Performance Assessment of Functionalized Electrospun Nanofibres for Removal of Pathogens

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Abstract: The aim of this study was to evaluate the use of functionalised electrospun nanofibre microfiltration membranes, spun by an innovative electrospinning technique in water desinfection. As such, this study bridges between developments in electrospinning techniques for the production of flat sheet membranes and the application of these membranes in water disinfection. This study demonstrates that the electrospun membranes can be used for water disinfection applications as up to 5 $\log_{10}$ removal can be obtained, but that further research towards leaching is necessary.

Keywords: functionalised nanofibre; membrane filtration; pathogen removal; WSCP

INTRODUCTION

The electrospinning technique is a process for making continuous nanofibres in a non-woven form. This process spins fibres ranging from 80 nm diameter to several hundred nanometers. The non-woven structure is produced by applying a high voltage to the anode, submerged in a spinning solution. This produces a charged jet of fluid when the electrical force is higher than the surface tension of the solution and the fibres are collected on a grounded aluminium plate (Ahn et al., 2005). Nanofibres have a small pore size and a large surface area to volume ratio compared to nonwovens (this ratio for a nanofibre can be as large as 10^3 times of that of a microfibre). This, together with their low density and interconnected open pore structure, make the nanofibre nonwoven appropriate for a wide variety of filtration applications (Huang et al., 2003). One of the potential applications of the nanofibres is water filtration.

Due to the large effective surface areas, nanofibres can carry functional agents with different properties, such as biocides. In previous studies (Daels et al., 2009; Decostere et al., 2010) WSCP was found to be the best tested biocide as functional agent on the electrospun nanofibres. WSCP is a bactericide that can be applied on electrospun nanofibres and it has also effect on gram positive bacteria (Chen et al., 2008), in contrary to silver nanoparticles that have only effect on gram negative bacteria (Sondi, I. And Salopek-Sondi, B. 2004). WSCP is used as a cooling tower biocide and is applied directly into the water. The aim of the study is to study the added value of the tested nanofibre microfiltration membranes functionalized with biocide to pathogen removal was studied. Possibly the membranes should be considered as anti-biofouling membranes. Zodrow et al. (2009) found polysulfone ultrafiltration membranes impregnated with silver nanoparticels nog only

antimicrobial, but also preventing bacteria attached to the membrane surface and reducing in this way, biofilm formation.

MATERIALS AND METHODS

Electrospinning and functionalisation

The standard setup for electrospinning consists of a spinneret with a metallic needle, a syringe pump, a high-voltage power supply, and a grounded collector. A polymer, sol-gel, composite solution (or melt) is loaded into the syringe and this liquid is driven to the needle tip by a syringe pump, forming a droplet at the tip. When a voltage is applied to the needle, the droplet is first stretched into a structure called the Taylor cone. If the viscosity of the material is sufficiently high, varicose breakup does not occur (if it does, droplets are electrosprayed) and an electrified liquid jet is formed. The jet is then elongated and whipped continuously by electrostatic repulsion until it is deposited on the grounded collector. The electrospinning set-up used in this study is a scaled up multi nozzle system, which is developed at Ghent University. This production process results in a flat sheet non – woven nanofibre membrane (see Figure 1) with a mean pore size of 0.4 µm, fibre diameter between 50 – 100 nm and a thickness of 120 µm (Decostere et al., 2009).

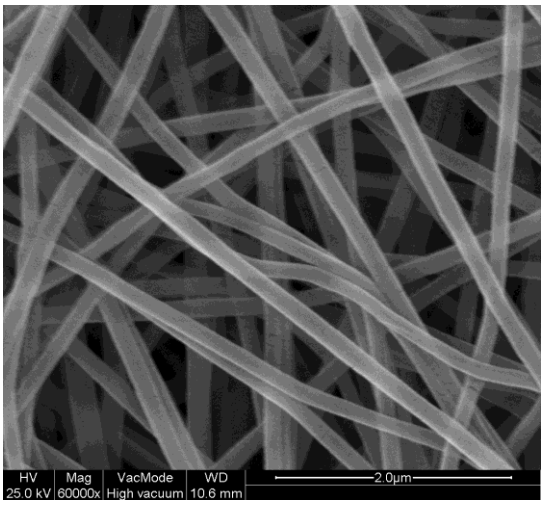

Figure 1 a SEM picture of a nanofibre polymer

The functional agent used in the experiment is a commercial biocides, WSCP (given in Figure 2). The membranes were functionalised by adding WSCP to the polymer solution before the electrospinning process starts. In this way the biocide is impregnated into the membrane. The added concentrations are expressed as ‘on mass fibre percent’ (omf%). As such 5 omf% equals 5 mg WSCP on 100 g membrane.

