A novel electrospun polyurethane nanofibre membrane – production parameters and suitability for wastewater (WW) treatment

Jaroslav Lev, Marek Holba, Michal Došek, Libor Kalhotka, Přemysl Mikula and Dušan Kimmer

ABSTRACT

The aim of this study was to investigate the suitability of a novel electrospun polyurethane nanofibre material for water-treatment purposes. Bacterial removal efficiency was tested in the laboratory by filtering artificial water spiked with *Escherichia coli* through a 0.25 μm nanofibre membrane. The results were compared with those obtained using a commercial microfiltration material (MV020T) with a similar pore size (0.20 μm). Alongside the laboratory experiments, we also determined filtration efficiency with semi-pilot scale experiments using actual wastewater from the secondary sedimentation tank of a wastewater treatment plant. The laboratory experiments indicated very high $\log_{10}$ removal efficiency, ranging from 5.8 to 6.8 CFU (colony-forming units)/ml. These results were better than those of the commercial membrane (3.8–4.6 CFU/ml). The semi-pilot scale experiment confirmed the membrane's suitability for microbial filtration, with both *E. coli* and total culturable microorganisms (cultured at both 22 and 36 °C) showing a significant decline compared to the non-filtered control (wastewater from the secondary outlet).

Key words | bacteria, electrospun nanofibres, membrane filtration, pathogen removal

Jaroslav Lev (corresponding author)
Marek Holba
Michal Došek
ASIO, s.r.o., Kšírova 552/45,
619 00 Brno, Czech Republic
E-mail: *lev@asio.cz*

Marek Holba
Přemysl Mikula
Department of Experimental Phycology and Ecotoxicology,
Institute of Botany of the Academy of Sciences of the Czech Republic,
Lidická 25/27, 602 00 Brno, Czech Republic

Michal Došek
Libor Kalhotka
Mendel University in Brno,
Faculty of Agronomy, Zemědělská 1/1665,
613 00 Brno, Czech Republic

Dušan Kimmer
SPUR, a.s., třída Tomáše Bati 299,
Louky, 763 02 Zlín, Czech Republic

INTRODUCTION

Dynamic human population growth over recent centuries has led to serious environmental problems. Of these, the lack of suitable (drinking) water in many areas of the world is one of the most important. As a result, there have been increasing efforts to develop more efficient technologies to improve (waste)water treatment and water recycling (Tanik *et al.* 2005; Zhang *et al.* 2007). Even in areas not affected by a lack of water, water quality is a significant factor with huge potential impacts on human health (Figueras & Borrego 2010).

Improvements in the microbial quality of water can be achieved in a number of different ways. Chemical disinfection (e.g. with chlorine) has been the most commonly used approach in the past; however, recognition of the dangers posed by the formation of potentially toxic by-products (Nieuwenhuijsen *et al.* 2000; Gopal *et al.* 2007) has led to the introduction and spread of alternative methods, such as microfiltration through various kinds of membranes. The membranes used in water treatment are usually polymer-based, but can also be made from other materials, such as ceramics (Kim & Van der Bruggen 2010). Recently, a variety of new membrane technologies have come into being and are now being extensively used in drinking water and wastewater treatment (Ersahin *et al.* 2012; Skouteris *et al.* 2012; Stoquart *et al.* 2012).

Commercially available microfiltration membranes have a pore size of 0.2 μm or less and usually possess very high microbial removal efficiency. In recent years, research has focused on the enhancement of membrane flow rates that could potentially result in energy savings while maintaining excellent filtration efficiencies (Meng *et al.* 2009; Kang & Cao 2012; Lau *et al.* 2012). From this viewpoint, electrospun polymer nanofibre structures represent one of the most promising research directions (Gopal *et al.* 2006; Botes & Cloete 2010).

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During the electrospinning process, polymer nanofibres with diameters ranging from 50 to 500 nm can be produced using an electrostatically driven jet of polymer solution (Doshi & Reneker 1995; Chronakis 2005; Ramakrishna *et al.* 2005). The nanofibres can then be directed onto a support material, thereby forming a filtration layer. Through careful control of over 20 process variables (e.g. electric voltage, temperature, humidity, pressure, speed of application), a homogenous structure can be obtained with a very high porosity yet very small pore diameter (Kimmer *et al.* 2011).

