

Review

Fouling Issues in Membrane Bioreactors (MBRs) for Wastewater Treatment: Major Mechanisms, Prevention and Control Strategies

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Abstract: Membrane fouling is one of the most important considerations in the design and operation of membrane systems as it affects pretreatment needs, cleaning requirements, operating conditions, cost and performance. Given that membrane fouling represents the main limitation to membrane process operation, it is unsurprising that the majority of membrane material and process research and development conducted is dedicated to its characterization and amelioration. This work presents the fundamentals of fouling issues in membrane separations, with specific regard to membrane fouling in Membrane Bioreactors (MBRs) and the most frequently applied preventive-control strategies. Feed pretreatment, physical and chemical cleaning protocols, optimal operation of MBR process and membrane surface modification are presented and discussed in detail. Membrane fouling is the major obstacle to the widespread application of the MBR technology and, therefore, fouling preventive-control strategies is a hot issue that strongly concerns not only the scientific community, but industry as well.

Keywords: membrane fouling; fouling control strategies; membrane bioreactors

Table of Symbols

AA	acrylic acid	
AAG	2-acrylamidoglycolic acid	
AAm	acrylamide	
ACH	aluminium chlorohydrate	
AFM	atomic force spectroscopy	
AMPS	2-acrylamido-methylpropane sulfonic acid	
anMBR	anaerobic membrane bioreactor	
aniMBR	anaerobic immersed membrane bioreactor	
AS	activated sludge	
ASP	activated sludge process	
BAC	biologically activated carbon	
bEPS	bound extracellular polymeric substances	
BFM	Berlin filtration method	
BSA	bovine serum albumin	
C_A	concentration of component A	$\text{mol}\cdot\text{m}^{-3}$
CA	cellulose acetate	
CASP	conventional activated sludge plant	
CER	cation exchange resin	
CFV	cross flow velocity	$\text{m}\cdot\text{s}^{-1}$
C_g	gel layer concentration	$\text{g}\cdot\text{cm}^{-3}$
CIA	cleaning in air	
C_{im1}	concentration of component i inside membrane wall on feed side	$\text{mol}\cdot\text{m}^{-3}$
C_{im2}	concentration of component i inside membrane wall on permeate side	$\text{mol}\cdot\text{m}^{-3}$
CIP	cleaning in place	
CLSM	confocal laser scanning microscopy	
COD	chemical oxygen demand	$\text{mg}\cdot\text{L}^{-1}$
C_p	permeate concentration	$\text{g}\cdot\text{cm}^{-3}$
CP	concentration polarization	
C_r	retentate concentration	$\text{g}\cdot\text{cm}^{-3}$
CS	chitosan	
CST	capillary suction time	s
D	inside diameter of the pipe	ft
D_i	diffusivity of component i	$\text{m}^2\cdot\text{s}^{-1}$
DFC _m	Delft filtration characterization method	
DO	dissolved oxygen	
DOC	dissolved organic carbon	
DTAB	dodecyltrimethyl ammonium bromide	
DW	dry weight	g
EDA	ethylene diamine	
EDTA	ethylenediaminetetraacetic acid	
EEM	excitation-emission matrix	
eEPS	extracted extracellular polymeric substances	

EGSB	expanded granular sludge bed	
EPS	extracellular polymeric substances	
EPS _c	carbohydrate fraction of EPS	
EPS _p	protein fraction of EPS	
ESEM	environmental scanning electron microscopy	
F/M	food to microorganisms	
FISH	fluorescence <i>in situ</i> hybridization	
FOG	fats, oil and grease	
FS	flat sheet	
FTIR	Fourier transform infrared spectroscopy	
GAMA	d-gluconamidoethyl methacrylate	
gDMAEM	quaternized 2 (dimethylamino) ethyl methacrylate	
GFC	gel filtration chromatography	
h	height of the channel	m
HA	humic acid	
HEMA	2-hydroxyethyl methacrylate	
HF	hollow fiber	
HFRB	hair and fiber reinforced biomass	
HPSEC	high-pressure size exclusion chromatography	
iMBR	immersed membrane bioreactor	
IR	infrared spectroscopy	
J	membrane flux	$\text{m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$
J _i	flux of component i	$\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$
K	membrane permeability	$\text{L} \cdot \text{h}^{-1} \cdot \text{bar}^{-1} \cdot \text{m}^{-2}$
k	mass transfer coefficient	$\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$
L	length of the flow channel	m
MBR	membrane bioreactor	
MC	methylcellulose	
MF	microfiltration	
MLSS	mixed liquor suspended solids	
MPDSAH	[(methacryloylamino)propyl]-dimethyl (3-sulfopropyl) ammonium hydroxide	
MW	molecular weight	
NF	nanofiltration	
NMR	nuclear magnetic resonance	
NOM	natural organic matter	
NVC	<i>N</i> -vinyl-caprolactam	
NVF	<i>N</i> -vinyl-formamide	
NVP	<i>N</i> -vinyl-2-pyrrolidone	
OC	organic carbon	
PA	polyamide	
PAC	powdered activated carbon	
PAN	polyacrylonitrile	
PCR-DGGE	polymerase chain reaction denaturing gradient gel electrophoresis	
PDA	2,4-phenylenediamine	
PE	polyethylene	
PEGDA	poly(ethylene glycol) diacrylate	
PEGMA	poly(ethylene glycol) methacrylate	

PEI	polyethylenimine	
PEO	polyethylene oxide	
PI	polyimide	
PP	polypropylene	
PS	polysulfone	
PSS	poly(sodium 4-styrene sulfonated)	
PVA	polyvinyl alcohol	
PVP	polyvinylpyrrolidone	
PVS	polyvinyl sulfate-potassium salt	
QS	quorum sensing	
RAS	return activated sludge	
R_{col}	resistance attributed to colloidal matter	m^{-1}
Re	Reynolds number	
R_m	resistance to flow through the membrane	$psi \cdot s \cdot cm^2 \cdot cm^{-3}$
R_g	resistance to flow through the gel	$psi \cdot s \cdot cm^2 \cdot cm^{-3}$
RI	refractive index	
RO	reverse osmosis	
R_{sol}	resistance attributed to soluble matter	m^{-1}
SBR	sequencing batch reactor	
SDS	sodium dodecyl sulfate	
sEPS	soluble EPS	
SLS	static light scattering	
sMBR	submerged membrane bioreactor	
SMP	soluble microbial product	
SMP_c	carbohydrate fraction of soluble microbial product	
SMP_p	protein fraction of soluble microbial product	
SPMA	3-sulfopropyl methacrylate	
SRF	specific resistance to filtration	
SRT	sludge retention time	d
SS	suspended solids	
SUVA	spectrophotometer using ultraviolet	
t_{crit}	critical time	s
TFC	thin film composite	
TIPS	thermally induced phase separation	
t_m	thickness of the membrane	m
TMC	trimesoyl chloride	
TMP	transmembrane pressure	bar
TOC	total organic carbon	
u	fluid velocity	$ft \cdot s^{-1}$
u_b	linear velocity through the channel	$m \cdot s^{-1}$
UF	ultrafiltration	
UMFI	unified membrane fouling index	
UV	ultraviolet	
VFM	VITO fouling measurement	
VSS	volatile suspended solids	
WS_2	tungsten disulfide	
XPS	X-ray photoelectron spectroscopy	

ΔP or ΔP_m	pressure difference	bar
η	viscosity	Pa·s
μ	fluid viscosity	lb·ft ⁻¹ ·s ⁻¹
ν	fluid kinematic viscosity	ft ² ·s ⁻¹
ρ	fluid density	lb·ft ⁻³

1. Introduction

The membrane bioreactor (MBR) is an increasingly used technology which offers the possibility to overcome a lot of the current problems encountered in the conventional Activated Sludge Process (ASP), mostly linked to the separation of biomass from the treated water. However, despite its widespread application and plentiful benefits (good effluent quality, high possible biomass concentration, reduced reactor volume and footprint), the MBR technology is constrained by membrane fouling which is regarded as the most serious drawback of process efficiency. Fouling leads to permeate flux decline which in turn decreases time intervals for membrane cleaning and replacement resulting both in higher operating costs. Therefore, most MBR studies aim to identify, investigate, control and model membrane fouling [1–3].

With specific regard to filtration of activated sludge in aerobic MBRs, it is widely recognized that the main foulants are the extracellular polymeric substances (EPS) [4–7] which constitute a matrix of high molecular weight molecules excreted from cells. Functions of the EPS matrix include aggregation of bacterial cells in flocs and biofilms, formation of a protective barrier around the bacteria, retention of water and adhesion to surfaces [8]. With its heterogeneous and changing nature, EPS can form a highly hydrated gel matrix in which microbial cells are embedded [9] and can thus help create a significant barrier to permeate flow in membrane processes.

Fouling is a three-stage process (Conditioning fouling-Slow/steady fouling-TMP jump) [10] and proceeds according to a number of widely recognized mechanisms which have their origins in early filtration studies [11]: blocking, standard blocking, intermediate blocking and cake filtration. Over the last few years, numerous attempts have been made in order to prevent and control fouling in membrane bioreactors. The most common methods to achieve this include the application of conventional physical or chemical methods, the optimal operation of the MBR process by permeate flux reduction and aeration increase [3,12–17], whereas more recent methods focus on: the (bio)chemical mixed liquor modification—such as the addition of specific chemicals (coagulants [18–23] or other (re)agents [24–27]) and the application of the Quorum Sensing (QS) method [28–31]—the application of ultrasound [32,33], electric field [1,34] and ozone [35,36], or membrane surface modification. The latter may include physical coating/adsorption [37–42] or grafting methods [43–45] on the membrane surface, the use of patterned membranes [46–50], plasma treatment [51–54], chemical reaction on the membrane surface [55,56] or surface modification with nanoparticles [57–80].

Over the last few years, several strategies have been employed to prevent or control membrane fouling. The present review deals with the burning issue of fouling in membrane separations and the most prevalent techniques/strategies used for the alleviation of the above phenomenon with specific regard to MBRs.

2. Major Mechanisms

2.1. The Driving Force

The driving force for a process is usually a pressure gradient, although both extractive and gas transfer systems operate via a concentration gradient. In almost all pressure-driven membrane processes applied to water treatment the desired permeate is water, such that the retained or rejected material (the retentate) is concentrated. Extractive systems rely on depletion of the permeating component on the permeate side of the membrane to generate a great enough concentration gradient across the membrane to transfer matter through it via diffusion. In gas transfer processes the concentration gradient is achieved by increasing the partial pressure on the unpermeated side [81].

The driving force can be natural or artificially imposed, and the two most important transport mechanisms in membrane processes for wastewater treatment are convection and diffusion.

Convection results from the movement of the bulk fluid, rather than any components dissolved or suspended in it. Hence, any flowing liquid constitutes convective transport. The type of flow produced, or the flow regime, is dependent upon the flow rate. At high flow rates the flow is described as turbulent, whereas at low flow rates, it is defined as laminar. Higher flow rates usually yield greater mass transport, and hence it is always desirable to promote turbulence on the retentate side of a membrane [81]. The Reynolds number, Re , is a dimensionless number that indicates whether a fluid flowing is in the laminar or turbulent flow regime. Laminar flow is characteristic of fluids flowing slowly enough so that there are no eddies (whirlpools) or macroscopic mixing of different portions of the fluid. In laminar flow, a fluid can be imagined to flow like a deck of cards, with adjacent layers sliding past one another. Turbulent flow is characterized by eddies and macroscopic currents. For flow in a pipe, a Reynolds number above 2100 is an indication of turbulent flow. The Reynolds number is dependent on the fluid velocity, density, viscosity, and some length characteristic of the system or conduit; for pipes, this characteristic length is the inside diameter:

$$Re = \frac{Du\rho}{\mu} = \frac{Du}{\nu} \quad (1)$$

where Re = Reynolds number; D = inside diameter of the pipe, ft; u = fluid velocity, $\text{ft}\cdot\text{s}^{-1}$; ρ = fluid density, $\text{lb}\cdot\text{ft}^{-3}$; μ = fluid viscosity, $\text{lb}\cdot\text{ft}^{-1}\cdot\text{s}^{-1}$; ν = fluid kinematic viscosity, $\text{ft}^2\cdot\text{s}^{-1}$.

For laminar flow through a channel, the average mass transfer coefficient can be estimated using the following equation:

$$k = 1.177 \left[\frac{u_b D^2}{hL} \right]^{1/3} \quad (2)$$

where k = mass transfer coefficient, $\text{m}^3\cdot\text{m}^{-2}\cdot\text{s}^{-1}$; u_b = linear velocity through the channel, $\text{m}\cdot\text{s}^{-1}$; D = diffusivity, $\text{m}^2\cdot\text{s}^{-1}$; h = height of the channel, m; L = length of the flow channel, m [82].

Brownian diffusion results from the transport of individual ions, atoms or molecules by thermal motion. The basic law defining diffusive transport (originally developed by Fick and known as Fick's first law of diffusion) dictates that its rate is dependent upon the concentration gradient coupled with the component Brownian diffusivity, which increases with decreasing size [81]. The diffusivity, or diffusion

coefficient, D_{AB} , of component A in solution B, which is a measure of its diffusive mobility, is defined as the ratio of its flux, J_A , to its concentration gradient and is given by

$$J_A = -D_{AB} \frac{\partial C_A}{\partial z} \quad (3)$$

This is Fick's first law written for the z direction. The concentration gradient term represents the variation of the concentration, C_A , in the z direction. The negative sign accounts for diffusion occurring from high to low concentrations. The diffusivity is a characteristic of the component and its environment (temperature, pressure, concentration, *etc.*). This equation is analogous to the flux equations defined for momentum transfer (in terms of the viscosity) and for heat transfer (in terms of the thermal conductivity). The diffusivity is usually expressed with units of (length)²/time or moles/time·area. As related to a membrane system, diffusive flux through the membrane can be expressed by Fick's law and given by

$$J_i = \frac{D_i}{t_m} (C_{im2} - C_{im1}) \quad (4)$$

where J_i = flux of component i , mol·m⁻²·s⁻¹; D_i = diffusivity of component i , m²·s⁻¹; t_m = thickness of the membrane, m; C_{im1} = concentration of component i inside membrane wall on feed side, mol·m⁻³; C_{im2} = concentration of component i inside membrane wall on permeate side, mol·m⁻³ [82].

2.2. Factors Opposing the Driving Force

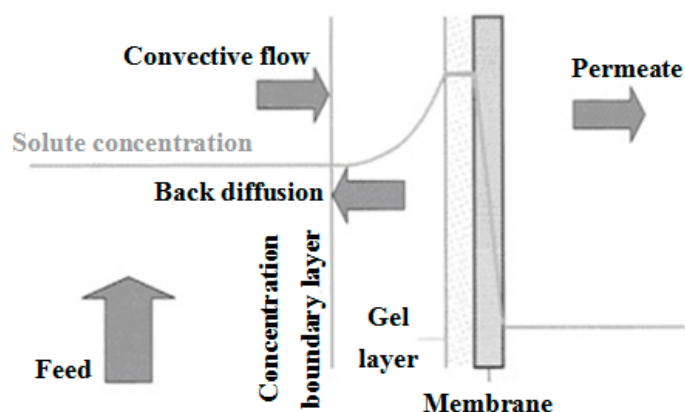
2.2.1. Concentration Polarization (CP)

For membrane filtration processes, the overall resistance at the membrane:solution interface is increased by a number of factors which each place a constraint on the design and operation of membrane process plant:

- (a) the concentration of rejected solute near the membrane surface,
- (b) the precipitation of sparingly soluble macromolecular polymeric and inorganic (gel layer formation and scaling, respectively) at the membrane surface and
- (c) the accumulation of retained solids on the membrane (cake layer formation).

All of the above contribute to membrane fouling, and (a) and (b) are promoted by concentration polarization (CP). CP describes the tendency of the solute to accumulate at the membrane:solution interface within a concentration boundary layer, or liquid film, during crossflow operation (Figure 1). This layer contains near-stagnant liquid, since at the membrane surface itself the liquid velocity must be zero. This implies that the only mode of transport within this layer is diffusion, which can be two orders of magnitude slower than convective transport in the bulk liquid region. However, it has been demonstrated [83] that transport away from the membrane surface is much greater than that governed by Brownian diffusion and is actually determined by the amount of shear imparted at the boundary layer; such transport is referred to as "shear-induced diffusion".

Figure 1. Concentration polarization. Reproduced with permission from Reference [81]. Copyright 2000 IWA Publishing.



Rejected materials nonetheless build up in the region adjacent to membrane, increasing their concentration over the bulk value, at a rate which increases roughly exponentially with increasing flux. The thickness of the boundary layer, on the other hand, is determined entirely by the system hydrodynamics, decreases and when turbulence is promoted. For crossflow processes, the greater the flux, the greater the build-up of solute at the interface; the greater the solute build-up, the steeper the concentration gradient and so the faster the diffusion. Under normal steady-state operating conditions, there is a balance between those forces transporting the water and constituents within the boundary layer towards, through and away from the membrane. This balance is determined by CP [10].

CP may occur with or without gel formation. Concentration polarization occurs in many separations, and for large solutes where osmotic pressure can be neglected, concentration polarization without gelling is predicted to have no effect on the flux. Therefore, if a flux decline is observed, it can be attributed to the formation of a gel layer with a concentration C_g . The gel layer, once formed, usually controls mass transfer and when this happens, Equation (3) can be used to determine the solvent flux:

$$J = \frac{\Delta P}{R_m + R_g} \quad (5)$$

where R_m = resistance to flow through the membrane, $\text{psi} \cdot \text{s} \cdot \text{cm}^2 \cdot \text{cm}^{-3}$; R_g = resistance to flow through the gel, $\text{psi} \cdot \text{s} \cdot \text{cm}^2 \cdot \text{cm}^{-3}$ [82].

The value of R_g varies with pressure, bulk concentration, and cross-flow velocity at lower transmembrane pressure, but tends to become pressure independent at higher transmembrane pressures. This value can be, and often is, measured experimentally.

When the gel layer controls mass transfer and $C_p = 0$ or the apparent rejection is unity, the solvent flux can be expressed in terms of a mass transfer coefficient, k , as follows:

$$J_s = k \ln \left(\frac{C_g}{C_r} \right) \quad (6)$$

where C_g = gel layer concentration, $\text{g} \cdot \text{cm}^{-3}$.

