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Membrane manufacturing via simultaneous electrospinning of PAN and PSU solutions

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ABSTRACT

Even though nanofiber membranes have wide unique characteristics, such as high surface porosity, high flux ratios, and lower production costs, they still show some shortcomings in terms of irreversible clogging, large pore sizes, and nanofiber rupture during filtration. This paper addresses a study to overcome such limitations with simultaneous electrospinning technique. Two different types of nanofibers were collected on the same layer. Polyacrylonitrile (PAN) nanofiber membranes have lower pore size than polysulfone (PSU) nanofiber membranes, while PSU component allowed easier toughening since it requires lower temperature for mechanical improvement against fiber rupture. As a result, pore size of simultaneous nanofiber membranes was provided by PAN (around 0.8 μm), whereas heat treatment at 185°C improved the strength of nanofiber membranes against rupture during filtration. Wastewater and surface water were filtered for filtration characterization. For both, removal rates were great. Thermal treatment improved membranes against fiber rupture. While fibers of heat-treated membrane were not broken, non-heat-treated membranes' fibers were broken and membrane disintegrated. But significant irreversible fouling was observed in wastewater filtration.

Keywords: Simultaneous electrospinning; Polyacrylonitrile; Polysulfone; Nanofiber; Heat treatment

1. Introduction

Electrospinning is a versatile method to produce very fine (micro/nano) scale fibers from solution or melt. It could be considered as a novel and popular method to produce highly porous filters [1] and a relatively new trend in membrane fabrication. In conventional membrane fabrication, it is possible to apply many types of techniques, but the most preferred one is phase inversion. But this process requires a coagulation medium which complicates the production and increases the cost. Membranes produced through conventional techniques, such as phase inversion, show low flux ratios depending on the distribution and geometric structures of pores. Nanofiber membranes produced with the electrospinning method have very high porosity. All the spaces between the fibers are

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connected to each other and generally have the porosity of around 80%. By means of interconnected porous structures, better permeability than conventional membranes would be expected. Likewise, electrospun membrane fabrication method is comparatively cheaper than other conventional methods. A commercial membrane production cost is around 50 €/m^2, whereas the estimated cost of nanofibrous membranes is around 20 €/m^2 [2].

There are several recent papers discussing the filtration performance of nanofiber membranes. Gopal et al. investigated the filtration performance of PVDF nanofiber membranes using polystyrene microparticles [3]. They found that larger particulates than pores rejected well, but smaller particles than pores were trapped between nanofibers and clogged the membrane irreversible. Similar results were observed with polysulfone (PSU) nanofibers [4]. Bilad et al. investigated the performance of nanofiber membranes in MBR system. Beside the same irreversible fouling problem, they are faced with nanofiber rupture caused by swollen nanofibers filled with activated sludge particles [5]. Bjorge et al. suggested that the nanofiber membranes could be a good pretreatment alternative before RO systems in the future [6]. Mirtalebi et al. found that nylon 66 nanofiber membranes have the same rejection performance of about 99% in coke removal from wastewater which is similar to commercial nylon 66 membranes but with higher permeation flux than commercial ones [7]. Nanofiber membranes are also a good alternative for antimicrobial filter production after proper functionalization [2,8,9]. Recent studies revealed that nanofiber membranes could be used effectively even in desalination processes, such as forward osmosis [10,11], membrane distillation [12], and nanofiltration/reverse osmosis membranes [13,14].

There are very few publications in the literature discussing the simultaneous electrospinning technique as well. Zhang et al. applied simultaneous electrospinning by using two nozzles with the aim of producing pH sensor with better stability and strength [15]. Zhan et al. produced superhydrophobic film with simultaneous electrospinning [16]. Ding et al. focused on collecting two different polymers on the same collection layer which has solubility in different solvents. They produced PVA/SA nanofiber film [17]. However, filtration properties of such multicomponent nanofibrous membranes have never been discussed so far.

