Removal of Pigment from Textile Wastewater by Electrospun Nanofibre Membrane

*Nor Dalila Nor Affandi, Nur Najiha Abdul Razak**
Textile Research Group, Faculty of Applied Sciences,
Universiti Teknologi MARA, 40450 Shah Alam, Selangor

**dalila@salam.uitm.edu.my*

ABSTRACT

The removal of contaminants in textile effluent using electrospun Nylon 6 nanofibre membrane has been investigated in the study. The electrospun Nylon 6 nanofibre membrane was fabricated using electrospinning process at different parameters. The resultant electrospun membrane was characterized for pore diameter and morphological structures. Permeate properties and flux of electrospun Nylon 6 nanofibre membrane were compared with the commercial filter membrane. From the results, it shows that the electrospun Nylon 6 nanofibre membrane exhibited lower flux than the commercial membrane. The accumulation of suspended solid particles onto the electrospun Nylon 6 membrane surface reduced the permeate flux which about 14 minutes slower than the commercial membrane. Although the electrospun Nylon 6 nanofibre membrane exhibited lower flux, this membrane gave the best removal of suspended solids with approximately 99%. As a result, a clear permeate was obtained after the filtration. The electrospun membrane also gave higher reduction of chemical oxygen demand (COD) as compared to the commercial filter membrane. For commercial membrane, it was found that the membrane gave a much lower removal of effluent with approximately 34%. The presence of a large pore diameter of the commercial membrane allows more suspended solids to pass though the membrane, resulting in a cloudy permeate.

Keywords: *Electrospinning; Nanofibre membrane; Textile wastewater, Filtration, Flux*

ISSN 1823- 5514, eISSN 2550-164X

Received for review: 2017-02-12
Accepted for publication: 2017-05-12
Published: 2017-10-15

Introduction

Removal of contaminants from industrial waste waters such as textile effluent is crucial to safeguarding the environment. In many cases particularly in third world countries, effluent is discharged directly into waterways without pre-treatment, which can be damaging to local aquatic ecosystems [1-3]. As reported by Judd and Jefferson [1], effluent from textile wet processing particularly dying, printing and finishing generate large volumes of salinity, chemical oxygen demand (COD), turbidity, suspended solids and colour. In waste waters, there are two types of solids, suspended solid and dissolved solid [2]. Solids that will not pass through 0.45µm filter are referred to suspended solids, whereas solids smaller than 0.45µm are defined as dissolved solid [2]. Both types of solids are present in textile effluent and can cause damage to the aquatic system. Thus, the remediation of textile effluent is of paramount importance and necessary before discharging the wastewater into the environment. Several conventional methods such as chemical coagulation, oxidation and flotation have been implemented for the removal of contaminants from waste water [4-6].

Filtration is a potentially simpler and easier method for wastewater remediation compared to the above methods, where the membrane separates dispersed particles from liquid [7-9]. Membranes are relatively thin, semi-permeable and flexible sheets, which are made by several processes and materials to produce different structures. Generally, the porosity of the membrane used in an application depends upon the separation process and are categorized into microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) [10, 11].

The application of membranes as a filter medium for textile effluent has been reported by a number of studies [12, 13]. Fersi *et al.* [12] reported that MF membranes have good performance for pre-filtering suspended solids from dyeing, whereas the NF membranes perform better removal of dissolved solids. Acaina-Mirande *et al*. [13] demonstrated that UF and NF membranes have successfully improved water quality by removing particles and organic compounds from the textile finishing effluent [13].

However the search of new membrane technology for more effective filtration is ongoing. A simple and versatile method to fabricate filter media is by a technique known as electrospinning [11-13]. Electrospun nanofibrous membrane has been reported to provide good properties for filtration applications. Mahapatra *et al*. [14] reported that the electrospun $Fe^{2}O^{3}$–$Al^{2}O^{3}$ nanocomposite fibers have successful removed heavy metal ions from aqueous solutions. Gopal *et al.* [15, 16] have observed that electrospun PVDF nanofibrous membranes are able to remove 5-10µm particles without damaging the membrane structure or surface.

The unique properties of electrospun membranes for liquid filtration are well recognized. However, the use of electrospun nanofibre membrane for the removal of pigment from textile wastewater has not been reported. Therefore, the objectives of the study is to investigate the feasibility of electrospun nanofibre membrane to remove suspended solid from textile effluent and also to compare the filtration efficiency with commercial membrane used for the removal of suspended solid from wastewater.

