

REVIEW ARTICLE OPEN

Chlorination disadvantages and alternative routes for biofouling control in reverse osmosis desalination

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With an ever-increasing human population, access to clean water for human use is a growing concern across the world. Seawater desalination to produce usable water is essential to meet future clean water demand. Desalination processes, such as reverse osmosis and multi-stage flash have been implemented worldwide. Reverse osmosis is the most effective technology, which uses a semipermeable membrane to produce clean water under an applied pressure. However, membrane biofouling is the main issue faced by such plants, which requires continuous cleaning or regular replacement of the membranes. Chlorination is the most commonly used disinfection process to pretreat the water to reduce biofouling. Although chlorination is widely used, it has several disadvantages, such as formation of disinfection by-products and being ineffective against some types of microbes. This review aims to discuss the adverse effect of chlorination on reverse osmosis membranes and to identify other possible alternatives of chlorination to reduce biofouling of the membranes. Reverse osmosis membrane degradation and mitigation of chlorines effects, along with newly emerging disinfection technologies, are discussed, providing insight to both academic institutions and industries for the design of improved reverse osmosis systems.

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INTRODUCTION

More than 71% of the earth's surface is covered with water, but only 1% clean drinkable water is available for direct consumption to sustain life. The permissible limit of salinity in drinking water is 500 ppm as provided in World Health Organization (WHO) guidelines. Seawater usually has salinity in the range of 35,000–45,000 ppm in the form of total dissolved solids.¹ The scarcity of fresh water is a strong issue already in an area of land affecting over one-third of the world's population, which is expected to double by 2050. The overuse of natural fresh water resources in several countries is already showing signs of the unsustainable approach, for example as the severe depletion of water in the Jordan River. Desalination offers the only viable solution to the water crisis estimated to affect at least 40% of humanity by 2050.² It is necessary for stakeholders and experts to commit resources and efforts for removing the roadblocks that currently make it an expensive and inefficient process.

Typical seawater desalination processes for high production of treated water are reverse osmosis (RO), multi-stage flash (MSF), and multiple effect distillation (MED). The most common desalination technology is RO accounting for over 60% of the total worldwide installed capacity.³ Seawater contains suspended particles, natural organic matter, mono- and multivalent ions, microorganisms, and organic and inorganic colloids. Some of these constituents block the pores of the RO membranes, also

known as fouling, rendering them inefficient after short operation times. Colloidal, particulate, organic or biological fouling (biofouling) as well as scaling occurs very easily during desalination using RO membranes. It is essential to remove the foulants to prevent the failure of the RO processes.⁴

Biofouling—the process by which organisms colonize all forms of submerged substrata—negatively affects materials and structures and can even destroy man-made installations. Such microorganisms, mainly bacteria, fungi, and diatoms, rapidly foul the RO membranes and create a sudden increase of differential pressure by restricting water flux, which ultimately impairs the salt rejection process, an issue which costs billions of US dollars to the desalination industry to address and prevent.⁵

The purpose of disinfection in RO desalination is to prevent the colonization of microbes at the surface of membranes. An ideal disinfectant should be inexpensive, non-hazardous, but highly toxic to microbes without affecting the productivity of the desalination plants. There are many disinfection methods currently practiced in water treatment using chlorine and its derivatives or ozonation or ultraviolet (UV) radiation. Ozone has been frequently used as a disinfectant of water as it effectively eliminates microorganisms by oxidative effects, however it is an expensive process, it is unstable and sometimes produces carcinogenic bromates in the treated water as by-products.⁶ Iodine, hydrogen peroxide, and peracetic acid are other oxidative

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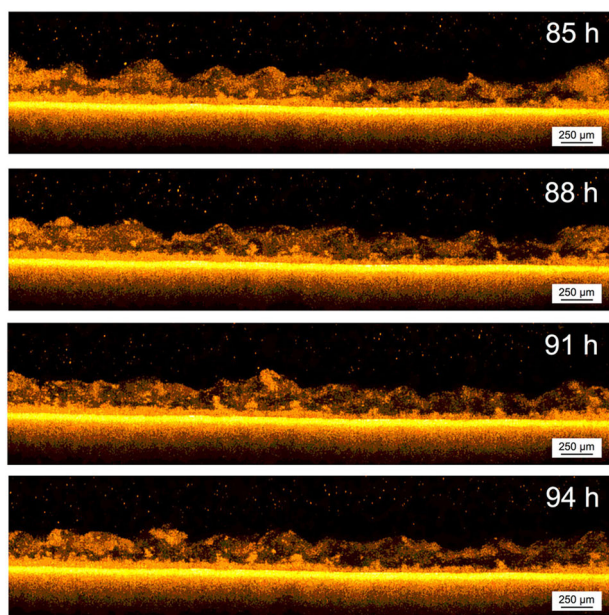


Fig. 1 Optical coherence tomography image presenting a time-resolved monitoring of biofouling development on a flat sheet membrane, from ref. ¹⁸ (Article distributed under a Creative Commons CC-BY license). OCT cross-sectional scans of the double layer biofouling morphology. The scans were acquired with a frequency of 5 min from 84 to 96 h of the experiment. The lower layer remains constant, whereas the upper one moves

compounds frequently used in water treatment processes. These are mainly used for disinfection of pre-treatment sections of membrane components, such as pipes and folds.⁷ The antimicrobial effect of UV radiation is based on the production of hydroxyl radicals that inhibit bacterial growth.⁸ Additionally, UV radiation can break down bacterial DNA and denature proteins. However, UV treatment has relatively high cost with limited applicability.⁹

Nitric oxide (NO) can regulate biofilm's dispersal.¹⁰ In laboratory conditions, NO-induced dispersal of industrial Gram-positive and Gram-negative biofilms at picomolar doses has been demonstrated.¹¹ It has been shown that NO is effective in combination with other traditional chemical biofouling treatments. The disadvantage of this method is that NO has a low solubility and stability in water, which prevent direct application of NO to water treatment.¹⁰

Quorum sensing (QS) is a process of production and perception of simple chemical signals by bacteria.¹² This process helps these microorganisms to coordinate their behavior and control biofilm formation. It has been shown that inhibitors of QS suppress and prevent biofouling.^{12,13} demonstrated that more than 60% of bacteria on RO membranes produce QS signals. It was demonstrated that inhibitors of QS suppress biofilm formation on RO membranes.¹⁴ Thus, it was concluded that treatments with QS inhibitors may be applied to control biofouling in industrial applications, but it is yet to be demonstrated in practice.

Fouling deteriorates membrane performance for both water flux and selectivity. The prevention of biofouling in desalination plants is still usually based on disinfection by a chlorine agent (as gas or in the hypochlorite form),¹⁵ as it can stop most microbes effectively at a low concentration, whereas being inexpensive and easy to deploy. However, chemical cleaning is expensive and adversely affects membrane life. It also increases energy consumption and operating costs. Biofouling is the Achilles heel of membrane desalination.¹⁶ This review provides a description of biofouling and strategies for RO desalination disinfection. It provides a comprehensive view on new RO membrane materials

used to overcome adverse effects of chlorination as well as different membrane modifications reported in the literature. Novel disinfection processes that have been demonstrated to be active against biofouling are also presented and discussed.

BIOFOULING OF REVERSE OSMOSIS MEMBRANES

Membrane fouling, the major obstacle for the efficient operation of membrane systems, is the accumulation of substances on the membrane surface or within the membrane pores.¹⁶ Membrane fouling is due to organic fouling as well as direct biological fouling (biofouling). The first is associated to the adsorption of dissolved organic matter, due to deposition of precipitated salts or by surface nucleation and growth of sparingly soluble salts, whereas biofouling is due to the deposition and growth of microorganisms that form strongly adherent biofilms.¹⁷

Figure 1 presents the time-resolved monitoring of biofouling development on a flat sheet membrane using optical coherence tomography (OCT) as studied by.¹⁸ The OCT scans acquired with a frequency of 5 min from 84 to 96 h of the experiment, shows that the lower layer remains constant, whereas the upper one moves.

