

SOLUTION PARAMETER EFFECT ON POLYSULFONE FIBERS VIA ELECTROSPINNING: FABRICATION, CHARACTERIZATION AND WATER FLUX PROPERTY

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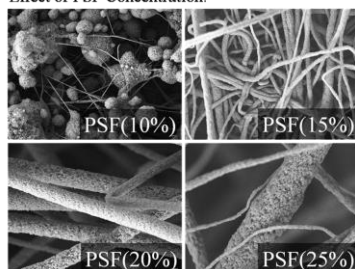
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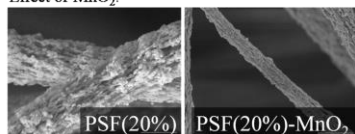
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Graphical abstract

Effect of PSF Concentration:



Effect of MnO₂:



Abstract

This research investigates the solution parameters, i.e., polymer concentration and addition of manganese (IV) oxide (MnO₂) nanoparticles, for the fabrication of polysulfone (PSF) fibers via electrospinning. Initially, PSF was dissolved in N,N-dimethylformamide (DMF) solvent and electrospun fibers with different morphologies were obtained using the range of PSF concentration of 10% (w/v) to 25% (w/v). Subsequently, PSF with the concentration of 20% (w/v) (denoted as PSF(20%)) was chosen to blend with 0.2% (w/v) of MnO₂ as it gave the most stable electrospinnability and uniform fiber diameter. The fabricated electrospun PSF(20%) and PSF(20%)-MnO₂ fibrous membranes were characterized to determine the morphology, wettability property, zeta potential, and tensile strength. The presence of MnO₂ improved tensile strength as it reduced the fiber diameter that eventually made a more compact fiber mat membrane. The results of contact angle confirmed that the fabricated fiber exhibited more hydrophobic property in the presence of MnO₂ nanoparticles. Thus, it reduced the pure water flux of PSF fiber membrane. The more hydrophobic nature of the proposed nanofiber might be useful in enhancing the application of PSF fiber in oil-water separation process.

Keywords: Electrospinning, polysulfone, manganese(IV) oxide nanoparticles

Abstrak

Kajian ini menyiasat parameter larutan, iaitu kepekatan polimer dan penambahan nanopartikel mangan (IV) oksida (MnO₂), untuk fabrikasi polisulfon (PSF) melalui elektrospinning. Pada mulanya, PSF telah dilarutkan dalam pelarut N,N-dimetilformamida (DMF) dan gentian elektrospun dengan morfologi berbeza diperoleh menggunakan julat kepekatan PSF dalam lingkungan 5% (w/v) hingga 25% (w/v). Seterusnya, PSF dengan kepekatan 20% (dilabel sebagai PSF(20%)) dipilih untuk diadun dengan 0.2% (w/v) MnO₂ kerana ia memberikan keelektrospinan yang paling stabil serta diameter gentian yang paling seragam. Gentian membran elektrospun PSF(20%) dan PSF(20%)-MnO₂ yang dihasilkan telah dicirikan untuk menentukan morfologi, kebolehasahan, keupayaan zeta, dan kekuatan tegangan. Kehadiran MnO₂ meningkatkan kekuatan tegangan kerana ia mengurangkan diameter gentian yang akhirnya menghasilkan lapisan membran gentian yang lebih padat. Keputusan eksperimen bagi sudut sentuh mengesahkan bahawa gentian fabrikasi mempamerkan lebih sifat hidrofobik setelah nanopartikel MnO₂ ditambah. Oleh itu, ia mengurangkan fluks air tulen membran gentian PSF. Sifat hidrofobik nanofiber yang dicadangkan berkemungkinan berguna untuk meningkatkan penggunaan gentian PSF dalam proses pemisahan air-minyak.

