The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM)
ISSN: 2602-3199

The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 2022

Volume 21, Pages 363-370

IConTES 2022: International Conference on Technology, Engineering and Science

Effect of Additive on the Structure and Performance of PVDF Hollow Fibre Membrane on Phosphorus Removal

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Abstract: Similar to plants, algae are tiny creatures that inhabit watery settings and use photosynthesis to harness the energy of the sun. Depending on the kind of algae, the excessive growth, or algal bloom, can be green, blue-green, red, or brown and becomes apparent to the human eye. The phenomena are caused by excessive phosphorus in the water body. There are many methods including chemical removal, advanced biological treatment, or a combination of the two methods can remove phosphorus from wastewater. Calcium, iron, and aluminum salts are added as part of the chemical removal of phosphorus in order to achieve phosphorus precipitation by a variety of methods that are explained. However, despite the efficient chemical phosphorus removal systems, it is important to note that they may increase sludge production rates and need additional storage requirements. Using hollow fibre ultrafiltration membrane has great potential to be the alternative in treating. This study observes the effect of TiO2 as additive on the structure and performance of PVDF hollow fiber membrane for phosphorus removal. A comparative study between 0 wt% and 0.5 wt% of TiO2 with a 16 wt% and 84 wt% of polymer and solvent respectively are used in designing and fabricating the hollow fibre membrane. The morphology, water contact angle and pure water flux were being observed. The presence of nanoparticles as additive in membrane enhance the structure and performance of the hollow fiber membrane by forming more porous structure, nano pore size for nanofiltration, increase the permeability and hydrophilicity nature, increase pure water flux and increase fouling resistance that capable to remove phosphorus in wastewater treatment.

Keywords: Hollow fiber membrane, Hydrophilic, Nanofiltration, Phosphorus

Introduction

Hollow fiber membranes are thin and porous semi-permeable layer of material in hollow shape that able to separate contaminants from water when a driving force is applied. In a membrane process, fluid is passed through a barrier (Xu et al., 2016). Hydrophobic is a characteristic of membrane's layer that does not allow water molecules to pass through the membrane which make the water molecules attached on the outside layer of the membrane and caused fouling. While, hydrophilic is a characteristic of membrane's layer that allow water molecules to diffuse easily through the membrane (Gao, Thong, Yu Wang, & Chung, 2017). Nowadays, government is very concern and aware of the phenomena of the eutrophication or algae blooms cause by excessive phosphorus in wastewater (dos Santos, Ribeiro, & Ribau Teixeira, 2015).

Phosphorus is a nutrient, usually in the form of phosphates with ionic radius of 1-10 nanometers (nm) (Zeng, 2012). It is not only produced in agricultural activities, but it is also present in industrial and domestic wastewater. Excessive phosphorus in wastewater causes eutrophication and further induces to negative environmental effects. For treating phosphorus, nanofiltration (NF) provide high separation efficiency as it has a porous membrane filtration process, made from thin film layer composite of polymer that uses nanometer sized through pores that pass through the membrane. Nanofiltration membranes have pore sizes from 0.1 until 10 nanometers, nm (Wang, Zhao, Li, Li, & Wang, 2015). In order to overcome this issues, hollow fiber membrane nanofiltration which is a portable wastewater treatment is being studied by designing and fabricating the membrane with polymer, solvent and additive to observe the characteristic and also the performance of hollow fiber membrane in treating phosphorus in wastewater.

Materials and Method

This study is conducted through experimental work. The main idea is to produce hollow fibre membrane and to observe the effect of different concentration of additive on the characterization and performance of membrane. There are two parts in membrane fabrication which are designing parameters for making dope solution and fabrication parameters during spinning process.

