverse osmosis membranes. For instance, Mi et al. (2004) reported the poor rejection of bacteriophage MS2 using spiral-wound RO elements. This improper rejection might be because the virus may permeate through the imperfections in the elements (Mi et al. 2004).

In addition to this, one of the recent studies reported the possible formation of intrinsic defects nano-size during the fabrication of polyamide NF membranes by interfacial polymerization (IP) (Guo et al. 2022). These may function as hot spots for virus transportation, resulting in incomplete virus rejection. To maintain the safety

of reused water from pathogens, hugely sensitive methods are required to check the integrity of membranes and elements. Polishing is also considered one of the methods to improve membrane integrity to achieve satisfactory virus removal.

11.3 Definition and Types of Membrane Fouling

Fouling can be defined as the accumulation of non-dissolved matter on the surface of the membrane. The accumulation can be found on the walls of the membrane, at the pore mouths, or a combination of both. Membrane fouling can be classified into the following types: organic fouling, biofouling, and inorganic fouling (Al-Qadami et al. 2020) (refer Table 11.1). Fouling also can be differentiated into reversible and irreversible fouling. These various kinds of fouling are briefly explained in the following sections.

11.3.1 Organic Fouling

Organic fouling refers to the adsorption of dissolved organic compounds on the membrane surface. Various organic foulants such as proteins, humic acids, polysaccharides, etc., can adhere and form a gel layer on the membrane surface. Consequently, the permeate flux significantly reduces, and concentration polarization increases. This will provide nutrients that may further promote the formation of biofilm.

Table 11.1 Different types of fouling with an explanation

Fouling type	Foulant	Explanation
Biofouling	Bacteria and fungi	The development of bacteria on the surface of the membrane as well as the excretion of the extracellular polymers
Colloidal fouling	Clay minerals, silica, suspended matter, salt precipitates and metal oxides	Deposition of colloidal matter takes place on the surface of the membrane
Organic fouling	Polysaccharides, effluent organic matter (EOM) and proteins	Deposition of organic matter or colloidal matter takes place on the surface of the membrane
Scaling	Calcium carbonate, barium sulphate, calcium sulphate and silica	On the membrane surface, the ionic product of the sparsely soluble salt lags behind the equilibrium solubility product, forming a scale layer because of the precipitation

11.3.2 Inorganic Fouling

Inorganic fouling can be defined as the formation of precipitation/scaling on the membrane surface due to inorganic foulants such as Ca, Mg, Mn, and Fe. A study investigated CaCO₃ Fouling on ceramic ultrafiltration membrane (Ognier et al. 2002). In that report, Ognier et al. (2002) prepared wastewater using hard tap water (with 8 mg/L of Mg²⁺ and 120 mg/L of Ca²⁺). The alkalinity of activated sludge increased with the precipitation of CaCO₃. In another study, Lyko et al. (2007) investigated the presence of metal substances (Lyko et al. 2007). Inorganic fouling is harder to remove, even with the chemical cleaning process. Inorganic fouling usually takes place by two kinds of precipitations. That is of chemical and biological precipitations. Ions such as Al³⁺, Ca²⁺, Fe³⁺, PO₄³⁻, Mg²⁺, OH⁻, CO₃²⁻ are present. Chemical precipitation occurs when anion and cation bond to form an insoluble salt. Ions such as PO₄³⁻, OH⁻, SO₄²⁻, CO₃²⁻ are present in biological precipitation. In some cases, acidic functional groups containing ions and calcium ions may form gel layers, decreasing flux (Muntha et al. 2017).

11.3.3 Biofouling

It is a type of fouling caused by the accumulation of microorganisms such as bacteria and their secretions on the membrane surface. It starts to accompany the precipitation of bacterial cells, and it multiplies to form bio cake. Yun et al. (2006) studied and analyzed cake's arrangement and membrane permeability for wastewater treatment (Yun et al. 2006). It was found that the membrane filterability depends on the biovolume and porosity of bio cake. Furthermore, bacterial cells' affinity toward the membrane also affects the deposition on the surface (Kirschner et al. 2018).