To determine an experimental value for k , data can be measured when $R \approx 1$, for the flux as a function of the bulk concentration. This information can be graphed using Equation (7) which is a rearrangement

of Equation (6) above. This plot is obtained for a constant temperature and cross flow velocity. A plot of J_s vs $\ln C_g$ on arithmetic coordinates has a slope of $-k$ and the Y-axis intercept is the \ln (natural log) of C_g [82],

$$J_s = \ln C_g - \ln C_r \quad (7)$$

2.2.2. Fouling

Fouling is the general term given to the process by which a variety of species present in the water increase the membrane resistance, by absorbing or depositing onto its surface, adsorption onto the pore surfaces within the bulk membrane material (pore restriction) or by complete pore-blocking. Fouling can occur through a number of physicochemical and biological mechanisms, and is exacerbated by concentration polarization since this effectively increases the concentration of foulants in the vicinity of the membrane [81]. Fouling can be classified into three major categories:

- *inorganic fouling* which refers to the deposit of inorganic material like salts, clay and metal oxides,
- *organic fouling* which includes all kind of deposit of organic material like grease, oil, surfactants, proteins, polysaccharides, humic substances and other organic biopolymers and
- *biofouling* which designates the formation of biofilms by compounds and microorganisms attached and growing at the membrane surface [3].

Much research work has been carried out on membrane separation of protein because of its industrial importance, and a number of review articles are available [84–87]. Proteins can cause severe fouling of a many different MF membrane materials, in particular hydrophobic polymers such as polypropylene, causing flux declines of an order of magnitude or more [88,89] ultimately due to irreversible deposition onto and penetration into the bulk membrane material. UF membranes, on the other hand, are somewhat less prone to fouling by macromolecules because the smaller pores are more impenetrable. For both UF and MF surface chemistry, specifically hydrophilicity and surface charge, plays an important part in determining the extent of fouling; hydrophobic materials are more prone to protein deposition leading to irreversible fouling. Proteins can arise either as dissolved or suspended matter, but their behavior within membrane separation systems is complex. Membrane fouling takes place both by adsorption and by deposition, with deposition being the most deleterious to performance with regards to flux decline in MF systems. It is thought that the high shear conditions prevailing at the membrane:solution interface promote aggregation of the protein or else produce other conformational changes which produce deposits of widely varying structures and hydraulic behaviour [90,91]. It has been proposed by Kelly *et al.* [92] that deposited protein aggregates may serve as nucleation sites for non-aggregated, dissolved proteins. The relative extent of internal to external fouling appears to be governed as much by physical phenomena such as surface porosity and flux as by membrane surface chemistry. Meuller and Davis [91] found high surface porosities to be deleterious to maintaining a high flux in their studies of membrane fouling of different membrane materials of the same nominal pore size. Marshall *et al.* [93] found internal fouling to be promoted at lower fluxes.

Colloidal and particulate materials are similarly affected by physical changes in structure as a result of permeation. In this case, it is the aggregation rate which is affected by the physicochemical conditions via hydrodynamic and surface force effects. Aggregation (or flocculation) may be promoted

orthokinetically (*i.e.*, by virtue of a velocity gradient) at the membrane solution interface or within the membrane pore. Flocculation, however, is dependent upon the extent of particle destabilization, or coagulation, generally resulting from the reduction in the magnitude of surface charge—which itself is dependent on both the bulk material properties and solution chemistry. The abstruse nature of colloidal behaviour and its sensitivity to surface forces makes particle aggregation kinetics difficult to predict, even in ideal systems. However, in their study of municipal wastewater treatment, Pouet and Grasmick [94] identified the supracolloidal fraction, *i.e.*, above 1 µm in particle size, as being principally responsible for fouling of a sidestream ceramic MF of sub-micron pore size.

With specific regard to filtration of activated sludge in aerobic MBRs, it is widely recognized that the main foulants are the extracellular polymeric substances (EPS) excreted from cells [4–7]. *Chang and Lee* [5] experimentally determined that a 40% reduction in EPS (by cultivating the activated sludge under nitrogen-deficient conditions) resulted in an equivalent reduction in the hydraulic resistance of the cake. *Nagaoka et al.* [7] similarly linked hydraulic resistance to EPS levels, including empirical parameters for EPS production and degradation in their phenomenological model [81].

2.2.3. Clogging

Clogging is the agglomeration of solids within or at the entrance to the membrane channels. Whilst this is to be clearly distinguished from membrane surface fouling regarding both its mechanism and amelioration, the impact of both fouling and clogging is identical in that both are manifested as a decrease in the membrane permeability. However, whereas fouling can generally be substantially removed through the application of an *in situ* chemical clean, *i.e.*, cleaning in place (CIP), this course of action is not necessarily effective against clogging since in this case the materials are physically lodged between the membrane surfaces rather than coated onto them. Severe clogging is generally only countered by removal of the membrane from the tank and cleaning the membrane modules individually with a low pressure hose. Such a level of manual intervention risks compromising the integrity of the fibers.

As well as being indistinguishable in terms of impact, fouling and clogging can be related—as in the case of localized dewatering. When fouling takes place in a region of a membrane other unfouled regions become hydraulically overloaded. This can then cause rapid draining of the sludge in that region. If the forces causing solids deposition and sludge dewatering are greater than those associated with the scouring air then clogging (or “sludging”) takes place in that region.

Whilst clogging is inferred by an ineffective chemical clean, for FS modules clogging may also be deduced from a visual inspection of the top of the stack if the sludge level is lowered to expose the permeate outlet tubes and the top of the membrane panels. Clogging can sometimes be visible to the naked eye as a dark brown color completely filling the 6–9 mm membrane channel. For transparent permeate outlet tubes, clogging may be inferred from a distinct dark brown discoloration which arises from extensive biofilm growth in the stagnant permeate water when no permeate flow takes place. Such an effect may also arise either from absolute fouling or from panels for which the membrane integrity has been compromised, but such effects are much less commonly encountered than channel clogging.

Anecdotal evidence from operation of full-scale wastewater treatment works indicates clogging to be a more significant problem than fouling. In a survey of 15 European MBR plants published in 2008, eight had experienced problems of clogging [95]. Clogging within membrane channels has been noted

in both of the main membrane configurations employed for iMBRs, hollow fiber and flat sheet. In the case of municipal wastewater treatment the problem of clogging of membrane channels by gross particles in the MBR is exacerbated by their apparent tendency to agglomerate into long “rags” or “braids” up to 1 m in length which may collect at the channel entrances. The rags appear to be made up primarily of cellulosic fibers, from bathroom tissue, and hairs. Such extensive agglomeration is referred to as “reconstitution of rags”, “ragging” or “braiding”, and the occlusion of the channel entrances sometimes referred to as “matting”. Rags may also agglomerate at the membrane aerator, which is extremely deleterious to the process since clogging rapidly ensues without scouring air to displace the solids from the membrane interstices.

There is currently no accepted non-intrusive method of assessing clogging propensity, other than (a) filtration of the mixed liquor through a coarse screen (3–6 mm) and (b) visual observation of aeration patterns in the tank. Whilst clogging impedes the passage of air bubbles passing through the membrane channels, there is a synergistic relationship in that reduced aeration encourages clogging. This underlines the importance of aerator design and installation, and specifically rigorous leveling of the diffusers to prevent poor air distribution between tanks or stacks. Also, small variations in water levels between reactors can significantly disturb air distribution, which is exacerbated in small plants equipped with less automation to remediate such imbalances.

Amelioration of clogging is primarily through the rigorous screening of the feedwater and, for the HF configuration especially, limiting the solids concentration in the membrane tank. Sludging/localized dewatering tends to arise only within some regions of specific units in some of the rains; it rarely arises throughout the plant and can normally be attributed to local regions of high fluxes (>~40 LMH), inadequate air scouring and, in the case of hollow fibers where direct air scouring of the membrane is more limited, high MLSS concentrations. A common scenario is that encountered during storm flows when the recycle ratios subsequently decrease to below 2 and the membranes become hydraulically overloaded. In the case of the FS membranes where permeation is driven by the hydrostatic head, an unregulated change in differential pressure across the membrane can cause high fluxes, which may then lead to clogging. On the other hand FS membranes are less prone to clogging from high MLSS; FS-based membranes thickeners operate at around 10 LMH and solids concentrations up to 4%–5% without clogging problems, provided aeration is maintained and the flux is regulated by controlling the pressure differential.

Notwithstanding the paucity of information in this area, there are a number of aspects of clogging which are self-evident:

1. The solids agglomeration rate in the channels relates to the rate at which water is drained from the sludge. This in turn is dependent on both the flux and the residence time of the sludge in the membrane channels, since the extent of dewatering increases at longer residence times.
2. The residence time in the membrane channel itself is directly related to membrane aeration, with respect to both the distribution of the air bubbles throughout the channels and the overall aeration rate.
3. Agglomeration must also depend both on the concentration and the characteristics of the particles, since particles which, for whatever reason, more readily adhere to the membrane and/or each other can be expected to agglomerate faster. These may be presumed to be partly related to

feedwater physicochemical parameters, since these are known to impact on sludge quality and the physical nature of the inert solids specifically.

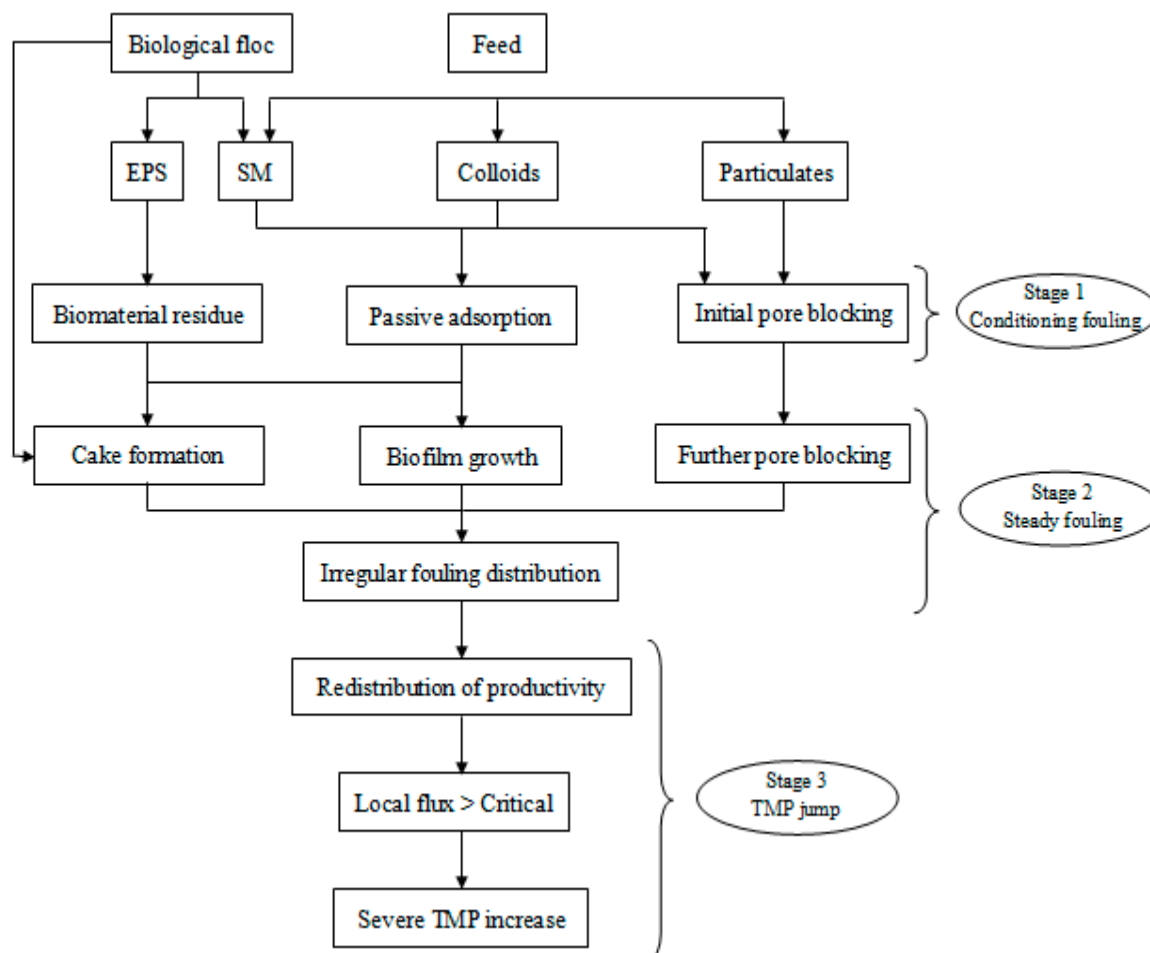
In fact, the same parameters which determine the extent of membrane fouling also similarly influence membrane channel clogging, and the manifestation of the two phenomena (reduced permeate flow) is also the same. It can only be speculated as to whether precisely the same chemical foulants which have been associated with fouling, such as colloidal polysaccharides or proteinaceous materials, are also responsible for particle agglomeration and/or irreversible deposition within the membrane channels. However, monitoring of the physical sludge characteristics can provide an indication as to whether incipient clogging is likely. The time to filter standard method 2710H [96], modified slightly with a smaller pore size filter paper, provides data on changes in sludge filterability and thus some indication of biomass health. Also, most obviously for immersed systems: (a) the solids concentration must be kept as low as possible, generally no more than 25% more than that of the biotank and a maximum of ~15 g/L for most HF systems; and (b) the membrane aeration system must be functioning correctly to ensure an even distribution of air over the membrane surface, possibly with increased aeration during storm flows. For pumped sidestream systems the high shear imparted by the crossflow permits rather higher MLSS concentrations and thus greater contingency, albeit at the expense of energy demand. Air-lift sidestream systems, on the other hand, are susceptible to clogging and matting, though the latter is apparently readily removed by periodic draining of the membrane tubes [10].

2.3. Membrane Fouling in Membrane Bioreactors (MBRs)

2.3.1. Fouling Mechanisms in MBRs

Various reviews of MBR fouling encompassing fouling mechanisms have been presented in the literature [3,97–99]. MBRs are routinely operated under notionally constant flux conditions with convection of foulant towards the membrane surface therefore maintained at a constant rate. Since fouling rate increases roughly exponentially with the flux [15,100,101], sustainable operation dictates that MBRs should be operated at modest fluxes and preferably bellow the so-called critical flux. Even sub-critical flux operation can lead to fouling according to a two-stage pattern: a low TMP increase over an initial period followed by a rapid increase after some critical time period. Pollice *et al.* [102] reviewed the sub-critical fouling phenomenon, introducing the parameters t_{crit} and $dTMP/dt$ to represent the critical time over which low-fouling operation at a rate of $dTMP/dt$ is maintained. Prior to these two filtration stages, a conditioning period is generally observed [103–106]. The three-stage process, wherein various mechanisms prevail, is summarized in Figure 2 [10].

Figure 2. Membrane Bioreactors (MBR) fouling mechanisms for operation at constant flux. Reproduced with permission from Reference [10]. Copyright 2011 Elsevier.



2.3.1.1. Stage 1: Conditioning Fouling

The initial conditioning stage arises where strong interactions take place between the membrane surface and the EPS/SMP present in the mixed liquor. Ognier *et al.* [107] described rapid irreversible fouling in this initial stage and passive adsorption of colloids and organics have been observed even for zero-flux operation and prior to particle deposition [103]. Another detailed study based on passive adsorption revealed the hydraulic resistance from this process to be almost independent of tangential shear and the initial adsorption to account for 20%–2000% of the clean membrane resistance depending on the membrane pore size [108]. In a more recent study, the contribution of conditioning fouling to overall resistance was found to become negligible once filtration takes place [109]. By applying a vacuum pump (rather than suction) coupled with air backflushing, Ma *et al.* [110] were able to reduce colloidal adsorption onto the membrane. These studies suggest that colloid adsorption onto new or cleaned membranes coupled with initial pore blocking may be expected in MBRs [12]. The intensity of this effect depends on membrane pore size distribution, surface chemistry and especially hydrophobicity [107]. In a test cell equipped with direct observation through a membrane operating with crossflow and zero flux, flocculant material was visually observed to deposit temporarily on the membrane [103]. This was defined as a random interaction process rather than a conventional cake

formation phenomenon. While some flocs were seen to roll and slide across the membrane, biological aggregates typically detached and left a residual footprint of smaller flocs or EPS material. Biomass approaching the membrane surface was then able to attach more easily to the membrane surface to colonize it and contribute to Stage 2 [10].

2.3.1.2. Stage 2: Slow/Steady Fouling

Even when operated below the critical flux for the biomass, temporary attachment of the floc can contribute to the second fouling stage. After Stage 1, the membrane surface is expected to be mostly covered by SMP, promoting attachment of particulate and colloidal biomass material. Because of the low critical flux measured for SMP solutions, further adsorption and deposition of organics on the membrane surface may also occur during Stage 2. Since adsorption can take place across the whole surface and not just on the membrane pore, biological flocs may initiate cake formation without directly affecting flux in this initial stage. Over time, however, complete or partial pore blocking takes place. The rate of EPS deposition, and resulting TMP rise, would then be expected to increase with flux leading to a shorter Stage 2. Such fouling would prevail even under favorable hydrodynamic conditions providing adequate surface shear over the membrane surface. However, since uneven distribution of air and liquid flow is to be expected in iMBRs, correspondingly inhomogeneous fouling must take place [10].

2.3.1.3. Stage 3: TMP Jump

With regions of the membrane more fouled than others, permeability is significantly less in those specific locations. As a result, permeation is promoted in less fouled areas of the membrane, exceeding a critical flux in these localities. Under such conditions, the fouling rate rapidly increases, roughly exponentially with flux. The sudden rise in TMP or “jump” is a consequence of constant flux operation and several mechanisms can be postulated for the rapid increase in TMP under a given condition. As with classical filtration mechanisms (Figure 3), it is likely that more than one mechanism will apply when an MBR reaches the TMP jump condition and a number of models can be considered:

- (i) *Inhomogeneous fouling (area loss) model*: This model was proposed to explain the observed TMP profiles in nominally sub-critical filtration of upflow anaerobic sludge [111]. The TMP jump appeared to coincide with a measured loss of local permeability at different positions along the membrane, due to slow fouling by EPS. It was argued that the flux redistribution (to maintain the constant average flux) resulted in regions of sub-critical flux and consequently in rapid fouling and TMP rise.
- (ii) *Inhomogeneous fouling (pore loss) model*: Similar TMP transients have been observed for the crossflow MF of a model biopolymer (alginate) [112]. These trends revealed the TMP transient to occur with relatively simple feeds. The data obtained have been explained by a model that involves flux redistribution among open pores. Local pore velocities eventually exceed the critical flux of alginate aggregates that rapidly block the pores. This idea was also the base of the model proposed by Ognier *et al.* [113]. While the “area loss” model considers macroscopic redistribution of flux, the “pore loss” model focuses on microscopic scale. In MBR systems, it is expected that both mechanisms occur simultaneously.