Kata kunci: Elektrospinning, polisulfon, nanopartikel mangan (IV) oksida

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1.0 INTRODUCTION

Electrospinning is a spinning technique that uses electrostatic forces to fabricate ultrafine fibers. It has been acknowledged as one of the most promising nanotechnologies as electrospun fibers exhibit superior properties, such as small diameter (in micro- or even nanometer), long length, large surface area, and sometimes complex fiber structure. Besides, electrospinning has been acclaimed as a simple technique, in which its typical set-up simply consists of three major components including a feeding unit (e.g., a syringe pump with a syringe), a high voltage supply (0–30 kV), and a counter-charged collecting site (e.g., a rotating drum or a metal plate) [1, 2].

The study of operational parameters of electrospinning is very significant because it reinforces the versatility of the technique in designing fibers with different morphology, structure, and function for a variety of applications. Basically, the operational parameters of electrospinning can be categorized into three different groups, i.e., solution parameters (material, solvent, and solution), processing parameters (feed rate, voltage supply, and distance between a feeding unit and a counter-charged collecting site), and ambient parameters (temperature and humidity). Among solution parameters, concentration and conductivity of a polymer solution particularly hold an unequalled position.

The fabrication of fibers through electrospinning can be divided into four steps: (1) the formation of a Taylor cone (a cone structure of solution droplets after being charged) at the needle tip; (2) the continuously flowing solution through a needle tip and forming a charged jet; (3) the stretching of the charged jet; and (4) the formation of fibers via solvent evaporation. Polymer concentration influences prominently the stretching of the charged jet during electrospinning. Haider *et al.* (2013) reported that at low concentration, due to the applied electric field and surface tension, entangled polymer chains tend to break into fragments that subsequently form beads or beaded fibers before reaching the collector. When the concentration is increased, the viscosity of the polymer solution and chain entanglement among polymer chains are also increased. These conditions affect surface tension and result in relatively uniform beadless electrospun fibers. However, if the concentration keeps increasing and exceeds the critical concentration (the minimum concentration of a polymer solution to form beadless uniform electrospun fibers), the high viscosity of polymer solution hinders the flowing of solution via the needle tip, which results in defective or beaded fibers [3, 4].

On the other hand, solution conductivity affects the Taylor cone formation and the stretching of charged jet. When salt is added to a polymer solution, it increases the number of ions in the solution and enhances the conductivity of the solution.

Electrospinning cannot be conducted in a solution with low conductivity because the solution droplets at the needle tips cannot be transformed into a Taylor cone. When solution conductivity is increased by adding salt, the polymer solution will have sufficient free charges to form a Taylor cone and electrospinning process is initiated. Additionally, the increase of solution conductivity will increase the stretching and whipping of the charged jet that results in smaller fiber formation. Similar to concentration, it is not recommended to increase solution conductivity beyond a critical value as it will hamper the formation of a Taylor cone [5, 6].

In this work, the effect of polymer concentration and solution conductivity (by adding manganese (IV) oxide (MnO_2) nanoparticles) on the fabrication of polysulfone (PSF) fiber via electrospinning is investigated. MnO_2 nanoparticles are effective adsorbents of metal ions and organic contaminants that have excellent physiochemical properties including high specific surface area, a wide range of surface charge, polymorphic nature, and environmentally friendly [7-9]. Nonetheless, due to the electrostatic interactions or Van der Waals forces between them, MnO_2 nanoparticles tend to coalesce into larger particles, which eventually puncture their effectiveness as sorbents. As a result, researchers have combined MnO_2 nanoparticles with other suitable materials such as polymers to produce composite adsorbents in order to maintain their advantages [10-12].

PSF is a synthetic hydrophobic polymer with outstanding physicochemical properties, such as thermal stability, chemical resistance, and good processability [13]. It is considered as one of the most common commercial polymers used in membrane formation because the membrane maintains its strong mechanical and thermal properties in dry and wet conditions [14]. To date, electrospun PSF has been widely employed in many applications encompassing blood hemodialysis [15], fuel cells [16], oil spill sorbents [17], and water treatment [18]. The limitation of PSF membrane is that it is quite susceptible to fouling upon contact with organic permeates. Hence, a lot of studies have been conducted to improve its hydrophobic properties in order to overcome the limitations [19-21].