Biofouling is a process that happens in various stages:¹⁹ first, a film of organic matter present in seawater forms on the membrane. Second, hydrophobic forces favor the attachment of randomly floating microbes to the surface of the membrane.¹⁵ Third, microbes feeding on the organic matter grow a surface biofilm, where they are embedded in a structure formed essentially of proteins and carbohydrates, that constitute a matrix of extracellular polymeric substances (EPS).²⁰ The final stage happens when the biofilm maturation is advanced enough that fluid shear forces can rip away part of the biofilm and propagate the phenomenon.²¹

Biofilm is an irreversible process that permanently damages the surface of the RO membrane, forcing periodic chemical cleaning to free the membrane from the accumulated films,²² which nevertheless reduces the active life of the RO membrane and constitutes a large part (up to 50%) of desalination plants operating costs.²³

The microorganisms responsible for biofouling include bacteria, Archaea, microalgae, protozoa, and fungi;²⁴ however, research suggests that the biofilm is composed mainly of two bacterial phyla, the Proteobacteria and the Bacteroidetes.²⁵ Interestingly, the biofilms that form on RO membranes differ in bacterial composition from the communities present in the seawater.²⁶ Although, fungi and Archaea were found to have little presence on RO membranes, research shows that the composition of the archaeal communities are mainly constituted of *Crenarchaeota* and *Euryarchaeota*, whereas the fungal communities chiefly contain *Ascomycota*.²⁶

Environment conditions favouring growth, such as quantity of nutrients, significantly affect the microbial composition, and density of biofilms.²⁷ Additionally, membrane characteristics such as type, roughness, charge, and hydrophobic/hydrophilic characters influences the formation of the biofouling microbial films.²⁸ The challenge still lies ahead for the development of RO membranes that are good at resisting both biofouling and the associated antifouling treatments, whereas delivering an acceptable desalination performance.

CHLORINE DISINFECTION

Microbes can be eliminated by disinfection with a chemical agent, which should at the same time be highly performing in eliminating microbes but also be inexpensive and harmless to human beings. Typically, two approaches are taken to tackle biofouling, including pre-treatment of sea water and adequate membrane surface modification.²⁹ The pre-treatment of water is usually carried out with agents having antimicrobial properties,

followed by cleaning detergents and subsequent flushing of dead cells and organic particles from the membrane surfaces.¹⁵

The most commonly available forms of chlorine are the gaseous form and the hypochlorite compounds it forms with sodium and calcium. By their instant hydrolyzation in water, hypochlorous acid is formed, which then dissociates in water to yield hydrogen and hypochlorite ions, a process depending on the water pH. Hypochlorite ions and hypochlorous acid (range 0.2–1 mg/l) effectively lead to the disinfection of microbial contamination.³⁰ The effective chlorine dosage for disinfection purposes should be at the break point concentration or slightly higher. This concentration should be sufficient to break chemical bonds of the contaminating organic compounds and to destroy waste products and pathogens. It is necessary to maintain a free available chlorine residual by applying a sufficient quantity of chlorine in water for disinfection purpose. The breakpoint chlorination curve is shown in Fig. 2 with four main stages/process. In the first stage, the amount of chlorine is low, with no free residual chlorine as complete oxidation occurs, thus reducing the final substances available in water. The second stage process shows that the amount of chlorine added is proportional to the total amount of chlorine residual, as the formation of chloramines and chloro-organic is occurring at this stage. In the third stage, the oxidative destruction is complete when the amount of chlorine further increased, and oxidation of chloramines take place. Therefore, the amount of residual chlorine decreases and reached the point called breakpoint or dip. After this point, there is no more reactions because of added chlorine, thus residual chlorine keeps on increasing. The actual breakpoint concentration varies with the water quality of the raw water—and the desired residual.

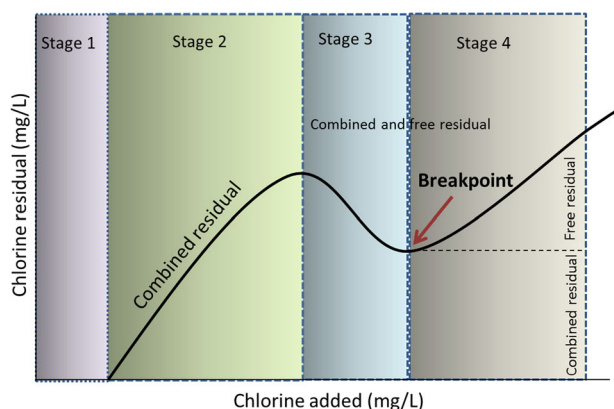


Fig. 2 Breakpoint chlorination curve

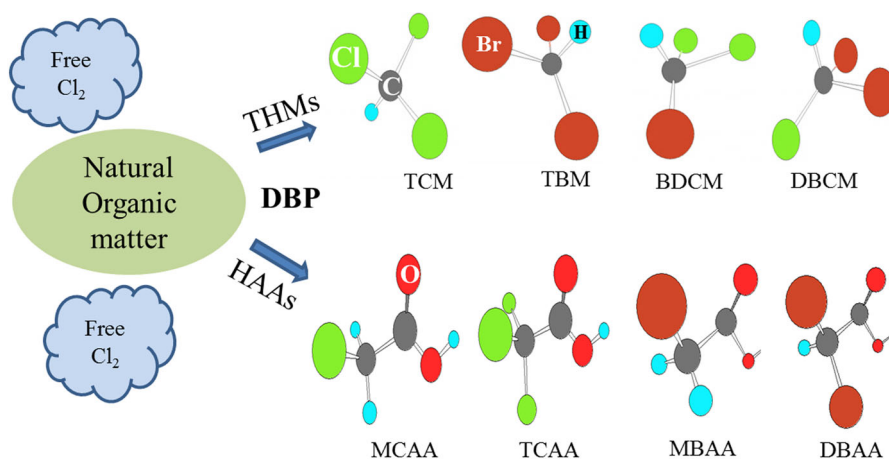


Fig. 3 Illustration of disinfection by product of trihalomethanes (THMs) and haloacetic acid (HAAs) species

This is typically about 0.2 mg/l at the furthest point in the distribution system.³¹

When the RO membranes are damaged by chlorine, disinfection by-products (DBP) are present in the pre-treated water. The organic DBP precursor are mostly natural organic matter (NMO), like humic and fulvic acids, wastewater effluent organic matter (EfOM), algal organic matter (AOM) and inorganic DBP precursor like bromide, iodide, and nitrile. Chlorine reactions with organic matter leave behind unwanted compounds such as trihalomethanes (THMs) and haloacetic acid (HAAs), which are the most prevalent DBP formed. Moreover, haloacetonitriles (HANs), chlorophenols and chlorate formed with trace amount,³² which together with other DBPs are suspected of carcinogenic activities.³³ Figure 3 illustrated the species of the most DBPs available in water. The concentration and formation of those DBPs strongly depends on raw water composition, residual chlorine available in the water distribution system and operational parameter. Furthermore, not all microbes are eliminated by chlorine disinfection, especially those that can form spores and spherical clusters, such as the *Bacillus* species; even if the microbes on the surface of the cluster are eliminated, the ones inside or their spores can survive and produce contamination after the treatment has concluded.³⁴

DISADVANTAGES OF CHLORINATION

RO membranes are commercially built either from polyamide (PA) or from cellulose acetate (CA), both being very effective in desalination, but with important differences. CA derived membranes have a long membrane life and good chlorine resistance, but also a lower water flux compared to PA, which somewhat limits their adoption.³⁵

However, cellulose acetate (CA) membranes can be damaged by chlorination,¹³ as shown in Fig. 4, whereas polyamide (PA) membranes are more resistant to chlorine, but do not take chemical treatments well.³⁶

Moreover, they can be used only in the pH range between 3.5 and 6.5 and being organically derived make them more vulnerable to microbial attacks.³⁷ Additionally, hydrolysis and oxidation degradation phenomena slowly impair their performance, as the first phenomenon causes a conversion of the polymer acetyl groups into hydroxyl groups over time, reducing the ability of the membrane to retain salt.³⁸

The most commonly used RO membranes in the desalination industry are made of multi-layered PA thin film composites (TFC), based on a thin cross-linked polyamide layer less than 0.2 μm thick, offering higher water flux, good chemical stability, and requiring a lower operating pressure differential. The PA layer is supported by a porous polysulfone (PSf) layer and a non-woven

polyester web. The fully-aromatic thin top PA layer offers high salt retention, whereas the support bottom layers offer high water permeability,³⁹ and their performance is enhanced with respect to single-layered membranes by improving the selectivity of the top active layer, whereas increasing the flux of the bottom support layers. PA membranes, however, suffer from low chlorine tolerance, expressed as the product of free chlorine concentration (ppm) with exposure time (h). Commercial PA membranes have a tolerance around 1000 ppm-h,⁴⁰ leading manufacturers to recommend a continuous exposure lower than 0.1 ppm,⁴¹ in case free chlorine ions damage the membrane, causing dramatic increase in water flux and reduction in salt retention.³⁹