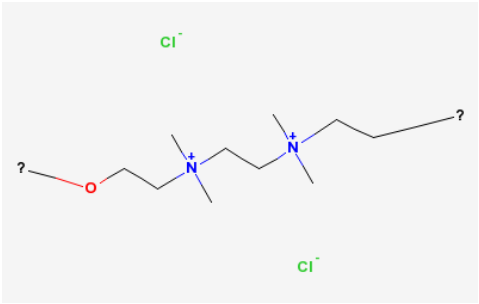

Figure 2 chemical structure of the biocide WSCP used as functional agent on the nanofibre membranes

Removal of pathogens

The tests were performed in a flow through system (Decostere et al., 2009) in which the samples (100 ml) were filtered over a functionalized nanofibre membrane (11 cm² diameter) with a pressure filter (1-1.5 bar) in a dead-end filtration cell, placed on a filter support (see Figure 3). The filtration cell was previously autoclaved at 121°C for 15 min. Water samples were collected and diluted as needed. Further the culturable micro–organisms were enumerated by inoculation in a nutrient agar culture medium (www.oxoid.com) at 37°C (EN ISO 6222, 1999) for 48 hours.

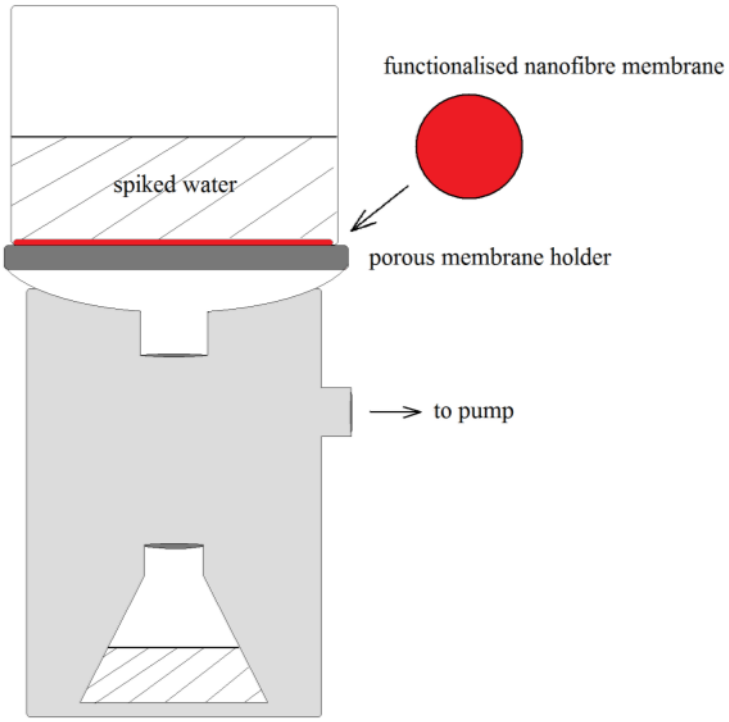

Figure 3 filtration set-up

For tests conducted to measure bacteria removal, a lab culture of *Staphylococcus aureus* (*S. Aureus*) LMG 8224 in nutrient broth to 10^6 CFU/ml (Bielefeldt et al., 2009) to serve as the influent "spike" water. Previous tests (Daels et al., 2009; Decostere et al., 2009) were done on the removal of pathogens on water samples taken from waste water from a general hospital (10^7-10^8 colony forming units / 100 ml). So both influents are compared for disinfection.

Leaching

Leaching of the added biocide in the functionalised membrane, was determined by measuring conductivity, expressed in µS and photospectromectric by Hach Lange Quaternary ammonium compound (QAC) tests, expressed as Cetyl Trimethyl Ammonium Bromide (CTAB). Ten batches of 100 ml demineralised water was poured into the functionalised nanofibre membrane (0,0011 m² diameter). Also a

monster was taken after 2 l of demineralised water. Each batch was analysed for conductivity and QAC-compounds. The test was repeated four times.