As seen in the literature, nanofiber membranes produced with polyacrylonitrile (PAN) polymer had lower pore size characteristics than PSU nanofiber membranes. The pore sizes were about 0.6–0.7 μm for PAN [13], while the pore sizes of PSU nanofiber membrane were between 2 and 4 μm [4]. For better stability and strength of nanofiber membranes, heat treatment is commonly used. Differential scanning calorimetry analyses showed that heat demand for PSU nanofiber membrane treatment was 180–190˚C and whereas it was about 270–300˚C for PAN nanofiber membrane [18]. The aim of this study is to fabricate a nanofiber membrane derived from two different polymer solutions as simultaneously collecting different polymer nanofibers on same collection layer. Two different features of PAN and PSU nanofiber membranes will be combined. While PAN was determining the pore size, the strength and stability were provided by PSU. So a nanofiber membrane containing lower pore size with better stability was aimed to be fabricated and used in water filtration application for the first time using simultaneous electrospinning technique.

2. Experimental

2.1. Materials

PSU, S6010 was purchased from BASF Chemical Co. PAN (with molecular weight of 150,000 Da) and N-methyl pyrrolidone (NMP) were taken from Sigma-Aldrich. Sodium chloride (NaCl) was purchased from Merck. Dimethylformamide (DMF) was obtained from AKSA Chemical. PET nonwoven support was used as a support layer.

2.2. Electrospinning and nanofiber membrane production

The illustration of simultaneously produced nanofiber membrane and its setup are given in Fig. 1. Nanofiber membrane production was performed with an automated line (NE100, Inovenso Co. Ltd., Turkey). It has a grounded collection drum which rotates constantly at 350 rpm and strokes to the both side in order to collect nanofibers uniformly. Each polymer solution was electrospun through four metallic nozzles, each having 700 μm inner diameter.

Firstly, optimum values were found for electrospinning of PSU and PAN polymers. After single optimization of each polymer, two solutions were processed together. Simultaneous electrospinning setup is given in Fig. 1. Each polymer solution was pumped from different syringe pumps. Nanofibers were collected on a PET non-woven support layer. Heat treatment was applied to nanofiber membranes in the interest of improve their mechanical strength. PAN, PSU, and PAN/PSU blend nanofiber membranes were kept in oven for 5 h at 185˚C.

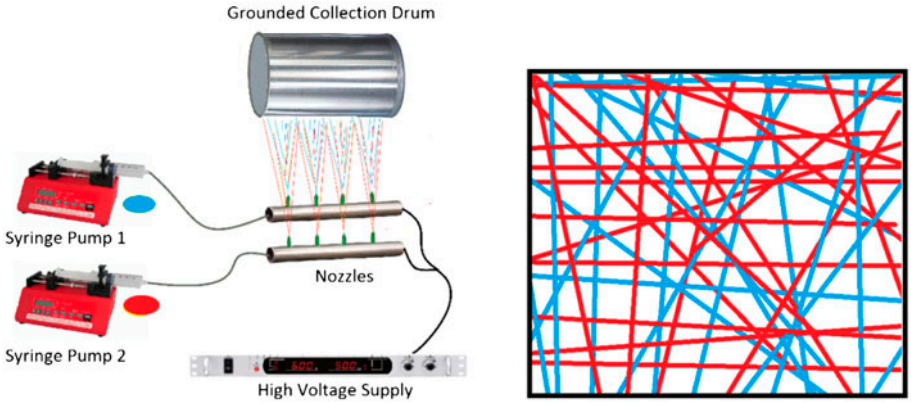

Fig. 1. Simultaneous electrospinning setup and the illustration of nanofiber membrane produced by simultaneous electrospinning technique. (Blue lines belong to PAN; red lines belong to PSU.)

2.3. Characterization of nanofiber membranes

2.3.1. Nanofiber and membrane characterization

Morphological characterization of nanofiber membranes was done with Quanta FEG 250 scanning electron microscope. Before and after filtration, fiber structures, thicknesses, and surfaces were analyzed. Pore sizes and pore size distribution were determined via capillary flow porometer (Quantachrome Porometer 3G). Effective measurement diameter of equipment was 1 cm. Samples were well wetted with wetting liquid (Porofil) before experiment. Contact angles were measured using KSV Nima Attention Theta model instrument. For dynamic mechanical analysis, SII DMS 6100 model instrument was used.

