



PVDF Electrospun Nanofiber Membranes for Microfiltration: The Effect of Pore Size and Thickness on Membrane Performance

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Abstract

Microfiltration membranes are needed in wastewater treatment, water purification and concentration processes. To separate microorganisms and suspended particles from process liquid, a contaminated fluid, especially water, is passed through a porous membrane. Electrospun nanofiber membranes could be used for this aim with their nanoscale fibers, small pore size, low weight and high permeability. The main purpose of this study is to show the relationship between the average fiber diameter and thickness of the PVDF nanofiber membrane and the pore size and liquid filtration efficiency. PVDF is a widely used polymer in water treatment processes. It is highly non-reactive thermoplastic fluoropolymer with outstanding physical and chemical properties. In this study, PVDF nanofibers were produced from 12, 14 and 16% (w/v) polymer solutions by electrospinning method to achieve three different mean diameters. 15 min, 30 min, 60 min, 3h and 5h of production periods were used for producing various thicknesses. According to pore size measurements, the differences in mean flow pore size (MFP) of 16PVDF and 14PVDF nanofiber membranes were not distinct. However, due to thin nanofiber diameter (278.58 nm) and high amount of nanofibers, biggest pore size (FBP) of 12PVDF-5h was the smallest. There was also significant difference between 12PVDF-5h and 12PVDF-3h, and FBP of these two membranes were smaller than other three 12PVDF nanofiber membranes. Liquid filtration property of produced electrospun PVDF nanofibers were evaluated by turbidity rejection of a kaolin solution. In correlation with the pore size results it was seen that best turbidity rejection percent was belonging to 12PVDF-5h and worst was belonging to 16PVDF-15min nanofiber membranes. Nevertheless, all of the produced electrospun PVDF nanofiber membranes can be effectively used to remove contaminants from wastewater at a relatively low cost.

Keywords: Nanofibers, Liquid Filtration, Pore Size, Turbidity.

Mikrofiltrasyon için elektrolif çekim yöntemi ile üretilmiş PVDF nanolifli membranlar: Gözenek boyutu ve kalınlığının membran performansına etkisi

Öz

Atık su arıtma, su saflaştırma ve konsantrasyon artırma işlemlerinde mikrofiltrasyon membranlarına ihtiyaç duyulmaktadır. Mikroorganizmaları ve askıda bulunan parçacıkları işlem sıvısından ayırmak için, kontamine sıvı, özellikle su, gözenekli bir membrandan geçirilir. Bu amaçla, elektrolif çekim yöntemi ile üretilmiş nanolifli membranların nano boyuttaki lifleri, küçük gözenek boyutları, düşük ağırlık ve yüksek geçirgenlik ile kullanılabilirler. Bu çalışmanın esas amacı ortalama lif çapı, PVDF nanolifli membranların kalınlıkları ve gözenek boyutlarının sıvı filtrasyon verimleri arasındaki ilişkiyi göstermektir. PVDF atık su arıtma proseslerinde yaygın olarak kullanılan bir polimerdir. Fiziksel ve kimyasal özellikleri ile dikkat çeken reaktif olmayan termoplastik floropolimerdir.- Bu çalışmada, üç farklı lif çapı elde etmek için %12, 14 ve 6 (w/v) PVDF çözelti konsantrasyonu ile nanolifler elektrolif

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çekim yöntemi ile üretilmiştir. Çeşitli kalınlıkların elde edilmesi amacı ile 15 dakika, 30 dakika, 60 dakika, 3 saat ve 5 saat üretim süreleri kullanılmıştır. Gözeneklilik ölçüm sonuçlarına göre, 14PVDF ve 16PVDF nanolifli membranlarının ortalama gözenek boyutları arasındaki büyük bir fark yoktur. Ancak, ince nanolif çapı (278.58 nm) ve fazla miktardaki nanolif nedeni ile, 12PVDF-5h nanolifli membranların en büyük gözenek boyutu (FBP) diğerlerine göre daha düşük olmuştur. Ayrıca 12PVDF-5h ve 12PVDF-3h arasında anlamlı bir farklılık gözlenmiştir ve bu iki membrana ait FBP diğer üç PVDF nanolifli membrandan daha küçük olmuştur. Üretilen PVDF nanoliflerin sıvı filtrasyon özellikleri, hazırlanan kaolin çözeltisinin bulanıklığının giderilmesi ile değerlendirilmiştir. Gözenek boyutları da göz önünde bulundurulduğunda, en iyi bulanıklık giderilme %'sinin 12PVDF-5h'e, en kötü bulanıklık giderilmesinin ise 16PVDF-15min nanolifli membranlara ait olduğu görülmüştür. Bununla birlikte, üretilen PVDF nanolifli membranların tümü, nispeten daha düşük bir maliyetle atık sudan kirleticilerin giderilmesi amacı ile etkili bir şekilde kullanılabilecek filtrasyon performansına sahiptir.

