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PREPARATION AND CHARACTERIZATION OF TIO_2 NANOFIBER COATED PVDF MEMBRANE FOR SOFTDRINK WASTEWATER TREATMENT

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ABSTRACT

In this study, Polyvinylidene Fluoride (PVDF) nanocomposite membrane consisting of electrospun titanium dioxide (TiO2) nanofibers (PVDF/e-TiO2) was prepared by hot pressing the as-spun TiO2 nanofibers onto PVDF flat sheet membrane. The hot press technique was carried out by applying the operating pressure at 1 bar, 1.5 bar and 2 bar for 30 seconds. The nanocomposite membrane was characterized by Scanning Electron Microscope (SEM) spectroscopy. The SEM images and analysis shows good adhesion and dispersion of TiO2 nanofibers in PVDF membrane. Based on the results, it can be concluded that a fine-tuning on the optimization study of the membrane hydrophilicity by several approaches such as pure water flux, glucose rejection and contact angle is desirable in order to ensure the developed PVDF/e-TiO2 membranes can be simultaneously efficiently functioned by means of filtration applications. Membrane successfully done glucose rejection and then COD analysis is carried out with higher efficiency. As the pressure increases the chemical oxygen demand (COD) increases because dissolved oxygen is removed in retentate side together with glucose.

KEYWORDS

PVDF membrane, TiO2, SEM, glucose rejection, pure water flux, contact angle, COD.

1. INTRODUCTION

Wastewater from soft drink industry faces one of the huge challenges to the industrial waste treatment system. In order to produce soft drink, 12 billion gallons of water needed every year [1]. Waste water streams generated from this soft drink manufacturing have been heavily contaminated with different type of chemicals, toxins and organic contents. Since COD levels in soft drink wastewaters are moderate, it is generally accepted that anaerobic treatment offers several advantages compared to aerobic alternatives. Anaerobic treatment can reduce COD from a few thousands to a few hundreds mg/L and it is advisable to apply aerobic treatment for further treatment of the wastewater so that the effluent can meet regulations [1]. Membrane technology is dominant in providing promising and modernization approach in upgrading and expansion of wastewater treatment plant among other wastewater treatment [2]. This type of technologies become more appealing because of many advantages over conventional processes like can improve the purification of the wastewater [3]. Membrane technologies are looking forward to develop the performances of treating pollutants in wastewater treatment but it also has some restrictions relates to fouling that will consequently decrease the permeate flux and efficiencies of the separation process [4].

Soft drink wastewater consists of wasted soft drinks, syrup, glucose and water from the washing of bottles and cans, which contains detergents and caustics, and finally lubricants used in the machinery. Therefore, the significant associated wastewater pollutants will include total suspended solids (TSS), 5-day biochemical oxygen demand (BOD5), chemical oxygen demand (COD), nitrates, phosphates, sodium, and potassium [1]. In this case, a variety of organic micro-pollutants contained in wastewater effluent could create problems. High pressure-driven membranes such as nanofiltration (NF) or reverse osmosis (RO) might be a powerful option to deal with such micro-pollutants [5]. One of disrupting compounds that contribute to large abundance in wastewater is glucose. Glucose is an important raw material in the production of soft drinks.

Use of membrane filtration processes have increased rapidly over the past decade. These filters are employed mainly to remove the unwanted micro- and macro- particles. However, membrane fouling which are unwanted particles that attached the outer layer of membrane thus forming a cake layer became the main obstacle in membrane filtration efficiency as it affects the productivity [6]. This phenomenon has practically and economically retarded membrane applications in water treatment development. The reduction in productivity caused by membrane fouling can be interpreted as the declined in flux with time of operation due to the increased of hydraulic resistance.

Nanofibers membrane is one of the advanced technologies used because of the small pore size and has very large surface area to volume ratio. It also has a good flexibility of its surface function and high mechanical performance such as tensile strength [7]. There are several techniques to produce nanofibers such as melt blowing, forcespinning and electrospinning. Electrospinning is the simplest and attractive method in order to produce fibers which is the diameters is about 10μm to 10nm simply by accelerating a jet of charged precursor solution in an electric field [8,9].

