



Review Paper

Recent Developments in Fouling Minimization of Membranes Modified with Silver Nanoparticles

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Keywords

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Highlights

- Acrylamide grafts/Ag⁰ on polyethersulphone membranes kill 99.9% E. coli
- Ag⁰ on surface of polysulphone membrane inhibits 98% of bacterial growth
- Polyamide/Ag⁰ membrane gives ~100% kill of E. coli and B. subtilis in 1.5 h
- 99.9% inhibition of E. coli for Ag⁰ grafted onto thiol modified cellulose membrane
- Ag⁰ on ZrO₂ capillary membrane removes all E. coli with no apparent silver loss

Abstract

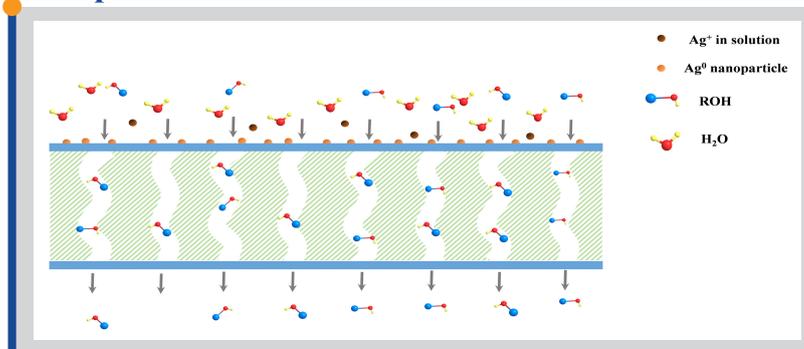
When incorporated in membranes, Ag⁰ nanoparticles are effective antifouling and antibacterial agents, arising from the presence of Ag⁺ ions either in solution or adsorbed onto nanoparticles. A variety of organic and inorganic composite membranes involving silver show good results. Long-term prevention of biofouling by such membranes does not seem to have been satisfactorily obtained yet. Ways of counteracting silver loss from the membranes need to be sought. Recovery by the reduction of soluble silver ions to elemental silver at regular intervals may be one possible method, but this is not feasible when the silver ends up in the product water. However, the regenerating and recycling of Ag⁺ ions could be especially relevant in the case of organophilic pervaporation, where the aqueous phase is retained and does not pass through the membrane. There is a potential for creating a practical long-lasting antifouling system for that process.

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Graphical abstract



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1. Introduction

Fouling is a major issue in membrane technology [1], especially in processes that make use of hydrophobic membranes, as in membrane distillation and organophilic pervaporation. Many studies have been carried out on membrane modifications for fouling prevention, which have been comprehensively reviewed [2], with nearly 200 examples of modification with hydrophilic entities being listed, and about 20 examples of charge modification incorporated into membranes used for water treatment. So far, no long lasting system has been perfected.

The use of nanoparticles in changing the membrane surface properties in terms of hydrophilicity and charge has been discussed [3-12]. Very recent broad and comprehensive reviews of such composite membranes and their antifouling prospects have appeared [13, 14]. Some of the nanocomposite membranes reported include metal-based nanoparticles such as TiO₂, SiO₂, Al₂O₃, Si, Ag, ZnO, ZrO₂, Mg(OH)₂, CaCO₃, and TiSiO₄, plus SiO₂, Si and carbon-based nanoparticles like graphene oxide and carbon nanotubes. The present article is focused on the use of surface deposits of elemental silver nanoparticles on membranes made from various organic polymers.

The antibacterial properties of silver are well known, and silver nanoparticles have been incorporated into a wide variety of consumer products for microbial control [15-18]. These authors point out that the use of such antimicrobial materials is widespread, with items ranging from simple methods of storing drinking water and milk in silver containers to the silver coating of medical instruments and implants. They emphasise the 100 µg/L silver limit in drinking water that has been established [19].

The antibacterial activity has been found to be dependent on the size of silver particles, which in turn is dependent on their method of preparation [20]. Smaller particles lead to a greater contact with bacteria and easier oxidative dissolution to release silver ions. The interaction of Ag⁺ with thiol groups and the formation of S-Ag or disulphide bonds can damage bacterial proteins, interrupt the electron transport chain, and dimerise DNA [21-23]. Similarly, the antiviral properties of silver ions involve interaction of viral DNA with the thiol groups in proteins [24]. The bactericidal action of silver ions increases with increasing temperature and pH level [22].

2. Membranes utilised

Silver nanoparticles have been successfully introduced into various membrane materials such as polyethersulphone (PES), polysulphone (PS), polyamide (PA), polyvinylidene fluoride (PVDF), polysaccharide and inorganic structures.

2.1. PES membranes

The effects of polyvinylpyrrolidone (PVP) and 2,4,6-triaminopyrimidine on the surface properties of silver-filled PES membranes have been described [25]. It was shown that smaller silver particles were formed in the PES membranes when the additives were applied during the preparation of the membrane, and that silver leaching was then significantly reduced by 57-63%. The improved silver dispersion on the membrane surfaces enhanced antibacterial activity against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), inhibiting almost all bacterial growth in a rich medium of the bacteria, making the membranes attractive for water treatment applications. Further work has appeared on PES-silver composite membranes fabricated using a simple phase inversion method with silver nitrate and PVP of molecular weights 10,000 to 360,000 Da as dispersant [26]. A membrane with 2.0 wt% Ag and PVP of MW 360,000 had a high level of Ag particle entrapment in the membrane structure, which resulted in a 100% inhibition of *E. coli* growth within a 24 h incubation time. This was concluded to offer a huge potential for bacteria removal and disinfection using this membrane for ultrafiltration (UF).

A study has been done to reduce membrane fouling by modifying the surface of commercially available PES membranes by using polyelectrolyte multilayers of anionic poly(styrene sulphonate) or PSS, alternating with cationic poly(diallyldimethylammonium chloride) or PDADMAC, together with silver nanoparticles integrated into the membrane surface in stable thin films of 15 nm thickness [27]. The presence of the silver in the top PSS layer imparted biocidal characteristics to the modified surface. Fouling was simulated by filtering solutions of humic acid (5 and 20 mg/L), a suspension of *E. coli* (106 colony-forming units (CFU)/mL), and a mixture of both foulants through the unmodified and modified PES membranes. The additions significantly reduced organic and biological fouling. It was noted that humic acid did not have a significant effect on the biocidal properties of the silver-containing membranes.

Acrylamide has been grafted onto a PES hollow fiber membrane and

silver nanoparticles were then formed within the acrylamide layer [28]. The hydrophilicity of the membrane surface was improved by the acrylamide grafting, leading to a reduction in fouling by bovine serum albumin (BSA). The antibacterial activity of the membrane was evaluated against *E. coli* in an agar culture medium. The parent PES membrane had no antibacterial activity, as bacteria grew on the membrane surface, but the membranes containing silver nanoparticles had a very high antibacterial activity. This was examined by immersing the membranes in an *E. coli* suspension, when after incubating for 8 h at 37 °C more than 99.9% of the cells were killed.