Materials and methods

Membrane formation

The electrospinning conditions for polyamide 6 (Nylon 6, Ultramide BS700 have been described elsewhere [17]. The electrospun Nylon 6 nanofibre membrane was electrospun for 22 hours onto an aluminium foil placed on a rotating drum (Ø95mm).The drum surface speed was approximately 30mm/s (Figure 1). The membrane was dried at room temperature for 24 hours.

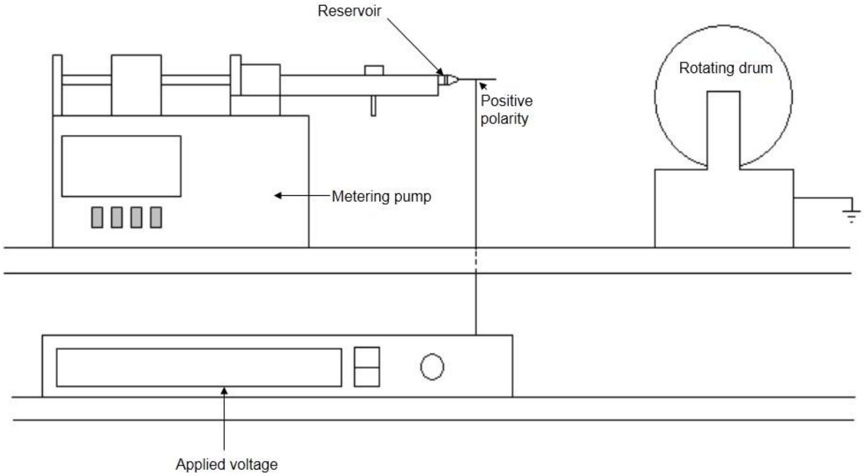


Figure1: Schematic diagram of electrospinning system.

Membrane characterization

The membrane morphologies were characterized using a Philips XL30 Field Emission Scanning Electron Microscope (FESEM). The samples were iridium coated at 50 to 60mA for 10 to 15 seconds. Nanofibre diameter was determined by taking the average of fifty measurements at random.

Membrane pore size

The pore diameters of electrospun Nylon 6 nanofibre membrane and commercial membrane were measured using a capillary flow porometry (Porous Materials Inc.) with the lower limit of approximately 0.03µm. Each membrane was tested under both dry and wet conditions. For wet conditions, the membrane was saturated with a defined surface tension liquid using galwick (γ= 15.6 dynes/cm) as a wetting agent. The membrane was pressurized with N_2 at 200psi. The pore diameter and distribution were derived from differences between the dry and wet curves. Details about capillary flow porometry can be found elsewhere [18-20].

Pre-filtered Effluent

Textile wastewater was supplied by Dyechem Industries Pty Ltd, Australia. It was taken directly at the end of a pigment padding process. The pigment contains pigment, acrylic binder and waxes. The concentrated effluent was diluted with deionised water, 10:1 (deionised water:pigment ratio) and pre-filtered using a cellulose filter paper (Whatman, Grade 1, particle size retention approximately 11µm) to remove the larger solids.

Membrane filtration

A 30ml of pre-filtered effluent was filtered using a circular electrospun Nylon 6 nanofibre membranes and a standard commercial nylon filter membrane (GE Water & Process Technologies), respectively. Each membrane has a diameter of 54mm. The test was carried out using a simple laboratory filtration system shown in Figure 2. The pressure used for the filtration was 20psi. Pressure higher than 20psi was not studied because some membranes were damaged during the test. The separation time was recorded using a HP webcam. The permeate flux was measured and then compared to the flux of commercial nylon membrane.

Characterization of pre-filtered effluent and permeate.

Samples of pre-filtered effluent and permeate (after membrane filtration) were measured for turbidity (or clarity) and chemical oxygen demand (COD). The results were also compared to the permeate from the commercial nylon filter membrane. The turbidity of permeate was measured using a turbidimeter (HACH 2100). For COD, 20µl of permeate was pipetted into COD reagent (solution range 0 to 1500ppm from HACH company) and heated at 150°C for

3 hours in a COD reactor (HACH). The solutions were analysed using a spectrophotometer (HACH DR/4000) and the results were recorded and compared with pre-filtered effluent values.