2.3.2. Filtration performance tests

Dead-end stirred cell system (Sterlitech, HP4750) was used to perform both water filtration and flux tests. Membranes were placed in the stirred cell. The effective filtration area of the cell was 14.6 cm^2. The permeability tests were performed with distilled water and filtration performance tests were carried out at 0.2 bar for 1 h using the surface water and activated sludge sample. The surface water sample was taken

Table 1
Final parameters for electrospinning process

Solution	Process	Electricity	Distance to collector	Polymer feed rate (ml/h)
17% PSU + 40% DMF + 43% NMP + trace amount of NaCl	During single electrospinning	31 kV[a]/36 kV[b]	16 cm/13 cm[a]	3.5
	During simultaneous electrospinning	36 kV	13 cm	3.5
6% PAN + 84% DMF	During single electrospinning	31 kV[a]/36 kV[b]	16 cm/13 cm[a]	10.5
	During simultaneous electrospinning	36 kV	13 cm	10.5

[a]Electricity voltage during single electrospinning process.
[b]Electricity voltage during simultaneously electrospinning process.

Table 2
Contact angles of produced nanofiber membranes

	PSU	PSU-HT	PAN	PAN-HT	SNFM	SNFM-HT
Contact angle	135.44 ± 0.1°	120.92 ± 0.6°	34.34 ± 6.6°	30.48 ± 18.1°	123.59 ± 0.04°	126.28 ± 0.16°

from Istanbul Technical University Ayazaga Campus Lake, Turkey. The activated sludge was received from aeration basin of Atakoy Advanced Biological Wastewater Treatment Plant, Turkey. MLSS content of activated sludge was 3,957 mg/l. Performances of nanofiber membranes were compared with commercial flat sheet Microdyn Nadir MV020 phase inversion membranes.

3. Results and discussion

3.1. Manufacture optimization of nanofiber membranes

PSU polymer solution concentration was optimized due to two main problems faced during electrospinning process. While the first problem was caused by clogging of nozzles due to rapid evaporation of solvent in solution, another problem was the insufficient drying of nanofibers and wet sample fabrication. Problems were solved using DMF and NMP solvents together, which have different vapor pressures. Also, trace amount of NaCl salt is added to the solution in order to improve electrospinning ability. Adding salt into solution decreased jetting height which was bridged over to have drier sample via electrospinning. The optimized final solution proportion was 17% PSU, 40% DMF, 43% NMP, and trace amount of salt. Electrospinning of PAN polymer solution was tried under the same conditions, with the same distance to collector and electricity. There was no problem occurred in electrospinning of PAN solution. Final parameters for each process are given in Table 1.

As soon as complete single optimization, simultaneous electrospinning tests started with the same polymer solutions and conditions. But simultaneously electrospinning system needed higher electric field as 40 kV to obtain electrospinning jet. Merely decreasing of electricity to 36 kV and distance to collector was 13 cm, electricity demand has lowered that provided successful simultaneous electrospinning. For the next step, simultaneous electrospinning of PAN and PSU solutions tried with same conditions in the simultaneous process. Nanofibers collected perfectly on nonwoven support for 2 h with 40 μm thickness without any problem.

Table 3
Water fluxes for membranes under 0.2 bar

	Distilled water flux (0.2 bar) (l/m^2 h)	Wastewater flux (0.2 bar) (l/m^2 h)	Surface water flux (0.2 bar) (l/m^2 h)
MV020	156	41	39
Heat-treated nanofiber membrane	1,605	20	146
Non-heat-treated nanofiber membrane	1,302	15	222

3.2. Characterization of nanofiber membranes

SEM micrographs of nanofiber membranes are given in Fig. 2. All three membranes did not have significant amounts of beads which indicate a successful nanofiber production. PAN nanofibers were slightly thinner than PSU nanofibers, as seen from the measurements on pictures. There were no physical changes on the membranes except PSU nanofibers become slightly curvy after heat treatment. PSU and PAN nanofibers could not be distinguished in SEM micrographs of simultaneous electrospinning and no structural changes observed in simultaneous electrospinning.