Materials

The chemicals used in fabrication the membrane includes the 16 % of PVDF polymer, 84 wt % of N,N-dimethylformamide as the solvent, and different variation of Titanium Dioxide ($TiO2$) at 0 wt% and 0.5 wt% has been used in the preparation of the dope solution. The polymer and the solvent were mixed in glass bottle to get 500 ml of dope solution. The dope solution was stirred at 300 rpm to 400 rpm with the temperature of 60^{o}C to 65^{o}C on the heated plate for 24 hours until the polymer is dissolved. The dope solution is then allowed to be cooled and homogenized at room temperature for another 24 hours.

Methods

The dopes prepared were used in the spinning process. Hollow fibre spinning machine was used to produce the hollow fibre membrane. The water bath (bore fluid) and 500 ml of dope solution were then extruded from the spinneret to form hollow fibre membrane. All the fabrication parameters were adjusted using the controller of the hollow fibre spinning machine. During the process, the hollow fibre membrane were immersed into water bath to solidify the membrane. This process takes about 1 hour to complete the production of hollow fibre membrane for 500 ml of dope solution. Then, the hollow fibre membranes were immersed in the water bath for 1 day for more solidification process. The hollow fibre membranes were then immersed with glycerol for 30 minutes to avoid the membranes from stick to each other. Finally, the hollow fibre membranes were dried in the drying oven for 1 day to remove residual solvent on the membrane before membrane characterization for analysis.

Table 1. Characterization of hollow fibre membrane.

Spinneret outer/inner diameter	1.0 mm/ 0.5 mm
Air gap distance	1.5 cm
Velocity of gear pump inverter/spinning drum	14 rpm/
Inverter (casting speed)	5 rpm
Room temperature	27.6^{o}C
Room humidity	71.7 g/m^3

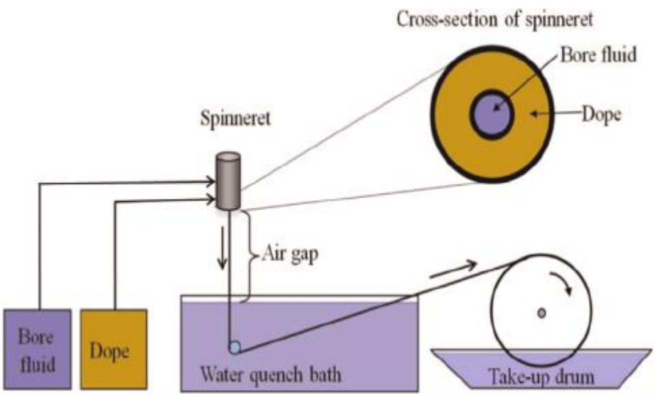


Figure 1. Hollow fibre membrane spinning process diagram (Ma et al., 2015)

Membrane Morphology

Scanning electron microscopy (SEM) was used to observe the structure and cross-section, pore size of surface and thickness of membrane. For cross-section analysis, each membrane were prepared two samples and need to dipped in the liquid nitrogen for 10 seconds so that the membrane will be hard and easy to fractured them by using knife for getting proper hollow shape of membrane. For surface analysis, no need to dipped in the liquid nitrogen and only need one sample for each membrane. Then, the samples were mounted on the brass plate and coated with platinum to increase the conductivity in the scanning electron microscopy when SEM cross-section analysis was carried out.

Water Contact Angle

Water contact angle measurement was carried out to identify the characteristic of hydrophilicity of the membrane. For water contact angle measurement, five samples of membrane were selected to measure the water contact angle accurately using the water contact angle instruments. A water drop was lowered onto the surface of the membrane from a needle tip. A magnified image of the droplet was recorded by a digital camera. Static contact angles were determined from these images with SCA20 software. The water contact angle measurement was taken as the mean value of ten different points from each membrane.