The percentage of turbidity (%) and COD reduction (%) were calculated using the equation of separation factor, which can be calculated using equation (1) [15, 16],

$$SF = \left[1 - \frac{C_{permeate}}{C_{feed}}\right] \times 100\% \qquad (1)$$

where SF is the separation factor (%), $C_{permeate}$ and C_{feed} are the permeate concentration and feed (pre-filtered effluent) concentration, respectively. The permeate and feed (pre-filtered effluent) concentrations are usually measured using UV-visible spectrophotometry. However, solid particles interfere with the spectroscopic measurements. Thus, the turbidity values (NTU) and COD (mg/L) were extrapolated to determine the separation factor (equation 1).

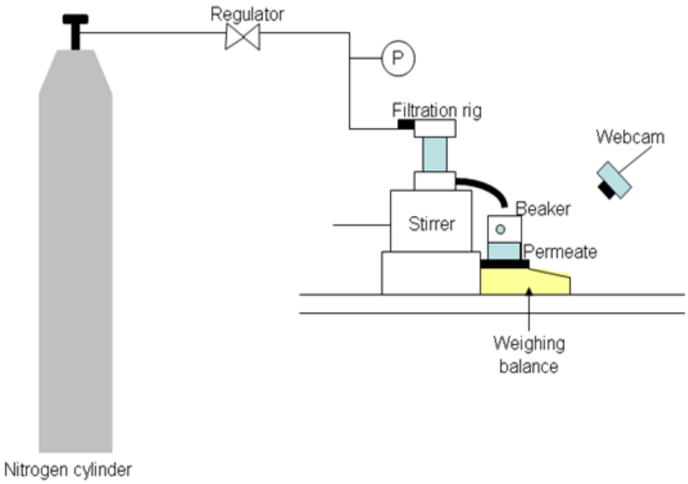
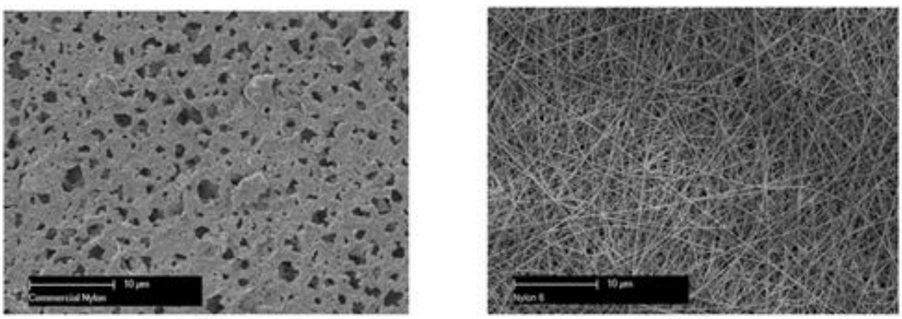


Figure 2 : Schematic diagrams for filtration systems.

Results and Discussion

Membrane characterization

As shown in Figures 3(a-b), the commercial and electrospun Nylon 6 membranes have different morphologies. The commercial Nylon membrane has porous structure, whereas the electrospun Nylon 6 nanofibre membrane has fibrous structure. In electrospinning process, an electrically charged jet of the polymer solution is accelerated and deposited onto a collector to form nanofibres. The accumulation of these nanofibres forms porous and fibrous membrane known as electrospun nanofibre membrane. In Figure 3 (b), the average fibre diameter of the electrospun Nylon 6 nanofibres is approximately 109 ± 0.32 nm.

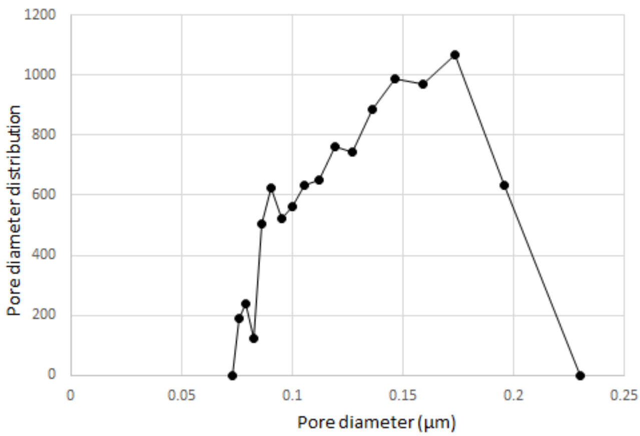


(a) (b)