Anahtar Kelimeler: Nanolifler, Sıvı Filtrasyonu, Gözenek Boyutu, Bulanıklık.

1. Introduction

Microfiltration (MF) membranes are used to filter particulates from liquids (Baker, 2004). Most importantly, these membranes are much needed in wastewater treatment, water purification and concentration processes and are highly utilized (Renuga Gopal, Satinderpal Kaur, Zuwei Ma, Casey Chan, Seeram Ramakrishna, 2006). In MF, to separate microorganisms and suspended particles from process liquid, a contaminated fluid, especially water, is passed through a porous membrane. The most important property characterizing a porous membrane for MF applications is the pore diameter or pore size (Baker, 2004). Size of the particle that is capable of penetrating the medium relates to the pore size which mainly effects the efficiency of the filtration medium (Hutten & Wadsworth, 2007) and fine fibers of low diameters give small pore size, high density and high filtration efficiency to filter media. Electrospun nanofiber membranes could be the good candidates for MF with their nanoscale fibers, small pore size, low weight and high permeability (Eichhorn & Sampson, 2005). These membranes also offer unique properties like high specific surface area, and good interconnectivity of pores (Letizia & Chiara, 2018).

In electrospinning, pores are created mainly by the entanglement of nanofibers and they are highly interconnected. Therefore, a nanofiber membrane or a composite structure containing a nanofiber layer could find use in MF applications (Hutten & Wadsworth, 2007). Moreover, these membranes can overcome the low-flux limitation of conventional porous membranes, due to their high porosity and high surface area-to-volume ratio. Since water molecules can move with low hydraulic resistance through the membrane, the high porosity is beneficial for improving the permeation flux (Letizia & Chiara, 2018). The diameter of the electrospun nanofibers could be modulated by electrospinning conditions such as polymer concentration, tip-to collector distance, applied voltage along with the surface-to-volume ratio (Letizia & Chiara, 2018).

Gopal et al. electrospun polyvinylidene fluoride (PVDF) nanofibers into membranes and characterized their structural properties to relate membrane performance and their separation properties. 1, 5 and 10 μm polystyrene particles were used for separation process. They found PVDF membranes were successful in rejecting approximately 90% of the micro-particles from solution (Renuga Gopal, Satinderpal Kaur, Zuwei Ma, Casey Chan, Seeram Ramakrishna, 2006). Bae et al. fabricated polyethersulfone (PES) nanofiber membranes for water purification. They improved the mechanical properties and surface roughness of the membranes by the solvent-induced fusion and were able to get clean water with regeneration ability (Bae, Baek, & Choi, 2017a). At their another work, they developed piezoelectric PVDF nanofiber membrane with antifouling ability through the vibrational inducement for water treatment applications (Bae, Baek, & Choi, 2017b). Jang et al. prepared PVDF/graphene oxide (GO) hybrid nanofiber membrane for water treatment application. They were able to control the pore-diameters by ~ 0.2 micron with narrow distribution and produced PVDF/GO nanofiber composite membranes. These membranes showed hydrophilic character and achieved high pure water flux results (Jang, Yun, Jeon, & Byun, 2015).

