Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.996778

57 (2016) 4906–4912
March

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Taylor & Francis Group

Long-term disinfection performance of silver nanoparticles impregnated membranes

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Received 25 October 2014; Accepted 4 December 2014

ABSTRACT

There is a major need for effective and sustainable point-of-use (POU) methods for drinking water treatment especially in remote rural areas. We present a study on the effectiveness and sustainability of POU woven fabric microfiltration (WFMF) membranes impregnated with silver nanoparticles (AgNPs) for water disinfection. The critical aspects investigated include: the period of effective disinfection performance; quantification of silver elution from the membranes with time; and the relationship between silver elution and the disinfection efficacy. The disk diffusion and glass bottle tests confirmed the antimicrobial effectiveness of the coated membranes as distinguished from the uncoated membranes which showed no antimicrobial properties under similar conditions. Synthetic feed water (10,000–85,000 Colony Forming Units/100 mL *Escherichia coli*) was treated for 90 d and no *E. coli* was detected in permeate for 63 d of continuous operation. Silver elution from the membranes was far below the maximum acceptable limit of 0.1 mg/L for drinking water throughout the period of investigation. To the best of our knowledge, this is the first study to investigate the long-term performance of AgNPs-coated WFMF membranes. The cost effective and extremely robust-coated membranes provided clean and safe drinking water for at least two months of continuous operation.

Keywords: Disinfection; *E. coli*; Membranes; Silver nanoparticles; Silver elution

1. Introduction

There is a major need for effective and sustainable point-of-use (POU) methods for drinking water treatment especially in remote rural areas of developing nations. This is due to the fact that implementation of conventional centralized water treatment is expensive and unfeasible in such areas [1]. The main objective of water treatment is the removal of suspended matter and pathogens in order to prevent the occurrence of waterborne diseases and to make water fit for drinking. The presence of pathogens, therefore, necessitates the disinfection of water [2].

In rural areas, disinfection of drinking water is commonly performed by individuals at their households using chemical disinfectants (chlorine and its derivatives); solar disinfection; and filtration media

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such as membranes. However, these POU water treatment technologies are faced with significant drawbacks that limit their application and disinfection effectiveness. For instance, chlorine-based disinfectants form disinfection by-products that are carcinogenic; solar disinfection using bottles only treats small volumes of water, while the use of current commercial membranes is limited by their relatively delicate nature. This has necessitated research into more effective, appropriate and sustainable POU technologies for remote areas.

Modification of existing technologies to attain superior performance is one viable option. For instance, advances in nanotechnology have resulted in nanomaterials with unique physical and chemical properties such as antimicrobial ability and high conductivities, which are significantly different from those of the same material in larger bulk form [3]. The incorporation of nanomaterials with antimicrobial into treatment processes, therefore, has the potential to replace or enhance conventional disinfection methods [4].

Silver nanoparticles (AgNPs) have been previously incorporated in polyurethane foams [5], ceramic filters [6], carbon [7] and fibres [8] for water treatment. They have depicted good disinfection ability using a variety of micro-organisms including bacteria, fungi, protozoa and viruses [9]. However, these studies were mainly focused on showing the disinfection capability of the AgNPs. They were short term in nature and could not provide useful insight into the effectiveness of the technologies over long periods, and hence could not inform decisions on practical application of these systems. Similarly, the use of AgNPs in water filters may cause leaching of AgNPs into the drinking water [10] which if at high concentrations may have adverse health effects on consumers. Although a number the studies identified above have investigated the elution of silver from the filters, this too was done for short periods, which are not representative of practical application of a POU system.

Therefore, a major challenge that has prevented the implementation of numerous POU technologies is the lack of sufficient information regarding long-term application and how the performance is affected over time. This, therefore, necessitates evaluation of such technologies under conditions that reflect practical application. The information obtained from such tests is invaluable in the determination of the robustness of the system and the potential challenges in application. The critical performance aspects for POU AgNPs impregnated membrane-based water disinfection include: the period of effective disinfection performance; quantification of silver elution from the membranes with time; and the relationship between silver elution and the disinfection efficacy.

