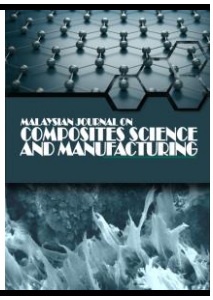
Penerbit Akademia Baru

Malaysian Journal on Composites Science and Manufacturing

Journal homepage:

https://akademiabaru.com/submit/index.php/mjcsm
ISSN: 2716-6945



Relationship of Additive Dosages to Polyvinylidene Fluoride (PVDF) Ultrafiltration: Dye Rejection Study

Khairul Anwar Mohamad Said[1, 2,*], Aiman Nabil Mohd. Ikhmal[1], Md Rezaur Rahman[1,2], Mohamed Afizal Mohamed Amin[1,2] , Muhammad Khusairy Bakri[3]

[1] Department of Chemical Engineering and Energy Sustainability, Faculty of Engineering, Universiti Malaysia Sarawak (UNIMAS), Kota Samarahan, Sarawak, Malaysia
[2] UNIMAS Water Centre, Faculty of Engineering, Universiti Malaysia Sarawak (UNIMAS), Kota Samarahan, Sarawak, Malaysia
[3] Composite Materials and Engineering Center, Washington State University, 2001 East Grimes Way, 99164, Pullman, Washington, United States of America

ARTICLE INFO

Article history:
Received 10 September 2024
Received in revised form 10 December 2024
Accepted 31 December 2024
Available online 30 March 2025

Keywords:
PVDF; ultrafiltration; dye rejection; membrane; copper; magnesium

ABSTRACT

Ultrafiltration membrane is often used in wastewater treatment plants to remove dyes and other contaminations. This study aims to improve the properties and methylene blue rejection efficiency of the polyvinylidene fluoride (PVDF) ultrafiltration (UF) membranes by introducing copper acetate monohydrate/magnesium sulphate (CuMgNTs) at different loading dosages. The flat sheet membranes were successfully fabricated using the phase inversion method. The physicochemical properties of membranes were characterized by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) and Fourier transform infrared spectroscopy (FT-IR). The pure water flux tests showed that the M3 membrane with 3wt.% of CuMgNTs loading exhibits the highest pure water flux of 47 L/m^{2}h. For methylene blue rejection efficiency M3 membrane possessed the highest rejection efficiency up to 94%. The M3 membrane performance showed an increase in pure water flux and methylene blue dye rejection up to 224% and 74%, respectively, compared to pristine PVDF membrane. Therefore, it can conclude that 3wt.% of CuMgNTs is the optimum loading for PVDF UF membrane in improving its permeability towards pure water and performance to reject methylene blue dyes.

1. Introduction

In this modern era, the rapid growth of economy root to the activities of factories, chemical plant, manufacturing industries, etc. become more active. This has increased the amount of wastewater effluent from the processes and led to the pollution of our natural water sources, consequently causing a water shortage. Many industries such as textile, leather, paper, food, and plastics industries released high levels of hazardous and recalcitrant substances, such as dyes, which can cause negative impacts on the environmental and human health [1].

* *Corresponding author.*
E-mail address: mskanwar@unimas.my

https://doi.org/10.37934/mjcsm.16.1.201211

There are many types of membranes that are used for effluents treatment containing dyes, such as ultrafiltration (UF), reverse osmosis (RO) and nanofiltration (NF) membranes [2]. UF membranes are usually utilized as a preferable pre-treatment method for NF or RO processes when treating dyeing wastewater. Nevertheless, the hydrophobicity nature and substantial surface energy of PVDF membranes frequently result in severe membrane fouling and a decline in flux during the treatment of dyeing wastewater [3]. To overcome this problem, incorporating hydrophilic substances into the membrane is one the method that can be applied to improve the PVDF membrane performance. The dye removal rate had been improved by incorporating the TiO_2 nanoparticles into the PVDF membrane. Other nanoparticles such as CuO, Fe_2O_3 and Al_2O_3 as well as thiourea also can be used to improve the membrane performance [4].

In recent decades, the modification of PVDF UF membrane for dye removal has been widely studied. Membrane modification by blending membranes with fillers of additives has shown an improvement in the removal of methylene blue up to 97% dye removal and 92% COD reduction [2]. However, the loading dosage of the additives also influenced the performance of the membranes. As stated by Ibrahim *et al.,* excessive loading of additives can lead to reduce in membrane performance [5]. According to Suresh *et al.,* the amount of additive in PVDF membrane is between 0.15 to 4 wt% with the removal of various types of dye such as congo red, methylene blue, direct blue 14 and sunset yellow FCF can reach up to 98% [6]. Therefore, it is crucial to determine the optimum loading of additives to be applied on the PVDF UF membrane so that the membrane can achieved the highest performance, especially in removal of dyes.