PES UF membranes have been made by phase inversion using silver loaded sodium zirconium phosphate nanoparticles (nano AgZ) in the casting solution [29]. The thermal stability of the membranes and their hydrophilicity were enhanced. The membrane with 1% nano AgZ present had the best permeation performance, with the pure water flux increasing from 82.1 to 100.6 L/m²h. The BSA rejection was 96.7%.

PES UF membranes with antibacterial properties have been prepared by blending them with SiO₂-Ag composites [30]. The silica particles were prepared from tetraethoxysilane by hydrolysis and polymerization, and the silica was then mixed with AgNO₃ solution. The silver nanoparticles were deposited on the surface of the SiO₂ by a reduction reaction. The modified membranes had a 270% higher water flux than the parent PES membrane. The structure of the membrane was not obviously affected by the addition of the SiO₂-Ag particles. The antibacterial effect of the composite membrane was tested with *E. coli* and *S. aureus* cultures. The antibacterial rates of the hybrid membranes could reach 100%, confirming their capability against biofouling. The antibacterial and anti-biofilm formation properties of the membranes were studied with pure cultures of both *E. coli* and *Pseudomonas* sp. and also with a mixed bacteria culture from an activated sludge bioreactor. The Ag-SiO₂/PES membranes gave the better filtration performance.

Chemically produced silver nanoparticles often have problems with particle stability and tend to aggregate at high concentration or when the average particle size is less than 40 nm. As an answer to this, biological processes have been developed using microorganisms to produce another variant, in the form of bio-Ag [31]. The incorporation of bio-Ag into PES membranes as a biocidal agent has been investigated. The bio-Ag/PES nanocomposite membrane was tested with pure cultures of *E. coli* and *Pseudomonas aeruginosa* (*P. aeruginosa*) and a mixed culture from an activated sludge bioreactor. The membranes had excellent antibacterial activity, not only preventing the attachment of bacteria onto the membrane surface, but also inhibiting the reproduction and development of biofilms [32]. The membrane hydrophilicity, porosity, water uptake and membrane surface smoothness were also enhanced.

As a bio-mediated synthesis route, *Bacillus subtilis* bacterial supernatants have been employed in the preparation of bio-Ag nanoparticles [33]. The particles had a size of less than 50 nm. A significant amount of the silver was in the form of silver oxide. The nanoparticles were used to modify PES membranes and tested for their performance in protein separation. The composite membranes showed higher hydrophilicity and enhanced permeability compared to the parent membrane, having a flux of 68 L/m²h when the BSA concentration was 500 mg/L. The BSA separation was then 92%, and there was reduced fouling. The membranes were seen as deserving candidates for future industrial separations.

Thin film composite membranes with silver-polyethylene glycol (PEG) nanocomposite coatings have been installed on the surface of PES membranes with the aim of reducing both organic and bacterial fouling in water treatment processes [34]. Analogous membranes were also made that had different functionalities, such as carboxylic acid, amine or PEG, which provided useful platforms for comparing the anti-fouling properties of the three kinds of functional groups. Significant improvements in hydrophilicity were found with all modifications. They showed reduced attachment of BSA and *E. coli*. Among them, the silver-PEG nanocomposite membrane was subjected to the least fouling, with a 99.8% reduction.

Modification of PES hollow fiber membranes has been carried out by thermal grafting of PEG and silver nanoparticles [35]. Poly(acrylonitrile-co-maleic acid) was used as a link to chemically attach the PEG and silver to the UF membrane via the acid group. This treatment increased the pure water flux by ~36% because of the improved hydrophilicity. In addition, antibacterial studies using the zone of inhibition test showed that the composite membrane had antibacterial properties. As a consequence, there was a lower flux drop when tests were carried out on reservoir water.

A layer-by-layer assembly method has been employed to modify a commercial PES membrane by successive adsorption of chitosan and alginate as cationic and anionic polyelectrolytes, respectively [36]. Then AgCl/TiO₂ xerogels were incorporated in the top layer of the modified membranes. Organic and biological fouling were addressed separately using alginate and

E. coli bacteria suspensions as the organic and biological model foulants, respectively. The AgCl/TiO₂-containing membranes showed higher water permeability and less organic fouling. There was also an improved resistance to biological fouling as compared to the parent PES membrane. Antibacterial activity tests showed that layers incorporating AgCl/TiO₂ do not permit bacterial growth on the membrane surface. However, after the tests it was noted that there was a 4.2% reduction in the amount of immobilized silver. With continued operation, the silver loss per filtration cycle was stabilized at 7.4 µg/L, which extrapolates to a 265-day time span for all the remaining silver to be released. Even though this was regarded as a low loss, it indicated that further work should be done on lowering the release, for example changing the texture of AgCl/TiO₂ xerogels by varying the pore size of the TiO₂ and the crystallite size of the AgCl. The challenge was seen in preparing membranes with a controlled release of silver and also to have the silver on the top layer of the membrane.

Silver nanoparticles of size ~40-50 nm have been successfully introduced onto the surface of sulphonated PES membranes by an ion exchange interaction, followed by the use of Vitamin C ascorbic acid as a reducing agent [37]. Detailed studies were made of the antibacterial activity of the composite membranes, carried out with *S. aureus*, *S. albus* and *E. coli*. The composites exhibited significant inhibition capacity, and had a strong bactericidal impact over a long period. It was anticipated that such sulphonated membranes might expand the usage of PES membranes in the food processing field and in the medical instrument industry. It was noted that silver release was higher in saline solutions. It was postulated that if Na⁺ contributed to Ag⁺ release, the higher concentration of Ag⁺ might suppress the dissolution of Ag⁰ nanoparticles. The mechanism of antibacterial activity has been further discussed [13], with one version being that the presence of nanoparticles leads to the breaking of bacterial cell membranes and the subsequent penetration of nanoparticles or ions into the cell [38]. There is still much to be learnt about the toxic effects of silver in either form.

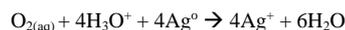
Sulphonated PES and Nafion membranes have been the host polymers for silver nanoparticles and have provided systems that claim complete disinfection of water containing *E. coli* in 1-2 h. [39]. It was postulated that the membranes provided a reservoir of Ag⁺ ions, with removal of less than 0.5% of the nanoparticles in under 2 h.

A summary of the results for PES membranes is given in Table 1. All have been shown to have enhanced anti-bacterial activity that is of a useful duration. Silver leaching was observed and seen to be low in the most recent example.