RESULTS AND DISCUSSION

Disinfection

In this study the term disinfection includes both physical removal and inactivation. The results of the enumeration of culturable micro-organisms (37°C) represented in Figure **4** where enumeration values are represented as $\log_{10}$ values. A $\log_{10}$ reduction value of 5 means that if the membrane is challenged with 10^5 bacteria, only one bacterium will be recovered in the permeate. When the water samples were filtered onto a non functionalised membrane (NF) with a dead-end filtration cell, a 2 $\log_{10}$ reduction in culturable micro-organisms was observed in the filtrate. This is comparable to what other studies have found on microfiltration membranes. Sadr Ghayeni et al. (1999), stated that larger pores in membranes, the presence of ultramicrobacteria (with a diameter of 0,2 µm) in the feed and the deformability of some bacteria are suggested to be possible mechanisms of bacterial passage through microfiltration membranes. The tested membranes in that study had a pore size of 0,2 µm with a bacterial transmission of 1,5 $\log_{10}$ reduction which is comparable to the values found in Figure 4 with non-functionalised nanofibre membranes (mean pore size 0,4 µm). Sadr Ghayeni et al. (1999) concluded that if the pore size decreases to 0,1 and 0,05 µm, the disinfection increases with 2 $\log_{10}$.

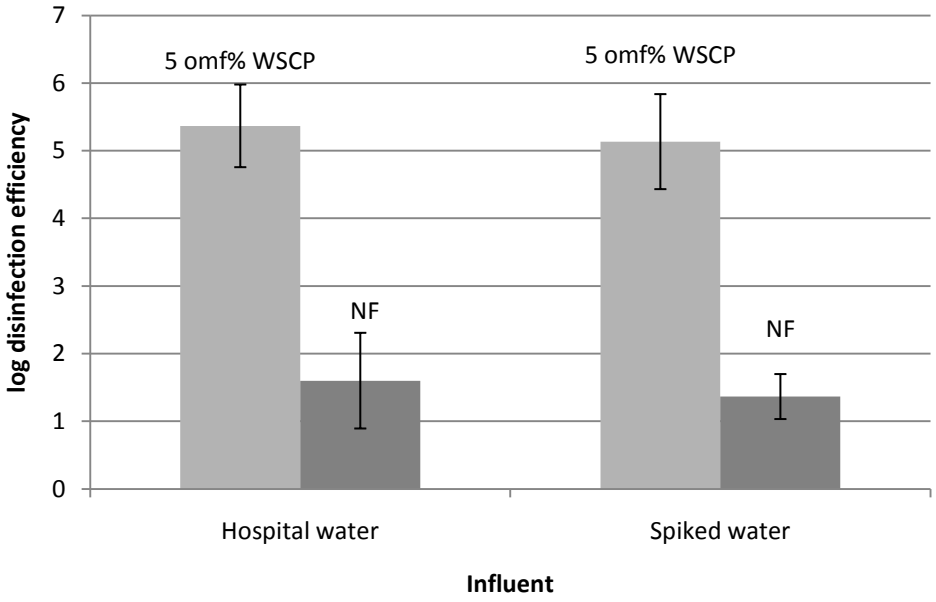

Figure 4 Pathogen removal by membrane filtration. Plate counts were performed on the influent (hospital water and spiked water) and filtrated through a n non-functionalized membranes (NF) and a functionalised membrane with 5 omf% WSCP.

Figure 5 shows the flow of bacteria in the effluent, after filtration of the spiked influent. A 1 flog$_{10}$ reduction could be seen after 200 ml, due to the physical removal by the cake layer on the membrane. The $\log_{10}$ reduction is stable during the 650 ml filtered and gives a constant value of log 5,15.