11.3.4 Reversible and Irreversible Fouling

If foulants cannot be removed by physical cleaning methods such as backflushing and surface cleaning, fouling is irreversible. Therefore, the study of irreversible fouling is important for defendable and far usage of membranes. Solutes that are very small such as colloids and microbial cells are the main reason for irreversible fouling since they can go via the membrane and precipitate inside it. Therefore, chemical cleaning methods are required to remove the irreversible fouling.

Loosely attached foulants cause reversible fouling, which can be removed using physical methods. In general, reversible fouling causes cake layer formation on the surface and irreversible fouling cause pore blockage. Membrane fouling is an inevitable occurrence that occurs in membrane filtration. Therefore, membrane selection, operating conditions and membrane cleaning must be appropriately selected to

decrease the membrane fouling. Various membrane cleaning methods include biological, chemical and physical processes. Biocides, specific microorganisms, are used in biological cleaning to remove foulants. Physical cleaning methods to remove foulants include water jets, sponges and backflushing. Acids and bases are used in chemical cleaning to remove impurities (Muntha et al. 2017).

11.4 Fouling Mechanism

In membrane separation processes, permeate flux, and thus membrane performance gradually decreases with time. Therefore, it is important to know the reasons for the reduction in permeate flux. In general, the reduction of permeate flux occurs in more than one step. Firstly, as the membrane is selective, it permeates desired components and stops undesired components from passing through, resulting in concentration polarization. This causes the solutes or the particles to accumulate in a mass transfer boundary layer next to the surface of the membrane. The activity of the solvent deteriorates as dissolved molecules accumulate at the surface, reducing the flow of solvent through the membrane. Because of this reason, an osmotic pressure difference between the filtrate and the feed solution directly next to the surface of the membrane rises, and the effective transmembrane pressure (TMP) driving force is reduced. Though this effect is unavoidable, it can be reversed by reducing TMP and hence flux. Fouling, or accumulation of material, is the second issue. Fouling can be observed in various forms such as adsorption, pore blockage, layer-by-layer deposition, and gel formation. Adsorption happens as a result of interactions between membrane and solute particles. Even in the absence of permeate flux, a single layer of particles and solutes could form, resulting in increased hydraulic resistance. Concentration polarisation will exacerbate adsorption quantity if the adsorption's degree depends on the concentration. Pore blocking can occur during filtration, resulting in flux decline due to complete or partial closure of pores. Also, solutes may deposit layer-by-layer on the membrane surface, reducing the flux significantly due to extra hydraulic resistance. In some cases, such as the concentration of proteins, the level of concentration polarization can cause gel formation in the immediate proximity of the surface of the membrane (Field 2010).

In the present chapter, the focus will be on porous membranes at first to grasp the foundations of fouling, an understanding of transportation to the surface of the membrane, and the physical rules that control transportation across the membrane, along with a suitable model. Fouling increases resistance, resulting in less flux for a given TMP or a higher TMP is needed for a constant flux which can be employed with the help of external devices such as a metering pump. As discussed earlier, concentration polarization decreases the driving force across the membrane, whereas fouling adds additional resistance. Therefore, the concept of concentration polarisation is explained in detail, followed by fouling models.

11.4.1 Concentration Boundary Layer

Membrane separation processes including MF, UF, and RO are used to separate oil droplets, salt, and proteins. In any membrane separation process, the rejected component (oil in oil–water emulsion, salt in desalination, etc.) would be in higher composition in the concentration boundary layer. This higher-concentration layer is a mass transfer boundary layer over which the concentration alters, and the total procedure is known as concentration polarisation. This entire process is unavoidable as it is a result of membrane selectivity. Moreover, as rejected components' concentration is higher at the concentration boundary layer, it may diffuse back into the bulk solution. The equations described below can be used to determine the extent of deposition in this layer and its thickness. The relevant fluxes (in $\text{kmol/m}^2 \text{ s}$) are described by the following relations under steady-state circumstances. These equations are given based on Fig. 11.1.