- (iii) *Critical suction pressure model*: The two-stage pattern of a gradual TMP rise followed by a more rapid increase has been observed from studies conducted based on dead-end filtration of a fine colloid by an immersed HF. At a critical suction pressure it is suggested coagulation or collapse occurs at the base of the cake, based on membrane autopsy evaluations supplemented with modeling [114]. A very thin dense layer close to the membrane surface, as observed in the study, would account for the rapid increase in resistance leading to the TMP jump. Although this work was based on dead-end rather than crossflow operation, the mechanism could apply to any membrane system where fouling continues until the critical suction pressure is reached, where-upon the depositing compound(s) coalesce or collapse to produce a more impermeable fouling layer.
- (iv) *Percolation theory*: According to percolation theory, the porosity of the fouling layer gradually decreases due to the continuous filtration and material deposition within the deposit layer. At a critical condition, the fouling cake loses connectivity and resistance, resulting in a rapid increase in TMP. This model has been proposed for MBRs [115], but indicates a very rapid change (within minutes), which is not always observed in practice. However, the combination of percolation theory with the inhomogeneous fouling (area loss) model could satisfy the more typically gradual inclines observed for TMP transients. Similarly, fractal theory was successfully applied to describe cake microstructure and properties and to explain the cake compression observed during MBR operation.
- (v) *Inhomogeneous fiber bundle model*: Another manifestation of the TMP transient has been observed for a model fiber bundle where the flow from individual fibers was monitored [116]. The bundle was operated under suction at constant permeate flow, giving constant average flux and the flow was initially evenly distributed among the fibers. However, over the time the flows became less evenly distributed so that the standard deviation of the fluxes of individual fibers started to increase from the initial range of 0.1–0.15 up to 0.4. Consequently, the TMP rose to maintain the average flux across the fiber bundle, mirroring the increase in the standard deviation of the fluxes. At some point, both TMP and standard deviation rose rapidly. This is believed to be due to flow maldistribution within the bundle leading to local pore and flow channel occlusion. It was possible to obtain steadier TMP and standard deviation profiles when the flow regime around the fibers was more rigorously controlled by applying higher liquid and/or airflows.

More recently, the TMP jump has also been explained by poor oxygen transfer existing within the fouling layer. As a result of transfer limitation, bacteria present in the biofilm layer can die, releasing extra levels of SMP. Experimental data have shown an increase in SMP concentration at the bottom of the fouling layer when the level of DO declines [10,117].

2.3.2. Biomass Foulants

Two types of foulant study dominate the MBR scientific literature: characterization and identification. Characterization refers to properties (usually relating to membrane permeability) the foulant demonstrates either *in situ*, that is, within the MBR, or *ex situ* in some bespoke or standard measurement, such as capillary suction time (CST) or specific resistance to filtration (SRF). Identification refers to

physical and/or chemical classification of the foulant, invariably through extraction and isolation prior to chemical analysis. Of course, foulant isolates may also be characterized in the same way as the MBR biomass.

In general, foulants can be defined in three different ways (Table 1):

1. Practically, based on permeability recovery,
2. Mechanistically, based on fouling mechanism, and
3. By material type, based on chemical or physical nature or on origin.

Table 1. Foulant definitions. Reproduced with permission from Reference [10]. Copyright 2011 Elsevier.

Practical	Mechanism	Foulant material type
Reversible/temporary: <ul style="list-style-type: none"> • Removed by physical cleaning 	Pore blocking/filtration models (Figure 3): <ul style="list-style-type: none"> • Complete blocking 	Size: <ul style="list-style-type: none"> • Molecular, macro-molecular, colloidal or particulate
Irreversible/permanent: <ul style="list-style-type: none"> • Removed by chemical cleaning 	<ul style="list-style-type: none"> • Standard blocking • Intermediate blocking • Cake filtration 	Surface charge/chemistry: <ul style="list-style-type: none"> • Positive or negative (cationic or anionic)
Irrecoverable */absolute: <ul style="list-style-type: none"> • Not removed by any cleaning regime 		Chemical type: <ul style="list-style-type: none"> • Inorganic (e.g., scalants) or organic (e.g., humic materials, EPS) • Carbohydrate or protein (fractions of EPS) Origin: <ul style="list-style-type: none"> • Microbial (autochthonous), terrestrial (allochthonous) or man-made (anthropogenic) • (Extracted) EPS (eEPS) or soluble microbial product (SMP) **

* Irrecoverable fouling is long-term and insidious; ** eEPS refers to microbial products directly associated with the cell wall; SMP refers to microbial products unassociated with the cell (Figure 3).

Of these, evidence suggests that it is the physical nature, and specifically the size, of the foulant that has the greatest impact on its fouling propensity. Hence, activated sludge biomass can be fractionated into three categories: suspended solids, colloids and solutes. The fractionation methodology critically affects the measurements made. Typically, the biomass sample is centrifuged. The resulting supernatant is then filtered with a dead-end membrane cell, with the calculated hydraulic resistance being attributed to colloidal and soluble matter combined (R_{col} and R_{sol} , respectively). Another portion of the biomass suspension is then microfiltered at a nominal pore size of 0.5 μm and the fouling properties of this supernatant (R_{sol}) attributed solely to the soluble matter. The relative fouling contributions of the suspended and colloidal matter can then be calculated [118]. The resistance provided by colloidal matter has also been attributed to the difference between the levels of TOC present in the filtrate passing through 1.5 μm filtration paper and in the permeate collected from the MBR membrane (0.04 μm) [119].

Fractionation methods may vary slightly for different studies, but results are often reported in terms of hydraulic resistance for suspended solids, colloids and soluble matter, the sum of which yields the resistance of the activated sludge. Although an interesting approach to the study of MBR fouling,

fractionation neglects coupling or synergistic effects which may occur both among different biomass components and with operating determinants. Such interactions are numerous and include feedwater quality [120], membrane permeability, particle size and hydrodynamics conditions [118].

The relative contribution of the biomass supernatant to overall fouling ranges from 17% [118] to 81% [121]. Such variation is probably attributable to the different operating conditions and biological state of the suspended biomass. It appears from these data that fouling by suspended solids is rather less than that of the supernatant. The latter is generally regarded as comprising soluble microbial product (SMP) which is soluble and colloidal matter that derives from the biomass. With respect to fouling mechanisms, soluble and colloidal materials are assumed to be responsible for membrane pore blockage, whilst suspended solids account mainly for the cake layer resistance [121]. However, since iMBRs are typically operated at a modest flux, cake formation is limited and deposition of physically smaller species is more likely to take place. Whilst there has been much interest in colloidal materials and their contribution often assessed, it has been argued that their impact on MBR fouling is relatively minor [122].

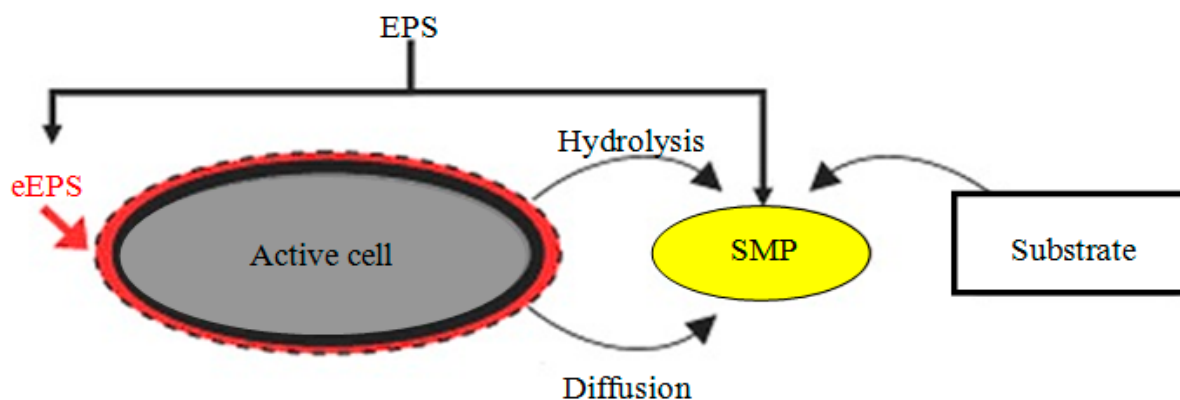
Biofouling can be described as the undesirable deposition of materials of biological origin on a surface [123] and contributes to the reduction of hydraulic performances in MBR systems. It can be further described as the initial attachment of SMP onto the membrane surface through adhesive forces during either passive adsorption or filtration. During MBR operation, bacteria then attach by cohesive mechanisms to the membrane surface already covered by SMP. As the mixed liquor filters through the fouled membrane, it provides nutrients and DO to the deposited bacteria. As a result, the immobilized bacteria assimilate to the surrounding environment by producing EPS and by forming a complex structure, generally termed the biofilm [124].

Advanced characterization of the biofilm formed on the membrane surface has formed the basis of much study. Efforts have focused on two main areas: (a) use of state-of-the-art visualization techniques to examine the morphology of the biofouling/biofilm and (b) identification of the microbial community present in the biofilm. The various observation techniques have been recently reviewed, along with the advantages and limitations for their potential use in MBRs [125]; confocal laser scanning microscopy (CLSM) in particular has been shown to offer great potential in characterizing the complex structure of the MBR membrane fouling layer [126]. In terms of community analysis, methods like fluorescence *in situ* hybridization (FISH) and polymerase chain reaction denaturing gradient gel electrophoresis (PCR-DGGE) are usually used to study the nature of the microbial population and structure on the membrane surface. From this work, specific bacteria have been identified as having a propensity to deposit and adsorb onto the membrane surface and to initiate biological growth [127]. The large number of cultures present makes the unambiguous identification of the microbial communities predominating in the MBR biofilm challenging [3]. However, of practical importance are the filamentous bacteria, which lead to sludge bulking in clarifiers of CASPs and promote foaming and EPS production, usually accompanied by TMP increase [128,129]. Strategies proposed to control the development of filamentous bacteria include use of selectors, addition of coagulants, high DO conditions and supplementing alkalinity [130], though appropriate ameliorative measures rely on the precise identification of the species concerned [10].

2.3.2.1. Extracellular Polymeric Substances (EPS)

Extracellular Polymeric Substances (EPS) are present outside and inside microbial cells. They constitute a matrix of high molecular weight molecules. They are secretions from microorganisms, and the products of cellular lysis and hydrolysis of macromolecules [131]. Membrane fouling in MBRs has been largely attributed to EPS [5,6,111,132,133], the construction materials for microbial aggregates such as biofilms, flocs and activated sludge liquors. “EPS” is a general term encompassing all classes of autochthonous macromolecules such as carbohydrates, proteins, nucleic acids, (phosphor) lipids and other polymeric compounds found at or outside the cell surface and in the intercellular space of microbial aggregates [134]. These consist of insoluble materials (sheaths, capsular polymers, condensed gel, loosely bound polymers and attached organic material) secreted by the cell shed from the cell surface or generated by cell lysis [12]. Functions of the EPS matrix include aggregation of bacterial cells in flocs and biofilms, formation of a protective barrier around the bacteria, retention of water and adhesion to surfaces [8]. With its heterogeneous and changing nature, EPS can form a highly hydrated gel matrix in which microbial cells are embedded [9] and can thus help create a significant barrier to permeate flow in membrane processes. Finally, bioflocs attached to the membrane can provide a major nutrient source during biofilm formation on the membrane surface [135]. Their effects on MBR filtration have been reported for more than 15 years [136] and have received considerable attention in recent years [3].

Figure 3. Simplified representation of extracted extracellular polymeric substances (eEPS) and Soluble Microbial Products (SMP). Reproduced with permission from Reference [10]. Copyright 2011 Elsevier.



Regardless of the extraction method used, a distinction can be made between EPS which derives directly from the active cell wall and that which is not associated with the cell but is solubilized in the mixed liquor. The former is usually referred to as “EPS” in the literature, although a less ambiguous term would be “eEPS” (extracted EPS) or “bEPS” (bound EPS) (Figure 3). The latter is normally termed sEPS (soluble EPS) or SMP (soluble microbial product) and invariably refers to clarified biomass, although for some more recalcitrant feedwaters, clarified biomass will inevitably contain feedwater constituents which remain untransformed by the biotreatment process. SMP comprises soluble cellular components released during cell lysis, which then diffuse through the cell membrane and are lost during synthesis or are excreted for some purpose [8,137]. In MBR systems, they can also be provided from the feed substrate. It is widely accepted that sEPS and SMP are identical [8,10,138,139].

2.3.2.2. Selection and Evaluation of EPS Extraction Methods

For the extraction of bEPS from microorganisms growing in suspension or in aggregates, there is not a universal extraction method [9]. The methods used for the extraction of EPS vary, giving each one of them different extraction efficiency and therefore different quantity and quality of the EPS extracted [140–142]. Therefore, the evaluation and selection of the appropriate extraction method of EPS according to the sample characteristics or/and the optimization of the selected method is a crucial step for further analysis of EPS. The optimal EPS extraction method should be effective, causing minimal cell lysis and not disrupt the EPS structure [143]. The extraction efficiency for a given sample can be defined as the total amount of EPS extracted from the total organic matter [9]. It should be noted that none of the extraction methods can extract all the EPS completely from microbial aggregates [131].

For the extraction of soluble EPS, centrifugation is usually used. For the extraction of bEPS, the methods which are used are classified into physical, chemical and a combination of physical and chemical methods. In order to study the composition of loosely bEPS and tightly bEPS separately, the bEPS can be extracted in two phases. A mild method can be used for the loosely bEPS extraction, like high-rate shear, heating at low temperatures or high speed centrifugation. Thereafter, a harsh method should be applied for the tightly bEPS extraction, such as heating at high temperatures, sonication or chemical extraction methods [131].

The physical extraction methods utilize the external forces to detach the EPS from cells and dissolve them in the solution. Physical methods contain centrifugation, shaking, sonication or heat treatment [9].

In the chemical extraction methods, chemical compounds, such as cation exchange resin (CER) [143], EDTA [141] or formaldehyde combined with NaOH [140], are added in order to disrupt the bonds between the EPS and the cells and dissolve the EPS in the solution. Chemical extraction methods are more efficient in comparison with the physical extraction methods. Among the chemical methods, the combination of formaldehyde with NaOH gives the highest extraction yields and seems to be the most efficient one [140,142]. However it must be pointed out that most of the chemical methods cause problems in the extraction process itself or in the subsequent EPS analysis, such as cell lysis, disruption of macromolecules and contamination of the EPS extracts by chemicals.

Cell lysis can be defined with various methods; however the extent of cell lysis is difficult to be evaluated. For the detection of cell lysis, nucleic acid content can be used as an indicator. The nucleic acid content in EPS is usually low, so a large quantity of nucleic acids after EPS extraction indicates intense cell lysis [131,144]. Some other methods consist of the counting of cells in conjunction with microscopy methods, the counting of live/dead cells, staining methods and UV-visible spectrum analysis [131,141].

The disruption of macromolecules can be evaluated via high-pressure size exclusion chromatography (HPSEC) [143].

According to D'Abzac *et al.* [142], the contamination of EPS extract by the extraction chemicals can be specified with various parameters. One parameter is the measurement of extraction yield. In case the yield surpasses 100% (Dry Weight of extracted EPS/Dry Weight of sludge) contamination has been occurred. Moreover, when the amounts of organic carbon surpass 1000 mg C/g DW is one more indicator of chemical transfer in the EPS extract. Finally, IR analysis can be used for the same reason.

2.3.2.3. EPS Quantification and Characterization

According to Raunkjaer *et al.* [145], for the quantification of the various components of EPS, conventional chemical colorimetric analyses should be used.

The proteins are analyzed by the Lowry method, the Bradford method and the total N-content method. The Lowry method has better recovery of proteins than the Bradford method [143]. The total N-content method is more precise compared to the other methods but it is more complex [131]. Generally, the method usually used for this case is Lowry method [146]. Bovine serum albumin (BSA) can be used as standard.

The polysaccharides content, with the form of carbohydrates, should be analyzed using the Dubois method [147,148] and the Anthrone method [143,149]. Both methods give similar results but in the anthrone method the coefficient of variation is lower than the other one [143]. On the other hand, Dubois method is sensitive and the color which it gives to the samples is stable. Typically, Dubois method is used in this case. Glucose can be used as standard.

Standard Addition Method is used in most cases to study eventual interferences between the sample and the analytical method [147].

Some indicative results of the concentration of extractable EPS from different MBR systems are the following. According to the research of Le-Clech *et al.* [99] the variation of proteins was found equal to 11–120 mg/g SS and of polysaccharides was found equal to 6–40 mg/g SS.

Nowadays the methods and instruments of analytical chemistry have evolved considerably, facilitating the study of the complex structure and composition of EPS and thus their behavior in wastewater treatment systems, such as MBR systems, can be explained.

The shape of EPS should be observed by environmental scanning electron microscopy (ESEM) [150], atomic force microscopy (AFM) [151] and confocal laser scanning microscopy (CLSM) [152]. The spatial distribution of carbohydrates, proteins and nucleic acids of EPS can be identified by confocal laser scanning microscopy (CLSM) [131,153].

Thereafter spectrophotometry techniques are presented, which can be proved useful for the study of membrane fouling by comparing the individual characteristics of EPS in a MBR system in operating conditions with and without fouling. The changes in the functional groups of EPS, which will probably be identified, should be related to the adsorption of pollutants on EPS [154,155]. After this conclusion, the bond strength of these pollutants on EPS can be determined [129,131,156]. Specifically, the functional groups and element compositions of EPS can be determined by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), 3-dimensional excitation-emission matrix fluorescence spectroscopy (3D-EEM), and nuclear magnetic resonance (NMR). Specifically, the X-ray photoelectron spectroscopy (XPS) can be used to define the elemental composition and evaluate the functionalities of EPS associated with carbon and oxygen [157–159]. Regarding the Fourier transform infrared spectroscopy (FTIR), it is widely used for the characterization of foulants adsorbed on membranes in MBR systems, in order to identify the functional groups of EPS [160,161]. The 3-D excitation-emission matrix fluorescence spectroscopy (3D-EEM) has many advantages for EPS characterization, as it can thoroughly characterize the sample with respect to its fluorescence characteristics [154,162]. Nuclear magnetic resonance (NMR) spectroscopy ($^1\text{H-NMR}$ or $^{13}\text{C-NMR}$) can, also, be used in order to identify the characteristics of organic matter in EPS samples, such as proteins,

aromatic carbons, carbohydrates, and other functional groups [146,163,164]. The hydrophobicity of EPS can be studied by the specific UV absorbance, which can be calculated by the division of the absorbance at 254 nm with the DOC concentration [165–167].

Finally, chromatography methods are also used widely for the characterization of EPS. The most appropriate method is High Pressure Size Exclusion Chromatography (HPSEC) or Gel Filtration Chromatography (GFC), which fractionates EPS according to their Molecular Weight (MW). A series of detectors such as UV, diode array, refractive index (RI), organic carbon (OC) and static light scattering (SLS) can be applied in this case [168–170].

2.3.2.4. Soluble Microbial Products (SMP)

Whilst the impact of dissolved matter on fouling has been studied for over 15 years, the concept of SMP fouling in a MBR is more recent [97], with available data being reported within the last 8 years. Experiments conducted with a dual compartment MBR, where the membrane was challenged ostensibly with the mixed liquor supernatant (*i.e.*, the SMP) rather than the whole biomass [171], have revealed greater filtration resistance from the SMP than from the biomass at 4 g/L MLSS concentration. This implies that SMP characteristics have a significant impact on membrane permeability. During filtration, SMP materials are thought to adsorb onto the membrane surface, block membrane pores and/or form a gel structure on the membrane surface where they provide a possible nutrient source for biofilm formation and a hydraulic resistance to permeate flow [139]. SMP materials appear to be retained at or near the membrane. Biomass fractionation studies conducted by Lesjean *et al.* [172] revealed levels of carbohydrates, proteins and organic colloids to be higher in the SMP than in the permeate, a finding similar to those previously reported [173,174].