2.0 METHODOLOGY

2.1 Chemicals

PSF (MW = 1700 g/mol) was obtained from DSM Co. and Solvay Company and used without further purification. MnO_2 nanoparticles were purchased from Sunnano and functionalized according to Subramanian *et al.* (2008) [22]. N,N-dimethylformamide (DMF) was acquired from QR&C. Meanwhile, ultrapure water was obtained from Arium-Pro ultrapure water system and used to wash

PSF membranes after electrospinning, and also acted as a feed stream for the pure water flux analysis.

2.2 Fabrication of PSF and PSF-MnO₂ Electrospun Fibers

In this study, PSF in the form of pellets was used as a polymer and electrospun together with a solvent. 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 g of PSF were dissolved in DMF to form PSF solution with the concentration of 5, 10, 15, 20, 25, and 30% (w/v), respectively. The polymer solution was stirred until homogeneous at the room condition. After electrospinning, only PSF with the concentration ranging from 10 to 25% (w/v) could be electrospun into fibers and the products were denoted as PSF(10%), PSF(15%), PSF(20%), and PSF(25%).

In the case of PSF-MnO₂ electrospun fiber, PSF(20%) was selected due to its stable electrospinnability and uniform fiber structure. 0.2% (w/v) of MnO₂ nanoparticles was added to the homogeneous PSF solution. Prior to electrospinning, the solution was kept in an ultrasonicator bath for 30 h. The product was denoted as PSF(20%)-MnO₂.

Electrospinning operational parameters such as applied potential energy (high voltage), working distance of the spinneret and the collector, flow rate, needle size, and temperature were optimized at 20 kV, 150 mm, 4.0 ml/h, and ambient temperature, respectively.

2.3 Characterization of Electrospun Fibers

The morphology of the electrospun fibers was observed using a field-emission scanning electron microscope (FESEM); Zeiss Supra 35VP operated at 5 kV. Before the observations, all the samples were sputter-coated with Au. The fiber diameter was analyzed from FESEM images by ImageJ software.

The mechanical properties of electrospun PSF(20%) and PSF(20%)-MnO₂ fibers were obtained from LRX 2.5 kN Lloyd tensile tester. A minimum of five strips with the dimensions of 30 mm × 13 mm × thickness for each membrane were tested. A controlled force module was selected with the speed set at 10 mm/min. The electrospun fibers thickness was measured using an electronic external micrometer.

The static surface contact angle of electrospun PSF(20%) and PSF(20%)-MnO₂ fibrous membranes was measured using the contact angle analysis system by Dataphysics OCA. 0.5 µl droplet of distilled water was dispensed onto the membrane using sessile drop method and the measured angle was recorded. A picture of the drop was captured after the drop set onto the sample. The contact angle could be calculated by the software through analyzing the shape of the drop. The contact angle θ was an average of five measurements.

The zeta potential (SurPASS Electrokinetic Analyzer for Solid Surface Analysis) of electrospun PSF(20%)

and PSF(20%)-MnO₂ fibrous membranes were conducted by using streaming method in a cylindrical cell. Prior to measurement, 500 mg of membrane sample was cut into very tiny pieces and soaked in 0.001 M of potassium chloride (KCl) solution. Then, the sample was compacted until approximately 5 mm. The operating pressure for the whole process was set at 400 mbar and the pH was adjusted for pH 2 to pH 11 using 0.1 M of hydrochloric acid (HCl) and 0.1 M of sodium hydroxide (NaOH).

2.4 Flat Sheet Membrane System and Filtration Protocol

The investigation of the water permeability of electrospun PSF(20%) and PSF(20%)-MnO₂ fibers was conducted using a flat sheet testing unit with direct liquid penetration [23].

First, the fabricated fibers were conditioned with distilled water for 24 h and dried at room temperature. Circular electrospun fibrous membranes with the diameter of 52 mm and an effective area of 21.24 cm² were cut out and subsequently used for flux studies.

