

Optimizing Fabrication of Electrospinning Nanofiber Membranes for Water Filtration using Response Surface Methodology

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ABSTRACT

Nanofiber Polyethersulfone (PES) membrane fabrication using the electrospinning method incorporating dry/wet phase inversion was investigated. The electrospinning process is a straightforward and versatile method to produce one-dimensional nanostructures, especially nanofibers. The electrospun's outcome can be affected by the various process parameters and solution parameters, making it an interesting study subject and an opportunity for customized nanofiber membrane. In this work, the analysis includes dope formulation and electrospinning parameter influence to membrane morphology dimensional structure based on Scanning Electron Microscopy (SEM) and filtration capability. Fibrous membranes were electrospun at 1 to 3 ml/h feeding rate and at 12 to 25kV voltage rate in a fixed 10 to 12 cm distance between the filter membrane and the syringe needle tip. The PES dope solution with N-methyl-2-pyrrolidone (NMP) as solvent electrospun onto a wet filter base membrane (5A 90 mm Advantec Filter Paper) to refine the fabricated fibrous membrane and to induce the dry-wet phase inversion process. The results indicate that the PES fiber dimension reduced at a lower feeding rate and higher voltage rate. In terms of liquid separation performance, experimental results showed that pure water permeation flux was reduced with the increased flow spinning rate of 1 to 3ml/hr but triple times higher than the increased concentration PES formulation, even at higher voltage spinning. The electrospun performance of polyethersulfone was also explained using Response Surface Methodology (RSM). It focused on the polymer content, tip-to-collector distance, and flow rate parameters toward fiber diameter and contact angle. Among these factors, the effect of PES content (f -value = 65.87) was the most significant, followed by tip-to-collector distance (f -value = 11.26) and flow rate (f -value = 2.59).

Keywords: Polyethersulfone (PES), tight ultrafiltration, electrospinning, water separation performance Response-Surface Methodology (RSM).

INTRODUCTION

Membrane-based technology has been highlighted as a separation tool in the industrial process of biotechnology, the food industry, and water treatment (Baker 2004). As one of the most important approaches for filtered water purification and biomaterials concentration, ultrafiltration has its role in water filtrations (Zhao et al. 2012). In water treatment, ultrafiltration membrane could remove contaminants, such as colloids, proteins, polysaccharides, most bacteria, and certain viruses (Schoupe, 2010; Mary-Theresa et al. 2011). Realizing the potential of nano or tight ultrafiltration, a tremendous improvement was performed by many researchers in this membrane separation technology in terms of flux (Qin et al. 2005; Yoon et al. 2006; Qin et al. 2003), anti-fouling (Shen et al. 2003; Dai et al. 2008) and chlorine resistances (Han et al. 2013; Zhang et al. 2013).

For decades, membranes have been fabricated using various techniques such as drawing, template synthesis, phase separation, self-assembly, and electrospinning (Homaeigohar 2011). Electrospinning appears as a novel,

versatile, simple, cost-effective, and straightforward technique to produce fibers with diameters down to tens of nanometers from various materials such as polymers, metal oxides, and composites (Caratao et al. 2014). In this study, ultrafiltration membranes were prepared via the electrospinning method. Electrospinning is an efficient technique for the fabrication process to assemble fibrous polymer mats composed of fiber diameters less than 100 nm (Frenot et al. 2003). This fabrication method was discovered in the early 1930s. Then, Formhals develop his invention relating to the process and the apparatus to produce yarns and has patented in 1934 (Teo et al. 2006). Electrospinning setup has various parameters that can significantly influence fibers' production classified into the process, solution, and ambient constraints. Process parameters comprise applied voltage, tip to collector distance, and feeding rate. In contrast, solution parameter consists of viscosity, conductivity, volatility, molecular weight and surface tension whereas temperature and humidity are the ambient parameters (Subbiah et al. 2005; Bhardwaj et al. 2010).

