Jurnal Teknologi

Stand-Alone Water Treatment: Performance Of Electrospun Nanofibers

A. Mataram[a,b]*, A. F. Ismail[a], E. Yuliwati[a], T. Matsuura[c], S. Rizal[d], A. Zamheri[d]

[a]Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Department of Mechanical Engineering, Universitas Sriwijaya, Sumatera Selatan, Indonesia
[c]Department of Chemical Engineering, Industrial Membrane Research Institute, University of Ottwawa, Ont., Canada KIN 6N5
[d]Department of Mechanical Engineering, Sriwijaya Polythecnic, Sumatera Selatan, Indonesia

Graphical abstract
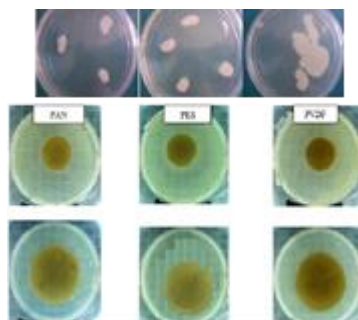
Abstract

The aim of this study was to evaluate the use of nanofiber microfiltration membranes, spun by an innovative electrospinning technique, in water filtration applications. This study bridges between developments in electrospinning techniques for the production of flat sheet membranes and the application of these membranes in water filtration. The functionalized or non-functionalized for the removal of pathogens was investigated, in term of chemical oxygen demand, total suspend solid and ammonium in the waste water. Physical properties such as clean water permeability (CWP) and strength were also examined. The results showed a very good removal of TSS (range 94.83-97.34%), COD (89.32-95.27%) and NH_3-N (64.48-72.87%). These test showed that the electrospun membranes can be used for water filtration applications.

Keywords: Electrospinning, Nanofiber, Microfiltration, Pathogen removal

Abstrak

Tujuan dari penelitian ini adalah untuk menilai penggunaan membran mikrofiltrasi nanofiber, berputar dengan teknik electrospinning inovatif, dalam aplikasi penapisan air. Penyelidikan ini menjembatani antara perkembangan teknik electrospinning untuk pengeluaran membran lembaran datar dan penerapan membran dalam penapisan air. Penggunaan untuk menghapuskan patogen diselidiki, dalam hal keperluan oksigen kimia, jumlah menangguhkan solid dan amonium dalam air sisa. Sifat fizikal seperti ketelapan air bersih dan kekuatan juga diperiksa. Hasil kajian menunjukkan penyingkiran sangat baik TSS (94.83-97.34%), COD (89.32-95.27%) and NH_3-N (64.48-72.87%). Ujian ujian ini menunjukkan bahawa membran electrospun boleh digunakan untuk aplikasi penapisan air.

Kata kunci: Electrospinning, nanofiber, mikrofiltrasi, penghapusan patogen

1.0 INTRODUCTION

The research and development of nanofibers have gained much interest in recent years due to the heightened awareness of its potential in medical and engineering applications. A number of processing techniques such as drawing, template synthesis, phase separation, self-assembly and electrospinning have been used to prepare polymer nanofibers in recent years. Among the most successful methods for producing nanofibers is the electrospinning process [1]. Electrospinning is a process that produces continuous ultrafine polymer fibers through the action of an external electric field imposed on a polymer solution or melt. Recently, polymer nanofibers have been attractive materials for a wide range of application because of their large surface area to volume ratio and the unique nanometer scale architecture built by them (Figure 1).
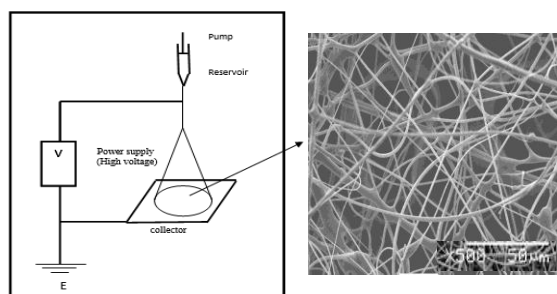

Figure 1 Electrospinning principle and resulting of nanofibre mat (SEM picture)

One of the possible applications of the nanofibers is water filtration. For this application a nanofiber flat sheet membrane can be produced that can be used as water filtration membrane. More specifically, this can be used in microfiltration. Nanofibers due to their higher porosities and interconnected pore structures offer a higher permeability to water filtration over conventional materials being used [2].