This TiO2 nanofiber is immobilized because to improve and increase hydrophilicity of the hydrophobic based PVDF membrane which is tend to fouling. In several studies, hot pressing methods were applied by application of pressure and heat to improve the connectivity between fiber and membrane intersection [10,11]. Membrane compactness, mechanical properties and chemical stabilities of membrane will be improved by applying the concurrent application of pressure and heat [11]. The losses strands of the nanofibers that are present on the top of the surface would also be eliminated as reported by Na et al., who studied the effect of hot press treatment on the electrospun PVDF membrane.

The main aim of this study is to investigate the removal efficiency of glucose by the developed nanocomposite membrane from a PVDF-based membrane coated with electrospun TiO2 nanofibers. In order to achieve the above-mentioned objectives, the following scopes are outlined:

1) Preparing TiO2 precursor solution about 1.0g of polyvinylpyrrolidone (PVP) in 1.5g of titanium tetraisopropoxide (TTIP) under electrospinning process.

2) Conducting the coating process of PVDF membrane with as-spun TiO2 nanofibers by using hot press method by varying the pressure at 1 bar, 1.5 bar and 2bar for 30 seconds each.

3) Characterizing the PVDF/e-spun TiO2 toward membrane separation through the membrane physical characteristics in terms of membrane hydrophilicity, pure water flux and membrane rejection on glucose.

4) Determining the Chemical Oxygen Demand (COD) of the soft drink treated by PVDF/e-spun TiO2 membrane.

Ultrafiltration modules operate free of process problems and produce permeate water with low turbidity and reduced COD. Polyvinylidene fluoride (PVDF) polymeric hollow fibers for high strength and chemical resistance that lead to longer membrane life. Hydrophilic PVDF fibers easy for cleaning and wettability that help maintain long-term performance. Furthermore, the immobilization of TiO2 nanofibers on the PVDF membrane support can simplify the conventional membrane filtration process by eliminating the post treatment of separation process. This improvement also indicated that this study significant as the membrane filtration is vital to sustain a clean and healthy environment [11].

2. EXPERIMENTAL

The experimental procedures were carried out in four main stages. The first stage of the methods involved two phases which are the fabrication of flat sheet PVDF membrane and the preparation of TiO2 nanofibers (e-spun TiO2). The second stage of this study was the development of PVDF/e-TiO2 nanocomposite membrane using hot press method. The third stage covered the performance of the prepared PVDF/e-TiO2 nanocomposite membrane which was studied for the membrane physical characteristics in terms of membrane hydrophilicity, pure water flux, contact angle and glucose rejection while the fourth stage is involving the Chemical Oxygen Demand (COD).

2.1 Preparation of PVDF Flat Sheet Membrane

The PVDF dope solution prepared by drying the PVDF powder in an oven at 60°C for a day was then added slowly into DMAC solution in flange reaction flask and mixed thoroughly under constant mechanical stirring at 60°C for 24 hours until dissolved was first spread onto the glass flat sheet at a certain thickness (30-40µm). Glass rod was used to spread the dope solution onto the glass plate to produced flat sheet membrane. After 30seconds exposure to air, the plate was immersed in the deionized water coagulation bath and the membrane slowly formed the polymer precipitation. After several minutes, the membrane was detached from the plate and was soaked in the deionized (DI) water overnight. In order to reduce the shrinking effect of the PVDF membrane, the membrane was undergone the post treatment process. After it was soaked in the DI water overnight, the membrane was soaked in the 50% of ethanol in water for about two hours and 100% ethanol for 1 hour. Finally, the membrane was dried at room temperature and was ready to used [12].

