Strategies for controlling biofouling in membrane filtration systems: challenges and opportunities†

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Biofouling is a critical problem in many membrane filtration processes. This review highlights the emerging strategies for polymer membrane modifications using organic and inorganic additives and surface modification to mitigate foulant deposition and biofilm formation. Constraints and opportunities for future implementation in membrane systems are outlined from the perspectives of water and wastewater treatment applications.

1. Introduction

Increasing global need for water and wastewater treatment has driven the widespread development of large-scale membrane filtration processes. Higher quality as well as supply and environmental demands have made microfiltration (MF) and ultrafiltration (UF) membranes attractive processes to complement or replace conventional filtration and sedimentation processes to remove particulate and organic matter. They are also now being integrated into membrane bioreactor (MBR) applications to replace activated sludge processes for wastewaters. Municipal reverse osmosis (RO) plants have also expanded rapidly and MF and UF pre-treatment of brackish or seawater are now being actively considered as a replacement for conventional granulated or sand filters. Nanofiltration (NF) has grown to a lesser extent but still plays an important role in removing industrial and domestic pollutants such as recalcitrant humics, organics and dye effluents.

However, the decrease of permeate flux or irreversible membrane fouling is recognized as the main problem in the application of membrane filtration technologies. Several types of membrane fouling have been introduced including inorganic fouling or scaling, colloidal fouling, organic fouling, and biofouling.[1–3] Among them, the formation of biofilms on the membrane surfaces or membrane biofouling has been regarded as the most serious problem.[4–8] Biofouling is a pervasive problem in materials design for applications ranging from biomedical devices to ship hulls to water treatment processes. For membrane systems, biofouling has severe impacts not only on the performance in terms of flux and separation but also on the lifetime of membrane

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filters and modules. Autopsy studies of nanofiltration and reverse osmosis membranes fouled during the treatment of surface water and wastewaters have shown that more than 50% of the dry weight of the fouling layers is biological in origin.[9,10] Biofouling refers to the deposition, growth and metabolism of bacteria cells or flocs on the membranes.[11,12] There are several distinct phases in the development of a bacterial biofilm. In the first stage single cells associate loosely with the surface which is usually covered by a conditioning film of proteins or macromolecules. They can move across the surface and in some cases masses of them actually swarm out in a co-ordinated waves. This stage can take place in seconds. In the second stage there is irreversible attachment (on a time scale of seconds to minutes) as the cells express exo-polymers that bind to the surface. Over subsequent hours and days cell proliferation in specific areas leads to structures called microcolonies which can dominate a mature biofilm. In the final stage there can be dissolution of the centre of microcolonies which may occur over days and months. Cells can disperse and leave behind remnant structures (Fig. 1).

For example, in MBRs most foulants (microbial flocs) are much larger than the membrane pore size. Biofouling may start with the deposition of individual cells or cell clusters on the membrane surface, after which the cells multiply and form a biofilm.

Micro-organisms actively colonize membranes using a broad range of behaviors that can be categorized into a series of defined stages that include: reversible and irreversible attachment (mostly electrokinetic and hydrophobic interaction), movement of reversibly attached cells across the surface and initiation of microcolony formation, maturation, differentiation and finally biofilm dissolution and dispersal (Fig. 1).[14] Movement of bioflocs across the membrane surface by rolling and sliding has been visualized.[15–18]

Compared to smooth nonporous surfaces, membrane biofouling is a much more complicated process and is affected by many factors, including operating conditions such as shear and pressure, some characteristics of the bacteria themselves, the membrane surface, and environmental factors such as pH, ionic strength, and ion species.[19,20] Most polymeric membranes are made from hydrophobic-based materials and therefore are more adherent to non-polar solutes, hydrophobic particles or bacteria.
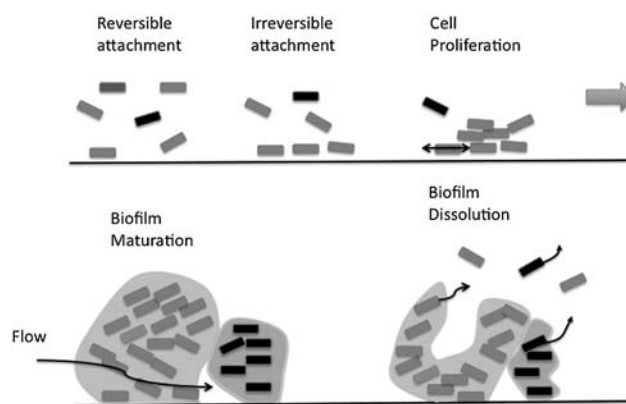

Fig. 1 Stages in the formation of biofilms (redrawn from reference 13).

Unlike other sources of fouling, biofouling cannot always be substantially reduced by pretreatment of the feed. This is because of the self-replicating nature of biofouling organisms. Any form of sterilization that is less than 100% effective will leave some cells alive and able to reproduce; the remains of dead bacteria provide an ample food source. Materials associated with biofouling include proteins, carbohydrates, cells, and biofilms, which can colonize the membrane surface. Initially, there is often the deposition of a conditioning film of organic molecules. This is followed by bacterial colonization, and subsequently by other microfouling such as microalgae and fungi. These organisms produce extracellular polymeric secretions (EPS) comprising polysaccharides, proteins, glycoproteins, lipoproteins and other biomacromolecules. As the biofilm matures, new species enter and additional organic and inorganic debris is incorporated. It is important to note that the composition of the foulant layer and the microbial community on the membrane may be very different from that in the suspended biomass.[21–23] Metzger et al. showed that the distribution of proteins and carbohydrates in membranes used in bioreactors varied between external and internal fouling as well as operating conditions.[23] The EPS matrix is held together by multiple noncovalent interactions, which must be disrupted in order to remove the biofilm. It is not sufficient simply to kill the bacteria by application of a biocide, as the biofilm will remain and provide a ready home for new bacterial colonization.[5] Additionally, the EPS matrix provides some protection from antibacterial agents, rendering microorganisms embedded in biofilms more difficult to kill.[24] Finally, microbial communities are adaptive. Thus environmental pressures (such as chemical or physical stress) will eventually select for organisms that can tolerate those condition to colonize the surfaces.

Once the surface has become coated in a layer of foulants, subsequent buildup of fouling depends largely on the interaction between the fouled surface and suspended foulant. If the suspension is thermodynamically stable, no further absorption will occur, resulting in a relatively small decrease to a stable flux. If, on the other hand, the suspension is unstable, additional layers of fouling will build up, and a sustained decline in flux is observed.[25]

Process parameters such as the permeate flux, pH, temperature[26,27] and ionic strength also have a large effect on fouling

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behavior.[28–31] Organic macromolecule solutions show limiting flux behavior, such that fluxes greater than the limiting flux rapidly decline to the limiting flux, while lower initial fluxes are unaffected.[32] Changes in pH, temperature, ionic strength and the concentrations of divalent cations (*e.g.* calcium and magnesium) affect the extent of protein fouling on reverse osmosis membranes.[28] Goosen *et al.*[33] and Chen *et al.*[21] have recently reviewed the literature dealing with bacterial growth on RO and MF membranes, techniques for measurement of fouling and pretreatment of feed to reduce fouling.

The depositions form a hydraulic resistance on the membrane surface that reduces flux or throughput as well as changing the porosity and pore size distribution on the membrane surface. In membrane filtration systems, convective transport (commonly on the order of 20 L m^{-2} h to 200 L m^{-2} h) and the concentration polarization provides additional driving force for deposition of macromolecules and cells as well as providing a steady supply of nutrients to the surface to grow the biofilms. In addition to the hydraulic resistance provided by the biofouling layers to liquid transport through the membranes, more severe impacts can be caused by the buildup of a stagnant liquid layer on the membrane surface that can enhance concentration polarization by reducing back transport of soluble components such as salts. The presence of a biofilm hinders back diffusion of salt ions and alters the crossflow hydrodynamics, resulting in enhanced concentration polarization and osmotic pressure.[34]

This can result in both flux loss due to increased osmotic pressure and loss of selectivity as demonstrated by Herzberg and Elimelech who inoculated *Pseudomonas aeruginosa* bacteria into a reverse osmosis filtration system.[35] They also showed a further polarization due to the presence of extracellular polymeric substances (EPS) due to biofilm growth. The complex matrix of the biofilms can also help entrap inorganic ions and precipitates. On the other hand, Vrouwenvelder and colleagues suggested that the more severe impacts of biofouling result from the narrowing and plugging of narrow channels of spiral wound membranes initiated by biofilm formation from the turbulence promoting spacers.[36] Biomass accumulation in the feed channel can cause a severe increase in pressure drop within the module, reducing the driving force for separation. Biofilms can grow to a thickness of up to 1 mm, blocking membrane channels and causing differential pressures in excess of 7 bar across multi-element pressure vessels, compared to 1.5 bar for clean elements.[37] Extreme cases may result in destruction of the membrane module due to displacement of the membrane sheets and breach of the membrane module (Fig. 2 and 3). The membrane lifetime depends on the application: in sea water desalination plants, membranes typically last for 4–5 years and are cleaned during normal plant maintenance procedures while in the dairy industry heavy biofouling necessitates daily cleaning and membranes last for only 3 years.[38]

There are three major strategies commonly used to control biofouling in membrane processes:

1. biocide dosing (continuous or intermittent),

2. optimization of operating conditions including pre-treatment of feed to reduce nutrient availability and cleaning procedures (chemical and physical),

3. new membrane development or modification of existing membranes to make them less prone to biofouling.
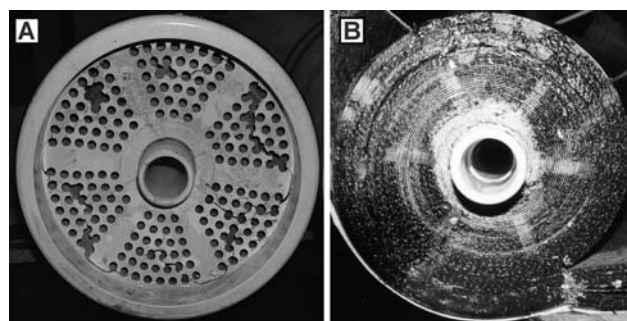

Fig. 2 Damage to module end cap due to biofouling in feed spacer channel of spiral wound membranes (photo courtesy of J. Vrouwenvelder).

While there is commonality between many of the approaches taken to control biofouling in biomedical and nautical applications, membrane filtration systems pose particular challenges due not only to the architecture of the membranes (pore size, surface roughness, porosity, *etc.*) and modules (complex distribution in spiral wound membrane modules) but also to the chemical and hydrodynamic environment in which they must perform. These important constraints include:

- hydraulic resistance,
- separation performance,
- mechanical stability,
- chemical stability,
- cost and flexibility of assembly.

Ultrafiltration and microfiltration membranes have porous submicron and nanometre structures that cannot be excessively compromised by coatings or surface modifications. The separation performances of reverse osmosis membranes are sensitive to subtle changes in interfacial chemistry and nanopore structures. Due to the convective flow through membranes, the effects of fluid hydrodynamics of membrane systems are intimately intertwined with their performance thus subtle changes in pore or surface morphology can strongly affect fouling performance and make it difficult to distinguish between the effects of surface chemistry and pore morphology/porosity.
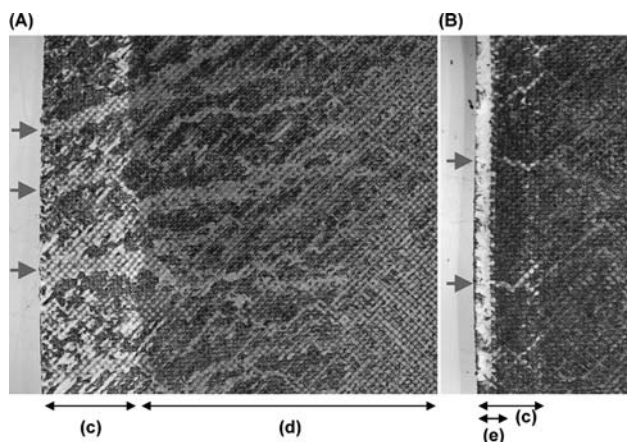

Fig. 3 Severe biofouling in spiral wound membrane flow channels (photo courtesy of J. Vrouwenvelder).

In addition, many water treatment and filtration processes frequently require exposure to aggressive hydrodynamic/physical and chemical cleaning. These may involve aeration of feed solution, backwashing (reversing permeate flow for short bursts to backflush the pores), high tangential shear, and highly turbulent flow to control the deposition of particulates and other solutes on the membrane surface. Chemical cleaning protocols involve intermittent exposure to high concentrations of alkali/acidic/chlorinated solutions as well as continuous dosing of hypochlorite and other oxidizing chemicals in some cases. Typical chemical cleaning involves a combination of alkali cleaning at 0.1 M, acid cleaning to remove scaling, and hypochlorite treatment (0.01 to 0.5%).[39] The frequency and aggressiveness of such cleaning depend on fluxes, membrane transport mechanisms, surface chemistry, and feedwater composition. In food and biotechnology processes, sanitation and sterilization impose additional chemical stability issues.

If aggressive cleaning procedures are required to remove the fouling, this causes further damage to the membrane, shortening its operating life. Due to better module manufacturing, the expected lifetime of membrane filtration units now ranges from 3 years to 10 years depending on cleaning frequency and mechanical stability. Thus endurance of chemical modification or new materials needs to be considered for much longer periods than is usual for biomedical or marine biofouling applications. While the chemical or mechanical robustness requirements may be mitigated or eliminated by new low-biofouling surfaces, water treatment and other membrane operators are cautious about adopting new materials that cannot withstand these rigors. Finally filtration systems such as desalination plants are now large scale facilities, and cost and footprint issues mean that material design must allow assembly into relatively low cost, high surface area modules. Thus from a material design or modification perspective, these constraints need to be taken into consideration.