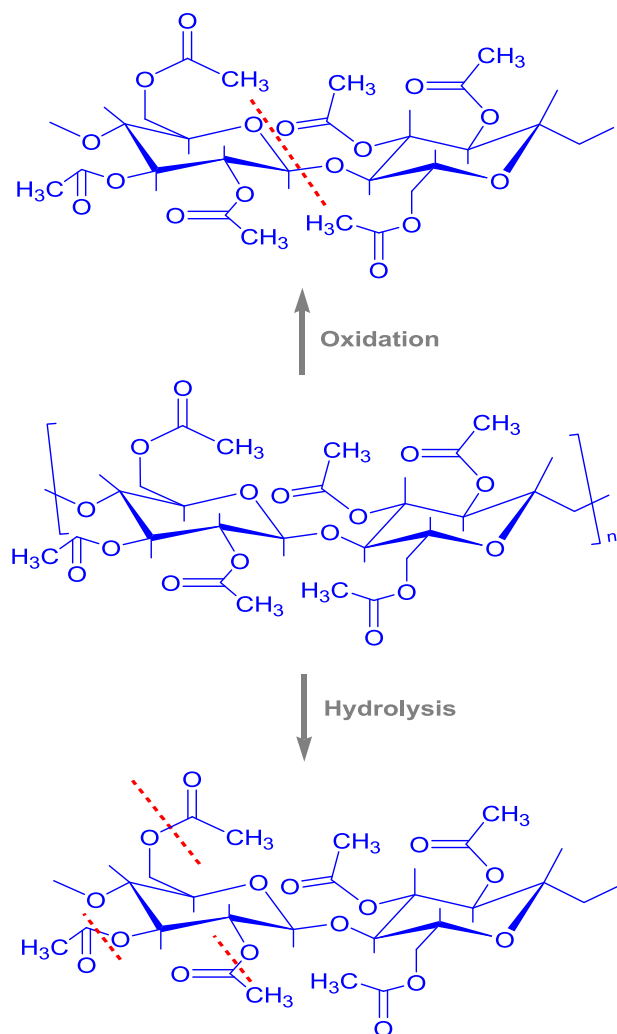


Fig. 4 Hydrolysis and oxidation degradation of cellulose acetate

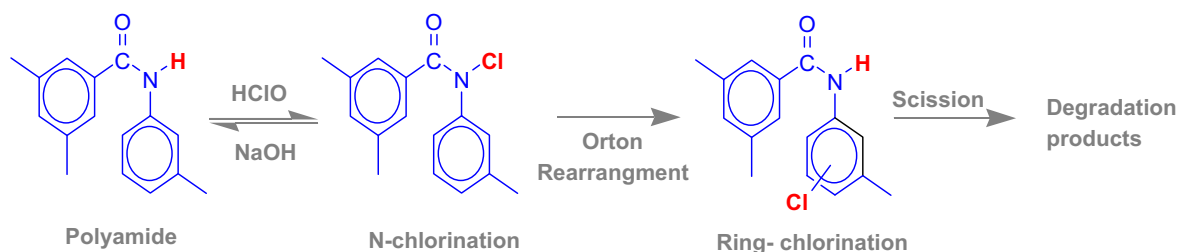


Fig. 5 Mechanism of Polyamide RO membrane degradation by aqueous chlorine

The mechanical properties of the polyamide active layer are governed by the membrane network structure,³⁹ whereas the selectivity in separating salt is affected by the free volume of the PA active layer and hydrated state mobility. Both the network structure and selectivity are dependent on the molecular density, cross-linking density and the chain stiffness of the polymers.⁴²

No direct methods are available to gauge chlorine-induced PA layer failure, though morphological changes have been investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM), as well as surface zeta potential and contact angle measurement.⁴³ To determine the involved chemical processes, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) have been utilized.⁴³

Understanding of PA membrane degradation hinges on clarifying the physio-chemical mechanisms involved in the active layer⁴⁴ such as conformational deformation upon chlorination,⁴⁵ as membrane performance is directly affected by any changes in the mechanical structure of the PA active layer. It has been shown that chlorination increases the surface roughness of the PA layer,⁴⁶ whereas also reducing active sites leading to a lowering the zeta potential and surface charge, ultimately yielding lower salt retention.⁴⁵ Chlorination provokes irreversible changes in the active layer structure, reducing ductility and strength. The active layer thus becomes brittle, leading to permanent mechanical damage as cracks and ruptures that can be induced at high operating pressures. These failures cause the observed increase in water flux and decrease in salt retention.⁴⁷ If chlorine exposure is continued, even destruction of the membranes has been reported as the top layer was found to separate from the bottom support layers.⁴⁷

The degradation mechanism involves the reaction of chlorine with the amide nitrogen in the active layer, which is converted to N-chloro derivative (N-chlorination).³⁵ This is the result of replacing the hydrogen in the amide group ($-\text{CO}-\text{NH}-$) with a chlorine atom, thus breaking the hydrogen bond that holds the PA chains together,³⁵ a reversible structural modification if the N-chlorinated PA is reverted to the amide chain as shown in Fig. 5. It can also rearrange into a chlorinated aromatic ring through an irreversible modification known as “Orton ring arrangement”, causing a scission of the amide bonds and breaking the polymer chains, upon which the RO membrane degrades severely.³⁵ The secondary amide nitrogen and aromatic rings of RO membranes are badly affected by chlorine, whereas the tertiary amide nitrogen and aliphatic rings bonded to secondary amide nitrogen of piperazine-based PA layers of NF membranes are more resistant.⁴⁶ Fully aromatic PA layers (RO) are more sensitive to chlorine than semi-aromatic ones (NF).⁴⁸

N-chlorination and amide bond cleavage thus cause the irreversible degradation of the top PA active layer with increased chain mobility and loss of cross-linking density,^{42,45} which loosens the PA layers and lowers the mechanical strength.⁴⁷ Water flux thus increases due to the lower cross-linking density that increases the diffusion process, which transports water through the membrane.⁴⁹ Lower cross-linking density also reduces retention of salt as salt transport depends on both the steric nature of the

free volume described by a pore size and pore size distribution, and the fixed surface charge of the PA active layer.⁵⁰ The packing tendency is increased by the cleavage of the amide bonds and the increase in chain mobility as the time of exposure to chlorine is increased, thus leading to an incremental mechanical damage of the active layer,⁵¹ until the membrane undergoes structural collapse with a consequent reduction in the flux of water.⁵²

It is important for the RO membranes to be hydrophilic, as this increases the flux of water, whereas reducing biofouling by hydrophobic species.⁵³ Polyamide layer hydrophilicity increases when exposed to chlorine,^{43,45,46} as it introduces unbalanced dipole moments on the surface,⁴⁵ causing an increase in water flux.

In acidic environments, there is a severe decrease of water flux through the PA membrane with chlorine which then stabilizes, whereas in basic environment the flux increases first and then gradually decreases with exposure time. More severe outcomes of chlorination are observed when the pH is very acidic, as bond breakage mechanism is very high, and the chain mobility leads to irreversible Orton ring arrangement and compaction of the membrane. This process increases its resistance to water flux, with a flow reduction, which eventually stabilizes when no further structural changes could occur.⁵⁴ In contrary, at high basic pH there is less effect of chlorine on hydrogen bonds and chain mobility, thus the membrane structure does not collapse. The active layer swells upon increased chain mobility, causing lower resistance to the flux of water. As the exposure to chlorine under high differential pressure is continued, free chlorine keeps diffusing into the membrane, increasing hydrogen bond breakage and membrane compaction. Therefore, the membrane water flux decreases with time of chlorine exposure.^{35,54} However, the dependence of these phenomena on pH chlorination, varies from membrane to membrane, as there is proven evidence of retention of salt in both conditions, either basic or acidic.⁵⁵ Further independence of salt retention with changing pH,⁵⁴ and/or greater drop of retention at basic conditions were observed.³⁵ The balance of these two competing processes, i.e., Orton ring arrangement and amide bond hydrolysis, causes the observed discrepancies effectively of chlorine on the PA layer of RO membranes. In fact, both processes depend on the layer active species, on the chlorine concentration, and on the exposure time.⁵⁶

CHLORINE MITIGATION

In-line SBS/SMBS injection

Mitigation of chlorination effects are tackled through in-line sodium bisulfite (SBS)/sodium meta-bisulfite (SMBS) injection, new membrane materials and surface coatings or grafting of polyamide membranes. To prevent oxidation of RO or NF membranes, pre-treatment involving dechlorination of the feed water is usually applied in the industry. Vulnerability of polyamide top layer of thin film composite (TFC) membranes to free chlorine, leads to the addition of a dechlorination unit. Sodium meta-bisulfite (SMBS) is commonly used as a reducing agent to react with free chlorine before it is fed to the RO unit. SMBS dissociates in water to form sodium bisulfite (SBS). Free chlorine as HOCl reacts with SBS forming sulfuric acid, hydrochloric acid and sodium sulfate salt. The ratio of SMBS to free chlorine is ~3:1. Excessive SMBS is essential in the dechlorination step as incomplete dechlorination may result in TFC membrane deterioration and reducing of its life time.⁵⁵

In field applications, adding SBS as dechlorination may influence the water flux and salt rejection as demonstrated in ref. ⁵⁷. Therefore, stimulated the concentration of SBS that required to be injected was inevitably after enquiring the consequences of residual chlorine attack on polyamide RO

membrane. Kim and his team studied the effect of high concentration of chlorine added to PA membrane concluding that this addition lead to decreased salt rejection and increased water flux. However, addition of SBS caused a replacement of chlorine by hydrogen in chlorinated membrane, which compensated the decrease in flux.