Component 1:

$$j_{1,con} = j_1 \tag{11.1}$$

Component 2:

$$j_{2,con} = j_{2,diff} + j_2 \tag{11.2}$$

To get the mass balance, some assumptions have been taken into consideration. First, the concentration gradient parallel to the membrane is insignificant; Fickian diffusion, steady-state, no chemical reaction, constant density, and the diffusion coefficient are independent of the solute's concentration.

For general component i , with the incorporation of volumetric flux J , the equation becomes:

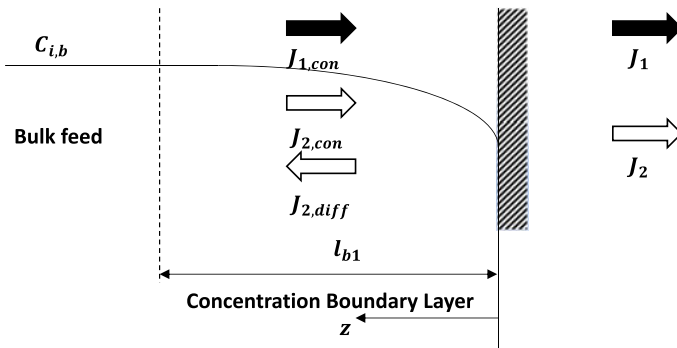


Fig. 11.1 Concentration polarization

$$J.C_i = J.C_{i,P} - D_{ji} \frac{dC_i}{dz} \quad (11.3)$$

The following boundary conditions are considered for the integration of the Eq. (11.3)

$$z = 0 \quad C_i = C_{i,M}$$

$$z = l_{bl} \quad C_i = C_{i,b}$$

Post integration of the Eq. (11.3) results in the following equation by considering the above conditions

$$J = \left(\frac{D_{ji}}{l_{bl}} \right) \cdot \ln \left(\frac{C_{i,M} - C_{i,P}}{C_{i,b} - C_{i,P}} \right) \quad (11.4)$$

where l_{bl} is the mass transfer boundary layer's thickness, subscript M denotes the membrane surface, and subscript P denotes the permeate.

According to Eq. (11.4), the concentration at the surface of each component i is exponential to the flux:

$$C_{i,M} = (C_{i,b} - C_{i,P}) \cdot \exp \left(\frac{J.l_{bl}}{D_{ji}} \right) \quad (11.5)$$

The mass transfer coefficient $k_{i,b}$ can be described as (D_{ji}/l_b) in Eqs. (11.4) and (11.5). Because of the exponential relationship from Eq. (11.5), the average concentration within the mass transfer boundary layer is much higher than in bulk; it is also known as the concentration polarization layer. Because the concentration profile curve is affected by flux, the relation among the mass transfer coefficient $k_{i,b}$ ($=D_{ji}/l_b$) and those derived from the conventional correlations in chemical engineering must be considered with caution. As the flux through the membrane tends to 0 ($J \rightarrow 0$), it could be proved that $k_{i,b}$ approaches a typical mass transfer coefficient. The correlations between Reynolds number, Schmidt number and Sherwood number, which employs the mass transfer coefficient, can be employed in systems with low fluxes, such as electrodialysis, reverse osmosis, and ultrafiltration. However, conventional correlations must be utilized with much care when there is moderate to high concentration polarization, which could be related to the boundary layer Peclet number's ($J/k_{i,b}$) value. Usually, the mass transfer coefficient is determined from the experimental way by using Eq. (11.4).

In case of complete rejection of the solution, the equation becomes Eq. (11.6)

$$J = k_{i,b} \cdot \ln \left(\frac{C_{i,M}}{C_{i,b}} \right) \quad (11.6)$$

Now that $C_{i,M}$ has been determined to be almost constant, a plot of flux versus $\ln(C_{i,b})$ frequently yields a straight line with a negative slope, referred to as $k_{i,b}$. In a broad sense, the Peclet number of the boundary layer is a significant process variable on the feed side in liquid membrane processes. In contrast, the polarization effect in gas phases is much less significant due to the larger (about 10^5 higher) diffusion coefficient in gas phases compared to liquid phases. The mass transfer boundary layer is thin, as was indicated in passing; its thickness is determined by $D_{ji}/k_{i,b}$. The boundary layer is thin when D_{ji} is merely small, but D_{ji} is extremely small for macromolecules, and the boundary layer is skinny. Fouling is related to the highly localized high concentrations that arise.

