Can fouling in membranes be ever defeated?

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Abstract

Fouling continues to be a major problem in membrane technology when water is the separation medium. In this review, the recent advances in strategies for fouling minimization are summarized and critically discussed. Different grafting approaches for surface modification are highlighted, particularly those promoting the integration of zwitterionic building blocks in the membrane top layer. We compare layer-by-layer and other coating methods, and emerging technologies such as 3D printing for pattern development, laser induced graphene formation and integration of other carbon-based materials to assist electrically driven processes of fouling mitigation. Finally, we emphasize the relevance of developing membranes with higher stability in chlorine, acid and base agents, since regular cleaning has been still mandatory to maintain the membrane performance in long periods of operation.
Seawater desalination, treatment of domestic and industrial wastewater, blood purification, and food processing are the applications that contribute to the largest fraction of the synthetic membrane market. While membrane technology is considered energy-saving and environmentally beneficial, membranes in these fields suffer from a common problem: fouling, where the flow rate decreases during operation due to the adhesion and accumulation of organic and/or biomolecules on the surface and pores. Decades of investigation have been dedicated to understand, characterize and minimize fouling, but this remains one of the biggest challenges in membrane technology for the water sector. This paper summarizes some of the scientific advances in the membrane modification for the fouling minimization in the last few years, critically discussing their perspectives of success. Besides membrane development itself, control approaches continue to be applied, promoting aeration, chemical cleaning (e.g. chlorine-based), biological control (e.g. enzymatic and bacterial degradation of biofilms), and more recently electrically-assisted process for fouling mitigation.[1]

Chlorine resistant membranes.

While the development of membranes with intrinsic fouling resistance has been a worldwide topic of research for decades in long-term operations, chlorine-based cleaning is frequently used. Despite being applied worldwide in large-scale desalination, thin-film composite (TFC) membranes based on polyamide do not have a satisfactory resistance to chlorine.[2] Scalable membranes with better chlorine-resistance are highly desired. New efforts with this goal have been reported in recent years. One of the reports on chlorine resistance proposes the modification of polyamide with 2,6-diaminopyridine and subsequent quaternization with 3-bromopropionic acid on membranes. [3] However, chemistries other than polyamide, such as poly(arylene ether
sulfone)s [4] or poly(epoxyether) [5], might be more effective to provide the needed higher chlorine resistance. A promising concept proposes multilayer membranes based on complexes of sulfonated polystyrene and poly(allylamine) hydrochloride, crosslinked with glutaraldehyde. [6]

*Development of membranes with intrinsic fouling resistance*

The first stages of the fouling process are driven by the interaction between the foulant and the membrane. With that in mind, strategies for fouling mitigation are mainly based on surface modification. [7-9] Figure 1 summarizes the most relevant approaches. They are based on (1) the incorporation of chemical groups by grafting, coatings or polymerization with anti-fouling building blocks; (2) integration of engineered nanomaterials; (3) introduction of surface patterns and (4) conductive layers.

![Figure 1. Surface modification methods for enhancing fouling resistance.](image-url)
A comprehensive demonstration of the most effective anti-fouling functionalization groups has been conducted by Belfort and co-workers, using high throughput plasma-induced graft polymerization. [10] Zwitterionic and ethylene glycol functional groups have been the preferred ones. Hydration prevents the adhesion of proteins, bacterial cells and extracellular polymeric substances to the membrane. Their results have motivated different approaches. Venault and Chang [11] recently summarized a broad variety of concepts their group explored for interfaces, hydrogels and membranes. This includes in-situ modification, synthesis and self-assembly of copolymers, and coating. Derivatives of sulfobetaine are the most explored zwitterionic functionality for anti-fouling membranes, compared to other options, such as caboxybetaine and phosphobetaine. A reason for that is the simpler and cheaper synthesis of sulfobetaine compounds. Effective approaches have been also explored by other groups. Figure 2 indicates approaches that have been under investigation by our group. Le et al. [12] grafted zwitterionic poly(sulfobetaine) in the lumen of polyetherimide hollow fibers. Modifications of hollow fibers with poly(ethylene glycol) (PEG) and zwitterionic poly(sulfobetaine) hydrogels were compared under common cleaning conditions. [13] To mention some quantitative results, the protein adsorption was reduced to 23 and 11 %, respectively, relative to unmodified membranes. The flux recovery after cleaning was 63 and 94 % for modified membranes, while the unmodified ones had only 42 % recovery. Stability is a clear difference between the two modifications. The poly(sulfobetaine) hydrogel was stable in acid, base and chlorine solutions, while PEG suffered alkaline hydrolysis in base and oxidative conditions. For the grafting of PEG a pre-treatment with dopamine was performed to provide adhesion. The use of polydopamine for anti-fouling membranes has been successfully
introduced by the Freeman’s group [7] and have been further explored by several groups in the field. More recently, his group proposed a one-step modification, combining polydopamine and a zwitterionic polymer, poly(2-methacryloyloxyethyl phosphorylcholine). [14] In another approach based on dopamine, Liu et al. [15] used its hydrochloride derivative as starting material for the modification, followed by reaction with 2-bromoisobutyryl bromide and triethylamine. The resulting bromine functionalized coating surface was then used as platform for atom-transfer radical polymerization (ATRP) and incorporation of zwitterionic brushes.