Three methods of separating the water phase from the biomass, so as to isolate the SMP, have been investigated. Simple filtration through filter paper (12 µm) was shown to be a more effective technique than either centrifugation or sedimentation [174]. It is likely that removal of colloidal material would demand more selective pre-filtration, e.g., 1.2 µm pore size (Figure 3). As with EPS, the SMP solution can be characterized with respect to its relative protein and carbohydrate content [174], TOC level [175,176] or with SUVA measurement [177], as well as MW distribution. HPSEC analysis conducted on SMP solutions has revealed the SMP MW distribution to differ significantly across a range of full-scale reactors operated under different conditions [178], although the MW distribution for the eEPS fraction has been found to be similar [179]. However, the SMP solution fingerprint was largely unchanged in weekly analysis conducted on a single reactor, indicating no significant change in SMP characteristics for biomass acclimatized to specific operating conditions. When compared to eEPS MW distribution, the SMP solution featured generally larger macromolecules.

Comparison between acclimatized sludges obtained from MBR and ASP pilot plants revealed similar levels of EPS_{sp}, EPS_c and EPS humic matter [180]. The membrane did not seem to affect the floc EPS content. However, corresponding levels of the SMP fractions were significantly higher for the MBR sludge. Critical tests carried out under the same conditions for both MBR and ASP sludge revealed a higher fouling propensity of the MBR sludge over that of the ASP; critical flux values were around 10–15 and 32–43 LMH, respectively. Since the measured levels of EPS were unchanged, it was surmised that the higher fouling propensity related to the SMP level. During this study, Spérandio *et al.* [180] observed

significant biological activity in the MBR supernatant, indicating the presence of free bacteria which may have contributed to fouling.

Between the years 2004 and 2005, a number of different studies indicated a direct relationship between the carbohydrate level in the SMP fraction and MBR membrane fouling directly [172], or fouling surrogates such as filtration index and CST [181–184], critical flux [185] and permeability [139]. The hydraulic nature of carbohydrate may explain the apparently higher fouling propensity of SMP_c over that of SMP_p, given that proteins are more generally hydrophobic than carbohydrates. Strong interaction between the hydrophilic membrane generally used in MBRs and hydrophilic organic compounds may be the cause of the initial fouling observed in MBR systems. However, the nature and fouling propensity of SMP_c has been observed to change during unsteady MBR operation [186] and, in this study, it was not possible to correlate SMP_c to fouling. Subsequent studies from Drews *et al.* [187] demonstrated that no direct link exists between the concentration of carbohydrate in the supernatant and the extent of fouling in MBR systems. However, the contribution of SMP, and not exclusively the carbohydrate fraction, to the formation of the fouling layer is undeniable.

The correlation of MBR membrane fouling with SMP protein has been less widely reported although, since a significant amount of protein is retained by the membrane—about 15%, according to Evenblij and van der Graaf [174], to 90% [186] it must be presumed that such materials have a role in fouling. The specific resistance apparently increased by a factor of 10 when the SMP_p increased from 30 to 100 mg/L [188]. Against this, analysis of the fouling layer has revealed higher levels of carbohydrate and lower protein concentrations compared to those in the mixed liquor [103,189], tending to reinforce the notion that SMP_c is more significant than SMP_p in MBR membrane fouling. Humic matter, on the other hand, may not significantly contribute to fouling due to the generally lower MW of these materials [186].

Many research studies have been based on synthetic/analogue wastewaters. Those analogues comprising the most basic constituents, such as glucose, are very biodegradable and, as such, would be expected to yield rather lower SMP levels than those arising in real systems. Since it may be assumed that there are almost no substrate residuals from glucose in the supernatant, the less biodegradable SMP induced by cell lysis or cell release would account for most of the supernatant EPS measured in such analogue-based studies and may explain the reduced influence of SMP compared with that of EPS reported in some of these studies [190]. SUVA measurements carried out on MBR mixed liquor supernatant have confirmed the presence of organic matter originating from the decayed biomass and of larger MW and greater aromaticity and hydrophobicity in this fraction than in the analogue wastewater feed [177]. This would seem to confirm that fouling materials are generated by biological action and arise as SMP, though once again the chemical nature of these products is obviously affected by that of the feed.

In another important study based on synthetic wastewater, Lee *et al.* [191] revealed that levels of soluble organic matter in isolation cannot be used to predict MBR fouling. By comparing filterabilities of attached and suspended growth micro-organisms, Lee *et al.* [191] observed the rate of membrane fouling of the attached growth system (0.1 g/L MLSS and 2 g/L attached biomass) to be about seven times higher than that of a conventional suspended growth MBR at 3 g/L MLSS. With similar soluble fraction characteristics in both reactors, it was concluded that the discrepancy arose from the formation

of a protective dynamic membrane created by suspended solids in the suspended growth system, a conclusion subsequently corroborated by the work of Ng *et al.* [171].

As expected, many operating parameters affect SMP levels in MBRs, and it is very unlikely that the level of carbohydrate or protein in the SMP could, alone, predict foiling propensity. As for EPS, SMP levels decrease with increasing SRT [179]. For SRTs ranging from 4 to 22 days, SMP_p and SMP_c levels have been reported to decrease by factors of 3 and 6, respectively [183].

The lack of a direct relationship between the biological parameters measured in the reactor and the extent of MBR fouling is also due to the preferential deposition of materials onto the membrane surface. Recent characterization of the fouling layers has established that the composition of the fouling layer differs significantly from that of the bulk activated sludge or supernatant [168,192,193] the relative concentrations of protein and carbohydrate in particular being larger on the membrane surface. The more detailed characterization of three cleaning solutions obtained after rinsing, backwashing and chemical cleaning clearly highlighted this preferential deposition [14]. Non-uniformity of the cake layer is also manifested across the module as a whole, where regions of both static sludge cake (not removed by aeration) and thinner sludge film (readily removed by the passage of bubbles) have been reported [10,189].

2.3.2.5. Organic Fouling by EPS

Comparison of aerobic and anaerobic systems by Liao *et al.* [194] and Jia *et al.* [195] revealed more EPS to be generated under anaerobic conditions but the ratio of proteins to carbohydrates to be higher in aerobic systems. However, analysis of literature data suggests that both the total EPS and the protein:carbohydrate ratio are higher in aerobic systems, though data are highly scattered. Expressed as a percentage of total VSS, the range of the EPS content of aerobic and anaerobic sludges is 2.5%–13.3% and 2%–5.7%, respectively. Comparison of anaerobic and aerobic MBRs operated with complete retention of solids and fed with settled sewage [196] showed EPS levels to decrease continuously to a concentration of 27 and 33 mg/g_{vss}, respectively. Another study of anMBRs [197] attributed the fast fouling rate observed following stable operation for 28 days to the sudden increase in extracted EPS from 30 to 235 mg_{TOC}/L. A similar trend was reported by Fawehinmi [198], who observed an increase in specific resistance to filtration as the EPS content of crushed granular sludge increased from 20 to 130 mg/g_{vss}. These EPS concentrations are among the highest found in anMBRs, probably resulting from the rupture of the granules. Unusually low EPS levels in aniMBRs have been reported for an expanded granular sludge bed (EGSB), in which granules provided 4.4–6.6 and 0.6–1.6 mg/g_{vss} of EPS_c and EPS_p, respectively [199]. Reported levels of extractable EPS from the membrane surface deposit were twice those found in the granules and the ratio of proteins to carbohydrate 2.5 times higher. For dispersed/flocculant aniMBR systems the EPS levels appear to be closer to those of the aerobic systems, though slightly lower. Regardless of the major fouling component, differences between biomass and cake layer EPS composition suggest that soluble or colloidal compounds are as responsible for the increase in membrane resistance in anaerobic as in aerobic MBRs, but that they are more onerous to permeation.

It has been recognized for some time that, as with EPS, the concentration of SMP normalized against influent COD is higher in aerobic (3.1%) than in anaerobic systems (0.2%–2.5%), as reported by Barker

and Stuckey [200] based on earlier reported work [201,202]. This is due to the lower biomass uptake and decay rates of anaerobic microorganisms compared to aerobic biomass. Comparative studies of MBR systems with conventional reactors, however, have revealed the concentration of SMP to be higher in MBRs than for conventional biotreatment for both aerobic [203] and anaerobic processes [204]. This arises both because the high-molecular-weight organic fraction is retained by the membrane [203] and because higher SMP production arises by endogenous decay and cell lysis as a consequence of long sludge age operation and high loadings. Conversely to trends reported for conventional reactors, anaerobic MBRs have slightly higher SMP levels than aerobic systems. Analysis of literature data shows SMP levels normalized against influent COD to range from 10% to 22% and 10%–50% for aerobic and anaerobic MBRs, respectively. Direct comparison between aerobic and anaerobic MBR systems operated in parallel [196] revealed residual COD concentrations in mixed liquor supernatant to be higher in anaerobic MBRs. Available data indicate that proteins generally dominate over the carbohydrate content in the SMP fraction in anMBRs.

Of greatest significance, however, is the colloidal matter. An order of magnitude difference in colloid concentration between aerobic and anaerobic systems has been reported for only an 80% difference in soluble COD concentration [205], supporting earlier observations by Choo and Lee [206,207]. As with all membrane systems, colloidal matter is transported more slowly back into the bulk solution than coarser particulate materials due to the lower diffusion rates [207]; they thus tend to accumulate at the membrane surface to form a low-permeability fouling layer. They are also of a size which can plug the membrane pores, particularly for the larger pores of MF membranes, if able to migrate into the membrane. It is this that may account for the markedly diminished permeability of anaerobic MBRs as compared to the aerobic processes, notwithstanding the lower SMP organic carbon concentrations. The high colloid concentration is thought to reflect differences in biodegradation, which is much slower for the anaerobic process and involves several sequential steps such as hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is thought to be a surface-based reaction taking place on influent solids which are converted to simple monomers by extracellular enzymes excreted by hydrolytic and fermentative bacteria. As a result, and due to the low hydrolysis rates and biomass yield of anaerobic bacteria, the reactor solid inventory is considered to be mainly constituted by influent particulates [208] that are of reduced particle size [209]. AnMBR solids properties, unlike those of aerobic processes, are thus more dependent on influent characteristics than on bioreactor operational parameters. Some physical characteristics such as particle charge, which affects colloidal interactions, have been reported to remain unchanged after digestion [196], and various studies [210] reported aerobic sludge to deflocculate under anaerobic conditions, due to the release of EPS from the biological matrix, increasing the supernatant turbidity and reducing filterability.

While the higher colloidal content of the anMBR sludge may reflect higher levels of free bacteria in the mixed liquor, the higher soluble organic concentration may result from lower biodegradation rates or SMP biodegradability under anaerobic conditions [211]. There is also evidence of high MW polymeric matter (up to 1000 kDa) being retained by the cake layer in anMBRs, supported by observed changes in SMP composition as a result of permeation [212]. The apparently increased rejection capability accounts for the relatively high SMP levels found in the mixed liquor supernatant and the low MW (<1.5 kDa) of the permeate organic matter [213]. Analysis of SMP concentrations from anMBRs seems to corroborate trends reported from conventional anaerobic chemostats, which indicate higher

levels of SMP produced at higher wastewater strengths, sludge retention times [201,202] and low temperatures. For instance, SMP concentrations of 150 mg/L [199,214] have been reported at SRTs of 145–150 days, whilst at lower SRTs of 30 and 60 days only 39 and 56 mg_{COD}/L were found, respectively [215]. Decreasing temperature from 25 °C by 10–14 °C has been shown to decrease COD removal efficiency by up to 16% [216,217].

The use of supplementary dosing with PAC to ameliorate fouling has been extensively studied in membrane filtration of potable water and in aerobic MBRs, and such studies have also been conducted on anMBRs [218]. It has been suggested [206] that the addition of an adsorbent or a coagulant can enhance the permeate flux by agglomerating colloids to form larger particles of lower fouling propensity. The coarser and more rigid particles additionally improve scouring of the membrane surface. Dosing of anMBRs with ion-exchange resin has also been studied [219], with beneficial effects noted only at very high concentrations of 5 wt% [10].

3. Prevention and Control Strategies

Whilst an understanding of fouling phenomena and mechanisms may be enlightening, control of fouling and clogging in practice is generally limited to five main strategies:

1. Applying appropriate pretreatment to the feedwater,
2. Employing appropriate physical or chemical cleaning protocols,
3. Reducing the flux,
4. Increasing the aeration,
5. Chemically or biochemically modifying the mixed liquor and
6. Membrane surface modification.

All of the above strategies are viable for full-scale operating MBRs and each is considered in turn below [10].

3.1. Feed Pretreatment

It is generally recognized that the successful retrofitting of an ASP or SBR with an MBR is contingent on upgrading the pretreatment and, specifically, the screening. Whilst an MBR can effectively displace primary sedimentation, biotreatment and secondary solid-liquid separation, as well as tertiary effluent polishing, classical screens of around 6 mm rating are insufficient for an MBR. Such relatively coarse screens increase the risk of clogging of the membrane module retentate flow channels, especially by hairs in municipal wastewaters, which aggregate and clog both the membrane interstices and aeration ports. HF membranes have a tendency to form aggregates of hair and other debris, which collect at the top of the membrane element. Hairs may then become entwined with the membrane filaments and are not significantly removed by backflushing or cleaning. FS membrane clogging occurs when inhomogeneous fouling takes place, causing localized dewatering or sludging in the membrane channels, as well as at the channel inlet. If the aeration fails to remove this solids build-up, sludge accumulates above the blockage, increasing the affected excluded area. Fibers collecting in the aeration system can change the flow pattern and volume of air to the membranes, reducing the scouring and so promoting

membrane fouling and clogging. Aerators are thus normally designed to resist clogging and/or allow periodic flushing with water.

Screening for clogging amelioration has been discussed by Frechen *et al.* [220] for 19 European MBR plants. This report revealed most of the 10 German plants considered, to be fitted with horizontal or vertical slit screens of 0.5 or 1 mm diameter, most of these being protected by 3–6 mm slit screens, regardless of the membrane configuration. The same report also revealed marked differences in the performance of identically rated screens with differently shaped apertures. A 0.75 mm mesh screen was found to remove 66% more solids and 2.5 times more COD than an identically rated slit screen [10].

3.1.1. Screening

Screening is generally recognized as being crucial in suppressing clogging of both the membrane modules and the aerators. Whilst the standard rating of a screen at the inlet of a classical sewage treatment works is 6 mm, for an MBR the rating ranges from 3 mm for a FS membrane down to 1 mm or less for the HF configuration. The quantities of the screening generated in a MBR process are therefore considerably greater than that produced by conventional sewage treatment and the management of this waste stream has to be taken into account.

A comprehensive testing program of screens challenged with raw municipal wastewater has been conducted at the Chester Le Street WwTW in the United Kingdom [221] and more limited smaller scale tests have been conducted in Germany [220]. The performance of different types of screens varies significantly for a given aperture shape and available screen types for fine screening of sewage upstream of the MBR comprise bar, wedgewire and perforated plate. For municipal wastewaters in particular, screens with circular aperture (*i.e.*, perforated plate) are preferred for rigorous removal of fibrous material which might otherwise pass through the slit-like apertures provided by bar or wedgewire screens. However, 1 mm bar or wedgewire screens provide a similar performance to 3 mm perforated plate; such systems may be considered more suited to small sites or industrial sites.

The other critical component of the screen system is the mode of cleaning. Most fine screens have automated cleaning, although coarse bar screens can be periodically manually raked clean. Brush cleaning of the screens produces a lower volume waste but the action of the brushes can force some fine material through the apertures. Washing of the screens can also introduce the risk of screenings being washed downstream. Backwashing offers the lowest risk of entrainment of fibrous matter, with band screens being the least exposed in this regard. Plants should be designed to prevent any bypassing of the fine screens; they must be operated and maintained correctly-preferably through a maintenance contract with the supplier. An advantage of a hybrid system is that excessive flows that would otherwise bypass the screens can be directed to the conventional activated sludge stream. For a classical MBR, on the other hand, duty and standby screens are essential to ensure that fine screening is never compromised.

However, some plants appear to be susceptible to ragging despite rigorous inlet screening and, in such cases, RAS screening would appear to be the only reasonable solution. Given that ragging has thus far attracted no research and quantitative information from full-scale plant is also extremely limited it is unclear as to whether such remedial action is effective. The company Eflo have fitted simple manually raked 10 mm bar screens to the RAS lines of two MBR plants in the UAE, having encountered problems with ragging (or “Hair and Fiber Reinforced Biomass”, HFRB) at smaller plants in the region over a

prior 18-month period. There are now an increasing number of plants operating with RAS screening, specifically Swanage, Heenvliet and Ulu Pandan [10].

3.1.2. Other Feed Pretreatment Methods

Aside from screening, pre-sedimentation has also been proposed as a method of pre-treatment. *Moustafa* [222] has investigated the effect of fine screening and pre-settling on the performance of a lab-scale submerged membrane bioreactor. The obtained results revealed that pre-sedimentation is more effective than the fine screening as a pre-treatment method.

Two other important pretreatment steps are flow balancing and FOG traps (for fats, oil and grease). Flow balancing is highly desirable to limit the shock loads imparted on the MBR system, since rapid changes in both the hydraulic load and the F/M ratio can promote a number of deleterious effects, principally membrane fouling foaming and nitrification inhibition. FOG can similarly promote both foaming and fouling, with fouling arising from both direct adsorption of FOG onto the membrane and from EPS generated by the filamentous micro-organisms [10].

3.2. Physical and Chemical Cleaning Protocols

The classification of the fouling types is often based on the method used to recover the initial permeability. With the wide range of strategies employed to remove fouling from the membrane surface, it is no surprise that different (and sometimes confusing and contradicting) definitions have been introduced. A practical definition of the various fouling types is given in Table 2. This is based on the rate at which the fouling is expected to form and the time interval between cleaning strategies applied to remove them [13] and includes the term “residual fouling” to differentiate between fouling removed by maintenance cleaning and that by recovery cleaning [10].

Table 2. Classification of fouling. Reproduced with permission from Reference [13]. Copyright 2009 Elsevier.

