

**Special Issue: Microfiltration and Ultrafiltration
Membrane Science and Technology**

Guest Editors: Prof. Isabel C. Escobar (University of Toledo) and
Prof. Bart Van der Bruggen (University of Leuven)

EDITORIAL

Microfiltration and Ultrafiltration Membrane Science and Technology

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Fouling control on microfiltration/ultrafiltration membranes: Effects of morphology, hydrophilicity, and charge

Rajेशha Kumar, A. F. Ismail

Advanced Membrane Technology Research Center, Universiti Teknologi Malaysia, 81310 UTM, Skudai Johor, Malaysia
 Corresponding author: A. F. Ismail (E-mail: afauzi@utm.my or fauzi.ismail@gmail.com)

ABSTRACT: Membrane-based separation processes are very susceptible to flux decline because of concentration polarization and fouling problems. Despite the immense applications of low-pressure driven microfiltration (MF) and ultrafiltration (UF) membranes in various fields, fouling is considered a major negative aspect, and it renders the membrane with a reduced lifetime. The important membrane properties, hydrophilicity, charge, and morphology mainly gained by the membrane during its formation process are considered to be deciding factors in fouling. In this review, we spotlight the effects of the hydrophilicity, charge, and morphology on MF and UF fouling, the principles of the most frequently used instrumentation techniques in predicting these factors, and measures that can be taken for fouling control. The review also focuses on the UF and MF membrane modification techniques used to attain high antifouling characteristics. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42042.

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INTRODUCTION

Ultrafiltration (UF) and microfiltration (MF) membrane separation process are used in a wide range of applications. UF and MF are separating processes of extremely small suspended particles and dissolved macromolecules (surface pore size range = 50–1 nm) that passes them through the membranes.¹ Numerous polymers, including poly(ether sulfone) (PES), polysulfone (PSF), poly(vinylidene difluoride) (PVDF), and polyacrylonitrile (PAN), are commonly used for UF and MF applications.² Properties such as a good mechanical strength and physicochemical stability, excellent film-forming properties, stability over a wide range of pH, and thermal stability (high glass-transition temperatures) make these polymers good membrane materials.³ Apart from the pore size and operating pressure, the main difference between MF and UF membranes lies in their applications in various fields. For example, MF membranes are effective in removing bacteria, and only parts of viral contamination are caught up in the process. UF membranes can remove viruses completely. Nowadays, MF membranes are used extensively in the cold sterilization of beverages and pharmaceutical products; clearing of fruit juice, wines, and beer; separation of bacteria from water (biological wastewater treatment); effluent treatment; separation of oil/water emulsions; pretreatment before nanofiltration or reverse-osmosis processes; and solid-liquid separation in the pharmaceutical and food industries. UF is useful for applications in the dairy industry (milk, cheese fil-

tration), food industry (juice filtration), blood filtration and treatment (hemodialysis), protein purification, sterile filtration, polymer separations, metal industry (oil/water emulsion separation, paint treatment), and textile industry (dye removal and effluent treatment) and also as a pretreatment for membranes in nanofiltration and reverse-osmosis processes.

Despite the enormous applications of MF and UF membranes in various fields, their permeability and selectivity deteriorates over time because of an accumulation of solids, suspended particles, colloids, and bacteria on the membrane surface and within the membrane pores; this is known as *membrane fouling*. Fouling is the deposition of retained particles, colloids, macromolecules, salts, biomolecules, and so on on the membrane surface or inside the pore at the pore wall. Fouling reduces the membrane flux either temporarily or permanently.⁴ The main mechanisms of fouling are (1) the adsorption of partially rejected matter within the membrane pores (*pore constriction*), (2) the plugging of individual pores by particles similar in size to the pores (*pore blocking*), and (3) the accumulation of completely rejected particulate matter on top of the membrane surface also (*cake formation*).⁵ Fouling is due to the overall effects of concentration polarization, adsorption, and cake layer deposition.

The fouling phenomenon is caused by the interaction between the membrane surface and the foulants, which include inorganic, organic, and biological substances in many different

Rajेशha Kumar obtained a master's degree in chemistry from Mangalore University, India, in the year 2004. He has research experience in the field of synthetic organic chemistry (2005–2010) from Syngene, Biocon India, Ltd. He obtained his Ph.D. in the field of membrane technology from the National Institute of Technology Karnataka, Surathkal, India, in the year 2013. He is the author of 12 publications in refereed journals and one book chapter. Since March 2014, he has been a postdoctoral fellow at the Advanced Membrane Technology Research Center, Universiti Teknologi Malaysia. His areas of research are the preparation of polymeric membranes for water and wastewater treatment and crude palm-oil purification.



Ahmad Fauzi Ismail is the Founding Director of Advanced Membrane Technology Research Center and also the Deputy Vice Chancellor (Research and Innovation), Universiti Teknologi Malaysia. Fauzi obtained a Ph.D. in Chemical Engineering in 1997 from University of Strathclyde and bachelor and master's degrees in science from Universiti Teknologi Malaysia in 1989 and 1992, respectively. He has authored and coauthored over 350 articles in refereed journals. He has authored two books, 25 book chapters, and three edited books and has three patents granted and 17 patents pending. He has won more than 120 awards, and among these outstanding awards are the Malaysia Young Scientist Award in 2000 and the ASEAN Young Scientist Award in 2001. He has won the National Intellectual Property Award two times, in 2009 (patent category) and 2013 (product category). He has also won the National Innovation Award twice, in 2009 (waste to wealth category) and 2011 (product category). He won the National Academic Award (Innovation and Product Commercialization Category) in August 2013 and the Malaysian Toray Science and Technology Foundation Award on November 28, 2013. Fauzi also won the IChemE Malaysia Innovator of the Year Award, awarded by IChemE UK on October 20, 2014. Most recently, on December 8, 2014, he won the Merdeka Award Winner in the outstanding scholastic achievement category (Malaysian Nobel Prize Winner).



He is a Fellow of the Academy of Sciences Malaysia, a Chartered Engineer in the United Kingdom (CEng), and a Fellow of the Institution of Chemical Engineers (FIChemE). At present, he is the editor of *Desalination*. Fauzi's research focuses on the development of polymeric, inorganic, and novel mixed-matrix membranes for water desalination, wastewater treatment, gas separation processes, membranes for palm-oil refining, photocatalytic membranes for the removal of emerging contaminants, and polymer electrolyte membranes for fuel cell applications. Fauzi has been involved extensively in Research & Development & Commercialization (R&D&C) for multinational companies related to membrane-based processes for industrial applications. He is also the an editorial board member of the *Journal of Membrane Water Treatment* (impact factor 0.436) and an advisory editorial board member of the *Journal of Chemical Technology and Biotechnology* (impact factor 2.494).

forms.⁶ The foulants does not only physically interact with the membrane surface but also chemically degrade the membrane material. For example, colloidal particles, such as natural organic matter (NOM), not only physically interact with the membrane surface but also chemically degrade the membrane material. In both MF and UF processes, the separation performance and membrane fouling are both strongly influenced by the skin-layer pore structure (size, shape, length, and porosity) and the chemistry (functionality, charge, and hydrophilicity).^{6,7} Not all MF or UF membranes undergo fouling at the same rate, presumably because of differences in the polymer composition and other membrane surface properties (e.g., hydrophobicity, roughness, pore size and geometry, charge density) that are believed to control how rapidly foulant matter undergoes initial surface attachment.^{8,9} In this review, we mainly focus on the control of fouling in UF and MF membranes. We cover the effects of the hydrophilicity, charge, and morphology on MF and UF fouling,

the principles of the most frequently used instrumentation techniques in predicting these factors, and measures that can be taken in fouling control. The review also focuses on the UF and MF membrane modification techniques used to attain high antifouling characteristics.