Pure Water Flux Performance

Filtration experiment was conducted using cross-flow equipment in laboratory to measure the pure water flux. This experiment is carried out to characterize the permeation performance of the prepared membranes. For membrane preparation of pure water flux test, five samples of each membrane with length of 15 cm were glued together with cotton using epoxy inside the screw adapter which was called a module after it was done. All the modules were left in room temperature for 1 day to dry. Then, the modules were soaked in the water for 30 minutes while setting up the apparatus for cross-flow filtration test. The modules were fixed into the apparatus and the water (retentate) with pressure of 30 psi was flowed through the modules for 30 minutes to get the steady static flow. After that, the reading of water flux (permeate) will be collected every two minutes for 20 minutes. The steady pure water flux (J_w) was calculated as follows:

$$J = \frac{V}{A \times \Delta t}$$

Where V is the volume of permeated pure water (L), A represents the effective area of membrane, (m2), Δt denotes the permeation time (h). The unit for the pure water flux was L/m^2.hr. (Vatsha, Ngila, & Moutloali, 2014)

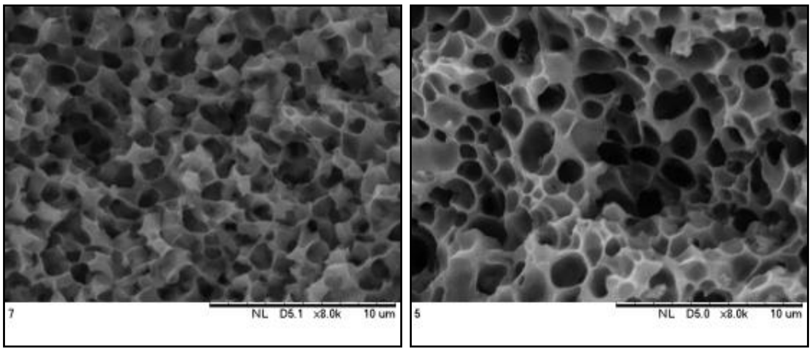
Results and Discussion

Membrane Morphology

Scanning electron microscope (SEM) was used to observe the morphology of the membrane which are pore and porosity of the membrane surface, cross-sectional of hollow fibre membrane and structure of hollow fibre membrane. Based on the Figure 2, From the observation, surface membrane with TiO_2 is more porous than the surface membrane without TiO_2. The addition of TiO_2 increases the porous structure of the hollow fibre membrane which will create better performance for the water permeation and pure water flux. This will increase the ability of the hollow fibre membrane to filter the phosphorus in wastewater. By comparing with previous research, (Abdullah et al., 2018), the addition of the TiO_2 increases the porous structure of the membrane same with this result.

For the pore sizes of the surface membrane, IMAGEJ software was used to measure the size of nano pores. The mean value for the nano pore sizes of PVDF/DMF/TiO_2 membrane is 0.32 nm which is smaller than the nano pore sizes of PVDF/DMF membrane which is 1.418 nm. The combination of smaller pore size and higher porosity was required in order to obtain porous structure membrane (A.L. Ahmad et al., 2014). PVDF and DMF are good combination in forming nanofiltration membrane which can be tested for the application for phosphorus removal in wastewater treatment. By referring to the previous journal by (Ekambaram &

Doraisamy, 2016), the combination of PVDF as polymer and DMF as solvent showed that this formula can produced nano pore sizes as the nano pore sizes that has been achieved by the previous researcher is 2.619 nm. This experiment has the same result with the previous researcher as both of the membrane produced nano pore size which is 1.418 nm for the membrane without TiO_2 and 0.32 nm for the membrane with TiO_2.