Definition (with Preferred Term)	Fouling Rate (mbar/min)	Time Interval	Cleaning Method Applied
Cake, reversible or removable fouling	0.1–1	10 min	Physical cleaning (e.g., relaxation, backflush)
Residual fouling	0.01–0.1	1–2 weeks	Maintenance cleaning (e.g., chemically enhanced backflush)
Irreversible fouling	0.001–0.01	6–12 months	Chemical cleaning
Permanent, long-term or irrecoverable fouling	0.0001–0.001	Several years	Cannot be removed

3.2.1. Physical Cleaning

Key general cleaning parameters are duration and frequency, since these determine process downtime and if backflushing is used a further key parameter is the backflush flux. Less frequent, longer backflushing (600 s filtration/45 s backflushing) has been found to be more efficient than more frequent but shorter backflushing (200 s filtration/15 s backflush) [12]. In another study based on factorial design, backflush

frequency (between 8 and 16 min) was found to have more effect on fouling removal than either aeration intensity (0.3–0.9 m³/h per m² membrane area) or backflush duration (25–45 s) for n HF iMBR [223], with backflush strength having an intermediate impact [14]. Whilst more effective cleaning would generally be expected for more frequent, stronger and longer backflushing, possible permutations need exploring to minimize energy demand. This has been achieved through the design of a generic control system with automatically optimized backflush duration according to the monitored TMP value [224]. However, many such studies have not always taken account of the loss of productivity which results from the use of permeate during the backwashing.

Air can also be used to affect backflushing [225] or to enhance backflushing with water. Up to 400% increase in the flux over that attained from continuous operation has been recorded using an air backflush, although in this case 15 min of air backflush were required every 15 min of filtration [226]. Whilst air backflushing is undoubtedly effective, anecdotal evidence suggests that it can lead to partial drying out of some membranes, which can then produce embrittlement and so problems of membrane integrity.

Membrane relaxation encourages diffusive back transport of foulants away from the membrane surface under a concentration gradient, which is further enhanced by the shear created by air scouring [227]. Detailed study of the TMP behavior during this type of operation has revealed that, although the fouling rate is generally higher than for continuous filtration, membrane relaxation allows filtration to be maintained for longer periods before the need for chemical cleaning arises [171]. Relaxation is almost ubiquitous in modern full-scale iMBRs and studies assessing maintenance protocols have tended to combine relaxation with backflushing for optimum results [228,229]. A more systematic comparison of backflushing and relaxation operating conditions was proposed during short-term filtration periods of 24 h [14]. Although the overall degree of fouling (in terms of TMP increase) was similar in the various operating conditions, tests revealed the nature of the incipient membrane fouling varied significantly with filtration mode.

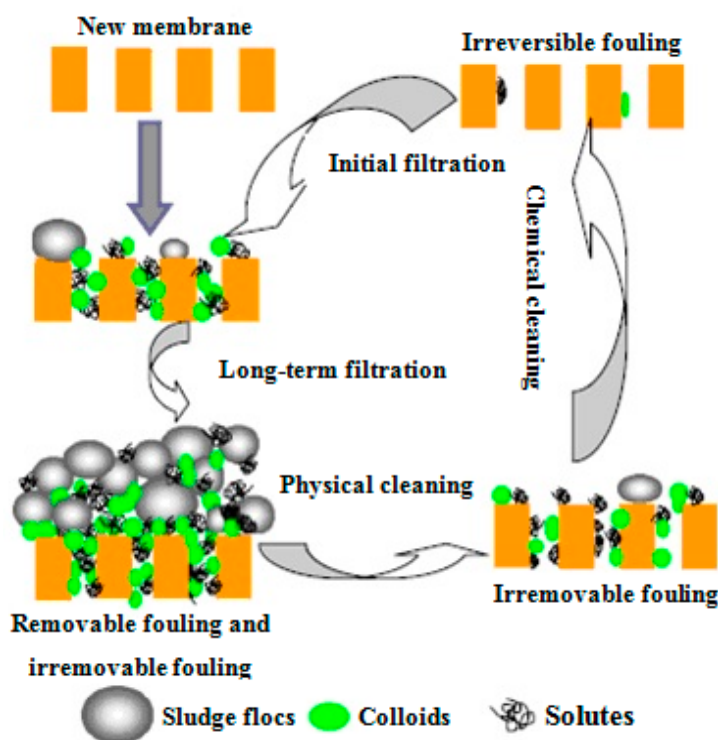
In practice, physical cleaning protocols tend to follow those recommended by the suppliers. Relaxation is typically applied for 1–2 min every 8–15 min of operation, both for FS and for HF systems. For HF systems, backflushing, if employed, is usually applied at fluxes of 1–3 times the operating flux and often supplements rather than displaces relaxation. It is likely that operation without backflushing, whilst notionally increasing the risk of slow accumulation of foulants on or within the membrane, conversely largely preserves the biofilm on the membrane, which affords a measure of protection. This fouling layer is substantially less permeable and more selective than the membrane itself and thus can be beneficial to the process provided that the total resistance it offers does not become excessive [10].

3.2.2. Chemical Cleaning

Physical cleaning is supplemented with chemical cleaning to remove residual and irreversible fouling (Figure 4) with this type of cleaning tending to comprise some combination of:

- Maintenance cleaning at moderate chemical concentrations on a twice weekly to monthly basis, designed to remove residual fouling and
- Intensive (or recovery) chemical cleaning (once or twice a year), used to remove the so-called irreversible fouling.

Figure 4. Fouling and cleaning. Reproduced with permission from Reference [3]. Copyright 2009 Elsevier.



Maintenance cleaning is designed to maintain membrane permeability and so reduce the frequency of intensive cleaning. It is performed either with the membrane *in situ*, a normal CIP, or in the case of an immersed system sometimes with the membrane tank drained (referred to as “cleaning in air”, CIA). Intensive, or recovery, cleaning is either conducted *ex situ* or in the drained membrane tank to allow the membranes to be soaked in cleaning reagent. Intensive cleaning is generally carried out when further filtration is no longer sustainable because of a diminished permeability. Recovery chemical cleaning methods recommended by suppliers are all based on a combination of hypochlorite, generally at 0.1–0.5 wt%, for removing organic matter and organic acid (either citric or oxalic, possibly supplemented with mineral acid to achieve a target pH of ~3) for removing inorganic scalants. Whilst some scientific studies of the impacts of chemical cleaning on the MBR system, such as the microbial community [230], have been conducted, there has been no systematic study comparing the efficacy of a range of cleaning reagents or cleaning conditions on MBR permeability recovery. Some experiments with augmented cleaning, such as sonically enhanced processes [231,232], have been conducted. Whilst ultrasonic cleaning can undoubtedly enhance flux recovery, tests conducted in potable water suggest that it can result in adverse impacts on membrane integrity [233].

Maintenance cleaning, usually taking 30–120 min for a complete cycle, is normally carried out every 3–7 days at moderate reagent concentrations of 200–500 mg/L NaOCl for classical aerobic MBRs. Recovery cleaning employs rather higher reagent concentrations of 0.2–0.3 wt % NaOCl, coupled with 0.2–0.3 wt% citric acid or 0.5–1 wt% oxalic acid [10].

More recently, Ramos *et al.* [16] applied different chemical cleaning methods to hollow fiber membranes from an anaerobic membrane bioreactor treating wastewater with a high oil and grease content: chemically enhanced backwashing, chemical cleaning in air and submerged chemical cleaning.

Concentrations of between 500 and 2000 ppm of NaClO and volumes per unit of membrane area of between 3 and 17.5 L/m² were employed. The best results were obtained with dynamic submerged chemical cleaning which allows a better distribution of the chemical reagent, increasing the cleaning effect over different fouled parts of the membrane module. On the contrary, non-uniform fouling on the module produced significant reductions in the cleaning efficiency of the backflux-driven chemical methods.

Vanysacker *et al.* [17] investigated the effect of the cleaning efficiency by NaOCl and citric acid treatments on 3 types of microfiltration membranes. For this purpose, membranes were fouled using biofoulant model organisms with increasing complexity (monospecies, duospecies and complex community). The cleaning efficiency was measured in terms of bacterial cell density and exopolymeric substance concentration. Citric acid, which was still able to kill most bacteria cells, was less effective, especially when the more complex activated sludge was used as biofoulant. Both chemicals had an impact on the membrane surface properties, reflected by increased pore size and porosity, although no changes in hydrophobicity and surface chemistry were detected. Overall NaOCl had the highest cleaning efficiency, irrespective of biofoulant or membrane type.

Membrane cleaning studies on anaerobic systems have generally indicated that a combination of caustic and acid washes is required to remove organic and inorganic (namely, struvite) foulants from organic anMBR membranes [234–236]. For inorganic membranes, acid washing has been found to be less effective and this has been attributed to surface charge effects [236]. However, the membrane ageing, and fouling history, variations in feedwater and biomass characteristics and differing operation and maintenance protocols make systematic optimization of cleaning protocols challenging. Such optimization is generally only achieved heuristically and a thorough testing of various cleaning agents in a large pilot plant has enabled recovery cleaning to be delayed by ~2 years in one case [10,237].

3.2.3. Feedback Control Systems

Given the constant variations in the biomass nature and the temporal development of the fouling layer on the membrane surface, for any MBR system a pre-determined operating mode is likely to be sub-optimal for at least some of the time. Since 2003, feedback control systems have been proposed to optimize the use of anti-fouling strategies in MBRs. Based on a simple polynomial model calibrated by consecutive cycles [238], or simply based on permeability drop [239,240], control systems developed have resulted in a reduction of backflush duration up to 25% or up to 50% in membrane aeration. Another relatively simple on-line method involved the combined monitoring of permeate flow rate, TMP and temperature to determine permeability and optimize the maintenance process on this basis [241]. More complex systems, taking into account the impact of growth of biofilm, concentration polarization phenomena and pressure drop in the permeation line, have been successfully designed, although they still require extensive calibration [31,238]. The successful application of control devices is possible only if appropriate inputs and outputs are properly defined and the integrity of the data is assured. System outputs can include control of the permeate pump (on/off or speed), the relaxation frequency, duration and membrane aeration rate, the backflush frequency, duration and flux and the filtration membrane aeration rate, although adjustment of the aeration rate is also possible only if variable-speed blowers have been installed.

Another strategy has been developed recently to attempt to better predict high fouling rate and involves the use of a small dedicated filtration apparatus to assess the filterability of the biomass at a given time. The Delft filtration characterization method (DFCm) comprises a sidestream membrane system in which 30 L of sampled biomass is filtered following a standardized protocol [242]. To avoid biomass handling and to obtain a faster response, two other filtration systems have been developed to be directly submerged into the MBR. The VITO fouling measurement (VFM) uses a single tubular membrane and the Berlin filtration method (BFM) is based on flat sheet configuration [243]. Whilst these systems all have the advantage of employing a standard method for sludge characterization, it is uncertain as to whether they offer a significant advance on feedback control based on permeability measurement of the actual process membranes [10].

3.2.4. Chemical/Biochemical Mixed Liquor Modification

The biomass quality can be controlled biochemically through adjustment of the SRT or chemically. In practice, SRT is rarely chosen on the basis of foulant concentration control. Instead a target value is almost invariably based on target water quality (for nitrification in particular), sludge production rate, membrane module clogging propensity and/or biomass aeration efficiency. However, studies have shown that a modicum of fouling control can be attained through the addition of chemicals [10].

3.2.4.1. Coagulant Addition

Ferric chloride and aluminium sulphate (alum) have both been assessed for fouling amelioration, most extensively for potable systems but also for MBRs [18]. In MBR-based trials, addition of alum to the reactor led to a significant decrease in SMPc concentration, along with an improvement in membrane hydraulic performances [244]. Small biological colloids (from 0.1 to 2 μm) have been observed to coagulate and form larger aggregates when alum is added to MBR activated sludge [245]. Although more costly, dosing with ferric chloride was found to be more effective than alum. Ferric dosing of MBRs has been used for enhancing the production of iron-oxidizing bacteria responsible for the degradation of gaseous H_2S [19]. In this study, specific ferric precipitated like ferric phosphates and K-jarosite ($\text{K-Fe}_3(\text{SO}_4)_2(\text{OH})_6$) were observed to foul the membrane. Pre-treatment of the effluent by pre-coagulation/sedimentation has been shown to provide some fouling reduction [246] and pre-clarification is employed at some sewage treatment works. In another example, the ferric dosing was shown to control both irreversible fouling and suspension viscosity [121]. Pre-coating of MBR membranes with ferric hydroxide has also been studied as a means of increasing permeability and improving permeate quality [247]. In this study, additional ferric chloride was added to remove non-biodegradable organics which accumulated in the bioreactor [10].

Chen and Liu [20] investigated the possibility and applicability of coagulation-membrane bioreactor (MBR) hybrid system in reclaiming dairy wastewater. Different types of coagulants such as inorganic (alum, aluminum sulfate, and ferric chloride), polymeric (polyaluminium chloride, PACl) and organic (polyacrylamide) were tested. The results showed that biological flocs in MBR could improve the fouling level of the membrane signifying that the hybrid system is feasible and applicable in dairy wastewater reclamation.

Ivanovic and Leiknes [21] underline that the addition of inorganic coagulants in the membrane filtration stage of the biofilm-MBR had a positive effect on improvement of mixed liquor filterability and dewaterability, resulting in lower fouling rates. Two dosages in the range of 9 to 22.5 ppm were chosen and tested in sets of experiments in two membrane bioreactors operated in parallel. Membrane fouling was reduced in a similar manner for both lower dosages of alum and iron applied, however, iron performed better at the higher dose.

Kimura *et al.* [22] investigated the effectiveness of pre-coagulation and showed that polyaluminum chloride could effectively mitigate membrane fouling using hollow fiber PVDF membranes. In addition, a remarkable relationship between the fouling index calculated from fairly long-term microfiltration experiments and concentrations of biopolymers in the feed waters collected from various parts of Japan was demonstrated in this study. Coagulation reduced the concentrations of biopolymers, to some extent, which might explain the mitigation of membrane fouling.

Zhang *et al.* [23] evaluated the fouling mitigation effect of four widely used water treatment coagulants, *i.e.*, alum, ACH, $\text{Fe}_2(\text{SO}_4)_3$ and FeCl_3 , on water containing algal organic matter using a lab scale ceramic MF membrane system. Treatment of the algal organic matter solutions with the four coagulants led to marked reductions in both the reversible and irreversible fouling for the ceramic MF membrane at the optimal coagulant dosages. ACH, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ performed similarly in reducing the flux decline, while alum gave a considerably lower reduction in flux decline. It is suggested that further investigations should be conducted in order to gain a better insight into the key mechanism controlling the removal of the high MW biopolymer molecules, with a view to further optimizing the coagulation process.

3.2.4.2. Adsorbent Agents

Addition of adsorbents into biological treatment systems decreases the level of organic compounds [10]. Powdered activated carbon (PAC) is a commercial porous adsorbent with a significant surface area [24]. Dosing with PAC produces biologically activated carbon (BAC) which adsorbs and degrades soluble organics and has been shown to be effective in reducing SMP and EPS levels in a comparative study of a sidestream and immersed hybrid PAC-MBR [248]. Decreased membrane fouling has also been demonstrated in studies of the effects of dosing MBR supernatant with up to 1 g/L PAC [249] and dosing activated sludge itself [250] for which an optimum PAC concentration of 1.2 g/L was recorded. In the latter study, floc size distribution and apparent biomass viscosity were identified as being the main parameters influenced resulting in a reduced cake resistance, when PAC was dosed into the bioreactor. Conversely, no significant improvement in performance was recorded when a concentration of 5 g/L of PAC was maintained in the bioreactor without sludge wastage [171]. It was postulated that under these conditions the PAC was rapidly saturated with organic pollutants and that fouling suppression by PAC relies on its regular addition brought about by lower SRTs [10].

Pramanik *et al.* [25] have also employed BAC filtration in order to reduce the organic fouling of a 0.1 μm PVDF membrane in the treatment of a biologically treated secondary effluent from a municipal wastewater treatment plant. BAC treatment led to a greater reduction of the high MW molecules such as biopolymers and humic substances through biodegradation and adsorption, respectively, resulting in a marked improvement in the permeate flux.

Hu *et al.* [24] carried out a study by initially dosing different amounts of PAC into a MBR, employing a combined PAC-MBR pilot-scale system for micro-polluted surface water treatment. Clearly, 0 and 3 g/L PAC-MBR had relatively higher fouling propensity *versus* 1 and 2 g/L PAC-MBR. The permeate flux decreased from 22 to 19 m²/h and 16 m²/h, while from 22 to 21 m²/h and 20 m²/h after 30 days' continuous operation. These differences are likely caused by the different characteristics of floc in the bulk mixture and cake layer on the membrane surface. Indeed, the positive effect of 1 or 2 g/L PAC addition on membrane filterability *versus* 0 g/L could be attributed to the following aspects: (1) more adsorption capacity of the fine colloids and solutes in the bulk mixture; (2) a stronger floc structure with an incompressible nature. However, increasing the PAC dosage to 3 g/L did not necessarily bring about an enhanced membrane flux; on the contrary, more rapidly deteriorated flux was observed in its later operational phase. This serious flux decline in the relatively higher PAC-dosed system can be attributed to its higher EPS content in the bulk mixture and the correspondingly increased floc viscosity which gave rise to the membrane filtration resistance and reduced the permeate flux as a consequence.

Experiments conducted with different system configurations based on immersed HF membranes allowed direct comparison of hydraulic performances for pre-flocculation and PAC addition. Under the operating conditions employed, pre-flocculation provided higher fouling mitigation than that of PAC addition [251]. However, the use of both strategies simultaneously provided the greatest permeability enhancement [251,252].

A detailed mathematical model has been proposed for predicting performances for hybrid PAC-MBR systems [26]. The model encompasses sub-processes such as biological reaction in bulk liquid solution, film transfer from bulk liquid phase to the biofilm, diffusion with biological reaction inside the biofilm, adsorption equilibria at the biofilm-adsorbent interface and diffusion within the PAC particles. Numerous other studies in which the use of PAC has been reported for fouling amelioration have generally been limited in scope and have not addressed the cost implications of reagent usage and sludge disposal. Tests have been performed using zeolite [245] and aerobic granular sludge, with an average size around 1 µm [120] to create granular flocs of lower specific resistance. Granular sludge was found to increase membrane permeability by 50% but also lower the permeability recovery from cleaning by 12% which would be likely to lead to unsustainable operation. There have additionally been studies on the use of granular aerobic sludge in aerobic MBRs [27,253], as well as anMBRs [10,199].

3.2.4.3. Proprietary and Other Reagents

Other types of additives, based on cationic polymer-based compounds have been recently developed to enhance membrane performance. The first product to appear on the market was *MPE50*, developed by Nalco for use in iMBRs which has been tested by a number of authors [197,254,255]. The addition of 1 g/L of the reagent directly to the bioreactor has been shown to reduce the SMPc level from 41 to 21 mg/L [254]. The interaction between the polymer and the soluble organics in general, and SMPc in particular, was identified as being the main mechanism responsible for the performance enhancement. In another example, an MBR operated at a MLSS level as high as 45 g/L yielded a lower fouling propensity when 2.2 g/L of polymer was dosed into the bioreactor. A number of other "anti-fouling" products have since become available, including *MPL30* (Nalco), *KD452* (Adipap), as well as generic chemicals such as chitosan and starch. A recent study has comprehensively compared a wide range of

these flocculants, adsorbents and additives [256] and revealed high SMP removal by *KD452* and an increased critical flux by *MPE50*, *KD452* and starch. Details of pilot testing of these three compounds were also reported by the authors. Biological side effects, clearly observed during overdosing of the compounds, were observed for the use of FeCl_3 and chitosan [2,10].