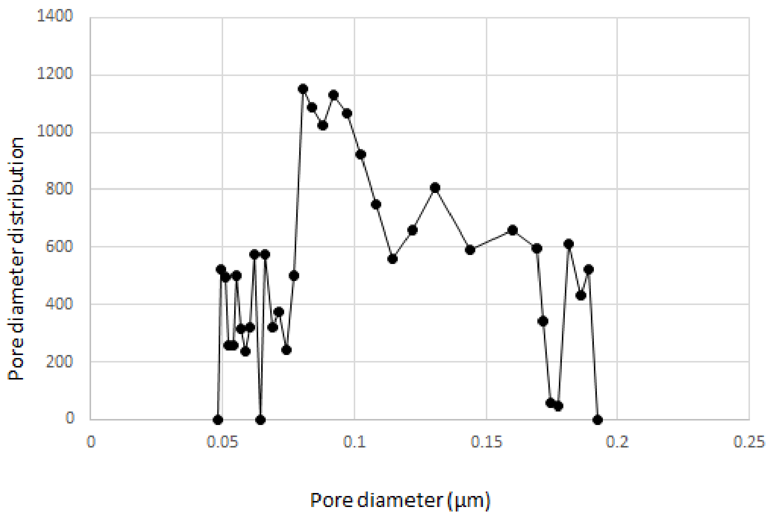
Figure 3 : SEM images of membranes, a) Commercial Nylon and b) electrospun Nylon nanofibe.

Figures 4 (a-b) illustrate pore diameter for commercial Nylon and electrospun Nylon 6 nanofibre membrane, respectively. In the product specification, the pore diameter of commercial Nylon membrane was reported to be 0.45µm. However, our measurements indicate a spread of pore diameters ranging from 0.08 to 0.19µm.

For electrospun Nylon 6 nanofibre membrane, the deposition of fine fibre diameter of electrospun Nylon 6 nanofibres has resulted in smaller pore diameter ranging from 0.05 to 0.19µm.



(a)



(b)

Figure 4 : Pore diameter of membranes. a) Commercial Nylon and b) electrospun Nylon 6 nanofibe.

Flux of membranes.

Figure 5 depicts the permeate fluxes of pre-filtered textile effluent passing through a commercial Nylon membrane and electrospun Nylon 6 nanofibre membrane,respectively. The commercial Nylon membrane had a greater flux than the electrospun Nylon 6 nanofibre membrane because of the larger pore diameter of the commercial membrane. The larger pores of the commercial membrane are clearly evident from the SEM (Figure 6a). A cloudy permeate was obtained after the filtration, indicating that some suspended solid particles passed through the larger pores of the commercial membrane. This explains the higher flux through the commercial membrane compared to the electrospun Nylon 6 nanofibre membrane.

The electrospun Nylon 6 nanofibre membrane exhibits lower flux as compared to the commercial Nylon membrane (Figure 5). This is probably due to membrane fouling, where a suspended solid cake forms on the membrane surface (Figure 6b). Fouling is defined as blockage due to particles caught in membrane or filter media [11]. As the feed flows through the membrane, the solids start to accumulate into the membrane pores causing blockage to the flow. This blockage has resulted in the reduction of the permeate flux as shown in Figure 5. Due to the fouling, the total filtration time for 30ml effluent was approximately 22 minutes which was 14 minutes slower than the commercial membrane.

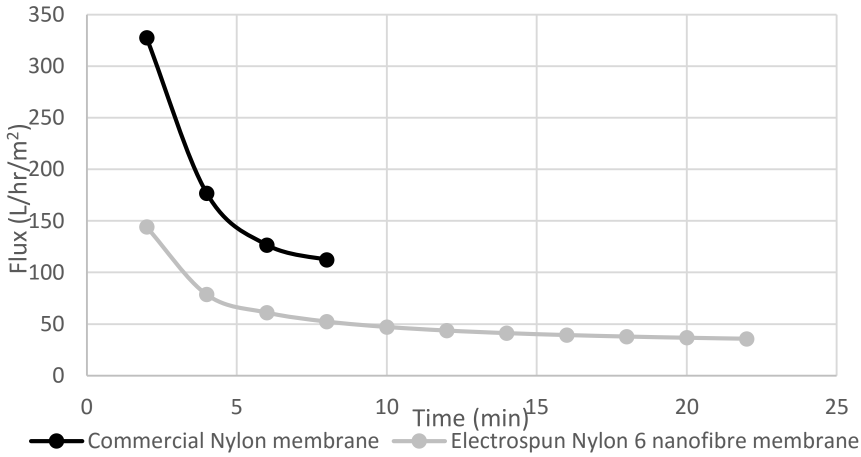


Figure 5 : Plots of fluxes for commercial and electrospun Nylon 6 nanofibre membranes.