Apart from these studies, the main purpose of this study is to show the relationship between the average fiber diameter and thickness of the PVDF nanofiber membrane and the pore size and liquid filtration efficiency. PVDF is a very hydrophobic polymer with high thermal and chemical resistance, and good mechanical properties (Li & Liu, 2014; Yeow, Liu, & Li, 2004). It is highly non-reactive thermoplastic fluoropolymer (Jang et al., 2015). PVDF is also widely used polymer in ultrafiltration, microfiltration, membrane distillation and some other membrane processes (Cheng et al., 2017; Cui, Drioli, & Moo, 2014; F. Liu, Hashim, Liu, Abed, & Li, 2011) such as affinity membranes. Some other examples of the applications of PVDF nanofibers are nanopressure sensors (Garain, Jana, Sinha, & Mandal, 2016; Mandal, Yoon, & Kim, 2011), polymer electrolytes or separators (Choi et al., 2004), proton exchange membranes in fuel cells (Li & Liu, 2014), and thin film composite membranes for forward osmosis (Huang, Arena, & McCutcheon, 2016). In this study, 12, 14 and 16% (w/v) PVDF nanofibers were produced by laboratory scale electrospinning method to achieve three different mean diameters and the pore size. Liquid filtration property of produced electrospun PVDF nanofibers were evaluated by turbidity rejection of a kaolin solution (Isoyama et al., 2017). Turbidity is a measure of the degree to which the water loses its transparency due to the presence of suspended particulates (Lenntech Water treatment & purification, 2019). Kaolin has been commonly utilized as a turbidity standard solution for a long time. Since kaolin is a clay mineral, it is free of anything harmful, is a low-cost material, and is easy to handle (Isoyama et al., 2017). Pore size comparison was also conducted which were directly related to filtration performance (Jang et al., 2015). Pore size measurements of PVDF nanofiber membranes were measured as maximum pore size (often

referred to as first bubble point (FPS), mean flow pore size (MFP) and smallest pore size (SPS). 15 min, 30 min, 60 min, 3h and 5h of production periods were used for producing various thicknesses in order to evaluate the change in pore size.

2. Material and Method

2.1. Materials

PVDF (Kynar 761A) was provided from Abalioğlu Teknoloji as a gift. Kaolin, Acetone, dimethylacetamide (DMAc) and tetraethyl ammonium bromide (TEAB) were purchased from Sigma Aldrich Company. Properties of PVDF powder is given in Table 1.

Table 1. Properties of PVDF (Kynar 761A) (Kynar & Pvd, 2014)

KYNAR® PVDF Grade	Fabrication	Melt Viscosity Method (ASTM D3835)	Melt Flow Rate (ASTM D1238)	Melting Point
Kynar 761A (Powder)	Binders, Additives, etc	. 30.5 - 36.5	0.5 - 3.5	165 - 172°C

2.2. The preparation of electrospinning solutions

Homogeneous PVDF solutions were prepared by dissolving 12, 14 and 16% (w/v) of PVDF powder in acetone/ Dimethylacetamide (DMAc) (1:4 v/v) and 0,015 g tetraethylammonium bromide (TEAB) was added to each 30 ml PVDF solution and stirred for 3h. Electrospun PVDF solutions were coded with 12PVDF, 14PVDF and 16PVDF along with their collection periods (15min, 30min, 60min, 3h and 5h).

2.3. Electrospinning

Electrospinning of the polymer solutions was carried out by a set-up consisting of a syringe (10 mL) with a stainless steel needle (22 gauges, and flat tip), a ground electrode and a high voltage supply (Simco, MP Series CM5 30 P, Charging Generator Output 30 kV DC). 12PVDF, 14PVDF and 16PVDF solutions were electrospun at a voltage of 15 kV, a tip-to-collector distance of 15 cm with a feeding rate of 0.5 ml/h. A grounded rotating metal drum collector covered by a 20 g/m² spunbond polypropylene nonwoven fabric was used as deposition material. Each polymer solution was electrospun for 15min, 30min, 60min, 3h and 5h. All electrospinning experiments were performed at room temperature (22±2 °C), where the relative humidity was 22-40%.

2.4. SEM analysis

The morphology of the PVDF nanofibers was analyzed by a scanning electron microscope (SEM; Phenom G2 pro scanning electron microscope). The electrospun PVDF nanofibers were sputtered by Quorum Q150R S ion sputtering device with a thin layer of gold prior to SEM observation.

2.5. Measurement of thickness, weight per square meter and fiber diameters

The thicknesses of the PVDF nanofiber mats were measured by Mitutoyo digital micrometer at 0,01 mm accuracy. Weights of nanofiber mats were calculated from the weights of small rectangular pieces. 8 and 3 measurements were carried out from the different parts of each sample for thickness and weights, respectively. The mean diameter of the resultant fibers was calculated from measurements on SEM images of 10000× magnification by using Image J program. Approximately 50 measurements were carried out from the different parts of each sample. All thickness, weights and fiber diameter measurements were expressed as mean ± SD.