3.2.4.4. Quorum Sensing (QS)

Bacteria use the language of small diffusible signaling molecules called autoinducers to communicate and assess their population densities in a process called quorum sensing (QS). The sensing mechanism is based on the synthesis, release and uptake of autoinducers in the surrounding medium, whose concentration correlates to the density of secreting bacteria in the vicinity [28]. QS has been shown to regulate gene expression mediating some bacterial behaviours such as the production of SMP and EPS, exocellular enzyme secretion, and biofilm formation. Accordingly, this discovery opens a new avenue to manage the behaviour of bacteria and control biofouling in membrane systems [29].

Yeon *et al.* [31] used acylase attached to magnetic carrier to inhibit QS in MBR for advanced wastewater treatment. They showed that this approach reduced biofouling effectively and enhanced the membrane permeability. Since then, this biofouling control technique has attracted a lot of attention, and is now viewed as a promising alternative technique for mitigating membrane biofouling [29,31].

Lv *et al.* [30] used vanillin, a QS blocker, and proteinase K to investigate the effect of QS and extracellular proteins on the microbial attachment of aerobic granular activated sludge. They found that microbial attachment of aerobic granular activated sludge could be inhibited by both vanillin and proteinase K. The contents of *N*-acylhomoserine lactones and extracellular proteins were decreased with vanillin and proteinase K. Besides, it was found that extracellular proteins were in favor of microbial attachment of aerobic granular activated sludge, and *N*-acylhomoserine lactones mediated QS might be involved in microbial attachment of aerobic granular activated sludge through the regulation of extracellular proteins. These results clearly indicated that both QS and extracellular proteins played important roles in the development of “aerobic granular activated sludge biofilm”.

Quorum sensing, which was earlier known for pathogenesis, seems to be a key factor which regulates biofilm formation, thus playing a key role in membrane biofouling [28]. However, as every new biofouling control paradigm, it should be more intensively studied and its efficiency in full-scale MBR plants needs further verification.

3.2.5. Application of Ultrasound, Electric Field and Ozone

Over the last few years several attempts have been made to control membrane fouling by using ultrasound, ozone and electric field [33,257–259].

Ultrasound proved to be able to enhance membrane permeability and mitigate membrane fouling effectively in crossflow filtration of macromolecules [260–262]. The enhancement of membrane flux depended on the ultrasound intensity, irradiation radiation and direction. Sui *et al.* [33] investigated the ultrasound working time for membrane fouling control under different sludge concentrations and operated an anaerobic membrane bioreactor (anMBR) to show the feasibility of employing ultrasound for on-line membrane fouling control. It was shown that the higher the sludge concentration, the longer the ultrasound radiation time should be for membrane fouling control. Xu *et al.* [32] employed an

on-line ultrasonic equipment to control membrane fouling in an anMBR for waste activated sludge digestion. It was found that intermittent ultrasonic irradiation was able to control the membrane fouling efficiently in the anMBR, with a power intensity of 0.18 W/cm^2 and a timing of 3 min/h regarded as the optimal ultrasonic condition in consideration of the efficiency of membrane fouling control and the lifetime of the membrane.

In order to stabilize membrane flux and slow up membrane fouling Chen *et al.* [257] built a new type of MBR with the ability to control membrane fouling in order to investigate the influence of electric field on membrane flux in the presence of appending direct-current field. Appending electric field has significant effects on the membrane flux of the new MBR: the electrophoresis of particle will increase; the sedimentation layer will become thinner and the resistance of filtration drop with the electric field strength. Liu *et al.* [34] demonstrated that employing a very low electric field (0.2 V/cm) in a MBR results in improved performance both in terms of fouling control and effluent water quality. Akamatsu *et al.* [1] proposed a novel MBR system to suppress membrane fouling caused by activated sludges: the membrane filtration proceeds in crossflow mode and an electric field is applied to the membrane intermittently during the filtration progress. It was possible to remove the foulant sludge particles from the membrane in the MBR process because they were negatively charged and the novel MBR system combined with the use of an intermittent electric field was very effective in suppressing membrane fouling and maintaining higher permeate flux.

Most researchers found that ozonation reduced membrane fouling in low pressure membrane filtration of natural waters and wastewaters [263–265]. Nguyen and Roddick [36] investigated the effects of ozonation and biologically activated carbon (BAC) filtration on the characteristics and UF filterability of the activated sludge (AS) effluent collected from the wastewater treatment plant. It was found that ozonation reduced the UMF_I (unified membrane fouling index) of the raw AS effluent by 32% and BAC filtration resulted in a further 29% reduction in the UMF_I of the ozonated effluent to give an overall fouling reduction of approximately 51% for the ozonation/BAC filtration sequence. Wu and Huang [35] confirmed the anti-fouling effect of adding ozone operating two MBRs, one with and one without ozonation. Ozonation was found to be able to effectively retard membrane fouling and prolong the chemical cleaning cycle by 1–2 times in long-term running MBRs with dosage of 0.25 mg/g SS at 1 day intervals.

3.3. Optimal Operation of MBR Process

3.3.1. Flux Reduction

Reducing the flux always reduces fouling but obviously then impacts directly on capital cost through membrane area demand. A distinction must be made between operating (*i.e.*, gross) flux and the net flux (the flux based on throughput over a complete cleaning cycle), as well as peak and average flux. Historically there appear to have been two modes of operation of an MBR regarding operating flux which then determine the cleaning requirements and thus net flux:

- *Sustainable permeability operation*: In this instance, the conditions are chosen so as to maintain stable operation (little or negligible increase in TMP at constant flux) over an extended period of time (*i.e.*, several weeks or months) with only moderate remedial measures (namely relaxation),

if any. Most immersed FS and all sidestream systems have traditionally operated under these conditions, with sMBRs operating continuously (*i.e.*, without relaxation) between chemical cleans.

- *Intermittent operation*: In this mode of operation, the operational flux is above that which can be sustained by the filtration cycle operating conditions and, as a result, intermittent remedial measures are employed. These comprise relaxation supplemented with backflushing and usually some kind of maintenance chemical cleaning procedure. All immersed HF systems operate in this manner.

Modern practice appears to favor operation at net fluxes of 18–25 LMH for iMBRs challenged with municipal wastewater, incorporating physical cleaning, regardless of membrane configuration. Maintenance cleaning, if employed, adds insignificantly to downtime. The greatest impact on operating vs net flux is therefore peak loading, often from storm waters if no flow balancing is provided. It is these increased hydraulic loads, coupled with feed water quality fluctuations which represent one of the major challenges to MBR design and operation. Most of the MBR suppliers allow their system to be operated at high flux (up to twice the normal value) to cope with potential peak loadings. However, these periods of high permeation are generally limited to a maximum of 1–2 h and are sometimes coupled with increased aeration requirement and followed by extended relaxation periods (at lower flux) to allow the fouling accumulated during the peak flow operation to be removed physically [10].

3.3.2. Aeration Increase

Whilst increasing aeration rate invariably increases the critical flux up to some threshold value, increasing membrane aeration intensity is normally prohibitively expensive. Much attention has been focused on commercial development of efficient and effective aeration systems to reduce the specific aeration demand, with possibly the most important publications arising in the patent literature [266,267] and including cyclic aeration [268] and jet aeration [269]. The use of uniformly distributed fine air bubbles from 0.5 mm ports has been shown to provide greater uplift and lower resistance compared to a coarse aerator having 2 mm ports at similar aeration rates [270]. In the same study, a bi-chamber (a riser and down-comer) in a FS MBR has been shown to play a significant role in inducing high CFVs. The use of a variable aeration rate to increase the flux during peak loads has been reported for short-term tests [271] and on full-scale plants [240,272]. There have additionally been a number of studies where flux has been correlated with aeration [15,273], but it is generally recognized that increasing aeration beyond some threshold value has no impact on the membrane permeability and, as such, the value of increasing aeration during the filtration cycle to control fouling is questionable. On the other hand, effective uniform distribution of aeration to suppress clogging is of paramount importance [10].

3.4. Membrane Surface Modification

Several of the surface characteristics of membranes such as hydrophilicity, charge and roughness are known to be strongly related to fouling because they determine the interaction between the membrane and the foulants [274].

The majority of the commercial membranes for pressure-driven processes are made from hydrophobic polymers with high thermal, chemical, and mechanical stabilities. Because of the hydrophobicity of these materials, they are prone to adsorption of the fouling substances. It has been well documented that

membranes with hydrophilic surfaces are less susceptible to fouling [275,276]. Therefore, an increase in the hydrophilicity of the membrane surface is often a key goal to reducing membrane fouling by organic pollutants and microorganisms. Due to the formation of hydrogen bonds, a thin layer of bounded water exists on the surface of the hydrophilic membrane. This layer can prevent or reduce undesirable adsorption or adhesion of the foulants on the membrane surface.

The charge of the membranes is an especially important consideration for reducing membrane fouling where the foulants are charged, which is often the case. Usually, it is appropriate to use a membrane carrying the same electrical charge as the foulants. When the surface and the foulant have a similar charge, the electrostatic repulsion forces between the solute and the membrane prevent the solute deposition on the membrane, thereby reducing the fouling [277,278]. There have been a number of attempts to reduce fouling by incorporating ionizable functional groups on the membrane surface. For example, a negative surface charge on the membrane will have a beneficial effect on the separation of the proteins around neutral pH, because most proteins also have a negative charge in such conditions [279]. In addition, most of the colloidal particles, such as NOMs, that deposit on the membrane surface are negatively charged [280]. Similar to the negatively charged surface, the positively charged membrane surfaces exhibited electrochemical repulsion against positively charged solutes [281,282].

3.4.1. Physical Coating/Adsorption on the Membrane Surface

Coating a thin layer of water-soluble polymers or surfactants from solution by physical adsorption is a flexible technique to optimize the hydrophilicity, smoothness, and surface charge of the membrane surface [37–42,283–288]. The first studies in this field dealt with the modification of the UF membranes to reduce their fouling with proteins [289–291]. Kim *et al.* [289] showed that the fouling of the UF membranes with proteins may be reduced by surface adsorption with watersoluble polymers, such as PVA, methylcellulose (MC) and PVP. The treatment provided an increase in the initial UF flux and a slower flux decline. MC was the most effective of the polymers tested in enhancing UF flux, showing an average flux advantage of 30%–40% for the first usage. Non-ionic, hydrophilic polymers were found to be the most effective in minimizing lactoglobulin adsorption as well as in decreasing membrane resistance during UF, while the application of surfactants and ionic polymers was less successful [291]. On the other hand, it was shown that modifying the PS membrane with polyethylenimine (PEI) decreased the flux reduction during UF of the ovalbumin solutions due to increased hydrophilicity and electrostatic repulsion between the protein molecules and the modified membrane [290]. Thereafter, many hydrophilic polymers, such as PVA, PAA, PEG-based hydrogels, and chitosan, have been coated on different MF, UF, NF, and RO membranes using casting [39,40,286,287], adsorption [42,284], or filtration [38,283,285] techniques [282].

3.4.1.1. Coating via Filtration

Li *et al.* [283] prepared PVA-coated TFC membranes by filtrating aqueous solutions containing PVA and cross-linking agents through the porous membrane support, followed by heat treatment. As a result, a cross-linked PVA gel layer was formed on the surface and in the pores of the modified membranes. The modified membranes show higher antifouling characteristics compared with the unmodified membranes during UF of the pepsin solutions.

The UF PES membranes containing negatively charged sulfonic acid groups on the surface were obtained on filtration of an aqueous solution of poly(sodium 4-styrenesulfonate) (PSS) for about 100 min using a dead-end filtration cell [285]. It was shown that thin porous membranes are modified only on the top surface because the PSS macromolecules are not able to enter the pores. However, for membranes with wider pores, PSS permeation results in the formation of charged groups on both the surface and the pore walls of the membrane. The major difference between the modified and the unmodified membranes was found in their flux recovery after UF of the PEG and dextran solutions. Flux recovery ratios of >90% were obtained for the modified membranes compared with 55% for the unmodified membranes. Thus, the surface-modified membranes have better “cleanability” and “antifouling” characteristics than the base membranes.

Boributh *et al.* [38] compared three different methods for modifying MF PVDF membranes with chitosan to reduce BSA fouling. These were: (i) An immersion method, when the membrane was immersed in a chitosan solution for a fixed time; (ii) A flow-through method, when the chitosan solution was filtered through the membrane; and (iii) The combined flow-through method and the surface flow method. It was shown that the membranes modified by a combined flow-through method and a surface flow method showed better antifouling properties compared with others. This is due to the deposition of the chitosan both on the surface and in the pores, resulting in the prevention of BSA adsorption. For a membrane modified by immersion, the chitosan was deposited only on the membrane surface. Therefore, BSA could be adsorbed easily on the pore walls, which led to a high flux decline and irreversible fouling.

At this point, it should be mentioned that depending on the adsorption affinity with the membrane surface, the adsorbed coating layer can be stable or removable. The thin-coated films prepared via the deposition of positively and negatively charged polyelectrolytes show good stability due to the electrostatic attraction between the membrane surface and the deposited layers [37,42]. On the other hand, for hydrogen-bonded modified layers, the strength of the hydrogen bonding between the membrane surface and the deposited layer can be altered by changes in the solution pH, thus these layers can be removed and replaced [292,293]. For example, the cleaning procedure for PVA-coated membranes included membrane treatment with HCl at a pH of 2 and stirring for 15–20 h [42]. Thus, if membrane fouling occurs, the PVA layer and the attached foulants can be removed by acid cleaning to refresh the membrane. It may be much easier and more cost-effective to remove and replace the film instead of replacing the membrane.

In general, the adsorbed coatings are relatively simple to apply and the process can be performed in commercial membrane elements. In addition, the type of coating can be tailored to the specific application of interest. However, despite the flexibility of the coating and the adsorption methods to change the hydrophilicity, smoothness, and charge of the membrane surface, their main drawback is the limited stability of the modified layer over time because of the possible desorption of the coated/adsorbed polymers from the membrane surface into the bulk of the feed solutions [282].

3.4.1.2. Coating via Adsorption

Maartens *et al.* [284] used the adsorption of the non-ionic surfactants, Triton X-100 and Pluronic F108, to modify the tubular UF PES membranes, which were used for filtering the pulp and paper effluents. Triton X-100 is adsorbed to the membrane by hydrophobic interaction with the hydrophobic

C₆H₄ groups, with the hydrophilic CH₂CH₂O groups facing toward the aqueous phase. Pluronic F108, on the other hand, is anchored onto the hydrophobic membrane surface by means of the hydrophobic poly(propylene oxide) center group. The two hydrophilic poly(ethylene oxide) groups at both ends of the molecule face toward the aqueous phase. It was shown that increasing the hydrophilic characteristics of the membranes due to the surfactants' adsorption could reduce the amount of phenolic foulants adsorbed onto the membranes. Precoating of the PES membranes with Pluronic F108 drastically diminishes the foulants' adsorption over a 90 h filtration time under cross flow conditions. It should be noted that the membrane modification not only reduced fouling, but also improved the efficiency of cleaning to remove the foulant layers. The flux through the fouled membranes was successfully restored by cleaning with the non-ionic detergent Triton X-100 and sponge balls. Pluronic F108-coated membranes were more easily cleaned. The antifouling effect induced by this agent was, however, lost after cleaning with Triton X-100, thus the membranes had to be recoated with the surfactants after the cleaning procedure.

The hydrophilicity of the MF PP membranes may be increased by increasing the amount of surfactant Tween-20 adsorbed onto the surface or in the pores of the membrane [288]. The PP membrane modified with a monolayer of the adsorbed surfactant showed higher flux and stronger antifouling ability than the unmodified membrane after operating in an MBR for about 12 days.

Charge reversal on a low-pressure RO PA membrane surface, due to the electrostatic self-assembly of PEI, was found to increase the fouling resistance of the modified membrane to the cationic foulant DTAB, owing to the enhanced electrostatic repulsion and the increased surface hydrophilicity [41]. It was shown that the improved fouling resistance and the increased surface hydrophilicity compensated for the reduction in the membrane permeability due to the adsorption deposition of the PEI layer on the membrane surface.

Ba *et al.* [42] used the adsorption of water-soluble polymers, such as PVA, polyacrylic acid (PAA), and polyvinyl sulfate-potassium salt (PVS) on the surface of the positively charged P84-PEI membrane to form a protective coating layer to improve the membrane fouling resistance. PVA, PAA, and PVS as the coating materials represented neutral, partially charged, and highly charged polyelectrolytes, respectively. Surface coating experiments were carried out in a cross-flow filtration cell with the circulation of 50 mg/L of a PVA, PAA, or PVS polyelectrolyte aqueous solution over the base membrane for 8–12 h. It was shown that by applying these coatings, the hydrophilicity, smoothness, and surface charge may be modified and optimized. This reduced the membrane fouling with BSA, HA, and sodium alginate. Membrane surface charge was observed to play the most important role in foulant adsorption. The uncoated membrane had a strong positive charge so that foulants such as BSA, HA, and sodium alginate were adsorbed quickly and firmly. The PVA-coated membrane also had a positive charge, and fouling by negatively charged materials such as HA and sodium alginate was still high. The PVS coated and PAA-coated membranes had a low surface charge and, as a result, the fouling with BSA and HA was diminished due to a reduction in the charge interactions [282].

3.4.1.3. Coating via Casting

Asatekin *et al.* [287] prepared novel composite NF membranes by casting the synthesized amphiphilic copolymer PAN *graft*-poly(ethylene oxide) (PAN-g-PEO) onto UF PAN membranes. The coated

membranes were immersed in isopropanol for 30 min and thereafter in a water bath. It was shown that during precipitation, the copolymer undergoes microphase separation, forming interpenetrating networks of PAN-rich and PEO-rich nanodomains. Transmission electron microscopy reveals that PEO domains act as water-permeable nanochannels and provide the size-based separation capability of the membrane. A small decline in flux (15%) was observed in a 24 h dead-end filtration experiment with 1 g/L BSA solution using the modified membrane, while the base UF membrane lost 81% of its flux irreversibly in the same conditions. It was concluded that the PEO “brush” layer, formed on the membrane surface, acts as a steric barrier to protein adsorption, endowing these membranes with exceptional fouling resistance.

Composite UF PVDF membranes modified with a self assembling graft copolymer PVDF-*graft*-poly(oxyethylene) methacrylate showed a good fouling resistance for BSA, HA, and sodium alginate at feed concentrations of 1000 mg/L and activated sludge [286]. For example, dead-end filtration of the activated sludge with 1750 mg/L of volatile suspended solids resulted in a constant flux throughout the 16 h filtration period. Interfacial force measurements with an atomic force microscope showed the presence of steric foulant membrane repulsive forces and a lack of adhesion forces between the foulant and the membrane. However, a possible ester bond linkage of the PEO side chain in acidic or basic media may restrict the application of the modified membranes.