In this study, the PVDF membrane will be doped with different dosages of nanomaterials, which are copper acetate monohydrate and magnesium sulphate heptahydrate that is synthesized using thiourea (denoted as CuMgNTs). The role of thiourea is to assist the growth of CuMgNTs [7]. This modified membrane will be label as PVDF/CuMgNTs in this study and will be applied on an ultrafiltration application for removing dyes from wastewater. The kinetic and isotherm models were also studied to better understand the adsorption mechanism.

2. Methodology

2.1 Materials

Polyvinylidene fluoride (resin, PVDF), N, N-dimethylacetamide (99%, DMAc) and methylene blue (powder, MB) were purchased from Sigma Aldrich. Copper acetate monohydrate/magnesium sulphate (powder, CuMgNTs) was supplied by Comilla University, Bangladesh.

2.2 Membrane Fabrication

A total of six CuMgNTs nanoparticles were prepared by varying the polymer dopes content from 0 to 5 wt% per wt% PVDF. By using a roller, the dope solution was casted on a glass plate and immersed in ultrapure water at room temperature for a minimum of 24 hours. Table 1 shows the nanoparticles loadings that were tested in this research.

Table 1
PVDF membrane configuration

Type of membrane	CuMgNTs loadings		PVDF, wt%	DMAc solvent, wt%
	wt.%	g		
M0	0	0	15	85
M1	1	0.045		
M2	2	0.090		
M3	3	0.135		

2.3 Membrane Characterization

The morphology of the prepared membranes was analyzed by using scanning electron microscopy (SEM, Hitachi TM4000 plus, Japan) combined with energy dispersive X-ray (EDX, Bruker instrument, Germany) for elemental analysis. The prepared membrane samples were cut into smaller pieces to fit on the specimen stage. The membrane samples were immersed in liquid nitrogen for several minutes in order to obtain a better image and eliminate surface bends. Then, the membranes were fractured spontaneously.

2.4 Porosity and Mean Pore Size

The method to analyze the porosity and mean pore size of the membranes was obtained from [8]. For measuring the porosity of the membranes, wet and dry membrane gravimetric methods were employed. The membranes were cut into a circular size with a diameter of 44 mm and soaked in ultra-pure water. The porosity of the membranes was measured by weighing them after soaking and weighing the dry membrane. The formula that was involved in the calculation is as follows:

$$\varepsilon = \frac{(\omega 1-\omega 2)/\rho_w}{(\omega 1-\omega 2)/\rho_w+\omega 2/\rho_p} \quad (1)$$

where, ε: the porosity of the membrane (%), ω1: wet weights of the membrane (g), ω2: dry weights of the membrane (g), ρ_w: water density (0.998 g/cm3), and ρ_p: density of the PVDF (1.765 g/cm3).

Meanwhile, for the mean pore size, the value of volume of permeate water in unit time (V) was obtained from pure water flux experiment. The mean pore size of the membranes was calculated according to Guerout–Elford–Ferry equation as follows:

$$r_m = \sqrt{\frac{(2.9-1.75\varepsilon)\times 8\eta LV}{\varepsilon \times S \times \Delta P}} \quad (2)$$

where, r_m: Mean pore size (µm), ε: Membrane porosity (%), η: viscosity of water (8.9×10^{-4} Pa s), L: membrane thickness (m), V: Volume of permeate water in unit time (m^3/s^{-1}), S: Effective filtration of the membrane (m^2), and ΔP: transmembrane pressure (Mpa).

2.5 Pure Water Flux

The prepared membranes were cut into a circular size with a diameter of 44 mm. The pure water flux, also known as pure water permeability, was determined by measuring the pure water flux using an Amicon® Stirred Ultrafiltration Cell with constant transmembrane pressure of 2 bar. Every 10 minutes, the volume of water passing through the PVDF membrane was collected and recorded until

at least three constant volumes were obtained. The pure water flux (J_p) was calculated using following formula.

$$J_p = \frac{V}{A \times t} \quad (3)$$

where, J_p: pure water flux ($L.m^{-2}.h^{-1}$), V: Constant volume of filtered pure water (L), A: effective membrane area (m^2), and t: permeation time (h).

2.6 Dye Rejection

The method to evaluate the membrane performance for the removal of dye was referred to [1]. In this experiment, methylene blue (MB) solution was prepared in 10, 20 and 30 ppm concentrations. Every 5 minutes, the MB dye solution was passed across the membranes for 1 hour using a Amicon® Stirred Ultrafiltration Cell at 2 bar operating pressure. The absorbance of the MB solution was then measured using a UV spectrophotometer at 663 nm, and the corresponding concentration was calculated based on standard curve. The MB solution rejection ratio was estimated using the formula below.

$$R = \left(1 - \frac{C_P}{C_f}\right) \times 100\% \quad (4)$$

where, C_p: permeate concentrations, and C_f: feed concentrations of the dye solutions.