2.6. Pore size measurements

The pore size and pore size distribution of the PVDF nanofiber membranes were measured by capillary flow porometry (Porolux 1000- Germany). All samples were wetted by Galpore 16 (a wetting liquid with a low surface tension of 16 dyne/cm) and tested. The mean pore size of the membranes was calculated from wet, dry and half dry conditions. MFP, FBP, SPS and pore size distribution (PSD) were measured by wet-up/dry-up method and the analysis was done by using Automated Capillary Flow Porometer system software according to the ASTM F316-03 (2011) (ASTM International, 2014). Pore size measurements were expressed as mean ± SD.

2.7. Evaluation of the liquid filtration performance

Filtration performance was evaluated by turbidity test. It was performed to observe the rejection of particulates and changes in the turbidity. Sizes of kaolin particles were measured by Malvern Hydro 2000S Master Sizer v3.50, Malvern Instruments Ltd. Turbidity rejection of the PVDF nanofiber membranes were tested using a dead-end filtration cell, Amicon® stirred cell (UFSC05001) (Fig. 1) (Bae, Baek, & Choi, 2016). The cell has a volume of 50mL and an effective membrane filtration area of 44.5 mm². The sample in the filtration cell was stirred with 200 rpm by using a magnetic stirrer, in order to avoid the settlement. A Delta OHM Turbidity meter (Italy) was used to measure the contaminant concentration of the feed solution and the permeation. A suspension of kaolin particles with a diameter of 3.79 µm was diluted in water to prepare a solution of 100 nephelometric turbidity units (ntu) turbidity to serve as the feed solution. The test was carried out at 1 bar pressure. For each nanofiber membrane 50 mL kaolin solution (100 ntu) was used. The turbidity rejection rate was calculated according to Eq. (1)(Bae et al., 2016; Y. Liu, Wang, Ma, Hsiao, & Chu, 2013):

$$\text{Rejection rate (\%)} = \left(1 - \frac{C_f}{C_i}\right) \times 100 \quad (1)$$

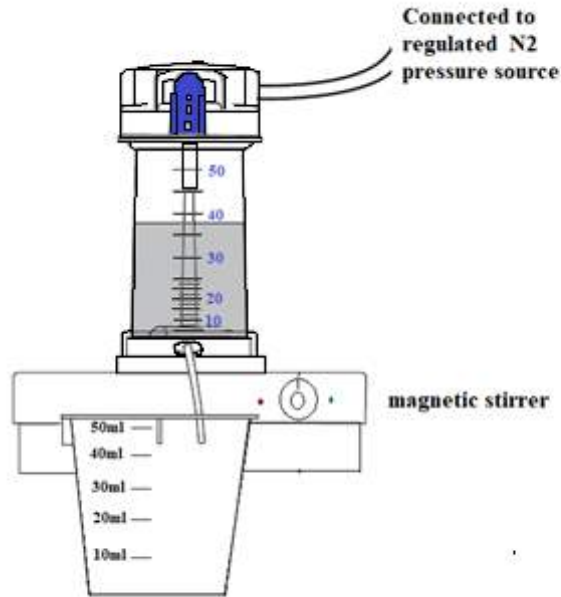


Figure. 1 Schematic diagram of a dead-end-cell device (Amicon® Stirred Cell, Merck (EMD Millipore Corporation, 2015).

3. Results and Discussion

3.1. Morphology of produced PVDF nanofiber membranes

The surface morphology of the PVDF nanofiber membranes were investigated by SEM analysis. SEM images of 12PVDF, 14PVDF, 16PVDF nanofibers were given in Fig. 2 (a), (b) and (c), respectively. Bead free, uniform PVDF nanofibers were produced. Mean nanofiber diameters were given in Table 2. and were about 278.58, 458.77 and 870.358 nm for 12PVDF, 14PVDF, 16PVDF, respectively. Differences in the mean fiber diameters were analyzed by one-way ANOVA followed by Tukey HSD test for pairwise comparison. It was observed that, there was a statistically significant difference between each polymer concentration ($p < 0.05$). Because of the decreasing polymer concentration mean fiber diameter decreased significantly.