(a) (b)

Figure 2. Pores structure of the surface membrane of (a) PVDF/DMF and (b) PVDF/DMF/TiO_2

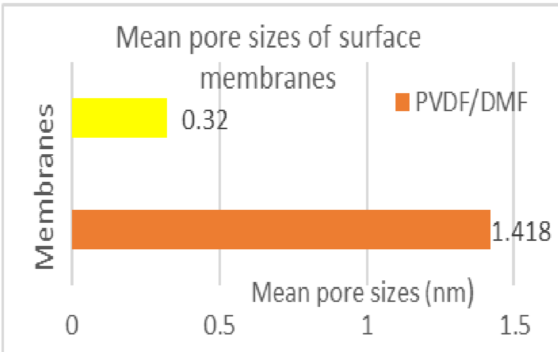
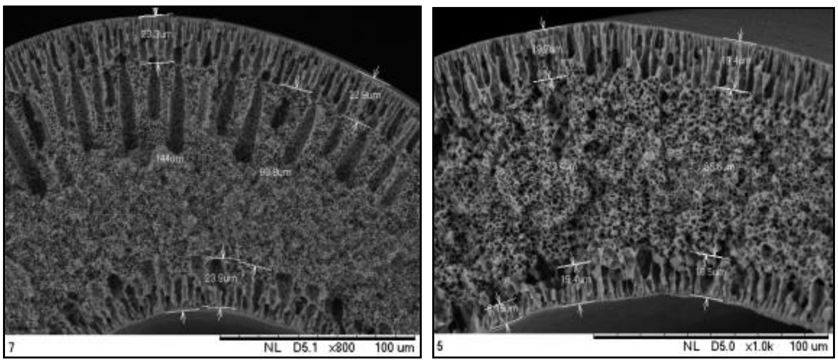


Figure 3. The horizontal bar chart graph of mean pore sizes of both membranes.

Figure 4 shows that the cross-sectional area of PVDF/DMF/TiO_2 membrane exhibit thinner wall of membrane which is 144 ųm length compared to membrane without TiO_2 which is 93.1 ųm. The structure of membrane with TiO_2 also forming more porous structure compared to membrane without TiO_2. The length of finger-like of membrane without TiO_2 is longer than the hollow fibre membrane with TiO_2.



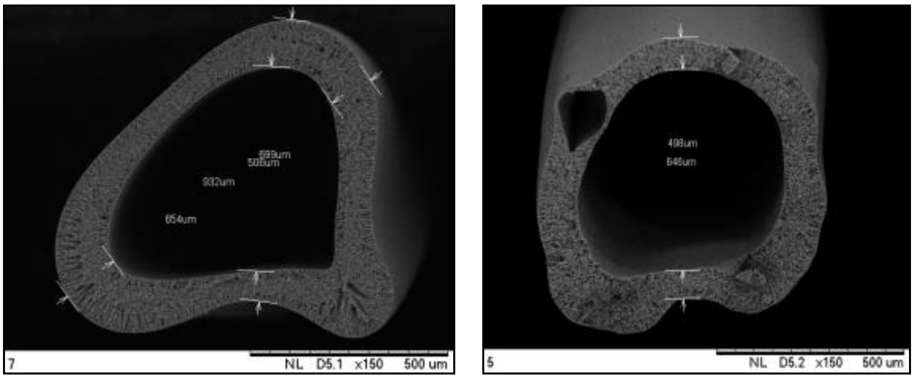
(a) (b)

Figure 4. Cross-sectional area of (a) PVDF/DMF and (b) PVDF/DMF/TiO_2.

Based on Figure 5, both of the hollow fibre membrane's structure are in irregular hollow shape. This is due to the low usage of PVDF percentage which lead to soft and improper hollow fibre membrane structure. The percentage of PVDF polymer must be increases in order to produce proper and rigid hollow structure of hollow fibre membrane. This hollow shape failure is also due to the human error when handling the sample of hollow fibre membrane such as the use of knives and hand touch during membrane preparation process.

In Figure 5 (b), there is a macrovoid defect in the structure of membrane with TiO_2 which is due to the present of voids inside the tubes of dope solution that connected to the spinneret during the hollow fibre membrane spinning process. The SEM image shows that both hollow fibre membranes with and without TiO_2 formed porous structure, have finger-like structure at outer layer and sponge-like structure at inner layer, formed nano pore sizes and also have asymmetric structure (Yuliwati & Ismail, 2011). The sponge-like structure at the inner layer is due to the water bath as bore fluid during hollow fibre spinning process which can filter phosphorus. The formation of finger-like structure occurred because of the instantaneous demixing cause by high mutual affinity of solvent and non-solvent.