3. Results and Discussion

3.1 Membrane Morphology

The cross-section morphology of the membranes was observed via SEM at 1500× magnification as shown in Figure 1. All membranes possess a typical asymmetric structure consisting of a thin dense top-layer with finger-like pores linked by sponge walls. This sponge-like walls formed between the pores comprise a porous network of interconnected PVDF polymer chains, which provide structural support to the membrane while enabling fluid flow through the interconnected pores.

Due to the addition of CuMgNTs nanoparticles, it is observed that the formation of a finger-like structure was enhanced and seems to extend to the central of the membranes. This may be due to the hydrophilic properties of the CuMgNTs nanoparticles, which increase the solvent/non-solvent exchange rate during the phase inversion [9]. This hydrophilic additive increases the surface tension of the casting solution, which makes it more difficult for the solvent to evaporate. This means that the solvent will remain in the casting solution for longer, which will give the non-solvent more time to diffuse into the casting solution and cause phase inversion. Hence, it led to the formation of membranes with improved properties, such as higher permeability and selectivity.

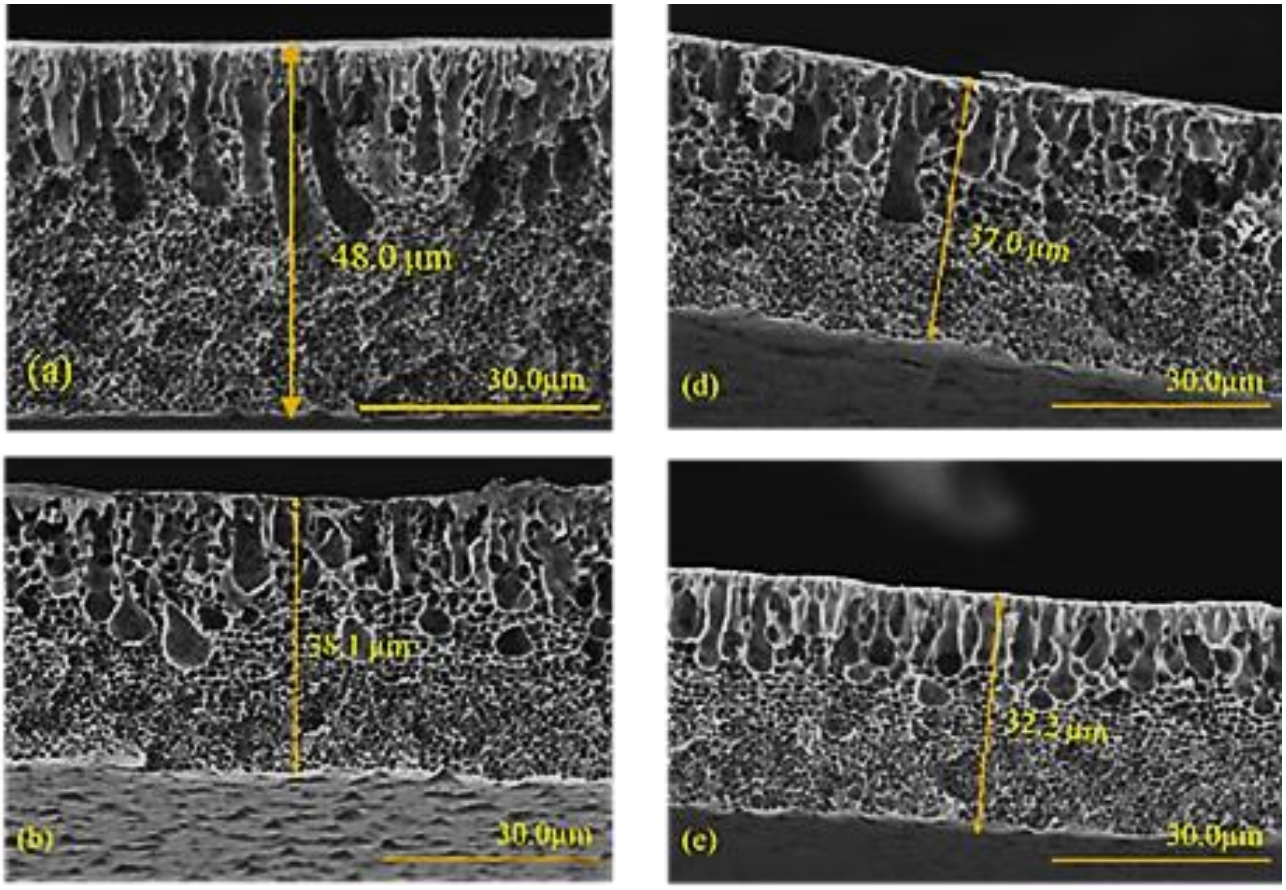


Fig. 1. SEM cross-section morphologies of CuMgNTs-PVDF membranes at 1.5k× magnification; (a) M0 (b) M1 (c) M2 (d) M3

Figure 2 illustrates the presence of Cu and Mg elements in membrane M3, whereas these elements are absent in the pristine membrane (M0). Thus, it can be confirmed that the integration of CuMgNTs into the PVDF membranes was successfully achieved.

