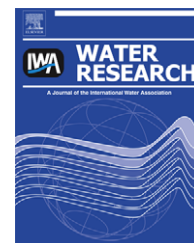


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Application of nanosilver surface modification to RO membrane and spacer for mitigating biofouling in seawater desalination

Hui-Ling Yang, Justin Chun-Te Lin, Chihpin Huang*

Institute of Environmental Engineering, National Chiao Tung University, 1001 University Road, Hsinchu, Taiwan

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ABSTRACT

Biofouling is one of the most critical problems in seawater desalination plants and science has not yet found effective ways to control it. Silver compounds and ions are historically recognized for their effective antimicrobial activity. Nanosilver particles have been applied as a biocide in many aspects of disinfection, including healthcare products and water treatment. This study proposes an innovative biofouling control approach by surface modification of the RO membrane and spacer with nanosilver coating. A chemical reduction method was used for directly coating nanosilver particles on the membrane sheet and spacer. The surface-modified membrane and spacer were tested for their antifouling performance in a cross-flow flat-sheet membrane cell, which is a part of a pilot plant in Wukan desalination plant. The silver-coating membranes and spacers, along with an unmodified membrane sheet, were tested in the membrane cell and compared on the basis of their antifouling performance. Permeate flux decline and salt rejection was continuously monitored through the testing period. Meanwhile regrowth of microbial populations on the membrane cell was quantified by a unique microbial counting every three to four days.

The results showed that both silver-coated membrane (Ag-cM) with uncoated spacer and silver-coated spacer (Ag-cS) with uncoated membrane performed better than the unmodified membrane and spacer (Un-MS), in terms of much slower decrease in permeate flux and TDS rejection. However, the effect of silver-coated spacer on antimicrobial activity was more lasting. In the silver-coated spacer test, there was almost no multiplication of cells detected on the membrane during the whole testing period. Besides, the cells adhering to the membrane seemed to lose their activity quickly. According to the RO performance and microbial growth morphology, the nanosilver coating technology is valuable for use in biofouling control in seawater desalination.

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1. Introduction

Fouling is often regarded as an inevitable hurdle in the membrane process as it is a major problem causing deteriorating membrane performance and yielding subsequent

operation and maintenance costs for cleanings and replacing. Seventy percent of seawater desalination plants suffering biofouling problems in the Middle East area (Gamal Khedr, 2000), while 58 of 70 surveyed reverse osmosis (RO) plants in the US reported the occurrence of fouling problems (Paul, 1991).

* Corresponding author. Tel.: +886 3 5726463; fax: +886 3 5725958.

E-mail addresses: tracy.hl.yang@gmail.com (H.-L. Yang), jlin0623@gmail.com (J.C.-T. Lin), cphuang@mail.nctu.edu.tw (C.P. Huang).
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Biological fouling (biofouling) results from assimilable organics accumulation, biofilm formation and the regrowth of microorganisms on the membrane surface. Among all types of membrane fouling, biofouling is the most complicated one and difficult to eliminate since inorganic fouling and scaling could be more easily predicted by monitoring feed characteristics and prevented by chemical or physical pretreatments.

The critical issue of biofouling occurs because microbes are able to grow with tiny amounts of nutrients (Sommariva et al., 2007). Moreover, biofouling has more significant impacts on decreasing the membrane flux, deteriorating the membrane structure, and increasing salt passage. (Kramer and Tracey, 1995; Schneider et al., 2005). Current studies revealed biofouling can arouse more problems in membrane module, such as biofilm-enhanced osmotic pressure (Herzberg and Elimelech, 2007), feed spacer channel pressure drop (Vrouwenvelder et al., 2008, 2009a) in conjunction with the well-known transmembrane pressure drop. Even operating under a critical flux, it did not eliminate biofouling in spiral-wound RO systems (Vrouwenvelder et al., 2009b). Besides, the release of extracellular polymeric substance (EPS) during microbial growth could enhance the ability of inorganic ions to stay on the membrane surface (Al-Ahmad et al., 2000; Yang et al., 2008). For these reasons, the means to minimize biofouling of membranes are always addressed as high concerns by both engineering and fundamental aspects in RO desalination plants.

Antifouling strategies of RO for seawater desalination are normally carried out either by feed water pretreatment, cleaning-in-place programs or by membrane surface modification (Pontié et al., 2005). Physical pretreatments (such as sand or cartridge filters, dissolved air flotation, microfiltration, or ultrafiltration) and chemical pretreatments (such as introducing chloride, coagulants, flocculants, and antiscalants) are able to control scaling, inorganic, and part of the organic fouling. However, most antifouling efforts by pretreatments are not effective in eliminating biofouling in RO desalination plants. Chemical-free pretreatment by sole ultrafiltration leaves refractory biofoulants remaining in the RO train (Pontié et al., 2005; Xu et al., 2007). Applying biocides such as chlorination was reported effectively to decrease the concentration of microbes prior to cartridge filter (Dudley and Darton, 1996; Kim et al., 2009); however, chlorine disinfection was also shown to enhance biofouling by providing small molecular nutrients for microbial growth in the RO unit (Saeed, 2002; Applegate et al., 1989). Even though bacteria counts were null in the feed water prior to the cartridge filters, it still has a chance for biofouling to raise to a significant level on RO membranes (Dudley and Darton, 1996). Hence, the most immediate method is to control biofouling in situ, i.e. by applying antifouling efforts to membrane directly. Therefore, an innovative approach to eliminate biofouling through surface modification applied to RO membranes and spacers by nanosilver is discussed in this study.

Silver compounds and silver ions have long been known to possess strong inhibitory and bactericidal effects as well as a broad spectrum of antimicrobial activities (Cho et al., 2005; Zhang et al., 2007; Kawashita et al., 2000; Xu et al., 2006). It is generally believed that silver ion reacting with thiol (-SH) groups in microbial cells play an essential role in bacterial

inactivation (Cho et al., 2005). Recently, various inorganic antibacterial materials containing silver have been developed and some of them are in commercial use (Kawashita et al., 2000). A wide variety of products in this respect has already been available on the market (Chen and Schluesener, 2008). In medical applications, silver is used for treatment of wounds, surgical instruments, and bone prostheses (Chen and Schluesener, 2008). In daily life, consumers may have room sprays, laundry detergents, wall paints, water purificants, water disinfectants, and pipelines containing silver (Chen and Schluesener, 2008; Cheng et al., 2004; Zhang and Sun, 2007). Silver nanoparticles are also incorporated into textiles for the manufacture of clothing, underwear and socks (Lee et al., 2007; Vigneshwaran et al., 2007; Chou et al., 2005).