Sagle *et al.* [40] used a drawdown coating of cross-linked PEG-based hydrogels modified with RO membranes to reduce their fouling. The cross-linked PEG-based hydrogels were synthesized via the photoinitiated copolymerization of PEG diacrylate as the cross-linker and PEG acrylate, 2-hydroxyethyl acrylate, or AA as the comonomers. It was evaluated that the coatings deposited on the membrane surface were approximately 2 μm thick. It was shown that the water fluxes of the coated membranes were smaller than those of the uncoated membranes, but the fouling of the modified membranes with cationic dodecyltrimethyl ammonium bromide (DTAB), anionic sodium dodecyl sulfate (SDS) surfactants, and oil/water emulsions was essentially reduced. At the filtration of the oil/water emulsion made with DTAB, the flux of the base membrane after 24 h decreased to 26% of its initial value, while the water flux of a PEGDA-coated RO membrane was 73% of its initial value. It was shown that the membrane surface charge correlates with the fouling properties of the membranes; negatively charged membranes foul extensively in the presence of positively charged surfactants and experience minimal fouling in the presence of negatively charged surfactants.

Commercial UF PVDF membranes with a cutoff of 120 kDa were modified by surface coating with a PVA aqueous solution followed by solid–vapor interfacial cross-linking with glutaraldehyde [39]. Fouling tests using a 5 mg/L protein solution showed that a short period of coating and cross-linking improved the antifouling performance. Additionally, after UF of the surface water with a total organic carbon of approximately 7 mg/L during 18 h, the flux of the modified membrane was twice as high as that of the unmodified membrane. The cake fouling layer could also be more easily removed from the PVA-modified membrane by alkaline cleaning. The improved fouling resistance of the modified membrane was related to an increase in membrane smoothness and hydrophilicity after coating with the PVA layer [282].

3.4.2. Development of Low-Fouling Polymer Membranes via Photoinitiated Grafting

Currently, UV-initiated graft polymerization has been widely used for the surface modification of polymer membranes in attempts to develop composite membranes with enhanced resistance toward organic fouling and biofouling. Different hydrophilic monomers, such as *N*-vinyl-2-pyrrolidone (NVP), *N*-vinyl-formamide (NVF), *N*-vinyl-caprolactam (NVC), 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AA), acrylamide (AAM), 2-acrylamidoglycolic acid (AAG), quaternized 2 (dimethylamino) ethyl methacrylate (gDMAEM), 2-acrylamido-methylpropane sulfonic acid (AMPS), 3-sulfopropyl methacrylate (SPMA), poly(ethylene glycol) (PEG), poly(ethylene glycol) methacrylate (PEGMA), d-gluconamidoethyl methacrylate (GAMA), [(methacryloylamino)propyl]-dimethyl (3-sulfopropyl) ammonium hydroxide inner salt (MPDSAH inner salt), 2,4-phenylenediamine (PDA), ethylene diamine (EDA), and poly(dimethylsiloxane) have been used for modification of the MF, UF, NF, and RO base membranes of various chemical natures. These include polyvinylidene fluoride (PVDF), polyethersulfone (PES), polysulfone (PS), polypropylene (PP), polyacrylonitrile (PAN), and polyethylene (PE). In general, modification of the membrane surface by UV-graft polymerization can be performed via “grafting-from” and “grafting-to” approaches.

In the case of the “grafting-to” method, preformed polymer chains, carrying reactive groups at the end or on the side chains, are covalently coupled to the surface [294]. The “grafting-to” procedure allows precise control of the grafted chain structure; however, because of a low density of grafted polymer chains [281], this method is seldom used for membrane modification. An example is functionalization of UF PAN membranes with low-molecular weight aromatic azide derivatives composed of different hydrophilic and hydrophobic components [295]. The separation characteristics and the protein fouling tendency were essentially changed depending on the type of functional groups introduced. This was explained by the increased hydrophilicity and the charge of the active membrane layer.

Compared with the “grafting-to” method, the “grafting-from” approach is widely used for the surface modification of various types of polymer membranes [44,296–318]. The majority of the studies have focused on antifouling modification of the UF and MF membranes, because a very high grafting density is required to use the grafted polymer layer as a selective barrier in RO. In general, membrane modification via the “grafting-from” approach may be realized with or without using a photoinitiator [270].

3.4.3. Miscellaneous Grafting Methods on the Membrane Surface

In contrast to UV-initiated graft polymerization, redox-initiated grafting gives the possibility of modifying the polymer membranes *in situ*, inside commercial wound membrane elements [319]. A redox system composed of potassium persulfate and potassium metabisulfite was used to generate the starting radicals for the graft polymerization of AA and other hydrophilic monomers on the surface of the CA membranes [320,321]. It was shown that despite the gradual decrease of the flux, the surface-modified membranes had a lower protein sorption and a better and more reversible flux recovery after cleaning.

A similar approach was used for the *in situ* preparation of the NF PES membranes containing hydrophilic functional groups such as SO₃H, COOH, or C(=O)NH₂ [45]. Testing the modified and unmodified membranes over a period of 30 days demonstrated that the surface-modified composite

membranes have better fouling resistance characteristics. In the case of the unmodified membranes, the flux decreased from 41.65 to 19.21 L/(m²·h), while for the surface-modified membranes under similar conditions, the flux reduced from 46.75 to 31.62 L/(m²·h). However, in the case of the NF PA membranes, it was observed that polymerization could take place inside the pores of the base support membrane as a result of the penetration of the monomer through the active layer, particularly for high degrees of grafting [322].

Gullinkala and Escobar [43] used porcine pancreatic lipase to catalyze the polycondensation of PEG to the surface of the CA membranes. The main advantage of this proposed “green” approach, based on catalytic polymerization, is a low degree of homopolymerization because the reaction occurs between the two functional groups present in the monomers and the membrane surface. The unmodified and the modified membranes displayed comparable initial flux values, flux decline curves, and rejections of dextran and BSA. This is suggested to be due to high hydrophilicity and the similar charge characteristics of both membrane samples. However, the flux recovery after UF of NOM followed by backwashing was quite different; the modified membrane regained nearly 97% of its initial flux value within 40 min of filtration, while the unmodified membrane recovered only 85%. A lower cake accumulation on the membrane surface was also found for modified membranes. These improvements are believed to be due to the high flexibility of the highly hydrophilic grafted PEG chains that prevents the membrane fouling. It should be noted, however, that the membrane modification via the proposed “green” approach takes rather a long time, about 50 h [282].

3.4.4. Patterned Membranes

Membranes with a patterned surface have become attractive for the mitigation of biofouling in membrane processes for water and wastewater treatment [46]. Won *et al.* [46] showed that a longer pattern height in a prism-patterned membrane reduced membrane biofouling because of the higher local shear stress near the apex of the prism pattern. To mitigate membrane fouling Won *et al.* [47] introduced a patterned morphology on the membrane surface using a lithographic method. Diverse patterned membranes, such as pyramid-, prism- and embossing-patterned membranes were prepared and compared with a flat sheet membrane in terms of morphology, permeability and biofouling. The patterned membrane surface augmented the water flux in proportion to the roughness factor of the patterned membrane. Deposition of microbial cells on the patterned membrane was significantly reduced compared to that on the flat sheet membrane in the membrane bioreactor used for wastewater treatment. Lee *et al.* [48] use a patterned surface to get over membrane fouling. In their experiments, they observed the local distribution of microbials; more fouling in the lower part of the pattern and less fouling in the upper region.

In order to mitigate thin film composite (TFC) membrane fouling, Maruf *et al.* [49] demonstrated, for the first time, a successful fabrication of a patterned TFC membrane. Compared with their non-patterned counterparts, the patterned TFC membranes demonstrated higher flux and rejection values when convection was present as a result of stirring. The results suggest that the surface patterns induced hydrodynamic secondary flows at the membrane feed interface which were effective in decreasing concentration polarization as well as in reducing scaling effects. Maruf *et al.* [50] also conducted systematic cross-flow filtration experiments of colloidal suspensions on UF membranes with sub-micron

surface patterns. The results showed that the presence of surface patterns increased the critical flux associated with filtration of colloidal feed solutions. The origin of this enhanced anti-fouling behavior was attributed to enhanced shear-induced diffusion whereby the presence of sub-micron surface patterns increased the effective shear rate near the membrane surface.

Although optimization has yet to be achieved, current studies provide important perspective regarding the promise of surface patterning as an effective method for fouling mitigation, indicating that it can be employed as an effective approach to fouling mitigation in membrane bioreactors as well.

3.4.5. Plasma Treatment of Polymer Membranes

Over the last two decades, the plasma treatment of the polymer membranes has been intensively studied in attempts to increase the hydrophilicity and induce low-fouling properties for membrane surfaces [51,52,54,323–342]. Usually, plasma treatment of the membranes can be carried out in three different modes: (i) with non-polymerizable gas molecules; (ii) with polymerizable vapors; and (iii) with plasma-induced grafting of the polymer chains to the membrane surface, where the plasma treatment with non-polymerizable gases and plasma-induced grafting are the most widely used [282].

3.4.6. Chemical Reactions on the Membrane Surface for Fouling Reduction

As discussed above, the introduction of charged groups on the membrane surface is a useful approach to reduce membrane fouling with charged organic compounds. In this context, various chemical reactions may be used for creating different functional groups, such as $-\text{SO}_3$ [343] or $-\text{CO}_2\text{H}$ [344,345], on the membrane surface. The quantity of the introduced functional groups and the thickness of the modified surface layer depend on the treatment time, temperature, and concentration of the modification agent.

For example, during the prolonged exposure of the PAN membrane to 1 M NaOH, the surface nitrile groups turned into carboxylic groups [345]. The modified membranes were less prone to fouling with BSA with a reduction in the average pore diameter of about 80% for the untreated membranes and 20% for the surface-modified membranes.

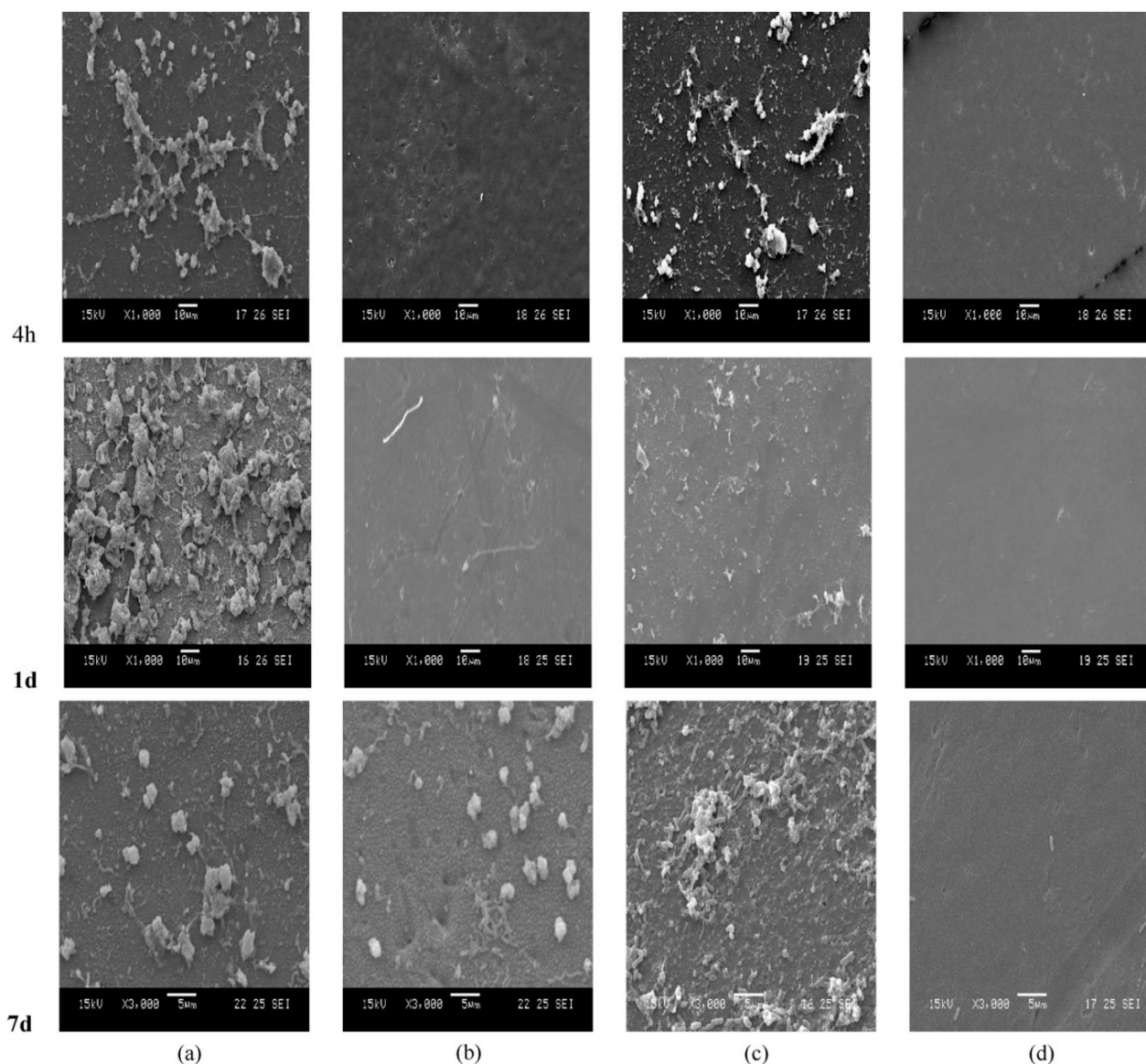
The blend UF PES/PAN membranes treated with aqueous NaOH solutions at room temperature for 24 h showed higher flux recovery ratios compared with the unmodified membranes after the UF of the PEG, dextran and PSS solutions. The increase in the fouling resistance is believed to be due to the higher hydrophilicity of the modified-membrane surface [55].

To improve the performance of the DS5DL (Osmonics) NF membrane, it was immersed for 14 days in 1% w/v hydrofluoric acid (HF). Such a prepared membrane was used for the purification of industrial phosphoric acid (8 M) and for the removal of Na_2SO_4 from industrial wastewater. In both cases, the treated membrane showed an increase in flux and an improvement in the rejection of impurities as compared with the base membrane. The additional advantage was a reduced membrane fouling after treatment with HF [56]. On the other hand, it was shown that despite the modification of many membrane characteristics, such as charge, hydrophilicity, porosity, and pore size, by hydrolysis and oxidation of the CA membrane, neither treatment prevented HA adsorption on the modified membranes [346].

Liu *et al.* [347] modified blended chitosan (CS)/CA membranes via surface treatment with heparin or a quaternary ammonium to change the hydrophilicity and the membrane charge or via a reaction with AgNO_3 to introduce a biocide on the membranes. The reaction of the heparin with the CS/CA base

membrane was through the formation of a polycations-polyanion complex, where the $-\text{CH}_2\text{SO}_3^-$ and $-\text{NHSO}_3^-$ groups in the heparin interacted with the $-\text{NH}_3^+$ groups in the CS (CS/CA-H membranes). The attachment of quaternary ammonium to the base membrane was realized via both the $-\text{CH}_2\text{OH}$ and the $-\text{NH}_2$ positions on the CS polymer chains (CS/CA-QN). Silver ions were loaded onto the membrane through surface complexation with the amine groups in CS and through physical adsorption (CS/CA-Ag or CS/CA-H/Ag membranes). It was shown that membranes modified with heparin or the quaternary ammonium became much more hydrophilic, with a water contact angle for CS/CA-H of 42.3° and that for CS/CA-QN of 39.8° , compared with 69.6° for that of the base CS/CA membrane. The ζ -potential of the CS/CA membrane was relatively small, while the CS/CA-H membrane had negative ζ -potentials at around -10 mV and the CS/CA-Ag membrane had positive ζ potentials at about $+12$ mV.

Figure 5. Bacterial adhesion and growth on the (a) chitosan/cellulose acetate (CS/CA); (b) chitosan/cellulose acetate-heparin (CS/CA-H); (c) chitosan/cellulose acetate-silver (CS/CA-Ag) and (d) chitosan/cellulose acetate-heparin/silver (CS/CA-H/Ag) membranes after immersion in an activated sludge bioreactor for a period of up to 7 days. Reproduced with permission from Reference [347]. Copyright 2010 Elsevier.



As can be seen in Figure 5, the CS/CA and CS/CA-Ag membranes had large numbers of bacterial cells on the surfaces, in contrast to the CS/CA-H and CS/CA-H/Ag membranes, after immersion in an activated sludge bioreactor for several periods of time. The high hydrophobicity of the CS/CA membrane and the strong attractive electrochemical interactions between the CS/CA-Ag membrane and the bacteria probably promoted and contributed significantly to the adhesion of the bacterial cells on these membrane surfaces. After 1 week of immersion, a number of bacterial flocs were also observed on the surface of the CS/CA-H membrane. Some of the initially adhered bacteria, even though at a very small number, may eventually grow and develop into the observed bacteria films because the membrane did not have an antibacterial function. However, the CS/CA-H/Ag membrane was still very clean after 1 week. Even if a small number of bacteria adhered on the surface, they were killed by the loaded silver ions, so could not grow on this membrane. Thus, the best performance for minimizing biofouling has been realized when the highly effective anti-adhesion function of the CS/CA-H membrane was supplemented by the antibacterial properties of the CS/CA-H/Ag membrane [282].

3.4.7. Surface Modification with Nanoparticles

The use of nanoparticles in preparing and modifying polymeric membranes has received much attention during the last few years in the attempts to enhance flux and reduce fouling [57–80,348–353]. Two different methods are used for preparing nanoparticle-based membranes. One is the deposition of the nanoparticles on the membrane surface via dipping the porous support in an aqueous suspension of nanoparticles [350]. The other is the entrapment of the nanoparticles in a polymer matrix via a phase inversion method by the addition of the nanoparticles to a casting solution [64,70].

3.4.7.1. Membrane Modification with Deposited Nanoparticles

Kwak *et al.* [349] performed one of the first studies in this field. TiO₂ nanoparticles of approximate size of 2 nm were immobilized via self-assembly with the terminal functional groups on the surface of the RO PA membrane. X-ray photoelectron spectroscopy demonstrated quantitatively that TiO₂ particles were tightly self assembled with a sufficient bonding strength to the membrane, which meant that particles could withstand various washing procedures and RO operating conditions. The self-assembly mechanism of fixing TiO₂ on the membrane surface with COOH functional groups may include bonding with the two oxygen atoms of the carboxylate group via a bidentate coordination to Ti⁴⁺ cations or through the formation of a hydrogen bond between a carbonyl group and the surface hydroxyl group of TiO₂ [350].