In this paper, the material design approaches used to control biofouling in membrane filtration systems are reviewed in terms of strategies, challenges, and potential new directions. This review will focus on techniques for reducing fouling by modifying the surface properties of the microporous and dense film filtration membranes, either by application of a coating or by changing the chemistry of the discriminating (separation) layer itself. While there are a large number of polymers and inorganic materials which may be used to form membranes, the vast majority of commercial membranes are limited to a small number of polymeric materials due to the mechanical and chemical stability constraints indicated earlier. As a result these membrane materials are relatively chemically inert and frequently form intrinsically hydrophobic or somewhat hydrophobic substrates which must be modified to allow both wetting of the pores and reduction in fouling propensity. While modifications have been extensively studied, broad-spectrum biofouling control remains elusive.

The main general approaches to control biofouling in terms of material design can be divided into "anti-adhesion" approaches to reduce initial macromolecular adsorption or attachment of organisms and "antimicrobial" approaches which attack, disperse or suppress the activity of attached organisms. These approaches include creating surface architecture to reduce macroscale roughness, preventing or slowing adsorption of the conditioning film (macromolecules and other solutes) and initial organism attachment, biocidal agents or effects to kill the organisms, and suppression of biofilm formation by disrupting bacterial communication or EPS production (Fig. 4).

Despite a number of community analyses and autopsies of biofilms in membrane filtration systems, there are few studies which examine systematically the effects of membrane surface properties on long-term biofouling performance. However, there have been a number of studies which identified some trends in regards to short-term cell adhesion and biofilm growth with controlled bacterial strains such as *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa*.[40] Generally they identify zeta potential, surface roughness, and hydrophobicity as key predictors of cell adhesion with neutral, smooth hydrophilic surfaces having the lowest propensity of biofouling. Ridgway *et al.*[41] evaluated the biofouling potentials of "hydrophobic" *Mycobacterium* and "hydrophilic" *Flavobacterium* onto nine modified polysulfone membrane surfaces, containing sulfonated polyether-ether-sulfone/polyethersulfone block copolymer. Their results suggested that hydrophobic bacteria tended to attach better to more hydrophobic membranes. They also found that physical properties of membranes (pore size, roughness, porosity) affected the attachment of microorganisms. However, the correlation of increasing microbial attachment with increasing hydrophobicity does not always hold when other varieties of organisms are examined on reverse osmosis membranes. Ghayeni *et al.* showed that microbial attachment increased with contact angle for some bacteria but others show little increase or even decreased adsorption with increasing contact angles (Fig. 5).[42]

The fluidity and brush-like surface structure have been shown to play crucial roles in repelling adsorption *via* hydrophilic
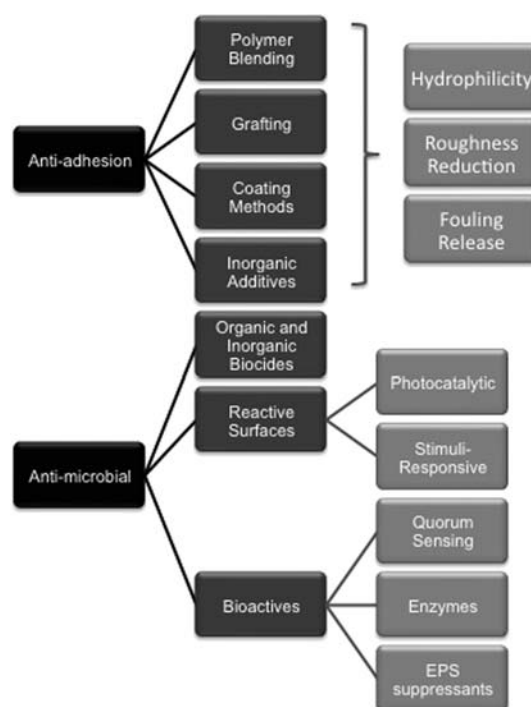

Fig. 4 Strategies to control biofouling in membrane filtration systems.
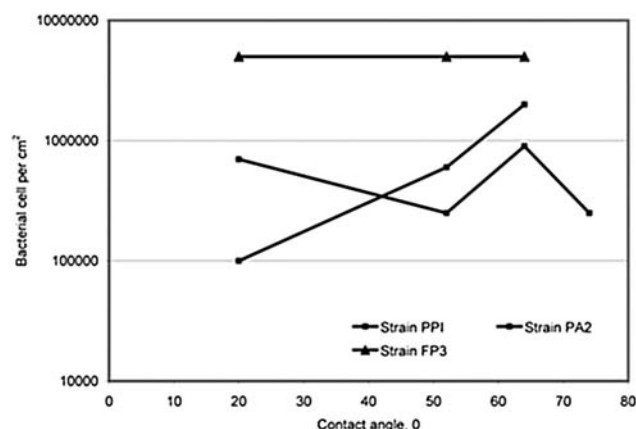
Fig. 5 Relationships of membrane hydrophobicity, measured as contact angles, to densities of initial colonisation by the three bacterial isolates. From left (most hydrophilic): BW30, NF45, PVD, CAB2 (most hydrophobic) membrane.[42] (Reproduced with permission).

modifications. Surfaces can be made resistant to biofouling by attachment of a dense brush of neutral hydrophilic polymer chains.[43] These brushes retard the adsorption of proteins and other biomacromolecules. The mechanism is complex, but includes contributions from the following factors:[44]

• shielding electrostatic interactions between the surface and the protein by interposing a neutral polymer layer with length greater than the Debye length (∼1 nm under physiological conditions),

• van der Waals interactions between the brush and the protein (always attractive),

• hydration/solvation interactions due to the formation of a layer of structured water associated with the brush. This results in a repulsive force that opposes protein adsorption.

In contrast, some researchers found that increasing hydrophobicity decreases biofouling, and low surface energy materials with "fouling release" characteristics may be an attractive approach.[45] Callow and Fletcher pointed out that low surface energy surfaces form weaker attachments for many organisms compared to high energy, highly polar surfaces.[45] Thus while these low energy surfaces (such as silicone elastomers and fluoropolymers) may not show lower initial deposition, they are more readily cleaned. Zhao *et al.* commented that a minimum in bacterial adhesion with respect of surface free energy has been observed in a number of studies.[46] Their results with membrane diffusers showed a similar minimum in bacterial adhesion when the surface free energy was in the range of 21–29 mN m^{-1}.[46]

In recent years, more diverse approaches have seen the incorporation of biocidal and other functional modifications. Incorporation or coating from inorganic particles can provide both increased hydrophilicity and a reactive surface for photocatalysis. Reactive surfaces can also be generated with stimuli-responsive mechanisms triggered by temperature and pH.[47,48] While some of these approaches can be implemented in a similar manner in some cases for both microporous (UF, MF, NF) and dense film membranes (RO, forward osmosis (FO)), the different transport mechanisms, hydrodynamic and chemical environments require different strategies. The trend in membrane modification towards adding structural and reactive

functionalities complements passive approaches to resistance to adsorption *via* conventional and novel hydrophilic modifications.

2. Microporous membrane modifications

Most microporous membranes are prepared by non-solvent induced phase separation (NIPS) which includes preparation of membrane solution, casting and phase separation (Fig. 6).

Membrane solution (so-called dope) may include only polymer and solvent; however in most cases it contains other additives with the aim to improve processing conditions and/or performance of resulting membrane. Polyvinyl fluoride (PVDF), polysulfone (PSf) and polyethersulfone (PES) UF membranes are broadly manufactured for industrial applications. Nevertheless, the hydrophobicity of those materials can cause severe fouling problems; therefore, membranes are usually modified to increase their resistance towards fouling. By 1996, almost half of all commercial membranes were surface modified.[49] Three different approaches including (i) membrane polymer modification (pre-modification), (ii) blending of the membrane polymer with a modifying agent (additive), and (iii) surface modification (chemical and radiation-induced grafting) after membrane preparation (post-modification) have been proposed, for preparation of low fouling membranes.[50,51] Other approaches include coating the commercial or in-house made membranes with polymeric solutions and inorganic additives.[50,51]

In some cases membrane modifications can lead to some undesirable effects such as narrowing the pore size on the membrane surface or in the case of photochemical grafting to pore enlargement of the host membrane.[52,53] Reduced water flux was also observed due to either surface hydrophobicity or lower molecular weight cut off (MWCO) of modified membranes.[54] However the higher flux recovery after fouling and higher UF flux have compensated for these drawbacks.

2.1 Anti-adhesion strategies for microporous membranes

Polymer blending approach. Blends of an established 'matrix polymer'—for a tailored and stable pore structure—and a 'functional polymer'—for special (tailored) surface properties—are very attractive from the membrane preparation point of view. If a macromolecular additive would show pronounced surface segregation and sufficient surface coverage, it should be possible to change the surface characteristics with only minor influence on bulk (including pore) morphology and properties. Another advantage of the blending approach is that it can easily be adapted to existing membrane fabrication processes. The
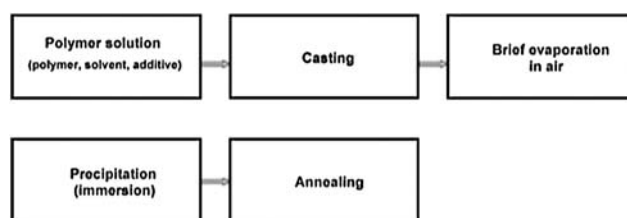

Fig. 6 Schematic presentation of different stages of polymer formation by the non-solvent induced phase separation method.

main issues of the blending approach are miscibility of polymer pairs and stability of modified surfaces.

The addition of hydrophilic polymers such as poly-vinylpyrrolidone (PVP) has become a standard method; commercial UF and MF membranes from so-called 'hydro-philized' polysulfone (PSf) or polyethersulfone (PES) are mostly produced using this approach. PVP was originally used as a pore forming additive.[55] One of the earliest studies in this area was on modification of PVDF and poly(ether-imide) membranes.[56] PVP and polyethylene glycol (PEG) have been extensively used as additives during preparation of PES UF membranes by phase separation methods. The mechanism of PES membrane formation with addition of PVP has been detailed in many publications.[57–59] Addition of PVP into PES–NMP (N-methyl-2-pyrrolidone) casting solution could suppress macrovoid forma-tion by decreasing the effect of delayed demixing.[57] However, the opposite effect, i.e., enlargement of the macrovoid structure, by addition of PVP into PES–DMF (dimethylformamide) has also been reported.[60] Increasing water permeability as well as MWCO of a PES membrane by the addition of PVP was another observation.[61] Moreover, it has been found that the character-istics and performance of PES–PVP blend membranes are influenced by the concentration and the molar mass of PVP.[62,63] The observed retention coefficient as well as surface roughness increased with increasing molar mass of PVP.[63] The effect of PVP content on the protein fouling behavior was also investigated; the presence of PVP could to some extent decrease the degree of fouling of the resulting membranes.[64]

PEG with various molar masses was added during the prep-aration of PES UF membranes.[65] The performance of the resulting membranes was influenced by both molar mass and concentration of PEG. Membranes prepared with higher molar mass of PEG had higher pure water permeation and larger pores. The water permeation increased as the concentration of PEG (400 and 600 g mol^{-1}) was increased, while the solute separation decreased. An optimum condition (high flux with acceptable solute rejection) was achieved at a PEG concentration of 10 wt%. In addition, differences in surface morphology and roughness could also be detected. A similar study was also performed using PSf–NMP and PSf–dimethylacetamide (DMAc) systems.[66] The results showed that the increase in PEG molar mass increased the membrane porosity leading to increased water permeability for both systems. Liu et al.[67] found an optimum PEG content in the PES–NMP system for increasing water permeability while further increase in PEG content would decrease the resulting water flux. Moreover, the addition of PEG alone could not suppress macrovoid formation even at high concentrations. A sponge-like membrane structure was obtained only when rela-tively large amounts of water were added to the dope solution. The effect of PEG/NMP ratio during preparation of PSf UF membranes was investigated.[68] As the PEG content was increased the pure water flux increased and the BSA adsorption decreased.

A variety of commercial surfactants from Pluronic (a triblock copolymer of PEO-PPO-PEO) series has been used in modifi-cation of UF membranes (Fig. 7). The resistance of PEO chains to the adsorption of proteins is generally considered to be a steric repulsion effect, by which the polymer prevents the protein from reaching the substrate.[69,70] Jeon et al. found that protein
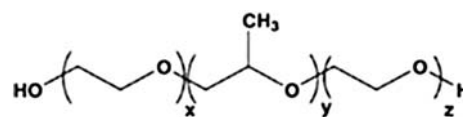

Fig. 7 Chemical structure of Pluronic surfactant.

adsorption on the surface was closely related to the balance between the attractive forces (van der Waals force and hydro-phobic force) and the steric repulsion. The steric repulsion has an osmotic (due to the solvation of the PEO chains) and an elastic (due to the conformational entropy of the PEO chains) compo-nent; these components become effective when the protein compresses the PEO layer. Consequently, the PEO layer thick-ness determined by the length and the density of PEO chains governs the steric repulsion. The relative lengths of the hydro-phobic and hydrophilic segments are critical in the extent of modification.[71] Among five Pluronic® polymers selected for modification of PES membranes, Pluronic® L44 type with the shortest PEO chain led to membranes with the poorest ability to resist fouling. On the other hand, Pluronic® F127 with 70 wt% PEO showed the best performance in terms of flux recovery and fouling resistant ability.

The performance of Pluronic® P123, an amphiphilic block copolymer with lower level of PEO segments, was improved by the incorporation of PEG as side chains.[72] The amount of protein adsorption as well as total membrane fouling, especially irre-versible fouling, decreased significantly by incorporation of PEG-b-P123-b-PEG into the membrane. Flux recovery up to 87% was obtained.

Polyacrylonitrile-graft-poly(ethylene oxide) (PAN-g-PEO) has been successfully incorporated as a surface segregating additive in the manufacture of novel polyacrylonitrile (PAN) UF membranes with improved flux, wettability and fouling resistance.[73,74] During membrane casting, PAN-g-PEO additive segregates to form a PEO brush layer on the membrane surfaces, including internal pores. Membrane with 20 wt% PAN-g-PEO (39 wt% PEO content) showed complete flux recovery after backwashing and cleaning.