Microfiltration membranes have pore sizes between 0.1 and 10 μm and pressure (TMP) between 0.01 and 0.2 bar is used. With these membranes it is possible to retain suspended solids and depending on the pore size even microorganisms such as bacteria, yeast and fungi. Earlier studies have indicated that in case of a 0.45 μm pore size, 0.2 to 0.4 μm bacteria reduction could be obtained, it seems very interesting to evaluate its bacteria removal capacity. [3,4]. As the membrane, which is subject of this study, has a nominal pore size of 0.2 to 0.4 μm it seems very interesting to evaluate its bacteria removal capacity. Further, the added value of silver functionalized membranes to pathogen removal was studied. These tests were performed in a flow through system as few studies have been carried out so far to test the filtration performance and disinfection efficiency of the silver impregnated

nanofiber membranes [2]. For the use in this research, the fouling characteristics and physical properties such as strength and thickness are very important parameters. These parameters are also the subjects of this study.

This study aims at assessing the possible use of electrospun nanofibers membrane in water filtration in two different areas: first, membranes for pathogen removal, to be applied as a membrane for antibacterial; and second, membranes for suspended solids, chemical oxygen demand, nitrogen ammonia and also pathogen removal; to be applied as stand-alone microfiltration unit.

2.0 METHODOLOGY

2.1 Materials and Dope Preparation

Polyacrylonitrile (PAN) powder, Polyethersulfone (PES) powder and Polyvinylidene fluoride (PVDF) powder, N, N-dimethylformamide (DMF) and acrylamide (AM) were obtained from Aldrich Chemicals and were used without further purification. Dope solutions were prepared by dispersing predetermined amount of silica nanoparticles (1 wt.% to solution) and silver nanoparticles (1 wt.% to solution) into 18 wt.% solution in DMF. The mixture was mechanically stirred for at least 24 h at 60 °C in order to obtain homogeneous dispersed solutions [5].

2.2. Membrane Production Process

For the preparation of nanofibers mat, a 100 mL reservoir was used to hold the electrospinning solution. The experimental set-up to electrospin nanofibers is shown schematically in figure 1, together with the picture of nanofibers mat. The solutions prepared in section 2.1 were pumped at a constant rate of 2 mL/h with the help of a metering pump through a stainless steel needle of inner diameter 0.8 mm. A drum of 15 cm diameter, connected to a variable speed motor, was used to collect the nanofibers. A high DC voltage was applied to the needle with the help of high voltage regulated DC power supply (Model ES 30P-5W, Gamma High Voltage Research, Ormond Beach, FL, USA). The applied voltage was set at 21 kV and distance between the tip of the needle and the surface of the drum at 10 cm. The collecting drum was ground so as to generate the desirable electric field strength between the tip of the spinneret and the collector surface. Polyacrylonitrile (PAN), Polyetylsulfone (PES) and Polyvinylidene fluoride (PVDF), supplied by Sigma-Aldrich, proved to be suitable for electrospinning because they can be electrospun under steady state conditions. This production process resulted in a flat sheet non – woven nanofiber membrane with a mean pore size of 0.4 μm (as measured with a bubble point test [6]), a fiber diameter between 50 and 100 nm and a

thickness of 120 μm. The nanofibrous mat was carefully removed from the collector, and the residual solvent associated with the nanofiber mat was removed by keeping the mat in an oven for at least 2 days at 40 °C. The dried electrospun mats were stored in desiccators.

2.3 Removal of Pathogens

2.3.1 Culture Mechanism of Bacterial Spot

To evaluate the removal of pathogens by filtration, different water samples were taken, namely, wastewater from a general hospital (Palembang, Palembang), water from a local pond (Inderalaya Pond) and water from local river (Inderalaya). Compositions of the water are summarized in Table 1.

Table 1 Composition of wastewater

Constituent, unit	Influent (hospital)	Influent (pond)	Influent (river)	National primary discharged standard (P.U. (A) 434, Standard B, December 10, 2009)
COD, mg/l	441	453	436	400
Suspended solid, mg/l	114	121	176	100
NH_3-N, mg/l	22	23	26	20
E. coli, spot/l	3	8	6	-