Figure 2. Selected building blocks recently explored for interfacial polymerization and surface modification.
Duong et al. [16] proposed a particularly effective method, incorporating zwitterionic building blocks during the formation of the membrane selective polyamide layers by interfacial polymerization. In this way the anti-fouling functionality was integrated as part of the membrane already during the preparation, not requiring post-treatments and forming thin and stable layers. A high permeance of 135 L m$^{-2}$ h$^{-1}$ bar$^{-1}$ and high rejection of organic dyes of molecular weight 700 g/mol were achieved. Mi et al. [17] worked with interfacial polymerization, but in two steps, first using 3, 3’-diamino-N-methyldipropylamine as building block and secondly reacting with 1,3-propanesultone. These approaches could in principle be performed in the same machines industrially used for commercial interfacial polymerization membranes, facilitating the scaling-up and translation into a product.

Besides modification with zwitterionic groups, Duong et al. investigated the incorporation of amino-functionalized dendrimers [18] and porphyrin [19] during the formation of the interfacial polymerization layer. Porphyrin gives a biocide capacity to the surface, when interacting with light. Considering the effect of light in a different way, Kaner et al. [20] modified polyacrylonitrile by ATRP, inserting photo-responsive side chains. A transition from a hydrophobic spiropyran to a hydrophilic zwitterionic merocyanine group, induced by light, gave a self-cleaning property to the membrane.

The membrane modification with peptides has been investigated to reduce biofouling. [21, 22] While purely hydrophilic groups act by inhibiting the adherence of foulants to the surface, the selected peptides have a killing activity. The peptide incorporation was done by simply graft polymerization and a combination of ink-jet printing, followed by covalently bonding and tethered peptides.
Some concepts were reported specifically for modification of poly(vinylidene fluoride) (PVDF) membranes, which are hydrophobic and quite susceptible to fouling. Bengani-Lutz et al. [23] prepared coatings based on random copolymers with zwitterionic and poly(trifluoroethyl methacrylate) monomers on PVDF porous membranes. The assembly led to pores of 1 nm, being tested for textile wastewater with high stability when exposed to acidic, basic and chlorinated cleaning solutions. Two other approaches to improve the fouling resistance of PVDF have been recently proposed. Li et al. [24] proposed a more complex multi-step procedure. Graft copolymers of PVDF with poly(hyperbranched polyglycerol methacrylamide) side chains (PVDF-g-PHPGMA copolymers) were synthesized via reversible addition−fragmentation chain transfer (RAFT), processed into membranes and further reacted by ATRP to form a dendritic hydrophilic hierarchical architecture based on N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine (SBMA). Meyer and Ulbricht [25] used pre-synthesized poly(ethylene oxide)-b-poly(methyl methacrylate) (PEO-b-PMMA) copolymers to modify PVDF membranes during their preparation. PMMA and PVDF are partially miscible, while the PEO blocks are exposed on the surface, turning it hydrophilic and potentially less susceptible to fouling.

Layer by layer (LBL)

LBL is a method of surface modification of growing interest for fouling resistance, consisting of the alternating deposition of different polymeric materials.[26] Recent examples include the deposition of poly(4-styrenesulfonic acid-co-maleic acid) sodium salt and 2-hydroxypropyltrimethyl ammonium chloride chitosan to minimize fouling in ion-exchange membranes. [27] In another approach, hydrogels were formed using thiol-ene click chemistry after LBL alternating deposition of functionalized precursors and loading of silver nanoparticles on
microfiltration membranes.[28] LBL deposition of polyethyleneimine and biocidal silver and copper nanoparticles on polylyethersulfone, followed by crosslinking, have been used to prepare cationic membranes for drinking water.[29] The co-deposition of polydopamine/polyethyleneimine (later gluteraldehyde-crosslinked) on electrostatic LBL-assembled polyethersulfone membranes has been also explored for antifouling nanofiltration membranes.[30] LBL has been used also for the development of chlorine-resistant membrane.[6]