PSU nanofiber membrane had 1.33, 1.02, and 1.21 μm as maximum, minimum, and mean pore size, respectively. After heat treatment, there were no significant changes in pore sizes observed. On the other hand, PAN had smaller pore sizes as expected. PAN nanofiber membrane had 0.901, 0.641, and 0.731 μm as max., min., and mean pore size, respectively. After heat treatment, the pore sizes decreased. But there were no significant changes once again. Simultaneous nanofiber membrane (SNFM) had 0.817, 0.681, and 0.764 μm as max., min., and mean pore size, respectively. With regard to these results, it could be said that PAN is decisive to adjust the pore size of SNFM. As expected, PAN gave smaller pore size characteristic to SNFM. Heat treatment did not have a significant effect on pore sizes of SNFM (Fig. 3).

Table 4
Flux decline and recovery rates during performance tests

Membrane type	J_t (l/m^2 h)	Flux decline rate (%) in WW	Flux decline rate (%) in LW	Flux recov. rate in WW filtration	Flux recov. rate in LW filtration
MV020	41	74	75	83	86
SNFM-2	20	99	91	3	9
SNFM-1	15	99	83	5	18

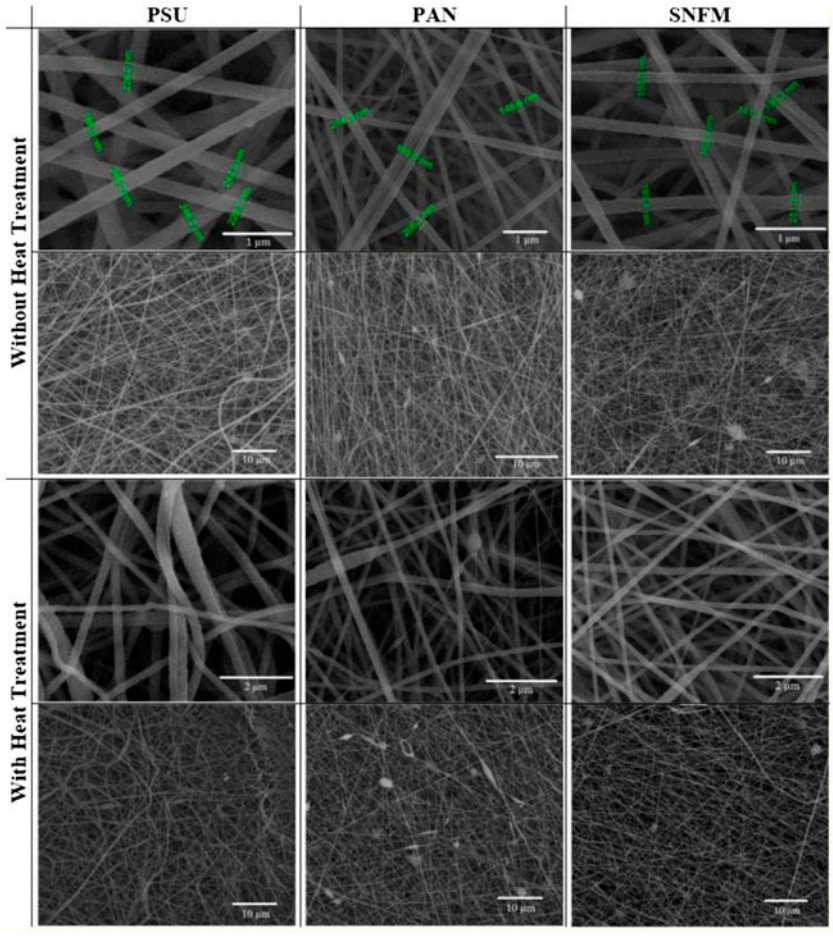

Fig. 2. SEM micrographs of nanofiber membranes.

PSU nanofibers are more hydrophobic than PAN nanofibers. Heat treatment decreased contact angles of nanofibers except SNFM (Table 2).