Polymers containing silver nanoparticles are intensively developed for the growing demands of different products (Son et al., 2004; Xu et al., 2006; Li et al., 2007; Liu et al., 2001; Clémenson et al., 2006; Chen, 2003). The majority of membrane materials used for water treatment are polymers, such as cellulose acetate (CA), polyamide (PA), polyacrylonitrile (PAN). The most often adopted method for the manufacture of these polymers is electrospinning technology. However, silver nanoparticles can be synthesized through numerous techniques, such as chemical reductions, gas condensation, laser irradiation, sonochemical deposition and nanostructured templates (Luo et al., 2005; Lo et al., 2007; Chen and Schluesener, 2008). Among them, chemical reduction methods are commonly used to synthesize silver nanoparticles (Jiang et al., 2006). Typical reducing agents include polyols (Sun and Xia, 2002), sodium tetrahydroborate (Sun et al., 2004; Muniz-Miranda and Innocenti, 2004; Muniz-Miranda et al., 2006), hydrazine (Zhang et al., 2007), and formaldehyde (Chen, 2003). In addition to direct coating on membrane surface, silver nanoparticles can be blended in membrane fabrication process (i.e. phase inversion) to improve biofouling resistance and virus removal properties of polysulfone (PSf) ultrafiltration in the laboratory (Zodrow et al., 2009). Apart from silver, titanium dioxide (TiO₂) nanoparticles are also introduced to PA thin-film to synthesize organic-inorganic hybrid RO membranes (by sol-gel process) for the purpose of anti-biofouling (Kwak et al., 2001). In this study, silver nanoparticles was chosen to coat directly on the surface of the RO membrane and spacer via a chemical reduction method. The surface-modified membrane and spacer were tested in a cross-flow membrane cell, and their anti-biofouling effects were performed in actual seawater feed.

2. Materials and methods

2.1. Process of seawater RO at the desalination plant and experimental set-up of pilot plant

In order to obtain constant seawater feed, a pilot plant was set-up in the Wukan desalination plant at Penghu, which is one of Taiwan's main off-shore islands. The raw water was taken from the nearby sea and pretreated by cross-media sand filter and 5- μ m cartridge filter. The one-stage RO system comprises eight suits in parallel, wherein seven RO membrane

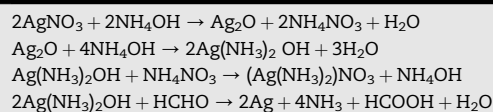
elements fit into a pressure vessel and thirteen pressure vessels comprise one suit. Neither antiscalants nor other common water treatment chemicals (e.g. coagulants and flocculants) were applied prior to the RO system. The RO membranes used in the full-scale plant are polyamide (PA) thin-film composite in spiral-wound modules (SW30HR-380, DOW-FILMTEC, USA). The RO permeate was then disinfected and used to supply the island residents with 7000 CMD potable water.

To simulate the actual process of the full-scale desalination plant, a pilot plant was set-up as shown in Fig. 1. Influent was drawn from cross-media sand filter unit in the full-scale desalination plant and feed water tank storage (T1). The seawater was pumped by P1 to pass through two in-series 5- μm cartridge filters (CF1 and CF2, 10 inches long each) and flow into a buffer tank (T2). Then, RO feed was constantly pumped into one commercial flat-sheet membrane filtration unit (Sepa™ CF II cross-flow test cell, GE Osmonics, USA) by a high-pressure pump (P2), where feed flowrates were set at 2 $\text{L}\cdot\text{min}^{-1}$. The system was operated at a constant pressure mode by a pressure release valve (V3), which was fixed at 800 psi (55.2 bar) throughout all the tests. Permeate was continuously collected in a tank (T3) and instant flowrate recorded by an electrical scale (S). Feed pressure (P) and concentrate flowrate (F) transmitters were monitored by a computer. The total dissolved solids (TDS) of the feed and permeate were measured four times a day by a portable water quality instrument (Ultrameter II™, MYRON L Co., USA).

2.2. Surface modification of RO membrane and spacer

For considering a feasible approach to mitigate membrane biofouling on site (Wukan desalination plant), a simple nanosilver-coating method (Chen, 2003) was applied to the RO membranes as a surface modification approach in this study. Silver nitrate (AgNO_3), ammonia water (NH_4OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), and formaldehyde (CH_2O) were starting materials to prepare the silver particles on the membrane surface (Mallory and Hajdu, 1990). All of the reactions are listed in Table 1.

Table 1 – The reactions of nanosilver preparer with silver nitrate solution and formaldehyde solution.



The major reactants include silver nitrate solution and the reduction solution. The 0.02 M silver nitrate (Sigma-Aldrich Co., USA) solution was prepared with adding NH_4OH (Merck Chemicals Ltd., USA) 10 vol.% to the solution. Reduction solution, 0.4 M formaldehyde solution (J.T. Baker Inc., USA), was prepared with 95% ethanol (Merck Chemicals Ltd.) by adding distilled water with 1.7% in volume of the solution.

All flat-sheet RO membrane sheets were taken from a spiral-wound membrane module (SW30-2514, FILMTEC-DOW), which is exactly the same membrane used in the full-scale desalination plant. The flat-sheet membrane and spacer were separated and then cut to fit the specific area of cross-flow cell ($14 \times 19 \text{ cm}^2$) for subsequent biofouling simulation tests (microbial incubation with real seawater feed). The membrane sheet was firstly soaked in a container filled up with silver nitrate solution for thirty minutes in order to facilitate silver ions adsorption on the surface. After that, the membrane was taken out and then soaked in another container filled with formaldehyde solution for the reduction reaction. Gently sway the container in a horizontal direction for forty minutes, which is the optimum reaction time based on our preliminary tests from twenty to sixty minutes. Details of the optimum reaction condition can be seen in our Supplemental information. Then the silver-coated membrane (Ag-cM) was taken out and washed with distilled water in order to remove any remaining reagents and non-strong adsorbed particles. The spacer, which was separated from the same spiral-wound module, received the same procedure to coat it with silver (Ag-cS). The coating of silver particles on the membrane and spacer were verified with field emission gun scanning electron microscopy (FESEM, JEOL, JSM-6330F).