Polymeric solution and melts are essential as they have a gigantic influence on producing the membranes (Zhou, 2007). PES and PES-based membranes have excellent characteristics in terms of high thermal, chemical resistance, hydrolytic stability, right mechanical property, and appropriate oxidative (Zhao et al. 2013; Homaeigohar et al. 2010). PES's outstanding features have made it one of the most significant polymeric materials and broadly used in membrane research as separation tools (Susanto et al. 2009; Xu et al. 2004; Ma et al. 2009; Wang et al. 2006).

PES solution in electrospinning has been conducted in numerous studies. Yoon et al. (2009) researched the formation of functional polyethersulfone electrospun membrane for water purification by mixed solvent and oxidation processes. They investigated two methods to enhance the mechanical properties and the hydrophilicity of the PES electrospun membrane. The first method used the mixed solvents (DMF/NMP) during electrospinning of PES and the second method was oxidizing the electrospun PES membrane by ammonium persulfate (APS). These steps successfully improved the influence of mixed solvents and oxidation processes on PES electrospun membranes' mechanical properties and hydrophilicity. However, these membranes were classified in the range of microfiltration membranes. Kwak et al. (2013) exposed that electrospun PES fibrous mats could be promising materials for ion-exchange by sulfonated the electrospun PES fibrous mats. Nakata et al. (2007) has studied the efficiency of PES electrospinning towards air filtration. The study was performed on the electrospinning PES behavior in four different solvents, namely m-cresol, N-N-Dimethylacetamide (DMAc), N-N Dimethylformamide (DMF), and 1-Methyl-2-Pyrrolidone (NMP). They found out that the PES/DMAc solution's electrospinning has achieved high-efficiency particulate air filter standards. They also conclude that the nano web's diameter is affected by the PES concentration, feeding rate of spinning dope, and needle collector distances.

Response surface methodology (RSM) is a useful tool in developing, improving, and optimizing the processes through a collection of statistical and mathematical techniques; particularly in the situations where multiple input variables may potentially influence the performance measure or quality characteristic of a product (Myers et al. 2009). Utilizing three-level designs such as Box-Behnken Design (BBD) allows the determination of optimum operation conditions (Bruns et al. 2006). The advantage of BBD is that all the factors are not simultaneously at the highest or the lowest levels. In this case, the extreme responses are at the vertices of the cube.

This work evaluates and compares the effect of electrospinning feeding rate and voltage on the PES polymer solution towards commercial cellulose ester membrane base support by integrating the phase inversion technique. The analysis was performed on the membrane morphology fibrous characterization, filtration performance, especially Pure Water Permeation (PWP), and rejection performance using sodium chloride (NaCl) and water kaolinite as

solutes. The evaluation of process and fabrication effects to membrane product were also statistically estimated using RSM focusing at PES formulation, tip to collector distance, and flow rate during the electrospinning process.

MATERIALS AND METHOD

ELECTROSPINNING FABRICATION OF PES NANOFIBROUS MEMBRANES

Polyethersulfone (PES) RADEL A-300 with a molecular weight of about 15,000 Da was purchased from Amoco Chemicals to be used as the base membrane material. Polyvinylpyrrolidone (PVP) with a molecular weight of 360K Da and 1-Methyl-2-pyrrolidone (NMP ACS reagent $\geq 99.0\%$) was obtained from Sigma-Aldrich. PES (with or without PVP additive) nanofibrous membranes were produced by electrospinning method, with 22% ratio solution to NMP as tabulated in Table 1.

A homogeneous solution of polymer (PES and/or PVP) in NMP was prepared by stirring at room temperature for 8-hours. The solution was then loaded into a 20 mL plastic syringe (Terumo Corporation, Japan) with a 21 gauge syringe needle. After that, the needle was connected to a high voltage supply (ES30P-5W, Gamma High Voltage Research Inc.) which voltage parameter was in the range of 12 kV up to 25kV.