Fig. 4 shows strain properties of SNFM and SNFM-HT membranes under increasing stress. SNFM-HT has lower strain level about 5.927% than SNFM in which strain is about 7.854 before rupture. Also SNFM-HT has capability to resist much more stress level than SNFM. SNFM-HT could resist to 2.507 N/mm^2, while SNFM could resist to 1.266 N/mm^2 until rupture point. These data provide that heat treatment redound endurance to SNFM. Lower strain level means less plastic property and much more solid structure.

3.3. *Activated sludge filtration*

Wastewater filtration performance tests were performed with activated sludge. Suspended solids' removal rates were higher than 99% for all three membranes. Membrane fluxes were decreased logarithmically and were found as 41 l/m^2 h. MV020 gave 20 l/m^2 h for heat-treated nanofiber membrane, and non-heat-treated nanofiber membrane gave 15 l/m^2 h for under 0.2 bar pressure (Table 3). MV020 membrane showed better flux rate than the others.

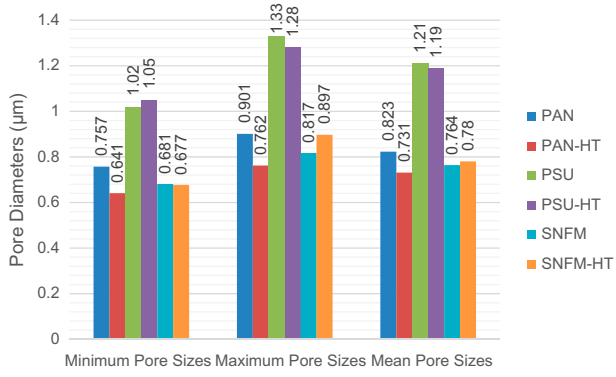

Fig. 3. Pore size comparisons of produced nanofiber membranes.

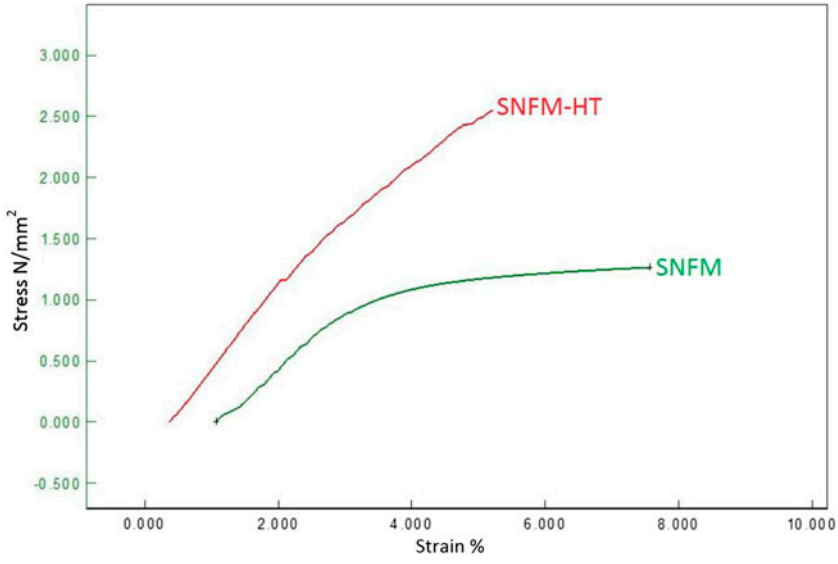

Fig. 4. Stress–strain graphic of SNFM and heat treated SNFM.

Flux decline rates express the difference between initial and final flux. While it was 74% for MV020, it was 99% for both nanofiber membranes as seen in Table 4. Nanofiber membranes showed significant flux decline. After filtration, the surface of the membranes was washed gently with distilled water. Flux recovery rates express ratio between distilled water flux after cleaning the surface and initial distilled water flux. Flux recovery rate was 83, 3, and 5% in MV020, SNFM-HT, and SNFM, respectively. Flux recovery rate is the indicator of one of the biggest problem in nanofiber membranes: irreversible fouling. Most probably particulate matters were trapped between nanofibers and clogged the pores.