SBS, known as preservation chemical, may lead to changes in membrane properties as well, which consequently affect the efficiency of salt rejection and permeability. Therefore, pH of the added solution should be maintained to avoid bad impact on the performance of PA RO membrane, as exhibited in RF.⁵⁸ Adding SBS with pH close to 7 was not detrimental for the RO membrane and its permeability, however, it impacted the rejection performance.

Sodium meta-bisulfite (SMBS) influenced the reduction and oxidation potential (ORP) quantity, which plays an important role in determining the effectiveness of disinfection. SMBS titrated chlorine in presence of sodium hypochlorite and performed using salinity water of different concentrations. Different dosage of chlorine and salinities were applied to study the changes in ORP. The study concluded that at higher dosage of chlorine, ORP was higher and lower at higher amount of added SMBS.⁵⁹

Optimization of the chlorination and dechlorination dosage was carried out in one of seawater RO plant⁶⁰ to inhibit the growth of the bacteria and biofouling. SBS was injected after the dual media filter to remove chlorine. However, the experiments concluded that as SBS dosing point moved forward along the pre-treatment line, biofouling increased. Moreover, in the chlorinated section of the plant the bacteria were capable of biofilm formation. Another investigation of optimum dosage of SBS has been done in another plant,⁶¹ after observing low performance because of biofouling problem. In the SHMP tanks 0.25% sodium meta-bisulfite was needed for sterilization. This concentration was not affecting SHMP reversion to orthophosphate and was found to inhibit bacteria growth.

New reverse osmosis membrane material

RO membranes are currently object of intense research, to remove active layer sites that show sensitivity to chlorine and give protection to the active layer's structure. Research has focused on varying the polymeric basis of the membrane fabrication and on using hybrid materials composed of polyamide together with other polymers, mostly making use of lab fabrication methods based on interfacial polymerization processes.⁶² This method was employed in ref. ⁶³ to build PA membranes, supported by polysulfone and based on a mix of metaphenylene diamine (MPD) and polyacyl chloride monomer (trimesoyl chloride, TMC). Improved chlorine tolerance was achieved.

Even more resistant than PA are membranes based on Sulfonated poly (arylene ether) (SPA), which is a promising material to replace PA for desalination applications, as it dispenses with the amide bond, that enables chlorine vulnerability. Such membranes are built as in ref. ³⁷ and studied for varying sulfonation amount, showing high resistance to chlorine, with however a significant drawback of salt retention percentage between 75% and 98%, too low for industrial applications as one-pass desalination membranes. PA membranes based on 17 different diamine compounds (aromatic, aliphatic, cycloaliphatic and heterocyclic) and isophthaloyl dichloride (IPC) or 1,3,5-benzenetricarbonyl trichloride (TMC) were fabricated as per ref. ⁶⁴ with comparable results³⁵ reported the effects of chlorine on a thin film composite (TFC), obtained from a polysulfone-polyamide composite, via sodium hypochlorite solution exposure, showing 65% flux improvement but 7% lower salt retention.

A film composite with PA top active layer is demonstrated in ref. ⁶⁵ showing that by substituting the amide group with the

more chlorine-resistant imide group, chlorine tolerance improves, with a reduction of flux of 43% with respect to PA at comparable salt retention. Similar observations were provided in ref. ⁶⁶.

In ref. ⁶⁷ hexafluoro alcohol-containing diamine and trimesoyl chloride (TMC) were employed as membrane basis. The hexafluoro alcohol group has high electron affinity on the aromatic ring and thus protects the PA from degrading due to chlorine. Better strength against chlorine was showed in ref. ⁶⁸ study by functional groups such as $-\text{CH}_3$ and $-\text{OCH}_3$ derived from *m*-phenylene diamine. Poly (N, N-dimethyl aminoethyl methacrylate) NF membranes were fabricated in ref. ⁶⁹ by including triazine rings in the active layer: the triazine ring links to the amide group in PA, increasing chlorine active layer resistance as the nitrogen atom's reactivity in the $-\text{NHCO}-$ group is reduced.⁷⁰ With respect to standard PA membranes, N-substituted PA active layer membranes are more tolerant to chlorine,⁷¹ as the aromatic ring position sensitive to attack is now occupied by a deactivating functional group.⁷²

N-methylated PA membranes were developed in ref. ⁷³ by secondary-to-tertiary amide replacement to increase chlorine resistance, but only reduced salt retention was achieved if compared to PA membranes. As reported by the authors in ref. ⁶⁹ Bis-2,6-N, N-(2-hydroxyethyl) diaminotoluene polyamide NF membranes showed higher resistance to chlorine than PA NF membranes, as water flux initially decreased and subsequently increased as chlorine concentration was increased, though with reduced retention of salt.

RO TFC polyamide membranes are prone to biofouling and other types of fouling, scaling, or organic. This is the result of surface hydrophobicity, charge, and morphology. *m*-phenylene diamine (MPD)-based TFC membranes have high surface roughness. This increases all types of fouling. The augmented surface area offers larger foulant-membrane interaction and more chances for attachment.⁷⁴ MPD-based TFC membranes are also hydrophobic. This amplifies the rates of organic and biological fouling.⁷⁵

Fouling for both MPD- and piperazine (PIP)-based TFC polyamide membranes increases because of surface charge. The carboxyl functional groups increase the binding of organic foulants, mostly partially aromatic macromolecules with high levels of carboxylic and phenolic functional groups, through calcium bridging.⁷⁶ Calcium sulfate scaling through surface nucleation and growth may also be induced by the enrichment of calcium at the surface.⁷⁷ A highly hydrophilic membrane surface by surface modification appreciably reduces organic fouling. It also decreases the adhesion of biofouling producing bacteria. Surfaces resistant to fouling are obtained by using hydrophilic materials such as polyethylene oxide (PEO)-based and zwitterionic polymers and epoxy open group.⁷⁸ Water molecules are bound by PEO (or polyethylene glycol, PEG) via hydrogen bonding and by poly(sulfobetaine) and poly(carboxybetaine) (zwitterionic polymers) via electrostatic interactions.⁷⁹ The adsorption of organic molecules and bacteria is prevented by the steric repulsive barrier provided by the hydration layer of the hydrophilic PEO and zwitterionic polymers. Prevention of protein and bacteria adhesion in a wide range of biomedical and industrial applications has been provided by brush layers of these hydrophilic materials.⁷⁹

Surface coating or grafting of polyamide membranes

Membrane coating and grafting are useful methods for surface modification of the active layer to increase chlorine tolerance of commercial PA membranes. Membrane coating is accomplished by immersion of the membrane in a casting polymer solution, and subsequent chemical cross-linking once the excess polymer is removed. Membrane coating is a more facile and convenient method to implement compared to membrane grafting. This last,

on the other hand, has the advantage of providing a more stable membrane due to the introduced permanent surface changes. In fact, membrane grafting exploits a chemical reaction between the top layer's active backbone with the side chains of the polymer used to affect the graft, causing a chemical structural change in the top layer. Thus, surface active sites increase in number and act as protectors for the PA sites sensitive to chlorine.

The usual mechanisms to obtain a graft include free radical graft polymerization,³ carbodiimide-induced graft copolymerization,⁸⁰ plasma polymerization,⁸¹ UV-induced photo grafting,⁸² surface-initiated atom transfer radical polymerization,⁸³ ring-opening polymerization⁷¹ and radiation-induced graft copolymerization.⁸⁴ The effect is either an increase in salt retention traded off with a decrease in water flux, or the opposite effect.⁸⁵ It remains a challenging problem to develop thin-film composite RO membranes that are at the same time resistant to chlorine and maintain competitive levels of water permeability and salt retention.

Coating the membrane gives protection to the PA aromatic rings and the sites of the membrane more sensitive to chlorine, and the coating has the role of a sacrificial layer,⁸⁵ further preventing the hydrolysis of the amide bonds and N-chlorination.⁸⁶ The coating polymer enhances membrane resistance as it increases density in the functional layer and seals sensitive pores, augmenting salt retention and rescuing the water flux.^{3,85} Using a low concentration of hydrophilic coating copolymer, decreased salt retention, and increased water flux has been reported.⁸⁶ Whereas, increasing the concentration of copolymer an increased salt retention with sharply decreased water flux is observed as the membrane resistance increases due to the increased hydrophilicity.