The electrospinning process was fixed at 2-hours, whereas the solution's flow rate was controlled by a syringe pump (Terumo Terufusion TE-331). A rotating drum was set at a rotation speed wrapped with filter membrane (5A 90 mm ADVANTEC Filter Paper) that soaked in water for 3 minutes before placed around the rotating drum as a pretreatment to allow for dry-wet phase inversion during electrospinning. The distance between the filter membrane and the syringe needle tip (tip to collector distance) was fixed at 10 cm to collect the electrospun by a rotating collector at about 100 rpm. The solution was subjected to electrospinning at a feeding rate (also termed here as flow rate spinning FRS) of 1.0 mL/h and several at 2.0 mL/h and 3.0 mL/h electrospun at 2 hours for each feeding rate parameters. Finally, these PES nanofibrous were treated in an oven at 200 °C for 2 hours to remove any excess solvent. The commercial filter membrane (C0) and the formulated membrane ID with electrospinning process conditions of membranes are summarized in Table 1. The schematic diagram of the electrospinning setup is shown in FIGURE 1.

TABLE 1. Membrane ID and experimental parameters of electrospinning PES membranes

Membrane ID	Formulation (weight %)	Flow Rate Spinning (FRS) (mL/h)	Voltage (kV)
C0	Mixed Cellulose ester	-	-
M1	PES/NMP (22)	1.0	12
M2	PES/NMP (22)	2.0	12
M3	PES/NMP (22)	3.0	12
M4	PES/NMP (26)	1.0	15
M5	PES/NMP (26)	1.0	20
M6	PES/NMP (26)	1.0	25
MP1	PES/PVP/NMP (22/4)	1.0	15
MP2	PES/PVP/NMP (22/4)	1.0	20
MP3	PES/PVP/NMP (22/4)	1.0	25
M7 (RSM statistical analysis)	22 to 30	0.5 to 1.5	15

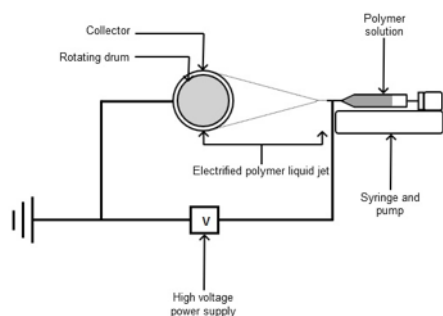


FIGURE 1. Schematic diagram of custom made electrospinning apparatus

CHARACTERIZATION AND PERMEABILITY TEST

The membranes' surface morphology was characterized by Scanning Electron Microscopy (TM3000 Hitachi) after gold coating. The PES electrospun nanofibrous membranes' static water contact angle was measured using a Canon EOS 700D setup. A droplet was dispensed on the membrane using a 1.20mm needle, and the resultant angle measured at 55mm focal length, ISO 2500, $f/5.6$, and shutter speed of 1/80 sec. All images measured from SEM micrographs and camera Canon were improved with the ImageJ software package.

For membrane ID M7n, a total of 17 experiments were fabricated based on the design approach of Box-Behnken Design (BBD) to analyze the responses of fiber diameter and mean contact angle. BBD was used to study the morphology and hydrophobicity of electrospun PES fiber under the process parameters of polymer content, tip-to-collector distance, and flow rate.

To obtain the membranes' filtration performance, permeability tests were carried out in a cross-flow filtration setup using distilled water in a flat sheet membrane testing unit. Approximately 4 Liters of distilled water filled into the feed tank. Then, the membrane placed in a membrane cell and was compacted for 30 minutes. The permeation volume was taken after 15 minutes for 60 seconds for each different pressure. In the testing unit, the pure water fluxes were calculated by:

$$J_w = \frac{V}{t \times A \times \Delta P} \quad (26.1)$$

Where V is the permeate volume (m^3), t is the time of permeate collection (sec), A is the surface area of the membrane (m^2), and ΔP is the transmembrane pressure (bar).

The rejection test was carried out by permeating the sodium chloride and the kaolin solutes in DI water for both M1 and M3 membrane types. First, the membrane was placed in the membrane cell and rinsed with distilled water for 10 to 15 minutes at 0 pressures. Then, either 1 L of NaCl at 0.01 M concentration of 500 mL of 10-100 ppm of kaolin solutes filled into feed tank for the first run. The rejection was measured after 50 to 100 mL of permeate had passed. The excess solution in the feed tank was removed, and the fresh permeation sample was filled into the feed tank for the

2nd run and 3rd run. Sodium chloride (NaCl) was supplied by (brand), and kaolinite with size 212 μm was used from locally synthesized kaolin.