The addition of TiO_2 nanoparticles as an additive increases the porosity of the structure of membrane which acts like pore former agent, decrease the thickness of the membrane's wall and forming smaller nano pore sizes compared to membrane without additive for nanofiltration process to remove phosphorus in wastewater treatment. The number of pores of membrane increase due to the enhancement of water affinity of $TiO_{2.}$ to water. (Abdullah et al., 2018)



(a) (b)

Figure 5. Structure of (a) PVDF/DMF and (b) PVDF/DMF/TiO_2.

Water Contact Angle Measurement

The characteristic of hydrophilicity and wet permeability of the membrane can be identified by carrying out the water contact angle measurement.

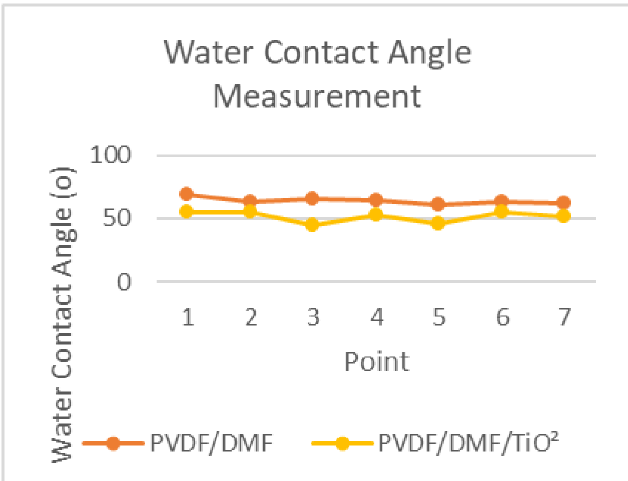


Figure 6. The line graph of water contact angle measurement of PVDF/DMF and PVDF/DMF/$TiO_{2.}$

Based on the line graph in Figure 6, the water contact angle of both hollow fibre membranes are non-uniformly pattern and fluctuated as they are increasing and decreasing but still in the same average of number of contact angle. The measurement of water contact angle of PVDF/DMF/TiO_2 are from 54.89^o to 44.70^o while the measurement of water contact angle of PVDF/DMF are from 68.73^o to 60.29$^{o.}$ This result shows that the water contact angle measurement for membrane with additive are lower than the membrane without additive. By comparing to the previous study (Shahruddin et al., 2018), combination of 15 wt% PES polymer, 84.5 wt% DMAc solvent and 0.5 wt% TiO_2 increased the hydrophilicity of the membrane as the mean water contact angle measurement was 50.1^o. This result gives slightly same contact angle measurement with the previous study as the result gained is 51.18^o.

From the observation, the addition of TiO_2 nanoparticles as an additive increase the number of pores of the surface membrane, yet increase the hydrophilicity of the membrane as the water contact angle is lower than the membrane without TiO_2 which enhance the performance of water permeation rate of the membrane and give positive effect on the water diffusion across the membrane surface. Even though the PVDF has hydrophobic characteristic, the tendency of the PVDF to have hydrophilic nature is increasing due to the addition of the TiO_2 as an additive which increase the fouling resistance of the membrane.

Pure Water Flux Performance

Pure water flux experiment was conducted by using cross-flow filtration equipment to observe the performance of the permeation of water with pressure of 30 psi through the hollow fibre membrane modules. Based on the Figure 7, the pure water flux performance of PVDF/DMF/TiO_2 decreases from 8.089 L/m².hr to 6.534 L/m².hr while pure water flux performance of PVDF/DMF decreases from 2.616 L/m².hr to 2.165 L/m².hr for every 2 minutes until 20 minutes. The bar chart graph shows the pure water flux performance of PVDF/DMF/TiO_2 is higher than the water flux performance of PVDF/DMF. The pure water flux performance of both hollow fibre membrane are decreasing for 20 minutes as the water molecules started to attach in the surface of the membrane which decrease the flux of the water during the filtration test. These results show that membrane with additive has higher pure water flux than the membrane without additive.