MF/UF MEMBRANE FOULANTS

Fouling in MF/UF membranes is classified into three categories: particle or inorganic fouling, biofouling, and organic fouling. In inorganic fouling, the fouling mechanism involves, first, the accumulation of particles on the membrane surface and inside the pores and, finally, cake layer formation.¹⁰ Biologically active organisms, such as bacteria, viruses, and algae, cause membrane biofouling as they adhere to the membrane and grow to form biofilms. The interaction between a bacterium and the separation membrane surface may be much more complex; bacterial

Table I. Common Foulants Used During the Application of MF/UF Membranes in Various Processes

| Filtration process | Foulants | References |
|------------------------------|--|------------|
| Wine clarification | Polyphenols, polysaccharides | 15 |
| Beer filtration | Sucrose, amylase, pure beer yeast, α -bitter acids, catechin | 16 |
| Skim milk filtration | Proteins, minerals | 17 |
| Textile wastewater treatment | Dyes (organic molecules) and detergents, salts (containing Cl^- , SO_4^{2-} , Ca^{2+} , K^+ , Mg^{2+} , Na^+ , and caustic soda) | 18 |
| Surface water treatment | Proteinlike substances, inorganic particles (iron oxides, aluminosilicates), soluble microbial products (bacteria, protozoa, algae) and NOM, colloids | 19 |
| Sugarcane juice filtration | 3–5% soluble solids in the form of colorants, color precursors, 0.85–1.45% of soluble solids in the form of organic nonsugars, such as proteins, polysaccharides, and waxes | 20 |
| Oil-in-emulsion filtration | Oil droplet | 21 |
| Hemodialysis | Blood proteins | 22 |

adhesion to the membrane surface can be initiated simply by nonspecific adsorption (e.g., through hydrophobic interaction). Once attached, the bacteria can grow on the membrane surface and synthesize insoluble exopolysaccharides that encase the adhered bacteria in a three-dimensional (3D) matrix. With the accumulation of exopolysaccharides and the reproduction of bacteria, a mature biofilm that cannot be easily removed by washing will develop on the membrane surface.¹¹ Membrane biofouling is often considered irreversible, and it is very difficult to handle because of the self-replicating nature of microbes.¹² NOM is the main source of organic fouling.¹³ NOM, on the other hand, can foul a membrane both internally and externally. Of the three types of foulants, NOM is thought to play a critical role in membrane fouling because it interacts with and/or adsorbs onto many surfaces in an aqueous environment.¹⁴ NOM can adsorb onto a membrane material and block or constrict the membrane pores. It can also coat the surfaces of particles and influence their interactions with one another or with the membrane.

Most importantly, the foulant will differ depending on the application of the MF/UF membranes. In MF membranes (pore size ≈ 0.1 – $1 \mu\text{m}$), inorganic particles and microorganisms are most likely to foul a membrane by the formation of caking on the external surface of the membrane. This fouling will be more or less severe depending on the properties of the cake (e.g., particle size, particle surface charge, compressibility). Table I represents the various types of foulants encountered during the application of MF/UF membranes in various fields.

FOULING MECHANISMS IN MF/UF

Generally, for MF and UF membranes, two types of fouling phenomena are distinguished. The first is *macrosolute or particle adsorption*, which refers to the specific intermolecular interactions between the particles and the membrane surface that occur even in the absence of filtration.²³ It is usually irreversible, adhesive fouling that cannot be removed by hydrodynamic methods. Irreversible fouling may be caused by hydrophobic interactions, hydrogen bonding, van der Waal's attractions, and

extracellular macromolecular interactions between the foulants and membrane surfaces.²⁴ Irreversible fouling is caused by pore blocking and strongly attached foulants during filtration. The second type is known as *filtration-induced macrosolute or particle deposition*; it is often reversible, nonadhesive fouling, where the accumulation of cells, cell debris, and other rejected particles on the top surface of the membrane is prominent.²⁵ This type of fouling is reversible in nature, can be removed by hydrodynamic methods (e.g., backwashing and cross-flushing). It occurs as external fouling or cake formation. Reversible fouling resulting from cake formation was found to be only weakly dependent on the membrane surface chemistry.

In membrane-based industries, the selection of MF or UF membranes suitable for preferred applications is vital. At the same time, vast knowledge about the foulants present in the feed is much essential. This is because the fouling mechanism changes from different foulants to different membrane surfaces. It is generally accepted that proteinlike substances significantly contribute to membrane fouling during MF and UF processes. Also, different foulants have different types of interactions with the same membrane surface.

ANALYTICAL TECHNIQUES FOR STUDYING FOULING

The three major parameters that affect the membrane fouling are the hydrophilicity, which offers better antifouling resistance because of the hydrophobic nature of most foulants; surface charge, which results in reduced scale formation, and surface roughness, which is likely to increase membrane fouling.²⁶ The other factors, such as the chemical composition and porosity, should also be taken into account. Various microscopic techniques, such as scanning electron microscopy (SEM), transmission electron microscopy, atomic force microscopy (AFM), confocal laser scanning microscopy, environmental SEM, and spectroscopic techniques, such as Fourier transform infrared (FTIR) spectroscopy, NMR, and surface-enhanced Raman spectroscopy, can be used to assess the fouling controlling factors, such as the morphology, charge, and hydrophilicity of the membrane surface. Among them, the following instrumentations are more

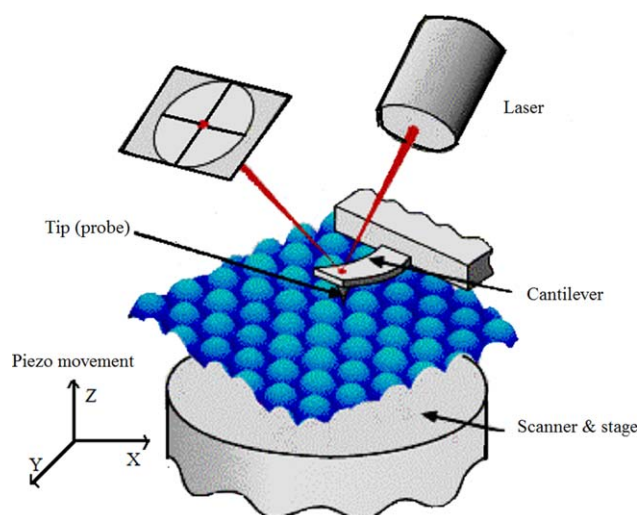


Figure 1. Schematic representation of an atomic force microscope.³⁶ [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

frequently used by researchers to evaluate the fouling tendency/resistance properties of the membranes.

Contact Angle

The contact angle is the angle where a liquid/vapor interface meets a solid surface. Generally, the solid surface is considered hydrophilic if the water contact angle is smaller than 90° , and if the water contact angle is larger than 90° , the solid surface is considered hydrophobic.²⁷ The hydrophobic membrane surfaces are formed by the disruption of intermolecular bonds within the polymer matrix; this leads to a low surface energy. The membrane sample preparation, measurement times, and drop volumes have a strong effect on the contact angle values.²⁸

The contact angle values of MF and UF membranes depend on their surface hydrophilicity (or hydrophobicity), roughness, porosity, pore size, and pore size distribution. For a membrane with a highly porous nature, the contact angle value may become very low, although the membrane is not necessarily hydrophilic. Similarly, the contact angle value of a membrane of higher surface roughness is higher compared to that of another membrane of lower surface roughness, although both membranes are of similar hydrophilic nature.⁴ It is believed that a membrane with a lower contact angle value will have high affinity toward water. The initial contact with the feed results in the formation of a hydrated layer, which prevents the further accumulation of hydrophobic foulants. Overall, contact angle estimates fouling-determining factors, such as the surface hydrophilicity, roughness, and porosity of the membrane. There have been few studies where researchers have used the contact angle itself as main tool in determining the membrane fouling.^{28,29}

Different contact angle measurement techniques are used for UF and MF membranes; these include the sessile drop,³⁰ immersion,²⁶ captive bubble,³⁰ and sticking bubble³¹ methods. The different contact angle values for different membrane surfaces indicates their variation in surface porosity, surface roughness, surface morphological alterations during the

measurement (e.g., that which results from surface drying), surface heterogeneity, and contamination of the solution(s) and/or solid surface.³² The rupture of the membrane morphological structure is considered a drawback during the measurement of the membrane surface contact angle with dry samples.³³

AFM and SEM

The morphological structures of different types of MF and UF membranes show considerable variations according to the application field and the underlying production process.³⁴ The microscopic techniques SEM and AFM are widely used to provide direct and detailed structural information, including the shape and size of individual pores inside the membrane and at the membrane surface.³⁵ AFM imaging can be implemented for fouling studies through the investigation of the foulant adhesion properties of membranes by force measurement. Atomic force microscopes use mechanical interactions with a probe scanned parallel to the mean plane (xy) of the surface to be studied. The probe tip is mounted on the end of a cantilever, as shown in Figure 1. When the tip touches the surface, the vertical deflection of the cantilever is measured by an optical system (a laser beam is bounced off the cantilever onto a dual-element photodiode). It is possible to adjust the mean plane of the surface by the subtraction of the surfaces to correct the imperfections of the chosen scan size. It is then possible to extract the roughness parameters, including the porosity of the membrane, which is directly related to the fouling.³⁶ A membrane with a hydrophilic surface interacts strongly with a hydrophilic probe, as indicated by a large phase shift, whereas the hydrophobic surface gives only a small phase shift.⁴ The surface roughness of the membranes calculated from the AFM analysis play a decisive role in the fouling propensity of the membranes.³⁷ The AFM 3D topographical images of the membrane surface allow for quantitative assessment of both the roughness and pore size distribution. The measurement of the roughness before and after the use of the membrane gives a quantitative measure of the degree of fouling on the membrane and allows for comparison between different membranes.³⁸

However, the AFM technique has few negative aspects: because of the size of AFM scanning probe tips, there are some limitations to the scanning depth, and in addition, AFM may distort the membrane pore size because of rounded corners near the pore entrance.³⁹ AFM scans a relatively small area at any given time, and roughness statistics derived from relatively small scan areas may be misleading.⁴⁰

SEM produces images of a membrane sample through the scanning of the surface with a focused beam of electrons. The electrons interact with atoms in the sample to produce various signals related to sample's surface topography and composition, which can be recorded. Image analysis by SEM or field emission SEM is also applied to visualize membrane structures and provide explanations of fouling mechanisms associated with the porosity, mean pore radius, and pore size distribution as they relate to pore blockage and/or surface (gel layer) coverage by image processing software.⁴¹ The rate of pore blockage is a strong function of the membrane porosity and pore structure. For example, membranes with interconnected pores were fouled more slowly because the fluid could flow around the blocked pores through the

interconnected pore structure.⁴² Membrane surface modification with techniques such as blending, grafting, coating, or irradiation will bring about morphological changes. To determine this, generally the membrane sample is scanned through the surface or cross section. Any morphological changes are closely related to the fouling resistance properties of the membrane.