The protection of the PA membrane active layer can also be achieved by membrane grafting: at low concentration of grafting polymer, the flux increases with a reduction of salt retention, as cross-linkable sites are reduced. Although higher polymer concentration results in a more dense and compact layer, which retains more salt at the cost of a lower water flux.⁷¹ The chlorine resistance of the grafted layer is increased, as the grafting introduces sacrificial groups that stop chlorine from diffusing to the surface of the membrane, and sacrificial pendant groups with high reactivity to chlorine, which stops chlorine attacks on the aromatic rings.⁵³

Surface grafting of hydrophilic polymers is one anti-fouling strategies for TFC membranes. One option is the binding of PEG-based materials to the free surface carboxyl or primary amine groups of the polyamide layer.⁸⁷ Other anti-fouling materials may also be used.⁸⁷ However, often this method grants limited fouling resistance. This is the result of the incomplete and non-uniform surface coverage of anti-fouling materials on the polyamide active layer because of the limited number of accessible pendant carboxyl/amine functional groups on the membrane surface.⁸⁸ Even when using a more ideal substrate, this method has drawbacks. The brush density that may be achieved is indeed limited by the steric repulsion of pre-formed polymers.⁸⁹

Better dense and uniform anti-fouling polymer brushes on TFC membranes are grafted by surface-initiated controlled radical polymerization techniques. The density, length and architecture of the anti-fouling brush layer can be controlled by using atom transfer radical polymerization (ATRP).⁸⁹ This technique improves robustness and versatility. ATRP grafting of a dense brush layer of poly (sulfobetaine methacrylate) to the polyamide surface of TFC RO membranes has been demonstrated in ref. ⁹⁰. Very low water contact angle ($<10^\circ$), negligible change in the permeability and selectivity of the membrane, or adsorption of biomolecules (proteins), and finally substantial reduction of foulant adhesion forces to the membrane surface were obtained. As a downfall, surface grafting may also result in reduced water permeability. There is a trade-off in between the gain in fouling resistance and the reduction in water permeability.⁹¹ The uniform immobilization

of the initiator molecules on the rough polyamide surface of TFC membranes is still an open issue. TFC surface modification must also ensure long-term anti-fouling performance and chemical stability of the grafted brush layer mostly under chemical cleaning operations. As only model surfaces have been used so far in laboratory experiments, upscale to membrane modules and cost reduction of membrane fabrication remains difficult.

ALTERNATIVE DISINFECTANTS

Ultraviolet (UV) disinfection

Alternative disinfection technologies include ultraviolet (UV) disinfection, ozone disinfection, silver for water disinfection and photo catalytic disinfection by nanomaterial. Ultraviolet (UV) light wavelength ranges between 100 nm to 400 nm (shorter than visible light but longer than X-rays) and this range is conventionally subdivided into four sub-regions, namely vacuum UV (from 100 to 200 nm), UV-C (from 200 to 280 nm), UV-B (from 280 to 315 nm), and UV-A (from 315 to 400 nm). UV has been used in treatment of water since the 1970s⁹² and is effective to disinfect water by killing microorganisms as it has the advantage that it does not produce chemical by-products that can affect health.⁹³ UV light penetrates the microbe cell wall and damages the genetic information contained in DNA and RNA, thus stopping it from reproducing.

UV light is commonly produced in low-pressure mercury lamps, which emit in the 200–300 nm wavelength range and are introduced into specific UV reactors along the water flux. To properly design and operate a UV reactor, the designer must consider several operating parameters, optimizing the lamp-to-wall distance and radiation dosage depending on water quality. UV dosage, that is the ratio between total incident radiation intensity (averaged on all directions and all wavelengths) and exposure time, is a fundamental parameter.⁹⁴ As the dosage is increased, its effect ranges from causing cell inactivation due to DNA/RNA damage up to causing cell wall damage due to protein absorption, with microorganism death.⁹⁵ The effective surface area and distribution of the microbes is another important factor,⁹⁶ as UV inactivation is significantly different for different microbes.⁹⁷ Therefore, UV disinfection effectiveness is a process that is heavily dependent on the type of microorganisms, their concentration, and the quality of the water.⁹⁵

Disinfection by UV light hinges on physical degradation on the microbes instead of the action of chemicals, starting from the seminal work in ref.⁹⁸ on the performance of UV irradiation for the treatment of *Cryptosporidium* and *Giardia*. This proved that UV treatment had higher efficiency than chemical processes⁹⁹ investigated the degradation of protozoan cysts under UV radiation, which showed that UV radiation impairs DNA and RNA replication and transcription, inhibiting microbe or virus reproduction. Microbes and virus reproduction was inhibited independently of physio-chemical parameters such as temperature, pH and reactive organic matter, parameters, which contrary strongly affect chemical disinfection.¹⁰⁰ The factors affecting disinfection efficacy have been studied by ref.⁹³ Here the physiological state of the microorganisms was correlated with the optical reflection, adsorption, and refraction of UV light through the water, as the lamp intensity was varied. It was shown that microbe sensitivity to UV is mainly related to the inactivation rate, as more sensitive organisms have higher rate constant and the effect of optical parameters such as reflection, refraction, and adsorption of UV light is lower.

Disinfection by UV light carries several advantages, being a faster method devoid of harmful or odorous by-products and volatile organic compounds (VOC) or toxic gas emission, and preserving water minerals, however it also has its limits. It is unsuitable for turbid water containing high percentage of solid

suspended matter or soluble organic matter, as the light cannot penetrate in depth and disinfection is less efficient. It is also difficult to determine the performance of UV disinfection for changing water quality.¹⁰¹ A UV system requires regular inspections to determine residual microbe activity in the case of drinking water, increasing maintenance costs, as a periodic disinfection assessment is required by performing a Heterotrophic Plate Count (HPC) test.¹⁰²

An interesting work have been done¹⁰³ to study a new way of pre-treatment disinfection step prior to RO desalination by utilizing medium pressure ultraviolet (MP-UV) treatment. The study was conducted for four months at a brackish water reverse osmosis (BWRO) desalination plant. It was reported that MP-UV prolonged the performance between cleaning in the desalination plant also affecting the characteristics of the microorganisms and creatures on RO membranes asextracellular polymeric substances (EPS) were found to be significantly reduced. In another work,¹⁰⁴ H₂O₂ with MP-UV was found to reduce the amount of heterotrophic counts biofilm cells and EPS on the RO membranes¹⁰⁵ studied the influence of suspended Nano-filler (TiO₂) as a photocatalyst and found that total organic carbon TOC increased probably due to larger number of organic by-products formed that was also corroborated in another work.¹⁰⁶

Ozone disinfection

The triatomic form of gaseous oxygen is called ozone (O₃), and it has powerful oxidizing properties due to its strong oxidation-reduction potential (E^H_O) of 2.07 V¹⁰⁷ as it undergoes the spontaneous transition back to oxygen, it forms a monoatomic oxygen radical that is extremely reactive, whereas having a short lifespan of a few milliseconds at ambient conditions. Ozone can be easily generated by feeding an electrical discharge across a flux of dry air and pure oxygen and then directing the gas into a down-flow contact chamber containing the contaminated water for disinfection. The initial ozone flux is quickly absorbed by the water-present matter and salts, and then the disinfection process happens as the ozone directly oxidizes the organic matter.¹⁰⁸ Ozone also undergoes instant decomposition due to a complicated reaction resulting in the production of free hydroxyl radicals (OH[•]), which further contribute to increase the disinfection efficacy,¹⁰⁹ though with a strong dependence on water type.