Since this is the first study on the long-term use of AgNPs-coated woven fabric microfiltration (WFMF) membranes in water disinfection, it is important that these performance aspects be addressed. In our previous study [11], synthesis and extensive characterization of AgNPs WFMF-coated membranes was performed in order to understand their properties such as morphology, hydrophilicity and permeability. In addition, short-term disinfection studies and silver elution tests were conducted. The results from these tests were positive in the sense that the coated membrane properties were better than the uncoated, the disinfection performance was excellent and silver elution was minimal. This, therefore, motivated the study reported here which is aimed at investigating the long-term performance of these membranes simulating practical performance.

2. Materials and methods

2.1. Materials

Nutrient agar was obtained from Prestige Lab Supplies cc in South Africa. The *Escherichia coli* inoculum was sourced from the Microbiology laboratory, department of Biotechnology at Durban University of Technology. Deionized-autoclaved water was used for all dilutions. Uncoated WFMF membranes were supplied by Gelvenor Consolidated Fabrics (Pty) Ltd in South Africa. All materials and apparatus used in the experiments were autoclaved at 121℃ for 30 min to ensure sterility and all tests were conducted under sterile conditions. Deionized water was spiked with specified colony forming units (CFU) of *E. coli* in order to make different concentrations of synthetic feed. Nutrient agar was used as the growth medium for the disk diffusion test. Silver nitrate, sodium borohydride and ethanol were all obtained from Laboratory Supplies Co in Durban, South Africa. The chemicals were of analytical grade and were used as received without further purification.

2.2. Methods

2.2.1. Incorporation of AgNPs on the WFMF membranes

AgNPs were incorporated using a modified chemical reduction method. Uncoated membranes were soaked in 0.05 M $AgNO_3$ solution in order to absorb silver ions, and then rinsed in ethanol to remove excess $AgNO_3$. They were, thereafter, soaked in 0.5 M $NaBH_4$ solution to reduce silver ions to AgNPs. The membranes were thoroughly rinsed using deionized water and dried in an oven at 100˚C for 3 h. The membranes were then used to fabricate A4 size flat sheet filtration modules as described in our previous study [11].

2.2.2. Disk diffusion test

Nutrient agar was poured into six petri dishes and allowed to solidify in a sterile environment. Thereafter, 1 mL of synthetic feed of different *E. coli* concentrations (61,310, 50,000 and 40,000 CFU/100 mL) was streaked on the lawn of agar and spread uniformly using sterile cotton swabs. For each feed concentration, two petri dishes were used. Sterile square pieces of the uncoated and coated membranes measuring 8 mm × 8 mm were placed on the lawn of agar. For each of the two petri dishes containing similar *E. coli* concentration, one piece of uncoated and coated membranes was used, respectively. The uncoated membranes were used as controls. The plates were incubated in an upside down position for 24 h at 37˚C. The inhibition ring formed after 24 h served as an indicator of the antibacterial activity and was determined by measuring the diameter of the inhibition zone around the membrane.

2.2.3. Glass bottle test

Synthetic feed water (100 mL, 61,310 CFU *E. coli*) was prepared and placed in sterile glass bottles. Square pieces (8 mm × 8 mm) of the uncoated (three) and coated membranes (three) were sterilized by autoclaving at 121˚C for 30 min and cooled to room temperature. The six membrane pieces were immersed in six glass bottles each containing 100 mL of synthetic feed with intermittent shaking for one hour. The uncoated membranes were used as the controls. The membrane pieces were removed from the feed water and the water tested for the presence of *E. coli* using the Colilert 18 method [12].

2.2.4. Flow test using AgNPs impregnated membranes

This test was conducted in order to investigate the disinfection efficacy of the membranes over time. The experimental rig consisted of a pack of three A4 size-coated membrane modules in a process feed tank (Fig. 1).

