MEMBRANE SURFACE MODIFICATION BY NANOSILVER FOR BIOFOULING RESTRICTION

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Abstract

Membrane biofouling limits widespread using of membrane technology in different fields. Several ways how to restrict this negative effect and achieve improving in long-term membrane filtration performances have been tested so far. Membrane modification by silver in the nanometre size-range can be a promising option for achieving high and long-term membrane permeabilities as well as antimicrobial features. Commercially available ultrafiltration membrane NADIR® UP 150 (commonly used for wastewater treatment) was modified by nanosilver. Modification methods were based on i) diffusion of silver together with its subsequent reduction, and ii) silver-doped nanofibers. Changes in permeabilities, antimicrobial properties, silver leaching and contact angles of modified membranes were examined.

While the membrane modified by diffusion method revealed higher permeabilities with demineralized water as well as diluted activated sludge, membrane modified through silver-doped nanofibers showed lower permeabilities, when comparing to unmodified one. The results of filtration tests well corresponded with contact angles which showed higher hydrophilic character of membranes modified through diffusion method. Both modified membranes also exhibited strong antimicrobial features and low silver leaching over time.

Keywords: Antibacterial properties, fouling, membrane modification, nanofibers, nanosilver, wastewater.

1. INTRODUCTION

Beside the numerous advantages of membrane technology, the most serious problem is fouling of the membrane surface [1]. It leads to a decrease in system hydraulic performance and an increase in operational costs. There are several ways to minimise membrane fouling and improve long-term membrane performance. One of the options is modification of the original membrane surface. Such modification reduces mutual hydrophobic interactions between the membrane surface, microorganisms and compounds present in the feed, thereby reducing membrane biofouling [2]. Modification using silver nanoparticles is a promising option for the restriction of biofouling. Silver nanoparticles have the potential to achieve the required long-term membrane permeability and antimicrobial properties. Both silver ions and silver nanoparticles have proven antibacterial properties as well as great potential for the development of strong hydrophilic membranes [3]; hence membranes containing silver nanoparticles have a great asset in wastewater treatment [4].

The main goal of this study was, therefore, to modify a commercially available ultrafiltration membrane, and to determine changes in membrane characteristics caused by modifications. Two modification techniques involving silver nanoparticles were used, i.e. functionalization through diffusion of silver ions, followed by their reduction and entrapment through heating (diffusion method); and fixation of silver-doped nanofibres (nanofibre method). Following modification, changes in filtration performance under different conditions as well as surface properties, silver leaching and antimicrobial properties were assessed.

2. MATERIALS AND METHODS

2.1. Membrane modification

a) Diffusion method: PES NADIR® UP150 membrane was soaked in 3.5% (wt.) silver nitrate and leached for 4 h at room temperature while stirring at 50 rpm. The membrane was then rinsed with demineralised water and the silver reduced by soaking in a 2% (wt.) ascorbic acid for 2 h. The membrane was again rinsed with demineralised water, and then heated for 2 h at 70°C while mixing at 50 rpm. Modified membrane was stored in demineralised water.

b) Nanofibre method: Polyurethane nanofibres were prepared based on ref. [5] using a free surface electrospinning device [6]. Heat-pressure lamination of the nanofibres onto the original membrane surface was performed using an Oshima Mini Press (OP-450GS) (Oshima, China). Pressure was set at 0.02 bar and the temperature kept within a range of 95-100°C to avoid structural changes to the nanofibres.

2.2. Filtration tests

Filtration performance of modified membranes was assessed using a LabUnit M10 laboratory-scale cross-flow filtration unit provided by Alfa Laval (Sweden), which allows for the testing of two membranes in parallel.

Three different filtration tests were carried out: **A) Test with demineralized water** at different transmembrane pressures (TMP), ranging from 0.3 to 1.95 bar; **B) Test with wastewater treatment plant (WWTP) effluent** withdrawn from secondary clarifier and used as the feed for filtration. The cross-flow volumetric flux was set at 3 $L \cdot min^{-1}$ and backwashing was conducted for 120 s. every 24 h. The retentate, and part of the permeate were recirculated back into the feed tank. Suspended solids in the feed were maintained at a stable concentration by adding new ratio of WWTP effluent (i.e. 200 $mL \cdot h^{-1}$ corresponding with flow of permeate discharged). This test lasted 72 h; **C) Test with increased suspended solids content** in feed of filtration unit (250 $mg \cdot L^{-1}$) due to the activated sludge addition and lasting 60 h. To evaluate changes in the retention of organic compounds, chemical oxygen demand (COD) was also determined. Hence, effluent from actual WWTP was filtered through an Amicon 8050 cell (EMD MilliPore), and COD concentration in feed and permeate was measured using the Hach-Lange cuvette test (LCK 414).