The solute concentrations in the feed, c_f , and permeate, c_p , were determined by a conductivity meter (Trans Instrument) for sodium solutes. In contrast, Kaolinite solutes were determined using a spectrophotometer (Hach DR 6000). The percent separation, R%, was computed by:

$$R\% = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (26.2)$$

RESULT AND DISCUSSION

EFFECT OF ELECTROSPINNING ON FIBER DIAMETER

The summaries of the average fiber dimensions are shown in FIGURE 2. The sizes of PES fiber membranes were estimated via the SEM image. The SEM pictographs of the fabricated membranes are shown in FIGURE 3 (a) the feeding rate effect and (b) the voltage, and (c) the PVP additive effect. The grouping was based on the electrospinning feeding flow rate parameter whereby FIGURE 3 (a) membranes were fabricated at 1 to 3 mL/h feeding rate, whereas FIGURE 3 (b& c) manufactured at a fixed feeding rate of 1 mL/h.

The influence of electrospinning feeding rate, voltage, and formulation in the formation of PES membrane on support filter paper resulted in fibrous trend rate difference and has significantly affected the membrane surface morphology. When electrospun, an electric field between a droplet of polymer solution at the tip of the needle and drum collector were created. The force of the electric field causes the droplet to elongate or ejected and accelerated to the collector. While accelerated onto the collector, the solution (or jet) rapidly thins and dries as the solvent (NMP) evaporates and depositing random nonwoven solid nanofibers on the surface of the grounded collector. On the drum collector, phase inversion plays an essential role in modifying the base membrane, where the polymer solution was contacted to liquid (water), causing diffusional mass exchange. The inversion produces a change in the local composition of the polymer film, and demixing was induced. The wetted membrane base surface has provided a wet-phase. Hence, during membrane formation, an extended period from initial phase transformation to complete solidification of the PES membrane wall and membrane base. PES is a hydrophobic polymer that produces more vital interaction between PES and water. The diffusion of water has initialized liquid-liquid phase separation and solidified fibrous network onto the base membrane, a commercial filter membrane of mixed cellulose ester as used in this work.

Results indicate that an increased feeding rate from 1 to 3 mL/h has increased the PES membrane size. The observed images of M1-M3 in Figure 3(a) suggests that a high feeding rate of 3mL/h during electrospinning has produced the largest diameter of fibrous of 9 μm , followed by 2mL/h feeding rate that made approximately 400nm

and the smallest fibrous of roughly 200nm at the slowest feeding rate of 1mL/h. This is attributed to the volume flow rate that increases the jet's radius during electrospinning and thinning the fibrous. The lower the feeding rate solution, the smaller the fibers with spindle-like beads were formed as similarly observed by other work (Zong et al. 2002).

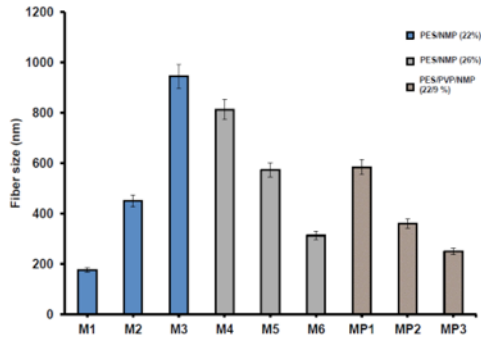


FIGURE 2. Effect of Electrospinning feeding rate (M1-M3), voltage (M4-M6), and additive formulation (MP1-MP3) on the membrane fiber size