Synthetic feed (20 L) was filtered and 100 mL of permeate was collected into a sterile glass bottle within five minutes and analysed for the presence of *E. coli*. The study was conducted for 90 d with a daily introduction of fresh synthetic feed (10,000–85,000 CFU/100 mL) after every 24 h. The removal efficiency *R* (%) was calculated using the equation,

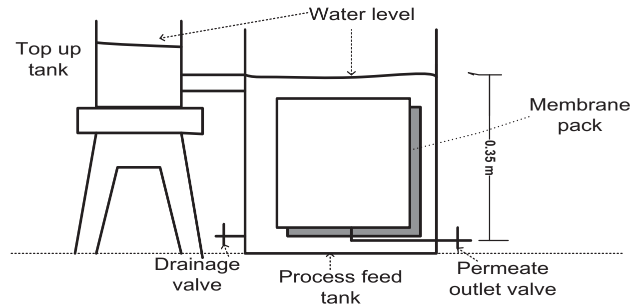

Fig. 1. Laboratory-scale rig for long-term disinfection performance conducted for 90 d. The coated membranes were used to filter synthetic feed (10,000–85,000 CFU/100 mL).

$$R\ (\%) = 100\ (1 - C_p/C_f) \tag{1}$$

where C_f is the *E. coli* concentration in the feed and C_p is the concentration in permeate.

Disinfection efficacy was also expressed in terms of log removal values (LRV) [13].

$$\mathrm{LRV} = \log10\ (C_f/C_p) \tag{2}$$

2.2.5. Analysis of silver elution with time

The stability of silver on the filters was investigated by filtration of deionized water, monitoring and quantification of silver leaching. This experiment was done using a set-up similar to the one shown in Fig. 1 using a flat sheet AgNPs-coated module. Deionized water was fed to the tank at a height of 0.35 m. Permeate was collected every 24 h and tested for the presence of silver using ICP-AES over a period of 90 d.

2.2.6. Effect of silver elution on the disinfection efficacy

Samples of permeate from the filters from the long-term disinfection performance rig (Fig. 1) were collected randomly and investigated for silver using ICP-AES. These results of silver leaching were compared with the disinfection results obtained from the Colilert 18 test method in order to evaluate the relationship between the degree of disinfection and the silver elution.

3. Results and discussion

3.1. Disk diffusion test

The results of the disk diffusion test are shown in Table 1.

The differences in the sizes of the zones of inhibition were due to different *E. coli* concentrations used. The lowest *E. coli* concentration resulted in the largest zone of inhibition (7 mm), while the highest *E. coli* concentration resulted in the smallest zone of inhibition (3 mm). The clear inhibition zone around the coated membranes was an indication of the antimicrobial effect [14]. Thus, the antimicrobial activity was only as a result of AgNPs impregnated in WFMF membrane and not due to membrane itself. This was in agreement with other previous studies, for instance, Maneerung et al. [15] obtained a zone of inhibition for *E. coli* of 2 mm, using 15 mm diameter cellulose impregnated with AgNPs. However, they did not indicate the concentration of *E. coli* used. Mollahosseini et al. [14] also noted a zone of inhibition using polysulfone ultrafiltration membranes coated with AgNPs; however, they did not quantify the zone. The zone of inhibition shows the migratory effect of the disinfectant to the surrounding medium [16] and the antimicrobial effect is determined by comparison of the size of the zone of inhibition around the silver-coated samples [17]. Silver ions released from the AgNPs diffused into the media which imparted antimicrobial activity under humid environment [18,19].

3.2. Glass bottle test

The control (uncoated membrane) did not display any disinfection ability when left in contact with synthetic feed. This was expected because the disinfection ability of uncoated membranes is as a result of size exclusion of bacteria during filtration. The coated membranes achieved complete disinfection (no *E. coli* was detected in permeate) when left in contact with synthetic feed for one hour. This was as a result of the migration of Ag^+ ions from the membranes due to the aqueous media and their deactivation of the *E. coli* [20]. This mechanism of antimicrobial effect is used in the medical field, whereby bandages containing AgNPs are used for wound dressing [15,21]. This test further demonstrated the antibacterial effect of the coated membrane.

3.3. Flow test

Disinfection performance of the coated membranes over a period of 90 d of continuous operation is shown in Fig. 2.

We observed that there was no *E. coli* detected in permeate for 63 d for a range of influent feed concentrations (10,000–85,000 CFU/100 mL). This showed that irrespective of the feed concentration, the filters produced water that is microbiologically safe for drinking. Similar findings have been reported by Quang et al. [22], using silica micro beads containing AgNPs; however, their study was done for a short period of time of one week. In the study reported here, we observed that from the 70th day onwards, the removal efficiency dropped below 100%. This was postulated to be as a result of loss of silver from the filters due to elution. The LRVs were between 4 and 5 for the 63 d, which is acceptable in municipal drinking water treatment [13]. The antibacterial mechanism of the coated filter is due to a combined effect of physical removal (filtration by size exclusion), which is attributed to the filtration of matter that cannot pass through the filter due to its large size and inactivation using the AgNPs [11].