TiO_2 nanoparticles has low tendency for aggregation and do not clogged the pores of the membrane which lead to high pure water flux. The wall of the membrane also thinner with the present of TiO_2 which make the water molecules easier to diffuse through the pores of the membrane. By comparing to the previous study by (Shahruddin et al., 2018), the membrane fabricated with 15 wt% PES polymer, 84.5 wt% Dmac solvent and 0.5 wt% TiO_2 additive gave 7.58 L/m2.hr for the mean value of pure water flux from 20 minutes to 120 minutes. This result also has slightly different mean value for the pure water flux which is 7. 14L/m^2.hr. This is due to the nano pore sizes of the hollow fibre membrane which decreases the rate of the water molecules diffusion movement through the membrane surface. The addition of TiO_2 nanoparticles as an additive increases the porosity of membrane, the permeability of the membrane's surface and the hydrophilicity nature of the membrane which enhanced high water diffusion through the membrane and high pure water flux performance due to high affinity of TiO_2 to water molecules.

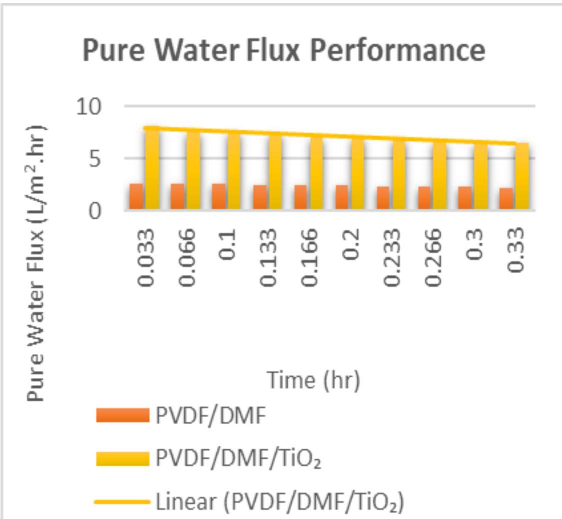


Figure 7. The bar chart graph of pure water flux performance of both modules.

Table 2. The summary of the analysis and characterization of both hollow fibre membrane.

Membranes	Mean Pore Size (nm)	Mean Water Contact Angle (^{o})	Mean Pure Water Flux (L/m².hr)
PVDF/DMF	1.418	63.75	2.40
PVDF/DMF/TiO_2	0.32	51.18	7.14

Conclusion

PVDF hollow fibre membrane with DMF as the solvent and TiO_2 as an additive and also another PVDF hollow fibre membrane without additive were successfully designed and fabricated. The effect of TiO_2 as additive on the structure and performance of the hollow fibre membranes such as the membrane morphology, the water contact angle measurement and the pure water flux performance have been studied and evaluated. The present of TiO_2 nanoparticles as an additive effect the structure and morphology of the hollow fibre membrane as the wall of the membrane became thinner, the porosity of the membrane's surface increased and formed nano pore size for nanofiltration process to remove phosphorus in wastewater treatment. Finger-like structure were formed at the outer layer and sponge-like structure were formed at the inner layer of the membrane and have asymmetric structure. The effect of additive increased the hydrophilicity of the membrane as hollow fibre membrane with TiO_2 has lower measurement of water contact angle as the permeability of membrane's surface increased. The addition of additive improved the hydrophilicity of the PVDF membrane and increase the fouling resistance on the membrane's surface.