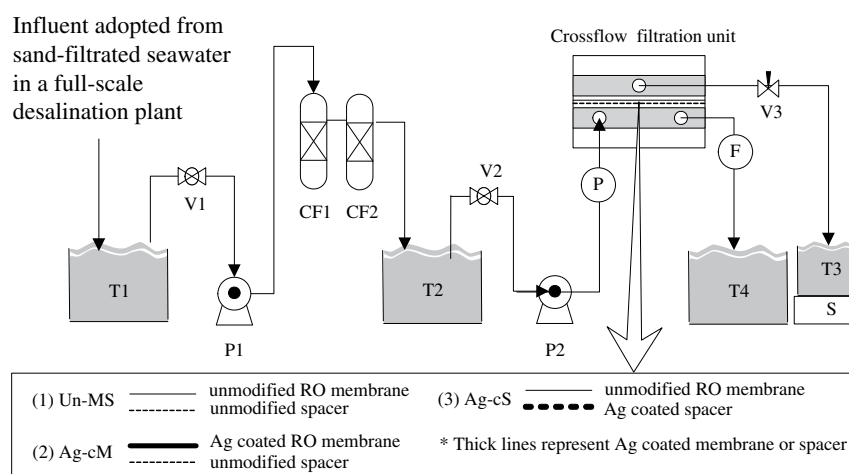


Fig. 1 – Schematics of seawater desalination pilot plant and cross-flow RO membrane cell for biofouling test (T1: feed water tank; T2: RO feed tank; T3: permeate tank; T4: concentrate tank; CF1, CF2: 5 μm cartridge filter; P1: pump; P2: high-pressure pump; P: pressure meter; F: flowrate meter; S: scale; V1, V2: ball valve; V3: Pressure release valve).

2.3. Microbial count for accessing biofouling

For long-term observation of microbial growth and to express their dynamic activity (e.g. microbial adherence and multiplication), a persistent labeling dye, namely PKH-26 (Red Fluorescent Cell Linker Mini kit, Sigma-Alorich) was selected and used to stain microbes which had accumulated on RO membranes. The dye is reported to be able to label a population of cells without affecting their morphology or function (Oh et al., 1999). Meanwhile, this dye can track their behavior, growth and the differentiation of individual cells. It is often used in the fields of medical and life science studies to express various cell types, such as hematopoietic cells, immune cells, blood, neurons, and cartilage (Holloway et al., 1999; Prendergast et al., 1998; Silverman et al., 2000; Hernit-Grant and Macklis, 1996; Dell'Accio et al., 2003). It has also been applied in research concerning microbes such as bacteria and parasites (Raybourne and Bunning, 1994; Shahabuddin et al., 1998; Kierbel et al., 2007).

A unique microbial counting protocol developed in our laboratory is detailed in Fig. 2. Two days after the test run started, the membrane was removed and stained with the PKH-26 labeling dye. In order to minimize site-specific difference of microbial counting on the membrane surface, the membrane sheet was spread out and divided into 3×3 arrays (nine zones). In each zone, nine different sites were selected to count based on the same geometry. So there are total eighty one sites on the membrane surface presenting general microbial fouling on the membrane. As a result, each 'Count' in the subsequent various stages was actually an average of the total 81 microbial numbers counted under a microscope. The first cell amount obtained after the second day was named as *Count A*. The inspected membrane was then put back into the cross-flow cell to continue the biofouling experiment. After three to four days, the membrane was removed for a microbial count again. The cell amount obtained at this stage was named as *Count B*. Then, the membrane was stained and analyzed to get the new cell amount, namely *Count C*. After

each microbial staining and counting, the membrane was put back to the cell. This procedure continued till the end of the whole test run. The multiplied cells were defined by subtracting the *Count A* from *Count B* (i.e. multiplied cells = $B - A$) and the newly adhered cells from the feed water was defined by subtracting *Count B* from *Count C* (i.e. adhered cells = $C - B$) as shown in note of Fig. 2.

3. Results and discussion

3.1. Performance of surface-modified RO membrane and spacer

The flat-sheet RO membrane specimen taken from the spiral-wound membrane module (SW30-2514) was separated into a membrane sheet and a spacer sheet, and both of them were surface modified with silver coating, named Ag-cM and Ag-cS respectively. Morphology of the silver-coated RO membrane (Ag-cM) was presented by FESEM as shown in Fig. 3(a). Most of the silver particles formed on the membrane surface by the chemical reducing reaction were round shaped and with a diameter of about 100 nm, while a few larger silver particles can be observed. The spacer taken out from the same spiral-wound module was also surface modified by the same procedure as that of the RO membrane. This silver-coated spacer (Ag-cS) was also examined by FESEM as shown in Fig. 3(b). The image proved silver particles were also successfully precipitated on the surface of the RO membrane spacer, where the sizes of the major formed silver particles were smaller than 100 nm. Both SEM pictures in Fig. 3 were taken at 30,000 times magnitude.

As shown in Fig. 1, the silver-coated membrane (Ag-cM) was put with a brand new spacer into the cross-flow cell to perform the biofouling simulation experiment. After finishing the first experiment, the silver-coated spacer (Ag-cS) also was put with a brand new membrane into the cross-flow cell to perform the same biofouling test. An unmodified membrane

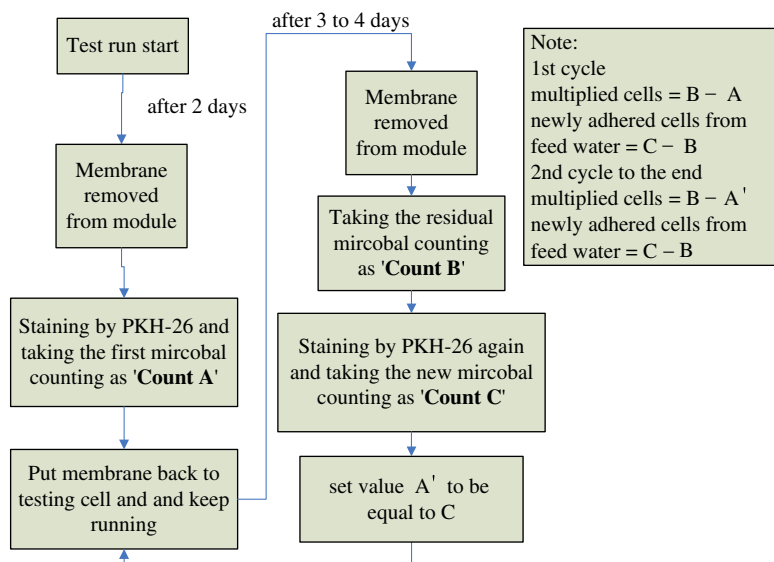


Fig. 2 – Microbial count protocol for identifying multiplied and adhered cells.