Before scanning, the membrane sample will be coated with a material such as gold, gold–platinum, gold–palladium, chromium, or iridium. The coating layer thickness may vary from 2 to 5 nm, and the metal used will affect the structure of the coating. Samples with an extremely thin layer of coating can be imaged at moderately high magnification. However, a thin layer may result in an uneven distribution of metal; this can lead to charging, image drift, and/or beam damage to the membrane. Polymeric membranes can be extremely beam sensitive and can shrink, swell, or rupture when exposed to the electron beam.⁴³ A thick layer can obscure details and/or add fine-scale texture. Furthermore, a thick layer can fill in nanoscale gaps and can also bridge nanopores, and this will lead to inaccurate measurements of the membrane surface properties.⁴⁴

ζ Potential

The ζ potential is a scientific term for the electrokinetic potential in colloidal systems, that is, the electric potential in the interfacial double layer at the location of the slipping plane versus a point in the bulk fluid away from the interface.⁴⁵ This term expresses the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The ζ potential is caused by the net electrical charge contained within the region bounded by the slipping plane, and it also depends on the location of that plane. Thus, it is widely used for the quantification of the magnitude of the charge present on the membrane surface. According to Lawrence *et al.*,⁴⁶ the fouling interactions, that is, electrostatic interactions between charged membrane surfaces and the charged foulants can be predicted with ζ-potential study. If the measured ζ potential is similar before and after fouling and cleaning, this suggests that the membrane surface was restored close to its original condition after the fouling and cleaning process.

Streaming potential measures the charge modifications on the surface of UF/MF membranes. The common instrumentation used to determine the membrane surface ζ-potential values can be obtained elsewhere.⁴⁷ The streaming potential was evaluated with a device constructed from two Plexiglas chambers with Ag/AgCl electrodes inserted at each end. Data were obtained with 10 mM KCl at pH 7, with the fluid flow directed through the membrane pores. The schematic of the membrane streaming potential measurement is shown in Figure 1. The apparent ζ potential was evaluated from the slope with the Helmholtz–Smoluchowski equation:

$$\zeta = \frac{\eta \Lambda_0}{\epsilon_0 \epsilon_r} \left(\frac{dE_z}{d\Delta P} \right) \quad (1)$$

where ζ is Zeta potential, η is the solution viscosity, Λ₀ is the solution conductivity, ε₀ is the permittivity of vacuum, ε_r is the dielectric constant of the medium, E_z is the Streaming potential and ΔP is the applied pressure.

Many researchers use ζ-potential measurement as the key factor to measure the fouling behavior of membrane surfaces.^{48,49} Xiao *et al.*⁵⁰ proposed that a more serious fouling of UF membranes could be observed with a more negative charge density of the feed solution. The fouling of MF and UF membranes by biological macromolecules such as proteins has been known to be dependent on the ζ potential of the membranes and the protein charge.⁵¹ In many cases, the charge present on the foulant surface is highly affected by the pH of the feed solutions.⁴⁶

Other Techniques

Today, new characterization techniques, such as confocal scanning laser microscopy (CSLM),⁵² provide a 3D representation of the membranes and their fouling. By means of a fluorescent contrast agent, this nondestructive technique reveals the presence in the porous structure of defects that do not propagate to the membrane surface. This is a clear advantage of CSLM over SEM, which provides only two-dimensional (2D) representations. Ferrando *et al.*⁵³ developed this technique to characterize the fouling of flat MF membranes with fluorescent probes. This technique provides information on the fouling at the surface of the membrane and also inside the porous matrix, the origin of the fouling, and the quantification of the blocked pore surface. However, the resolution of this technique is low, and thus, it has so far been applied only to MF membranes. Another technique, which also uses fluorescence labeling, was developed by Hughes *et al.*⁵⁴ to give a 3D representation of flat membrane fouling. With this optical technique, namely, two-photon FEM to second near-IR nonlinear optical imaging, they were able to show the influence of the concentration of a yeast fouling solution on cake formation. The use of modern synchrotron radiation sources provides 3D visualization of the membranes with 2D images. Real-time techniques are very useful for determining the earliest interactions between foulants and membrane materials during the formation of fouling layers, so that remedial measures, such as membrane cleaning or replacement, can be more efficiently implemented. Ultrasonic time-domain reflectometry (UTDR) and ultrasonic frequency-domain reflectometry can be used for this purpose in a manner that does not damage the membrane or alter the function of a liquid separation system.⁵⁵ UTDR can be successfully used to measure the rate of cake layer formation at different flow rates, monitor membrane cleaning, and evaluate the cleaning effectiveness of various cleaning methods. The working principle of UTDR is schematically presented in Figure 2. The cell consists of two poly(methyl methacrylate) (PMMA; Perspex) plates, and the ultrasonic transducer is mounted on top of the cell. During the filtration process, most of the feed solution flows over the top of the membrane, whereas the permeate is withdrawn from the bottom of the membrane. When fouling occurs on the membrane surface, the properties of the membrane change because of the accumulation of foulants on the surface of the membrane. If a fouling layer with thickness ΔS is present on the membrane surface, the reflected echoes A, B, and C are produced from the different interfaces in the cell. Echo A is associated with the top plate or feed interface, and echo B is associated with the initial feed solution or membrane interface. If the fouling layer is dense and thick enough to produce a

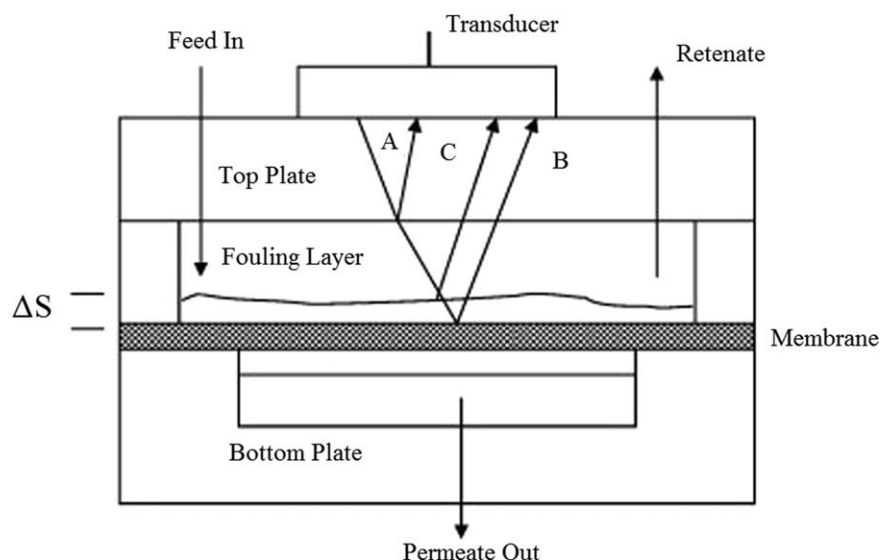


Figure 2. Schematic representation of the principle of UTDR measurement of fouling in flat-sheet membranes. Redrawn from Shugman *et al.* 2013.⁵⁶

reflected ultrasonic signal, a new echo signal will appear as a consequence of the new feed/fouling interface.⁵⁶ ΔS can be determined with the following equation:

$$\Delta S = 0.5c\Delta t \quad (2)$$

where c is the ultrasonic velocity in the medium through which the wave travels and Δt is the change in the arrival time of the fouling peak.

UTDR can provide an approach for understanding the protein-fouling behavior related to flux decline. Ultrasonic methods can also be correlated and verified with standard postmortem characterization techniques, such as microscopic and gravimetric analysis. It can be applied for postmortem characterization via scanning acoustic microscopy. This novel approach, leveraging both *in situ* and postmortem analysis, provides the basis for a comprehensive monitoring methodology for fouling formation and to characterize the distribution and abundance of conglomerate fouling layers.

FTIR spectroscopy could provide chemical and structural information of the membrane surface. FTIR/attenuated total reflectance is not very surface sensitive because of its large penetration depth, although it is a common technique for quick analysis of the membrane surface.⁴ It gives information about the presence of important functional groups, such as $-\text{NH}_2$, $-\text{COOH}$, $-\text{CONH}_2$, and $-\text{POOH}$, and this helps in determining the charge (positive or negative) on the membrane surfaces.