PVDF hollow fibre membrane with TiO_2 showed higher pure water flux performance. TiO_2 nanoparticles is the best additive to produce nanofiltration for PVDF hollow fibre membrane which can enhanced the structure and performance to treat phosphorus. TiO_2 could serve as a basis for further work to demonstrate the capabilities of photocatalytic membrane to degrade organic pollutant such as phosphorus from industrial effluent. From this study, the present of nanoparticles as an additive in membrane formation enhanced the structure and performance of the hollow fibre membrane by forming more porous structure, nano pore size, increase the permeability and hydrophilicity nature, increase pure water flux and increase fouling resistance of the membrane that capable to remove phosphorus in waste water treatment.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgements

* This article was presented as an oral presentation at the International Conference on Technology, Engineering and Science (www.icontes.net) held in Antalya/Turkey on November 16-19, 2022.

References

Abdullah, N., Ayodele, B. V., Mansor, W. N. W., & Abdullah, S. (2018). Effect of incorporating TiO_2 photocatalyst in PVDF hollow fibre membrane for photo-assisted degradation of methylene blue. *Bulletin of Chemical Reaction Engineering & Catalysis, 13*(3), 588–591.

Ahmad, A.L., Ideris, N., Ooi, B. S., Low, S. C., & Ismail, A. (2014). Influence of polymer concentration on pvdf membrane fabrication for immunoassay analysis. *Journal of Applied Sciences, 14*(12), 1299–1303.

dos Santos, C., Ribeiro, A., & Ribau Teixeira, M. (2015). Phosphorus recovery from waters using nanofiltration. *Desalination and Water Treatment, 55*(5), 1308–1315.

Ekambaram, K., & Doraisamy, M. (2016). Study on the fabrication, characterization and performance of PVDF/calcium stearate composite nanofiltration membranes. *Desalination, 385*, 24–38.

Gao, J., Thong, Z., Yu Wang, K., & Chung, T. S. (2017). Fabrication of loose inner-selective polyethersulfone (PES) hollow fibers by one-step spinning process for nanofiltration (NF) of textile dyes. *Journal of Membrane Science, 541*, 413–424.

Shahruddin, M. Z., Zakaria, N., Diana Junaidi, N. F., Alias, N. H., & Othman, N. H. (2018). Study of the effectiveness of Titanium Dioxide (TiO2) nanoparticle in Polyethersulfone (PES) composite membrane for removal of oil in oily wastewater. *Journal of Applied Membrane Science & Technology, 19*(1), 33-42.

Vatsha, B., Ngila, J. C., & Moutloali, R. M. (2014). Preparation of antifouling polyvinylpyrrolidone (PVP 40K) modified polyethersulfone (PES) ultrafiltration (UF) membrane for water purification. *Physics and Chemistry of the Earth, Parts A/B/C, 67*, 125-131.

Wang, T., Zhao, C., Li, P., Li, Y., & Wang, J. (2015). Effect of non-solvent additives on the morphology and separation performance of poly(m-phenylene isophthalamide) (PMIA) hollow fiber nanofiltration membrane. *Desalination, 365*, 293–307.

Xu, Z., Wu, T., Shi, J., Teng, K., Wang, W., Ma, M., & Fan, J. (2016). Photocatalytic antifouling PVDF ultrafiltration membranes based on synergy of graphene oxide and TiO2 for water treatment. *Journal of Membrane Science, 520*, 281–293.

Yuliwati, E., & Ismail, A. F. (2011). Effect of additives concentration on the surface properties and performance of PVDF ultrafiltration membranes for refinery produced wastewater treatment. *Desalination*, *273*(1), 226–234.

Zeng, Z. (2012). *Phosphorus removal by ceramic tight ultra-filtration (CTUF) membranes for RO pre-treatment* (master thesis), Delft University of Technology, Delf.

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To cite this article:

Mansor, H. & Mohd Sobran, N.H. (2022). Effect of additive on the structure and performance of PVDF hollow fiber membrane on phosphorus removal. *The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 21*, 363-370.