Ozone was first employed for water disinfection in 1886 by De Meritens, leading to its popularity as a replacement for chlorination, as ozonation does not produce trihalomethanes (TMH) and organochlorine,¹¹⁰ also leading to a better water disinfection.¹¹¹ The ozonation process is also affected by parameters such as pH, temperature, and quality of water, though the pH effect was found to be negligible,¹¹² whereas higher temperatures reduce water solubility and stability of ozone,¹¹³ and disinfection rate was shown to be temperature-independent.¹¹⁴

Ozone is also effective against protozoan cysts in water¹¹⁵ and to inactivate bacteria and viruses¹¹⁶ without having significant regrowth processes.¹¹⁷ The reactivity of ozone though, has corrosive effects, requiring-resistant materials such as high grade stainless steel, bringing the cost higher with respect to UV disinfection and chlorination. As it reacts with natural organic matter, ozone produces by-products like carboxylic acids, aldehydes, and ketoacids,¹¹⁸ which can be harmful in high concentrations. The presence of bromide ions brings about brominated by-products, which can result in brominated organ halogen compounds such as *halobenzoquinones*, which have been mentioned as one cause for bladder cancer.¹¹⁹

Silver for water disinfection

Silver (Ag) has been known to have antibacterial properties as Roman times and in the modern era it has been used extensively for water disinfections, including potable water.¹²⁰ The remarkable

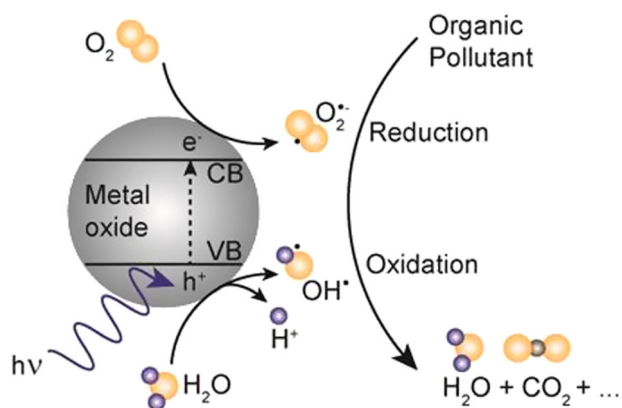


Fig. 6 Schematic representation depicting the photo catalysis process on the surface of a nanostructured metal oxide semiconductor (e.g. ZnO, TiO₂ etc.) photocatalyst

antimicrobial property of silver is mainly attributed to its strong binding with disulfide (S–S) and sulfhydryl (–SH) groups found in the proteins of microbial cell walls, which disrupts the normal metabolic processes leading to cell death.¹²¹ Silver is considered as an alternative to the harmful chlorine-based water disinfection processes and used widely across the world, even extending its use up to the space shuttles.¹²² Application of nanoparticulate and ionic forms of silver are reported for water disinfection demonstrating their antimicrobial effect against many different types of microorganisms, including bacteria, viruses, and protozoa.¹¹⁷ Silver's antimicrobial and antiviral mechanisms are summarized in a study carried out by ref. ¹²¹.

Mechanisms to remove bacteria includes: release of silver into the system;¹²³ oxidative destruction catalyzed by silver;¹²³ Targeting of Na⁺-translocating NADH: ubiquinone oxidoreductase (NQR) at low concentration of Ag⁺;¹²⁴ Targeting of membrane proteins;¹²⁴ Inhibition of oxidative metabolism required by the cells;¹²⁵ Inhibition of uptake of nutrients;¹²³ Metabolite leakage.¹²³ Mechanisms to remove viruses includes: Site-specific Fenton mechanism;¹²⁶ Immobilization of the virus to a surface;¹²⁶ Inactivation of the nucleic acid within the viral capsid;¹²⁶ Destruction of blockage of host-cell receptors.¹²⁶ Finally, mechanisms to remove both bacteria and viruses are: Affinity for sulfhydryl groups,^{117,125} binding to DNA.¹²⁶

Apart from drinking water, silver together with copper has been used in hospitals as an effective disinfectant, which does not produce toxic by-products.¹²⁷ Silver is also effective against biofilm formation and used successfully in diverse applications for the prevention of biofouling.¹²⁸

Nano photocatalytic disinfection

Photocatalysis has recently emerged as a promising avenue for disinfection of water, based on a nanostructured light-activated catalyst, which causes degradation of the organic and inorganic compounds and microorganisms that pollute the water. Photocatalysis can be described as “change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible, or infrared radiation in the presence of a substance—the photo catalyst—that absorbs the light and is involved in the chemical transformation of the reaction partners”.¹²⁹ Photo catalysis is a complex process based on a five-step mechanism:¹³⁰ (i) reactant diffusion, (ii) catalyst surface adsorption of reactants, (iii) catalyst surface reaction, (iv) catalyst surface by-products desorption, and (v) by-products diffusion.

The catalyst is typically based on metal oxide-semiconductor (MOS) nanostructures containing zinc oxide (ZnO), titania (TiO₂), tungsten oxide (WO₃), zinc stannate (Zn₂SnO₄) etc. creating an

interesting alternative for water disinfection because of their ability to degrade both chemical and biological pollutants.¹³¹ When hit by optical radiation, electron–hole (e–h) pairs are generated in the photocatalysts, which cause oxidation and reduction processes resulting in the formation of radicals with highly reactive properties, like super oxides (O₂^{•−}) and hydroxyl radicals (OH[•]), as shown in Fig. 6. The diffusion of these highly reactive radicals then causes the degradation and removal of organic/inorganic pollutants from the contaminated water, and results in the death of microbes as the radicals destroy their cell walls.^{132,133} reported a possible course for photocatalytic degradation of organic pollutants (OP) in water. A FLV–MoS₂ disinfection schematic is proposed by ref. ¹³⁴.

A nanostructured photocatalyst is more effective than bulk, as it offers a higher surface-to-volume ratio, which increases the density of photo-electrons just where the surface reactions happen. An effective photocatalyst of a wide semiconductor bandgap (bandgap between 2 and 4 eV) produces electron–hole pairs that have enough energy to kick off the secondary reactions, but have a low recombination probability of the generated charges in their migration to the surface. Ideally, an efficient photocatalyst should be: (i) highly photoactive, (ii) biologically and chemically inert, (iii) highly photo stable, (iv) non-toxic, and (v) cost-effective.¹³⁵

Photocatalyst-based systems are in wide use for the disinfection of contaminated water, as harmful organic matter is broken down into harmless by-products, carbon dioxide, and water, being effective on such diverse substances as alcohols, carboxylic acids, phenolic derivatives, and chlorinated aromatic contaminants.¹³⁵ Photo catalytic compounds such as ZnO, TiO₂ etc., are very effective to degrade organic dyes present in water.¹³⁶ It has also been used to successfully degrade natural organic matters or humic substances.¹³⁷ In this regard, in ref. ¹³⁸ TiO₂ nanoparticles were used to photo catalytically degrade humic acids in potable water. Photocatalysis is also effective against inorganic contaminants, like halide ions, cyanide, thiocyanate, ammonia, nitrates, and nitrites.¹³⁹ An antimicrobial effect is also the property of many photocatalysts, which inhibit the growth of microbes in water by diffusing highly reactive radicals that destroy the walls of the microbial cell. This process has proved to be effective against such microorganisms as *Streptococcus mutans*, *Streptococcus natuss*, *Streptococcus cricetus*, *Escherichia coli*, *Scaccharomyces cerevisias*, *Lactobacillus acidophilus* etc.¹⁴⁰ Antimicrobial effect of ZnO nanorods have been reported by ref. ¹⁴¹ showing almost 99% microbial removal from water, which was used to develop portable water purification system. Similarly, ¹⁴² have reviewed the heterogeneous photocatalytic inactivation of water borne microorganisms, including plausible mechanisms of microbial degradation as well as a kinetic model of the inactivation process and analyzed various factors involved in the photo catalytic process, such as light intensity, pH and water quality. The photocatalytic properties of ZnO nano rods have also been investigated against marine micro and macro fouling organisms in laboratory,¹⁴³ mesocosm¹⁴⁴, and field experiments.¹⁴⁵

Photocatalytic compounds such as TiO₂, ZnO can be nanostructured at low cost and the results they have shown for water purification are promising, leading to prospective applications to disinfect water in homes, as well as in small and large industries. However, the bandgap of these semiconductors pushes their light absorption range in the UV light band, so they can only be activated by a high-energy UV source, whereas the power distribution of the solar spectrum is split between 46% visible light, 47% infrared radiation, and only 7% UV light. For this reason, a research effort is underway to discover photocatalysts that can use the sizable visible light power available from the sun. Wide bandgap semiconductor catalysts have been modified in the attempt to harvest visible light and disinfect water, using a variety of techniques: (i) Transition-metal semiconductor doping with