3.4. Silver elution test

The results of silver elution from the filters are shown in Fig. 3.

We observed that silver leaching decreased with time (*see dotted trend line*) probably due to decrease in silver concentration on the filters. This could have led

Table 1
Disk diffusion test results for the uncoated and coated membranes for different concentrations of *E. coli*. There were no zones of inhibition observed around the uncoated membranes; however, there were clear zones of inhibition around the coated membranes

E. coli concentration (CFU/100 mL)	Zone of inhibition on uncoated membranes (mm)	Zone of inhibition on AgNPs-coated membranes (mm)
40,000	0	7
50,000	0	5
63,310	0	4

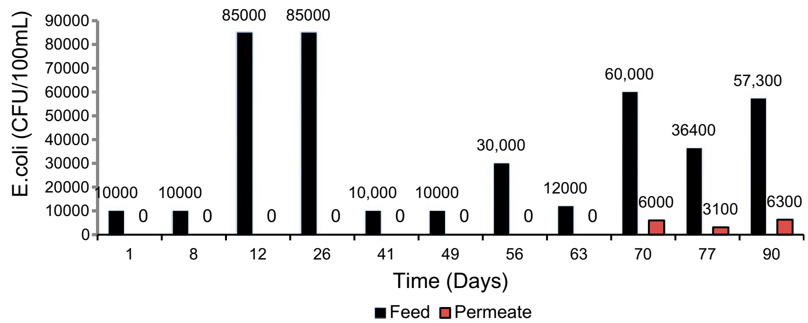

Fig. 2. *E. coli* concentrations in feed and permeate during 90 d of continuous operation. The variation in *E. coli* concentrations in the feed water simulates real application, where the level contamination in raw water varies with time. There was no *E. coli* detected in permeate for 63 d.

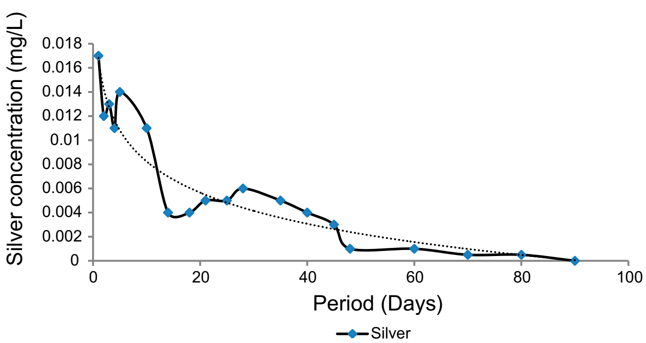

Fig. 3. Concentrations of silver in permeate with time. The silver leaching was far below the WHO guideline limit (0.1 mg/L) for the 90 d period of the study.

to a decrease in the concentration gradient, which is the driving force for the dissolution. The silver elution is mainly due to the weak adhesion forces between the AgNPs and polyester fabric matrix as well as the dissolution of nanosilver in water leading to release of silver ions [22,23]. Silver elution also depends on the concentration of the silver in the substrate [24]. Silver elution was generally far below the World Health Organization (WHO) limit (0.1 mg/L), which is considered not posing health risk to consumers [25].

We suggest that, the coated membranes can be regarded as providing low amounts of disinfectant (silver) in permeate just like the slow release techniques for small-scale water treatment such as chlorine and iodine tablets. This is a significant advantage especially, because the lack of residual disinfection to guard against water re-contamination before consumption is regarded a major limitation in the use of disinfectants such as solar disinfection, UV radiation and Ozone. However, leaching of silver from the membranes causes the performance of the membranes to drop over time [10], because it reduces the amount of nanosilver on the filter and the disinfection performance of the filter. The average amount of silver on the coated membrane module was determined by acid digestion to be 0.0117 wt.% corresponding to a silver content of 0.0139 mg cm^{-2}. However, after 90 d of continuous filtration, there was no silver detected in permeate.