2.3. Silver leaching

Released silver from the modified membranes during filtration in LabUnit M10 (TMP 1.0 bar, cross-flow volumetric flux 3 $L \cdot min^{-1}$) was measured. Samples were taken at 0, 30, 120, 240 and 480 minutes and stabilised with 1% (wt.) nitric acid. To evaluate the total silver concentration on the surfaces, membranes were soaked for 24 h in 15% (wt.) nitric acid at stirring of 100 rpm. Silver concentration was measured using an Optima 2100 DV (Perkin Elmer) ICP-OES.

2.4. Surface visualization and wettability

A Carl Zeiss ULTRA Plus scanning electron microscope (SEM) was employed to visualise the cross-sections of membranes at 2,500x magnification. The SEM was equipped with a secondary electron detector, employed to analyse the chemical composition of the membrane surface, and a built-in energy dispersive X-ray (EDX) detector (Oxford instruments), which was used to determine the amount of silver bound to the membrane surface.

Surface wettability (i.e. hydrophobicity or hydrophilicity) of the modified membranes was assessed based on contact angles determined using the See System E portable computer-based device (Advex Instruments, Czech Republic).

2.5. Antimicrobial test

For each membrane, 4 cultivation tests, based on colony forming units (CFU), were undertaken for increasing contact time between the microorganisms and the membrane. First, 100 mL of 100-times diluted municipal WWTP effluent containing around $4.3 \cdot 10^3$ of bacteria was filtered through each membrane. After filtration, the membranes were stored on a wet cell for the appropriate contact time (i.e. 0, 3, 6 or 24 h) and then placed onto an agar cultivation plate for 30 minutes. The membrane was then removed and the agar plate cultivated in accordance with the method ČSN EN ISO 6222 (75 7821) [7].

3. RESULTS AND DISCUSSION

3.1. Membranes modification

The results obtained from SEM are shown in Fig. 1. SEM images of membrane modified by diffusion method showed no significant changes in cross-section morphology (Fig. 1-B) while structure of nanofibre layer onto the surface is evident (Fig. 1-C). Compression of original active membrane layer and its “replacing” for nanofibre layer is obvious when compared with reference (unmodified) membrane (Fig. 1-A).

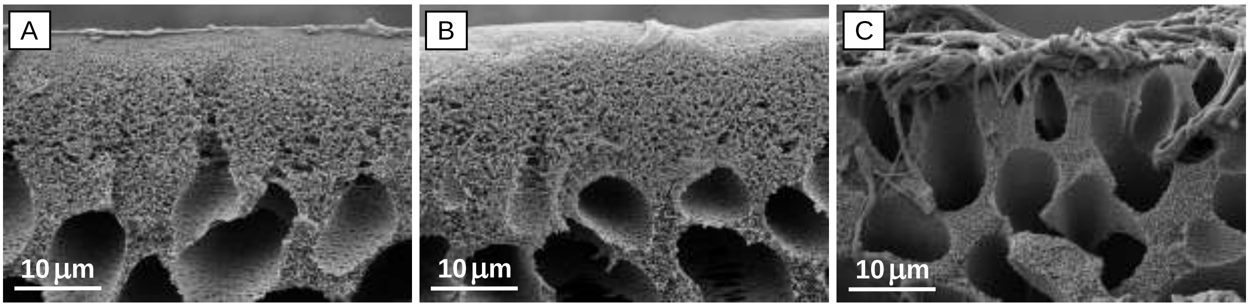

Fig. 1 Cross-sections visualised by SEM under magnification of 2,500x: A) unmodified membrane; B) membrane modified by diffusion method; and C) membrane modified by silver-doped nanofibres

3.2. Filtration tests

a) Test with demineralized water: The main purpose was to determine the changes in membrane permeabilities caused by modifications. Firstly, dependence of flux on the applied TMP only with demineralized water was determined. This test was conducted in parallel set-up with modified and unmodified membranes. The highest permeability over all tested TMP was found for membrane modified by diffusion method (Table 1). Membrane modified by silver-doped nanofibers achieved the lowest permeability. These findings correspond with contact angle measurement (section 3.4). Significantly lower permeabilities for membrane modified by silver-doped nanofibres could be likely caused by process conditions during lamination used for fixation of nanofibers on membrane surface.