Inspired by antifouling marine coatings, the antifouling characteristics of modified membranes made from PES and an amphiphilic comb copolymer PS-b-PEG made from hydro-phobic polystyrene (PS) and hydrophilic poly(ethylene glycol) (PEG) were examined.[75] Similar to other comb copolymer modifications, the hydrophilic segments of the comb polymer spontaneously segregated to the membrane surface during the phase inversion process, while the hydrophobic parts were strongly trapped within the membrane matrix. A flux recovery of 80.4% after three BSA ultrafiltration–cleaning cycles was ach-ieved. An ultrahigh molecular weight ($M_W > 10^6$) styrene-maleic anhydride (SMA) copolymer that is synthesized in supercritical carbon dioxide was used as a hydrophilic additive in fabrication of PES membranes via an immersion precipitation process.[76]

During membrane formation, the hydrolysed copolymer preferentially segregated to the membrane–coagulant interface. The surface modification was achieved without compromising the mechanical properties of membrane. However AFM images revealed a rougher surface. The increase in surface roughness with the addition of SMA limits this modification, since it could

intensify bacteria and protein adsorption. However, the enrichment of SMA simultaneously improved the surface hydrophilicity, which endowed the PES/SMA blend membranes with superior protein-adsorption resistance.

The stability of membranes was improved by blending a comb copolymer of poly(styrene-*alt*-maleic anhydride) (SMA) backbone with PEG side chains. Modified membranes were hydrophilic with 90% higher resistance to protein adsorption than control membranes.[77] In fact, after the modified membrane underwent 25 days of cleaning, it exhibited even higher hydrophilicity and stronger fouling resistance. SMA-*g*-MPEGs appeared to be well anchored in the membrane near the surface and were not leached out during membrane washing due to their ultra-high molecular weight as well as the comb-like architecture.

The application of low surface energy coating materials such as siloxane, fluoropolymers, and fluorosiloxanes as alternatives to paints containing lead and other toxic materials in marine applications is well documented.[78,79] For example, poly(dimethyl siloxane) (PDMS) elastomers are widely used in commercial marine foul-release coatings because of their combination of properties such as low surface energies, low micro-roughness, and low modulus. Another class of materials with dual effect of hydrophilicity and low surface energy are novel amphiphilic polymers composed of PEG and perfluoroalkyl units.[80,81]

The high removal of diatoms from the amphiphilic surface was explained by the fact that the surface could reconfigure to become as hydrophilic as a PEGylated surface when immersed into water and that diatoms adhered weakly to hydrophilic surfaces. Inspired by antibiofouling marine paints, amphiphilic polymers have been the subject of extensive research on membrane modification.[73,82–85]

It is also believed that amphiphilic additives could improve the stability of modification and therefore lead to membranes with long lasting antifouling characteristics.[86–88] The presence of the hydrophobic segment improves the compatibility of additive and membrane (anchoring effect), while the surface segregation of the functional blocks leads to a modified membrane with most of the modification at the outer active side and outer surface of pores (Fig. 8).

PES modified with surface modifying macromolecules containing zonyl BA-L fluorotelomer had higher flux in treatment of oil/water emulsions than control unmodified membranes[86] due to its more hydrophobic surface and low fouling. Modified membranes had lower water flux, probably due to the migration of the hydrophobic block polymer to the membrane surface. Also copolymers with special side groups such as phosphorylcholine have been used as surface-modifying additives in formation of UF membranes.[89,90] Hester *et al.* have prepared very interesting block copolymers *via* controlled (ATRP) graft copolymerization of PEG methacrylates onto PVDF.[91] Such polymers are not only promising additives for surface modification but they could also be used as a bulk material for NF membranes.

Type, polarity, and average molecular weight could affect the solubility of surface active additives in the base polymer. It has been reported that amphiphilic polymers with block,[92,93] comb[82,94] and branched[95,96] structures can be used to reduce the biofouling of UF membranes. The high retention degree of a comb-like copolymer of polysiloxane with polyethylene oxide
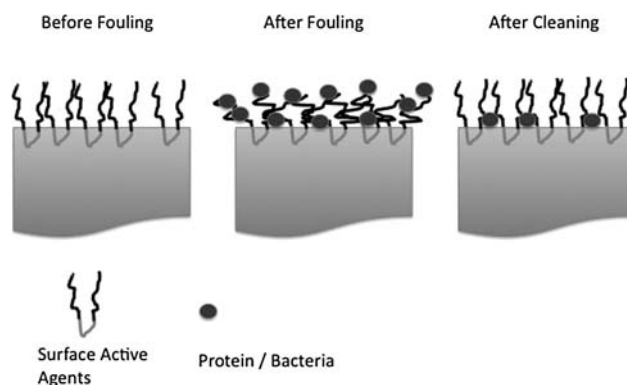

Fig. 8 Schematic presentation of modification of membranes with surface active macromolecules.

and polypropylene oxide side chains (ACPS, $M_n = 25000$) was attributed to high MW, large hydrophobic parts (both polysiloxane in backbone and PPO segment), which is expected to improve compatibility between the additive and PVDF, and the comb-like structure which generates the high diffusive hindrance.[85]

For solid non-porous surfaces it has been shown that compositional and morphological heterogeneity might be the key to achieving surfaces that can prevent biofouling.[97] It is quite possible that the low biofouling for membranes modified by amphiphilic or surface active additives is partly due to the nanoscale heterogeneities in topography as well as composition of the surface. More research in this area would be very useful in further understanding the behavior of these additives during application of membranes.

Grafting approaches. Grafting techniques to produce antifouling surfaces have been extensively studied.[50] Both "grafting to" and "grafting from" using hydrophilic polymers are used to generate dense brush structures.[98] The growth of polymer brushes, which usually includes the attachment of an initiator to a surface followed by polymerization from the initiator, is also very versatile and can take place on any substrate that allows for initiator attachment and is stable to polymerization conditions (Fig. 9). In comparison to the layer by layer deposition approach the approach allows easy control of the composition since the coating consists of only one polymer, and functionality can be introduced through the appropriate choice of the monomer unit or by the derivatization of the polymer. Another advantage of polymer brushes compared to multilayer films is that, in principle, it is possible to control the density of chains growing from the surface.[99]

The effects of surface charge, surface roughness and surface hydrophilicity on bacteria attachment on chemically modified polyethylene membranes were systematically studied.[100] Conventional and novel materials were ranked against solid PE film (as baseline) and the results are given in Table 1 and plotted *versus* contact angle and zeta potential (Fig. 10). Hydrophilic, non-charged, smooth surfaces had the lowest biofilm coverage as compared to unmodified polyethylene membrane. It was also shown that of all of the materials tested, the different variations of PEG grafted to the surface had the lowest coverage of *P. aeruginosa*. Over the range of values examined, zeta potential
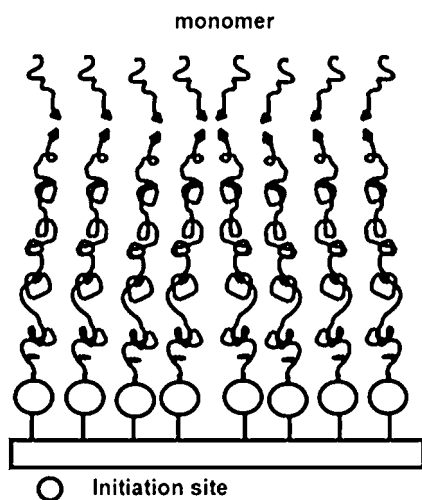
Fig. 9 Schematic presentation of grafting method (comb and copolymers) for membrane modification (redrawn from Bao *et al.*, 2006).[99]

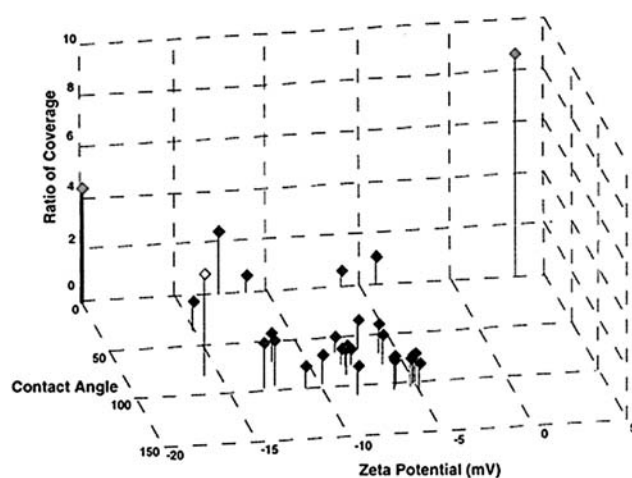**Fig. 10** Ratio of bacterial coverage for various materials *vs.* contact angle and zeta potential (reproduced with permission).[100]

had a greater effect on bacterial coverage than did contact angle as shown in Fig. 10.

Plasma treatment can be used to introduce hydrophilic functional groups on membrane surfaces but does not provide the additional steric and entropic barrier of brush or hydrogel structures.[51] Ageing due to chain migration, further oxidation, and migration of reacted species can contribute to loss of surface modification. UV and plasma grafting provide more permanent surface modification, primarily with poly-2-hydroxyethyl methacrylate (HEMA), polyacrylic acid (PAA), polymethacrylic acid (MAA), and similar families of compounds. These techniques were recently reviewed by Khulbe *et al.* (2009) and van der Bruggen (2009) for the modification of polyethersulfone nanofiltration membranes but are widely applicable to other membrane materials.[50,51] While hydrophilicity and surface smoothness are often conferred on the surface, there are few studies which examine the long term stability of such membrane modifications after cyclical fouling and cleaning.

Table 1 Ranking of different materials *vs.* solid PE film using percent biofilm coverage[100]

Material	Coverage ratio: material/solid PE film
Nylon	9
PTFE	2
PP	2
PE membrane	1
CA (pore size = 0.22 μm)	0.7
Polyphosphazene–CH_2CF_3	5
1H,1H-pentadecafluorooctyl methacrylate grafted to PE	2
Polyphosphazene (92%) –OC_6H_5, (8%) –OC_6H_4COOH	2
Polyphosphazene–OC_6H_5	1
Poly(dimethylsiloxane) methacrylate grafted to PE	1
PEG(1000)MMA grafted to PE	0.7
PEG(200)MMA grafted to PE (weight gain = 9.16)	0.3
Polyphosphazene–$O(CH_2CH_2O)_4CH_3$	0.6

Coating methods. Although surface grafting has shown high fouling resistance, this approach inevitably leads to permanent change of membrane chemistry and other properties such as membrane permeability and pore size. Grafting density is also hard to control between the surface and the internal pore structure of the membranes, frequently resulting in severe reduction of pore size and flux as grafting density and chain length increase. Thus a compromise between fouling resistance and pore reduction is required. Unlike grafting, coating is usually simple to apply and the process can easily adapted to the existing membrane manufacturing processes. The membrane surface is contacted with a solution/dispersion of modifying additive and after evaporation a thin layer of coating is formed. Membrane surface properties such as hydrophilicity, roughness and charge are modified to give improved resistance to biofouling.

Both amphiphilic and hydrophilic additives have been used. Simple passive adsorption with anionic and nonionic surfactants provides temporary resistance to protein fouling.[101,102] Poly-(methyl methacrylate)-based coating materials with short non-fouling oligoethylene glycol side chains have been used to coat commercial polysulfone membranes. Membranes coated with this comb polymer showed higher flux recovery than control membranes after a five-cycle filtration-washing process.[103] Other examples are hydrophilic coatings such as polyvinyl alcohol (PVA) and negatively charged polymers such as polyacrylic acid (PAA) on NF membranes,[104] polyamide-*b*-poly(ethylene oxide) coating on porous PVDF membranes,[105] polyolefin-*graft*-PEG amphiphilic copolymers coating of PVDF UF membranes,[106] coating of micron-scale films of an amphiphilic graft copolymer consisting of a PVDF backbone and side chains of poly(oxyethylene methacrylate)[107] on PVDF UF membranes. Boudjouk and Johnson worked on the coating of UF membranes with solutions of block copolymers with biocidal and/or fouling release characteristics.[108,109] The copolymers may include one or more polymers grafted onto a polysiloxane backbone. A stable coating of PVA can also be formed on the surface of PES UF membranes by a surface adsorption-crosslinking process.[110] The PVA coating was stabilized by crosslinking with borax. Flux recovery of 86% was obtained with a coating of 2 wt% PVA

solution through three adsorption-crosslinking cycles. The main drawback of the coating approach is the potential reduction in permeability and delamination of coating during use, especially during harsh conditions of frequent chemical cleaning. More recently, hydrophilic coatings using 3,4-dihydroxyphenylalanine (DOPA) and dopamine have been used to treat microporous PE, PVDF, and PTFE membranes.[111] The strong adhesive properties of these compounds formed films that attached well to the hydrophobic membranes and decreased the contact angle from 50° to 30°. PEG modified polydopamine coatings showed additional resistance to protein and bacterial adhesion.[112]

Table 2 summarises a number of studies on the surface grafting along with membrane performance.

Inorganic additives. Incorporation of nanoparticles into polymeric filtration membranes included mostly silica,[119] Al_2O_3[120] and titanium dioxide, TiO_2.[121–126] Nano-sized TiO_2 has received significant interest for its high hydrophilicity, chemical stability, and antibacterial properties. In addition anatase TiO_2 could serve as a photocatalyst to degrade pollutants in waste water treatment while having an antimicrobial effect in the presence of UV. Different methods have been examined for the incorporation of TiO_2 in membranes as follows:;

(1) dispersion of nanoparticles in the casting solution directly and preparation of the composite membranes *via* phase inversion;[127,128]

(2) addition of the prepared sol containing nanoparticles to the casting solution and preparation of the composite membranes *via* phase inversion;[129]

(3) dip-coating of membrane in the aqueous suspension containing nanoparticles and preparation of the composite membranes *via* self-assembly.[121,130]

Most work on the antifouling properties of TiO_2 modified membranes includes the requirement of UV irradiation to achieve superior performance compared to unmodified membranes. Membranes with deposited TiO_2 nanoparticles and UV irradiation at 365 nm had 50% less fouling in filtration of a natural surface water.[131] The antifouling property of TiO_2 nanowire membranes was significantly improved when UV irradiation was carried out during filtration. The improvement was attributed to the dual effect of photocatalyst degradation of foulants and filtration.[132] Similar results were reported for membranes modified with TiO_2 nanoparticles and TiO_2 coating.[125,126,133,134] There are also some reports which show that the improved performance of composite membranes with TiO_2 was the result of solely microstructural changes and/or higher hydrophilicity. For example Luo *et al.*[130] showed that antifouling properties of membranes could be improved by self-assembly of hydroxyl groups on the TiO_2 nanoparticle surface and the sulfone groups and ether bonds in PES structure *via* coordination and hydrogen bond interactions.