In wastewater filtration, with the heat-treated nanofiber membrane showed better structural strength than non-heat-treated nanofiber membrane. Non-heat-treated nanofiber membrane is torn and scattered,

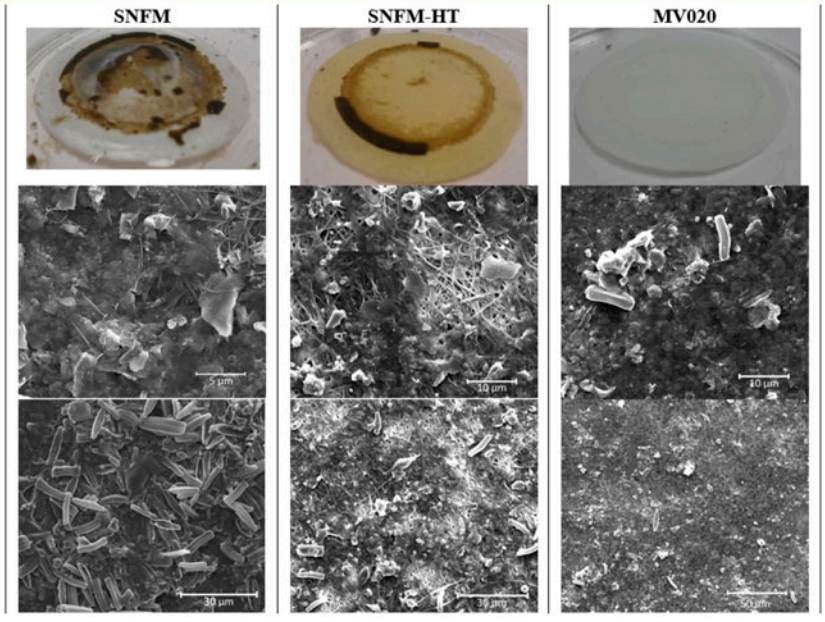

Fig. 5. Normal images and SEM micrographs of membranes after wastewater filtration.

Table 5
Performances of membranes in surface water filtration

Parameter/ membrane	Surface water	MV020	Non-heat-treated nanofiber membrane	Heat treated nanofiber membrane
Suspended solids	6.25 mg/l	Under measurement range	Under measurement range	Under measurement range
Turbidity (NTU)	3.68	0.49	0.58	0.45

while heat-treated nanofiber membrane keeps its structural unity as seen in Fig. 5. Two possible mechanisms could be leading to that: tiny sludge flocs may be entered among the fibers, made nanofibers swell up, and broke them. Secondary reason would be cross-flow effect that could cause that. Sterlitech had a magnetic stirrer in its cell to create cross-flow filtration effect on the surface. This effect may tear and scatter the surface of nanofibers as seen in Fig. 2. In the same figure, there is scanning electron microscope image of the surface of SNFM. The top of the nanofiber membranes and MV020 membrane was covered completely with biomaterials.

Heat treatment improved the mechanical strength of nanofiber membrane as seen in Fig. 2. SNFM-HT kept its structural and physical unity after filtration, which shows its robustness compared to SNFM. This result was confirmed previously by DMA analysis. In SEM micrographs (Fig. 2), it can be seen that nanofiber membrane surface is covered locally with sludge. SNFM-HT is in better conditions than SNFM.

3.4. Surface water filtration

Surface water filtration fluxes were found as 39 l/m^2 h for MV020, 146 l/m^2 h for heat treated nanofiber membrane, and 222 l/m^2 h for non-heat-treated nanofiber membrane under 0.2 bar pressure. Results are given in Table 5. In the surface water filtration, the suspended solids' removal rates were very efficient for all membranes. Raw surface water turbidity was 3.68 NTU. After filtration, the turbidity values were found as 0.45 NTU for heat treatment membrane, 0.58 NTU for non-heat treatment membrane, and 0.49 NTU for MV020 membrane. Turbidity removal is more efficient in the heat treated nanofiber membrane.