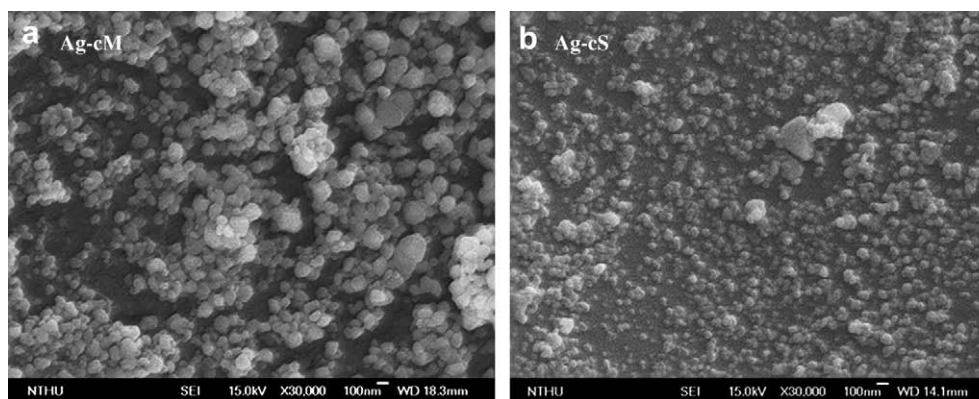


Fig. 3 – FESEM photographs of silver modified (a) RO membrane (b) spacer.

specimen containing both membrane and spacer (Un-MS) served as a blank experiment. The three experiments were all continuously fed by the same pretreated seawater. And the experimental conditions (e.g. feed flowrate and pressure) in the pilot plant were controlled as close to the actual operation parameters of the full-scale desalination plant as possible. Variations of permeate flux and their trends in the three experiments were shown in Fig. 4. Fig. 4(a) represents the permeate flux of the blank experiment, i.e. original unmodified membrane and spacer (Un-MS). The permeate flux dropped quickly from 1.3 to 0.15–0.2 $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ which was one-ninth to one-seventh of the initial permeate flux of the clean RO membrane. This blank experiment demonstrates a serious decline in the flux of uncoating RO membranes even though the seawater was pretreated by cross-media sand filter and double steps of 5- μm cartridge filters.

Fig. 4(b) shows the permeate flux recordings in the experiment of silver-coated RO membrane (Ag-cM) with one uncoated spacer. The initial permeate flux of the test was 0.8 $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ and was much lower than that in the Un-MS test (1.3 $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{day}^{-1}$). The lower initial permeate flux could have resulted from the increased permeate resistance on the coated silver particles on the RO membrane surface. The permeate flux fluctuated around 0.8 $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{day}^{-1}$ for the first seven days, and began to decrease slowly to the seventeenth day. This result shows the Ag-cM could prolong the performance of the RO flux parabolic decline in comparing with the uncoating membrane (Un-MS). The decrease of permeate flux was consistent with the initial low microbial growth count that appeared in the initial seven incubation days (Fig. 6(b)). Silver nanoparticles produce bactericidal effects by releasing silver ions that reacting with thiol (-SH) groups in microbial cells and make them inactive. The loss of the antibacteria effect could be induced by foulants which have accumulated on the silver-coated membrane (Ag-cM) and caused the silver ions to release difficultly. In order to improve this limitation, an alternative approach was developed in this study. This alternative approach is to coat silver nanoparticles on the spacer instead of the membrane itself. In the Fig. 4(c), a fluctuation of permeate flux presents in the experiments of silver-coated spacer (Ag-cS). It can be observed that the permeate flux in the Ag-cS test was generally higher

than that in the Ag-cM test. The permeate flux remained at the same level as initially recorded and showed the minimum decrease among the three tests. Besides, the permeate decline did not occur until the thirteenth day of the experiment. These results implied a modified spacer can also contribute to the improvement of the RO performance to extend the required clean interval.

Variations of TDS rejections with respect to time in the three biofouling tests were plotted in Fig. 5. Rejection of the unmodified membrane and spacer (Un-MS) performed high levels of fluctuation among the three tests. In the beginning four days, the TDS rejection of Un-MS was remained at 95%. It declined quickly in the next two days, and then fluctuated dramatically (from 83% to 30%) until the end of the test. On the contrary, TDS rejection in the Ag-cM test remained almost constant at 95% throughout the seventeenth-days testing period. In the Ag-cS test, the TDS rejection curve shows less fluctuation than the Un-MS test and most of the values varied gently between 97% and 80% in the twenty-days testing period.

According to the results shown in Fig. 4 and Fig. 5, both silver-coated membrane (Ag-cM) and spacer (Ag-cS) performed antifouling properties in the continuous seawater feed tests. The nanosilver surface modification approach demonstrated it is able to eliminate permeate flux decay rate and mitigate TDS rejection rate.

Spacers are normally regarded as providing mechanical support for the membranes in spiral wound modules, but they also act as vortex promoters in the feed channels (Li et al., 2002). They provide the benefit of reducing concentration polarization phenomena on the membrane surface and minimizing membrane fouling (Geraldes et al., 2003; Koutsou et al., 2007). The vortex phenomenon near the surface of the spacer could decrease the adherence of foulants, hence the release of silver ions is less affected. As a result, the anti-fouling ability is able to extend longer.

3.2. Variation of microbial population

Biofouling, or more specifically ‘microbial regrowth on the membrane matrix’, was expressed as the variations of total accumulated, adhered, and multiplied cells. The three cell