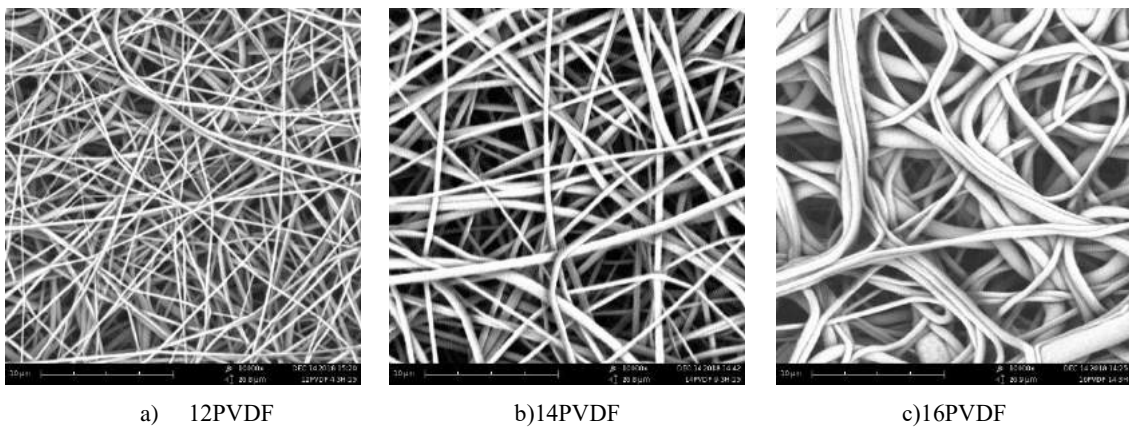


Figure 2. SEM images of (a) 12 PVDF, (b) 14 PVDF and (c) 16 PVDF nanofibers

Table 2. lists the mean thickness and mean weight of 12PVDF, 14PVDF, 16PVDF nanofibers based on collection period. Collection period had an effect on thicknesses and weights of nanofiber membranes. Because of the higher polymer concentration, 16PVDF

nanofiber membranes were thicker and heavier than 14PVDF, and 14PVDF nanofiber membranes were thicker than 12PVDF nanofiber membranes. Weight of lighter nanofiber membranes of 15 min collected PVDF nanofibers were ranged 2.86 to 2.13 g/m². Significant differences occurred after 3h, and long collection periods significantly increased the weights of the membranes. The weights of the 5h collected membranes were ranged 35.60 to 51.62 g/m².

Table 2. Thickness, Weight and Fiber Diameter of the electrospun 12PVDF, 14PVDF, 16PVDF nanofibers

	Mean Thickness (mm) ±SD	Mean Weight (g/m ²) ±SD	Mean Nanofiber Diameter (nm) ±SD
12PVDF-15min	<0.01	2.16 ± 0.82	
12PVDF-30min	0.024 ± 0.014	6.52 ± 1.79	
12PVDF-60min	0.035 ± 0.019	11.68 ± 0.96	278.58 ± 111.13
12PVDF-3h	0.055 ± 0.019	28.13 ± 4.30	
12PVDF-5h	0.070 ± 0.017	35.60 ± 0.67	
14PVDF-15min	<0.01	2.63 ± 1.78	
14PVDF-30min	0.030 ± 0.017	7.18 ± 2.59	
14PVDF-60min	0.039 ± 0.015	9.17 ± 2.07	458.77 ± 155.15
14PVDF-3h	0.073 ± 0.021	28.82 ± 2.15	
14PVDF-5h	0.146 ± 0.026	47.20 ± 2.31	
16PVDF-15min	0.026 ± 0.019	2.86 ± 0.18	
16PVDF-30min	0.036 ± 0.014	8.64 ± 0.88	
16PVDF-60min	0.040 ± 0.013	13.95 ± 0.50	870.38 ± 391.16
16PVDF-3h	0.108 ± 0.025	32.58 ± 1.41	
16PVDF-5h	0.156 ± 0.022	51.62 ± 1.75	

3.2. Pore size analysis

Since the pores of nanofiber membranes are caused by the entanglement of the nanofibers, more nanofibers covering a specific area would result in narrower pore size distribution along with smaller pores when nanofiber diameter is constant (Y. Liu et al., 2013). However, membrane thickness may reach a level with the increase of the collection period which won't affect the pore size anymore. Thus, it is important to determine this level to avoid unnecessary extension of collection period in order to optimize the production speed.