2.2. PS membranes

Flat sheet porous PS-silver nanocomposite membranes have been synthesized by a phase inversion process [40]. The effects of the casting mixture composition and nanoparticle incorporation method on the morphological and separation properties of the membranes were studied by comparing nanocomposites of different preparations with silver-free controls.

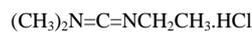
The silver nanoparticles were either synthesized and then added to the casting solution as an organo-sol or produced in the casting solution by *in situ* reduction of ionic silver by the polymer solvent. The effects of filler incorporation were more pronounced for less porous membranes. For casting mixtures that yielded membranes with relatively low porosity, there was a macro-void broadening and an increase in surface pore size and density. This translated into an improvement in separation properties with a significant decrease in the hydraulic resistance, accompanied by only a minor decrease in rejection. There was an antibacterial capacity because of the gradual release of ionic silver by the following mechanism, with a leachate level of less than 1 µg/L:



This implies that the oxidation would be inhibited by alkaline conditions. It could also be reduced by lowering the level of dissolved oxygen in the water, which could be done by adding sulphite. However, this may diminish, if not eliminate, the antibacterial activity.

Silver nanoparticles have been incorporated into PS UF membranes, which were then shown to exhibit antimicrobial properties towards a variety of bacteria, including *E. coli* and *P. mendocina* [18]. It was also observed to increase membrane hydrophilicity. Analysis indicated a sharp loss of silver from the membrane surface after a relatively short filtration period, but 90% of the added silver remained in the membrane. The silver loss resulted in a significant decrease in antibacterial and antiviral activity. To slow the release of silver ions it was suggested that the nanoparticles should be located in the surface layer of the membrane and anchored there, or they should be encapsulated in an appropriate polymer. Furthermore, silver lost from the membrane could be restored by the deposition and reduction of silver salts [41].

Silver nanoparticles encapsulated in positively charged poly(ethyleneimine hydrochloride) (PEI) were incorporated in a PS UF membrane that had been modified by oxygen plasma [42]. The crosslinking agent 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) was used:



The primary amino groups of the PEI reacted with carboxylic acid residues in the PS, whether or not EDC was present. The extra binding via EDC maximised the density of nanomaterials on the membrane surface and imparted significant antimicrobial activity to the membrane. Without EDC, a 94% inactivation of *E. coli* was achieved, but with EDC this was increased to > 99.9%, which was attributed to the higher concentration of silver on the membrane surface, raised from 1.5 to 5.2 wt%. The Ag-loaded membranes displayed an initial Ag⁺ release of 28.4 µmoles/m²day, which declined steadily with time.

Table 1
Effects of various treatments when Ag nanoparticles are inserted into PES membranes.

Reagent	Antibacterial activity, fouling	Other, Ag ⁺ leaching, flux change	Reference
Polyvinylpyrrolidone & triaminopyrimidine	Enhanced anti-bacterial activity	Ag ⁺ leaching 55 and 63% less	[25]
Polyvinylpyrrolidone of >MW 360,000	100% inhibition of <i>E. coli</i>	High level of Ag ⁰ entrapment	[26]
PSSA/PDADMAC/ Ag ⁰ layers	Significant reduction in organic & biofouling	Humic acid did not affect biocidal activity	[27]
Acrylamide graft	99.9% <i>E. coli</i> kill and less BSA fouling	Not reported	[28]
Ag ⁰ loaded sodium zirconium phosphate	96.7% BSA rejection	Flux increase, 82 to 101 L/m ² h	[29]
SiO ₂ -Ag composite	Excellent, less fouling	270% higher water flux	[30]
Bio-Ag ⁰	Excellent, less fouling	Enhanced porosity	[31, 32]
Bio-Ag ⁰	BSA separation facilitated, less fouling	High fluxes, good BSA recovery	[33]
Ag ⁰ -PEG thin film	99.8% BSA and <i>E. coli</i> fouling reduction	Less attachment of all foulants	[34]
PEG/Ag ⁰ graft	36% flux increase, antibacterial properties	Less drop in flux over time with real water	[35]
AgCl/TiO ₂ xerogels	Increased ease of rinsing	4.2% reduction in Ag ⁰ per filtration cycle	[36]
Sulphonated PES/Ag ⁰	Significant bactericidal effect	Long non-fouling period. Na ⁺ inhibits release?	[37]
Sulphonated PES and Nafion/Ag ⁰	100% kill of <i>E. coli</i> after 1-2 h	0.5% silver loss in 2 h	[39]

Table 2
Effects of various treatments when Ag nanoparticles are inserted into PS membranes.

Reagent	Antibacterial activity, fouling	Ag ⁺ leaching, flux change	Reference
Ag ⁺ reduced by polymer solvent	Ag ⁺ release gives antibacterial effect	Ag ⁺ in leachate <1 µg/L	[40]
Ag ⁰ loaded	Best when Ag ⁰ located on surface	Encapsulate Ag ⁰ in appropriate polymer?	[18]
Ag ⁰ loaded	Regenerate Ag ⁰ by depositing more	Reduce mobile Ag ⁺ ?	[41]
Ag ⁰ in polyethylene-imine plus crosslinker	94% <i>E. coli</i> removal increased to >99.9%	Crosslinking assists silver retention	[42]
Smaller Ag ⁰ particles better than 70 nm	Higher bacteria removal with 30 nm	Higher flux and BSA rejection too	[43]
Polyvinylpyrrolidone to assist smaller size	More hydrophilic	Less adsorption of organics	[44]
Ag ⁰ particles in top skin of membrane	Growth 98% inhibited	Properties unaltered by 7 day soaking	[45]
Supporting membrane contained CNTs	More antiadhesive and antibacterial	Water permeability enhanced	[24]
Ag ⁰ on membrane surfaces or within pores	Surface product better, 90% less <i>E. coli</i> adherence	Ag ⁺ in leachate 2 µg/L	[47]
PAN membrane and CNTs	Enhanced antibacterial effect with <i>E. coli</i>	Flux drop of 6% vs. 55% for parent membrane	[46]

The membranes with EDC-facilitated grafting and released higher concentrations of 110.2 µmoles/m²/day at the start of the experiment, but after 14 days the rate of Ag⁺ release was similar to that of the membranes where EDC was not employed. It was observed that more work was necessary on a regenerating process to improve the functionality of the membrane. The effect of silver nanoparticle size on the performance and bacterial resistance of PS UF membranes has been explored [43]. A less crystalline structure was obtained with smaller silver nanoparticles, and surface pore sizes were also smaller. Tighter finger-like structure structures appeared on adding 70 nm silver nanoparticles, but with 4 wt% of silver nanoparticles of size 30 nm the membranes had smoother surfaces. The membranes were then more hydrophilic and had higher antibacterial behaviour. In addition, there was a higher flux of pure water and higher BSA rejection. This was ascribed to the increased silver release and higher surface to volume ratio obtained with smaller silver nanoparticles.