2.2 Preparation of Titanium Dioxide (TiO2) Nanofibers by Electrospinning Process

In the preparation of homogeneous precursor solution, the solution was divided into two sections which are PVP/ethanol and TTIP/acetic acid solution. PVP/ethanol was prepared by mixing 1g of PVP and 7.9g of ethanol while TTIP/acetic acid solution was prepared by mixing 1.5g of TTIP and 3g of acetic acid solution and were mixed for 2 hours. A TTIP/acetic acid solution was then wisely drops into the PVP/ethanol solution and vigorously stirred until the clear yellow solution formed. Meanwhile the TiO2 nanofibers were prepared through electrospinning (V=12kV, flowrate= 1mL/hr and tip to collector distance= 15cm) by using the TiO2 precursor solution.

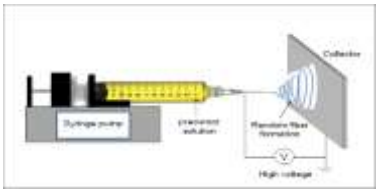


Figure 1: The schematic diagram electrospinning process to produce TiO2 nanofibers

2.3 Preparation of Hot Press Method between TiO2 Nanofibers and PVDF Membrane

The PVDF-TiO2 nanofibers material was clipped with two clean aluminium plates to minimize contamination of the membrane. The most important thing was that the hot press pressure must be achieved first. The plate containing PVDF-TiO2 membrane was placed in hydraulic press system (CARVER) and the temperature set to be at T=60˚C [13]. The hot press technique was carried out by varied the operating pressure of (1 bar, 1.5 bar and 2 bar) for 30 seconds. The PVDF-TiO2 membrane was cooled down and allowed to remain compressed by the pressure after a certain time to make the nanofiber attached to the PVDF membrane.

2.4 Rejection of Glucose

The rejection of glucose was conducted through cross-flow filtration system. 2 L of water contained 1000ppm of glucose was used as a feed. The concentration of feed and permeate of glucose solutions was characterized. The glucose rejection was expressed in terms of Chemical Oxygen Demand and in the percentage of rejection according to the following equation.

$$\text{Rejection (\%)} = (Cf\text{-}Cp)/Cf \times 100\%$$

Where Cf and Cp was the concentration of glucose in feed and permeate solution respectively.