The fiber membranes were subjected to compaction for stabilization for 1 h with the pressure of 1.5 bar, whereas the flux pressure was set at 1.0 bar. Flux can be calculated by using the following formula:

$$\text{Flux, J} = \frac{\text{Volume permeation rate, (V/t)}}{\text{Fibrous membrane area, A}}$$

Where J is the flux (L/m²h), V is the permeate volume (L), A is the effective fibers membrane area (m²), and t is time (h). The effective nanofibers membrane area is 21.24 cm².

The pure water flux was measured for every 200 ml of permeate collected.

3.0 RESULTS AND DISCUSSION

Effects of PSF Concentration on Electrospun Fibers Characteristics

In this experiment, the ability of PSF to be electrospun into fibers at different concentrations was evaluated. Polymer concentration plays a crucial role for the formation of electrospun fibers. When PSF concentration was extremely low, i.e., 5% (w/v), no fiber was formed but instead, a wet collector was obtained. This is because the applied electric field and surface tension hampered polymer chains entanglement, which subsequently led to electrospraying. Electrospinning occurred when the PSF solution achieved the concentration of 10% (w/v). However, fiber formation at this concentration was still very low and beaded fiber was obtained as shown in Figure 1(a). The noticeable fiber diameter was as small as 100–300 nm.

Less beaded fiber mats (Figure 1(b) and (c)) with fiber diameter ranging from 200 to 2,500 nm and 600 to 1,250 nm were formed at the concentrations of 15% (w/v) and 20% (w/v), respectively. Increasing polymer concentration increased solution viscosity and polymer chain entanglement. PSF(15%) was the critical concentration of PSF solution with DMF as the solvent. Nonetheless, the solution was not chosen as the optimum concentration of PSF because PSF(20%) provided more stable electrospinnability and much more uniform fiber formation than PSF(15%). Electrospinnability is the ability of a polymer solution to form fibers through electrospinning.

Moreover, at the concentration of 25% (w/v), although less beaded fiber was obtained, the fiber formation was disrupted. In more concentrated and viscous solutions, a formation of many fiber branches was obtained (Figure 1(d)) as the electric field used was higher than the minimum value required for producing a single jet [24]. PSF(25%) had two different groups of fiber diameter, in the range of 450–1,000 nm (fiber branch) and 1,500–5,500 nm (fiber). Beyond the concentration, continuous electrospun fibers could not be formed. At the concentration of 30% (w/v), the fibers broke down into small pieces, as illustrated in Figure 2, before reaching the collector. Notably, this is the first work that successfully displayed the effect of concentration of the fabrication of electrospun fiber membrane, although the idea has been proposed previously [1, 2].

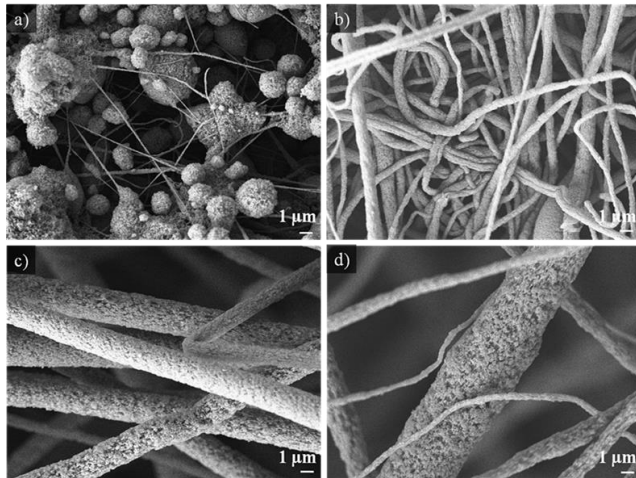


Figure 1 FESEM micrographs of (a) PSF(10%), (b) PSF(15%), (c) PSF(20%), and (d) PSF(25%) fibers at magnification of 5 k

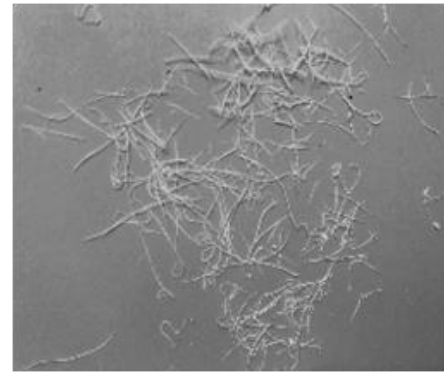


Figure 2 Brittle fibers of PSF(30%)