The aim of this study was to investigate the filtration efficiency of a novel electrospun polyurethane (PU) nanofibre material in the laboratory, and to compare the results with those from a commercial flat-sheet polyvinylpyrrolidone (PVDF) membrane of similar pore size. We then evaluated the suitability of the electrospun nanofibre filtration material for (waste)water treatment using actual wastewater.

MATERIALS AND METHODS

Materials

A modified PU solution was prepared for electrostatic spinning from diisocyanate, polyesterdiol and 1,4-butanediol in dimethylformamide (DMFA) using the *per partes* (integration by parts) synthesis method (temperature 90 °C; 6 hours). The solution was further diluted with DMFA in order to achieve a viscosity of 1.30 Pa s. Conductivity was increased to 150 μS/cm.

Nanofibre layers were prepared from the polymer solution using a commercially available SpinLine 120 device (SPUR a.s., Zlín, Czech Republic) that uses nanofibre forming jets (see Figure 1). The experimental conditions were as follows: 28% relative humidity, 23 °C, 75 kV applied to the PU solution, 210 mm distance between electrodes and a speed of 0.30 m/min for the supporting textile collecting the nanofibres. The nanofibres were collected on a surface-treated polyester fabric weighing 50 g/m^2.

The nanofibre membrane produced (named SPURTEX M247) was characterised using a scanning electron microscope (Vega 3, Tescan, Czech Republic; Figure 2); pore size distribution, average pore size and maximum pore size measurements were analysed in accordance with Czech Standard ASTM F316-03 (2011) (see Table 1 for membrane physical parameters).

A circular filter with a diameter of 48 mm (functional diameter 38 mm) was cut from both the M247 test membrane and a commercial flat-sheet PVDF microfiltration membrane (code MV020T) of similar pore size (see Table 1) for the short-term laboratory experiments. In addition, a 100 × 200 mm flat-sheet two-sided membrane was prepared from the M247 test membrane for the semi-pilot scale experiments. All filters were sterilised for 4 hours under UV radiation prior to the experiments.

Short-term laboratory-scale tests using artificial wastewater

A sterile bouillon was inoculated with *Escherichia coli* CCM 7929 and, after 24 hours of cultivation at 37 °C, 100 ml of the culture was inoculated into 900 ml of sterile physiological saline in order to produce an artificial wastewater containing around 5×10^6 colony-forming units (CFU)

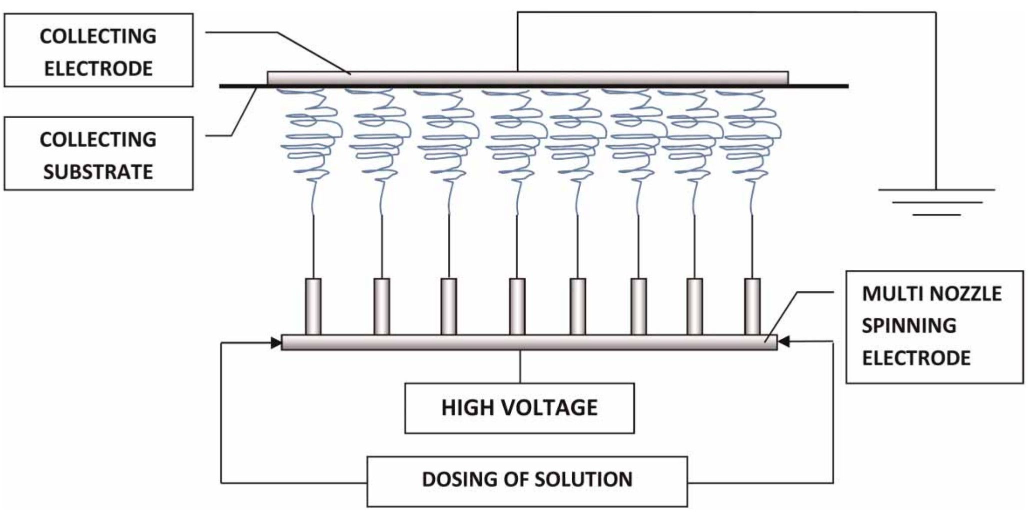

Figure 1 | A schematic diagram illustrating the principle of multi-nozzle electrospinning of nanofibre membranes.