Before filtered by using nanofibers mats, the sample water has checked for the content of e. coli. The cultural microorganisms were identified by inoculation in nutrient agar (NA) culture medium. The water samples were added by swapping method into nutrient agar medium in petri dish. Then, the samples were left for 24 hr at room temperature. After leaving, the bacteria spots were identified in the nutrient agar medium of all three water samples. The water samples were then filtered by nanofibers membrane by the filtration system illustrated in figure 2.
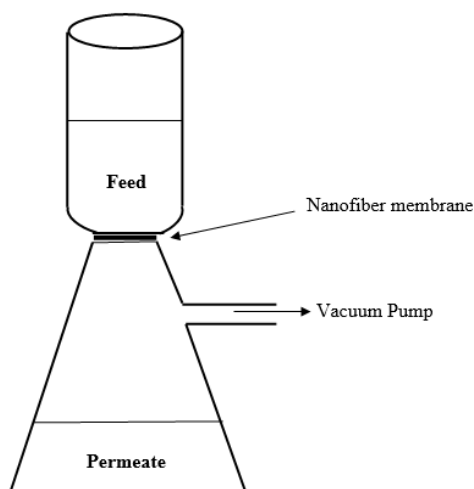

Figure 2 Illustration of nanofibre membrane filtration set up for stand-alone

2.3.2 Antibacterial Activity

The technique was adopted from Zodrow et al. by using vacuum filtration cell [13]. The membrane used in the filtration was put in medium to investigate the inhibition of bacteria growth at 37 °C for 24 h. Considering the membranes were sterilized before filtration, the growth of E. coli must come from the filtration process.

2.4 Evaluation of the Physical Characteristics

2.4.1 Clean Water Permeability

Clean water permeability (CWP) with used the water permeation system represents the maximum flux achievable dependent on the state of the membrane. It can be determined by measuring the flux at different trans membrane pressures (TMP). The slope of the resulting curve is considered as the CWP [6]. The CWP test was performed at 25 °C.

2.4.2 Tensile Strength Test

A tension testing machine ((LRx2.5 KN LLYOD Instrument with a load cell of 1 N, accordance with ASTM D 3379) was used to examine the tensile strength of the nanofiber membrane. A specific test strip (5 cm) was stretched at a pulling speed of 50 mm/min until rupture. This resulted in the maximum tensile strain. The tensile strength test was performed at ambient temperature. Tensile stress was calculated as follow: σ = P/A, where P is the maximum load and A is the cross-sectional area.

2.4.3 COD, TSS, NH_3-N Removal Guide Method

COD, TSS and NH_3-N concentrations were measured using the spectrophotometer (DR5000, HACH) in accordance to the standard proceduresHR (Method 8000, TNT822, 20-1500 mg/L COD) that are measured at 620 nm for COD, Method 8006, Photometric method, 5-750 mg/L TSS, that are measured at 810 nm for TSS and Method 10031, Salicylate method, HR 0.4-50.0 mg/L NH_3-N, that are measured at 655 nm for NH_3-N.

The COD removal efficiencies are calculated with Equation:

$$\text{COD removal (\%)} = \frac{COD_0 - COD}{COD} \times 100 \qquad (1)$$

where COD_0 and COD are the initial concentration of wastewater and the concentration of permeate produced.

The TSS removal efficiencies are calculated with Equation:

$$\text{TSS removal (\%)} = \frac{TSS_0 - TSS}{TSS} \times 100 \qquad (2)$$

where TSSoand TSS are the initial concentration of wastewater and the concentration of permeate produced.

The NH₃-N removal efficiencies are calculated with Equation:

$$NH_3\text{-N removal (\%)} = \frac{NH3-N_o\_NH3-N}{NH3-N} \times 100 \qquad (3)$$

where $NH_3\text{-}N_o$ and $NH_3\text{-}N$ are the initial concentration of wastewater and the concentration of permeate produced.

3.0 RESULTS AND DISCUSSION

3.1. Removal of Pathogens

3.1.1 Culture Mechanism Of Bacteria Spot

Figure 3 illustrates the amount of bacteria spot in the water samples. The water sample from pond has the largest bacteria number of spots among all water samples. Hence, pond water was used for the ring-test.
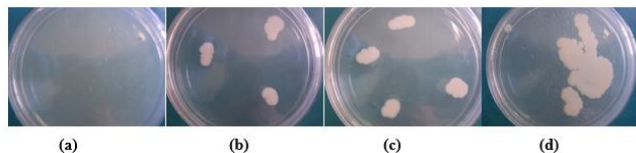

Figure 3 Content of E.coli; (a) control E. coli, (b) water from hospital, (c) water from river and (d) water from pond

3.1.2 Antibacterial Activity

The results of the antibacterial activity are shown in Figure 4. Each membrane displayed (after filtration, below figure) the large inhibition ring, diameter increment around 8%. Silver is believed to act as an antibacterial agent either upon contact to the bacteria or as released ion in the media [10]. For silver ion, as studied by Kumar and Munstedt, the release system is controlled by the rate of water diffusion in the composite [11]. As for silver particles, the ability to inhibit bacterial activity is depending on the particle size which corresponds to surface-to-volume ratio in which the smaller particle with larger surface area will lead to more bactericidal effect [12].