Table 1. Surface modification of polyamide TFC RO membranes

Materials	Treatment	Fabrication method	Salt rejection	Water permeability (L/m ² h), Operating pressure	Tolerance (Chlorination and biofouling test), chlorine testing period	Modification properties improving the tolerance	References
Metaphenylene diamine (MPD) and polyacryl chloride monomer (trimesoyl chloride, TMC)	Post-treatment (hydroxyl and cross-linking agents)	Interfacial polymerization	[NaCl]: 100 ppm, R: 90%	Flux 135, 60 psi, Ph 19.8	[NaClO]: 3450 ppm for 10 h, chlorine tolerance	Thermal cross-linking and cross-linking density of PA, cross-linking contain hydroxyl groups	⁶³
Sulfonated poly(arylene ether) (SPA) 1. End-group Cross linked 2.C-ESFx-BP Non-cross-linked N-ESFx-BP	Thermal treatment	Polycondensation interfacial polymerization	[NaCl]: 2000 ppm 1. R: 98.4% 2. R: 90.3%	1. 0.6 L μ m ² h bar pH 4, 1000 psi 2. 0.81 L μ m ² h bar	[NaClO]: 4000 ppm for 30 days, chlorine tolerance	Partial fluorinated polymer membrane, cross-linking and the degree of sulfonation of the membrane	³⁶
N,N'-DMMPD and 1,3,5-benzenetricarbonyl trichloride (TMC)	—	Interfacial polymerization	[NaCl]: 1500 ppm, R: 90.0%	48 L/m ² h, 1.5 MP	[NaClO]: 200 ppm [CaCl ₂]: 500 ppm 96 h, Chlorine tolerance	Electron-withdrawing properties for aromatic diamines and amide bonds is sterically hindered at ortho position	⁶⁴
m-phenylene diamine (MPD) and 1,2,4,5-benzene tetracarboxyl chloride (BTC)	Thermal imidization	Interfacial polymerization	[NaCl]: 2000 ppm, R: 98.8%	32 L/m ² h, 1.5 MP	[NaClO]: 6000 ppm, chlorine resistance, 168 h.	Amide linkage replaced by imide linkage	⁶⁵
Film poly(amide-urethane@imide)	—	Two-step interfacial polymerization	[NaCl]: 2000 ppm, R: 95%	35 L/m ² h 1.55 MPa	[NaOCl]: 8000 ppm, 24 h chlorine-tolerant property, antifouling property.	Formation of the imine-like and quinone-like	⁶⁶
Hexafluoro alcohol(HFA)-and diamine and trimesoyl chloride (TMC)	Pre-treated PSF membrane with UV-Ozone	Interfacial polymerization	[NaCl]: 2000 ppm, R: 100%	65 L/m ² h 27.6 bar	[HOCl]: 1000 ppm, 24 h, chlorine-tolerant property	Steric hindrance and electron-withdrawing properties of the HFA group.	⁶⁷
2,6-DAT and MPD	—	Interfacial polymerization	[NaCl]: 1000 ppm, R: 100%	0.23 L/m ² h 1 MPa	[NaClO]: 2000 ppm, 100 h chlorine-tolerant property	Electron donating (CH ₃ and OCH ₃) attached to the phenyl ring of MPD group	⁷⁰
Sorbitol polyglycidyl ether (SPGE)	—	-Interfacial polymerization -In situ polymerization	0.2 wt% NaCl, R: 98%	44 L/m ² h 1.5 MP	[NaClO]: 100 ppm, 1 h chlorine-tolerant property	Glycerol prevented membrane drying out during the ring-opening reaction.	⁷¹
PA N,N'-dimethyl-m-phenylene diamine (N,N'-DMMPD)	Heat treatment	Interfacial condensation polymerization	[NaCl]: 1500 ppm, R: 92%	22 L/m ² h 1.5 MP	[NaClO]: 200 ppm, [CaCl ₂]: 500 ppm, 96 h, chlorine-tolerant property	Secondary-to-tertiary amide replacement and a highly crosslinked structure.	⁷³
Layered double hydroxide (LDH) FO	—	Induced immobilization	—	Over 0.015 L/m ² h	[NaClO]: 1000 ppm, 1 h Chlorine-resistant 96 times, resistance to organic fouling and reduce the attachment of bacteria.	The LDH layer served as a barrier	¹⁶¹
	—	—	—	—	—	—	⁷⁹

Table 1 continued

Materials	Treatment	Fabrication method	Salt rejection	Water permeability (L/m ² h), Operating pressure	Tolerance (Chlorination and biofouling test), chlorine testing period	Modification properties improving the tolerance	References
Zwitterionic polymers poly(sulfobetaine) and poly(carboxybetaine)	Heat treatment	Interfacial polymerization	[NaCl]: 2000 ppm R: 99.2%	21.26–4.90 L/m ² h 1.52 MPa	Biofouling property and has biomedical and industrial applications [NaClO]: 1000 ppm, at improve the chlorine tolerance	Electrostatic interactions and steric repulsive barrier Hydrophilic epoxy compound	¹⁶²
Glycidoxypropyltrimethoxysilane (GPPTMS)	Heat treatment	Interfacial polymerization					

manganese, copper, nickel, cobalt etc.;¹⁴⁶ (ii) Non-metal doping with nitrogen, sulfur, boron, halogens etc.;¹⁴⁷ (iii) Coupling with narrow bandgap semiconductors;¹⁴⁸ (iv) Introduction of organic dyes and polymers sensitive to visible light on the nanostructured catalyst surface;¹⁰⁴ (v) Introduction of defect states in the mid-bandgap region of the semiconductor;¹⁴⁹ (vi) Addition on plasmonic metal nanoparticles for visible-range surface-plasmon resonance enhanced photo catalysis.¹⁵⁰

Reference. ¹⁰⁵ studied the influence as photocatalysis of suspended Nano-filler (TiO₂) and thin film mode, using solar energy by continuously re-circulated sea water. The research concluded that the total organic carbon (TOC) increased probably because of increasing organic by-products due to complexity of sea water. Suspended TiO₂ showed better degradation results than thin film mode.¹⁰⁶ By using a tubular photo catalytic reactor in the presence of TiO₂ thin film coating mode, the same results as in ref. ¹⁰⁵ were obtained, with an appreciable decrease in total inorganic carbon.

The free and abundant nature of solar radiation gives a big advantage to photocatalytic methods using sunlight, and is also well suited for outdoor applications, like wastewater treatment processes.

OUTLOOK

Several technologies are available for removing salt from saline water for the provision of clean and safe water. MSF is the more energy- hungry technology, as it needs up to 282 MJ/m³ of thermal energy, whereas energy consumption in MSF unit ranges between 19.58 and 27.25 kWh/m³. MED requires about 230 MJ/m³ with net energy consumption ranging from 14.45 to 21.35 kWh/m³. RO doesn't require any thermal energy with a total equivalent electricity that is about one quarter that of MED and one-fifth of that used by MSF and is thus one of the most effective energy efficient process for seawater and brackish water desalination.¹⁵¹

Adsorption desalination as well as pervaporation and humidification-dehumidification are some of the emerging thermal desalination processes having low energy consumption of purely thermal processes (1.38–45.3) kWh/m³. The developed technologies are still at demonstration scale and the cost of operation is dependent on the availability of a waste heat source to heat feed water stream.¹⁵² Reverse osmosis is by far the most accepted technology for water desalination for both seawater and brackish water as its invention in the 1950s as it is the most energy efficient desalination technology in common use today.¹

There are some newer alternative processes for desalination such as Microbial desalination cell, capacitive deionization technologies and Ion concentration polarization, but they are at initial stages of development and require further demonstrations and scaling up to demonstrate long-scale sustainable operations.¹⁵² Tables 1 and 2.

Biofouling aggravation must be mentioned as one disadvantage of chlorination. Chlorination is not effective in biofouling removal.¹⁵³ In recent study, biofouling of cellulose triacetate (CTA) membranes in a seawater RO desalination plant was investigated. Results suggested that chlorination was not able to prevent biofilm formation on RO membranes. This is probably because chlorination (especially pulse chlorination) kill only bacteria at the surface of a biofilm and cannot penetrate the biofilm's polysaccharide matrix. Moreover, chlorination has a different microbe removal efficiency and can lead to adaptation of certain bacterial populations. Whereas growth of some bacteria, like *Bacillus safensis* and *B. lechinoformis*, were affected by chlorination, other bacteria, like *B. aquimaris* were resistant and leads to irreversible membrane fouling.¹⁵⁴

The biggest disadvantage of silver and copper disinfection is the process cost and the processing times.¹⁵⁵ In addition, even small amounts of silver, especially in the form of nanoparticles, can