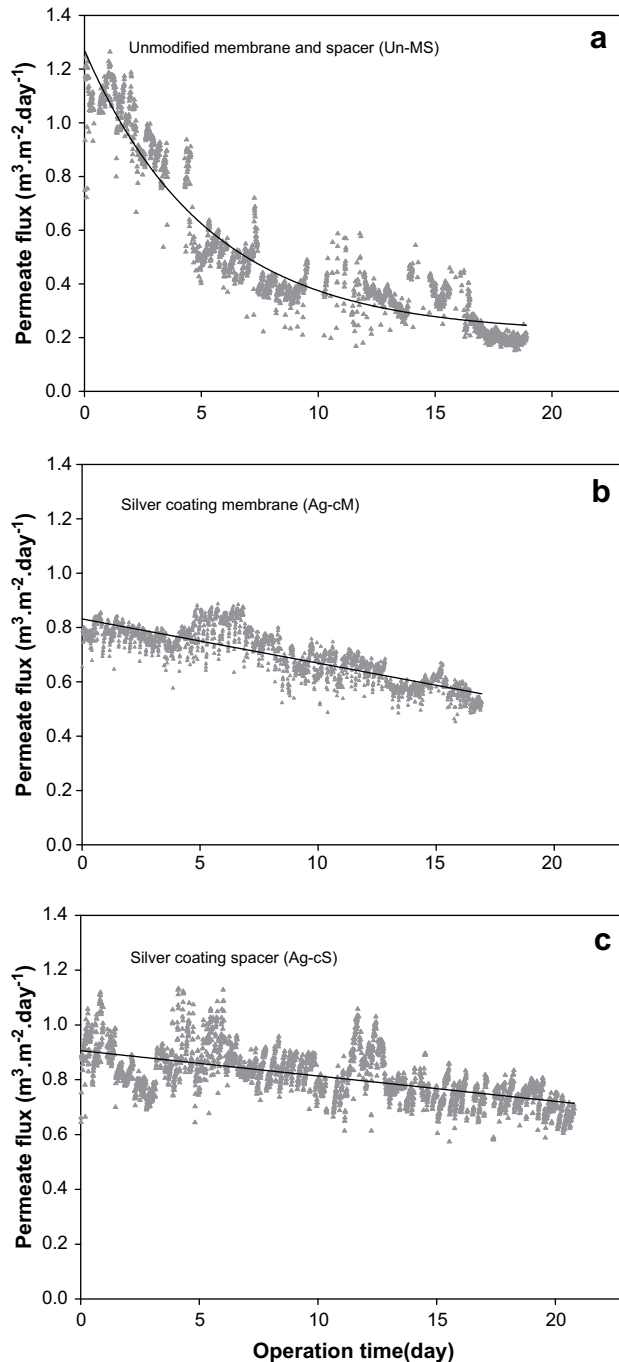


Fig. 4 – Variations of permeate flux in the three biofouling tests.

counts were carried out in the following three tests Un-MS, Ag-cM and Ag-cS as shown in Fig. 6(a), 6(b) and 6(c). The maximum counts of the total accumulated cells in the three tests appeared on the twelfth, fourteenth and tenth day respectively, where the peaks were 2.1×10^5 , 1.3×10^5 and 1.5×10^5 cells·cm⁻². The peak of total accumulated cell counts in the silver modified test came out slightly slower and was smaller than that in the unmodified test. This result indicates the silver-coated membranes not only prolongs the incidence of biofouling, but also minimizes the degree of biofouling. As

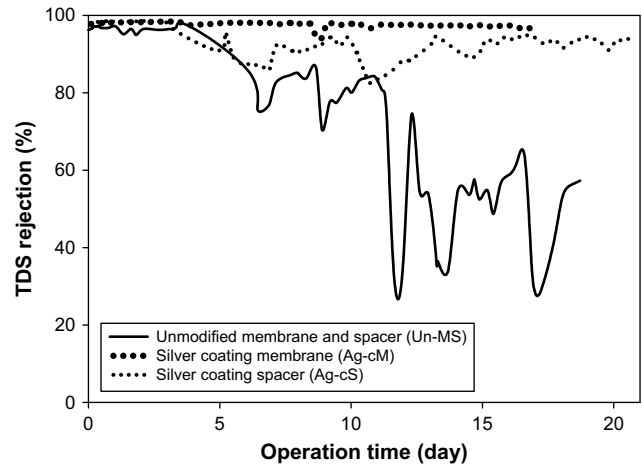


Fig. 5 – Variations of TDS rejection in the three biofouling tests.

shown in Fig. 6(a), the, microbial population variations on the unmodified membranes and spacers (Un-MS), an exponential growth in the 5th to 10th day can be observed, and then the growth curve reached a stationary phase after ten days of operation. This phenomenon proves that the microbes on the membrane grew without limitation. Besides the bar diagram, the variation of microbial population was clearly decided by microbial multiplication. However, once the membrane surface was modified by nanosilver particles, the results were very different, shown in Fig. 6(b). In the initial seven days, the microbial population remained at a very low level of about 2×10^4 cells·cm⁻². Furthermore, the microbial multiplication was non-detected. The antibacterial effect of silver-coated objective is clearly presented here. However, after the seventh day, microbial multiplication occurred and the population increased quickly. The antibacterial effect of coated silver nanoparticles on the RO membrane surface became less active. This could be due to the cover of foulant and its resistance on the release of silver ions. These results are also consistent with the flux decay in the biofouling simulation test of Ag-cM and could be resulted from abundant microbial multiplication.

Fig. 6(c) shows the result of the silver modified spacer test. Although the maximum total accumulated cells on the membrane was around equal to that in silver modified membrane test, the anti-bacteria effect was different. The bars revealed there were almost no multiplied cells detected until the end of the test. The disadvantage of resistance of silver ion release in silver modified membrane test was improved. The continuing released silver ions have controlled the microbial multiplication which will release EPS that is a major factor causing performance decay.

3.3. Morphology of microbial population

Morphology of microbial population distributions of the three testes were presented by gradient maps as shown in Fig. 7. The gradient maps were converted from the original pictures taken during the tests by a commercial software (SigmaPlot),