Performance and morphology of PVDF membrane and PVDF composite membranes with nanosized TiO_2 particles of different sizes have been compared.[135] It was found that the smaller nanoparticles produced a greater improvement in the antifouling property of the PVDF membrane due to their higher porosity (Fig. 11). Membranes coated with a mixture of TiO_2 and SiO_2 had higher permeability for whey solutions than the membrane coated solely with TiO_2 particles.[128] It is believed that by adding SiO_2 particles to TiO_2, surface acidity is increased and this leads to an increase in ultrahydrophilicity and photocatalytic properties of the membranes.

In spite of the significant reduction of fouling observed with TiO_2-membrane nanocomposites, the use of UV irradiation in some studies has potential complications for commercialisation since in most membrane processes it would not be practical to incorporate a UV light source in the membrane module.

2.2 Antimicrobial additives

As was shown in previous sections it is generally accepted that membranes with hydrophilic, electrically neutral and smooth surfaces are much less likely to foul with bacteria than hydrophobic, charged, rough surfaces. Control of these three properties, however, only focuses on the bacteria attachment and the rate of early biofilm initiation. To prevent biofilm formation for extended time and to maintain minimal bacteria growth and proliferation, an antimicrobial approach can potentially provide an additional layer of protection. Membranes with inherent biocidal properties may be helpful in reducing fouling by killing bacteria either before they are able to attach to a surface or before they proliferate, thus reducing the extent of biofilm formation. This approach will not prevent fouling altogether, as dead bacteria will still accumulate on the membrane surface.

Antimicrobial modification of surfaces to prevent growth of detrimental microorganisms is a highly desired objective in many fields and has been studied extensively in the biomedical and marine biofouling fields. In general, three broad classes of materials have been used for rendering surface antimicrobial properties: contact active amphiphilic polymers,[136] microbe-repelling anti-adhesive polymers[137] and polymeric or composite materials loaded with slow releasing biocides such as heavy metals.[138] Biocides must be mobile so they can migrate to the film surface and across the bacteria cell membrane to destroy bacteria. This necessary property also renders biocides prone to water leaching which is unavoidable in membrane applications. To overcome such losses it is necessary to design a carrier to release the biocides slowly.

Among the third class of antimicrobials, silver-based materials are of special interest. Silver is a widely used antibacterial agent, which has high toxicity towards many types of bacteria, but low toxicity for humans and animals. The antibacterial properties of silver in the form of silver salts or silver metal nanoparticles have been exploited in a wide range of applications, including socks, washing machines, antibacterial paints and wound dressings. Its mechanism of action is not well understood, but is likely to involve complexation with thiol groups on proteins, interaction with DNA and the cell wall, and interference with electron transport.[139] Ag^+ ion is known to deactivate cellular enzymes and DNA by coordinating to electron-donating groups such as thiols, carboxylates, amides, imidazoles, indoles, and hydroxyls.[140] There is no widely accepted value for the minimum inhibitory concentration (MIC) of silver, but reported values for the effect of $AgNO_3$ on *Staphylococcus aureus* range from 8–80 $\mu g\ mL^{-1}$, and for *Pseudomonas aeruginosa*, 8–70 $\mu g\ mL^{-1}$.[141] Surfaces coated with silver nanoparticles at a concentration of 10 $\mu g\ cm^{-2}$ completely inhibit the growth of *S. aureus* bacteria.[142]

Table 2 Modification used in UF and MF membranes by different methods

| Approach	Substrate/initial polymer	Functionality/modification	Tests	Modification extent	Ref.
Surface grafting	PVDF UF membrane (NIPS)	Poly(ethylene glycol) methacrylate (PEGMA)	Protein (BSA) adsorption (static, 1 mg ml⁻¹), UF experiments	Up to 60% lower BSA adsorption, 40% increase in water flux recovery (1 cycle of fouling/cleaning)	113
Bulk modification	Polyacrylonitrile	Poly(ethylene glycol)-*graft*-polyacrylonitrile copolymers (various MWs of PEG)	XPS	Surface coverage of PEG up to 56%	114
		UF membranes	Static BSA adsorption, BSA fouling/cleaning	Up to 10 times lower BSA adsorption, Up to two times flux recovery	
Surface grafting	PVDF MF membranes (Millipore)	Chlorosulfonic acid	Permeability, Contact angle	Higher permeability, Higher rejection, Lower contact angle	115,116
Surface grafting	Poly(acrylonitrile-*co*-maleic acid)	PEG (immobilisation on the surface)	Hydrophilicity, Platelet adhesion (SEM), Protein adsorption after chemical cleaning, Water and protein fouling, Flux recovery (after water and chemical cleaning)	CA reduced up to 100%, No platelet on modified membranes, Reduced to half, Protein flux increased 3 times, Flux recovery after chemical cleaning for unmodified membrane: 12 vs. 30 for modified membrane	116,117
Surface modification	Commercial MF PVDF membrane (Millipore)	Method 1: photoinitiated graft polymerisation with quaternized 2-(dimethylamino)ethyl methacrylate (qDMAEM) and 2-acrylamidomethylpropanesulfonic acid (AMPS) Method 2: interfacial polymerisation between polyethyleneimine and toluene diisocyanate	Filtration of *E. coli* suspension through membranes and bacteria count	Much lower bacteria attachment in comparison with control membrane; qDMAEM showed stronger bactericide effect	117
Surface modification	Commercial PE membrane, PVDF, Polymer surfaces (PC, PMMA, PTFE)	PEG and polydimethylsiloxane	Contact angle, roughness, surface charge, biofilm growth in rototorque(*P. aeruginosa*) and analysed by epifluorescence microscopy	Electrically neutral, smooth and hydrophilic surfaces were less fouled	100
Surface modification	UF PES membrane (10 kDa)	Photolysis using UV light and graft polymerisation of hydrophilic monomer *N*-Vinyl-2-pyrrolidinone (NVP), *N*-vinylformamide (NVF), *N*-vinylcaprolactam (NVC)	Contact angle, flux recovery	Best: PES-NVP; 25% increase in hydrophilicity, 49% reduction in BSA fouling compared to PES membrane	118
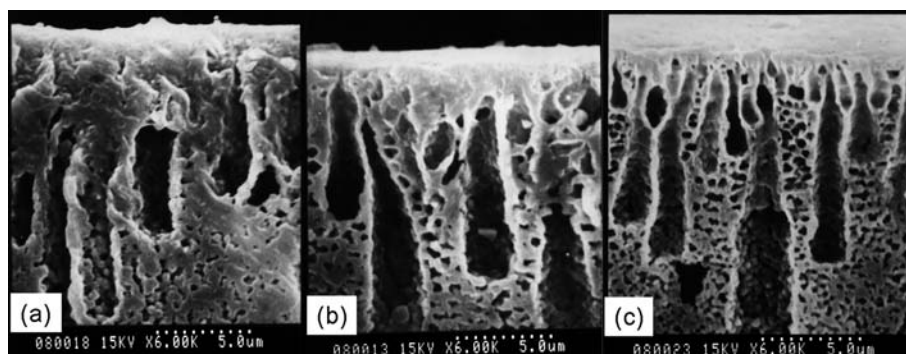
Fig. 11 SEM cross-sectional micrographs of the membranes: (a) PVDF; (b) TiO$_2$/PVDF (TiO$_2$ granular diameter 26–30 nm); (c) TiO$_2$/PVDF (TiO$_2$ granular diameter 10 nm) (reproduced with permission from Cao *et al.*, 2006).[135]

The efficiency of inorganic antimicrobial systems relies on the "delivery" of small quantities of ionic metal at the cell membrane. The metal ions are usually bound within a delivery system that stabilizes them such as zeolite (*e.g.* in Irgaguard® B5000), allowing their incorporation into the product, and then releases them through a process of ion exchange at the surface. While there is no migration of the ions, as with organic systems, it is the delivery system that ensures a constant replenishment at the surface. The level of additive in the polymer/membrane and also the delivery mechanism regulate how quickly ions are released. A significant constraint in membrane applications is the need for a controlled mode of action continuing over the lifespan of the membrane. Common delivery systems include those based on ceramic glasses and zeolites (aluminosilicates). Silver ions are placed at the specific position of the interior of the cage structures because of their electron density.

There has been very limited research work with specific focus on the antibacterial properties of membranes modified by organic and polymeric additives. Hilal *et al.*[117,143,144] developed membranes with lower biofouling properties by photo-induced grafting copolymerization of commercial membranes. Two types of hydrophilic and water soluble monomers; 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and quaternary salt of 2-dimethyl aminoethylmethacrylate (qDMAEMA), were grafted to the surface of commercial polyethersulfone (PES) microfiltration membranes. The membrane affinity to biofouling was tested experimentally in the presence of *E. coli* bacteria, and it was found that the number of bacterial cells able to reproduce was much lower for qDMAEMA-grafted samples compared with unmodified PES membranes. Of the two membranes studied, the modified membrane had a significantly smaller force of adhesion (evaluated by AFM), which also indicated the development of low or zero fouling properties.

Chitosan has also been tethered to the surfaces of cellulose membranes (Microdyn Nadir, Wiesbaden, Germany) to provide them with biocidal activity and thereby lower the membrane biofouling potential.[145] The membrane bactericidal activity was tested against *E. coli* and *Staphylococcus aureus* strains. The influence of the modification conditions, molecular weight of the chitosan, and morphological structure of the membranes on the antimicrobial properties of the prepared membranes was examined, and the highest antimicrobial activity of modified membranes was achieved when the degree of membrane modification is close to its maximal value. Antimicrobial efficiency improves with the use of higher molecular weight chitosan and membranes with smaller pore sizes (Fig. 12). Such trends are postulated to be associated with the effective length of chitosan chains protruding from the membrane surface. It is believed that immobilized biocides must be sufficiently long to traverse and damage the cellular membrane/wall of bacterial cells in contact with the surface. Modification of membranes with smaller pore sizes occurs entirely on the membrane surface when membranes are modified with higher molecular weight chitosan. This results in the most expanded layer of bound chitosan with the highest activity against both *S. aureus* and *E. coli.*
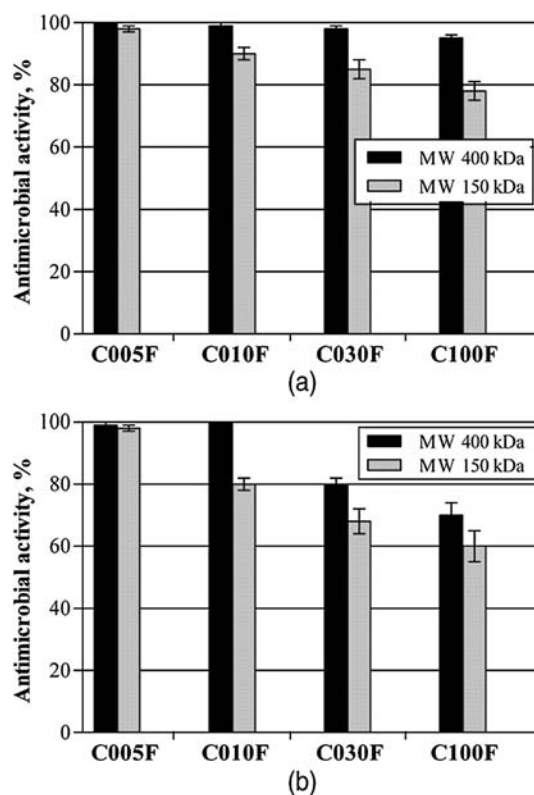

Fig. 12 Effects of the molecular weight of chitosan and the membrane pore size on antimicrobial activity against (a) *S. aureus* and (b) *E. coli* (reproduced with permission from Nigmatullin *et al.*, 2009).[145]

Although it is widely accepted that the antimicrobial activity of cationic polymers including chitosan is not fully understood, it is believed that the binding of positively charged polycations to the surface of negatively charged cells and the disruption of at least the outer layers of the cell membrane are involved in the processes affecting cell viability.[146]

In studies by GKSS[147] a coating layer of silicone polymer containing 4,5-dichloro-2-octyl-4-isothiazolin-3-one was employed in preparation of a polyimide membrane with high resistant to biofouling. Choi et al.[148] demonstrated that by incorporation of only 0.01 to 3 wt% of organic and inorganic antimicrobial agents in the hollow fiber membrane the bacteria inhibiting performance of these membranes could be improved. Incorporation of non-leaching antimicrobial additives such as 2,4,4'-trichloro-2'-hydroxydiphenol ether or 5-chloro-2-phenol(2,4-dichlorophenoxyl) have been patented by Patil for use in semi-permeable membranes.[149] The organic antimicrobial agents can also be selected from organic copper, organic zinc, phenyl ether based and organic silicon quaternary ammonium compounds. For inorganic antimicrobials, silver, copper, and zinc-based zeolites and aluminosilicates, or a mixture of these, have been suggested. In a more recent patent Mansouri et al. disclose up to 48% reduction in the attachment of P. aeruginosa to the membrane surface after incorporation of silver zeolite in PES UF membrane.[150]

Ciston et al.[151] modified ceramic membranes to reduce the tendency to biofouling. They gave a comparison of bacterial attachment among three photocatalytic ceramic ultrafiltration membranes for the prevention of biofilm formation. Zirconia ceramic ultrafiltration membranes were dip-coated with anatase and mixed phase TiO_2 photocatalysts to prevent biofilm growth. The membrane surface was characterized in terms of roughness, hydrophobicity, bacterial cell adhesion, and attached cell viability, all of which are important factors in biofilm formation. The TiO_2 coatings had minimal impact on the membrane roughness, reduced the hydrophobicity of membranes, prevented Pseudomonas putida attachment, and reduced P. putida viability. Degussa P25 TiO_2 is a particularly promising reactive coating because of its ease of preparation, diminished cell attachment and viability in solutions with low and high organic carbon concentrations, and reduced flux decline.