The work then focused and fixed at a feeding rate of 1 mL/h for membrane M4-M6 and MP1-MP3. The M4-M6 and MP1-MP3 have higher dope viscosity than M1-M3 due to more significant PES percentage (26%) and PVP addition (4%) as an additive in a particular formulation. In Figure 3(b), morphology observation on fabricated membranes of 26% PES at electrospinning voltage of 15 and 20kV showed less fibrous web as pictured in the SEM, due to high polymer dope concentration and viscosity that proceeded much slowly and thus affected the jet thinning onto the collector. Furthermore, during fiber formation, repulsive electrostatic forces from high electric fields induce jet instabilities that might cause breakage and form discontinued fibers (Ahmed et al. 2015). However, the 22% PES with 4% PVP additive has produced observable and more membrane fibrous onto the membrane cellulose acetate base as observed in Figure 3(c). Subsequently, the average fiber size reduced with the increasing voltage for both formulation types; for 26%PES (M4-M6) from 800 to 300 nm while for PES/PVP:22/4 w% (MP1-MP3) from 600 to 200 nm. The higher voltage has produce solution jet drop smaller, and when initiated, the jet moved to produce smaller fiber (Reneker and Yarin, 2008). Alike study conducted by Megelski et al. (2002) in micro and nanostructured surface morphology on electrospun polymer fiber also comes with the same observation as this current study. The increased voltage decreases fiber size.

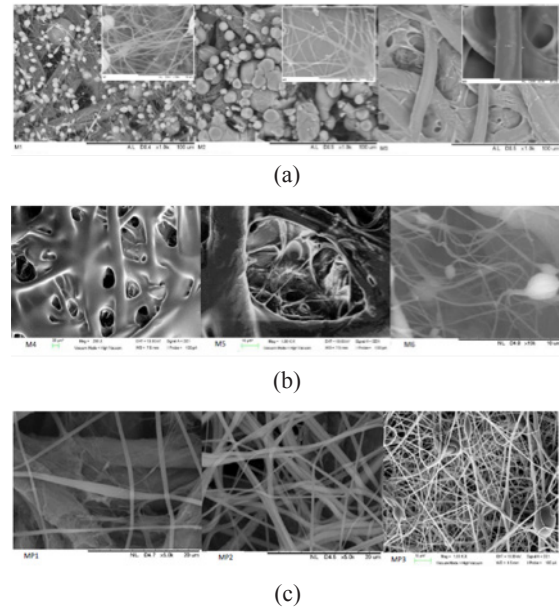


FIGURE 3. SEM morphology on the influence of (a) feeding rate toward 22% PES (M1, M2, and M3); (b)voltage and (c) PVP additive

WATER PERMEABILITY AND SOLUTES FILTRATION PERFORMANCE

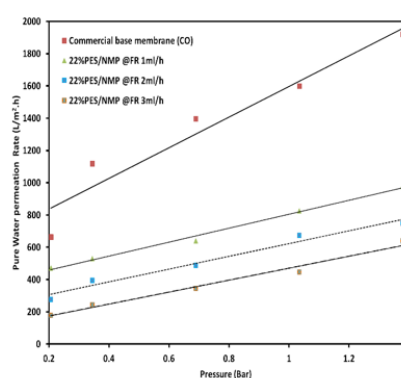
The results of permeability performance are portrayed in Figure 4 (a-c). In Figure 4(a), the pure water fluxes of nanofiber PES membranes increased with pressure, and the commercial filter membrane modified by PES fiber has reduced half of the filtration flux as observed for M1 to M3. From the slope, pressure normalized pure water flux was calculated as 950>431>396>371 L/m².h.Bar for M0>M1>M2>M3, respectively. The M0 is the commercial Filter Paper (Advantec) with a pore size of 5µm; mixed cellulose ester was used as a support base for PES membrane electrospinning. The filter paper of M0 was the base membrane layer, and thus the permeability is higher than the four types of membrane.

The flux reduction was observed when the feed rate spinning (FR) during electrospinning PES membrane increased from 1.0 ml/h to 3.0 ml/h. This indicates that a higher feeding rate during electrospinning produces thicker and condensed fiber when collected at 100rpm collector. The study observed a larger diameter size, as shown previously from SEM morphology.