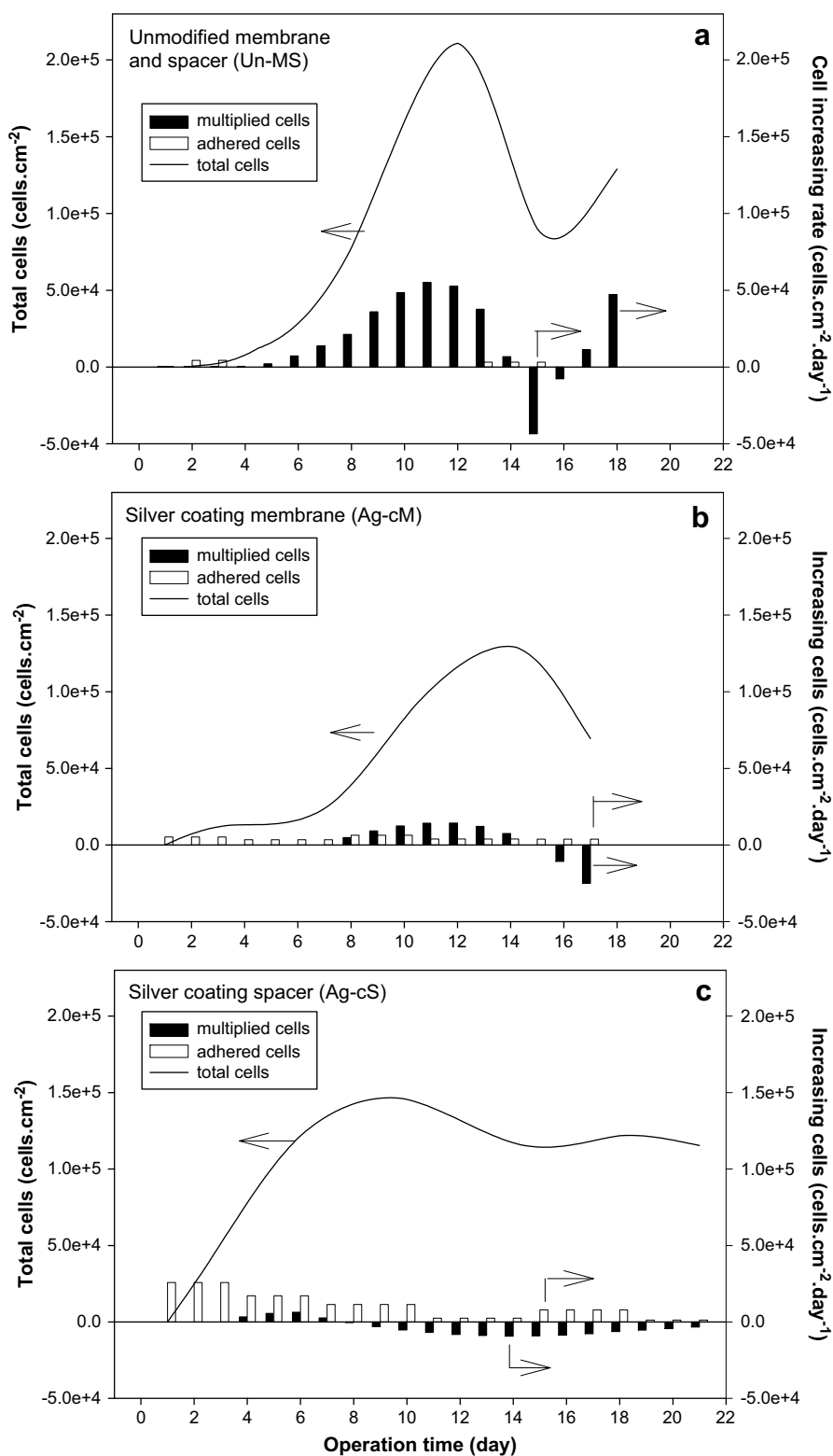


Fig. 6 – Growth curve of microbes in the three biofouling test.

and the intensity of the grey scale corresponds to the total microbe amount as shown in the right table of Fig. 7. In the blank test using an unmodified membrane and spacer (Un-MS), a comparison of the microbial population concentration from Day 4.5 to Day 15 in Fig. 7(a), clearly shows the difference

at the same sites (marked by arrow labels). The microbial concentration was 1.6×10^5 cell·cm⁻² on the 4.5th day. And then the microbial concentration increased and reached the highest amount of 2.5×10^5 cell·cm⁻² on the eighth day. After that it decreased to 1.15×10^5 cell·cm⁻² on the twelfth day,

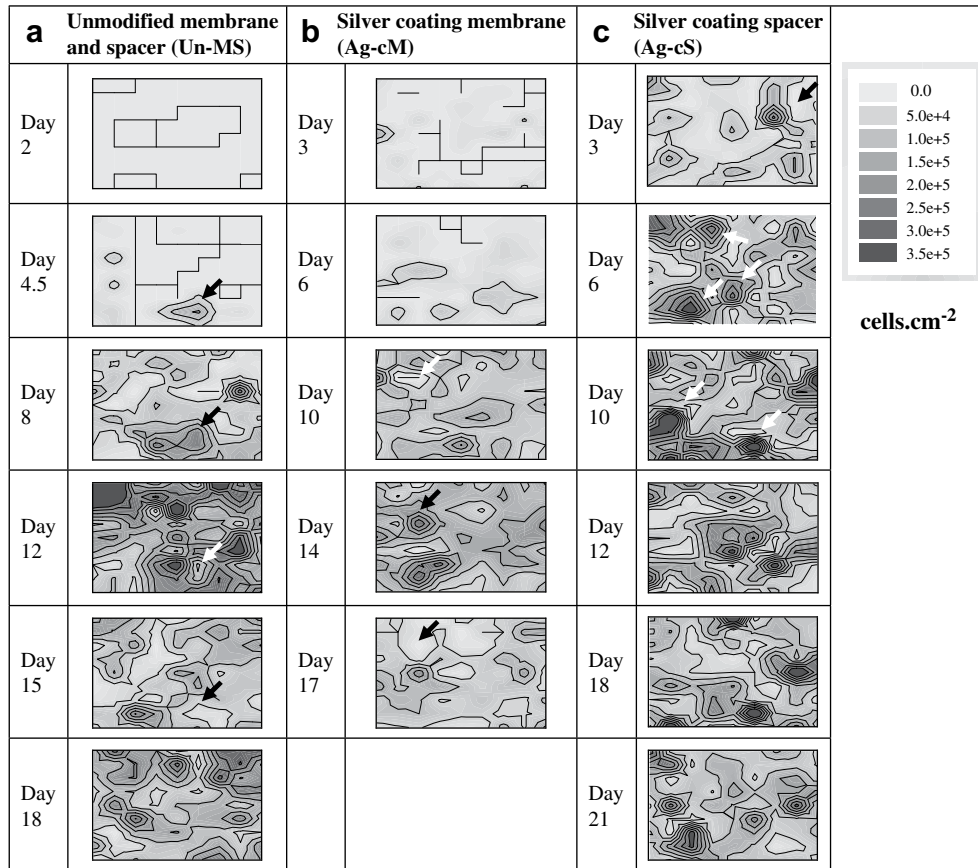


Fig. 7 – Microbes amount variation distributed on the membranes with operation time.

and 0.2×10^5 cell·cm⁻² on the fifteenth day. The microbial population grew and declined without limitations.

Similar developing trends of microbial population dynamics in the Ag-cM experiments are shown in Fig. 7(b). As the marked site shows, the microbial concentration increased to 0.6×10^5 cell·cm⁻² on the tenth day, reached the highest amount at 3.5×10^5 cell·cm⁻² on the fourteenth day, and then decreased to 0.3×10^5 cell·cm⁻² on the seventeenth day. The growth and decline of microbial population was observed, but the population growth occurred later than that in Un-MS experiment. The maximum amount of microbes in Un-MS test on the 4.5th day was 16×10^4 cell·cm⁻² and just 9×10^4 cell·cm⁻² in Ag-cM test on the 6th day. The slower development of microbial population revealed the influence of silver ion on microbes, although the antibacterial effect just remained for seven days.

Different from the Un-MS and Ag-cM tests, the microbial growth patterns of Ag-cS shown in Fig. 7(c) exhibited signs that abundant amounts were accumulated immediately after the experiment started (shown in Day 3) and microbial distribution changed very frequently in the next few pictures taken on the subsequent days (Day 6, 10, 12, 18, 21). The variation of microbial population distribution looks irregular. Microbial colonies at the site of arrow labels disappeared on the next count day. The silver-coated particles on the membrane surface was certainly affected the growth of microbes.

4. Conclusions

Previous antifouling focus and efforts of surface modifications were mainly addressed on the RO membranes itself, few were carried out on the spacer. The results of this study prove the silver-coated spacer also could mitigate biofouling in seawater desalination and the related surface modification studies should pay more attention to the spacer as well.