Membranes with engineered nanomaterials

While the examples above demonstrate chemical modification only by adding a functionalization or organic coating, approaches with inorganic or carbon additives have also been investigated for many years with the expectation of adding biocidal properties to membranes. Figure 3 summarizes the different kinds of engineered nanomaterials tested with the objective of reducing fouling. Used in the past due to its capacity for photocatalytically degrading organic contaminants in water treatment processes and self-cleaning, TiO$_2$ recently has been explored in conjunction with carboxylic groups to improve its dispersion when modifying a poly (aryl ether sulfone) membrane. [31]
Our group used silver coordinated with pyridine to add antifouling properties to block copolymer membranes.[32] However, the strategy of metal release is controversial in terms of potential toxicity at long time.

Carbon nanomaterials in different forms, as 1, 2 or 3D architectures, are being considered as membrane components. Graphene derivatives are being extensively explored for membrane development and are being also used as biocide additives. [33] More recently, carboxylated nanodiamonds [34], which are sp³ carbon-carbon bond structures, have been used as additive to improve the fouling resistance of PVDF membranes.

Other 2D materials have growing interest for membranes and are also being tested as antifouling fillers. Amine-functionalized boron nitride [35] nanosheets were incorporated during the interfacial polymerization of a polypiperazine amide layer. A more negative charge was achieved with the modification, 13 % increase of permeance and fouling resistance as high as similar
modifications with amino-functionalized multi-wall carbon nanotubes and zwitterionic polyelectrolytes.

Membranes for electrically-assisted fouling mitigation

There is a growing interest in electrically-assisted methods to minimize fouling. The application of an electric potential can lead to the oxidation of ions (e. g. Cl\(^-\)), H\(_2\)O\(_2\) formation by O\(_2\) reduction, water reduction to H\(_2\) bubbles and other reactions. Commercial membranes without further modification are not conductive and therefore not suitable for electrically-assisted approaches. The development of membranes with electron conductive layers is proliferating. [36, 37] Examples from our group are based on the use of atomic layer deposition of a thin metallic coating [38] and integration of conductive carbon nanotubes [39] for different electrochemical processes. An interesting way to induce the formation of graphene layers induced by laser on the surface of membranes has been proposed by the Arnusch’s group.[40] A polyimide film irradiated with a CO\(_2\) infrared laser could be transformed into a strong anti-fouling surface. The method was also demonstrated for polyethersulfone membranes [41] and has been extended to produce graphene composite layers with different materials. [42]

Pattern formation

The formation of surface patterns has been advocated as an anti-fouling method in general for marine vessels. [43] Similarly, Mattia’s group has been innovating in 3D printing supports with wavy structures for membranes with encouraging results in fouling reduction.[44, 45]
Conclusions

After decades of membrane seawater desalination, fouling continues to be an unsolved problem. However, even with the occurrence of fouling, membranes have been very successful in desalination and water treatment, following standard cleaning protocols. The expectation of having radical solutions able to completely eliminate fouling in long-term operations without the need of additional chemical cleaning are still a source of disappointment. Sophisticated and creative solutions have been proposed in recent years with the aim of retarding at least the initial stages of foulant adhesion and microbial growth. However, for industrial application, the substitution of current membrane systems will only be feasible, economically profitable and accepted by the industry, if the proposed approach would be simple, preferentially not requiring fundamental changes in the current fabrication and operation processes, involving low additional cost. Considering membranes with the intrinsic fouling resistance, from my point of view, only modifications that could be done in simple one-step processes, such as the integration of zwitterionic groups during the interfacial polymerization [16] and other related options, would have chances of success and industrial implementation. The risk of toxicity has to be essentially avoided in the production of drinking water, as well as in food and biomedical applications, and this compromises at least in part approaches involving the release of biocides. On the other hand, covalent bonds as part of the interfacial polymerization layer gives long-term stability and do not restrict the permeation, as it might be the case when applying a second coating layer. However, high selectivity must be guaranteed to compete with commercial membranes optimized for decades in the industry, particularly in processes like desalination. After all, investing in new membranes, more resistant to chlorine and extreme pH conditions, might be more effective and profitable, when considering fighting against fouling in long-term operations. Membranes with
higher chemical, thermal and oxidative resistance are potentially useful not only in the water sector, but could facilitate the implementation of membrane technology in the chemical industry, enabling sustainable processes that are currently not served by membranes, with an even higher and broader impact.

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References


Graphical Abstract

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