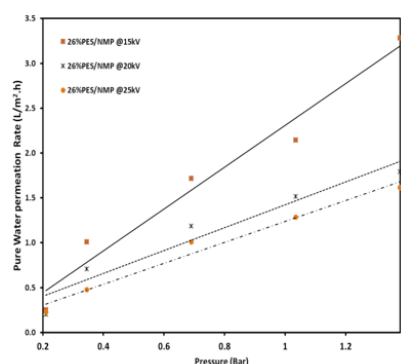
To target smaller nanosize fibers, further evaluation was then fixed at a flowrate spinning rate of 1 ml/h. As shown in

Figure 4(b), higher dope of 26% PES/NMP was fabricated and electrospun at an increased voltage from 15 to 25kV. The result shows that the permeation rate was prolonged, which ranges from 1-2 L/m².h.Bar. Furthermore, between the 26% PES membranes, the trend indicates that higher voltage produced denser and lower permeability membranes. At a slow feeding rate of 1 mL/h and higher PES concentration, it may anticipate creating a condensed PES fiber network and increased surface hydrophobicity, resulting in a significant reduction in water permeability. The experiment also showed that the increased voltage in electrospinning, even though it has reduced the fibrous diameter and has reduced membrane permeability attributed to the dominant influence of PES concentration.

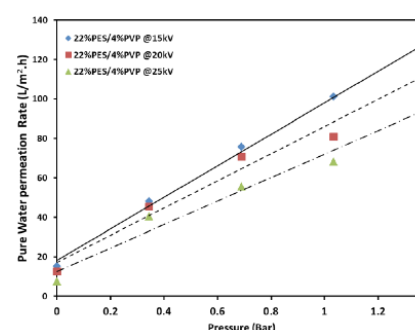
The formulation of 22% PES dope added with 4% polyvinylpyrrolidone (PVP) was further studied, and the pure water permeation is shown in Figure 4(c). Compared to the 22% PES membrane discussed previously, pure water permeation was three times higher than 22% PES with PVP additive. An increased permeation order was observed for the 22%PES/4% PVP formulation spun at 1 ml/h feeding rate when at reduced 25>20>15 kV electrospinning voltage. Figure 4(c) indicates a similar trend with Figure. 4-b when the higher voltage has produced a denser and less porous membrane. The formulation consists of 22%PES concentration. The addition of 4%PVP has improved the permeability might be attributed to the addition of PVP hydrophilicity characteristic (Bolong et al. 2009) but insufficient to increase the permeability. The summary of the calculated permeation rate is summarized in Table 2.



(a)



(b)



(c)

FIGURE 4. Membrane permeation rate result of (a) Flowrate Spinning (FR) from 1 to 3mL/h to 22%PES; (b) voltage from 15 to 25 kV to 26%PES and (c) voltage from 15 to 25 kV to PES/PVP (22/4 w%) formulation

TABLE 2. Calculated Permeation rate based on membrane electrospinning factors

Membrane ID	Formulation and electrospinning factors (weight %)	Permeation rate (L/m ² .h.Bar)	
C0	Mixed Cellulose ester	950.0	↑↑↑
M1	22%PES/NMP @ FR 1ml/h	431.9	↑↑
M2	22%PES/NMP @ FR 2ml/h	396.1	↑↑
M3	22%PES/NMP @ FR 3ml/h	371.2	↑↑
M4	26%PES/NMP @15kV	2.3	↓
M5	26%PES/NMP @20kV	1.3	↓
M6	26%PES/NMP @25kV	1.2	↓
MP1	22%PES/4%PVP/NMP @15kV	88.4	↔
MP2	22%PES/4%PVP/NMP @20kV	75.8	↔
MP3	22%PES/4%PVP/NMP @25kV	65.1	↔

Separation of solutes analysis discussed here for membrane M1 and M3 only due to its highest and lowest pure water permeability rates. The rejection results using 0.01M Sodium Chloride and kaolinite solutes are shown in Figure. 5 and Figure. 6, respectively, for both types of membrane fabricated at 1.0 mL/h (M1) 3.0 mL/h (M3) feeding rate. Despite the filtration runs, salt rejections were observed up to 10% removal in the early filtration. However, the PES membrane significantly reduced and poorly separated salt.