Flux decline rates in surface water filtration for MV020 are very similar to the value in wastewater

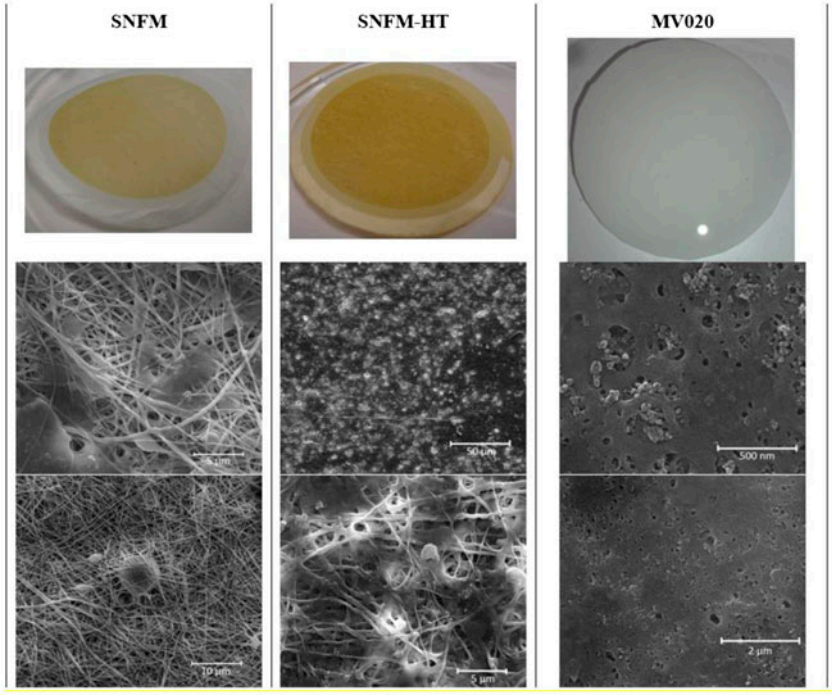

Fig. 6. Normal and SEM micrographs after surface water filtration.

filtration with the value of 75% as given in Table 4. While SNFM had 83% flux reduction, SNFM-HT had 91%. Flux recovery rate was 9% for SNFM-HT and 18% for SNFM. The difference between them can be explained with more robust fibers. Heat treated nanofiber membranes were more robust than without heat treatment as seen in DMA analysis and wastewater filtration. Surface fibers of SNFM could be move freely during the surface washing. During this movement, particulates trapped among nanofibers could be released easily. SNFM-HT may confine the particulates more effectively due to robust fibers. Normal and SEM micrographs are given in Fig. 6. SNFM membranes retained suspended solids between nanofibers which prove that the filtration area had different colors than the rest area. MV020 has cleaner surface than others.

4. Conclusion

The main conclusions of this work can be summarized as follows:

(1) Simultaneous electrospinning could bring novel design opportunities to be utilized from different characteristics.
(2) Nanofiber membranes were produced successfully via simultaneous electrospinning technique. Nanofiber membranes were produced with this technique for first time and used in water filtration applications.
(3) We have successfully combined two different features of PAN and PSU polymers via simultaneous electrospinning: smaller pore sizes of PAN nanofiber membrane compared to PSU nanofiber membrane would allow enhanced selectivity, whereas PSU will enhance mechanical properties.
(4) SNFM's pore sizes are similar to PAN nanofiber's pore sizes. It can be concluded that one of the aims in this study was achieved. During wastewater filtration, SNFM had scattered and torn, while SNFM-HT kept its unity. This shows heat treatment improved mechanical properties.
(5) Nanofiber membranes produced via simultaneous electrospinning technique were highly effective in SS removal during activated sludge filtration. But flux decline ratios were very high and flux recovery rates were very low. It was not suitable for wastewater filtration yet. Wastewater filtration performance could be improved using different polymer couple possibilities and/or adding antibacterial materials to the structure.
(6) SNFM-HT was very successful for turbidity and SS removal in surface water filtration. It can be used in the area of removing surface water turbidity after long-term operation tests.
(7) These types of membranes could also be used as disposable membranes such as are used in syringe filters. Although they have the same efficiency with phase inversion membranes, they could have cheaper fabrication cost.

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