The results of antibacterial activity shown in figure 4 are in agreement with the results reported by Kumar and Munstedt and Basri et al. in which silver containing polymer (PES, PAN and PVDF) exhibited better antibacterial activity due to content of silver ion released from the system. Thus we could conclude that the silver nanoparticles had a good retention on the membrane, indicating the successful application of the silver nanoparticles on the nanofiber membrane.
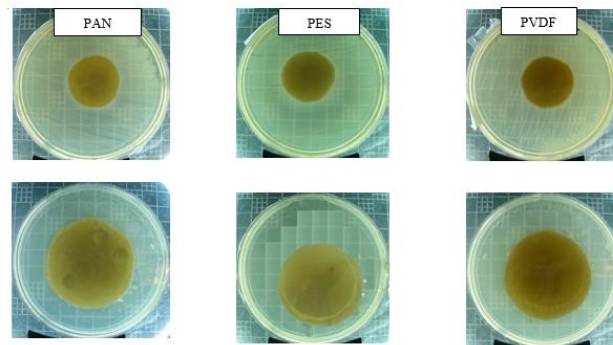

Figure 4 Antibacterial activity

3.2. Physical characteristics of the nanofiber membrane

3.2.1 Clean Water Permeability (CWP)

The CWP are given in Table 2 for different nanofibers membranes. Clean water permeability (CWP) gave an idea of the fouling on the membrane. The values showed a very high CWP value, which could be useful to treat large volumes of water in absence of particles that could obstruct the nanofibers membrane. Further this high CWP indicates that nanofiber membranes could be energy saving [14].

Table 2 Comparison of CWP-value

Membrane type	CWP (l/m² .h.bar)
Polyethyl Sulfone	2134
Polyacrylonitrile	1982
Polyvinylidene fluoride	2001

3.2.2 Tensile Strength Test

The results showed that the strength of the membrane was independent of the direction in dry condition. Also it could be concluded that in wet condition of the membrane, it is stronger lengthwise. The results of all nanofibers are listed in Table 3. These values show that the strength of nanofibres membranes is satisfying [7]. Meanwhile, PAN membranes were more brittle than PES and PVDF membranes and difficult to install in the water permeation system.

Table 3 The tensile strength of PES, PAN and PVDF

Membrane type	Tensile test (KPa)
Polyethyl Sulfone	986
Polyacrylonitrile	1065
Polyvinylidene fluoride	902

3.3 Nanofiber Membrane Used in Stand-Alone Applications

Other important parameters that were monitored are the removal of Total Suspended Solids (TSS), Chemical Oxygen Demand (COD) and Nitrogen Ammonia (NH$_3$-N). The results are illustrated in Table 4.

Table 4 Removal of COD, Suspended solid and NH$_3$-N

Membrane type	Parameter	Removal(%)
Polyethyl Sulfone	COD	95.27
	TSS	97.34
	NH$_3$-N	72.87
Polyacrylonitrile	COD	89.32
	TSS	95.23
	NH$_3$-N	64.48
Polyvinylidene fluoride	COD	93.62
	TSS	94.83
	NH$_3$-N	70.57

The results showed a very good removal of TSS (range 94.83-97.34%), COD (89.32-95.27%) and NH$_3$-N (64.48-72.87%). Only the removal of nitrogen ammonia (NH$_3$-N) was not satisfying. This was due to an unsatisfactory denitrification. A suspended solid is generally related to the membrane performance and efficiency [9, 15].

The nanofibers membrane was tested in a stand-alone application treating wastewater. This means that nanofibers membrane filtration is the only treatment technique applied before discharge. The challenge with this waste water treatment was that membranes for suspended solids, chemical oxygen demand, ammonium nitrate and also pathogen removal; to be applied as stand-alone microfiltration unit.