Figure 5 reflects that M1 has higher salt rejection than M3 due to smaller fiber diameter and better surface area. M1 recorded 10.5 % salt rejection; meanwhile, M3 only achieved 5.9 % salt rejection for the 1st run. The data shows that the observed rejection for the first run is higher than the subsequent rejection for both membranes. This might be due to some form of absorption that took place during the initial run as been reported (Bowen et al. 1997) and also due to an increased pore size attribute to repulsive interaction between counterions inside the fibrous network (Bouranene et al. 2009). Subsequently, both membranes were dropped drastically for 2nd run. M1 was able to reject only 4.4% and M3 at 1.1% of 0.01M NaCl. This situation also occurs for the 3rd run when the salt rejection has been poorly removed, 1.6% and 0.4% by M1 and M3, respectively.

Figure 6 portrayed the comparison between M1 and M3 membranes on kaolinite solute removal. The kaolinite is an organic solute at an approximate size of 0.2 nm. The result shows that M3 produced 77.8% removal whereas M1 slightly lower at 75.0 % for 100 ppm of kaolinite water due

to gradual build-up or increase of solute concentration at the membrane surface. However, between the two membranes, M1 has higher removal compared to M3 due to the smaller size fibrous diameter as observed and discussed previously via SEM. The recorded removal for M1 was 66% for 50ppm and 50% for 10ppm, whereby M3 able to remove less than M1, which at a value of 50% for 50ppm and 33% for 10 ppm kaolinite solute concentration.

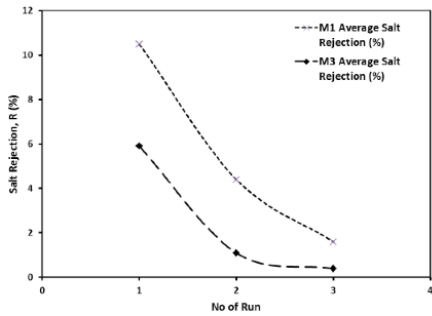


FIGURE 5. Salt removal performance by M1 and M3 membranes

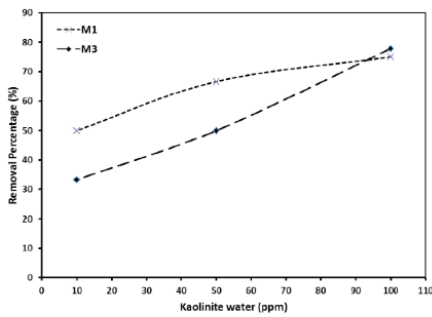


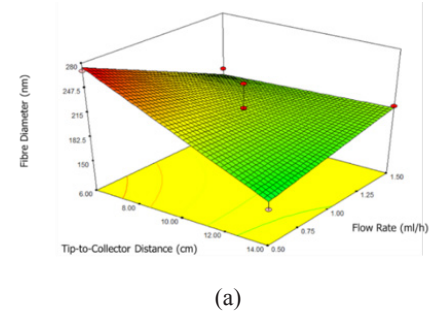
FIGURE 6. Influence of kaolinite solutes concentration to the removal performance of M1 and M3

RESPONSE SURFACE MORPHOLOGY ANALYSIS

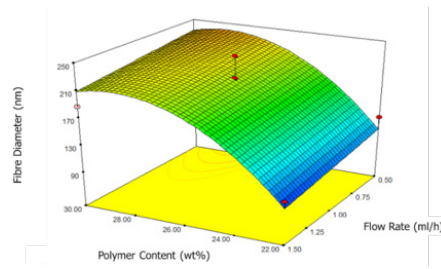
Response Surface Morphology (RSM) for PES polymer content variables, tip-to-collector distance, and flow rate spinning parameters toward fiber diameter and contact angle were studied. Design Expert (version 7.0.0, trail version) software was used for the experiments' statistical design and data analysis resulted in the 3D data surface plot shown in Figure 8 (a-f). A 3D response surface was obtained by keeping one of the variables constant at a zero level while varying the other two variables (Penjumras et al. 2015). The chosen variables were with polymer content = 26wt%, tip-to-collector distance = 10cm and flow rate = 1.0ml/hr.