This study performed the biofouling experiments under the practical conditions and provided a panorama of biofouling from the overall microbial activity on the membrane and spacer surface. The obtained results would be benefit to practical seawater desalination operation and biofouling prevention because the same seawater feed and operation parameters as the full-scale plant were synchronized in the pilot plant study.

According to the RO performance and microbial growth morphology, the coating of silver nanoparticles is capable of being applied in practical biofouling control operations in a seawater desalination plant. The simple coating approach (i.e. silver redox reactions) used for surface modification of the RO membrane and spacer proved effective to mitigate biofouling in this study. However, further investigations of other silver nanoparticles coating methods to modify the surface of the RO membrane and spacer are recommended in the future study.

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Appendix. Supplementary information

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.watres.2009.06.002.

REFERENCES

- Al-Ahmad, M., Abdul Aleem, F.A., Mutiri, A., Ubaisy, A., 2000. Biofouling in RO membrane systems Part 1: fundamentals and control. *Desalination* 132, 173–179.
- Applegate, L.E., Erkenbrecher Jr., C.W., Winters, H., 1989. New chloramine process to control aftergrowth and biofouling in Permasep B-10 RO surface seawater plants. *Desalination* 74 (5), 1–67.
- Chen, S.H., 2003. Development of chemical methods for production of silver nanoparticles for infrared surface enhancement and their application in surface-enhanced infrared absorption spectroscopy, Ph.D. dissertation, p. 121, Chung Yuan Christian University, Taiwan.
- Chen, X., Schluesener, H.J., 2008. Nanosilver: a nanoparticle in medical application. *Toxicology Letters* 176, 1–12.
- Cheng, D., Yang, J., Zhao, Y., 2004. Antibacterial materials of silver nanoparticles application in medical appliances and appliances for daily use. *Chinese Medical Equipment Journal* 4, 26–32.
- Cho, K.H., Park, J.E., Osaka, T., Park, S.G., 2005. The study of antimicrobial activity and preservative effects of nanosilver ingredient. *Electrochimica Acta* 51, 956–960.
- Chou, W.L., Yu, D.G., Yang, M.C., 2005. The preparation and characterization of silver-loading cellulose acetate hollow fiber membrane for water treatment. *Polymers for Advanced Technologies* 16, 600–607.
- Clémenson, S., Alcouffe, P., David, L., Espuche, E., 2006. Structure and morphology of membranes prepared from polyvinyl alcohol and silver nitrate: influence of the annealing treatment and of the film thickness. *Desalination* 200, 437–439.
- Dell'Accio, F., Vanlauwe, J., Bellemans, J., Neys, J., De Bari, C., Luyten, F.P., 2003. Expanded phenotypically stable chondrocytes persist in the repair tissue and contribute to cartilage matrix formation and structural integration in a goat model of autologous chondrocyte implantation. *Journal of Orthopaedic Research* 21, 123–131.
- Dudley, L.Y., Darton, E.G., 1996. Membrane autopsy a case study. *Desalination* 105, 135–141.
- Gamal Khedr, M., 2000. Membrane fouling problems in reverse osmosis desalination applications. *Desalination & Water Reuse* 10 (3), 8–17.
- Geraldes, V., Semiao, V., Pinho, M.N., 2003. Hydrodynamics and concentration polarization in NF/RO spiralwound modules with ladder-type spacers. *Desalination* 157, 395–402.
- Hernit-Grant, C.S., Macklis, J.D., 1996. Embryonic neurons transplanted to regions of targeted photolytic cell death in adult mouse somatosensory cortex re-form specific callosal projections. *Experimental Neurology* 139, 131–142.
- Herzberg, M., Elimelech, M., 2007. Biofouling of reverse osmosis membranes: role of biofilm-enhanced osmotic pressure. *Journal of Membrane Science* 295, 11–20.
- Holloway, W., Martinez, A.R., Oh, D.J., Francis, K., Ramakrishna, R., Palsson, B.O., 1999. Key adhesion molecules are present on long podia extended by hematopoietic cells. *Cytometry* 37, 171–177.
- Jiang, H., Moon, K., Zhang, Z., Pothukuchi, S., Wong, C.P., 2006. Variable frequency microwave synthesis of silver nanoparticles. *Journal of Nanoparticle Research* 8, 117–124.
- Kawashita, M., Tsuneyama, S., Miyaji, F., Kokubo, T., Kokuka, H., Yamamoto, K., 2000. Antibacterial silver-containing silica glass prepared by sol-gel method. *Biomaterials* 21, 393–398.
- Kierbel, A., Gassama-Diagne, A., Rocha, C., Radoshevich, L., Olson, J., Mostov, K., Engel, J., 2007. *Pseudomonas aeruginosa* exploits a PIP3-dependent pathway to transform apical into basolateral membrane. *The Journal of Cell Biology* 177, 21–27.
- Kim, D., Jung, S., Sohn, J., Kim, H., Lee, S., 2009. Biocide application for controlling biofouling of SWRO membrane – overview. *Desalination* 238, 43–52.
- Koutsou, C.P., Yiantsios, S.G., Karabelas, A.J., 2007. Direct numerical simulation of flow in spacer-filled channels: effect of spacer geometrical characteristics. *Journal of Membrane Science* 291, 53–69.
- Kramer, J.F., Tracey, D.A., 1995. The solution to reverse osmosis biofouling. In: *Proceedings of IDA world congress on desalination and water reuse, Nov, Abu Dhabi, vol. IV.* 3344.
- Kwak, S.Y., Kim, S.H., Kim, S.S., 2001. Hybrid organic/inorganic reverse osmosis (RO) membrane for bactericidal anti-fouling. 1. Preparation and characterization of TiO₂ nanoparticle self-assembled aromatic polyamide thin-film-composite (TFC) membrane. *Environmental Science & Technology* 35, 2388–2394.
- Lee, H.Y., Park, H.K., Lee, Y.M., Kim, K., Park, S.B., 2007. A practical procedure for producing silver nanocoated fabric and its antibacterial evaluation for biomedical applications. *Chemical Communications (Cambridge, United Kingdom)* 28, 2959–2961.
- Li, F., Meindersma, W., de Haan, A.B., Reith, T., 2002. Optimization of commercial net spacers in spiral wound membrane modules. *Journal of Membrane Science* 208, 289–302.
- Li, X., Hao, X., Na, H., 2007. Preparation of nanosilver particles into sulfonated poly(ether ether ketone) (S-PEEK) nanostructures by electrospinning. *Materials Letters* 61, 421–426.
- Liu, H., Ge, X., Ni, Y., Ye, Q., Zhang, Z., 2001. Synthesis and characterization of polyacrylonitrile–silver nanocomposites by γ -irradiation. *Radiation Physics and Chemistry* 61, 89–91.
- Lo, C.H., Tsung, T.T., Lin, H.M., 2007. Preparation of silver nanofluid by the submerged arc nanoparticle synthesis system (SANSS). *Journal of Alloys and Compounds* 434–435, 659–662.
- Luo, C., Zhang, Y., Zeng, X., Zeng, Y., Wang, Y., 2005. The role of poly(ethylene glycol) in the formation of silver nanoparticles. *Journal of Colloid and Interface Science* 288, 444–448.
- Mallory, G.O., Hajdu, J.B. (Eds.), 1990. *Electroless Plating: Fundamentals and Applications.* AESF Society, Florida.
- Muniz-Miranda, M., Innocenti, M., 2004. AFM and micro-Raman investigation on filters coated with silver colloidal nanoparticles. *Applied Surface Science* 226, 125–130.
- Muniz-Miranda, M., Innocenti, M., Foresti, M.L., 2006. Relation between the photoreaction of p-nitrobenzoic acid on to silver-coated filter and the surface roughness, as detected by SERS and AFM. *Surface Science* 600, 2096–2102.
- Oh, D.J., Lee, G.M., Francis, K., Palsson, B.O., 1999. Phototoxicity of the fluorescent membrane dyes PKH2 and PKH26 on the human hematopoietic KG1a progenitor cell Line. *Cytometry* 36, 312–318.