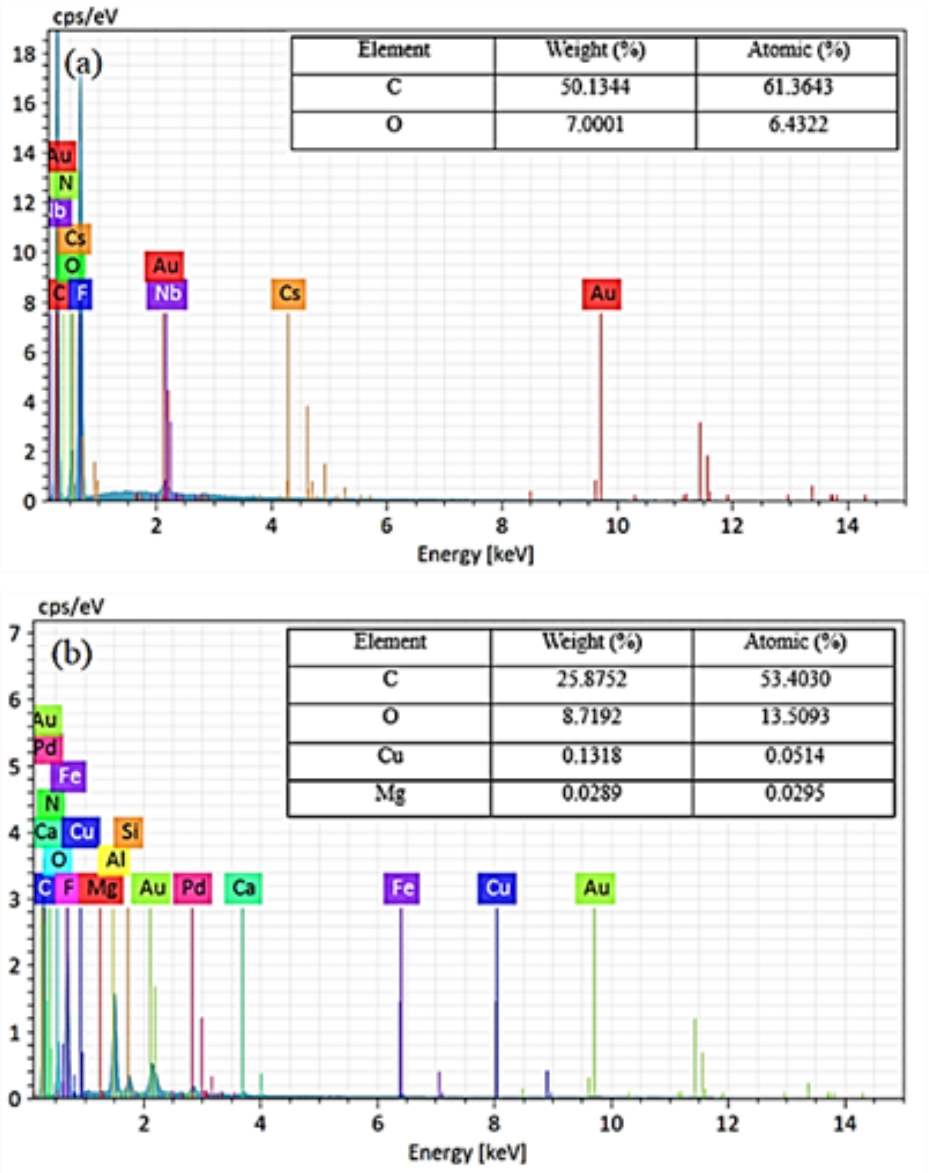


Fig. 2. EDX elemental analysis of the (a) M0 and (b) M3 membranes

3.2 Membrane Pore Characteristics

Table 2 present the pore characteristics of the membranes, which were determined by the gravimetric method. The average porosity and mean pore size were calculated by taking three samples of each membrane. The highest porosity was recorded for M2 (2 wt% CuMgNTs) at 78.01%, followed by M3, M0, and M1.

Table 2
Porosity, mean pore size, tortuosity, and pore density of the prepared membranes

Membrane	Porosity (%)	Mean Pore Size (nm)
M0	74.23	3.58
M1	73.25	5.09
M2	78.01	4.04
M3	74.92	6.78

In addition, the mean pore size of the CuMgNTs-PVDF membranes was determined by using the gravimetric method. According to Singh and Hankins (2016), the pore size of a membrane determines the classification of the membrane processes in water treatment [10,22]. In the case of the ultrafiltration process, the pore size falls under the range of 50.0-1.0 nm. As shown in Table 2, it was determined that the prepared membranes in this study possessed the mean pore size ranges from 3.58 nm to 6.78 nm, which falls under the range of ultrafiltration process. It was also observed that the mean pore size of all the modified membranes were also enlarged compared to the neat membrane (M0).