EFFECTS OF THE MEMBRANE HYDROPHILICITY, MORPHOLOGY, AND CHARGE ON FOULING

Hydrophilicity of the Membrane

Generally, most commercial UF and MF membranes are made up of hydrophobic polymers, such as PSE, PES, polypropylene (PP), polyethylene, and PVDF. Hydrophobic membranes, however, are easily susceptible to fouling, that is, the nonspecific adsorption of solutes on the membrane surface and pores,

which results in severe flux decline. It has also been generally acknowledged that membranes with hydrophilic surfaces are less susceptible to fouling and their fouling is often reversible. Fouling decreases with increasing hydrophilicity of the polymeric material.⁴ It is worth mentioning that many of the foulant molecules are hydrophobic in nature;⁵⁷ with an increase in the membrane surface hydrophobicity, hydrophobic foulant molecules are driven more toward the surface. This results in the enhancement of surface contamination. As the membrane surface becomes more hydrophilic, when an aqueous feed comes into contact with it, a hydrated layer is easily formed on its surface. It is assumed that increasing the hydrophilicity of the membrane will provide more opportunity for water, rather than foulants, to chemically associate with the membrane surface. Such a hydrated layer can prevent the adsorption and deposition of hydrophobic foulants onto the membrane surface and thus reduce fouling.

In the past few decades, attention has been given to the chemical and physical modification of UF/MF membrane surfaces with hydrophilic inorganic or organic molecules. The hydrophilic polymeric additives and functionalized nanomaterials have shown the immense effect of surface hydrophilicity changes of UF/MF membranes on reduced fouling, as illustrated in Table II. Through the incorporation of functionalized nanoparticles into the UF/MF membrane matrix, an enhancement in the hydrophilicity and better dispersion in dope solutions can be achieved.^{58,59} Moreover, it plays a major role in improving the membrane permeation and antifouling properties.⁶⁰ Hydrophilic polymers, such as poly(vinyl pyrrolidone) (PVP),⁶¹ poly(ethylene glycol) (PEG),⁶² and cellulose acetate phthalate,⁶³ often act as pore formers and introduce hydrophilicity to the membrane surface. It is noteworthy that hydrophilic polymer additives move to the surface during the membrane-formation process because of their high affinity toward water. Surface modification is one of the practical approaches for hydrophilicity enhancement and fouling mitigation strategies. The

Table II. Effects of the Surface Charge, Hydrophilicity, and Morphology on the MF/UF Membrane Antifouling Properties

| Base material | Major factor affecting fouling | Modification and antifouling results | Reference |
|--|--------------------------------|--|-----------|
| PES UF | Hydrophilicity | High flux recovery values were attributed to the surface hydrophilicity improvement with myoglobin. | 64 |
| Polyolefinic MF | Hydrophilicity | A modified interfacial polymerization technique was used to coat 1,8-octanediamine onto the internal surface. | 65 |
| Microporous PP | Hydrophilicity | It was coated with polyethylenimine and sequentially crosslinked with <i>p</i> -xylylene dichloride and quaternized with iodomethane to form a permanently positively charged layer. | 66 |
| PVDF MF | Hydrophilicity | The addition of nanosized ZnO particles enhanced the antifouling performance during the reclaimed water treatment. | 67 |
| PSF UF | Charge | It was chemically modified on its surfaces with propane sultone and SnCl ₄ ; there was better anti-absorption properties for BSA protein because of the high flexibility of the negatively charged sulfonated group. | 68 |
| PSF | Charge | SPEEK was used as a blend; humic acid deposits, forming on the charged membranes above the critical fluxes, had a loose structure, as visualized by AFM, and were consequently efficiently removed by simple rinsing. | 69 |
| PAN | Charge | The —SO ₃ H groups of the blending material electrostatically repelled the negatively charged particles of BSA, and the electrostatic repulsion promoted the low fouling of the membranes. | 70 |
| PSF | Charge | There was less static adsorption of foulant molecules on the PSF membrane with its higher degree of carboxylation and sulfonation; this resulted in negatively charged membrane surfaces. | 71 |
| Microporous PP | Charge | Poly[2-(dimethyl amino)ethyl methacrylate] was grafted onto the membrane surface by sequential UV-induced graft polymerization; this was followed by quaternization with benzyl chloride or iodomethane. A positively charged membrane surface achieved 100% antibacterial efficiency for tested bacteria. | 72 |
| PVDF | Charge | It was grafted by acrylic acid or methacrylic acid. The negatively charged carboxylic groups in poly(acrylic acid) or poly(methacrylic acid) and the negatively charged BSA protein molecular repulsion resulted in improved antifouling performance. | 73 |
| Poly(arylene ether sulfone) and aminated hydrophilic poly(arylene ether sulfone) | Charge | Membranes were incorporated with MWCNT-COOH; this induced a negative charge on the membrane surface, and the protein antifouling properties of the membranes improved with an increase in the MWCNT-COOH content. | 74 |

Table II. Continued

| Base material | Major factor affecting fouling | Modification and antifouling results | Reference |
|---------------|--------------------------------|---|-----------|
| PP | Charge | The tethering of zwitterionic PSBMA through UV-induced surface graft polymerization followed by surface-initiated atom transfer radical polymerization resulted in a good anti-protein-fouling performance. | 75 |
| PVDF | Charge | A zwitterionic polymer, poly[3-(methacryloylamino) propyl dimethyl(3-sulfopropyl) ammonium hydroxide], was grafted via a two-step polymerization; good BSA protein-fouling resistance and good membrane recycling properties were obtained. | 76 |
| PES | Charge | Zwitterionic monomers [2-(methacryloyloxy) ethyl]dimethyl(3-sulfopropyl) ammonium hydroxide and 2-(methacryloyloxy)ethyl phosphorylcholine were obtained by photografting. Better organic antifouling properties and a higher biofouling resistance were observed. | 77 |
| PVDF | Hydrophilicity/charge | Amphiphilic poly(vinylidene fluoride)-graft-poly(<i>N,N</i> -dimethyl amino-2-ethyl methacrylate) was obtained via radical graft copolymerization and was used as an additive to prepare a flat-sheet PVDF membrane; poly(<i>N,N</i> -dimethyl amino-2-ethyl methacrylate) side chains tended to aggregate on the membrane surface, pore surface, and internal pore channel surface and were converted with 1,3-propane sultone to yield a zwitterionic membrane surface; it exhibited a high flux recovery and anti-biofouling properties. | 78 |
| PVDF | Hydrophilicity/charge | A copolymer containing PVDF backbones and polyacryloylmorpholine side chains was synthesized by the radical polymerization method. The copolymer was used to fabricate membranes without the blending of PVDF. An improved resistance to protein fouling was observed. | 79 |
| PVDF | Hydrophilicity/charge | Zwitterionic PPO- <i>b</i> -PSBMA copolymers with various zwitterionic PSBMA lengths were coated onto a PVDF membrane surface. Resistance to human fibrinogen adsorption was enhanced with increasing PSBMA content. A coating consisting of high PPO- <i>b</i> -PSBMA containing a high number of zwitterionic sulfobetaine methacrylate units presented a high hydration capability, which was believed to allow significant improvements in the hemocompatibility characteristics of the PVDF membranes. | 80 |
| PVDF/PTFE | Pore size and shape | For PVDF membranes with a morphology resembling a particulate bed, the fouling evolution rate decreased with the pore size. For PTFE/PVDF membranes having a fibrous network with threadlike pore walls and | 81 |

Table II. Continued

| Base material | Major factor affecting fouling | Modification and antifouling results | Reference |
|---|--------------------------------|---|-----------|
| | | interconnected pore channels. The fouling evolution rate varied only slightly with the membrane hydrophobicity and pore size. | |
| Polycarbonate (track-etched) | Pore size | It was used for the filtration of a PMMA suspension. Filtration transformed it from membrane blocking to cake filtration at a lower filtration flux or lower particle accumulation for the membrane with a larger pore size or under a lower filtration pressure. | 82 |
| Sulfonated PEI/PEI | Pore size and shape | The addition of sulfonated PEI induced the formation of a nodular structure and suppressed the formation of fingerlike macrovoids. An increase in the air gap distance resulted in micropore formation in the outer fiber surface of a hollow-fiber membrane, and the pore size increased accordingly. This resulted in increased pure water flux and antifouling properties. | 83 |
| PEI/SPEEK | Pore size | Electrostatic repulsion between SPEEK molecules in the casting solution hindered the bundling of polymers. This resulted in a larger pore size or interconnected pores with reduced fouling. | 84 |
| Four MF membranes with polycarbonate, PVDF, mixed cellulose esters, and PES | Pore size and shape | For activated sludge filtration, a track-etched polycarbonate membrane with a dense structure and uniform cylindrical pores featured the lowest resistance because of pore fouling. The other three membranes presented a spongelike microstructure and tended to have more pore fouling because of their highly porous network. | 85 |
| Polycarbonate (track-etched), PVDF, PTFE | Pore shape | A membrane with straight trough (noninterconnected) pores showed a more rapid flux decline (polycarbonate) than membranes with an interconnected pore structure (PVDF). | 86 |
| PVDF | Roughness | With the incorporation of nano-ZnO, the roughness parameters of the membranes decreased; a higher loading of ZnO increased the roughness along and decreased the porosity, pore size, and antifouling properties because of the increased viscosity of the dope. | 67 |
| PVDF/PVA | Roughness | A PVA layer increased the smoothness and hydrophilicity of the membranes. As a result, the antifouling properties increased. | 87 |
| PTFE/PEGylation | Roughness | The surface roughness increased with the treatment time because of enhanced surface PEGylation, and the adsorption of fibrinogen and bacterial attachment decreased. | 88 |