4.0 CONCLUSION

The nanofiber membrane was tested in a stand-alone application wastewater. The challenge with this wastewater treatment was to removal unuseful organic in the water. The following results were obtained when The Clean Water Permeability (CWP) gave an idea of the fouling on the membrane. The values showed a very high CWP-value this could be useful to treat large volumes of water in absence of particles that could obstruct the nanofiber membrane. Further this high CWP indicates that nanofiber membranes could be energy saving. These nanofibers membrane filtration is the only treatment technique applied before discharge. The challenge with this waste water treatment was that membranes for suspended solids, chemical oxygen demand, ammonium nitrate and also pathogen removal; to be applied as stand-alone microfiltration unit.

References

[1] Huang, Z. M., Zhang, Y. Z., Kotaki, M., Ramakrishna, S. 2003. A Review on Polymer Nanofibers by Electrospinning and Their Applications in Nanocomposites. *Composite Science & Technology*. 63 (15): 2223-2253.
[2] Thavasi, V., Singh, G., Ramakrishna, S. 2008. Electrospun Nanofibers in Energy and Environmental Applications. *Energy & Environmental Science*. 1: 205-221.
[3] Gómez, M., de la Rua, A., Garralón, G., Plaza, F., Hontoria, E., Gómez, M.A. 2006. Urban Wastewater Disinfection by Filtration Technologies. *Desalination*. 190(1-3): 16-28.
[4] Ghayeni, S. B. S., Beatson, A. J., Schneider, R. P. 1999. Bacterial Passage through Microfiltration Membranes in Wastewater Applications. *Journal of Membrane Science*. 153(1): 71-82.
[5] Mataram, A., Ismail, A. F., Mahmod, D. S. A., Matsuura, T. 2010. Characterization and Mechanical Properties of Polyacrylonitrile/Silica Composite Fibers Prepared via Dry-Jet Wet Spinning Process. *Materials Letters*. 64(17): 1875-1878.
[6] Mulder, M. 1997. *Basic Principles of Membrane Technology*. Kluwer Academic Publisher, Dordrecht.
[7] Ma, X., Su, Y., Sun, Q., Wang, Y., Jiang, Z. 2007. Enhancing the Antifouling Property of Polyethersulfone Ultrafiltration Membranes through Surface Adsorption- Crosslinking of Poly(Vinyl Alcohol). *Journal of Membrane Science*. 300(1-2): 71-78.
[8] Bjorge, D., Daels, N., Vrieze, S. D., Dejans, P., Camp, T. V., Audenaert, W., Westbroek, P., Clerck, K. D., Hulle, S. W. H. V. 2009. Performance Assessment of Electrospun Nanofibers for Filter Applications. *Desalination*. 249: 942-948.
[9] Basri, H., Ismail, A. F., Aziz, M., Nagai, K., Matsuura, T., Abdullah, M. S., Ng, B. C. 2010. Silver-Filled Polyethersulfone Membranes for Antibacterial Applications- Effect of PVP and TAP Addition on Silver Dispersion. *Desalination*. 261(3): 264-271.
[10] Yu, D. G., Teng, M. Y., Chou, W. L., Yang, M. C. 2003. Characterization And Inhibitory Effects of Antibacterial PAN-Based Hollow Fiber Loaded with Silver Nitrate. *Journal of Membrane Science*. 225: 115.
[11] Kumar, R. and Münstedt, H. 2005. Silver Ion Release from Antimicrobial Polyamide/Silver Composites. *Biomed. Mater.* 26(14): 2081-2088.
[12] Baker, C., Pradhan, A., Pakstis, L., Pochan, D.J., Shah, S.I. 2005. Synthesis and Antibacterial Properties of Silver Nanoparticles. *Journal of Nanoscience & Nanotechnology*. 5(2): 244-249.
[13] 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 Improved Biofouling Resistance and Virus Removal. *Water Resources*. 43(3): 715-723.
[14] Daels, N., Vrieze, S. D., Sampers, I., Decostere, B., Westbroek, P., Dumoulin, A., Dejans, P., Clerck, K. D., Hulle, S. W. H. V. 2011. Potential of a Functionalize Nanofibre Microfiltration Membrane as an Antibacterial Water Filter. *Desalination*. 275: 285-290.
[15] Mataram, A. Ismail, A. F. Yuliwati, E. Matsuura, T. Zamheri, A. Rizal, S. 2015. Water Treatment Perfomance: Application Of Electrospun Nanofibers. *Jurnal Teknologi* 77(11): 263-267.