11.4.2 Overview of Fouling: Its Causes and Effects

Fouling of the membrane is described as a reduction in the active area, resulting in a flux that is less than the membrane's theoretical capacity for a particular driving force. This is true if the pores are partially blocked or restricted, but sometimes a cake layer on a membrane's surface becomes a resistance in series with the membrane resistance. Two types of substances cause problems: those that destroy the membrane and foul it. Because a fouled membrane must be cleaned, harm to the membrane may occur if precautions are not taken during the cleaning process. Fouling during filtering has a clear detrimental impact on the economy of any membrane process. Thus it should be recognized, and countermeasures should be taken to limit the impacts.

The fouling rate is influenced by various factors, including the nature of the membrane module's hydrodynamics, characteristics of the membrane's surface, the material of the membrane, concentration of the solvents and the solutes. For a few applications, such as wastewater treatment, biofilms are becoming a challenging issue as they form from the ingredients of feed itself instead of foulants. The effect of concentration polarisation exacerbates the negative impact of all of these foulants; as previously stated, surface concentration is projected to grow exponentially with flux Eq. (11.5). As a result, less fluxes will reduce fouling, with a non-linear effect. Also, Eq. (11.5) shows that improved mass transfer would result in low surface concentrations, which is the reason the membrane module's hydrodynamics were stated to influence the rate of fouling. Therefore, the mass transfer will be improved, and fouling will be reduced with a higher crossflow velocity. An electrostatic term could be included in the mass balance Eq. (11.3). Under these conditions, the critical flux is the flux at which the electrostatic convective term equals the convective term; Fouling will be high beyond this flux. In general, the net flux of material towards the membrane could be considered a mix of fluxes, a few of which tend to transport material away from the surface of the membrane while others, such as the convective flux, move the material towards it.

The overall material flux, which is denoted by N , is:

$$N = JC - D \frac{dC}{dz} + p(\zeta) + q(\tau) \quad (11.7)$$

where D denotes the diffusion coefficient of the Brownian. $p(\zeta)$ denotes the term for solute/particle migration caused by surface interactions between the membrane and the solute/particle. $q(\tau)$ represents the influence of local hydrodynamics on the mass flux. The possibility of non-buoyant particles settling on the membrane's surface had not been considered.

11.4.3 Fouling Mechanism Assessment

A couple of models are being utilized to understand the concept of fouling process. The foremost one is based on the total membrane resistance (Chang et al. 2011). Resistance in series is denoted by R_t (cm^{-1}), and this is further divided into reversible cake formation (R_c) and irreversible Fouling (R_i). The resistance in the series model can be represented by Eq. (11.8), which was obtained using Darcy's law considering a constant transmembrane pressure (ΔP).

$$J_v = \frac{\Delta P}{(R_m + R_t)\mu} = \frac{\Delta P}{(R_i + R_m + R_c)\mu} \quad (11.8)$$

where J_v , R_m , ΔP , μ are the water flux, membrane resistance, transmembrane pressure and dynamic viscosity, respectively.

The other approach uses semi-empirical fouling models to fit the experimental fouling data to recognize the corresponding fouling mechanisms. A general equation (Eq. 11.9) was developed for dead-end filtration by modifying the Hermia empirical model for the crossflow filtration given by Vincent Vela et al. (2009).

$$-\frac{dJ_p}{dt} = K_{CF}(J_P - J_{pss})J_p^{2-n} \quad (11.9)$$

where J_{pss} , J_p , K_{CF} and t are the steady-state permeate flux, permeate flux, the coefficient for the phenomenological dependent on the specific mechanism, and time-taken for the filtration. According to Vincent Vela et al. (2009), n represents the fouling mechanisms. The value of n is 0, 1, 1.5, and 2, which implies gel formation, standard blocking, intermediate blocking and complete blocking, respectively (Vincent Vela et al. 2009).