3.3 Water Flux

Figure 3 presents the results of the steady-state pure water flux for the prepared membranes. Due to its hydrophobic nature, the pristine PVDF membrane, M0, exhibited the lowest pure water flux at 14.6 L/m^2.h. Incorporating CuMgNTs into the PVDF membrane resulted in improved pure water flux, indicating that CuMgNTs can enhance the flux of polymeric membranes. The 3wt% CuMgNTs (M3) membrane achieved the highest stable flux at 47.4 L/m^2.h, demonstrating a remarkable improvement of 224.32% compared to the pristine membrane. Despite modifications, the lowest pure water flux was observed in M2 at 18.9 L/m^2.h, which still outperformed the pristine membrane. According to Jee *et al.,* pure water flux is influenced by membrane hydrophilicity and morphology [2]. Therefore, the increased pure water flux in the modified membrane can be attributed to the incorporation of CuMgNTs, which significantly improved membrane hydrophilicity and reduced mass transfer resistance [3].

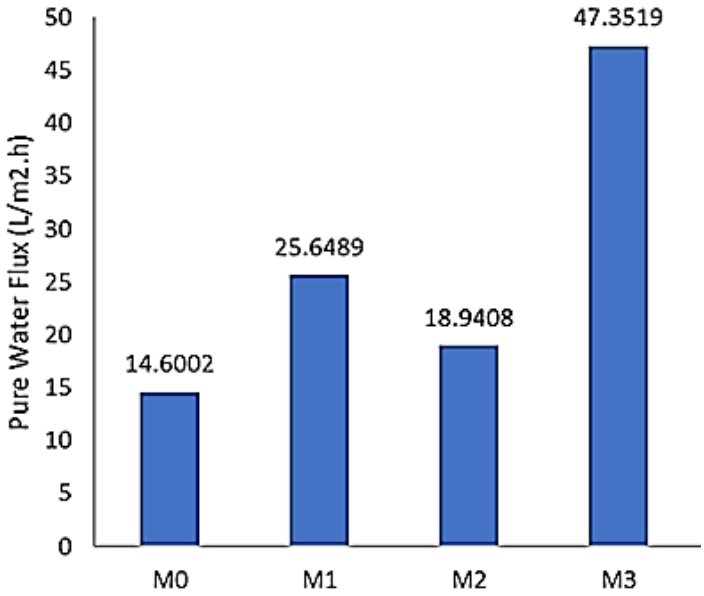


Fig. 3. Steady state of pure water flux of the prepared PVDF membranes

3.4 Methylene Blue (MB) Dye Rejection

The results of the average MB rejection during the first 30 minutes of filtration are shown in Figure 4. As can be observed, the results of this study showed that membrane M3 had the highest rejection efficiency for MB at all concentrations tested. The rejection efficiency of membrane M3 was 94.04%, 74.91%, and 78.91% for MB concentrations of 10 ppm, 20 ppm, and 30 ppm, respectively. In

contrast, M2 had a slightly lower rejection efficiency than membrane M3, with rejection efficiencies of 94.17% (10 ppm), 68.67% (20 ppm), and 71.8% (30 ppm). Meanwhile, the lowest rejection efficiency was found on M0, with rejection efficiencies of 53.83% (10 ppm), 57.60% (20 ppm), and 65.8% (30 ppm). Therefore, the initial adsorbent dosage (CuMgNTs) had a significant impact on the removal efficiency. This is because the increase in adsorbent dosage led to an increase in the available surface area and adsorption sites, hence, the more adsorbent there is, the more dye molecules can be adsorbed [13].

Other than that, by comparing the mean pore size in Table 2 and MB dye rejection in Figure 4, the rejection efficiency increases as the mean pore size increases from membranes M0, M2 and M3. In addition to that, the mean pore size of the membranes (ranging from 3.58 to 7.12 nm) was basically larger than the methylene blue dye molecules, which has approximately the size of a rectangular block that is 17×7.6 ×3.3 Å (or 1.7×0.76×0.33nm) [4]. According to study by Oyarce *et al.,* supposedly the smaller pore size will have the ability to remove higher percentage of dye [5]. However, there are some exceptions to this theory. For example, some dyes can be rejected by membranes even when the pore size is larger than the dye molecules. This is because the dye molecules can be electrostatically repelled by the membrane, which prevents them from passing through the pores [6]. In the case of methylene blue dye, it is negatively charged [7]. This means that they are attracted to positively charged surfaces of the PVDF membrane. Therefore, when the pore size of the membrane is larger than the dye molecules, the dye molecules can be electrostatically attracted to the membrane surface, which prevents them from passing through the pores [8]. This is why a larger pore size can actually lead to a higher percentage of methylene blue dye being rejected by the PVDF membrane.