PS membranes have been prepared by adding different amounts (0-1 wt%) of silver nanoparticles of less than 100 nm in size to a PS and PVP preparative mixture [44]. The presence of the silver improved the filtration performance of protein and carbohydrate solutions as the composite membranes had lower absorption and pore fouling behaviour than the silver-free PS membrane. A specific relationship between hydrophilicity and protein fouling was observed. Filtration of activated sludge was improved with the composite membrane, as pore fouling was decreased.

A nanocomposite membrane has been synthesised by embedding silver nanoparticles in the top skin of a PS membrane [45]. The silver component enhanced the anti-adhesive property of the membrane by decreasing the capability of *E. coli* bacteria to permanently attach to the membrane surface. On average, a 75% detachment was observed compared with 18% for the parent PS membrane. It was shown that bacterial growth was 98% inhibited, which did not decrease after the membrane had been soaked in water for seven days.

A new type of thin film nanocomposite membrane has been made by the interfacial polymerization of a PS support layer containing acid modified multi-walled carbon nanotubes (CNTs) and a thin top layer film containing nanosilver particles [24]. Microscopic characterization confirmed that CNTs and Ag⁰ particles were distributed in the support layer and the thin film layer, respectively. It was observed that membranes with 5.0 wt% of CNTs in the support layer and 10 wt% of Ag⁰ particles in the thin film layer enhanced the pure water permeability by 20-23%. This was attributed to the diffusive effect of the nano-pores in the CNTs. Tests with *P. aeruginosa* indicated that the composite membrane had greater antiadhesive and antibacterial properties than the silver free membrane. A very similar membrane has been made from a polyacrylonitrile (PAN) hollow fiber membrane and silver coated multi-walled CNTs [46]. There were enhanced antimicrobial activities and antifouling properties with *E. coli*. Also, the relative flux drop after 20 h of filtration was 6%, significantly lower than the 55% result for the unmodified PAN membrane.

Silver nanoparticles have been dispersed within a PS membrane matrix using two different methods [47]. Initially, the nanoparticles were synthesised and then dispersed in the preparative polymer solution, while in the second the formation of nanoparticles was carried out within an existing PS membrane. The first approach gave composite membranes that had the Ag⁰ particles uniformly distributed in the internal pores of the membrane, but the second gave a product where they were located on the top and bottom

surfaces of the membrane. This latter membrane exhibited better antibacterial activity and gave a 90% reduction in *E. coli* adhered cells compared to the parent PS membrane, but both types of composite membranes showed promising antibacterial activity against Gram-negative bacteria. The Ag⁺ released in the leachate was 2 µg/L. The best product had potential in the preparation of antifouling NF membranes for water and wastewater purification.

The results for PS membranes are summarised in Table 2, together with the one result for a PAN hollow fiber membrane. In addition to the good antibacterial behaviour, the fouling by organics was markedly reduced.

2.3. PA membranes

Hybrid membranes consisting of silver nanoparticles in thin film composite PA membranes on a PS supporting membrane have been prepared by *in situ* interfacial polymerization [48]. They were shown to possess dramatic anti-biofouling effects when exposed to *Pseudomonas* sp., with the colonies of *Pseudomonas* almost all being killed. The presence of the silver had little effect on the water flux and salt rejection in the nanofiltration (NF) process, with a flux of 92 L/m²/hr and 97% salt rejection at 200 psi being obtained.

Elemental silver nanoparticles have been deposited in Polyamide 6 (from BASF) at the level of 2 wt% by the thermal reduction of Ag⁺ during the melt processing of a Polyamide 6/ silver acetate mixture [49]. The composite membrane was shown to be active against *E. coli*, whereas the parent membrane did not exhibit any antimicrobial properties. Immersion of the membrane in water for 100 days did not reduce its antimicrobial efficacy, so it should be an effective antimicrobial material for long-term applications. This low silver release behaviour was ascribed to the high surface to bulk ratio of the silver nanoparticles and the strong hydrophilic properties of the PA matrix.

The potential of a hydrophilic polyether-block-polyamide copolymer (PEBA) on a PS support to alleviate membrane biofouling when incorporating silver nanoparticles has been investigated [50]. The composite membranes had improved hydrophilicity and inhibited the growth of *E. coli*. The irreversible biofouling, which was observed in the case of the parent membrane, was significantly reduced in the PEBA/nano-Ag membrane, the flux recoveries being 21 and 89%, respectively.

Silver nanoparticles of approximately 15 nm diameter have been attached to the surface of PA thin film composite UF membranes by covalent bonding, using cystamine as the bridging agent [51]. Thiol groups were first inserted on the surface of a freshly fabricated membrane by reaction with the NH₂-CH₂-CH₂-SH in ethanol, and then the nanoparticles were attached to the membrane surface by Ag-S chemical bonding. The water permeability was increased from 49.9 to 69.5 L/m²/h by this process, and there was an improved inhibition of *E. coli* growth. Silver loss was minimal, with the amount leached out during 14 days of batch tests accounting for 12% of the total amount of silver on the membrane.

The incorporation of ~7.6 nm silver nanoparticles in a thin film composite PA membrane used for RO has been carried out by plasma arc deposition [52]. The result was a membrane that had very strong antibacterial properties and *E. coli*, *P. aeruginosa* and *S. aureus* that were long lasting. There was 85% of the silver remaining after 7 days operation. In addition, there was an enhancement in the water flux of approximately 40% without

loss of RO performance. This was attributed to an increased membrane hydrophilicity and partial destruction of the PA layer.

Silver nanoparticles have been immobilised onto a commercial polyamide RO membrane by initially depositing an ultrathin layer of tannic acid/Fe³⁺/PEI complex onto the membrane surface [53]. The treated membrane was then immersed in ammoniacal silver nitrate solution, and as it is tannic acid is a reducing agent, it converted the Ag⁺ to Ag⁰, with *N*-vinylpyrrolidone used as a stabiliser to get an even distribution of the Ag⁰ nanoparticles on the membrane surface. The water flux and salt rejection of the modified membrane both increased, and there was excellent anti-bacterial behaviour with bacteria mortality reaching almost 100% after contact with *E. coli* and *B. subtilis* suspensions for 1.5 h. The water flux decreased by only 11 and 17%, respectively after contact with the two organisms, versus 35% for both bacteria with the unmodified membrane.

Biogenic silver nanoparticles with an average diameter of only 6 nm have been grafted onto the surface of a poly (piperazine amide) NF membrane [54]. The results were compared with hybrid membranes made from chemically prepared Ag nanoparticles. There was improved hydrophilic character and water flux with the bio-Ag membrane. In addition, this type of membrane showed better and longer lasting antibacterial properties towards *P. aeruginosa* and *E. coli*. The life of the membrane was better in that the amount of silver remaining was 95% after soaking in pure water for 50 days. After 4 months' of immersion, the salt rejection was more than 90% of the initial rejection. The membranes were seen as an effective strategy for decreasing biofouling in the NF process.