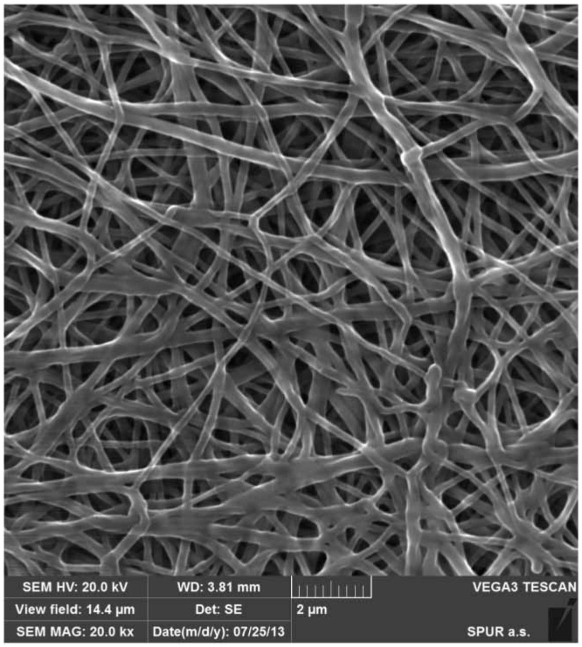

Figure 2 | Scanning electron microscopy image of the M247 test nanofibre's structure (magnification: 20,000 times).

Table 1 | Physical parameters of the membranes used in the laboratory filtration experiments

Parameters	Test nanofibre (SPURTEX M247)	Commercial membrane (MV020T)
Membrane material	PU[a]	PVDF[a]
Support material	PET[a]	PET
Nominal pore size [µm]	0.25 ± 0.10	0.20
Water flux [l/(m^{2}h)]	>500[b]	>500[c]
Thickness [µm]	250–300	210–250
Area weight of nanofibre layer [g/m^2]	2.82	–

[a]PU = polyurethane, PVDF = polyvinylidene fluoride, PET = polyethylene terephthalate.
[b]Test conditions: after 1 hour of distilled water filtration at 7.50 kPa; 23 °C.
[c]Test conditions: 0.70 bar; 20 °C; stirred cell (700 rpm).

per ml. The sample was then poured into the pre-sterilised filtration device, following which the test filter and support media were attached and the air pressure set to 50 kPa. The sample suspension of bacteria (100 ml) was then transferred to the filter via a drain valve. Sample filtrates were collected and diluted as needed for further analysis.

Samples of both filtered and non-filtered medium were analysed according to EN ISO 6222:1999 and EN ISO 9308-1:2000 standard international methodologies for inoculations of *E. coli*. We then prepared decimal dilutions of the artificial wastewater (non-filtered as control; plus samples filtered through each filter type). One ml of each dilution was inoculated onto a sterile Petri dish filled with VRBL Agar (Biokar Diagnostics, France) nutrient medium. The samples were then incubated for 24 hours at 37 °C, whereupon *E. coli* colonies growing on the agar plate were counted and number of bacteria calculated and expressed as CFU/ml. All measurements were performed in triplicate.

Semi-pilot scale tests using actual wastewater

Test wastewater was obtained from the secondary sedimentation tanks of a wastewater treatment plant (WWTP). The wastewater (120 l) was stored in a tank that also housed the flat-sheet nanofibre membrane frame. The water was filtered through this membrane via a suction tube and peristaltic pump fitted with a manometer and flow meter, the filtered water being delivered to a separate holding tank for further analysis (Figure 3).

Before the experiment started, the whole apparatus was sterilised using sodium hypochlorite solution. A potable water flush was used for the detection of background environmental contamination. Wastewater was pumped at a constant flow rate of 9 l/h, pressure changes being

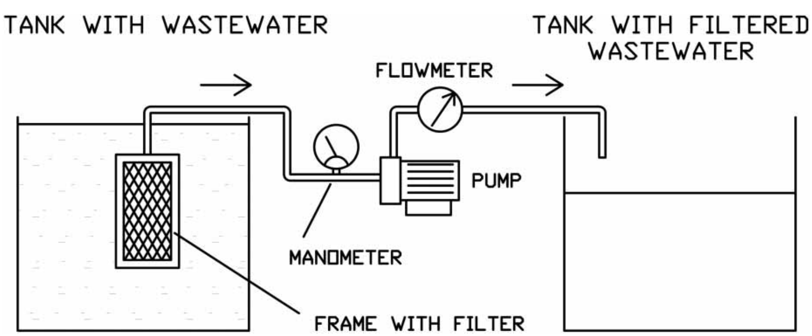

Figure 3 | Schematic diagram of the semi-pilot scale test apparatus.

monitored and adjusted. Samples of filtrate of 50 ml each were taken after 6, 25, 35, 50, 70 and 90 min for further analysis.