BSA, bovine serum albumin; PEI, poly(ether imide); PPO-*b*-PSBMA, poly(propylene oxide)-*block*-poly(sulfobetaine methacrylate); PSBMA, poly(sulfobetaine methacrylate); PTFE, polytetrafluoroethylene; SPEEK, sulfonated poly(ether ether ketone); PVA, polyvinyl alcohol; MWCNT-COOH, carboxylated multi walled carbon nanotube.

membrane surface hydrophilicity can also be improved by surface coating, the incorporation of zwitterionic additives, interfacial polymerization techniques, and so on, as illustrated in Table II.

Surface Charge of the Membrane

The antifouling properties of the UF and MF membranes depend on both the charge present on the membrane surface and the charge present on the foulant under selected operation conditions. The advantages of the charged membranes are underlined as a higher selectivity/retention or reduction of fouling phenomena. The repulsive forces working between the charged membrane surface and the charged foulants in the feed solution prevent the deposition of foulants on the membrane surface; this reduces fouling.⁴ Because of extensive applications of MF and UF in water pretreatment and protein separation, considerable research is ongoing in the development of membrane surfaces that can effectively inhibit protein adsorption. As most proteins, cells, and colloidal particles, such as NOM, are negatively charged in aqueous solution,⁸⁹ the presence of negatively charged groups on the membrane surface should increase the electrostatic repulsion between the membrane and foulants and thus reduce fouling on the membranes.⁹⁰ To achieve high resistance to biofouling by both positively and negatively charged foulant molecules, neutrally charged surfaces with highly hydrophilic surfaces are highly preferred. Recently, the development of membrane surfaces containing zwitterionic groups (containing both positively and negatively charged groups) has been found to be more effective in fouling mitigation.⁹¹ Overall, the selection of a suitably charged membrane surface relating to the nature of the foulant is the best method for fouling mitigation.

Usually, it is appropriate to use a membrane carrying the same electrical charge as the foulants. For example, charged membranes have been developed mainly for the separation of charged solutes, such as proteins. The membrane charge should be of the same sign as the charge on the product protein at the selected pH value to enhance the electrostatic exclusion of the product from the membrane pores.⁹² Electrostatic interactions are significantly important for achieving high humic acid removal and less fouling.⁹³ Several studies have shown that UF membranes with a negative charge had a greater NOM rejection and less fouling tendency than neutral membranes. Humic acid is highly negatively charged at a pH greater than 4.7; a modified membrane with a negative charge would reject the humic acid with the same kind of charge because of electrostatic repulsion and increase the rejection coefficient.⁹⁴

In general, the charge present on the polymer is mainly dependent on the type of chemical functional group present in its backbone. Most UF and MF membranes are uncharged, and chemical modification is essential to make them charged. Membranes prepared from chemically modified polymers with suitable functional groups have increased positive or negative charges on their surfaces.⁸⁴ Charged polymers not only change the hydrophilicity of the membranes but also provide charges on the surface.⁹⁵ The behavior of charged membrane surfaces for the different foulant molecules is distinct. Grafting and coat-

ing are the other techniques that help to attaining charges on the membrane surfaces, as illustrated in Table II. The incorporation of charged nanomaterials have a high tendency to impart charges on the surface of the membrane to reduce fouling (Table II). Several researchers have claimed that the polarity of MF and UF membrane surfaces highly influences the fouling rate because of electrostatic interactions.^{15,96} Zwitterionic groups have received increasing attention in the preparation of fouling control membranes because of their resistance toward adsorption of proteins from aqueous buffers.⁹⁷ Zwitterions with a balanced charge and minimized dipole are excellent candidates as nonfouling materials because of their strong hydration capacity via electrostatic interactions.⁹⁸ The contribution of zwitterions in membrane surface charge modification to mitigate fouling is illustrated in Table II.

Membrane Morphology

The UF and MF membranes prepared by the phase-inversion technique are asymmetric in nature. The different types of phase separation are responsible for the buildup of the dense skin layer and the porous supporting layer in asymmetric membranes. The formation of the porous sublayer can be explained in terms of liquid–liquid phase separation, coalescence, and gelation. Special attention needs to be paid to the formation mechanism of the fingerlike cavities in the sublayer.⁹⁹ The active thin layer decides the flux and selectivity, whereas the supporting layer provides mechanical strength for an asymmetric membrane. The incorporation of additives (organic or inorganic) into the UF and MF membrane matrix has a high influence on the formation of fingerlike cavities, porosity, and flux. The conversion of fingerlike cavities into spongelike structures in the sublayer may be possible for the higher loading of additives and result in reduced flux and porosity.^{100,101} The membrane flux can be tuned to a larger extent through membrane fabrication methods. The track-etching technique, in which the polymeric film is irradiated with energetic heavy ions, leads to the formation of linear damaged tracks across the irradiated polymeric film. The track-etched polymer membranes are usually in an MF range of pore sizes with low surface roughness, their unique features are practically ideal cylindrically shaped pores, and they have a very sharp pore size distribution. However, because of their low surface porosity, the membrane fluxes are rather low.¹⁰²

Usually, for UF and MF membranes, the fouling is strongly influenced by the membrane polymer properties, porous structure, and specific membrane surface features.¹⁰³ Polymer properties, such as the crystallinity of the base polymer, are essentially required for better mechanical strength and permeability of the membrane. In UF and MF membranes, membrane fouling takes place when the matter in the feed solution leaves the liquid phase to form a deposit on either the membrane surface or inside its porous structure.¹⁰⁴ The nonfouling or low-fouling membrane should have a much narrower pore size distribution, stronger hydrophilicity, and larger porosity. However, control over UF and MF membrane fouling with increasing porosity is a difficult task. Fouling and flux in the UF and MF membranes are primarily controlled by the porosity, pore size distribution, and pore tortuosity of the membranes. Surface

coverage is a dominant fouling mechanism for UF membranes, whereas pore blockage is dominant with MF membranes because of the a different interactions between the size of organic matter components and membrane pore size.¹⁰⁵ The membrane pore morphology is the other factor that effects the fouling. The effect of different pore sizes and shapes on membrane fouling is illustrated in Table II. For less fouling, it is necessary to make the membrane thinner than the pore size, make the porosity as high as possible, and give the pores a uniform size and distribution over the surface.¹⁰⁶

The UF and MF membrane surface smoothness and roughness will effect fouling. A smoother surface is commonly expected to experience less fouling, presumably because foulant particles are more likely to be entrapped by rougher surfaces than by smoother membrane surfaces.¹⁰⁷ The membranes with rougher surfaces are observed to be more favorable for foulant attachment, and this results in faster fouling rates. A greater roughness increases the total surface area to which foulants can be attached, and the ridge–valley structure favors the accumulation of foulants at the surface by providing more adsorption sites.¹⁰⁸ Foulant particles preferentially accumulate in the valleys of rough membranes; this results in valley clogging, which causes a more severe flux decline than in smooth membranes. In the case of composite or nanocomposite UF and MF membranes, the surface of the nascent membrane presents a high roughness with several obvious peaks and valleys. The surface roughness can amplify both the hydrophilicity and the hydrophobicity of the surfaces.¹⁰⁹ After the blending of hydrophilic polymers or nanomaterials, huge peaks and valleys are replaced by numerous small ones. Such internal modification results in the formation of smooth membrane surfaces with a reduction in fouling. The membrane surface roughness is highly influenced by its modification techniques, including blending, grafting, or coating. A few examples of altered membrane roughness by the incorporation of nanoparticles and zwitterionic molecules and coating via PEGylation are demonstrated in Table II. However, there are still concerns; for example, roughness has both positive and negative effects on the membrane flux. The available membrane area for transport increases with the surface roughness and has a positive effect on the flux, whereas fouling is the reason for negative effects.¹¹⁰

APPROACHES TO CONTROLLING MEMBRANE FOULING IN UF AND MF MEMBRANES

The main approaches that can be implemented in UF/MF membrane filtration processes to bring down the fouling problem are (1) the pretreatment of the feed, (2) membrane material/surface modification, and (3) cleaning procedures and operating parameters.