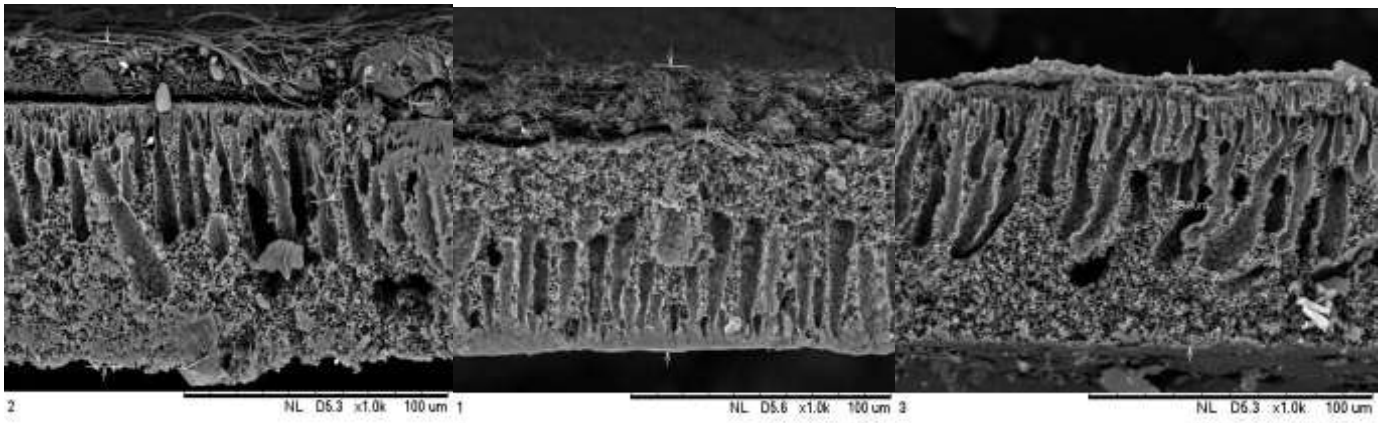
2.5 Chemical Oxygen Demand

The 2mL glucose rejection which are collected from each hot pressed PVDF/TiO2 membrane with operating pressure 1 bar, 1.5 bar and 2 bar are pipetted in the high range Chemical Oxygen Demand reagent which are been prepared. Then, after adding the solution the test tube are mixed by shaking gently. The cover of the test tube should be hold as the test tube becomes hot when mixing process takes place. Not only that, a blank sample is prepared to make zero reading at the beginning. All this sample are then kept in the reactor with operating temperature of 148˚C for 2 hours. Next, let the sample to cool until room temperature. Lastly, the Chemical Oxygen Demand is measured using DR5000 Spectrophotometer UV-VIS.

3. RESULTS AND DISCUSSION

3.1 PVDF/e-spun Membrane Characterization Scanning Electron Microscope (SEM)

The morphological structure of PVDF membrane to be greatly altered when the TiO2 nanofibers embedded by applying hot pressing technique using pressure of 1 bar, 1.5 bar and 2bar [14]. As can be seen in Figure 2 (a), (b) and (c), obviously different structures are clearly shown, which are finger like, porous and dense like structures between the nanofibre and PVDF membrane. It is probably due to the effect of pressure and temperature that applied to the membrane during the hot pressing process that forces the membrane morphology to be changed [15]. In addition, cross-sectional SEM analysis indicated that all resultant nanocomposite membranes exhibited that the TiO2 nanofibers layer adheres strongly onto the PVDF membrane only on Figure 2 (c) whereas there are visible lift off on the top of PVDF membrane in Figure 2 (a) and Figure 2 (b). As we know, that the membrane internal structure plays an important role in determining the membrane performance [13].



(a) (b) (c)

Figure 2: SEM cross section images of PVDF/e-TiO2 nanocomposite membrane a) PVDF/e-TiO2-1 bar, (b) PVDF/e-TiO2-1.5 bar and (c) PVDF/e-TiO2-2 bar

3.2 The Pure Water Flux Analysis of the PVDF/e-TiO2 Membranes

Incorporating the TiO2 nanofibers onto the PVDF membrane have changed the structure and characteristics of the membrane. Higher hot-pressing pressure used to incorporate TiO2 nanofibers onto PVDF membrane matrix displays reduction in pure water flux. This is due to the morphological structure of the membrane that is greatly changed after applying the hot-pressing technique. With the increasing of the hot-pressing pressure, the pure water flux of the PVDF nanocomposite membranes were found to reduce. It seems that the addition of TiO2 nanofibers has caused some pore blockage phenomenon that consequently hindered the filtration process.

Table 1: The pure water flux based on difference hot pressed pressure

Pressure (bar)	Volume (mL)	Pure Water flux, (L/m²hr)
1 bar	2	5.536
1.5 bar	2	2.135
2 bar	2	1.633

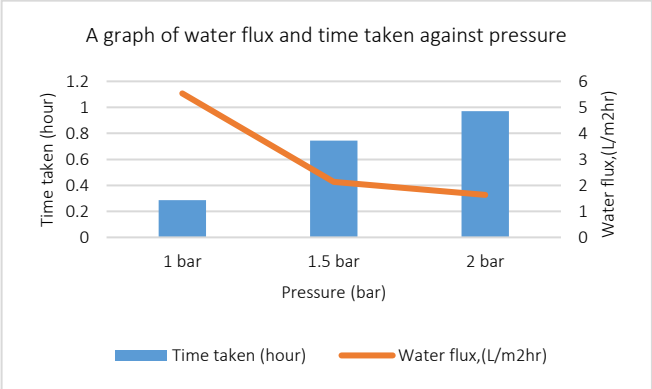


Figure 3: A graph of water flux and time taken against pressure

3.3 PVDF/e-TiO2 Membrane Hydrophilicity Analysis

The degree of hydrophilicity of the PVDF/e-TiO2-1 bar was found higher than PVDF/e-TiO2-1.5 bar and PVDF/e-TiO2-2 bar membrane as it has the lowest contact angle value because it is suggested that more hydroxyls group from the TiO2 nanofibers retained on the top layer of the membrane. It has been proven by the SEM images in Figure 3 (a) that there is a clear appearance of the TiO2 nanofibers on the nanocomposite membrane surface.