Effects of MnO₂ Nanoparticles on Electrospun PSF Fibers Characteristics

After the addition of 0.2% (w/v) of MnO₂ to PSF(20%), the fiber diameter decreased about twofold from 1,056 to 416 nm, without affecting the fiber surface morphology (Figure 3). This is because the addition of MnO₂ nanoparticles increased the conductivity of PSF solution, which subsequently created more whipping process in the charged jet before reaching the collector [25-26]. The presence of MnO₂ nanoparticles in PSF(20%) fibers is depicted in Figure 4.

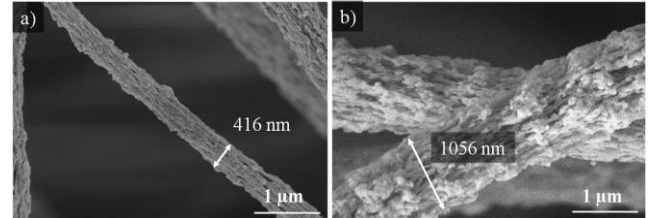


Figure 3 FESEM micrographs of (a) PSF(20%)-MnO₂ and (b) PSF(20%) fibers at magnification of 25 kV

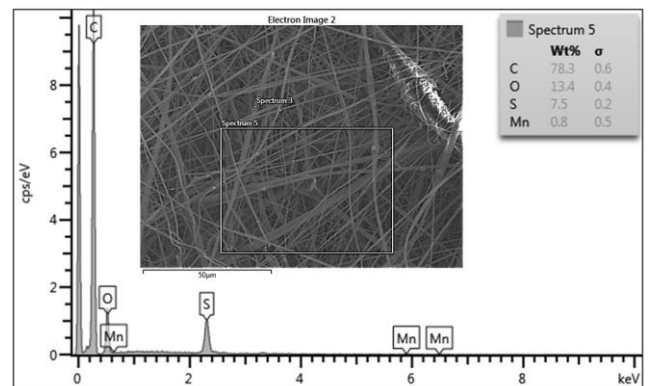


Figure 4 FESEM-EDX micrograph of PSF(20%)-MnO₂ fibers

The addition of MnO_2 improved the physical properties of PSF fibers. For example, it enhanced the tensile strength of PSF(20%) from 0.2303 to 3.3016 MPa as smaller fibers gave more compact structure of the fiber mat. The tensile strength of electrospun PSF membrane was very weak, and the tensile strength achieved in this work corresponds to the work of Uzal *et al.* (2017) [27]. Furthermore, it gave a positive effect on the surface properties of PSF(20%) fiber. PSF(20%)- MnO_2 exhibited a larger contact angle and a more hydrophobic surface than PSF(20%) (Figure 5). Although MnO_2 nanoparticles are hydrophilic, smaller fibers increased the hydrophobic interaction between PSF fibers and water. The improvement is vital as it may improve the antifouling properties of PSF against organic permeates during wastewater treatment and oil-water separation. Recently, Al-Husaini *et al.* (2019) proved that the addition of hydrous manganese dioxide (HMnO) nanoparticles in electrospun polyethersulfone nanofibers enhanced the ultrafiltration of an oily solution [28]. The surface charge of PSF fibers was investigated using zeta potential analysis. The variations in zeta potentials for analyzing fiber membranes surface charges as a function of pH are shown in Figure 6. It is noted that all fiber membranes possessed a negatively charged surface in all pH media. Nevertheless, the surface charge of PSF(20%)- MnO_2 (green line) was slightly positive than PSF(20%) (blue line).