A coating approach has also been used in the fabrication of antimicrobial polymeric membranes. Hardorfer et al.[152] showed that RO membranes modified by deposition of elemental silver using a galvanic procedure had higher permeate flux (up to 45%) and higher permeate recovery. The durability of antibacterial activities of cellulose acetate hollow fiber membranes with silver loadings was estimated by monitoring the relative silver residue on the surface and in the bulk and their activity against E. coli and S. aureus (Table 3). In similar work the antibacterial activity of modified polyacrylonitrile hollow fibers with low loadings of silver have been reported.[153]

One of the main challenges in the application of silver loaded membranes is the rate of silver release from the membrane. Effective methods are needed to anchor/immobilise silver particles to the surface of the membrane. This may include improved silver incorporation strategies such as encapsulation in a polymer which is compatible with the base polymer of the membrane. An interesting concept introduced by Loher et al.[155] is based on

Table 3 Silver content and antibacterial activity of hollow fiber samples from Chou and Yang, 2005[154]

Soaking time (days)	Relative silver residue (%)		Antibacterial activity	
	Bulk[a]	Surface[b]	E. coli	S. aureus
0	100	100	Active	Active
30	83	31	Active	Active
60	74	23	Active	Active
90	68	17	Active	Active
180	61	10	Active	Active

[a] Measured by inductively coupled plasma atomic emission (ICP-OES) method. [b] Measured by X-ray photoelectron spectroscopy.

encapsulation of silver in a substrate that is degraded by bacteria so that silver is only released in the presence of bacteria. The bactericidal effects of both silver and TiO_2 are affected by the feed conditions—any work on long term applications for these additives should consider their stability and controlled release behavior. The USEPA has set water quality criteria values for silver in salt and fresh water at 1.9 and 3.4 ppb, respectively, and a secondary drinking water standard for silver of 100 ppb. The growth in public concern over the use of silver and nanoparticles may pose a regulatory risk for applications in water treatment.

3. Biofouling control of dense film filtration membranes (RO/NF)

While dense film (RO and NF) membranes can be formed from conventional phase inversion, thin film composite (TFC) membranes[156,157] are the dominant form of membrane in reverse osmosis applications. They are produced by interfacial polymerization of polyfunctional amines and acid chlorides to form a thin layer of polyamide on a microporous substrate, typically polysulfone or polyethersulfone. The resulting composite membranes combine the excellent flux and salt rejection of the thin (10–200 nm) polyamide film with the mechanical properties of the thicker (∼100 μm) substrate. These membranes typically provide >97% salt rejection at fluxes of around 1 m^3 m^{-2} d^{-1} (15 bar pressure, 1500 ppm NaCl).[158,159] While TFC membranes have excellent salt rejection and water flux, fouling remains a significant problem. Fouling can be a combination of salt precipitation (scaling), colloidal fouling, organic fouling and biofouling.[29] Due to their polyamide chemistry, many TFC membranes are highly sensitive to oxidizing chemicals such as hypochlorite which may otherwise be used for removing bio-foulants. An autopsy of membrane elements collected from the Tajoura seawater desalination plant in Libya after 360 days operation showed the presence of a heavy coating of reddish-brown biofilm with bacterial counts of approximately 10^5 cfu cm^{-2}. Analysis by AFM, ATR-FTIR and XRD showed the presence of polysaccharides, silica, hematite and $CaCO_3$ as major components.[160] Biofouling can vary extensively between and within the desalination plants within the various treatment trains and element arrays, and their microbial community can be extremely diverse.[21] Biofouling has been referred to as the 'Achilles heel' of reverse osmosis due to its persistence.[5] In addition to cleaning with alkali and acid with chelating agents,

control measures have included intermittent dosage of biocides and removal of biodegradable or assimilable organic carbon (AOC) which serve as nutrients for biofilms.

3.1 Anti-adhesion strategies for RO and NF membranes

Fouling in reverse osmosis membranes is controlled by interactions between the membrane surface and solutes such as proteins, carbohydrates and bacteria. Thus surface properties such as roughness, charge and hydrophobicity are important in determining the susceptibility of a membrane to fouling. Of these factors, a number of studies suggest that surface roughness may be the most important.[30,31,34,161–164] Surface roughness was strongly correlated with flux decline in bench scale tests of a number of RO and NF membranes; weaker correlation was observed for surface charge.[161] Studies of direct microscopic observation of bacterial adsorption[30,163] also showed a strong correlation between the rate of adsorption and surface roughness. In the initial stages of fouling, colloids accumulate in the valleys of rough membranes, causing severe flux decline.[162] A colloid probe AFM study[165] of a rough reverse osmosis membrane (AFC99, PCI Membranes) found that adhesive forces between the colloid probe and surface were 20 times lower at the peaks than in the valleys, suggesting that colloid fouling could be greatly reduced if the periodicity of the roughness was small enough to prevent penetration of the colloids into the valleys. Thus the surface properties of the reverse osmosis membrane are critical to its susceptibility to fouling. One way to change these properties is to modify the chemistry of the membrane. This approach carries the danger of reducing the flux or salt rejection below acceptable levels, but obviates the need for an antifouling coating which may detach or degrade during operation.

Aryl-alkyl polyamide polyureas are produced by interfacial polymerization of 5-isocyanatoisophthaloyl chloride and meta-phenylene diamine (MPD). The resulting polymer contains both acid and amine groups (from hydrolysis of unreacted isocyanate) on the surface, and hence has a lower net charge than polyamide membranes, which are negatively charged under neutral conditions due to the presence of carboxylic acid groups on the surface. These membranes are more hydrophilic and smoother than conventional TMC-MPD membranes, and show improved fouling performance under some conditions.[166,167] This chemistry forms the basis of the commercial Trisep X20 membrane.

Another approach is to improve the chemical resistance of the membrane through the use of sulfonated polysulfone as the separation layer.[168] These lack the vulnerable amide bond of TFC membranes, and can be operated in the presence of chlorine to inhibit biofouling. Partially disulfonated poly(arylene ether sulfone) random copolymers are chlorine resistant and show good antifouling behavior.[169] Crosslinking the membranes has improved their salt rejection to a point where they may become viable alternatives to polyamide membranes[170]

Modification of surface roughness forms the basis of the GE Osmonics Duraslick™ membrane, in which a smooth surface is obtained by interposing a proprietary polymer layer between the polysulfone substrate and the polyamide thin film.[171] In a recent study, comparison of a number of commercial low-fouling membranes found that increased hydrophilicity, lower surface
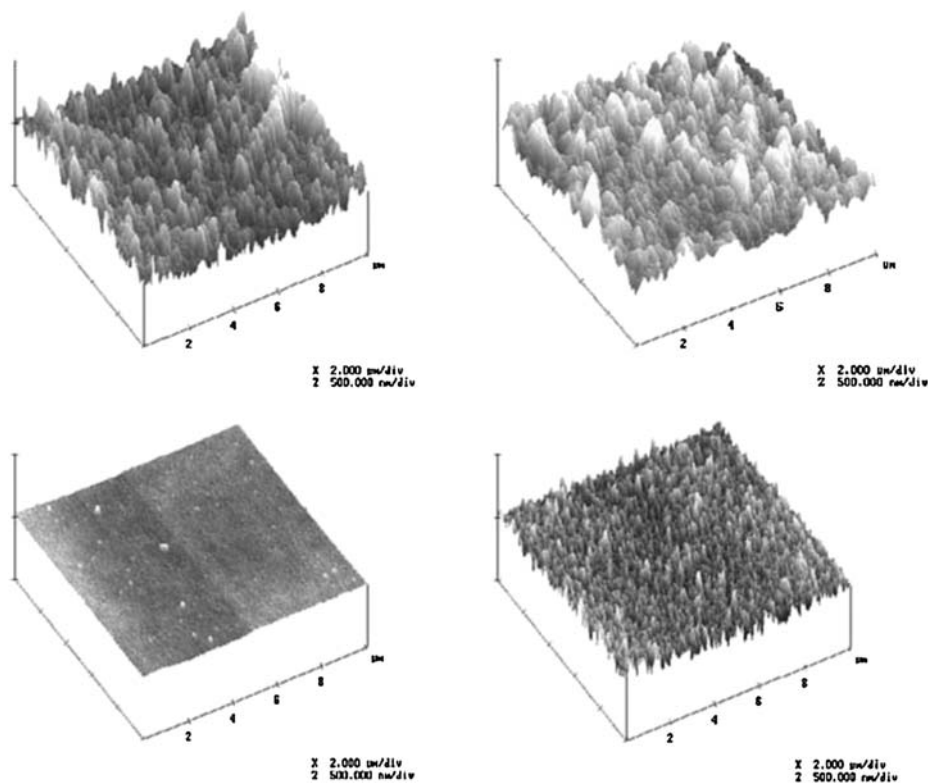

Fig. 13 AFM images of fouling resistant low pressure RO membrane surfaces (Dow BW30 FR1, Hydranautics LFC1, Osmonics SG and Trisep X20).[172] Surface roughnesses range from 13.1 nm (SG) through 41.6 nm (X20) to 65.0 nm (BW30FR1) and 67.4 nm (LFC1). Reproduced with permission.

charge and greater smoothness were associated with better antifouling performance (Fig. 13).[172]

RO membranes are frequently coated with a layer of hydrophilic polymer to improve their fouling resistance. The polymer must be either insoluble in water under the operating conditions (*e.g.* polyvinyl alcohol, Pebax™ block copolymers), or cross-linked—either to itself or to the membrane (*e.g.* polyfunctional epoxides). In most cases, these treatments result in a reduction in initial flux, with little change in salt rejection. Flux after filtration of fouling solutions is greater than that of comparable untreated membranes. Some examples of antifouling coatings are described below and shown in Table 4.

Non-covalent attachment. Neutral hydrophilic polymers such as polyethylene glycol, polyvinylpyrrolidinone or PVA have been used to shield the surface charge of RO membranes.[173,174] The treated membranes exhibited reduced loss of flux and salt rejection when exposed to a cationic surfactant solution. Highly saponified PVA is preferred for this application as it is insoluble in water at 25 °C due to intramolecular hydrogen bonding. In a related technique, coatings of PEBAX® polyamide-polyether block copolymers were applied to RO membranes.[175,176] These are water-insoluble, water-swellable polymers with glass transition temperatures below the membrane operating temperature. They can be coated onto a membrane without need for cross-linking or covalent attachment.

Epoxide-functional polymer coatings. A patent by Mickols (US Patent 6,280,853)[177] disclosed the use of PEG diepoxide (polyethylene glycol diglycidyl ether, M_W = 200 or 3400 g mol^{-1}) as an amine-reactive hydrophilic coating.[177] The treatment resulted in reduced flux (by a factor of 3 to 4) and improved salt passage (by a factor of 2 to 3). Resistance to fouling by surfactants (sodium dodecyl sulfate or dodecyltrimethylammonium bromide) was improved. Other polyfunctional epoxides such as sorbitol tetraglycidyl ether have been coated onto membranes then cross-linked with N,N,N',N' tetramethyl-1,6-hexanediamine.[180] The coated membranes show reduced flux compared to uncoated control, but improved fouling resistance to 2000 ppm NaCl containing 60 ppm dry milk. Flux after fouling was superior to the uncoated membrane. No change in salt rejection was observed. Polyethylene glycol (meth)acrylates were copolymerized with glycidyl methacrylate or 2-isopropenyl oxazoline to prepare a branched polyethylene glycol with amine-reactive functionality.[178] These were coated onto RO membranes to produce membranes with improved fouling resistant characteristics under treatment with sodium lauryl sulfate and dodecane. Salt passage was improved, but initial flux was slightly reduced compared to the control membrane.

Amine-functional polymer coatings. Amine-functionalized PEGs[177,182] or polyglycerols[181] have been used as antifouling coatings for thin film composite membranes. The amine functionality forms a covalent linkage with acid chloride groups on the membrane surface. Treatment with amine-functional PEGs resulted in reduced flux, improved salt passage and improved resistance to fouling by surfactants, while polyglycerols gave slightly reduced flux and salt rejection compared to unmodified membrane.

Other covalently attached polymers. Polyoxazolines such as poly(ethyl oxazoline) have been used to modify membranes, alone or in combination with PEG glycidyl ethers.[179] This results in increased boron and salt rejection and improved storage stability—no mention is made of the effect on fouling. The polyoxazolines are grafted onto the membrane by reaction between amine or acid chloride groups and the polymer endgroup.

Graft polymerization. Graft polymerizations have been carried out from the surface of RO membranes using a wide range of hydrophilic monomers.[183–187] Polymerizations are carried out in an aqueous system using low (~0.5 M) concentrations of monomers and redox initiator systems.[183] The treated membranes showed increased salt rejection without loss of flux. Membranes grafted with sulfopropyl methacrylate (SPM) or polyethyleneglycol methacrylate (PEGMA) showed reduced adsorption of foulants and easier foulant removal in tests with a highly fouling surface water.[186] Commercial membranes modified by graft polymerization of SPM or PEGMA also showed reduced decline in flux during tests under operating conditions in a pilot plant, although no improvement was seen during accelerated fouling tests.[188] The grafted polymer increases the hydrophilicity of the membrane (manifested as a reduced contact angle) and reduces the roughness of the surface.[187] Both effects are known to reduce fouling in membranes.

A recent concept in reverse osmosis membranes is the introduction of surface modifying macromolecules (LSMM) to the interfacial polymerization with the objective of making the surface more hydrophilic.[189] LSMMs are amphiphilic polyurethanes which may be prepared in advance or *in situ* (by addition of 4,4'-methylene bis(phenylisocyanate) and polyethyleneglycol to the organic phase of the interfacial polymerization). *In situ* formation of low levels of LSMM (0.25 wt% in solvent phase) gave improved salt rejection and reduced initial flux relative to a control membrane. These results were associated with a decreased contact angle and increased roughness. After 50 h of operation the flux of the control membrane was significantly reduced to below that of the LSMM-modified membrane.