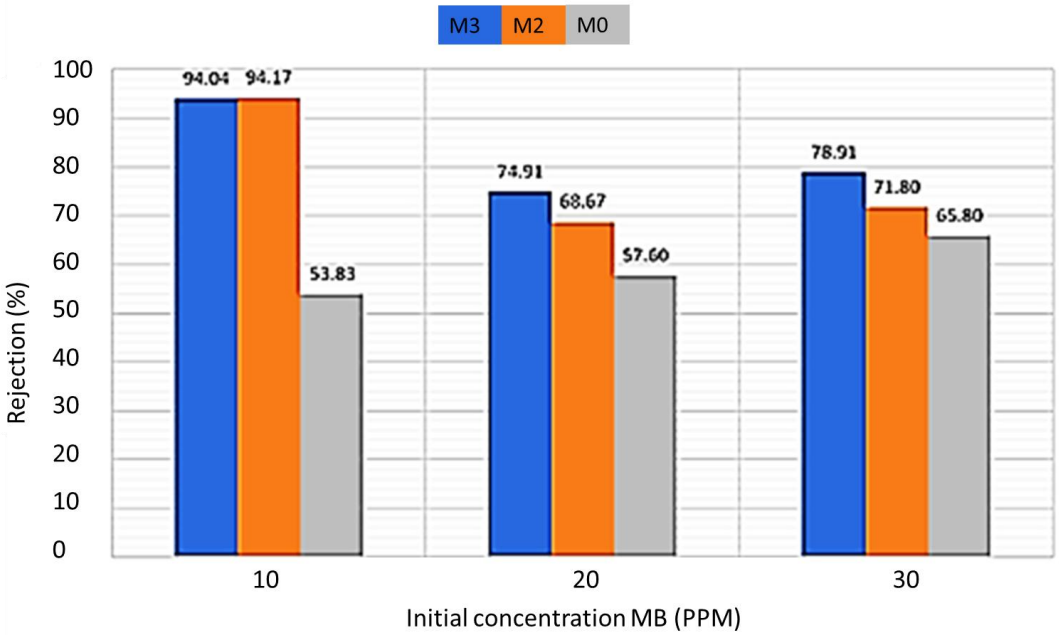


Fig. 4. 10, 20, and 30 ppm MB dyes average rejection efficiency by CuMgNTs-PVDF membranes

In terms of dye rejection over time, the focused was on the rejection of MB dye at 30 ppm concentration as shown in Figure 5. All the tested membrane (M3, M2 and M0) exhibited a similar rejection trend, which decreased gradually with time. At initial (t=5min), M3 possessed the lowest MB rejection efficiency (83.34%), followed by M0 (86.53%) and M2 (88.33%). However, with increasing in time, M3 able to have higher MB rejection efficiency among the membranes. The

highest rejection efficiency was recorded at t=10min which is 85.87%, and then gradually decreasing with time until it reached 69.91% rejection efficiency at t=30min. The reduced in dye rejection efficiency of the membranes is caused by pore blocking phenomenon, where the dye molecules accumulate on the membrane surface, then can block the smaller pores [9,23]. After a certain time, the smaller pores will be occupied by the dye molecules, which then leaves only the larger pores open, thus allowing more dye molecules to pass through the membrane.

In the previous study by Isawi, the nanocomposite PVA/PVDF membrane with CuO nanoparticles showed an enhanced dye rejection efficiency, up to 95% which almost similar our study [10]. Another study was also conducted by Karimi *et al.,* that also enhanced the dye rejection efficiency of PVDF-modified membrane with Cu_2S nanoparticles with highest rejection efficiency of reactive blue 21 dye, direct black 38 dye, and direct yellow 12 dye obtained were 99.8%, 99.2%, and 73.8%, respectively [11]. The low rejection efficiency for yellow 12 dye is due to the molecular size of the dye that very small that allows it to pass through the membrane. Therefore, comparing this study to the previous studies, it shows that CuMgNTs is also a great nanomaterial that can enhance the dye removal efficiency as well as permeability of the membrane.