A somewhat related polyamide has been formed from PEI and methacryloyl chloride are crosslinked with 2-hydroxyethyl acrylate [55]. The films were then loaded with silver nanoparticles by ascorbic acid reduction of silver ions complexed within the polymer network. Silver particles of 4-50 nm size were obtained, and were capable of killing bacteria or at least inhibiting bacterial growth and also of repelling microbes at the same time.

Polyimide (PI) membranes containing silver nanoparticles have been made from the precursor poly (3,3',4,4'-biphenyl-tetracarboxylic acid dianhydride-co-4,4'-oxydianiline) amic acid [41]. The membranes had nanoparticles in pores on one side of the membrane, on the bottom side and were dispersed evenly on the walls of the pores. More recently, antifouling PI membranes have been synthesized with surface-bound silver nanoparticles [56]. Silver ions were grafted onto the membrane surface by an ion exchange reaction, followed by thermal treatment at high temperature. With an increase in temperature, more silver ions were converted to metallic silver particles. After this modification, the membrane showed an enhanced bacteria-inhibition effect, and the antifouling properties in the BSA solution were also improved. This was ascribed to the inhibitory and biocidal properties of

elemental silver, not silver ions.

The results for PA and PI membranes are recorded in Table 3. Strong antibacterial activity was noted throughout, along with enhanced flux performance because of the more hydrophilic character of the membranes.

2.4. PVDF membranes

Biogenic silver nanoparticles of size ~11 nm produced with *Lactobacillus fermentum* have been immobilized in microporous PVDF membranes using an immersion-precipitation method and two different pretreatments of biosilver [57]. Virus inactivation by the membranes was demonstrated using UZ 1 bacteriophages. With a membrane containing 2.5 g/m² of silver and a flux of 75 L/m² h, there was at least a 3.4 log decrease in the phages achieved. This was ascribed to the release of silver ions release from the membranes. With a submerged plate membrane reactor operated at a flux of 3.1 L/m²h at the start, the silver concentration was 271 µg/L, but after filtration of 31 L/m² the concentration decreased to within the drinking water limit. By increasing the understanding of how the membrane structure affects the release rate of Ag⁺ from bio-Ag⁰, it was felt that the Ag⁺ concentration in the filtrate could be further lowered and the depletion of Ag⁺ from the material controlled.

A poly(acrylic acid) brush has been grafted onto a PVDF membrane, and then silver ions loaded onto the carboxylic acid groups [58]. There was a significant improvement in PVDF membrane surface hydrophilicity, and the antifouling performance of the membrane towards BSA was elevated. Some 80% of the foulant could be removed from the membrane by washing, to give a flux recovery of about 40%.

To improve the hydrophilicity and antifouling performance of PVDF membranes, silver nanoparticles have been immobilized in PVDF UF membranes, using *N,N*-dimethylformamide as the reducing agent for Ag⁺ and as the solvent for PVDF as well [59]. The organic antifouling and antibacterial performance of the composite membranes were evaluated using BSA solution and *E. coli*. The organic antifouling performance was illustrated by the water flux recovery, which was about 1.3 times that of the parent membrane. Regarding the antibacterial performance, the unmodified membrane had high amounts of bacteria on the surface, which almost completely covered the membrane, in contrast with the composite membrane, where only a small amount of surface bacteria could be observed.

Poly amidoamine (PAMAM) dendrimers have been used as templates to form silver-PAMAM dendrimer nanocomposites, which were then grafted onto PVDF membranes [60]. There was better flux recovery and antifouling performance versus humic acid and BSA as a result.

The results for the examples cited are listed in Table 4. All the benefits are attained to some degree.

Table 3
Effects of various treatments when Ag nanoparticles are inserted into PA or PI membranes.

Reagent	Antibacterial activity, fouling	Ag ⁺ leaching, flux change	Reference
Ag ⁰ particles in thin film of aromatic PA	<i>Pseudomonas</i> sp. almost all killed	Flux for NF was 92 L/m ² h	[48]
Ag ⁰ particles deposited on tannic acid/Fe/PEI film on aromatic PA	<i>E. coli</i> and <i>B. subtilis</i> ~100% kill in 1.5 h	Flux decrease of 11 and 17% respectively, vs. 35% for original membrane	[53]
In polyether-block-polyamide	<i>E. coli</i> growth inhibited	Flux recovery goes from 21 to 89%	[50]
Ag ⁰ bonded to PA by NH ₂ -CH ₂ -CH ₂ -SH	<i>E. coli</i> growth inhibited	Flux recovery from 50 to 69 L/m ² h	[51]
Used 6 nm biogenic Ag ⁰ particles	More antibacterial than chemical Ag ⁰	Better flux as well	[54]
Ag ⁰ bonded to crosslinked PEI	4-8 times less attachment	Microbe repelling properties too	[55]
Polyimide membrane, thermal oxidation of Ag	Higher temperatures gave better results	Less biofouling so better flux also	[56]
Plasma arc deposition of Ag ⁰ particles in RO thin film PA membrane	Long lasting killing of <i>E. coli</i> , <i>S. aureus</i> and <i>P. aeruginosa</i>	85% of Ag ⁰ retained after 7 days RO operation	[52]

Table 4
Effects of various treatments when Ag nanoparticles are inserted into PVDF membranes.

Reagent	Antibacterial activity, fouling	Ag ⁺ leaching, flux change	Reference
11 nm bio-Ag ⁰ used	3.4 log decrease in bacteriophages	Ag ⁺ release within limit eventually	[57]
Poly(acrylic acid) graft first	Washing removes 80% of foulants	Flux recovery then 40% higher	[58]
Dimethylformamide to reduce Ag ⁺ to Ag ⁰	Better antibacterial properties	Flux recovery improves	[59]
Polyamidoamine-Ag ⁰ graft	Less organic fouling	Better flux recovery	[60]

2.5. Polysaccharide membranes

Silver was immobilized onto the surface of a chitosan membrane, first as ionic silver and then after chemically treating the membrane surface, it was reduced to metallic silver [61]. Antibacterial and antibiofouling experiments were conducted with two types of typical bacteria, *E. coli* and *Pseudomonas* sp. Neither were found to be able to grow on the Ag⁺ or Ag⁰ membranes, but they attached and grew on the parent chitosan membrane as viable cells. Leaching tests showed that elemental silver on the membrane was more stable than ionic silver. They were similar in their anti-biofouling behaviour for the first 24 h, but the Ag⁰ membrane gradually exhibited more stable and eventually better anti-biofouling performance after that time.