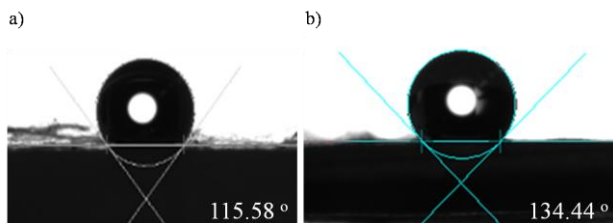


Figure 5 Photographs of surface contact angle of (a) PSF(20%) and PSF(20%)- MnO_2 fibers

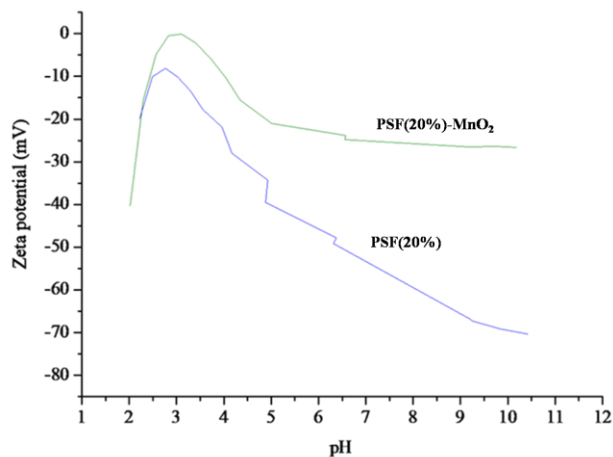


Figure 6 Zeta potential of PSF(20%) and PSF(20%)- MnO_2 fiber membranes

Influence of MnO_2 Nanoparticles on Electrospun PSF Fibers Characteristics towards Permeability Performance

The performance of electrospun PSF(20%) fiber membrane with/without MnO_2 nanoparticles was tested on a permeation cell. The permeation fluxes of pure water are shown in Figure 7. The addition of MnO_2 fiber membrane reduced the average water flux rate by twofold, from 4,809.81 to 10,451.78 $\text{L}/\text{m}^2\text{h}$. A possible reason for this phenomenon is related to their hydrophobic properties. Increasing hydrophobic properties of a fiber membrane decreases the interaction between water and the fiber membrane. Therefore, water could not be absorbed easily by the relatively hydrophobic fiber membrane. Besides, PSF(20%)- MnO_2 has a smaller fiber diameter than PSF(20%) and this may reduce the pore size of the fiber membrane, which ultimately creates more resistance against water flow. However, the water flux of both fiber membranes was considered high.

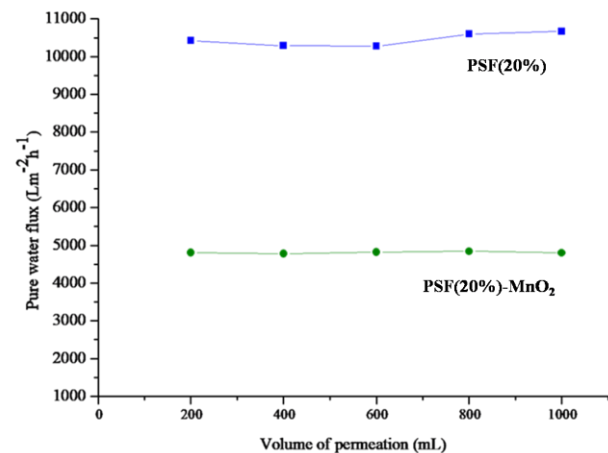


Figure 7 Pure water flux (J) of PSF(20%) and PSF(20%)- MnO_2 fiber membranes

4.0 CONCLUSION

Solution parameters play a very important role in the formation of fiber via electrospinning. From the structural analysis of the fiber membranes using FESEM conducted in this study, it is found that an optimum concentration is always required to produce fiber with less bead formation and a uniform structure. Besides, it is also proven that the addition of MnO_2 nanoparticles in PSF solution subsequently increased solution conductivity, giving a positive result in reducing fiber diameter, enhancing tensile strength, as well as increasing surface hydrophobicity of the PSF fiber. Nonetheless, the addition also negatively affects the PSF fiber membrane by decreasing pure water flux as small fibers created a much more compact fiber mat membrane than big PSF fibers. The electrospun PSF(20%)- MnO_2 fiber

membrane could be applied as a filter membrane for wastewater treatment or oil-water separation.

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