Table 1 Permeabilities over TMP applied, including reference membrane

Membrane / Pressure [bar]	0.3	0.9	1.45	1.95
Diffusion	797	700	667	801
Reference	636	542	547	523
Silver-doped nanofibre	198	459	429	431
Reference	271	529	512	526

b) Test with wastewater treatment plant effluent: During this test, the permeability difference was in favour of membrane modified through diffusion method as its gradual increase was observed. Although the initial permeability of this membrane was about 10% lower compared to reference membrane, about 5% higher permeability was reached at the end of test. Backwashing was also more effective for this membrane as showing higher tendency towards surface foulant removal. Significant differences were observed for membrane modified by nanofibers. The maximum negative difference was almost 50% of unmodified membrane. The permeability difference for membrane modified by nanofibres improved greatly over the latter stages reaching about 10% lower permeability than reference membrane. The subsequent sharp change in permeability was likely caused by the removal of part of the fouling layer prior to backwashing. Furthermore, no significant improvement in organic compounds removal compared to reference membrane was observed for membrane modified by nanofibers. Only slight improvement in COD removal efficiency (feed COD: 25.6 ± 0.2 mg·L^{-1}) was found for membranes modified by diffusion method (Table 2).

Table 2 Mean COD removal of modified and reference membranes, as feed used actual WWTP effluent

Modification method	COD removal eff. [%]
Reference	29.7 ± 4.5
Diffusion	33.5 ± 1.6
Nanofibre	32.7 ± 3.5

c) Test with increased suspended solids content

After ending the filtration test with WWTP effluent, suspended solids in the feed were increased (from 20 mg·L^{-1} to 250 mg·L^{-1}) through activated sludge addition. This filtration test lasted 60 h and backwashing was performed twice. It is clear that the permeabilities of membranes modified by diffusion method were higher in comparison with reference membrane, similarly as in the previous filtration tests. After 60 h, the permeability of membrane modified by diffusion method was about approx. 30% higher than the unmodified membrane. In the case of membrane modified by silver-doped nanofibers, significantly lower permeabilities compared to reference membrane were observed (Fig. 2).

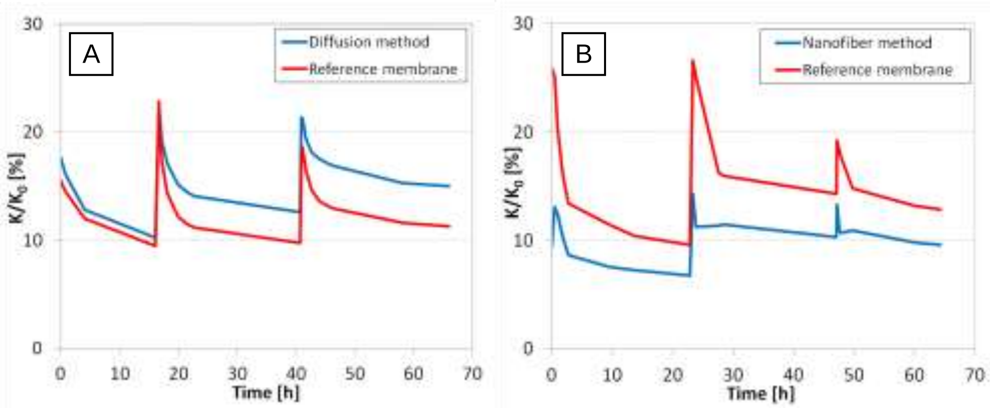

Fig. 2 Permeability difference (in %) of modified membranes (K) compared to original membrane (K_0) in the test with activated sludge addition (approx. 250 mg·L^{-1} of suspended solids in the feed)

3.3. Silver leaching

Dispersive X-ray energy (EDX) analysis performed after pre-leaching test by soaking the membranes in demineralized water revealed that membrane modified through diffusion method contained 2.9% of bound silver (silver content was calculated from all detected elements present on the surface). Results of silver leaching test proved the stability of bound silver on the membrane surface as the silver loss reached only 1.8% of the total amount of bond silver after 8 h. For membrane modified by silver-doped nanofibres, the surface contained 19.5% of silver. Silver leaching implied a decline in amount of bound silver, 1.4% of total bound silver after 30 minutes, and 3.2% at the end of this test. Detailed results and silver leaching kinetics are displayed in Table 3. Furthermore, the presence of silver was also confirmed by microscopic analysis carried out after the 3rd filtration test. From the SEM images, it was evident that large silver particles were washed out, and only the small silver particles remained in the surface monolayer. Chemical analysis conducted by dispersive X-ray energy (EDX) showed homogenous distribution of silver nanoparticles on the membrane surfaces even after ending filtration tests (Fig. 3).