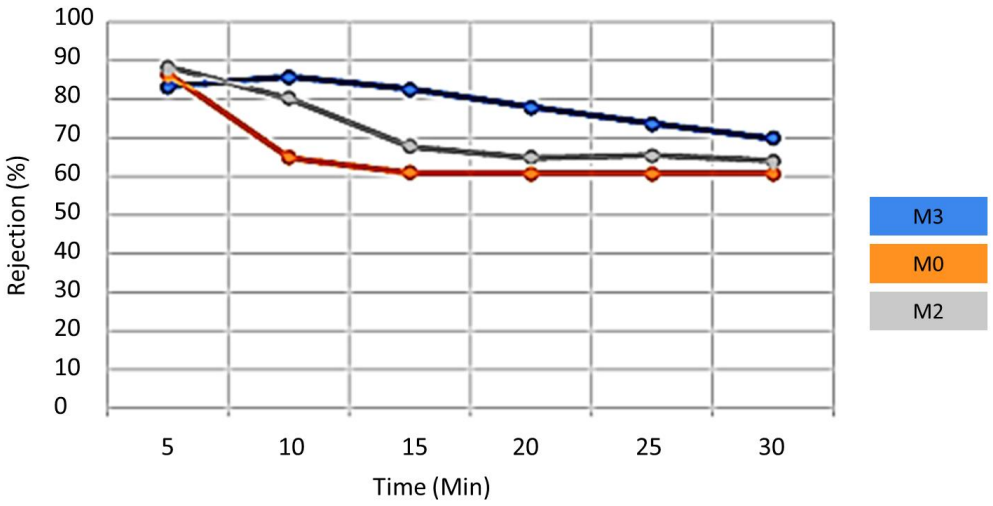


Fig. 5. 30 ppm MB dye rejection during 30 minutes filtration by CuMgNTs-PVDF membranes

4. Conclusions

The membrane performances were executed in terms of pure water flux and methylene blue (MB) dye rejection. Based on the performance, the pure water flux of the membranes was enhanced with the highest pure water flux obtained by M3, which increased by 224.32% compared to the pristine membrane. The performance of the membrane via MB dye rejection also shows a promising rejection efficiency by membrane M3, with 94.04% rejection efficiency for 10 ppm MB. This was increased 74.7% compared to pristine membrane. However, the rejection efficiency of the membranes was declined as the concentration of MB increases to 20 and 30 ppm.

Acknowledgement
The author would like to acknowledge Osaka Gas Foundation of International Cultural Exchange (OGFICE) for financing this research with grant number INT/F02/OSAKA-IG/85662/2023. The author also acknowledges Research, Innovation and Enterprise Centre (RIEC), Universiti Malaysia Sarawak (UNIMAS) for managing research activity.

References

[1] Lellis, Bruno, Cíntia Zani Fávaro-Polonio, João Alencar Pamphile, and Julio Cesar Polonio. "Effects of textile dyes on health and the environment and bioremediation potential of living organisms." *Biotechnology Research and Innovation* 3, no. 2 (2019): 275-290. https://doi.org/10.1016/j.biori.2019.09.001

[2] Buscio, V., M. Crespi, and C. Gutiérrez-Bouzán. "Application of PVDF ultrafiltration membranes to treat and reuse textile wastewater." *Desalination and Water Treatment* 57, no. 18 (2016): 8090-8096. https://doi.org/10.1080/19443994.2015.1021854

[3] Li, Renjie, Yanting Wu, Liguo Shen, Jianrong Chen, and Hongjun Lin. "A novel strategy to develop antifouling and antibacterial conductive Cu/polydopamine/polyvinylidene fluoride membranes for water treatment." *Journal of colloid and interface science* 531 (2018): 493-501. https://doi.org/10.1016/j.jcis.2018.07.090

[4] Arumugham, Thanigaivelan, Reshika Gnanamoorthi Amimodu, Noel Jacob Kaleekkal, and Dipak Rana. "Nano CuO/g-C3N4 sheets-based ultrafiltration membrane with enhanced interfacial affinity, antifouling and protein separation performances for water treatment application." *Journal of Environmental Sciences* 82 (2019): 57-69. https://doi.org/10.1016/j.jes.2019.03.001

[5] Ibrahim, N. A., M. D. H. Wirzal, N. A. H. Nordin, and N. S. Abd Halim. "Development of polyvinylidene fluoride (PVDF)-ZIF-8 membrane for wastewater treatment." In *IOP conference series: earth and environmental science*, vol. 140, no. 1, p. 012021. IOP Publishing, 2018. https://doi.org/10.1088/1755-1315/140/1/012021

[6] Suresh, R., Saravanan Rajendran, Lalitha Gnanasekaran, Pau Loke Show, Wei-Hsin Chen, and Matias Soto-Moscoso. "RETRACTED: Modified poly (vinylidene fluoride) nanomembranes for dye removal from water–A review." *Chemosphere* 322 (2023): 138152. https://doi.org/10.1016/j.chemosphere.2023.138152

[7] Ciapina, E. G., E. A. Carbonio, F. Colmati, and Ernesto Rafael Gonzalez. "The effect of adsorption of thiourea on the particle size of supported platinum nanocatalysts synthesized by chemical reduction." *Journal of power sources* 175, no. 1 (2008): 18-25. https://doi.org/10.1016/j.jpowsour.2007.09.094