- Paul, D.H., 1991. Reverse osmosis: scaling, fouling and chemical attack. *International Desalination & Water Reuse* 1, 8–11.
- Pontié, M., Rapenne, S., Thekkedath, A., Duchesne, J., Jacquemet, V., Leparç, J., Suty, H., 2005. Tools for membrane autopsies and antifouling strategies in seawater feeds: a review. *Desalination* 181, 75–90.
- Prendergast, R.A., Iliff, C.E., Coskuncan, N.M., Caspi, R.R., Sartani, G., Tarrant, T.K., Luty, G.A., McLeod, D.S., 1998. T cell traffic and the inflammatory response in experimental autoimmune uveoretinitis. *Investigative Ophthalmology & Visual Science* 39, 754–762.
- Raybourne, R.B., Bunning, V.K., 1994. Bacterium-host cell interactions at the cellular level: fluorescent labeling of bacteria and analysis of short-term bacterium-phagocyte interaction by flow cytometry. *Infection and Immunity* 62, 665–672.
- Saeed, M.O., 2002. Effect of dechlorination point location and residual chlorine on biofouling in a seawater reverse osmosis plant. *Desalination* 143, 229–235.
- Schneider, R.P., Ferreira, L.M., Binder, P., Bejarano, E.M., Goes, K.P., Slongo, E., Machado, C.R., Rosa, G.M.Z., 2005. Dynamics of organic carbon and of bacterial populations in a conventional pretreatment train of a reverse osmosis unit experiencing severe biofouling. *Journal of Membrane Science* 266, 18–29.
- Shahabuddin, M., Gayle, M., Zieler, H., Laughinghouse, A., 1998. *Plasmodium gallinaceum*: fluorescent staining of zygotes and ookinetes to study malaria parasites in mosquito. *Experimental Parasitology* 88, 79–84.
- Silverman, A.J., Sutherland, A.K., Wilhelm, M., Silver, R., 2000. Mast cells migrate from blood to brain. *Journal of Neuroscience* 20, 401–408.
- Sommariva, C., Comite, A., Capannelli, G., Bottino, A., 2007. Relationship between biofouling and recovery ratio: the theoretical approach and one experimental case. *Desalination* 204, 175–180.
- Son, W.K., Youk, J.H., Lee, T.S., Park, W.H., 2004. Preparation of antimicrobial ultrafine cellulose acetate fibers with silver nanoparticles. *Macromolecular Rapid Communications* 25, 1632–1637.
- Sun, Y., Xia, Y., 2002. Shape-controlled synthesis of gold and silver nanoparticles. *Science* 298, 2176–2179.
- Sun, Y.P., Atornjitawat, P., Lin, Y., Liu, P., Pathak, P., Bandara, J., Elgin, D., Zhang, M., 2004. Nanoscale cavities in ionomer membrane for the formation of nanoparticles. *Journal of Membrane Science* 245, 211–217.
- Vigneshwaran, N., Kathe, A.A., Varadarajan, P.V., Nachane, R.P., Balasubramanya, R.H.J., 2007. Functional finishing of cotton fabrics using silver nanoparticles. *Journal of Nanoscience and Nanotechnology* 7, 1893–1897.
- Vrouwenvelder, J.S., Manolarakis, S.A., Van Der Hoek, J.P., Van Paassen, J.A.M., Van Der Meer, W.G.J., Van Agtmaal, J.M.C., Prummel, H.D.M., Kruithof, J.C., Van Loosdrecht, M.C.M., 2008. Quantitative biofouling diagnosis in full scale nanofiltration and reverse osmosis installations. *Water Research* 42, 4856–4868.
- Vrouwenvelder, J.S., Graf Von Der Schulenburg, D.A., Kruithof, J.C., Johns, M.L., Van Loosdrecht, M.C.M., 2009a. Biofouling of spiral-wound nanofiltration and reverse osmosis membranes: a feed spacer problem. *Water Research* 43, 583–594.
- Vrouwenvelder, J.S., van Paassen, J.A.M., van Agtmaal, J.M.C., van Loosdrecht, M.C.M., Kruithof, J.C., 2009b. A critical flux to avoid biofouling of spiral wound nanofiltration and reverse osmosis membranes: fact or fiction? *Journal of Membrane Science* 326, 36–44.
- Xu, J., Ruan, G., Chu, X., Yao, Y., Su, B., Gao, C., 2007. A pilot study of UF pretreatment without any chemicals for SWRO desalination in China. *Desalination* 207, 216–226.
- Xu, X., Yang, Q., Wang, Y., Yu, H., Chen, X., Jing, X., 2006. Biodegradable electrospun poly(L-lactide) fibers containing antibacterial silver nanoparticles. *European Polymer Journal* 42, 2081–2087.
- Yang, H.L., Huang, C., Pan, J.R., 2008. Characteristics of RO foulants in a brackish water desalination plant. *Desalination* 220, 353–358.
- Zhang, Y., Sun, J., 2007. A study on the bio-safety for nano-silver as anti-bacterial materials. *Chinese Journal of Medical Instrumentation* 31, 35–38.
- Zhang, W., Qiao, X., Chen, J., 2007. Synthesis of nanosilver colloidal particles in water/oil microemulsion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 299, 22–28.
- Zodrow, K., Brunet, L., Mahendra, S., Li, D., Zhang, A., Li, Q., Alvarez Pedro, J.J., 2009. Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal. *Water Research* 43, 715–723.