A common technique for reducing fouling of surfaces is to apply a coating of a fouling resistant polymer. Many polymers have been evaluated for their antifouling activity.[190] These fall into two broad classes: hydrophilic polymers such as polyethylene glycol (PEG) that resist protein adsorption and cell adhesion, and low energy hydrophobic surfaces such as polydimethylsiloxane (PDMS) that have good fouling release properties. Only the first class of polymer has been investigated in reverse osmosis applications, perhaps due to concerns of reduced flux as a result of application of a hydrophobic coating.

Additionally, antifouling behaviour has been imparted through chemical treatment of the membrane. For example, membranes were prepared incorporating halophenyl acid chlorides such as 5-iodo- or 5-bromo-isophthaloyl chloride or 2-iodo- or 2-bromo-terephthaloyl chloride.[191]

Subsequent treatment with an inorganic persulfate imparts improved chlorine resistance and fouling resistance. In another example, the treatment of freshly formed membranes with 10 mM solutions of various anilines and amines,

Table 4 Antifouling polymer coatings for reverse osmosis membranes

Antifouling polymer coatings	Structure	Reference
PEBAX® 1657		175,176
Poly(vinyl alcohol)		173
Polyethylene glycol		173
PEG diepoxide		177
PEG diamine		177
Poly(PEG methacrylate)-*co*-(glycidyl methacrylate)		178
Poly(PEG methacrylate)-*co*-(2-isopropenyl-oxazoline)		178
Polyvinylpyrrolidinone		173
Polyethyloxazoline	I = initiator group X = end group (e.g. Cl, OH)	179
Sorbitol tetraglycidyl ether	R = H,	180
Polyglycerol		181

e.g. 3-aminoacetophenone, led to improvements in solute passage and reduced biofilm formation.[192] Other antifouling approaches have included the use of electrospun composite structures. The mechanism of operation of the electrospun substrate is unclear but may be due to decreased susceptibility to fouling as a result of the smoother surface compared to membranes prepared on a microporous substrate. Similarly, GE Osmonics Duraslick® membranes are prepared using
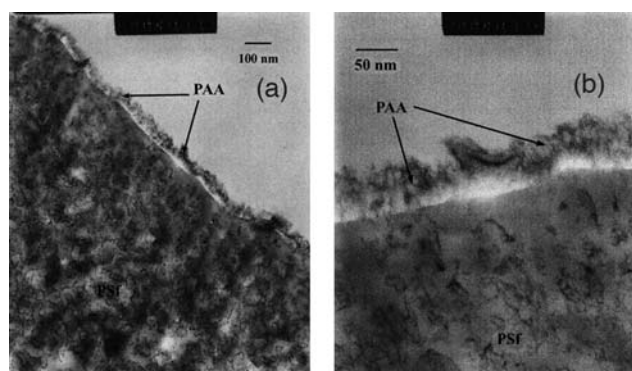
Fig. 14 TEM cross-sectional images of PAA-grafted NF-270 nanofiltration membrane: (a) magnification 60k, (b) magnification 200k. Reproduced with permission from Freger *et al.*, 2002.[187]

a proprietary coating in between the microporous support and the discriminatory layer.[171] This results in a smoother membrane surface which is less susceptible to fouling. Membranes which incorporate nanoparticles into the microporous substrate also exhibit increased compaction resistance and are less susceptible to internal fouling compared to traditional RO membranes. The fouling resistance is in part due to the increased hydrophilicity of the zeolite membrane, and in part due to the compaction resistance.[193]

3.2 Antimicrobial approaches for RO and NF membranes

A number of biocidal techniques have been used with reverse osmosis, including silver-impregnated membranes and membrane elements and use of titania coupled with UV irradiation.[194] *N*-Halamines (prepared by reaction of amides with hypochlorite) show significant antimicrobial activity and can be regenerated by exposure to additional sodium hypochlorite. These materials have been investigated in textile[195–197] and food[198] applications, and may be applicable to TFC membranes, which contain a high concentration of amide groups. However, the poor stability of polyamide membranes towards chlorine, which adversely affects the salt rejection,[199] will limit application of this chemistry.

Numerous patents cover the use of Ag in the pretreatment of RO membrane feed solutions.[200–204] Examples include the use of silvered activated carbon cartridges[200,201] or filters,[203] use of silver-coated pipes,[202] or a silver-coated membrane.[204] Additionally, there are a few examples in the literature of silver-functionalized reverse osmosis membranes.[205–208] Silver-functionalized reverse osmosis membranes have been prepared by interfacial polymerization where the organic phase contains dispersed silver nanoparticles.[205] The resulting membranes showed equivalent performance to membranes without silver (97% $MgSO_4$ rejection, 90 L m^{-2} h^{-1} at 200 psi), and were toxic to *P. aeruginosa*. Toxicity was evaluated by SEM analysis of the samples after incubation with bacteria. More recently, Yang *et al.* reported the application of nanosilver coating to reverse osmosis membranes and spacers.[209] This was achieved by soaking the membrane or spacer first in silver nitrate solution, then in reducing formaldehyde solution. The membranes showed

reduced fouling and flux reduction compared to untreated membranes.

In the patent literature, Ag-functional membranes have been prepared by passing a solution containing $AgNO_3$ and a polyphenol (*e.g.* tannin) through the membrane after fabrication.[207] The polyphenol does not pass through the membrane and complexes silver ions, trapping them on the surface. A recent patent by Nitto Denko[208] describes the preparation of silver-functionalized membranes by coating thin film composite membranes with a dispersion of a silver antimicrobial agent (Novalon 1100AG) in a solution of polyvinyl alcohol. The resulting membranes contained Ag concentrations of $\sim$100 mg m^{-2}, and were toxic to *E. coli* bacteria. Heat treatment of the antimicrobial agent at 1000–1300 °C was found to reduce the leaching of silver during use (95% silver retention after passage of 13 m^3 m^{-2} of water over 11 days). A further technology that may be used to provide silver-modified membranes is by dispersing zeolites in the organic phase prior to the interfacial polymerization reaction. These zeolites can be loaded with silver by ion exchange reactions.[193,210,211] A number of other antimicrobial treatments disclosed in the patent literature include the incorporation of inorganic nanoparticles into the polysulfone substrate.[193] The incorporation of titania nanoparticles into thin film composite membranes gives a membrane which becomes antibacterial when irradiated with UV light, due to the photo-induced formation of hydroxyl radicals on the surface of the titania nanoparticles.[194] As indicated earlier, the technical challenges of UV irradiation and potential polymer degradation in membrane modules are significant issues that have not been yet addressed.

4. Challenges and future opportunities

Biofouling control requires material development and modifications integrated appropriately into the chemical and hydrodynamic environment. Extensive studies have focussed on generating surface hydrophilic, neutral, brush or hydrogel structures on membrane surfaces that show lower initial fouling or microbial attachment. However, it is difficult to achieve the appropriate density on microporous membrane structures without occluding the pores or impacting the separation performance. In addition, many coatings do not have the long-term mechanical and chemical stability *and* the ease of removal of the residual foulants/biofilms accumulated over time. While biofouling cannot be permanently prevented, appropriate surface modification can slow down the adsorption process and growth of the biofilms so that less cleaning chemicals or biocides need to be used. As environmental regulation increases for chemicals such as hypochlorite used in the cleaning processes, there is a greater impetus to reduce their use. Lower usage of water and energy are also tangible benefits of low fouling membranes.

There are increasing efforts to utilize multi-pronged approaches. For example, biocidal moieties will not be sufficient to control biofouling if cellular debris remains to foul the membrane. Additional functionalization of the surface groups may improve performance by combining non-leachable biocidal moieties with anti-adhesion characteristics. Majumdar *et al.* showed that tethering quaternary ammonium salts (QASs) to

a cross-linked polysiloxane matrix formed a hybrid surface with both fouling release and biocidal performance.[212] A number of nanomaterials such as TiO_2, ZnO, peptides, silver nanoparticles and carbon nanotubes are being actively explored as antimicrobial components which can be incorporated into membrane structures or activated by UV light.[213] However leaching and long term activity towards micro-organisms encapsulated in EPS (in contrast to planktonic organisms in suspension) remain significant issues. New synthetic biocides also face large regulatory hurdles, and bacteria may develop resistance to non-oxidizing antimicrobial compounds.[214]

Other bioactive compounds have been shown to disrupt the formation of biofilms. Quorum sensing compounds disrupt signalling within the biofilms and encourage the transition from sessile to planktonic organisms.[215,216] Antifouling enzymes can be used to degrade many biofilm components.[217] Other compounds such bismuth dimercaptopropanol inhibit expression of EPS and proteins.[218] While there is potential to couple these types of compounds to the membranes themselves, embedding or coupling bioactives to spacers and other membrane module components may also mitigate fouling close to stagnant regions that would be prone to microbial attachment without impacting the morphology or surface chemistry of the membrane. For example, Hausman et al. functionalized polypropylene with metal chelating ligands charged with copper ions as potential biocide augmented feed spacer materials to prevent biofouling in spiral wound membrane modules.[219]

Stimuli-responsive coatings also provide additional tunable surface structures and hydrophobicity. Berndt and Ulbricht proposed block copolymers with poly(n-butyl acrylate) (PBA) to tether poly(N-isopropylacrylamide) (PNIPAAm) to functionalize polysulfone surfaces with a temperature switchable coating.[47] PNIPAAm forms a highly hydrated brush at room temperature but has a lower critical solution temperature (LCST) of 32 °C above which the chains collapse into a hydrophobic state. This allows variable hydrophobicity with the potential to discourage selective bacterial colonization by hydrophobic or hydrophilic species. Gorey et al. coupled hydroxypropyl cellulose (HPC) with divinyl sulfone (DVS) onto a cellulose acetate ultrafiltration membrane to form a stimuli-responsive membrane with a LCST of 46 °C.[48]

Antifouling hydrophilic or amphiphilic brushes may be supplemented by a combination of short and long moieties to optimize coverage of potential adsorption sites. A tiered nanostructure or mosaic structure offers other opportunities for increased fouling resistance by providing additional barriers to adsorption from those macromolecular species which have infiltrated the hydrophilic brush coatings. For example, enhanced resistance to protein fouling with mixed short chain anionic and long chain nonionic surfactants adsorbed onto ultrafiltration membranes have been observed by Chen et al.[102] Innovative grafting techniques using controlled radical polymerization such as surface-initiated atom transfer radical polymerization (ATRP) are constantly being developed to deliver better control of chain lengths and functionalization.[220] Mixed brushes (with chains with different chemical structures) can show local surface or phase aggregation or nanopatterning.[221] While these have been postulated as alternative methods to disrupt attachment of micro-organisms, this has not yet been verified in

membrane systems. Finally, enzyme-mediated hydrolysis as a less harsh means of hydrophilization for PAN and PA membranes has been proposed.[222]

The challenges of biofouling are being attacked on many fronts, but implementation of new technologies into broader water and wastewater membrane treatment systems remains limited. Currently many proposed polymers and functionalized surfaces have not been rigorously evaluated for long-term membrane filtration where more severe convective forces and chemical environment are common. Oxidative and hydrolytic attack may occur both from added chemicals or from micro-organisms themselves. Fouling propensity of novel surfaces can only be inferred with short-term adsorption tests with macromolecules such as proteins, polysaccharides, and bacterial adhesion tests. Cyclical cleaning (physical and chemical) protocols are rarely used to evaluate the stability of new coatings or surface modifications, particularly leaching and ageing issues. Finally use of new biocidal components and nanomaterials faces both potential regulatory barriers and potential public concern. These aspects need to be considered in the development of novel polymer modifications before they can be incorporated into widespread usage in water treatment processes.

Acknowledgements

References

1 H. Nagaoka, S. Yamanishi and A. Miya, *Water Sci. Technol.*, 1998, **38**, 497.
2 J. R. Pan, Y. C. Su, C. Huang and H. C. Lee, *J. Membr. Sci.*, 2010, **349**, 287–294.
3 J. S. Baker and L. Y. Dudley, *Desalination*, 1998, **118**, 81–89.
4 H. Y. Kim, K. M. Yeon, C. H. Lee, S. Lee and T. Swaminathan, *Sep. Sci. Technol.*, 2006, **41**, 1213–1230.
5 H. C. Flemming, G. Schaule, T. Griebe, J. Schmitt and A. Tamachkiarowa, *Desalination*, 1997, **113**, 215.
6 H. C. Flemming, *Appl. Microbiol. Biotechnol.*, 2002, **59**, 629–640.
7 H. C. Flemming, *Water Science and Technology*, 2003, **47**, 1–8.
8 H. C. Flemming and G. Schaule, *Desalination*, 1988, **70**, 95–119.
9 T. F. S. Speth, R.S. and A. M. Gusses, *Environ Sci Technol*, 1998, 32.
10 R. P. Schneider, L. M. Ferreira, P. Binder, E. M. Bejarano, K. P. Góes, E. Slongo, C. R. Machado and G. M. Z. Rosa, *J. Membr. Sci.*, 2005, **266**, 18–29.
11 S. Wang, G. Guillen and E. M. V. Hoek, *Environ. Sci. Technol.*, 2005, **39**, 6461–6469.
12 C. M. Pang, P. Y. Hong, H. L. Guo and W. T. Liu, *Environ. Sci. Technol.*, 2005, **39**, 7541–7550.
13 S. Rice and S. Kjellberg, *Microbiol. Australia*, 2007, **28**, 118–120.
14 S. Kjelleberg and M. Givskov, *Horizon Bioscience*, 2007, 5.
15 V. Chen, H. Li and A. G. Fane, *J. Membr. Sci.*, 2004, **241**, 23–44.
16 H. Li, A. G. Fane, H. G. L. Coster and S. Vigneswaran, *J. Membr. Sci.*, 2003, **217**, 29–41.
17 B. K. Hwang, W. N. Lee, P. K. Park, C. H. Lee and I. S. Chang, *J. Membr. Sci.*, 2007, **288**, 149–156.
18 W. N. Lee, I. S. Chang, B. K. Hwang, P. K. Park, C. H. Lee and X. Huang, *Process Biochem.*, 2007, **42**, 655–661.
19 M. F. A. Goosen, S. S. Sablani, H. Al-Hinai, S. Al-Obeidani, R. Al-Belushi and D. Jackson, *Sep. Sci. Technol.*, 2005, **39**, 2261–2297.
20 H. Ridgway, K. Ishida, G. Rodriguez, J. Safarik, T. Knoell, R. Bold and J. D. Ron, in *Methods in Enzymology*, ed. R. J. Doyle, Academic Press, 1999, p. 463.