Fairly uniform chitosan/poly(ethylene oxide) or PEO using ultrafine fibers of size ~100 nm that contained silver nanoparticles have been successfully prepared by electrospinning chitosan/ PEO solutions containing Ag/chitosan colloids, by means of the *in situ* chemical reduction of Ag ions [62]. The presence of silver nanoparticles in the fibers was confirmed by X-ray diffraction patterns. They were evenly distributed and had a size less than 5 nm. X-ray photoelectron spectroscopy suggested that the existence of Ag-O bonds in the composite fibers. Evaluation of the antimicrobial activity of the composite membranes against *E. coli* showed that there was significant inactivation of the bacteria, with their levels being at least halved.

Electrospun nanofibers containing silver nanoparticles have also been made from 70/30 wt% chitosan/poly(vinyl alcohol) to give composites. The silver component had a size of 58-73 nm and after crosslinking with glutaraldehyde, the size increased to 95-109 nm [63]. The fiber diameter was 59 nm, increasing to 96 nm after crosslinking. Silver leaching tests showed that for fibers made with 4 wt% silver nitrate, there was a release of almost 0.8 mg/L after 24 h, or 15% of the total silver content. About 2 log removals of *E. coli* were obtained in antibacterial experiments.

Films have been produced by solution casting using chitosan as both a stabilizing and reducing agent for the *in situ* synthesis of embedded silver nanoparticles [64]. Smaller silver nanoparticle sizes and a better dispersion were obtained using medium molecular weight chitosan, which gave films that were able to completely eradicate antibiotic resistant *S. Aureus* after short contact times. The films showed a strong attachment of the silver nanoparticles contained within their structure, even under sonication, which avoided their uncontrolled release. The best results were obtained with chitosan of a high degree of deacetylation, which gave a fast reduction of Ag⁺ to Ag⁰, leading to smaller nanoparticles. This observation is in agreement with earlier work [65], which compared the antimicrobial action of chitosan and chitosan-silver films. They suggested that the high bactericidal activity of silver nanoparticles could not be explained exclusively by the release of Ag⁺ ions, indicating that direct contact was involved between the bacteria and the membrane. The exudates from those films showed a reduced biocidal action. Other workers [66] have concluded that Ag⁺ release could not be solely responsible for the strong bactericidal action of silver nanoparticles on silver-resistant *E. coli* strains, and have attributed the effect to chemisorbed silver ions on the surface of the particles.

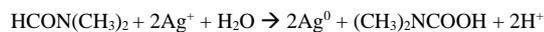
As a response to the threat of direct exposure of silver nanoparticles towards mammalian cells, and prompted by mussel chemistry to incorporate dihydroxybenzene groups [67], two kinds of dopamine-grafted functional biopolymers, chitosan and also heparin, have been used to reduce Ag⁺ ions pre-absorbed onto an oxidised carbon nanotube (CNT) surface. This simultaneously formed protective coating layers [68]. Tests revealed that a

3,4-dihydroxycinnamic acid-grafted chitosan when coated on a nanohybrid exhibited excellent bactericidal activity against both Gram negative and Gram positive bacteria, and was as effective as the bare Ag-CNT hybrid. The chitosan-coated samples were particularly effective because of the synergistic effects of chitosan and silver nanoparticles.

Chitosan, as a hydrophilic polymer, has been used to enhance the hydrophilicity and biocompatibility of polycaprolactone (PCL), frequently employed in biomedical uses because of its biocompatible properties, slow biodegradability, low-cost, non-toxicity and good mechanical properties [69]. PCL has been used as a core in coaxial nanofibers, and silver nanoparticles have been incorporated into the chitosan shell of the fibers. Tested as an antibacterial agent against *E. coli* and *S. aureus*, the inhibition capability was found to be acceptable so that the composite fiber could be used as an antibacterial agent.

Electrospun chitosan/PEO nanofibrous membranes containing silver nanoparticles as an implantable delivery vehicle have similarly been prepared for the dual release of chlorhexidine and silver ions [70]. A long-term antibacterial effect was possible up to 4 days against *S. aureus* using membranes made with 5 wt% AgNO₃.

Silver has been incorporated into cellulose acetate (CA) hollow fiber membranes by using a dry jet-wet spinning technique [71]. The spinning solution was made up of CA and AgNO₃ in dimethylformamide, with the AgNO₃ being reduced to silver nanoparticles in the spinning solution:



The resulting membrane had a sponge-like structure and dense inner and outer surfaces. The polymer matrix entrapped the silver nanoparticles so that leaching of the silver particles was substantially hindered. The membrane showed antibacterial activity against *E. coli* and *S. aureus* when the silver content was at least 100 mg/L. However, during use the silver content became depleted within 5 days and the membrane did not then show antibacterial activity, so that the silver had to be periodically replenished. To exhibit antibacterial activity in the long term, it was established that the AgNO₃ in the spinning dope should be 0.01-0.1 wt%.

Cellulose nanofibers have been coated with silver particles with an average diameter of 1.5 nm [72]. The composite material had strong antibacterial properties when tested against *E. coli* and *S. aureus*, with greater than a 99% reduction. The composites were postulated to be useful in preparing artificial skin.

Cellulose filters have been grafted with silver nanoparticles and silver nanowires by covalent attachment on thiol and amine modified commercial products [73]. They had an antibacterial activity of at least 99.9% growth inhibition versus *E. coli*, and showed no uncontrolled release of silver into the product water.

Also of interest is a recent report on the light-induced reduction of silver ions to silver nanoparticles in aquatic environments brought about by microbial extracellular polymers, or EPS [74]. The EPS molecules are postulated to be excited by UV light to produce strong reducing species, which enhance the reduction of Ag⁺.

A summary of the data obtained is shown in Table 5. The antibacterial effects are quite positive in all examples, with silver release is usually seen as essential for this behaviour. There is speculation as to whether this is an effect of free silver ions or adsorbed species.

Table 5
Effects of various treatments when Ag nanoparticles are inserted into polysaccharide membranes.