11.4.4 Hermia's Fouling Models

Hermia developed four fouling models: complete pore blocking, intermediate pore blocking, cake filtration, and standard pore blocking (Fig. 11.2). These models are derived considering dead-end filtration under constant pressure.

The following assumptions were taken in developing the models:

1. Pores are symmetrical and parallel to each other
2. Foulants are uniform spheres
3. Overall filter resistance is constant.

In cross flow filtration, the flow rate of the feed can detach some of the foulants from the surface, so a term of foulant removal has been added in the derivation. This term comes for all mechanisms except standard pore filtration since it is not a surface phenomenon. Constant flux can be maintained by increasing the pressure drop ΔP across the membrane since the membrane area decreases due to fouling. A study developed models for fouling in the case of cross flow filtration and constant flux as follows (Kirschner et al. 2018).

11.4.4.1 Complete Pore Blocking

This model assumes that the foulants occupy all the pores and do not occupy the space on the top of other foulants (single layer fouling).

According to Darcy's law for flow through a membrane

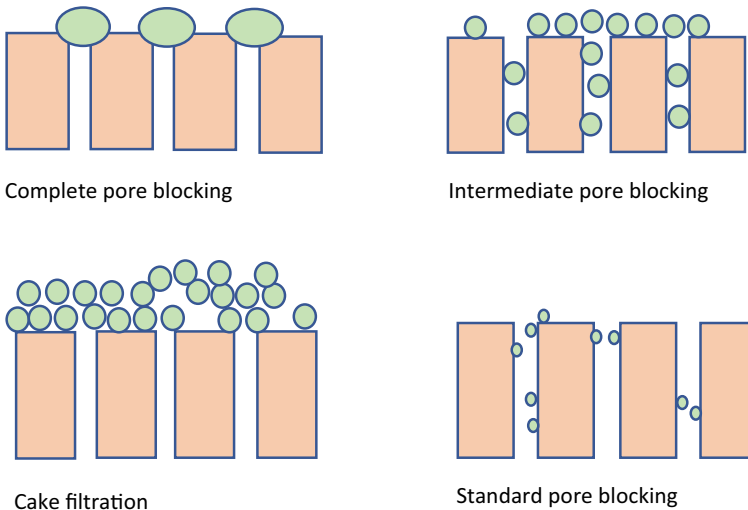


Fig. 11.2 Different types of Hermia fouling models

$$Q = \frac{\Delta P a}{\mu R} \quad (11.10)$$

where a , μ , ΔP , Q and R represent the free surface area, viscosity, transmembrane pressure, flow rate and overall resistance, respectively.

Since Q , μ , R are constant, we can write

$$\Delta P_t = \frac{\Delta P_0 a_0}{a_t} \quad (11.11)$$

0—initially at time = 0 s, t —at time = t s.

From Hermia,

$$a_t = a_0 - \sigma V \quad (11.12)$$

σ and V have occupied surface area per filtrate volume is filtrate volume, respectively.

As the permeation rate is constant,

$$V = Q_0 t = a_0 J t \quad (11.13)$$

Here, J is the permeation flux

Substituting Eq. (11.13) in Eq. (11.12), we get

$$-\frac{da}{dt} = \sigma a_0 J \quad (11.14)$$

Foulant removal term is added,

$$-\frac{da}{dt} = \sigma a_0 J - B(a_0 - a) \quad (11.15)$$

B is the particle resuspension rate.

On integrating Eq. (11.15) we get,

$$a_t = a_0 \left(1 - \frac{\sigma J}{B} (1 - \exp(-Bt)) \right) \quad (11.16)$$

Substituting Eq. (11.16) in Eq. (11.11) we get,

$$\Delta P_t = \frac{\Delta P_0}{\left(1 - \frac{\sigma J}{B} (1 - \exp(-Bt)) \right)} \quad (11.17)$$

The second term in the parentheses always lies between 0 and 1, which indicates that ΔP increases with time.