Samples from both filters and the water flush were analysed using the EN ISO 6222:1999 standard methodology, with the number of bacteria calculated and expressed as CFU/ml. The filtrates were treated in a similar manner to the laboratory experiments, with samples inoculated onto a sterile Petri dish filled with PCA agar nutrient medium (Biokar Diagnostics, France) incubated for 72 hours at 22 °C and for 48 hours at 36 °C. *E. coli* were detected and enumerated on VRBL Agar inoculated at 37 °C for 24 hours.

RESULTS AND DISCUSSION

Short-term laboratory experiments using artificial wastewater

The electrospun PU nanofibre membrane showed a very high bacterial removal efficiency, with just 0.44 $\log_{10}$ CFU/ml detected in the filtrate compared to the 6.8 $\log_{10}$ CFU/ml detected in the unfiltered control sample (Figure 4). In comparison, the commercial PVDF microfiltration membrane showed a lower level of bacterial removal, with appreciable numbers of culturable bacteria found even after filtration of *E. coli*. Indeed, thousands of bacteria were still detected after filtration, suggesting a bacterial removal efficiency of about 4 $\log_{10}$ CFU/ml. This seems surprising since filtration through a 0.2 μm pore size membrane would usually be expected to result in total removal of bacteria. Similar results have been found by Wang *et al.* (2007, 2008), however, who regularly observed the passage of a significant fraction of natural freshwater bacterial communities through 0.45, 0.22 and even 0.1 μm pore size filters. The same authors suggested that bacterial shape, rather than absolute size, was the key factor determining the ability of bacteria to pass through filters (Wang *et al.* 2008). Sadr-Ghayeni *et al.* (1999) also reported low bacterial removal efficiency through 0.2 μm membrane filters, although the authors also mention that the bacteria transmitted were not culturable. On the other hand, approximately half of the total number of cells that passed through the membranes still possessed functional electron transfer chains, which did suggest viability (Sadr-Ghayeni *et al.* 1999).

Cultivation of *E. coli* under various cultivation media and growth rates (Pierucci 1978) has indicated that the bacteria always exceed 1.5 μm length and 0.6 μm diameter, which is much higher than the denoted pore size of the PVDF commercial membrane (MV020T) used in this study. Note, however, that we have no relevant information on *E. coli* flexibility and we did not measure the actual pore size of the commercial PVDF membrane. In comparison, the results suggest that our unfunctionalised 0.25 μm electrospun PU nanofibre membrane (SPURTEX M247) has great potential for use in water filtration, in particular due to its multilayer nanofibre structure, structured surface and varied shape of pores. The removal efficiency achieved in the laboratory experiments was markedly higher than that of the 0.40 μm non-functionalised nanofibre membrane previously developed by Daels *et al.* (2011), which achieved only 2.20 $\log_{10}$ reduction, and comparable with that of the same membrane functionalised with 5 omf% (on mass fibre percent) water soluble cationic polymer antibacterial agent (5.60 $\log_{10}$ removal). Further, the 0.40 μm functionalised (silver particles) nanofibre membrane produced by Bjorge *et al.* (2009) displayed slightly lower removal efficiency (3.90–4.01 $\log_{10}$) than our membrane (5.8–6.8 $\log_{10}$).

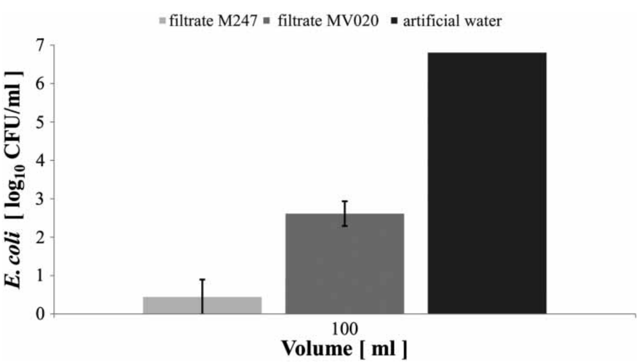

Figure 4 | Enumeration of *E. coli* in artificial test water and in samples following filtration through the test membranes.