The mean pore size (MFP) and pore size distribution are important parameters to determine the membrane arrestment capability [11, 13]. To compare the pore size of the 12PVDF, 14PVDF, 16PVDF nanofibers mats according to their collection period, pore size measurements were carried out by capillary flow porometry in triplicate. FBP, MFP and SPS were given for each PVDF nanofiber membrane in Table 3. Differences in FBP, MFP and SPS were analyzed by one-way ANOVA and followed by Tukey HSD pairwise comparison. Results were splitted by polymer concentration. For each PVDF concentration the difference in MFP was statistically important. According to the Tukey HSD post hoc tests, MFP of 12PVDF-5h and 12PVDF-3h were significantly smaller than 12PVDF-30min and 12PVDF-15min (p<0.05). However, for 16PVDF and 14PVDF nanofiber membranes the differences in MFP were not distinct. The differences in FBP of 12PVDF and 16PVDF nanofiber membranes were important but the differences in FBP of 14PVDF nanofibers were not statistically important, they were found to be in same subset. For 16PVDF nanofiber membranes FBP's were higher than 14PVDF and 12PVDF nanofibers and especially FBP of 16PVDF-15min nanofiber was higher than all other membranes due to

very thick nanofiber mean diameter (870.38 nm) and small amount of nanofiber collection. On contrary, due to thin nanofiber diameter (278.58 nm) and high amount of nanofibers, FBP of 12PVDF-5h was the smallest. There was also significant difference between 12PVDF-5h and 12PVDF-3h, and FBP of these two membranes were smaller than other three 12PVDF nanofiber membranes. It was also observed that for all three PVDF concentration collection period did not cause a significant effect in SPS ($p < 0.05$). It was decreased with decreasing polymer concentration but it was not affected from collection periods, they were all in same subsets ($p < 0.05$). For liquid filtration it is known that especially MFP plays a significant role along with FBP and it was seen that according to the pore size analysis, with finer nanofiber diameters it was possibly to achieve smaller pore size. In addition to this, the differences in FBP and MFP is more significant in case of finer fibers.

The membrane filtration process for the recycling of wastewater into drinking water is being used increasingly around the World. Water flows through semi-permeable and porous medias, often made of PVDF. The size of the pores of a commercial PVDF membrane is about 1 to 2 microns (Arkema Innovative Chemistry, 2019). It was seen that it is possible to achive 1 to 2 microns pore size with fine PVDF nanofiber membranes.

The pores of nanofiber membranes are caused by the entanglement of the nanofibers, thus more nanofibers that cover a specific area resulted in narrower pore size distribution along with smaller pores. However, membrane thickness may reach a level with the increase of the collection period which won't affect the pore size anymore.

Table 3. Pore size measurement of the electrospun 12PVDF, 14PVDF, 16PVDF according to collection period.

	First bubble point (FBP) $\mu\text{m} \pm \text{SD}$	Mean flow pore size (MFP) $\mu\text{m} \pm \text{SD}$	Smallest pore size (SPS) $\mu\text{m} \pm \text{SD}$
12PVDF-15min	4.11 \pm 0.26	2.45 \pm 0.01	1.35 \pm 0.06
12PVDF-30min	3.96 \pm 0.02	2.5 \pm 0.04	1.24 \pm 0.17
12PVDF-60min	3.71 \pm 0.15	2.02 \pm 0.09	1.21 \pm 0.03
12PVDF-3h	2.66 \pm 0.13	1.44 \pm 0.20	1.22 \pm 0.15
12PVDF-5h	1.96 \pm 0.07	1.81 \pm 0.09	1.39 \pm 0.02
14PVDF-15min	6.29 \pm 1.73	2.91 \pm 0.26	1.52 \pm 0.09
14PVDF-30min	4.91 \pm 1.03	2.70 \pm 0.37	1.37 \pm 0.07
14PVDF-60min	4.46 \pm 0.58	2.43 \pm 0.53	2.0 \pm 0.05
14PVDF-3h	3.59 \pm 0.15	1.77 \pm 0.02	1.33 \pm 0.19
14PVDF-5h	4.68 \pm 0.10	1.93 \pm 0.31	1.30 \pm 0.49
16PVDF-15min	16.80 \pm 1.71	5.88 \pm 1.26	4.52 \pm 2.0
16PVDF-30min	13.15 \pm 0.49	5.13 \pm 0.06	3.65 \pm 1.63
16PVDF-60min	11.05 \pm 1.20	4.18 \pm 0.29	3.62 \pm 0.77
16PVDF-3h	10.19 \pm 1.15	2.26 \pm 0.08	2.01 \pm 0.35
16PVDF-5h	7.50 \pm 0.47	3.58 \pm 0.34	2.92 \pm 0.33