21 V. Chen, J. Mansouri and T. Charlton, in *Membrane Technology: Volume 4: Membranes for Water Treatment*, ed. S. Nunes and K. Peineman, Wiley-VCH, 2010 (in press).

22 K. Zhang, H. Choi, D. D. Dionysiou, G. A. Sorial and D. B. Oerther, *Environ. Microbiol.*, 2006, **8**, 433–440.

23 U. Metzger, P. Le-Clech, R. M. Stuetz, F. H. Frimmel and V. Chen, *J. Membr. Sci.*, 2007, **301**, 180–189.

24 L. H. G. Morton, D. L. A. Greenway, C. C. Gaylarde and S. B. Surman, *Int. Biodeterior. Biodegrad.*, 1998, **41**, 247.

25 S. Kim and E. M. V. Hoek, *Desalination*, 2007, **202**, 333–342.

26 X. Jin, A. Jawor, S. Kim and E. M. V. Hoek, *Desalination*, 2009, **239**, 346–359.

27 A. Jawor and E. M. V. Hoek, *Desalination*, 2009, **235**, 44–57.

28 H. Mo, K. G. Tay and H. Y. Ng, *J. Membr. Sci.*, 2008, **315**, 28–35.

29 S. G. Yiantsios, D. Sioutopoulos and A. J. Karabelas, *Desalination*, 2005, **183**, 257–272.

30 A. Subramani and E. M. V. Hoek, *J. Membr. Sci.*, 2008, **319**, 111–125.

31 X. H. Zhu and M. Elimelech, *Environ. Sci. Technol.*, 1997, **31**, 3654–3662.

32 C. Y. Tang, Y. N. Kwon and J. O. Leckie, *J. Membr. Sci.*, 2009, **326**, 526–532.

33 M. F. A. Goosen, S. S. Sablani, H. Ai-Hinai, S. Ai-Obeidani, R. Al-Belushi and D. Jackson, *Sep. Sci. Technol.*, 2005, **39**, 2261–2297.

34 E. M. V. Hoek, S. Bhattacharjee and M. Elimelech, *Langmuir*, 2003, **19**, 4836–4847.

35 M. Herzberg and M. Elimelech, *J.l Am. Water Works Assoc.*, 2007, **295**, 11–20.

36 J. S. Vrouwenvelder, D. A. G. von der Schulenburg, J. C. Kruithof, M. L. Johns and M. C. M. van Loosdrecht, *Water Res.*, 2009, **43**, 583–594.

37 S. Coker and P. Sehn, *Desalination*, 2000, **132**, 211.

38 S. A. Avlonitis, K. Kouroumbas and N. Vlachakis, *Desalination*, 2003, **157**, 151–158.

39 P. Le-Clech, A. G. Fane, G. L. Leslie and A. Childress, *Filtr. Sep.*, 2005, **42**, 20–23.

40 S. Kang, E. M. V. Hoek, H. Choi and H. Shin, *Sep. Sci. Technol.*, 2006, **41**, 1475–1487.

41 T. Knoell, J. Safarik, T. Cormack, R. Riley, S. W. Lin and H. Ridgway, *J. Membr. Sci.*, 1999, **157**, 117.

42 S. B. S. Ghayeni, P. J. Beatson, R. P. Schneider and A. G. Fane, *J. Membr. Sci.*, 1998, **138**, 29–42.

43 P. Kingshott and H. J. Griesser, *Curr. Opin. Solid State Mater. Sci.*, 1999, **4**, 403–412.

44 P. Vermette and L. Meagher, *Colloids Surf., B*, 2003, **28**, 153–198.

45 M. E. Callow and R. L. Fletcher, *Int. Biodeterior. Biodegrad.*, 1994, **34**, 333–348.

46 Q. Zhao, S. Wang and H. Muller-Steinhagen, *Appl. Surf. Sci.*, 2004, **230**, 371–378.

47 E. Berndt and M. Ulbricht, *Polymer*, 2009, **50**, 5181–5191.

48 C. Gorey, I. C. Escobar, C. Gruden, M. Coleman and O. Mileyeva-Biebesheimer, *Sep. Sci. Technol.*, 2008, **43**, 4056–4074.

49 L. Zeman and A. L. Zydney, *Microfiltration and Ultrafiltration: Principles and Applications*, Marcel Dekker, New York, 1996.

50 K. C. Khulbe, C. Feng and T. Matsuura, *J. Appl. Polym. Sci.*, 2010, **115**, 855–895.

51 B. van der Bruggen, *J. Appl. Polym. Sci.*, 2009, **114**, 630–642.

52 B. Kaeselev, J. Pieracci and G. Belfort, *J. Membr. Sci.*, 2001, **194**, 245–261.

53 J. Pieracci, J. V. Crivello and G. Belfort, *J. Membr. Sci.*, 2002, **202**, 1–16.

54 L. Zhang, G. Chowdhury, C. Feng, T. Matsuura and R. Narbaitz, *J. Appl. Polym. Sci.*, 2003, **88**, 3132–3138.

55 C. A. Smolders, A. J. Reuvers, R. M. Boom and I. M. Wienk, *J. Membr. Sci.*, 1992, **73**, 259–275.

56 T. Uragami, Y. Naito and M. Sugihara, *Polym. Bull.*, 1981, **4**, 617–622.

57 R. M. Boom, I. M. Wienk, T. van den Boomgaard and C. A. Smolders, *J. Membr. Sci.*, 1992, **73**, 277–292.

58 R. M. Boom, T. van den Boomgaard and C. a. Smolders, *J. Membr. Sci.*, 1994, **90**, 231–249.

59 I. M. Wienk, R. M. Boom, M. A. M. Beerlage, A. M. W. Bulte, C. A. Smolders and H. Strathmann, *J. Membr. Sci.*, 1996, **113**, 361–371.

60 H. T. Yeo, S. T. Lee and M. J. Han, *J. Chem. Eng. Jpn.*, 2000, **33**, 180–184.

61 D. B. Mosqueda-Jimenez, R. M. Narbaitz, T. Matsuura, G. Chowdhury, G. Pleizier and J. P. Santerre, *J. Membr. Sci.*, 2004, **231**, 209–224.

62 B. Torrestiana-Sanchez, R. I. Ortiz-Basurto and E. Brito-De La Fuente, *J. Membr. Sci.*, 1999, **152**, 19–28.

63 N. A. Ochoa, P. Prádanos, L. Palacio, C. Pagliero, J. Marchese and A. Hernández, *J. Membr. Sci.*, 2001, **187**, 227–237.

64 J. Marchese, M. Ponce, N. A. Ochoa, P. Prádanos, L. Palacio and A. Hernández, *J. Membr. Sci.*, 2003, **211**, 1–11.

65 A. Idris, N. Mat Zain and M. Y. Noordin, *Desalination*, 2007, **207**, 324–339.

66 B. Chakrabarty, A. K. Ghoshal and M. K. Purkait, *J. Membr. Sci.*, 2008, **309**, 209–221.

67 Y. Liu, G. H. Koops and H. Strathmann, *J. Membr. Sci.*, 2003, **223**, 187–199.

68 J.-H. Kim and K.-H. Lee, *J. Membr. Sci.*, 1998, **138**, 153–163.

69 S. I. Jeon, J. H. Lee, J. D. Andrade and P. G. De Gennes, *J. Colloid Interface Sci.*, 1991, **142**, 149–158.

70 S. I. Jeon and J. D. Andrade, *J. Colloid Interface Sci.*, 1991, **142**, 159–166.

71 Y.-Q. Wang, Y.-L. Su, X.-L. Ma, Q. Sun and Z.-Y. Jiang, *J. Membr. Sci.*, 2006, **283**, 440–447.

72 Y. Q. Wang, Y. L. Su, Q. Sun, X. L. Ma and Z. Y. Jiang, *J. Membr. Sci.*, 2006, **286**, 228–236.

73 A. Asatekin, S. Kang, M. Elimelech and A. M. Mayes, *J. Membr. Sci.*, 2007, **298**, 136–146.

74 Pat., WO 2007/120631 A1, 2007.

75 X. L. Ma and Y. L. Su, *J. Membr. Sci.*, 2007, **292**, 116–124.

76 L. P. Zhu and X. X. Zhang, *Colloids Surf., B*, 2007, **57**, 189–197.

77 L.-P. Zhu, Z. Yi, F. Liu, X.-Z. Wei, B.-K. Zhu and Y.-Y. Xu, *Eur. Polym. J.*, 2008, **44**, 1907–1914.

78 S. Feng, Q. Wang, Y. Gao, Y. Huang and F.-L. Qing, *J. Appl. Polym. Sci.*, 2009, **114**, 2071–2078.

79 N. Clarkson and L. V. Evans, *Biofouling: J. Bioadhes. Biofilm Res.*, 1995, **9**, 129–143.

80 W. Senaratne, L. Andruzzi and C. K. Ober, *Biomacromolecules*, 2005, **6**, 2427–2448.

81 S. Krishnan, N. Wang, C. K. Ober, J. A. Finlay, M. E. Callow, J. A. Callow, A. Hexemer, K. E. Sohn, E. J. Kramer and D. A. Fischer, *Biomacromolecules*, 2006, **7**, 1449–1462.

82 J. F. Hester, P. Banerjee and A. M. Mayes, *Macromolecules*, 1999, **32**, 1643–1650.

83 S. Kang, A. Asatekin, A. M. Mayes and M. Elimelech, *J. Membr. Sci.*, 2007, **296**, 42–50.

84 K. Na, H. Jang, K. Kim, T. Tak and J. Hyun, *Proceedings of the 230th National Meeting of the American Chemical Society*, Washington, DC, 2005, p. U3661.

85 Y.-H. Zhao, Y.-L. Qian, B.-K. Zhu and Y.-Y. Xu, *J. Membr. Sci.*, 2008, **310**, 567–576.

86 A. Hamza, V. A. Pham, T. Matsuura and J. P. Santerre, *J. Membr. Sci.*, 1997, **131**, 217–227.

87 M. Khayet, C. Y. Feng and T. Matsuura, *J. Membr. Sci.*, 2003, **213**, 159–180.

88 D. Rana, T. Matsuura, R. M. Narbaitz and C. Feng, *J. Membr. Sci.*, 2005, **249**, 103–112.

89 S. Ye, W.J. and K. Ishihara, *J. Biomater. Sci., Polym. Ed.*, 2004, **15**, 981–1001.

90 S. H. Ye, J. Watanabe, Y. Iwasaki and K. Ishihara, *J. Membr. Sci.*, 2005, **249**, 133–141.

91 J. Hester, P. Banerjee, A. Akthakul, M. Acar and A. Mayes, *Macromolecules*, 2002, **35**, 7652–7661.

92 L. Hancock and F., *J. Appl. Polym. Sci.*, 1997, **66**, 1353–1358.

93 Y.-Q. Wang, T. Wang, Y.-L. Su, F.-B. Peng, H. Wu and Z.-Y. Jiang, *Langmuir*, 2005, **21**, 11856–11862.

94 J. F. Hester, P. Banerjee, Y. Y. Won, A. Akthakul, M. H. Acar and A. M. Mayes, *Macromolecules*, 2002, **35**, 7652–7661.