Semi-pilot scale tests using actual wastewater

To investigate the suitability of our material for wastewater treatment, we also performed semi-pilot scale tests using actual wastewater from the secondary outlet of a WWTP. As a control, background contamination of the measuring apparatus was assessed following a flush-through with potable water.

The amount of bacteria detected following filtration through our nanofibre was the same, or even slightly lower, than that measured for background contamination (Figure 5). Comparison of the filtrate and non-filtered

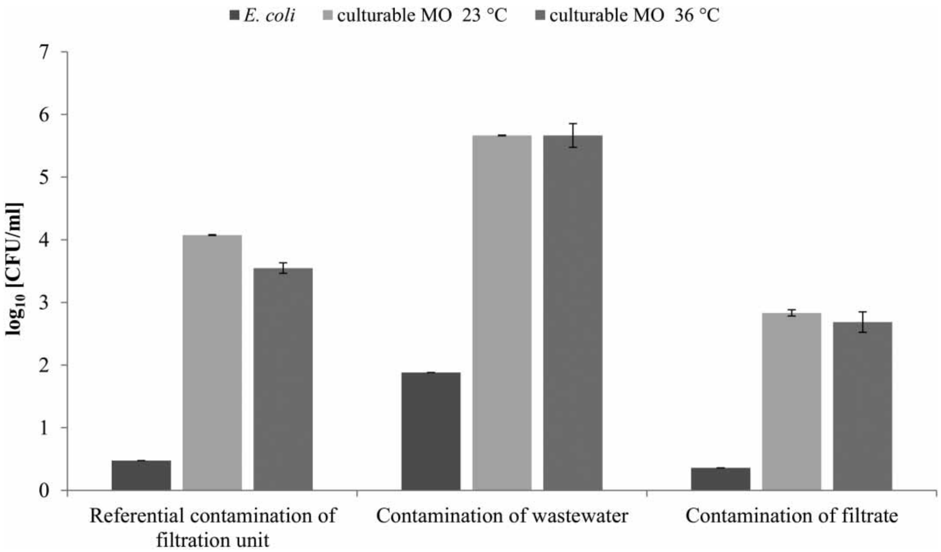

Figure 5 | Bacterial filtration efficiency for samples from the semi-pilot scale tests.

wastewater indicated a bacterial removal rate of 1.50 $\log_{10}$ CFU/ml for *E. coli*, and 2.83 $\log_{10}$ CFU/ml (23 °C) and 2.98 $\log_{10}$ CFU/ml (36 °C) for culturable microorganisms. While the bacterial removal values observed at the pilot plant were significantly lower than those detected during the short-term laboratory tests, they are very similar to the values previously reported by Bjorge *et al.* (2009). These authors filtered collected rainwater (initial contamination 5.48–6.98 $\log_{10}$ CFU/ml) and achieved removal rates of 3.16 $\log_{10}$ CFU/ml for *E. coli*, and 2.16 $\log_{10}$ CFU/ml (23 °C) and 2.23 $\log_{10}$ CFU/ml (36 °C) for culturable microorganisms.

CONCLUSION

The excellent removal efficiency observed during laboratory *E. coli* filtration experiments, and the promising results obtained during semi-pilot scale experiments, suggest that our new electrospun PU nanofibre material (SPURTEX M247) has great potential for the filtration of bacteria. Its application is not restricted to (waste)water treatment alone, however, as nanofibres are also used in separation technologies in the food and pharmaceutical industries (Barhate *et al.* 2006). What is more, the use of nanofibre membranes in (waste)water treatment can result in considerable energy savings due to their high flow capacity (e.g. see Meng *et al.* 2009); while functionalising of the material with antibacterial agents could enhance the antibacterial activity of the material still further (e.g. see Bjorge *et al.* 2009; Daels *et al.* 2011).

In every research field, however, there remain problems to be solved. For example, significant challenges remain regarding mechanical resistance and cohesion of nanofibre layers under long-term application in wastewater treatment (Barhate & Ramakrishna 2007), biofouling control (Drews 2010), filter regeneration and environmentally friendly disposal of used membranes. These are areas we hope to address in our future research.

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