3.3 Turbidity rejection results

For the rejection of turbidity test, 200 mg/L kaolin solution (100 ntu) was used, where distilled water showed a turbidity of 0.98 ntu. Fig. 3 shows the particle size distribution of kaolin for which specific surface area was 1.585 m²/g. By taking the average surface weighted mean of each of the trials, the mean particle size for the kaolin used was 3.79 μm . Filtrate rejection rate results of PVDF nanofiber membranes were shown in Fig. 4. Due to bigger pore sizes of 16PVDF nanofiber membranes, turbidity rejection percentage ranged between 80.08 to 90.19%. Higher rejection was achieved with 16PVDF-5h nanofiber membrane. For 15, 30 and 60min there were not any significant difference seen which was about 80%. Turbidity rejection percentages were ranged 89.50 to 95.87% for 14 PVDF nanofiber membranes. Similar to the 16 PVDF nanofiber membranes, turbidity rejection percentages of 14PVDF-15, 30 and

60min nanofibers membranes were very close (89.50, 89.89 and 90.73%, respectively). Higher turbidity rejection percentages were achieved with 12PVDF nanofibers due to its lowest nanofiber diameter which resulted smaller pore sizes. Even turbidity rejection of 12PVDF-15min nanofiber membranes was about 90.32% which is close to 14PVDF-60min and 16PVDF-5h. Highest rejection of 98.52% was belong to 12PVDF-5h nanofiber membrane. It showed a turbidity of 1.48 ntu which was very close to distilled water.

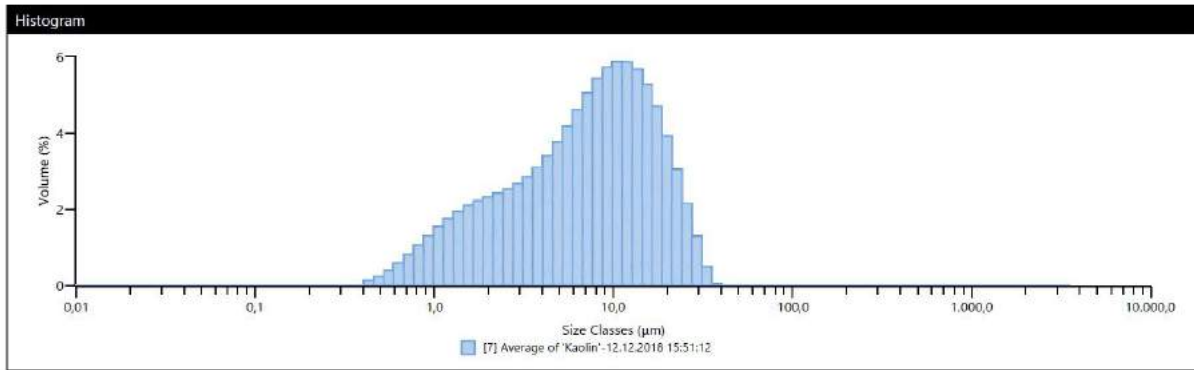


Figure 3. Particle size distribution of kaolin measured using Malvern Hydro 2000S Sizer