The self-assembly procedure was also used by Bae *et al.* [60] for modifying sulfonated PES membranes and by Mansourpanah *et al.* [68] for coating PES/PI blend membrane and the OH functionalized PES/PI membrane with TiO₂ nanoparticles. Luo *et al.* [58] also applied a similar approach to the deposition of TiO₂ nanoparticles onto the PES membranes. For the PES membranes, self-assembly can be due to the coordination of the sulfone group and the ether bond to Ti⁴⁺, or by a hydrogen bond between the sulfone group and the ether bond and a surface hydroxyl group of TiO₂ due to the strong electronegativity of oxygen in the ether bond and the sulfone group of the PES.

The self-assembly of the TiO₂ nanoparticles on a membrane surface is usually realized by dipping the porous membrane support in a colloidal suspension of TiO₂. The concentration of the aqueous colloidal suspension of TiO₂ may vary from 0.01 through 0.03 wt% [68] to 1 wt% [58,64], while the time of immersion

of the porous supports in the suspension was suggested to be 1 min [60], 1 h [58], and 1 week [65]. Rahimpour *et al.* [67] studied the effect of dipping time in a 0.03 wt% TiO₂ colloidal suspension by comparing 15, 30, and 60 min of dipping. They concluded that a 15 min immersion yielded the best performance in terms of permeability and hypothesized that longer dipping times led to more pore plugging.

Lee *et al.* [61] applied an *in situ* interfacial polymerization procedure on the PES support for preparing composite nanoparticle-based membranes. In this procedure, commercial TiO₂ nanoparticles of 30 nm were dispersed in an organic trimesoyl chloride (TMC) solution. The PES support was first immersed in aqueous *m*-phenyl diamine with 0.05 wt% NaOH; the excess reagent was removed from the surface so that a controlled reaction was obtained on subsequent immersion in the solution of TMC in 1,1-dichloro-1-fluoroethane. As a result, a thin modified layer with immobilized nanoparticles was obtained on the surface of the PES support.

Bae and Tak [118] prepared two types of TiO₂-immobilized UF membranes (TiO₂ entrapped and deposited) and applied them to an activated sludge filtration, to evaluate their fouling mitigation effect. It was shown that the entrapment of the TiO₂ nanoparticles in the membranes increased the hydrophilicity of their surfaces. The water contact angles were changed from 87.6° for neat PS to 73.1° for PS-TiO₂, from 86.7° for PVDF to 81.1° for PVDF-TiO₂, and from 45° for PAN to 43.1° for PAN-TiO₂ membranes. Such hydrophilization leads to a reduction in membrane fouling during the filtration of activated sludge, which contains a great number of different organic and microbiological foulants. The TiO₂-entrapped membrane showed a lower flux decline than the neat PS membrane. On the other hand, the TiO₂-deposited membrane showed a greater fouling mitigation effect compared with that of the TiO₂-entrapped membrane. Obviously, the degree of fouling mitigation is mainly affected by the surface area of the TiO₂ nanoparticles, which are located on the membrane surface and are exposed to feed solution. In the case of the TiO₂-deposited membrane, the degree of surface modification was higher than that for the TiO₂-entrapped membrane, and the fouling mitigation effect significantly improved. The cake layer resistance of the modified membrane, which is a major influence on membrane fouling during the filtration of the activated sludge, was dramatically decreased compared with that of the initial PES membrane [60]. As the introduction of nanoparticles increases the hydrophilicity of the polymeric membrane surfaces, the adsorbed foulants on the modified membranes can be more readily dislodged by shear force than those on the unmodified PES membranes. As a result, the hydrophilic modification of the membrane surface by the introduction of the TiO₂ nanoparticles inhibits the hydrophobic interactions between the organic foulants and the membrane surface. The increased hydrophilicity of the PES and PVDF membranes modified with TiO₂ results in improved permeability and antifouling ability compared with virgin membranes during filtration of the PEG-500 and BSA solutions, respectively [64,65].

It has been demonstrated that the antifouling potential of the TiO₂-modified membranes is much better realized with the application of UV irradiation [68]. Rahimpour *et al.* [67] compared TiO₂-entrapped PES membranes and self assembled TiO₂-coated membranes with and without UV irradiation during filtration of non-skim milk. The initial pure water flux and the milk water permeation of the TiO₂-entrapped membranes were low compared with the unmodified PES membrane. However, the antifouling property and the long-term flux stability were significantly enhanced. UV illumination further improved the membrane performance and antifouling properties, and the UV-irradiated TiO₂-deposited membranes had increased flux and higher antifouling properties compared with the TiO₂-entrapped membranes.

The authors believed that the membranes with TiO₂ nanoparticles on their surface and radiated by UV light obtained two main characteristics, namely, photocatalytic properties to decompose the organic compounds adsorbed on the membrane surface and superhydrophilicity that results in a decrease in the contact angle [67]. Therefore, foulants such as fats and proteins may be decomposed by photocatalysis and then removed from the surface by the feed flow. Furthermore, with the increase in the membrane hydrophilicity, there is a competition between the adsorption of water and the foulant molecules, which leads to improved removal of the pollutants from the membrane surface. The photocatalytic properties and enhanced hydrophilicity of the TiO₂-modified NF PES/polyimide (PI) blend membrane and the OH⁻ functionalized PES/PI blend membranes meant that they were also less fouled with BSA solutions [68].

Al₂O₃ nanoparticles have also been used for reducing the organic fouling of polymeric membranes. Al₂O₃-PVDF UF membranes have been applied to the oil-wastewater treatment [53]. The modified membranes had an improved antifouling performance, and the flux recovery for these membranes reached up to 100% after washing with a 0.1% solution of OP-10 surfactant. The authors suggested that this is a result of hydrophilicity, with significantly decreased contact angles for the modified membranes.

The photocatalytic bactericidal effect of the composite membranes with the deposited TiO₂ was examined by determining the survival ratios of *E. coli* [350] and *Pseudomonas putida* cells [66] with and without black UV illumination. A sharp drop in the number of *P. putida* cells on the membrane surface with the deposited TiO₂ particles was found after UV irradiation. The mechanism of the bactericidal action of TiO₂ under black UV light is based on the formation of OH[•], O₂^{-•}, and HO₂[•] radicals in water. The adhesion of the bacterial cells to the TiO₂ particles controlled by the hydrophobic and charge interactions allows the active oxygen-containing species to reach and damage the bacterial cell wall. Due to the strong photobactericidal properties under UV treatment, the modified membranes are capable of inhibiting the growth of microorganisms on their surface and thus membrane biofouling is reduced. This reduction in biofouling was demonstrated when the membranes were used for surface water treatment as the fluxes of the modified membranes were 1.7–2.3 times higher compared with those for the control samples [66].

Membrane biofouling may also be reduced via surface membrane modification with Ag nanoparticles. Silver-loading PAN hollow fibers were prepared via the dry jet–wet spinning technique from a dope containing 0.5 wt% silver nitrate [351]. It was shown that at an Ag loading of 0.1 wt%, bacterial growth for both *E. coli* and *Staphylococcus aureus* was not observed on the membrane surface. The antibacterial activity of the modified membrane is attributed to trace amounts of silver ions released from the fiber [348]. The interaction between the silver ions and the bacteria can change the metabolic activity of the bacteria and prohibit the growth of bacteria. However, after flushing with water for 60 days, the silver content in the hollow fibers decreased from 0.19 to 0.1 wt%, while still keeping the antibacterial activity of *E. coli* and *S. aureus*. During the membrane process operation, the permeating water reduces the silver content of the hollow fibers, thus requiring periodical replenish.

A dramatic effect on *Pseudomonas* fouling was observed when the silver nanoparticles were immobilized on a thin-film composite PA membrane [62]. SEM measurements confirmed that all *Pseudomonas* cells were made inactive on the modified-membrane surface, while water fluxes and salt rejections remained unchanged. High antibacterial activity toward *E. coli* and *S. aureus* was also found with CA membranes modified with Ag nanoparticles [353]. However, a significant loss of silver was found as a result of water permeation, and the antibacterial activity of the membranes disappeared after

5 days [57]. The loss of the entrapped silver nanoparticles was also reported for modified PS membranes, which have a high antimicrobial activity toward *E. coli*, *P. mendocina*, and the MS2 bacteriophage [69].

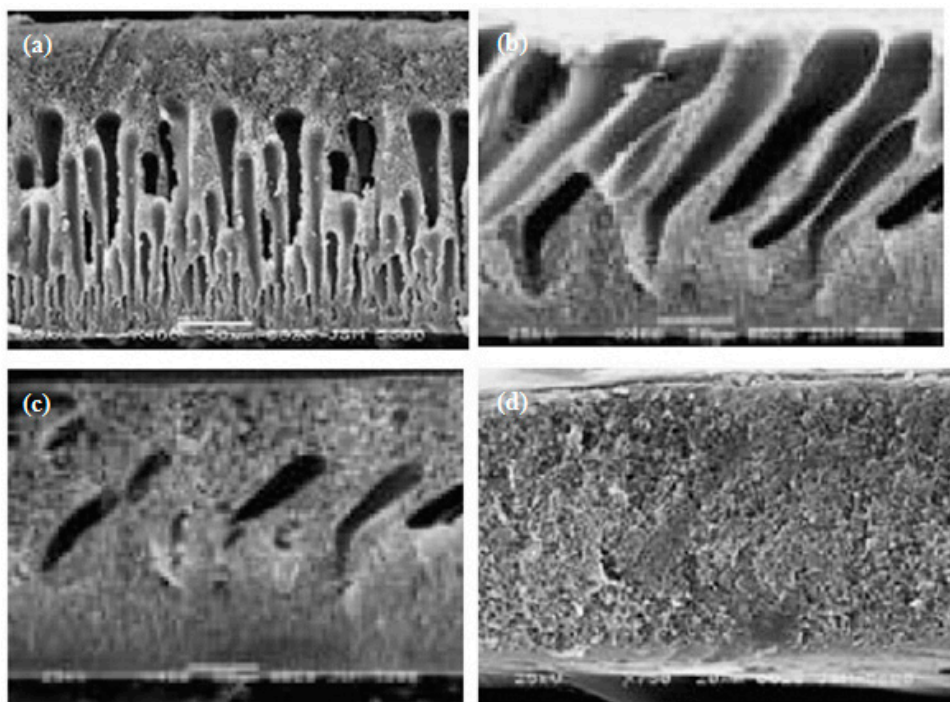
3.4.7.2. Phase Inversion Method

Phase inversion can be described as a demixing process whereby the initially homogeneous polymer solution is transformed in a controlled manner from a liquid to a solid state [71]. The use of inorganic nanoparticles as additives to polymeric membranes has begun to attract wide interest due to the improved membrane properties, including increased strength and modulus, which result from the strong interfacial interactions the nanoparticles have with the surrounding polymer matrix [72]. A comprehensive review on polymeric membranes incorporated with metal/metal oxide nanoparticles has been published recently by Ng *et al.* [73].

Zodrow *et al.* [52] prepared polysulfone membrane contained Ag nanoparticles (1–70 nm) via the phase-inversion process by dispersing nanoparticles in the casting solution. It was shown that polysulfone membranes impregnated with 0.9 wt% Ag nanoparticles possess similar permeability and surface charges compared with pure polysulfone membranes, however they were significantly more hydrophilic with 10% reduction in contact angle. It was found that the addition of Ag nanoparticles does not visibly alter the membrane structure. Similar results were obtained by Yan *et al.* [74], which used nano-sized Al₂O₃ particles in dimethylacetamide casting solutions for preparation of PVDF membranes. It was found that increased Al₂O₃ concentrations from 0 to 2% in the casting solution had led to increased water permeate fluxes due to an increase in the membrane hydrophilicity. SEM images showed that the addition of nano-sized Al₂O₃ particles did not affect the surface, cross-section, and inner pore membrane structures. Both pure PVDF and PVDF-Al₂O₃ membranes showed typical asymmetric morphology with finger-like pores.

On the other hand, Yang *et al.* [75] showed that the addition of TiO₂ nanoparticles has a large effect on the membrane structure of TiO₂/PS membranes casted from 18 wt% PS solution in *N,N'*-dimethylacetamide with *N*-methyl-2-pyrrolidinone. The cross-section morphologies of membranes are shown in Figure 6, which illustrates that the macrovoids grow and become run through at low TiO₂ concentrations and then are suppressed or disappear at higher additive dosages (≥ 3 wt%), the thickness of skin layer increases with the increase of TiO₂ dosage. Figure 6a–c shows a log-normal pore size distributions for the membranes with TiO₂ content of 1–2 wt% and the number of small pores increases compared with the PSF membrane without nanoparticles. While adding more TiO₂ ($\geq 3\%$) to the casting solution enhances the formation of larger pores (50070 nm) caused by the nanoparticle aggregate phenomenon, which leads to a bimodal pore distribution (Figure 6d). The mean pore radius of the membrane with 1–2 wt% TiO₂ content decreased and then increased at higher TiO₂ content due to the presence of large pores. These results demonstrate that adding appropriate TiO₂ nanoparticles to PS matrix can improve its porosity and increase the number of small pores. As a result, the flux through such membranes can be increased significantly. It was also shown that the addition of TiO₂ nanoparticles causes the decrease of contact angle from 85° for pure PS membrane to 41–52° for TiO₂/PS membranes, indicating that TiO₂ addition enhances the hydrophilicity of membrane as a few of hydrophilic TiO₂ nanoparticles adsorb and stick on the membrane surface [76].

Figure 6. SEM (nanoscale) images of the morphology of PS/TiO₂ membranes with (a) 0 wt% TiO₂; (b) 1 wt% TiO₂; (c) 3 wt% TiO₂ and (d) 5 wt% TiO₂. Reproduced with permission from Reference [73]. Copyright 2013 Elsevier.



Vatanpour *et al.* [77] prepared flat sheet asymmetric amine-functionalized multiwalled carbon nanotubes (NH₂-MWCNTs)/polyether-sulfone (PES) nanocomposite nanofiltration membranes with different nanofiller contents by the phase inversion method and evaluated the performance of the membranes in terms of pure water flux, static protein adsorption and bovine serum albumin (BSA) filtration. Antifouling experiments using BSA filtration showed that the three parameters hydrophilicity, surface charge and surface roughness together determine the antifouling properties of the membranes. The best antifouling membrane against protein fouling should have higher hydrophilicity, more negative surface charge and lower roughness. Results also showed that the hydrophilicity and pure water flux of the nanocomposite membranes were enhanced with increase of NH₂-MWCNTs dosages.

Jafarzadeh and Yegani [78] fabricated high density polyethylene membranes embedded with TiO₂ nanoparticles via thermally induced phase separation (TIPS) method. The fouling behavior of membranes was investigated by filtration of collagen protein solution the results of pure water flux test showed that incorporation of TiO₂ into polymer matrix improved water flux of polyethylene membranes.

Lin *et al.* [79] manufactured blended PES-WS₂ flat sheet membranes with the incorporation of ultra-low concentrations of nanoparticles (from 0.025% to 0.25%, WS₂/PES ratio) and investigated them in terms of permeability, fouling resistance and solute rejection. The incorporation of nanoparticles at ultra-low concentrations in the membrane had a determining influence on the characteristics and filtration performance of the modified membrane. Remarkably, a significant enhancement in the permeability was observed as a result of the incorporation of ultra-low fractions of nano-WS₂ to the membrane structure. The optimum permeability values were obtained for modified membranes with 0.075%–0.10% nanoparticle/polymer concentration ratios. In general, fouling resistance and solute rejection were

significantly enhanced by the incorporation of nanoparticles into the membrane structure. Specifically, fouling resistance increased by around 50%.

Vatanpour *et al.* [80] investigated the effect of types and sizes of TiO₂ on the morphology, performance and fouling control of nanofillers embedded membranes. The anti-biofouling performance of the membranes fouled by whey solution was investigated by measuring fouling resistance parameters. The biofouling of the membranes resulted from whey filtration was decreased by embedding TiO₂ nanofillers. At low TiO₂ concentration, the nanoparticles with small size caused more biofouling reduction due to the fact that the aggregation of the nanoparticles was not prominent at low amount.

It should be mentioned however, that one of the limiting factors for incorporation of nanoparticles into polymeric membranes is high aggregation of nanoparticles that results in a low dispensability in the casting solution. Also, careful control and monitoring of the nanoparticles released from the modified membranes are necessary to minimize potential (eco) toxicity effects [76].

In general, it may be concluded that despite the endeavor described earlier to develop low-fouling membranes via surface modification with nanoparticles, further research is still needed to investigate the combined effects of the water chemistry, the nature of the nanoparticles, and the coating conditions on the modified membrane performance and fouling mitigation. Also, careful control and monitoring of the nanoparticles released from the modified membranes are necessary to minimize potential environment (eco) toxicity effects [282,354].

4. Conclusions

Due to their unique advantages like good effluent quality, high possible biomass concentration, low space requirements and reduced footprint, membrane bioreactors have become the state of the art in wastewater treatment and are becoming increasingly popular. These advantages, with the more stringent discharge standards, steady decrease of membrane cost and increased water reclamation needs, have given remarkable impetus to the extensive research and applications of MBR for biological wastewater treatment. Notwithstanding the significant progress of MBR technology, membrane fouling remains the primary hindrance for its universal and large scale applications. Membrane fouling would reduce system productivity, increase the energy requirement for gas scouring and frequency of cleaning which might shorten the membrane lifespan and result in higher replacement costs. Therefore, there is great interest in investigating the causes, characteristics, mechanisms and control measures of membrane fouling in MBRs.

This review attempted to address the recent and current developments in MBRs on the basis of reported literature in order to provide more detailed information about the fouling mechanisms in MBRs and the most frequently applied preventive-control strategies. In this paper, the fouling behavior, fouling factors and fouling stages were discussed. An important part of the current work refers to EPS, biological substances which largely determine properties of sludge flocs, including hydrophobicity, adhesion, flocculation, settling and dewatering properties, and therefore significantly affect membrane fouling in membrane bioreactors (MBRs). Recent developments in fouling prevention and control strategies, such as feed pre-treatment, physical and chemical cleaning, flux reduction, aeration increase, chemical or biochemical modification of the mixed liquor, application of ultrasound, electric field and ozone and membrane surface modification, were also reviewed.

In order to further reduce fouling in MBRs and address the existing obstacles, the future researches maybe should focus on the following aspects:

- New aeration systems
- New cleaning/fouling mitigation methods
- Emerging technologies (forward osmosis MBRs) Finally, the basic question “*What should be the focus of research moving forward?*”
- Will further research in the mechanisms of fouling shed some light in the efficient operation of MBRs?
- Or should research move to more macroscopic approaches such as mathematical modelling based on empirical relationships?

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Author Contributions

Petros K. Gkotsis wrote the biggest part of the paper, Efrosini N. Peleka and Anastasios I. Zouboulis contributed to the article in some crucial parts and reviewed the paper, while Petros E. Samaras and Dimitra Ch. Banti introduced Extracellular Polymeric Substances (EPS).

Conflicts of Interest

The authors declare no conflict of interest.

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