11.4.4.2 Intermediate Pore Blocking

Intermediate pore blocking is similar to complete pore blocking, but particles are allowed to deposit on top of previously accumulated particles.

$$-\frac{da}{dt} = \sigma a J \quad (11.18)$$

Since the probability of occupying new pore decreases in intermediate pore blocking, we consider a in place of a_0 Eq. (11.14).

Foulant removal term is added,

$$-\frac{da}{dt} = \sigma a J - B(a_0 - a) \quad (11.19)$$

On integration, we get,

$$a_t = a_0 \left(\frac{1}{K_i} + \left(1 - \frac{1}{K_i} \right) \exp(-K_i B t) \right) \quad (11.20)$$

K_i —intermediate pore blocking constant.

$$K_i = \frac{B + \sigma J}{B} \quad (11.21)$$

$$\Delta P_t = \frac{\Delta P_0}{\left(\frac{1}{K_i} + \left(1 - \frac{1}{K_i} \right) \exp(-K_i B t) \right)} \quad (11.22)$$

The denominator of this equation is always positive and varies from $(1/K_i)$ to 1.

The ΔP initially increases and reaches constant since the foulant removal and deposition balance each other.

11.4.4.3 Cake Filtration

In cake filtration, foulants cover the membrane surface in multiple layers, forming a cake of foulants. The overall mass transfer resistance increases with an increase in cake thickness. Therefore, overall resistance is the sum of membrane resistance, cake resistance, and the foulant removal term.

$$R_t = R_0 + \frac{\alpha W}{a_0} - \alpha S t \quad (11.23)$$

α , W and S are specific cake resistance, cake mass and rate of erosion of cake per unit area, respectively.

From a mass balance on the cake,

$$W = \frac{V\gamma s}{(1 - ms)} \quad (11.24)$$

γ , s and m are filtrate density, mass fraction of solid in fouling solution, and the mass ratio of wet to dry cake.

Substituting Eqs. (11.13) and (11.24) in Eq. (11.23) we get,

$$R_t = R_0(1 + K_c Jt) \quad (11.25)$$

K_c is cake filtration constant for crossflow filtration (m^{-1})

$$K_c = \frac{\alpha\gamma s}{R_0(1 - ms)} - \frac{\alpha s}{JR_0} \quad (11.26)$$

Substituting Eq. (11.25) in Eq. (11.10) we get,

$$\Delta P_t = \Delta P_0(1 + K_c Jt) \quad (11.27)$$

This equation shows that ΔP increases linearly with filtration time. Therefore, cake filtration is the dominant fouling mechanism for long filtration times.

11.4.4.4 Standard Pore Blocking

In this mechanism, it is assumed that foulants occupy only inside the pores, i.e. reducing the pore diameter and pores are assumed to be straight and parallel.

Laminar flow through a straight cylindrical pore,
Hagen-Poiseuille equation

$$Q = N \left(\frac{\pi r^4 \Delta P}{8\mu L} \right) \quad (11.28)$$

N , r and L are the number of membrane pores, pore radius and pore length, respectively.

Since the initial and final flow rates are equal, we get

$$\Delta P_t = \Delta P_0 \left(\frac{r_0}{r_t} \right)^4 \quad (11.29)$$

Following Hermia, a solid mass balance gives,

$$N\pi(r_0^2 - r_t^2)L = CV \quad (11.30)$$

C —volume of particles deposited per unit volume of filtrate.

Rearranging Eq. (11.30), we get,

$$\left(\frac{r_t}{r_0}\right)^4 = \left(1 - \frac{CV}{N\pi Lr_0^2}\right)^2 \quad (11.31)$$

K_s is the standard pore-blocking constant.

Where

$$K_s = \frac{C}{N\pi Lr_0^2} \quad (11.32)$$

Substituting Eq. (11.31) in Eq. (11.29) we get,

$$\Delta P_t = \frac{\Delta P_0}{(1 - K_s a_0 J t)^2} \quad (11.33)$$

From the above equation, it can be observed that the ΔP increases with an increase in time.