Pretreatment of the Feed

UF and MF membranes are well known as low-pressure membranes and have relatively large membrane pores. During water treatment, this leads to undesirable removal efficiencies of NOM, in which the effluent cannot meet the quality of potable water. Meanwhile, foulants in raw water can cause severe flux decline in the membrane. Frequent membrane cleaning will

increase operation costs and decrease membrane module operation costs and performance. Thus, a proper pretreatment process before membrane filtration will not only improve the treatment efficiencies of the whole system but also mitigate membrane fouling, decrease the frequency of cleaning, and prolong membrane lifetime. Several pretreatment methods for preventing MF/UF membrane fouling include coagulation, sand treatment, flocculation, chemical treatment, adsorption, and ozone oxidation. The selection of a proper pretreatment technique for the MF or UF process strongly depends on the nature of foulants present in the feed.

Coagulation and flocculation are the techniques that are commonly used for the removal of organics, suspended solids, and phosphorous from wastewater. Such coagulated or flocculated particles can be easily removed by cross-flow MF. We assume that during the coagulation process, the stability of colloidal organic matter will be disturbed; this will lead to the formation of larger particles and provide opportunities for the adsorption of dissolved material adsorption and relieve membrane fouling. During the flocculation pretreatment process, the flocculator will produce uniform microsized flocs, which are removed by cross-flow MF. Flocculated particles can form a highly porous filtration cake on a membrane surface. This fouling can mitigate the membrane surface by preventing the deposition of particles and making membrane cleaning easier.¹¹¹

Adsorption pretreatment is the other technique; it consists of the combination technology of a powder-activated carbon low-pressure membrane particularly used in water treatment technologies. The adsorption of foulant molecules by activated carbon is the main principle of the treatment process. Similar to the coagulation pretreatment, the cake layer formed by activated carbon on the membrane surface can also facilitate filtration efficiency.

During water treatment applications with UF and MF membranes, the molecular weight distribution of organic matter in water has a great influence on membrane fouling. The degradation of organic macromolecules into smaller molecules with oxidizing agents is known as *oxidative pretreatment*. Ozone is a powerful oxidant that preferentially oxidizes electron-rich moieties containing carbon double bonds and aromatic alcohols.¹¹² It had an obvious effect on the modification of the molecular weight distribution of organic matter.¹¹³ Through ozone oxidation, macromolecular organics can be oxidized into small molecules, and small molecules can be oxidized into inorganic matters, which can further decrease the concentration of fouling pollutants and radically reduce membrane fouling. UF and MF integrated with other suitable treatment processes are effective in achieving separation efficiency along with control over fouling during water treatment applications. The MF/UF processes integrated with photocatalysis,¹¹⁴ ultraviolet (UV) irradiation,¹¹⁵ chlorination,¹¹⁶ slow sand filtration,¹¹⁷ and electrocoagulation¹¹⁸ have been found to be effective in fouling reduction.

FOULING CONTROL VIA MF/UF MEMBRANE SURFACE MODIFICATION

The recent methods for fouling control have been the selection of membrane materials that have a low affinity toward proteins,

colloidal particles such as humic substances, and NOM or bacteria. This may result in the loose binding of foulants to membrane surfaces. The flux of such membranes can be easily recovered by simple cleaning techniques. The membrane material influences fouling to a greater extent in UF and MF membranes, mainly because many UF and MF membrane polymers are hydrophobic in nature. The effects of solute adsorption in MF may not be very severe, but the solutes contribute significantly to flux reduction by reducing the pore sizes on the membrane. Thus, the other approach is to fabricate the membrane with resistance toward the adhesion of foulants through membrane surface modification. Usually, the membrane's surface-modifying groups are hydrophilic in nature and are retained on the surface after membrane fabrication. Membrane surface modifications can be achieved through various techniques such as polymer grafting, blending, irradiation, coating, and the use of inorganic or antimicrobial additives during membrane manufacturing. Overall, surface modification will affect membrane fouling by altering the charge, hydrophilicity, and smoothness of the membrane surface.

Surface Grafting

The grafting technique consists of the addition of a hydrophilic chain or electrostatically charged group to the membrane surface. The schematic representation of the membrane surface modification through grafting method is presented in Figure 3. Grafting uses hydrophilic polymers or plasma treatment to produce antifouling membrane surfaces. Surface grafting inevitably leads to a permanent change in the membrane chemistry, pore size, permeability, and fouling; this affects the overall performance of the membrane and the quality of the product water.¹²⁰ Furthermore, the grafting of the membrane surface can be achieved by chemical, radiation, radical, and photo-induced grafting techniques. Photo-induced grafting is a useful technique for the modification and functionalization of membrane surface because of its mild reaction conditions, selectivity to absorb UV light without affecting the bulk polymer, and permanent alteration of the surface functional groups. Zwitterionic groups exhibit great superiority in the field of polymer membrane surface functionalization due to simpler modification techniques involved. The grafting of zwitterionic monomers is the most commonly adopted procedure for membrane surface functionalization to attain both positive and negative charges. The antiprotein fouling of zwitterions is also associated with the uniformity of the distribution of charge and electrical neutrality. Charge uniformity can not only maximize the hydration ability of the zwitterion but also reduce the electrostatic interaction between the membrane surface and the protein.¹²¹ The grafting of a variety of zwitterionic monomers have been reported to increase membrane resistance toward foulants, as summarized in Table III.

Membrane Surface Coating

The surface coating in UF and MF membranes involves the use of a solution containing the polymer(s) bearing the antifouling properties. The coating is very water-permeable and resists foulant particles from reaching the underlying membrane structure and reducing internal fouling. The coating technique may involve coating via casting, adsorption, or filtration. General coating techniques involve coating via casting where the brush-

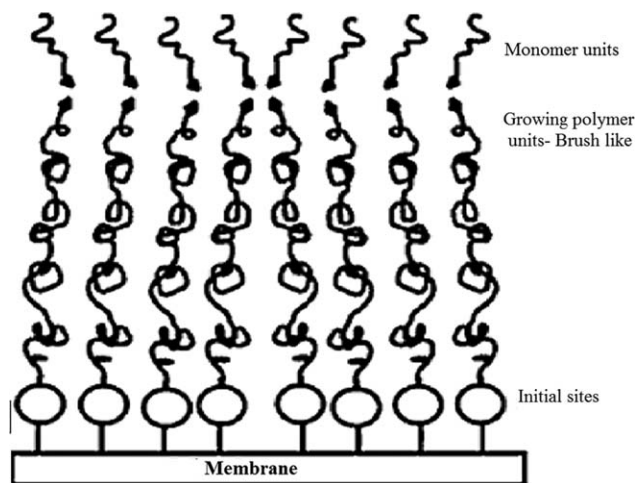


Figure 3. Schematic representation of membrane surface grafting. Redrawn from Mansouri *et al.* 2010.¹¹⁹

like layer of the polymer or copolymer, formed on the membrane surface, acts as a steric barrier to protein adsorption and endows these membranes with exceptional fouling resistance with a small reduction in flux.¹³⁵ Coating via adsorption usually imparts hydrophilicity to the membrane surface, whereas coating via filtration usually results in the deposition of hydrophilic additive polymers on the membrane surface and into the membrane pores.¹⁴⁹ The coating of a thin layer of water-soluble polymers or surfactants from solution by physical adsorption is a flexible technique that is used to optimize the hydrophilicity, smoothness, and surface charge of the membrane surface.¹⁵⁰ Hydrophilic materials, such as PEG-based materials, have been shown to be an ideal choice for surface functional moieties with antifouling characteristics.¹⁵¹ The formation of the bounded water layer on a highly hydrated surface was demonstrated as a crucial issue for repelling proteins, and it made the antibiofouling surface-generated. Membrane surface PEGylation can be achieved by the blending of PEG-containing polymers before membrane formation or surface grafting or the coating of PEG moieties after membrane formation. However, blending is the highly preferred technique, and the compatibility between the polymers and membrane matrix is a problem that easily causes hydrophilic polymers to be removed during the reaction or phase separation; this limits the performance of biofouling resistance.¹⁵² PEGylation via surface grafting has shown high efficiency in the improvement of biofouling resistance, but large-scale surface modification is still difficult because it usually needs membrane pretreatment and additional complicated steps during operation processes.¹⁵³ Surface PEGylation via physical coating is an effective approach, and it provides several distinct advantages, including easy operation and suitability for large-scale preparation.¹⁵⁴ However, coating stability is still a major concern and challenge. The UF/MF membrane fouling mitigation efforts via surface coating and PEGylation are summarized in Table III.