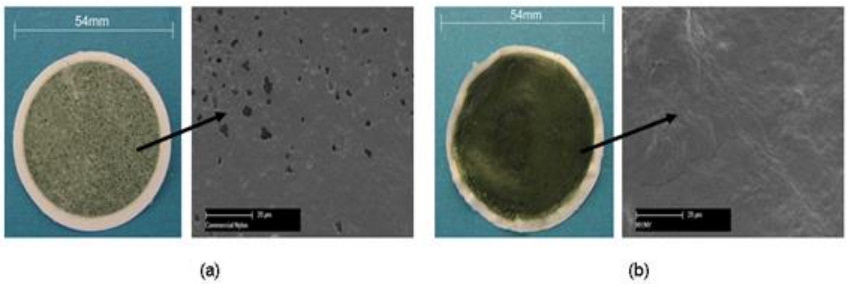


Figure 6 : Photographs and SEM images of typical membranes after filtration. a) commercial Nylon and b) electrospun Nylon 6 nanofibre membrane, respectively.

Table 1 : Properties of pre-filtered samples and permeate for commercial Nylon and electrospun Nylon 6 nanofibre membrane, respectively.

Parameter	Feed		Permeate	
	Raw pigment	Pre-filtered pigment	Commercial Nylon membrane	Electrospun Nylon 6 nanofibre membrane
Applied pressure (psi)	NA	NA	20	20
Turbidity (NTU)	>4000	183 ± 0.1	123 ± 0.3	1.97 ± 0.2
Turbidity (%)	NA	NA	33	99
COD (mg/L)	Off scale	2370 ± 1.0	2000 ± 3.0	840 ± 3.5
COD reduction (%)	NA	NA	16	64

Properties of pre-filtered effluent and permeate

The properties of pre-filtered effluent and permeate are shown in Table 1. The commercial Nylon can only remove 33 % of suspended solids from the pre-filtered effluent. The presence of a large pore diameter of the commercial membrane allows more suspended solids to pass though the membrane, resulting in a cloudy permeate as shown in Figure 7. In addition, the COD reduction was relatively low approximately 16% as compared the electrospun Nylon 6 nanofibre membrane.

Although the electrospun Nylon 6 nanofibre membrane exhibited lower flux than the commercial membrane, this membrane gave the best removal of suspended solids with approximately 99%. As a result, a clear permeate was obtained after the filtration (Figure 7). The COD value was also reduced up to 64% indicating that the electrospun nanofibrous membrane has the ability to reduce the chemical oxygen demand (COD) from textile wastewater.

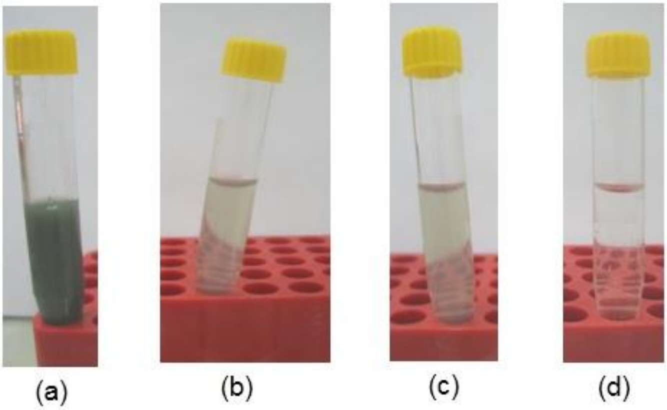


Figure 7 : Photographs showing the clarity of: a) raw effluent, b) feed (pre-filtered effluent) and permeate using: c) commercial Nylon and d) electrospun Nylon 6 nanofibre membrane, respectively.

Conclusion

This study has demonstrated the feasibility of electrospun Nylon 6 nanofibre membrane to remove suspended solids from textile wastewater using a lab scale filtration system. The electrospun Nylon 6 nanofibre membrane improved the effluent clarity by 99% and reduced the COD values by 64% as compared to a commercial Nylon membrane with a 33% reduction in turbidity and a 16% reduction in chemical oxygen demand (COD). Membrane fouling due to the formation of effluent cake is one of the drawbacks for the electrospun Nylon 6 nanofibre membrane. Therefore, more work is required to fully understand the mechanism for the prevention of fouling using electrospun nanofibre membrane while achieving high quality remediated water.