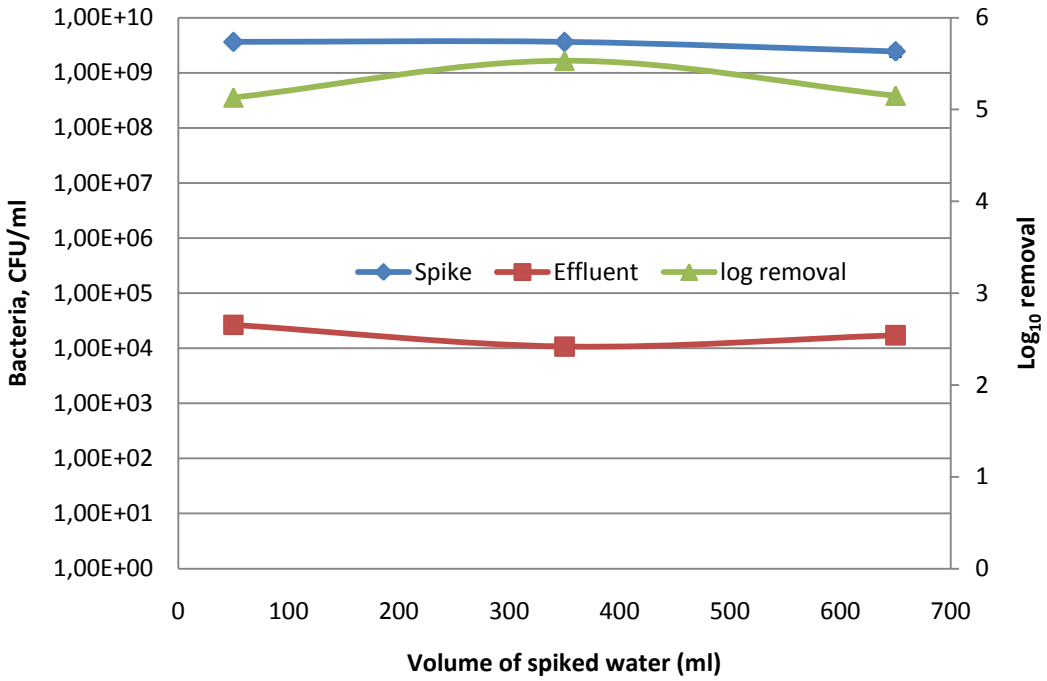

Figure 5 Measured bacteria concentrations in the spiked feed water and the filter effluent. On the secondary axis, the $\log_{10}$ removal is displayed.

Leaching

The values of the QAC leaching test are expressed in **Figure 6**. Conductivity results gave the same flow and are not displayed. Out of the results, there can be seen that the leaching is high in the beginning (15,07 ± 2,20 mg/l CTAB) but lowers in the end. After two litre (not displayed on the figure) the leaching is 0,05 ± 0,02 mg/l CTAB.

The area under this curve displayed in **Figure 6**, gives the total amount of WSCP, expressed as CTAB, that leached out of the membrane. In this case 0,945 mg CTAB leached. Knowing that the ratio CTAB/WSCP is 2,8/1, this equals 0,338 mg WSCP. The membrane was a 5 omf% WSCP nanofibre and had a mass of 0,1149 g. This means that 5/100*0,1149 g or 5,75 mg WSCP is present in the membrane. Of this 0,338 mg is leached. This equals 5,93% over the first two litres.