Polymer Blending

The blending of hydrophilic polymers is considered the simplest way to enhance the hydrophilicity of membranes. In this

Table III. Effect of the Surface Modification on the MF/UF Membrane Fouling

| Base membrane | Modification | Modifier group | Antifouling results | Reference |
|----------------|--------------|--|---|-----------|
| Zirconia MF | Grafting | Poly(acrylic acid) | Densely packed, brush-shaped poly(acrylic acid) chains reduced the protein adsorption on the membrane surface. | 120 |
| PP | Grafting | [2-(Methacryloyloxy)ethyl] trimethyl ammonium chloride and 3-sulfopropyl methacrylate potassium salt | It had the ability to resist both protein adsorption and biofilm formation. | 122 |
| PES | Grafting | 2-Acrylamido-2-methyl-1-propane sulfonic acid and quaternary salt of 2-dimethyl aminoethyl methacrylate | The grafted membrane had a smaller force of bacterial adhesion with low or zero fouling properties. | 123 |
| PSF | Grafting | N-(3- <i>tert</i> -Butyl-2-hydroxy-5-methyl benzyl) acrylamide | It exhibited excellent antibacterial properties. | 124 |
| PVDF | Grafting | 3-(Methacryloylamino) propyl-dimethyl(3-sulfopropyl) ammonium hydroxide and 2-(methacryloyloxyethyl) ethyl dimethyl(3-sulfopropyl) ammonium crosslinked with <i>N,N'</i> -methylene bisacrylamide | The protein-fouling resistance performance was improved. | 125 |
| Hydrolyzed PAN | Grafting | 3-Dimethyl aminopropyl amine first grafted by the activation of 1-(3-dimethyl aminopropyl)-3-ethyl carbodiimide hydrochloride followed by the quaternization of 1,3-propane sultone | There was excellent resistance to protein adsorption; the molecular weight cutoff of the substrate membrane had a great influence on the flux recovery rate of the modified membrane. | 126 |
| Cellulose | Grafting | Four different zwitterionic monomers: [2-(methacryloyloxy)ethyl] dimethyl(3-sulfopropyl)ammonium, PEGMA, <i>N,N</i> -dimethyl- <i>N</i> -(<i>p</i> -vinylbenzyl)- <i>N</i> -(3-sulfopropyl)ammonium, and 2-methacryloyloxyethyl phosphorylcholine | All of the coatings exhibited excellent blood compatibility without their cytocompatibility being compromised. | 127 |
| PES | Grafting | Zwitterionic monomers: <i>N</i> -(3-hydroxypropyl)methacrylamide, <i>N</i> -(4-hydroxybutyl)methacrylamide, <i>N</i> -(4-hydroxybutyl) methacrylamide, ethylene glycol monomer <i>N</i> -(3-methoxypropyl)methacrylamide, <i>N</i> -[2-(dimethyl amino)ethyl]- <i>N</i> -methyl methacrylamide, and <i>N</i> -[2-(diethyl amino)ethyl]- <i>N</i> -methyl methacrylamide, all terminated with tertiary amines | It exhibited both low protein adhesion (i.e., membrane plugging or fouling) and high flux. | 128 |
| PVDF | Grafting | PEGMA | Brushlike PEGMA led to lower protein adsorption and better antifouling for BSA filtration. | 129 |
| PEI | Grafting | Amino-terminated poly(propylene oxide)/poly(ethylene oxide) block copolymer | There was an improvement in the resistance to protein fouling. | 130 |

Table III. Continued

| Base membrane | Modification | Modifier group | Antifouling results | Reference |
|------------------------------------|-----------------------------|---|--|-----------|
| PVDF | Blending | Poly(vinylidene fluoride)-graft-poly(hydroxyethyl methacrylate) | The hydrophilicity was enhanced along with the anti-fouling properties. | 131 |
| PSF | Coating | PVA, methyl cellulose, and PVP | Treatment provided an increase in the initial UF flux and a lower flux decline. | 132 |
| PVDF | Coating | Chitosan | It exhibited good antifouling properties by reducing irreversible membrane fouling. | 133 |
| PSF | Coating | Anionic, nonionic, and cationic polymers and surfactants | There was a significant reduction in protein adsorption on the surfactant-modified membranes. ¹²⁸ | 134 |
| Ceramic MF | Coating | Nano-TiO ₂ | The coating prevented an oil droplet from adhering to or penetrating the membrane surface. | 135 |
| PVDF | Coating | PEG | There was a drastic reduction in internal fouling caused by the BSA protein molecules. | 136 |
| PSF | Coating | Nonionic and anionic surfactants | Steric hindrance between the bulky ionic surfactant and the protein at the pore entrance reduced the fouling potential of those proteins that could penetrate the first nonionic surfactant layer through electrostatic repulsion. | 137 |
| PVDF | Coating | Block and random PEGylated copolymers of PEGMA and PS | The specific and overall protein resistance of BSA on PVDF membranes coated with block copolymers was much higher than that with random copolymers; the protein resistance was enhanced with the PEGMA content. | 138 |
| PP, PDMS, PS, nylon, PVC, and PMMA | Coating | Zwitterionic sulfobetaine polymers with a catechol chain end (DOPA-PSB) | Among two DOPA-PSB polymers of different molecular weights tested on hydrophobic surfaces, the polymer with the higher molecular weight was found to have better nonfouling than the low-molecular-weight polymer because of increased surface coverage. | 139 |
| PSF-N ₃ | Coating via click chemistry | The copolymers alkynyl-PSBMA and azide-PSBMA were used to modify PSF-N ₃ , and alkynyl-citric acid was then clicked onto the membrane when the outermost layer was azide-PSBMA | It was resistant to protein adsorption and platelet adhesion and also prolonged clotting times; this indicated that the blood compatibility was improved. | 140 |

Table III. Continued

| Base membrane | Modification | Modifier group | Antifouling results | Reference |
|-------------------|----------------------|---|---|-----------|
| PSF | Blending and coating | Incorporation of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), Pluronic F108, followed by PEGylation | PEGylation was performed with the LIPS and VIPS methods. Through the control of the surface uniformity of the PEGylated domains, the adsorption of proteins and bacteria was resisted. The VIPS process showed great potential in the molecular design of antibiofouling membranes. | 141 |
| PAN | Blending | PAN-g-PEO | A dense brush layer of poly(ethylene oxide) chains on the membrane surface had a high affinity for water and resistance to protein adsorption. | 142 |
| PVDF | Coating | PS/PEGMA | An increase in the PEGMA content enhanced the protein resistance. Protein adsorption by membranes coated with block copolymers was much higher than that with random copolymers. | 143 |
| PES | Blending | Poly(ethylene oxide)- <i>b</i> -poly(propylene oxide)- <i>b</i> -poly(ethylene oxide) triblock copolymer and triethylene glycol | There was increased resistance toward the adsorption of protein molecules. | 144 |
| Poly(lactic acid) | Blending | Poly(lactic acid)-PEG-poly(lactic acid) | Antifouling properties improved for BSA and humic acid adsorption. | 145 |
| PSF | Blending | <i>N</i> -Succinyl chitosan and <i>N</i> -propylphosphonyl chitosan | Protein antifouling properties were enhanced. | 100, 101 |
| PPESK | Blending | PPESK- <i>g</i> -poly[poly(ethylene glycol) methyl ether methacrylate] | Protein anti-adhesion properties increased. | 146 |
| PES | Blending | Pluronic P123-PEG | There was superior fouling resistance toward protein; irreversible fouling decreased remarkably. | 147 |
| PES | Blending | Poly(butyl methacrylate)- <i>co</i> -poly[<i>N,N</i> -dimethyl- <i>N</i> -methacryloxethyl- <i>N</i> -(3-sulfopropyl)] | Irreversible protein fouling was reduced. | 148 |

BSA, bovine serum albumin; PAN-*g*-PEO, polyacrylonitrile-graft-poly(ethylene oxide); PDMS, poly(dimethyl siloxane); PEGMA, poly(ethylene glycol) methacrylate; PEI, poly(ether imide); PPESK, poly(phthalazinone ether sulfone ketone); PS, polystyrene; PSBMA, poly(sulfobetaine methacrylate); PSF- N_3 , azido-functionalized polysulfone; PVC, poly(vinyl chloride), PVA, poly(vinyl alcohol); LIPS, liquid induced phase separation; VIPS, vapor induced phase separation; DOPA-PSB, dopamine-polysulfobetaine.

process, the hydrophilic polymers are usually dissolved into solution, so they can be cast into membranes during the phase-separation process. Polymer blending with hydrophilic polymers changes the surface characteristics with only minor alterations of the bulk morphology and properties of the membrane.¹⁵⁵ The major problem associated with blending is the poor compatibility of the hydrophilic polymers with the hydrophobic polymer matrix. The main issues associated with the polymer blending approach are the miscibility of polymer pairs and the

stability of the modified surfaces. Generally, the blending of copolymeric additives will bring down the miscibility gap. In addition to hydrophilic polymer materials, the inorganic nanoparticles are another type of important modifier. The introduction of nanoparticles into membranes to enhance hydrophilicity has been proven to be an effective method and has attracted much attention. Polymer-nanocomposite membranes present an interesting approach for improving the mechanical, separation, physicochemical, and antifouling properties of polymer

membranes. There are two ways to introduce nanoparticles into membranes during the preparation process: (1) blending them in a polymer solution or (2) mixing them in a coagulation bath. The addition of inorganic nanoparticles to a polymer dope will produce membranes with different pore structures and surface properties. Generally, mixed-matrix membrane properties depend on the nature of the nanoparticles and polymer and the preparation conditions used.