Reagent	Antibacterial activity, fouling	Ag ⁺ leaching, flux change	Reference
Chitosan Ag ⁰ and Ag ⁺ forms prepared	<i>E. coli</i> could not grow on either	Ag ⁰ form performed better on use	[61]
Chitosan/PEO with Ag ⁺ electrospun for fibres	<i>E. coli</i> levels at least halved	Ag-O bonding indicated, so more stable	[62]
Chitosan/PVA with Ag ⁺ electrospun for fibres	2 log removals of <i>E. coli</i>	15% loss of silver by leaching	[63]
High degree of chitosan deacetylation	Can completely eradicate <i>S. aureus</i>	Ag ⁺ release not solely responsible	[64]
Ag ⁺ pre-adsorbed on CNTs on chitosan	Excellent antibacterial effect	Synergism of Ag ⁰ and chitosan	[68]
Ag ⁰ inserted in chitosan layer on PCL nanofibre	Acceptable inhibition of bacteria	Ag ⁺ release responsible	[69]
Ag ⁰ deposited in hollow fibre CA	Good versus <i>E. coli</i> and <i>S. aureus</i>	Need certain Ag ⁺ level for long term	[71]
Ag ⁰ on cellulose nanofibers	Good versus <i>E. coli</i> and <i>S. aureus</i>	Useful in preparing artificial skin	[72]
Ag ⁰ grafted onto thiol, amine modified cellulose	99.9% inhibition of <i>E. coli</i>	No uncontrolled release of silver	[73]

2.6. Inorganic membranes

Photocatalytic membranes containing silver nanoparticles incorporated in a TiO₂ matrix have been made using Pluronic P-123, a poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) copolymer [75]. Six different hierarchical architectures were obtained by multilayer coating of different Ag-TiO₂ sols. The porous structure of the resulting layers could be fine-tuned by altering the amounts of P-123 and AgNO₃ used during the preparation. The membranes possessed both photocatalytic and antibacterial activity. In a batch reactor operated in the dark, the membranes were able to remove more than 5 log of *E. coli*. In a photocatalytic membrane reactor with the membrane having the highest percentage of silver, the removal was close to 7 logs of *E. coli*. The best performing membrane was able to remove up to 1 g/m²h of Rhodamine B by two mechanisms, combined namely photocatalytic degradation and physical adsorption on the membrane.

Ceramic TiO₂ membranes have been impregnated with metals, including silver, and utilised in seawater desalination by reverse osmosis [76]. Titania is itself antibacterial and has antifouling properties, and these are enhanced by metals such as silver. Tests aimed at confirming this are being done to see if there is inhibition of fouling in RO desalination, using a membrane that contains 0.12 wt% silver. There was a 20% increase in salt rejection when compared with non-impregnated membranes, but fouling studies are yet to be completed.

Silver nanoparticles have been deposited on the surface of cellulose triacetate forward osmosis membranes by a photo-induced growth approach [77]. This was followed by a charge-driven self-assembly of TiO₂ nanoparticles on the silver nanoparticles. It was found that the bacterial growth on the Ag/TiO₂-coated membrane was about 11 times less than that on the parent membrane, at 2.0 mg/L versus 23.5 mg/L. The TiO₂ played an effective role in regenerating the silver nanoparticles by decomposing the organic matter that covered the nanoparticles. After cleaning it was observed that the water flux was recovered by 67-72%, versus only 33% for the parent membrane.

An anodic aluminium oxide UF membrane has been modified by stacking the surface with silver nanoparticles separately stabilized by the oppositely charged polyelectrolytes PEI and sodium polystyrene sulphonate, then sequentially attaching them to the supporting membrane in a layer-by-layer deposition [78]. The performance of the resultant membrane was comparable with that of commercial UF membranes, with an ability to reject dextran of 500 kDa molecular weight. The modified membrane was stable under severe conditions of low pH, organic solvents and sonification, but no mention was made of antibacterial properties.

Silver nanoparticles have been immobilized on porous zirconia capillary membranes to generate a nanocomposite material that is an efficient bactericide for water decontamination [79]. This was achieved by direct reduction of AgNO₃ with sodium borohydride to produce elemental silver on the surface of the capillaries. Silver nanoparticles of a particularly narrow size distribution can be obtained at high ratios of sodium borohydride to metal salt [80]. The filtration of suspensions of *E. coli* gave an 8-log removal of the bacteria, with maximum loading capacities of 3×10⁹ cells/750 mm² of capillary surface, when back flushing was then needed. The bacteria could be retained at up to a maximum load of 6×10⁸ cells/750 mm² of capillary surface, with regeneration efficiencies of 95-100% when there was backwashing for 10% of the run time. The silver release was only 0.8% of the initial silver loading over a three-day filtration experiment, leading to an average silver contaminant level of 100 µg/L.

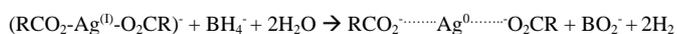
Porous ceramics can be made from refractory oxides such as alumina, Titania and Zirconia [81]. The authors have suggested a new method for fixing silver nanoparticles to the interior walls of porous ceramic channels by using an aminosilane coupling agent in the form of 3-aminopropyltriethoxysilane as a connecting bridge between the silver nanoparticles and silica groups on the ceramic surface. The resultant composite when tested on *E. coli* suspensions showed that none survived when the input water had a bacterial load of ~105 colony-forming units (CFU) per millilitre. There was no apparent loss of nanoparticles after

keeping the treated ceramic for several weeks in an atmospheric environment.

Data for the inorganic membranes are collected in Table 6. The ZrO₂ membrane had the best results, with a lot of other works still being preliminary.

2.7. Silver-graphene oxide hybrids

An antifouling PVDF hollow fiber membrane has been made by blending it with silver-loaded graphene oxide (GO) and carrying out a phase inversion process via a dry-jet, wet-spinning technique [82]. GO has an ultra-thin two-dimensional structure and a variety of functional groups such as epoxide, carbonyl and hydroxyl on its surface [83]. The stability of silver nanoparticles is known to be improved when they are adsorbed onto GO, when no silver release is claimed [84]. GO has been found to increase the surface hydrophilicity and imparted antimicrobial activity to membranes without altering their transport properties [85]. Its presence in the PVDF membrane gave it a resistance to organic fouling, and the silver improved its antibiofouling properties. In tests on an *E. coli* suspension, the permeation flux of the composite membrane was 8.2 times that of the parent PVDF membrane. In addition, the hydrophilicity and mechanical strength were improved. This raises the question of what happens to silver in the composite PVDF membrane when it is reduced to the zero valent state.



The ionic bonding no longer exists, so the silver is presumably locked into the membrane structure by purely physical forces. It is apparently inaccessible to oxidation as there are no free silver ions found in solution.

Regenerated cellulose membranes embedded with silver nanoparticles have been prepared with and without the presence of GO [86]. The parent cellulose membrane and the composite containing only GO had no antibacterial effect, while that with silver inhibited the growth of *S. aureus* and *E. coli*, as detailed in Table 7. It can be seen that the membrane with both silver and GO exhibited much stronger antibacterial activity towards *E. coli*, even though the metal content was a tenth of that in the silver-only composite. This was attributed to the more porous structure of the silver/GO version. The cumulative amount of Ag⁺ ions released after immersion for 4 h in distilled water was about 55 µg/L of Ag⁺ from the GO-free version, but there was no release when Ag/GO was used. This suggests an interaction between the silver nanoparticles and GO, which stops their release. This is contrary to the usually proposed mechanism, where soluble Ag⁺ is held responsible for the antibacterial activity. It would be useful to know the ultimate capacity of the Ag/GO membrane for bacterial absorption. The synergistic effect of GO and silver nanoparticles has been observed before [87, 88]. Another study found that for a 0.10 wt% GO-Ag content, the GO controlled the release of Ag⁺ ions to one twelfth that for the silver only PVDF membrane [89]. This was attributed to the functional groups on the GO providing anchoring sites for the silver.