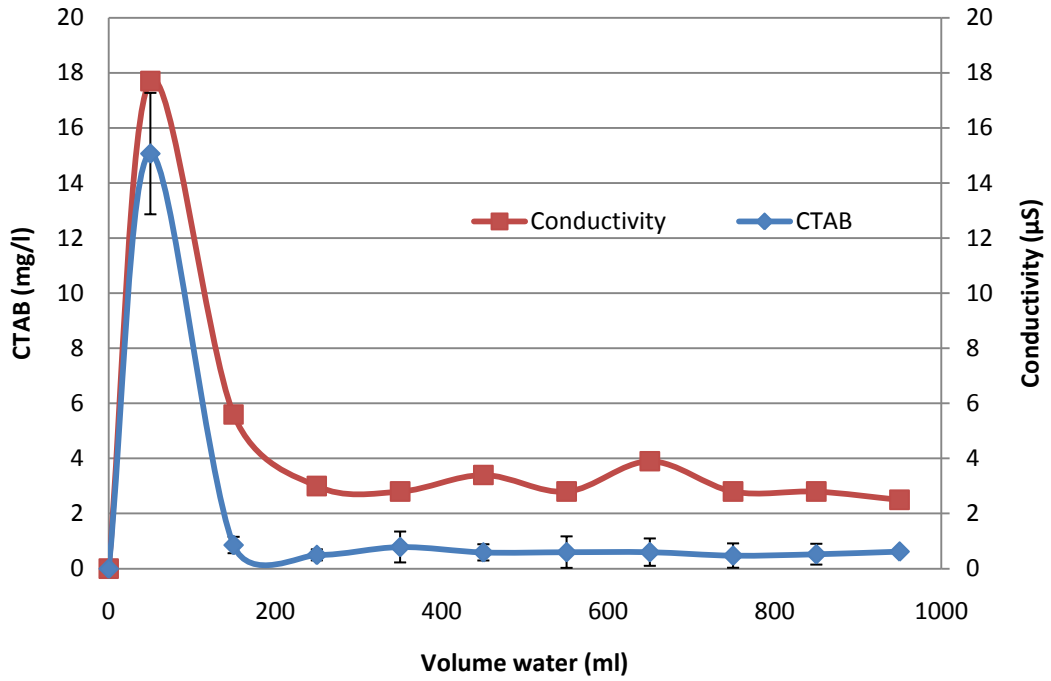

Figure 6 Measured CTAB concentration and conductivity after ten batches of 100 ml demineralised water

CONCLUSIONS

The 5,15 $\log_{10}$ removal stays stable after 650 ml of spiked water except for the extra $\log_{10}$ removal because of the cake layer. Further research should be done on functionalised nanofibres for pathogen removal on long term, and for the removal of *Escherichia coli*.

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REFERENCES

Ahn, Y.C., Park, S.K., Kim, G.T., Hwang, Y.J., Lee, C.G., Shin, H.S., Lee, J.K. (2005). Development of high efficiency nanofilters made of nanofibres. Current Applied Physics, 6, 1030-1035.

Bielefeldt, A.R., Kowalski, K., Summers, R.S. (2009). Bacterial treatment effectiveness of point-of-use ceramic water filters. Water Research, 43, 3559-3565.

Chen, L., Bromberg, L., Hatton, A. and Rutledge, G.C. (2008). Electrospun cellulose acetate fibres containing chlorhexidine as a bactericide. Polymer, 49, 1266–1275.

Daels, N., Decostere, B., De Vrieze, S., Dejans, P., Van Camp, T., Audenaert, W., Hogie, J., Westbroek, P., De Clerck, K., Van Hulle, S.W.H. (2009). Performance Assessment of Functionalized Electrospun Nanofibres for Removal of Pathogens. In:

Proceedings 1st IWA BeNeLux Regional Young Water Professionals Conference. Eindhoven, the Netherlands, 30 September - 2 October 2009.

Decostere, B., Daels, N., De Vrieze, S., Dejans, P., Van Camp, T., Audenaert, W., Hogie, J., Westbroek, P., De Clerck, K., Van Hulle, S. (2009). Performance assessment of electrospun nanofibres for filter applications, desalination, 249 (2009) 942-948.

Decostere, B., Daels, N., De Vrieze, S., Dejans, P., Van Camp, T., Audenaert, W., Westbroek, P., De Clerck, K., Boeckaert, C., Van Hulle, S.W.H. (2010) Initial testing of electrospun nanofibre filters in water applications. Water South Afrika, 36, 151-155.

EN ISO 6222:1999, Water quality – Enumeration of culturable micro-organisms – Colony count by inoculation in a nutrient agar culture medium

Huang, Z.-M., Zhang, Y.-Z., Kotaki, M., Ramakrishna, S. (2003). A review on polymer nanofibres by electrospinning and their applications in nanocomposites. Composites science and technology, 63, 2223-2253.

Sadr Ghayeni, S.B., Beatson, A.J. and Schneider, R.P. (1999). Bacterial passage through microfiltration membranes in wastewater applications. Journal of Membrane Science, 153, 71-82

Sondi, I., Salopek-Sondi, B. (2004) Silver nanoparticles as antimicrobial agent: a case study on E. coli as a model for Gram - negative bacteria, Journal of Colloid and Interface Science, 275, 177–182

Zodrow, K., Brunet, L., Mahendra, S., Li, D., Zhang, A., Li, Q., Alvarez, P.J.J. (2009). Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show imporved biofouling resistance and virus removal. Water research, 43, 715-723