Nanoparticles, such as TiO_2 ,¹⁵⁶ SiO_2 ,¹⁵⁷ $\text{Mg}(\text{OH})_2$,¹⁵⁸ lithium perchlorate,¹⁵⁹ silver nanoparticles,¹⁶⁰ zirconium dioxide,¹⁶¹ polydopamine,¹⁶² Al_2O_3 ,¹⁶³ ZnO ,¹⁶⁴ carbon nanotubes, and graphene oxide,¹⁶⁵ have been extensively incorporated into UF and MF membrane matrices to achieve improved antifouling properties. The UV irradiation of titanium-incorporated membranes have resulted in the photocatalytic degradation of foulants before they reach the membrane surface,¹⁶⁶ whereas silver nanoparticle provide resistance for biofouling on the membrane surface because of their antibacterial activity.¹⁶⁰ Apart from silver nanoparticles, there are many other antimicrobial additives, including quaternary ammonium–phosphonium salts,¹⁶⁷ chitosan or its derivatives,^{100,101,168} and poly(ethylene oxide),¹⁶⁹ which has shown good antibiofouling results. However, nanoparticles agglomerate during dope preparation and finally, in the resulting membrane, lead to changes in the membrane topography, microstructure, and performance, and also potential reduction in the antifouling ability of the membrane. Such a phenomenon is considered to be a major drawback during the preparation of mixed-matrix membranes. Generally, the preparation of mixed-matrix membranes is usually achieved by strong mechanical stirring or sonication. However, the effect is limited when the concentration of nanoparticles is high because of drastic viscosity changes in the dope.

Recently, more focus has been given to the *in situ* generation of nanoparticles by the sol–gel method,¹⁷⁰ the chemical hydrophilic functionalization of nanoparticles or nanotubes,¹⁷¹ to resolve the agglomeration effect. Madaeni *et al.*¹⁷² modified PVDF membranes by three different techniques, (1) the self-assembly of TiO_2 on the surface of the poly(acrylic acid)-grafted PVDF membrane, (2) the functionalization of TiO_2 by acrylic acid monomers, and (3) *in situ* grafting polymerization of this blend solution, which is called the *grafting-from technique*.¹⁷² Antifouling properties were tested with whey solution. Better resistance to fouling was observed for membranes prepared from functionalized TiO_2 because of the high grafting yield and low agglomeration of TiO_2 in this method. The amphiphilic copolymeric additives are of high interest because both their hydrophilic and hydrophobic groups are totally insoluble in water and are able to interact with hydrophobic membrane polymers.¹⁷³ The resulting membrane compatibility will be enhanced by hydrophobic chains, whereas hydrophilic chains will enrich the membrane surface during the phase-separation process. On the basis of the previous assumptions, many blending efforts have been made to enhance the MF/UF membrane antifouling characteristics, as summarized in Table III.

Cleaning Procedures and Operating Parameters

Because of fouling, the membrane resistance to flux increases with time because of the accumulation of foulants on the mem-

brane surface and/or inside the membrane. A well-designed membrane, with a high porosity and permeability, will inherently provide better flux and economics. It is essential to establish a good pretreatment to prevent or minimize fouling, so the productivity loss will be lower. Keeping the membrane clean as often and as long as possible allows the most efficient use of the membrane area and porosity. If foulants are not successfully removed, the membrane system performance will decline faster as it is easier for the foulant to deposit onto the membrane surface area. The time between cleanings will become shorter, and this will result in shorter membrane element lives and higher operating and maintenance costs. Most effective cleaning allows for a longer system operating time between cleanings and results in the lowest operating costs.

Membrane cleaning results in a membrane that is physically, chemically, and biologically clean and, thus, can provide adequate flux and separation. There are many ways to clean a fouled membrane. Generally, they can be divided into four categories: physical cleaning, chemical cleaning, physicochemical cleaning, and biological cleaning. Physical cleaning methods depend on mechanical and electrical treatments to dislodge and remove foulants from the membrane surface. A few of mechanical treatments include periodic backflushing, vibration, air sparging, automatic sponge ball cleaning, and ultrasonication. In constant-flux UF and MF systems, the most adopted membrane fouling control method is hydraulic cleaning, that is, the backwashing of the membrane at constant time intervals; this is believed to ensure higher water production. Electrical cleaning is achieved by the application of a voltage across the membrane, which thus pushes charged deposits away.¹⁷⁴ The chemical cleaning methods depends purely on chemical reactions to remove foulants from the membrane surface. Each type of foulant requires certain types of chemical agents. Chemical cleaning is generally applied to hydraulically irreversible foulants, that is, to the tough parts of the fouling. Chemical agents, particularly oxidants, are also used for disinfection to maintain the system free of microorganisms. Physicochemical cleaning methods use physical cleaning methods with the addition of chemical agents to effectively enhance cleaning.¹⁷⁵ Biological cleaning can be broadly described as the use of cleaning agents, which contain bioactive agents such as microorganisms or enzymes to enhance the removal of foulants.¹⁷⁶ Maartens *et al.*¹⁷⁷ tested enzymes as key components of biological cleaning regimes for PSF membranes fouled in abattoir effluent. They reported that enzymes are specific for the degradation of protein and lipids.

In addition to the membrane and solute (solution) properties, fouling is strongly influenced by operating parameters, such as temperature, flow rate (stirring rate), feed concentration, and pressure. For example, in comparison between filtration under stirred and nonstirred conditions, the flux decline trends with stirring were less than with nonstirring conditions in UF membrane filtration.¹⁷⁸ Nonstirred filtration provides a higher topography on the membrane surface than stirred filtration.¹⁰⁵ Generally, at a high flow rate or stirring rate, the accumulated solutes on the membrane surface tend to be swept from the membrane surface, and thus, the fouling layer is reduced. However, higher fouling at a higher flow rate has also been observed

by many researchers.^{179,180} Increasing the temperature can either decrease or increase the fouling of UF and MF membranes. This depends on the effects of the temperature on the solubility of the feed components, viscosity, diffusivity, or denaturation of the solute.¹⁸¹ Many researchers have studied the effect of the feed concentration on the UF and MF membrane fouling.^{182,183} During water treatment applications, a few investigations have been attempted to study the effects of the ionic strength on colloidal fouling in both dead-end¹⁸⁴ and cross-flow modes.^{185,186} The flux during UF and MF will increase as transmembrane pressure is increased. However, after concentration, polarization reaches a maximal point where the gel layer has been formed; then, the flux does not increase any more. In some cases, a further increase in the transmembrane pressure yields a decrease even in the flux. To minimize the possible effect of cake formation and compaction, the use of a relatively low operating pressure and high cross-flow velocity is highly recommended.¹⁸⁷

CONCLUSIONS

This review provides comprehensive insight into factors affecting fouling and the wide range of techniques used to control fouling in both MF and UF membranes. The many instrumentation techniques developed for membrane characterization are also supportive in predicting the antifouling properties of the membranes. However, all of these techniques have their own limitations. Despite the vast applications of UF and MF membranes in numerous fields, the long-term stability of these membranes due to fouling remains a problem. Attaining control over fouling or its mitigation have been the key areas of research in the past few decades. Basically, UF and MF membranes use filtration-based separation techniques. To achieve effective filtration and separation, immense control over fouling is obligatory. So, it is worth mentioning that superior knowledge about foulants in the feed is vital to controlling fouling. The fouling-determining factors, such as the morphology, hydrophilicity, and charge, are highly dependent on the properties of the polymer(s) and additives used, preparation method, and conditions applied.

For UF and MF membranes, to accomplish better fouling control the following methods are highly recommended. The appropriate choice of membrane materials, modification methods (blending, grafting or coating), pretreatment methods (coagulation, flocculation, adsorption, or oxidation) can lead to looser binding of the foulants to the membrane surfaces. However, surface modification techniques have their own drawbacks. For instance, the long-term stability of coating layers is difficult to achieve, there are miscibility issues between blending polymers, and control over the pore size and porosity of grafted layers is difficult. Consequently, further optimization of these processes is highly requisite to develop surface-modified membranes as commercial membranes. Among blends, nanocomposite MF and UF membranes are considered an emerging technology. Their high performance and antifouling properties make them an emerging technology from the laboratory/pilot scale to a reliable commercial technology. However, the cost of production of nanoparticles still remains a major issue. The most productive methodology to mitigate membrane fouling is considered to be optimization of hydrodynamic conditions;

these include the selection of proper operating parameters during filtration (temperature, flow rate, stirring rate, feed concentration, and pressure) and cleaning procedures (physical cleaning, chemical cleaning, physicochemical cleaning, and biological cleaning) after filtration, which can bring about high membrane recycling properties.

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