11.5 Cleaning Methods to Remove Fouling

Fouling is unavoidable, but its effects can be reduced by efficient cleaning and regeneration of membranes. Cleaning of the membrane is defined as removing the unwanted material and recovering the lost membrane efficiency. The membrane, after cleaning, should approximately act as the original membrane. The most recent development in membrane separation processes is carbon nanotubes (CNT) (Kramer et al. 2020). These tubes offer much less fouling potential than ceramic and polymeric membranes, but further research must be carried out to develop them to the industrial-scale level of wastewater treatment. Moreover, their potential toxicological effect on the environment is not yet studied (Wei 2015).

However, membrane cleaning is critical once the membrane is used for specific applications. Hence many researchers have focused on developing and modifying the mechanisms and cleaning techniques in the most economical and environmentally friendly way. Two cleaning methods exist to remove fouling, namely physical and chemical cleaning. In the following sections, these methods are described in detail.

11.5.1 Physical Cleaning

This cleaning method includes hydraulic permeate backwash, forward flush, electrical methods, and ultrasonic methods. Of these, backflushing is more advantageous

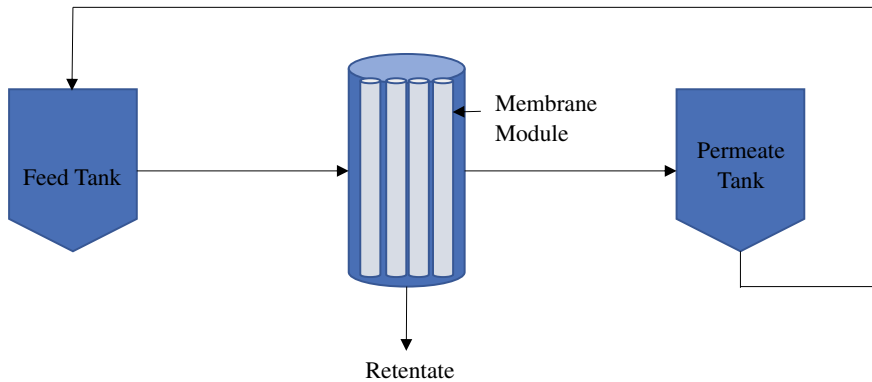


Fig. 11.3 Schematic representation of permeate backwash cleaning

compared to others. Many researchers worked out backwash efficiency and manipulated many parameters to obtain better output. Kramer et al. (2020) highlighted the disadvantages of chemical cleaning and employed hydraulic backwash, which failed in their case because backwash strength is not attained. Backwash strength is the ratio of backwash pressure to the permeate pressure (Kramer et al. 2020). Usually, backwash strength should reach 2.1 to avoid damage to the membrane. So, they employed precoating methods. Chang et al. (2011) studied irreversible fouling of ultrafiltration membrane, filtration mode, and backwash water as parameters (Chang et al. 2011). Figure 11.3 illustrates the permeate backwash cleaning.

11.5.2 Chemical Cleaning

In the chemical cleaning method, oxidants, chelating agents, caustic acids, enzymes and surfactants are usually used for membrane cleaning (Gitis 2016). Each group of chemical cleaners are used for different types of foulants. For example, caustic cleaners such as NaOH are used to cure microbial and organic fouling. And, acids including nitric acid and citric acid are used to remove metal oxides and scales from fouling layers.

Both physical and chemical cleaning methods can remove the foulants to their extent, but care should be taken such that the membrane's primary function should not be affected by these techniques.

11.6 Conclusions

Nanotechnology is emerging as an efficient technology in various sectors, including water purification. It is noteworthy that nanofiltration membranes are efficient enough to remove monovalent and multivalent ions. Therefore, they were widely used in several applications, including surface and groundwater treatment, removal of organic contaminants and pathogens, etc. However, the fouling phenomenon limits the large-scale application of the NF membrane. Consequently, the present chapter discussed fouling, including organic, inorganic, and biofouling. The performance of the membrane is affected in two steps, namely concentration polarization and fouling. Accordingly, the present chapter discussed the mathematical models for the concentration boundary layer and Hermia's models of fouling. As fouling is unavoidable, the membrane should be regenerated by proper cleaning methods for long term use. Depending on the nature of foulants and operating conditions, physical, chemical or biological cleaning methods should be employed.

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