A GO/PA thin film composite membrane (not containing silver) devised for desalination has been found to have good antibacterial properties [90]. For *E. coli* it had a cell viability of 22%, versus 87% for the parent PA membrane, showing that GO itself has strong antimicrobial activity. Likewise, thin film composite PA membranes have been made from *m*-phenylene diamine and 1,3,5-benzenetricarbonyl chloride by interfacial polymerization on the surface of a PS supporting membrane. GO was embedded in the membrane during membrane formation to see if it would improve the performance [91]. There was an increased resistance to surface fouling and chlorine attack.

Silver-GO oxide hybrids have also been used in biofouling control in forward osmosis membranes [92]. The membranes used were thin film composite membranes based on PA, grafted with silver-GO via reaction between the carboxylic acid groups in the GO and terminal amino groups in the PA membrane. It was found that silver nanoparticles of average size 16 nm were irreversibly bound to the GO. There was an 80% inhibition of *P. aeruginosa* attachment to the membrane.

Table 6
Effects of various treatments when Ag nanoparticles are inserted into inorganic membranes.

Membrane	Antibacterial activity, fouling	Ag ⁺ leaching, flux change	Reference
In photocatalytic TiO ₂ -polyether matrix	5 log <i>E. coli</i> removal, 7 with light	Photocatalytic and adsorption effects	[75]
Ceramic TiO ₂ impregnated with Ag	Salt removal better, need fouling studies	No loss of flux	[76]
TiO ₂ on Ag nanoparticles	Bacterial growth 11 times less than parent membrane	67-72% flux recovery versus 33%	[77]
On ZrO ₂ capillary membrane surface	8 log <i>E. coli</i> removal, with 95-100% regeneration	0.8% loss of initial Ag loading after 3 days	[79]
On ceramic surface via aminosilane bridge	All <i>E. coli</i> removed	No apparent loss of Ag in air	[81]

Table 7
Inhibition and leaching data for cellulose membranes containing silver, GO [86].

Membrane	<i>E. coli</i> inhibition, %	<i>S. aureus</i> inhibition, %	Silver release after 4 h in water, µg/L
Regenerated cellulose	0	0	55
Plus Ag ⁰	62	42	-
Plus GO and Ag ⁰	82	45	0

Table 8
Properties of some silver-graphene oxide hybrid membranes.

Composite membrane	Antibacterial activity, fouling	Ag ⁺ leaching, flux change	Reference
PVDF/GO-Ag ⁰ blend	<i>E. coli</i> resistance 8.2 times better	Improved flux recovery	[82]
Regenerated cellulose/ GO-Ag ⁰ blend	82% inhibition of <i>E. coli</i>	No leaching of silver	[86]
Thin film PA/GO-Ag ⁰ surface graft	80% less <i>P. aeruginosa</i> attachment	Silver irreversibly bound to GO	[92]
GO functionalised with polyamines	97.9% rejection of BSA	Flux 3 times higher	[94]

The membrane modified with silver-free GO showed no decrease in antibacterial activity, in contrast with the result mentioned above for a regenerated cellulose membrane [86]. However, GO alone and various composites, especially hydrophobic versions, have been widely acknowledged as having enhanced antibacterial properties [93].

The carboxylic acid groups on GO have been reacted with three different polyamines, ethylenediamine, diethylenetriamine, and triethylenetetramine. The modified GO was then incorporated into a PS membrane, and the mixed matrix product was tested for antifouling properties using BSA as the foulant [94]. The membranes had higher porosity and permeability, improved structural and mechanical properties, and better antifouling behavior, with a 3-fold higher flux and minimal change in the BSA rejection. Increasing the chain length of the amine gave the highest BSA rejection of 97.9% versus 98.5% for the parent PS membrane.

Results for Ag-GO modified membranes are summarised in Table 8. The lack of release with the Ag-GO combination is worthy of further study, as is the better bacterial resistance when the GO is present as well as silver.

2.8. Miscellaneous

Fibrous membranes with antibacterial activity have been prepared from 10% w/v polyacrylonitrile (PAN) solutions by electrospinning [95]. N,N-dimethylformamide was used as both the solvent and as a reducing agent for silver ions. An enhancement in the reduction process was achieved with UV irradiation, which resulted in the formation of larger silver nanoparticles in areas adjacent to and on the surface of the fibers. Without UV treatment, the size of the nanoparticles was smaller than 5 nm. After 10 min of UV treatment, the size of the particles increased from 5.3 to 7.8 nm with an increase in the initial silver nitrate concentration in the solutions. With or without UV treatment, the diameters of the composite fibers decreased with an increase in the initial silver nitrate concentration. The diameters of the composite fibers that had been subjected to UV irradiation exhibited lower values. Both the cumulative amounts of the released silver and the bactericidal activities of the composites against *S. aureus* and *E. coli* increased with increases in both the initial silver nitrate concentration and the UV irradiation time.

Hybrid fabrics containing nanowires of Ag-tetracyanoquinodimethane (TCNQ) have been made that show extremely high antibacterial behaviour against both Gram negative and Gram-positive bacteria, outperforming Ag itself [96]. The activity could not be explained solely by the presence of leached Ag⁺ ions.

3. Conclusions

As it is observed in the results provided in the tables, there is a need for more quantitative information on antibacterial effects, but the usefulness of silver nanoparticles in overcoming bacterial attack cannot be denied. PES, PS, PVDF- and cellulose-GO, together with inorganic membranes, show the best results. The membranes are more durable when binders such as poly (acrylic acid) are used to assist attachment of Ag⁺ via their carboxylate groups. Chemisorption using thiol or amino links from the membrane to the silver ion

can similarly prolong the life of the antibacterial system. After reduction to elemental Ag⁰ there is entrapment of the metal within the polymer matrix. Long-term prevention of biofouling by the incorporated silver does not seem to have been satisfactorily obtained yet. The life of composite membranes containing silver is now the main issue. Ion exchange sites will bind Ag⁺, but when reduction to Ag⁰ occurs, that mechanism will no longer prevail, with the nanoparticles now being held by physical entrapment and adsorption. Also, the protective role of GO in preventing loss of silver should be further investigated. Ag⁺ release is not a health problem when the membranes are used for the recovery of bio-alcohols from fermentation liquors.

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