These Figures show that flow rate spinning was less significant than the other variables (polymer concentration and tip to collector distance). Tip-to-collector distance has a considerable influence on the fiber diameter. The increment of the distance between the needle tip to collector allowed a longer time for the elongation and thinning of fiber as the solvent evaporates. Thus the thinning effect is better with a long-distance apart (Ray and Lalman 2011). The polymer content demonstrated the most significant influence on the fiber diameter. A low polymer content with a long tip-to-

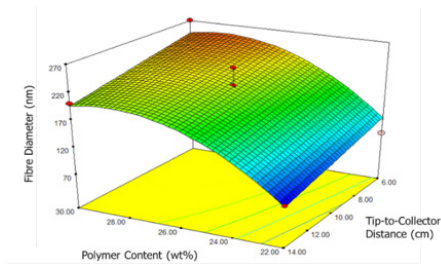
collector distance yielded smaller fibers. However, in the study of polyethersulfone, lower polymer content resulted in a higher amount of electrospinning that produces beads reported by Li and Wang (2013).



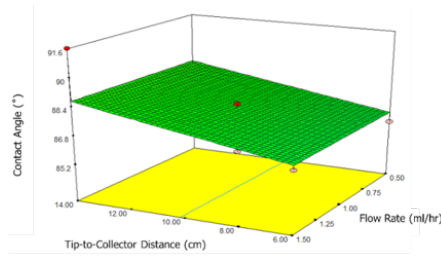
(a)



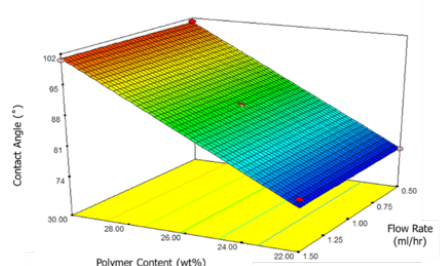
(b)



(c)



(d)



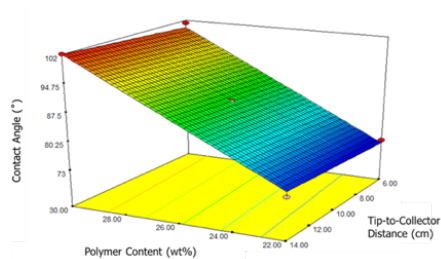
(e)

DECLARATION OF COMPETING INTEREST

None

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(f)

FIGURE 7. Three dimensional Surface Plot of electrospinning fabrication Parameter on Fibre Diameter (a,b,c) and Contact Angle (d,e,f)

CONCLUSION

The PES membrane was successfully fabricated via the electrospinning method by embedding the dry-wet phase inversion technique on the membrane support. The membranes' characterization and the filtration experiments led to the following conclusions: The observed SEM morphology indicates that PES fiber size increment is proportional to the increase of electrospinning flowrate rate. While at a fixed one ml/h flowrate spinning rate, the formulated PES fiber size reduced with the increment of voltage spinning. The electrospun PES membrane on microfibrinous support has reduced flux yet increase the retention performance of the membranes. The smallest fiber size (M1) has a larger surface area, better removal, and higher pure water permeability than M3. The increased concentration PES formulation either by weight percentage (M4-M6) or PVP addition (MP1-MP3), pure water permeability has reduced significantly despite reduced fiber size dimension when electrospun in increased voltage due to dope formulation dominancy. The fabricated PES membrane fiber was able to remove up to 70% of non-ionic kaolin of < 2micron size at a lower concentration (<100 ppm). In terms of salt rejection, the PES membrane fiber has a low capability with less than 10% removal of 0.01M NaCl. The Response surface method analysis also concluded that PES polymer content indicated the most significant influence on predicted fiber diameter and contact angle measurement.

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