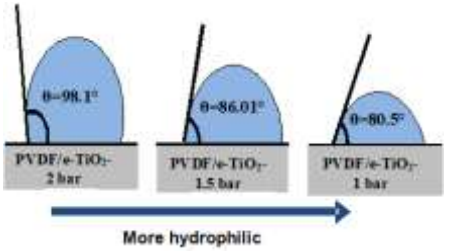


Figure 3: Contact angle of PVDF/e-TiO2-1 bar, PVDF/e-TiO2- 1.5 bar and PVDF/e-TiO2-2 bar

The recorded contact angle value for PVDF/e-TiO2- 2 bar was slightly higher than PVDF/e-TiO2-1.5 bar and PVDF/e-TiO2-1.bar because the higher pressure used to press the TiO2 nanofibers makes them merge together and tends to aggregate with the PVDF matrices, resulting in the decrease of hydrophilicity

3.4 Membrane Rejection Analysis of Glucose and Chemical Oxygen Demand by PVDF/e-TiO2 Membrane

As it can be seen in the Figure 4, PVDF/e-TiO2-2 bar membrane has lower value of glucose rejection. As the hot-pressing pressure increase, the glucose rejection (%) was slightly decreases. However, as the pressure increases the chemical oxygen demand(COD) increases because dissolved oxygen is used by the microorganism in the surrounding and the organic content removed in retentate side together with glucose.

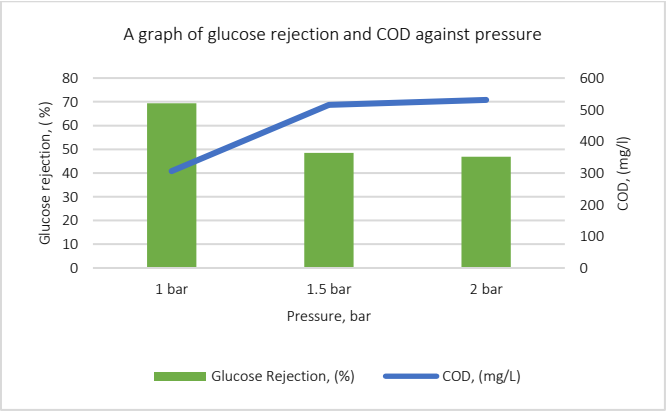


Figure 4: Glucose rejection and COD rejection of PVDF/e-TiO2-1 bar, PVDF/e-TiO2- 1.5 bar and PVDF/e-TiO2-2 bar

4. CONCLUSION

As the hot pressing pressure increases, the dense structure starts to form. Thus, nanocomposite membrane prepared at hot pressing pressure at 1 bar exhibited appropriate morphological structure and physical properties. Not only that, as the hot pressing temperature increased, the PVDF membrane melts and the membrane matrix has covered the TiO2 nanofibers surface. It will then minimize the direct contact between the TiO2 catalysts with the pollutants under filtration activity while simultaneously decreasing membrane hydrophilicity and pure water flux and as the pressure exerted on the PVDF/e-TiO2 nanocomposite

membrane increases. On the other hand, as the hot pressing pressure increase from 1 bar to 2 bar, the pure water flux for PVDF/e-TiO2 nanocomposite membrane was reduced from 5.536 L/h.m2, 2.135 L/h.m2 and 1.633 L/h.m2 respectively. Hence, PVDF/e-TiO2-1 bar possesses better water flux among the others nanocomposite membrane. Other than that, the glucose rejection of the PVDF/e-TiO2-1 bar was also found to be the highest among the other prepared PVDF/e-TiO2 nanocomposite membrane due to its high hydrophilicity. Not only that, the glucose rejection of PVDF/e-TiO2-1 bar shows lower amount of Chemical Oxygen Demand due to less organic content and high dissolved oxygen in the sample.

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