3.5. Effect of silver elution on the disinfection efficacy

The filters produced permeate with no *E. coli* detected for 63 d (Fig. 2). This correlated well with the silver loss from the membranes which was almost 0 mg/L after 60 d of continuous operation (Fig. 3). This was in agreement with Yu et al. [26] who observed significant reduction of silver loading after flushing poly acrylonitrile-based hollow fibre with water for 60 d; however, it still showed antibacterial activity against *E. coli*. They attributed the antibacterial activity of the hollow fibre to the silver ion released from the fibre.

Overall, this study succeeded in evaluating the long-term disinfection performance of the filters, the silver elution behaviour and its effect on the disinfection performance. These are core aspects of any AgNPs-based system intended for use as a POU system in drinking water disinfection. The information obtained is useful in design and practical implementation of the filters especially in the intended remote rural areas. The WFMF membrane employed here is very robust and can be easily cleaned and used, it is also cheaper compared with commercial membranes and locally available in South Africa [11]. The filters were operated for a period of 90 d with continuous filtration (24 h daily), which translates to 2,160 h of operation; out of these, no *E. coli* was detected in the treated water for 63 d (1,512 h). Therefore, practically, the filters can actually be used for a longer period of time considering the fact that under normal usage, they may not be left running the whole day except only when the household require water for drinking and cooking. For instance, if used for 4 h per day, then the household can typically use it for a period of one year before it is exhausted (1,512 h divided by 4 h per day translates to 378 d of use). Thus, the daily period of use will greatly determine the lifespan of the filters.

4. Conclusions

Critical long-term water disinfection performance aspects of AgNPs-coated membranes have been presented for the first time in this study. The coated membranes demonstrated excellent disinfection performance and produced clean and safe drinking water for at least two months of continuous operation. This can have a significant impact in provision of drinking water to people in remote rural areas who lack access to centralized water treatment. The membranes can also be useful during emergency situations when water distribution systems may be damaged due to floods or other natural disasters. The mechanism of disinfection of the coated membranes is due to a synergistic operation involving size exclusion of material larger than the membrane fibre spacing and by deactivation using the AgNPs. Furthermore, silver elution to permeate was far below 0.1 mg/L throughout the period of study which satisfies the drinking water standards. The study suggested that the presence of silver in permeate, although at low levels, may also provide residual disinfection against re-contamination of the water during storage. The coated membranes demonstrated tremendous potential for use in drinking water disinfection and the information obtained from this study is important for planning the implementation of this technology in communities of remote rural areas.

Acknowledgements

The authors would like to acknowledge Durban University of Technology for sponsoring this work. Sincere gratitude to Jimmy Chetty from the Department of Chemistry for the ICP-AES tests and the Institute of Water and Waste Water Treatment for the *E. coli* testing facilities.