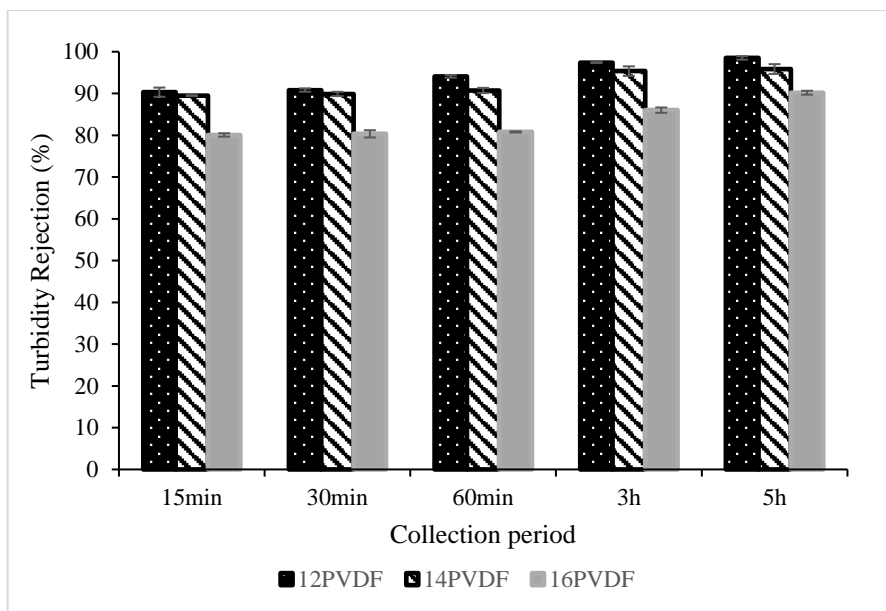


Figure 4. Turbidity Rejection (%) after filtration of 200 mg/L kaolin solution at 1 bar pressure

4. Conclusion

MF membranes are used to filter particulates from liquids and are needed in wastewater treatment, water purification and concentration processes. The most important property for characterizing a porous membrane for MF applications is the pore diameter or pore size. Fine fibers of low diameters give small pore size, high density and high filtration efficiency to filter media. Electrospun nanofiber membranes offer unique properties like high specific surface area, very small pores and good interconnectivity of pores. In this study, PVDF nanofiber membranes with three different mean fiber diameters were produced for MF applications. Decreasing polymer concentration significantly affected the mean fiber diameter and the mean nanofiber diameters were about 278.58, 458.77 and 870.358 nm for 12PVDF, 14PVDF, 16PVDF, respectively. Weight of lighter nanofiber membranes of 15 min collected PVDF nanofibers were ranged 2.86 to 2.13 g/m². Significant differences occurred after 3h, and long collection periods significantly increased the weights of the membranes. The weights of the 5h collected membranes were ranged between 35.60 to 51.62 g/m².

When all three polymer concentration taken into account, the biggest FBP was belong to 16PVDF-15min with 16.8 µm. But FBP of 14PVDF-30min, 14PVDF-60 14PVDF-3h and 14PVDF-5h, and all 12PVDF nanofiber membranes were in same subset which means the differences between the FBP these membranes were not significantly different. In case of MFP, there were five subsets, and the biggest MFPs were belonging to 16PVDF-15min and 16PVDF -30min with 5.88 and 5.13 µm, respectively. Except 16PVDF nanofiber membranes, MFP of 14PVDF and 12PVDF nanofiber membranes were not significantly different from each other. On the other hand, the results demonstrated that, when splitted to polymer concentration (16, 14 and 12%), for each PVDF concentration the difference in

MFP was statistically important. MFP of 12PVDF-5h was the smallest and the MFP of 16PVDF-15min nanofiber membrane was the highest.

In correlation with the pore size results it was seen that best turbidity rejection % was belonging to 12PVDF-5h and worst was belonging to 16PVDF-15min nanofiber membranes. Due to bigger pore sizes of 16PVDF nanofiber membranes, turbidity rejection percentage of 16PVDF nanofibers were ranged between 80.08 to 90.19%. Turbidity rejection percentages were ranged between 89.50 to 95.87% for 14PVDF nanofiber membranes and were ranged between 90.32 to 98.52% for 12PVDF nanofiber membranes. Highest rejection of 98.52% was belong to 12PVDF-5h nanofiber membrane. It showed a turbidity of 1.48 ntu which was very close to distilled water. Nevertheless, all of the produced electrospun PVDF nanofiber membranes can potentially be a candidate to effectively remove contaminants from waste water at a relatively low cost. However, when higher filtration efficiencies are required mean fiber diameters should be lower than ~280 nm.

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