95 C. Siegers, M. Biesalski and R. Haag, *Chem.–Eur. J.*, 2004, **10**, 2831–2838.

96 D. J. Irvine, A. M. Mayes and L. Griffith-Cima, *Macromolecules*, 1996, **29**, 6037–6043.

97 C. S. Gudipati, J. A. Finlay, J. A. Callow, M. E. Callow and K. L. Wooley, *Langmuir*, 2005, **21**, 3044–3053.

98 M. Ulbricht, *Polymer*, 2006, **47**, 2217–2262.

99 Z. Bao, M. L. Bruening and G. L. Baker, *Macromolecules*, 2006, **39**, 5251–5258.
100 M. Pasmore, P. Todd, S. Smith, D. Baker, J. Silverstein, D. Coons and C. N. Bowman, *J. Membr. Sci.*, 2001, **194**, 15–32.
101 K. J. Kim, A. G. Fane and C. J. D. Fell, *J. Membr. Sci.*, 1989, **43**, 187–204.
102 V. Chen, A. G. Fane and C. J. D. Fell, *J. Membr. Sci.*, 1992, **67**, 249–261.
103 J. Hyun, H. Jang, K. Kim, K. Na and T. Tak, *J. Membr. Sci.*, 2006, **282**, 52–59.
104 C. Ba, J. Langer and J. Economy, *J. Membr. Sci.*, 2009, **327**, 49–58.
105 B. D. Freeman and I. Pinnau, *Proceedings of the ACS Symposium Series 876 (Advanced Materials for Membrane Separations)*, ed. B. D. Freeman and I. Pinnau, American Chemical Society, Washington DC, 2004, 1–23.
106 R. Revanur, B. McCloskey, K. Breitenkamp, B. D. Freeman and T. Emrick, *Macromolecules*, 2007, **40**, 3624–3630.
107 A. Akthakul, R. F. Salinaro and A. M. Mayes, *Macromolecules*, 2004, **37**, 7663–7668.
108 US Pat., US20070021529A1, 2007.
109 US Pat., WO 2007/053163 A2, 2006.
110 X. L. Ma and Y. L. Su, *et al.*, *J. Membr. Sci.*, 2007, **300**, 71–78.
111 Z. Y. Xi, Y. Y. Xu, L. P. Zhu, Y. Wang and B. K. Zhu, *J. Membr. Sci.*, 2009, **327**, 244–253.
112 D. Miller, B. McCloskey, H. B. Park, H. Ju, B. Rowe, A. Ellington, D. Paul and B. D. Freeman, *19th North American Membrane Society Annual Meeting 2009 (NAMS 2009)*, Curran Associates Inc., 2009.
113 Y. Chang, C.-Y. Ko, Y.-J. Shih, D. Quémener, A. Deratani, T.-C. Wei, D.-M. Wang and J.-Y. Lai, *J. Membr. Sci.*, 2009, **345**, 160–169.
114 Y.-L. Su, W. Cheng, C. Li and Z. Jiang, *J. Membr. Sci.*, 2009, **329**, 246–252.
115 G. N. B. Baroña, B. J. Cha and B. Jung, *J. Membr. Sci.*, 2007, **290**, 46–54.
116 F.-Q. Nie, Z.-K. Xu, Q. Yang, J. Wu and L.-S. Wan, *J. Membr. Sci.*, 2004, **235**, 147–155.
117 N. Hilal, V. Kochkodan, L. Al-Khatib and T. Levadna, *Desalination*, 2004, **167**, 293–300.
118 J. Pieracci, J. V. Crivello and G. Belfort, *J. Membr. Sci.*, 1999, **156**, 223–240.
119 M. Khayet, J. P. G. Villaluenga and J. L. Valentin, *Polymer*, 2005, **46**, 9881–9891.
120 Y. J. S. Liang, L. Sun, X.Y. and L. J. Wang, *Technol. Water Treat.*, 2004, **30**, 199–201.
121 T. H. Bae, I. C. Kim and T. M. Tak, *J. Membr. Sci.*, 2006, **275**, 1–5.
122 T. H. Bae and T. M. Tak, *J. Membr. Sci.*, 2005, **266**, 1–5.
123 T. H. Bae and T. M. Tak, *J. Membr. Sci.*, 2005, **249**, 1–8.
124 J. B. Li, J. W. Zhu and M. S. Zheng, *J. Appl. Polym. Sci.*, 2007, **103**, 3623–3629.
125 L. Liu, L. Xiao and F. Yang, *J. Membr. Sci.*, 2009, **333**, 110–117.
126 A. Rahimpour, S. S. Madaeni, A. H. Taheri and Y. Mansourpanah, *J. Membr. Sci.*, 2008, **313**, 158–169.
127 Y. Yang, H. Zhang, P. Wang, Q. Zheng and J. Li, *J. Membr. Sci.*, 2007, **288**, 231–238.
128 S. S. Madaeni and N. Ghaemi, *J. Membr. Sci.*, 2007, **303**, 221–233.
129 G. Wu, S. Gan, L. Cui and Y. Xu, *Appl. Surf. Sci.*, 2008, **254**, 7080–7086.
130 M.-L. Luo, J.-Q. Zhao, W. Tang and C.-S. Pu, *Appl. Surf. Sci.*, 2005, **249**, 76–84.
131 V. Kochkodan, S. Tsarenko, N. Potapchenko, V. Kosinova and V. Goncharuk, *Desalination*, 2008, **220**, 380.
132 X. Zhang, D. D. Sun and J. O. Leckie, *J. Membr. Sci.*, 2008, **313**, 44–51.
133 J. H. Li, Y. Y. Xu, L. P. Zhu, J. H. Wang and C. H. Du, *J. Membr. Sci.*, 2009, **326**, 659–666.
134 S. J. Oh, N. Kim and Y. T. Lee, *J. Membr. Sci.*, 2009, **345**, 13–20.
135 X. C. Cao, J. Ma, X. H. Shi and Z. J. Ren, *Appl. Surf. Sci.*, 2006, **253**, 2003–2010.
136 T. Tashiro, *Macromol. Mater. Eng.*, 2001, **286**, 63–87.
137 N. P. Desai, S. F. A. Hossainy and J. A. Hubbell, *Biomaterials*, 1992, **13**, 417–420.
138 A. M. P. McDonnell, D. Beving, A. Wang, W. Chen and Y. Yan, *Adv. Funct. Mater.*, 2005, **15**, 336–340.
139 H. V. Rasika Dias, K. H. Batdorf, M. Fianchini, H. V. K. Diyabalanage, S. Carnahan, R. Mulcahy, A. Rabiee, K. Nelson and L. G. v. Waasbergen, *J. Inorg. Biochem.*, 2006, **100**, 158–160.
140 G. L. Feng, J. Wu and J. O. Kim, *J. Biomed. Mater. Res.*, 2000, **52**, 662.
141 I. Chopra, *J. Antimicrob. Chemother.*, 2007, **59**, 587–590.
142 J. C. Tiller, in *Polymeric Drug Delivery II*, 2006, pp. 215–231.
143 N. Hilal, V. Kochkodan, L. Al-Khatib and T. Levadna, *Desalination*, 2004, **167**, 293–300.
144 N. Hilal, L. Al-Khatib, B. P. Atkin, V. Kochkodan and N. Potapchenko, *Desalination*, 2003, **158**, 65.
145 R. Nigmatullin, V. Konovalova and G. Pobigay, *J. Appl. Polym. Sci.*, 2009, **111**, 1697–1705.
146 E. I. Rabea, M. E. T. Badawy, C. V. Stevens, G. Smagghe and W. Steurbaut, *Biomacromolecules*, 2003, **4**, 1457–1465.
147 Pat., EP 99–10212119990203, 1999.
148 Korea Pat., KR2004039907, 2004.
149 US Pat., 6, 540, 915 B2, 2003.
150 Australia Pat., WO 2008–EP63000, 2009.
151 S. Ciston, R. M. Lueptow and K. A. Gray, *J. Membr. Sci.*, 2008, **320**, 101–107.
152 F. Hardorfer and G. Hartel, *Chem. Eng. Technol.*, 1999, **22**, 313–316.
153 D. G. Yu, M.-Y. Teng, W.-L. Chou and M.-C. Yang, *J. Membr. Sci.*, 2003, **225**, 115–123.
154 W.-L. Chou and M.-C. Yang, *Polym. Adv. Technol.*, 2005, **16**, 600.
155 S. Loher, O. D. Schneider, T. Maienfisch, S. Bokorny and W. J. Stark, *Small*, 2008, **4**, 824–832.
156 J. E. Cadotte and L. T. Rozelle, *OSW PB-Report*, 1972, 927.
157 R. J. Petersen, *J. Membr. Sci.*, 1993, **83**, 81–150.
158 M. Kurihara and Y. Himeshima, *Polym. J.*, 1991, **23**, 513–520.
159 T. Matsuura, *Desalination*, 2001, **134**, 47–54.
160 I. M. El-Azizi and R. G. J. Edyvean, *Desalin. Water Treat.-Sci. Eng.*, 2009, **5**, 34–41.
161 C. Hobbs, S. K. Hong and J. Taylor, *J. Water Supply: Res. Technol.–AQUA*, 2006, **55**, 559–570.
162 E. M. Vrijenhoek, S. Hong and M. Elimelech, *J. Membr. Sci.*, 2001, **188**, 115–128.
163 A. Subramani, X. F. Huang and E. M. V. Hoek, *J. Colloid Interface Sci.*, 2009, **336**, 13–20.
164 M. Elimelech, X. Zhu, A. E. Childress and S. Hong, *J. Membr. Sci.*, 1997, **127**, 101–109.
165 W. R. Bowen and T. A. Doneva, *J. Colloid Interface Sci.*, 2000, **229**, 544–549.
166 L. F. Liu, S. C. Yu, L. G. Wu and C. H. Gao, *J. Membr. Sci.*, 2006, **283**, 133–146.
167 L. F. Liu, S. C. Yu, L. G. Wu and C. J. Gao, *J. Membr. Sci.*, 2008, **310**, 119–128.
168 H. B. Park, B. D. Freeman, Z. Zhang, M. Sankir and J. E. McGrath, *Angew. Chem., Int. Ed.*, 2008, **47**, 6019–6024.
169 H. B. Park, B. D. Freeman, Z.-B. Zhang, G.-Y. Fan, M. Sankir and J. E. McGrath, *PMSE Prepr.*, 2006, **95**, 889–891.
170 M. Paul, H. B. Park, B. D. Freeman, A. Roy, J. E. McGrath and J. S. Riffle, *Polymer*, 2008, **49**, 2243–2252.
171 G. Osmonics, *Duraslick™ Low Fouling Membranes for Surface and Natural Water*, http://www.desalwater.com/Featured-Duraslick.htm, Accessed November 25, 2009.
172 D. Norberg, S. Hong, J. Taylor and Y. Zhao, *Desalination*, 2007, **202**, 45–52.
173 Japan Pat., PCT/JP1997/000856, 1997.
174 US Pat., US6,177,011, 2001.
175 US Pat., US2005/077,243, 2003.
176 J. S. Louie, I. Pinnau, I. Ciobanu, K. P. Ishida, A. Ng and M. Reinhard, *J. Membr. Sci.*, 2006, **280**, 762–770.
177 US Pat., US6,280,853, 1999.
178 US Pat., US2007/251,883, 2007.
179 US Pat., US2008185332, 2008.
180 US Pat., US2003/121,844, 2003.
181 US Pat., US2007/175,820, 2007.
182 US Pat., US2007/175,821, 2007.
183 Pat., WO2006/030411, 2006.
184 S. Belfer, Y. Purinson and O. Kedem, *Acta Polym.*, 1998, **49**, 574–582.
185 S. Belfer, Y. Purinson., R. Fainshtein, Y. Radchenko and O. Kedem, *J. Membr. Sci.*, 1998, **139**, 175–181.
186 J. Gilron, S. Belfer, P. Väisänen and M. Nyström, *Desalination*, 2001, **140**, 167–179.

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J. Mater. Chem., 2010, **20**, 4567–4586 | 4585

187 V. Freger, J. Gilron and S. Belfer, *J. Membr. Sci.*, 2002, **209**, 283–292.

188 S. Belfer, J. Gilron, Y. Purinson, R. Fainshtain, N. Daltrophe, M. Priel, B. Tenzer and A. Toma, *Desalination*, 2001, **139**, 169.

189 B. J. Abu Tarboush, D. Rana, T. Matsuura, H. A. Arafat and R. M. Narbaitz, *J. Membr. Sci.*, 2008, **325**, 166–175.

190 S. Krishnan, C. J. Weinman and C. K. Ober, *J. Mater. Chem.*, 2008, **18**, 3405–3413.

191 US Pat., US2008/203,013, 2008.

192 Pat., WO2007133362, 2007.

193 US Pat., US2008237126-A1 2008.

194 S. Y. Kwak, S. H. Kim and S. S. Kim, *Environ. Sci. Technol.*, 2001, **35**, 2388–2394.

195 G. Sun and X. J. Xu, *Text. Chem. Color.*, 1998, **30**, 26–30.

196 G. Sun and X. Xu, *Text. Chem. Color.*, 1999, **31**, 21–24.

197 G. Sun, X. J. Xu, J. R. Bickett and J. F. Williams, *Ind. Eng. Chem. Res.*, 2001, **40**, 1016–1021.

198 J. M. Goddard and J. H. Hotchkiss, *J. Food Protection*, 2008, **71**, 2042–2047.

199 E. S. Kim, Y. J. Kim, Q. S. Yu and B. L. Deng, *J. Membr. Sci.*, 2009, **344**, 71–81.

200 Japan Pat., JP2006281023-A, 2006.

201 Japan Pat., JP2000288539-A, 2000.

202 Korea Pat., KR2004038971, 2004.

203 South Korea Pat., KR 2004074362., 2004.

204 Germany Pat., DE20203733–U1, 2002.

205 S. Y. Lee, H. J. Kim, R. Patel, S. J. Im, J. H. Kim and B. R. Min, *Polym. Adv. Technol.*, 2007, **18**, 562–568.

206 H.-L. Yang, J. C.-T. Lin and C. Huang, *Water Res.*, 2009, **43**, 3777–3786.

207 Japan Pat., JP2008142596, 2008.

208 Pat., WO2009008500A1, 2009.

209 H. L. Yang, J. C. T. Lin and C. Huang, *Water Res.*, 2009, **43**, 3777–3786.

210 B. H. Jeong, E. M. V. Hoek, Y. S. Yan, A. Subramani, X. F. Huang, G. Hurwitz, A. K. Ghosh and A. Jawor, *J. Membr. Sci.*, 2007, **294**, 1–7.

211 Pat., WO2006098872-A2 2006.

212 P. Majumdar, E. Lee, N. Patel, S. J. Stafslien, J. Daniels and B. J. Chisholm, *J. Coat. Technol. Res.*, 2008, **5**, 405–417.

213 Q. L. Li, S. Mahendra, D. Y. Lyon, L. Brunet, M. V. Liga, D. Li and P. J. J. Alvarez, *Water Res.*, 2008, **42**, 4591–4602.

214 T. E. Cloete, *Int. Biodeterior. Biodegrad.*, 2003, **51**, 277–282.

215 D. Paul, Y. S. Kim, K. Ponnusamy and J. H. Kweon, *Environ. Eng. Sci.*, 2009, **26**, 1319–1324.

216 K. M. Yeon, W. S. Cheong, H. S. Oh, W. N. Lee, B. K. Hwang, C. H. Lee, H. Beyenal and Z. Lewandowski, *Environ. Sci. Technol.*, 2009, **43**, 380–385.

217 J. B. Kristensen, R. L. Meyer, B. S. Laursen, S. Shipovskov, F. Besenbacher and C. H. Poulsen, *Biotechnol. Adv.*, 2008, **26**, 471–481.

218 A. R. Badireddy, S. Chellam, S. Yanina, P. Gassman and K. M. Rosso, *Biotechnol. Bioeng.*, 2008, **99**, 634–643.

219 R. Hausman, T. Gullinkala and I. C. Escobar, *J. Appl. Polym. Sci.*, 2009, **114**, 3068–3073.

220 N. Singh, Z. Chen, N. Tomer, S. R. Wickramasinghe, N. Soice and S. M. Husson, *J. Membr. Sci.*, 2008, **311**, 225–234.

221 I. Luzinov, S. Minko and V. V. Tsukruk, *Prog. Polym. Sci.*, 2004, **29**, 635–698.

222 G. M. Guebitz and A. Cavaco-Paulo, *Trends Biotechnol.*, 2008, **26**, 32–38.