References

[1] M. Peter-Varbanets, C. Zurbrugg, C. Swartz, W. Pronk, Decentralized systems for potable water and the potential of membrane technology, Water Res. 43 (2009) 245–265.
[2] B. Tansel, New technologies for water and wastewater treatment: A survey of recent patents, Recent Patents Chem. Eng. 1 (2008) 17–26.
[3] A. El-Badawy, D. Feldhake, R. Venkatapathy, State of the Science Literature Review: Everything Nanosilver and More, U.S. Environmental Protection Agency, Washington, DC, 2010.
[4] Q. Li, S. Mahendra, D.Y. Lyon, L. Brunet, M.V. Liga, D. Li, P.J.J. Alvarez, Antimicrobial nanomaterials for water disinfection and microbial control: Potential applications and implications, Water Res. 42 (2008) 4591–4602.
[5] T. Pradeep, P. Jain, Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter, Biotechnol. Bioeng. 90 (2005) 59–63.
[6] V. Oyanedel-Craver, J. Smith, Sustainable colloidal-silver impregnated ceramic filter for point-of-use water treatment, Environ. Sci. Technol. 42 (2008) 927–933.
[7] K.Y. Yoon, J.G. Byeon, C.W. Park, J.H. Wang, Antimicrobial effect of silver particles on bacterial contamination of activated carbon fibers, Environ. Sci. Technol. 42 (2008) 1251–1255.
[8] N.A.M. Barakat, M.F. Abadir, F.A. Sheikh, M.A. Kanjwal, S.J. Park, H.Y. Kim, Polymeric nanofibers containing solid nanoparticles prepared by electrospinning and their applications, Chem. Eng. J. 156 (2010) 487–495.
[9] A.D. Russell, W.B. Hugo, Antimicrobial activity and action of silver, Prog. Med. Chem. 31 (1994) 351–370.
[10] L.Y. Ng, A.W. Mohammad, C.P. Leo, N. Hilal, Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review, Desalination 308 (2013) 15–33.
[11] C.A. Mecha, V.L. Pillay, Development and evaluation of woven fabric microfiltration membranes impregnated with silver nanoparticles for potable water treatment, J. Membr. Sci. 458 (2014) 149–156.
[12] I. IDEXX Laboratories, Colilert®-18: A New Standard in Coliform/*E. coli* Detection, Westbrook, ME, 2013.
[13] R.W. Baker, Membrane Technology and Applications, Wiley, West Sussex, 2004.
[14] A. Mollahosseini, A. Rahimpour, M. Jahamshahi, M. Peyravi, M. Khavarpour, The effect of silver nanoparticle size on performance and antibacteriality of polysulfone ultrafiltration membrane, Desalination 306 (2012) 41–50.
[15] T. Maneerung, S. Tokura, R. Rujiravanit, Impregnation of silver nanoparticles into bacterial cellulose for antimicrobial wound dressing, Carbohydr. Polym. 72 (2008) 43–51.
[16] R. Nirmala, F.A. Sheikh, M.A. Kanjwal, J.H. Lee, S. Park, R. Navamathavan, H.Y. Kim, Synthesis and characterization of bovine femur bone hydroxyapatite containing silver nanoparticles for the biomedical applications, J. Nanopart. Res. 13 (2011) 1917–1927.
[17] E. Guibal, S. Cambe, S. Bayle, J.M. Taulemesse, T. Vincent, Silver/chitosan/cellulose fibers foam composites: From synthesis to antibacterial properties, J. Colloid Interface Sci. 393 (2013) 411–420.
[18] Q.L. Feng, J. Wu, G.Q. Chen, F.Z. Cui, T.M. Kim, J.O. Kim, A mechanistic study of the antibacterial effect of silver ions on *Escherichia coli* and *Staphylococcus aureus*, J. Biomed. Mater. Res. 52 (2000) 662–668.

[19] Y. Lv, H. Liu, Z. Wang, S. Liu, L. Hao, Y. Sang, D. Liu, J. Wang, R.I. Boughton, Silver nanoparticle-decorated porous ceramic composite for water treatment, J. Membr. Sci. 331 (2009) 50–56.
[20] K.A. Juby, C. Dwivedi, M. Kumar, S. Kota, H.S. Misra, P.N. Bajaja, Silver nanoparticle-loaded PVA/gum acacia hydrogel: Synthesis, characterization and antibacterial study, Carbohydr. Polym. 89 (2012) 906–913.
[21] S.L. Percival, P.G. Bowler, D. Russell, Bacterial resistance to silver in wound care, Hospital Infection 60 (2005) 1–7.
[22] D.V. Quang, P.B. Sarawade, S.J. Jeon, S.H. Kim, J.K. Kim, Y.G. Chai, H.T. Kim, Effective water disinfection using silver nanoparticle containing silica bead, Appl. Surf. Sci. 266 (2013) 280–287.
[23] H. Basri, A.F. Ismail, M. Aziz, K. Nagai, T. Matsuura, M.S. Abdullah, B.C. Ng, Silver-filled polyethersulfone membranes for antibacterial applications—Effect of PVP and TAP addition on silver dispersion, Desalination 261 (2010) 264–271.
[24] R. Kumar, H. Munstedt, Silver ion release from antimicrobial polyamide/silver composites, Biomaterials 26 (2005) 2081–2088.
[25] WHO, Guidelines for Drinking-water Quality, World Health Organization, Geneva, 2011.
[26] D.G. Yu, M.Y. Teng, W.L. Chou, M.C. Yang, Characterization and inhibitory effect of antibacterial PAN-based hollow fiber loaded with silver nitrate, J. Membr. Sci. 225 (2003) 115–123.