Table 2. Surface coating or grafting of polyamide membranes

Materials	Treatment	Fabrication method	Salt rejection	Water permeability	Tolerance Test (Chlorine and antifouling)	Modification properties affecting the tolerance	References
Base structure of X35iRy, where X is a $-OC_2H_5$ alkoxy group and Y is an alkyl (CH_3 , C_8H_{17} , or $C_{18}H_{37}$), vinyl.	Heat treatment	Coating	[NaCl]: 3500 ppm, R: 96.00–99.52	0.255–1.114 L/m ² h 55 kg/cm ²	[NaClO]: 2000 ppm 12 h	Alkyl and aryl groups	85
poly(N-isopropylacrylamide-co-acrylamide) (P(NIPAM-co-Am))	—	Interfacial polymerization, Coating	[NaCl]: 2000 ppm, R: 95.2%	45 L/m ² h, 1.5 MPa	[NaClO]: 3000 ppm, 1 h acid stability, chlorine resistance	Replace hydrogen with chlorine which enhanced intermolecular hydrogen bonding	86
Hydantoin derivative, 3-monomethylol-5,5-dimethylhydantoin (MDMH)	Heat curing at 80 °C	Free radical graft polymerization	[NaCl]: 200 ppm, R: 89%–90.5%	94.8–117.4 L/m ² h	[NaOCl]: 100–2000 ppm, chlorine resistances, anti-biofouling	Sterilize microorganisms on membrane surfaces, regenerate to MDMH	163
3-allyl-5,5-dimethylhydantoin (ADMH) using 2,2 - azobis (isobutyramidine) dihydrochloride as an initiator	—	Grafting polymerizations	[NaCl]: 2000 ppm, R: 85%	205 L/m ² h 1.5 MPa	(100–2500) ppm 1 h chlorine resistance, anti-biofouling property	Sacrificial pendant groups	80
3-allyl-5,5-dimethylhydantoin (ADMH) and then crosslinked by N,N'-Methylenebis (acrylamide) (MBA)	Heat treatment	Free-radical graft polymerization	[NaCl]: 2000 ppm, R: 96.9%	86.3 L/m ² h 1.5 MPa	[Free chlorine]: 1000 ppm, 1 h Enhance chlorine resistances and anti-biofouling properties	Presence of high amount of N atom, increased in hydrophilicity of membrane. MBA with amide II groups in aliphatic and MBA cross-linked aromatic PA	164
Imidazolidinyl urea	—	Carbodiimide-induced graft copolymerization	[NaCl]: 2000 ppm, R: 93.6%	150 L/m ² h 1.55 MPa	[NaClO]: 1000 ppm, 100 days	IU grafted as sacrificial pendant groups	53
Carbodiimide-induced graft copolymerization with Poly (ethylene glycol) derivatives	—	Interfacial polymerization Jeffamine ED600 modified membrane Jeffamine ED2001 modified	[NaCl]: 1500 ppm R: 96.4% R: 96.5%	1.05 MPa 32 L/m ² h 36 L/m ² h	[MLK]: 100 ppm, (DTAB, a cationic surfactant): 100 ppm, 5 h No adsorption of protein	Good steric repulsion	165
Glycylglycine Gly-grafted PA membrane	—	Interfacial polymerization Grafting	[NaCl]: 2000 ppm R: 90%	3.7 L/m ² h 1.6 MPa	[NaClO]: 1000 ppm, 1 h	Sacrificial pendants: N-H moiety of glycylglycine	87
Poly(ethylene glycol) (PEG) diglycidyl ether (PEGDE)	Heat treatment	Grafting	[NaCl]: 2000 ppm, R: 99%	40–60 L/m ² h 5.5 bar	[Surfactant] or [oil-in-water emulsion]: 150 ppm, 30 h preventing foulants from closely approaching the membrane surface	Steric hindrance by PEG	166
Graphene oxides coated by tannic acid (GOT)	—	-Interfacial polymerization -Coating	[NaCl]: 2000 ppm, R: 90%	44 L/m ² h 15.5 bar	[NaClO]: 500 ppm, 1 h -antimicrobial and anti-oxidant properties - tissue engineering, battery membranes, sensing, and gas se- paration processes	GOT enhanced oxidative stress capability, barrier property and hydrophilicity	91
Azide-functionalized graphene oxide (AGO)	UV exposure	Coating	[NaCl]: 2000 ppm [BSA]: 200 ppm R: 95.3%	36.3 L/m ² h	17-fold reduction in biofouling	Grafting of GO reduced the tendency to form gel layer so less accumulation of foulant. foulant deposition.	82
Sulfonated polyvinyl alcohol (SPVA)	Cross-linking treatment	Coating	[NaCl]: 2000 ppm, R: 99.18%	38.3 L/m ² h 1.55 MPa	2000 ppm of BSA, 12 h improved fouling resistance to BSA and CTAB	Electronegativity and hydrophilicity of PA-SPVA and	96

Table 2 continued

Materials	Treatment	Fabrication method	Salt rejection	Water permeability	Tolerance Test (Chlorine and antifouling)	Modification properties affecting the tolerance	References
Glutaraldehyde aqueous solution followed by polyvinyl alcohol (PVA) aqueous solution	Sequential surface treatment with glutaraldehyde (GA)	Coating	[NaCl]: 500 ppm, R: 98.48 – 97.29%	28.6–40.9 L/m ² h, 5 bars	[NaOCl]: 5000 ppm -6 h Chlorine stability -Anti-fouling property	strong ionization of sulfonic acid group. Enhanced surface hydrophilicity, reduced surface negative charge and increased surface roughness. Covalent attachment of PVA	¹⁶⁷
Terpolymer of 2-acrylamido-2-methyl propane sulfonic acid, acrylamide and 1-vinylimidazole (P(AMPS-co-Am-co-VI))	—	- Conventional free radical. - dip-coating process	[NaCl]: 80,000 ppm R: 85%	45 L/m ² h 0.4 MPa	[NaClO]: 2000 ppm, 40 h improve the chlorine tolerance	Terpolymer as a barrier layer	¹⁶⁸

enter mammalian body causing serious health issues.¹⁵⁶ It has been reported that silver ingestion can lead to severe mammalian liver and kidney damages.¹⁵⁷ The efficiency of silver disinfection process also depends on the levels of chlorine and nitrates present in water. Silver strongly reacts with these anions to form silver-compounds in water, dramatically reducing the disinfection efficiency.

Although the photocatalytic disinfection route produces harmless by-products and is effective against microbial disinfection, its applications are still limited to small or laboratory scale devices. One of the drawbacks is the cost for large-scale production of uniform nanoscale photocatalytic materials to meet the water demand. Some of the photocatalytic materials also show toxic effects against various aquatic organisms.¹⁵⁸ Moreover, the pollutants need to be in contact with the catalyst surface to get degraded into harmless products. Therefore, photocatalytic route is an adsorption limited process that hugely affects the overall efficiency of the disinfection process. Turbidity of water also affects the overall efficacy of the photocatalytic system by preventing light penetration.¹⁵⁹ If the nanoscale catalysts are in free form, then their removal after the disinfection process is extremely difficult and often needs additional filtering processes adding to the cost of operation.

Disinfection by-products (DBP) in seawater and fresh water are reported to be similar in wastewater as well as seawater. Halo acetaldehydes (HALs) were the main groups of DBP formed in either case. In seawater, the concentrations level of bromide and iodide in distribution systems are much higher. More toxic cytotoxic and genotoxic DBP species are formed in seawater with biotic water blend (where the precursor is e.g., amino acids and simulated algal blooms). Studies in Red Sea have shown DBAcAm, DBAA, DBAN as Dibrominated species of DBPs are formed.

There are quite a few recent papers on chlorine dioxide, an alternative for chlorine disinfection. Many are considering them as alternative to chlorine.¹⁶⁰

CONCLUSIONS

To prevent biofouling of RO membranes, chlorination is becoming the popular choice of the RO plants as facile and inexpensive method. Although chlorination can prevent the biofouling of the RO membranes up to a certain extent, it has several other disadvantages. Many of the DBPs formed during chlorine disinfection are carcinogenic posing a risk to human health. Additionally, chlorination is not effective against all microbe types and active chlorine species attacks the polymer network of the RO membranes, making them weaker over time, allowing additional post dechlorination treatment units, adding more operational costs to the RO plants. Although the choice of polymers for RO membranes is wide and careful selection of polymers and surface functionalization can avoid such attacks from active chlorine species, their wide spread application is mostly limited by their poor salt rejection. Disinfection using UV and/or ozone treatment as viable alternatives to chlorination has been widely studied as do not form harmful by-products and it is effective against most of the microbes present in the water. However, these techniques have their own limitations, such as they are ineffective against suspended solids, they are energy intensive process and they suffer of corrosion. Recently emerging techniques, materials, and methods attributed to the field of nanoscience and nanotechnology, have shown great potential as an alternative to chlorination. Techniques like photo catalysis and nano-silver have shown promising results towards disinfection, as they are efficiently effective against organic pollutants as well as microbes and do not produce harmful by-products. Using natural sunlight these nanomaterials can significantly reduce the contamination level in water due to their high reactivity and thus can prevent the biofouling of RO membranes. However, their applications are

mostly limited to the laboratory scale and need more attention for large-scale usage.

Next-generation desalination membranes are likely to overcome another limitation of current TFC membranes: the high sensitivity of the polyamide selective layer to oxidants, such as chlorine and ozone.

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AUTHOR CONTRIBUTIONS

M.A.-A., B.A.-G., T.B., and S.D. designed the manuscript, processed the references, prepared the original figures, and wrote the draft manuscript. J.D., S.C., L.R., and A.B. contributed discussing and expanding the manuscript, rewriting, and checking the final version of the manuscript. M.A.-A. and A.B. assembled the final version of the paper. A.B. further revised the manuscript.

ADDITIONAL INFORMATION

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