Acknowledgment

The authors would like to acknowledge the Institute of Research Management and Innovation (IRMI), Universiti Teknologi MARA (UiTM) for providing research funding under the LESTARI Grant (Project Number: 600-RMI/DANA 5/3/LESTARI (65/2015)). The authors are also thankful to Dyechem Industries Pty Ltd, Australia for supplying the textile wastewater, research groups from CSIRO for their assistance of feed and permeate analysis and Shane Cox from UNSW.

References

1. S. Judd and B. Jefferson, The Textile Industry, *Membranes for industrial wastewater recovery and re-use*, 1st ed. (Elsevier Science, UK, 2003), pp 132-149.
2. F. Woodard. Wastes from Industries, *Industrial waste treatment handbook*. (Butterworth-Heinemann, USA, 2006), pp 61-144.
3. M. Chandramowleeswaran and K. Palanivelu. " Treatability studies on textile effluent for total dissolved solids reduction using electrodialysis," *Desalination* 201(1-3), 164-174 (2006).
4. T. Xiaomin, Z. Huaili, T. Houkai , S. Yongjun, G. Jinsong, X. Wanying, Y. Qingqing and C. Wei." Chemical coagulation process for the removal of heavy metals from water: a review,"*Desalination* 57 (4), 1733-1748 (2014)
5. O. Mehmet A and A. Jean-Jacques. "Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review," *Critical Reviews in Environmental Science and Technology* 44 (23), 2577-2641 (2014)
6. A.Z Habis, I. Khalid A and A-S. Khaleel A." Removal of heavy metals from wastewater by economical polymeric collectors using dissolved air flotation process," *Journal of Water Process Engineering* 8, 19-27 (2015)
7. Y. Heyang and H. Zhen, "Integrating membrane filtration into bioelectrochemical systems as next generation energy-efficient wastewater treatment technologies for water reclamation: A review," *Bioresource Technology* 195, 202-209 (2015)
8. S.J Russell, Modelling Filtration Properties. *Handbook of nonwovens*. (Woodhead Publishing Limited, UK, 2007). pp 48-49.
9. O.Ruth, H. Daphne , M. Noemí, G. Antonio, N. Carlos and B. Ángeles. "Application of Multi-Barrier Membrane Filtration Technologies to Reclaim Municipal Wastewater for Industrial Use,"*Journal Separation & Purification Reviews* 43 (4), 263-310 (2014)

10. D. Purchas and K. Sutherland. Membranes. *Handbook of filter media*, 2nd ed (Elsevier Science, UK, 2002). pp 307-354.
11. M. Mulder. Characterisation of Membranes. *Basic principles of membrane technology* (Springer, Netherlands,1996). pp 157-209.
12. C. Fersi, L. Gzara and M. Dhahbi."Treatment of Textile Effluents by Membrane Technologies," *Desalination* 185(1), 399-409 (2005).
13. M. Alcaina-Miranda, S. Barredo-Damas, A. Bes-Pia, M. Iborra-Clar, A. Iborra-Clar and J. Mendoza-Roca. "Nanofiltration as a Final Step Towards Textile Wastewater reclamation," *Desalination* 240(1-3), 290-297 (2009).
14. A. Mahapatra, B.G Mishra and G. Hota. "Electrospun Fe^2O^3–Al^2O^3 nanocomposite fibers as efficient adsorbent for removal of heavy metal ions from aqueous solution," *Journal of Hazardous Materials* 258-259, 116-123 (2013)
15. R. Gopal, S. Kaur, Z. Ma, C. Chan, S. Ramakrishna and T. Matsuura."Electrospun nanofibrous filtration membrane," *Journal of Membrane Science*, 281(1-2), 581-586 (2006).
16. Gopal R, Kaur S, Feng C, Chan C, Ramakrishna S, Tabe S, and Matsuura T. "Electrospun nanofibrous polysulfone membranes as pre-filters: Particulate removal," *Journal of Membrane Science*, 289(1-2), 210-219 (2007).
17. N. Affandi, Studies on fabrication, morphology and performances of bi-layer electrospun nanofibre membrane, *Phd* Thesis, RMIT Univesity, 2010.
18. D. Li, M. Frey and Y. Joo. "Characterization of nanofibrous membranes with capillary flow porometry,". *Journal of Membrane Science*, 286(1-2), 104-114 (2006).
19. A. Jena and K. Gupta. " Liquid extrusion techniques for pore structure evaluation of nonwovens," *International Nonwovens Journal*, 45-53 (2003).
20. A. Jena and K. Gupta."Pore volume of nanofiber nonwovens," *Int Nonwovens J*, 14, 25-30 (2005).