Table 3 Silver leaching (c(Ag); mg·m^{-2}) and silver loss (%) of total silver present over time (t)

t [h]	Diffusion method		Nanofibre method	
	c(Ag) [mg·m^{-2}]	Silver loss [%]	c(Ag) [mg·m^{-2}]	Silver loss [%]
0.0	<0.07	0.0	<0.07	0.0
0.5	0.34 ± 0.09	0.7	23.1 ± 0.6	1.4
2.0	0.42 ± 0.17	0.8	38.2 ± 1.1	2.3
4.0	0.79 ± 0.19	1.5	46.2 ± 3.3	2.8
8.0	0.92 ± 0.32	1.8	52.9 ± 4.7	3.2
Total silver	50.34 ± 4.02	-	1638.1 ± 17.0	-

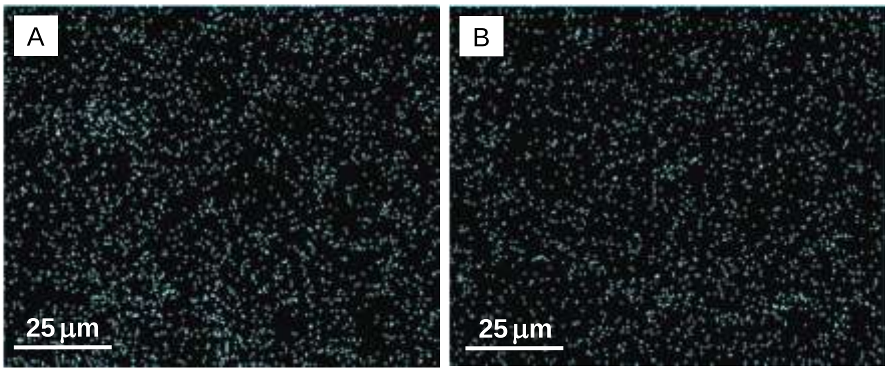

Fig. 3 Distribution of silver nanoparticles (AgLα) on the surfaces before (A), and after (B) filtration for membrane modified by diffusion method

3.4. Changes in wetting properties

The average contact angle of hydrophilic reference membrane was 66.6±10.2° while for membrane modified by diffusion method reached 52.6±2.6°, indicating its higher hydrophility. Higher hydrophility was caused by silver nanoparticles as already proved [8]. For membrane modified though nanofibres, average contact angle reached 80.6±3.2° mainly due to hydrophilic behaviour of polyurethane nanofibres. The results of contact angle measurement also well corresponded with the results of filtration tests (section 3.2).

3.5. Antimicrobial features

Antimicrobial cultivations revealed that the bound silver to the membrane surfaces exhibited positive effect towards microorganism's inhibition; thus restricted the growth of microorganisms on modified membranes. The results for different contact times with membranes are summarised in Table 4. Obvious antimicrobial effect was mostly observed already after 3 h, while unmodified membrane showed no inhibition.

Table 4 CFU of modified membranes after different contact times

Contact time [h]	Reference membrane		Diffusion membrane		Nanofibre membrane	
	CFU [-]	Inhibition [%]	CFU [-]	Inhibition [%]	CFU [-]	Inhibition [%]
0	>1000	-	>1000	-	>1000	-
3	>1000	-	492	89	402	91
6	>1000	-	156	96	71	98
24	>1000	-	34	99	73	98

The strongest inhibition, i.e. least CFU at contact time of 24 h exhibited the membrane modified by diffusion method, simultaneously having highest permeabilities. Differences between modified membranes for various contact times were, however, only negligible. The strongest inhibition after the shorter contact time (3 h) was observed for membrane modified by nanofibers likely due to the highest silver content (Table 3).

4. CONCLUSION

Commercial PES ultrafiltration membrane was modified through different procedures based on the silver nanoparticles immobilisation on membrane surface to restrict biofouling.

Conducted modifications led to changes in original membrane filtration characteristics. Compared to unmodified membrane, higher permeabilities in different filtration tests were observed for membranes modified by diffusion method. In contrast to that, the membrane modified by silver-doped nanofibers exhibited generally lower permeabilities in all filtration tests i.e. with demineralized water, WWTP effluent as well as activated sludge addition. The permeabilities corresponded with the results of surface contact angle measurements. Modifications also led to stable silver nanoparticles fixed to the membrane surface exhibiting low silver loss during the leaching test. Furthermore, modified surfaces exhibited strong antimicrobial features towards growth of microorganisms taken from actual WWTP effluent.

In general, membranes modified by diffusion method achieved the best results in conducted tests. Hence, membrane modified by this technique is promising for further testing.

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