[8] Said, Khairul Anwar Mohamad, A. F. Ismail, A. K. Zulhairun, M. S. Abdullah, M. Ariff Azali, and Mohd Nizam Zainal Abidin. "Magnetic induced asymmetric membrane: Effect of magnetic pattern to phenol removal by adsorption." *Materials Chemistry and Physics* 278 (2022): 125692. https://doi.org/10.1016/j.matchemphys.2021.125692

[9] Pishbin, Roshanak, Toraj Mohammadi, and Maryam Ahmadzadeh Tofighy. "PVDF ultrafiltration membranes containing copper oxide-charcoal based graphene oxide nanohybrids with enhanced performance and antifouling properties." *Process Safety and Environmental Protection* 176 (2023): 180-195. https://doi.org/10.1016/j.psep.2023.05.086

[10] Singh, Rajindar, and Nicholas Hankins, eds. *Emerging membrane technology for sustainable water treatment*. Elsevier, 2016.

[11] Jee, Ki Yong, Jae Sung Kim, Jinsoo Kim, and Yong Taek Lee. "Effect of hydrophilic Cu3 (BTC) 2 additives on the performance of PVDF membranes for water flux improvement." *Desalination and Water Treatment* 57, no. 38 (2016): 17637-17645. https://doi.org/10.1080/19443994.2015.1085912

[12] Cheng, Lilantian, Zixun Zhou, Lei Li, Pei Xiao, Yun Ma, Fei Liu, and Jian Li. "PVDF/MOFs mixed matrix ultrafiltration membrane for efficient water treatment." *Frontiers in Chemistry* 10 (2022): 985750. https://doi.org/10.3389/fchem.2022.985750

[13] Ghaedi, M., A. M. Ghaedi, M. Hossainpour, A. Ansari, M. H. Habibi, and A. R. Asghari. "Least square-support vector (LS-SVM) method for modeling of methylene blue dye adsorption using copper oxide loaded on activated carbon: Kinetic and isotherm study." *Journal of Industrial and Engineering Chemistry* 20, no. 4 (2014): 1641-1649. https://doi.org/10.1016/j.jiec.2013.08.011

[14] Arias, M., E. López, A. Nuñez, D. Rubinos, B. Soto, M. T. Barral, and F. Díaz-Fierros. "Adsorption of methylene blue by red mud, an oxide-rich byproduct of bauxite refining." *Effect of mineral-organic-microorganism interactions on soil and freshwater environments* (1999): 361-365. https://doi.org/10.1007/978-1-4615-4683-2_39

[15] Oyarce, Estefanía, Karina Roa, Andrés Boulett, Sebastián Sotelo, Plinio Cantero-López, Julio Sánchez, and Bernabé L. Rivas. "Removal of dyes by polymer-enhanced ultrafiltration: an overview." *Polymers* 13, no. 19 (2021): 3450. https://doi.org/10.3390/polym13193450

[16] Koulivand, Habib, Afsaneh Shahbazi, and Vahid Vatanpour. "Fabrication and characterization of a high-flux and antifouling polyethersulfone membrane for dye removal by embedding Fe3O4-MDA nanoparticles." *Chemical Engineering Research and Design* 145 (2019): 64-75. https://doi.org/10.1016/j.cherd.2019.03.003

[17] Zhang, Ye, Gongyi Li, Junming Liu, Tao Wang, Xue Wang, Bin Liu, Yunling Liu, Qisheng Huo, and Zengyong Chu. "Synthesis of hierarchical hollow sodium titanate microspheres and their application for selective removal of organic dyes." *Journal of Colloid and Interface Science* 528 (2018): 109-115. https://doi.org/10.1016/j.jcis.2018.05.069

[18] Liu, Gonggang, Hongqi Ye, Antai Li, Chenyuan Zhu, Heng Jiang, Yong Liu, Kai Han, and Yonghua Zhou. "Graphene oxide for high-efficiency separation membranes: Role of electrostatic interactions." *Carbon* 110 (2016): 56-61. https://doi.org/10.1016/j.carbon.2016.09.005

[19] Nawaz, Hifza, Muhammad Umar, Iqra Nawaz, Azeem Ullah, Muhammad Tauseef Khawar, Marek Nikiel, Humaira Razzaq, Muhammad Siddiq, and Xuqing Liu. "Hybrid PVDF/PANI membrane for removal of dyes from textile wastewater." *Advanced Engineering Materials* 24, no. 5 (2022): 2100719. https://doi.org/10.1002/adem.202100719

[20] Isawi, Heba. "Evaluating the performance of different nano-enhanced ultrafiltration membranes for the removal of organic pollutants from wastewater." *Journal of Water Process Engineering* 31 (2019): 100833. https://doi.org/10.1016/j.jwpe.2019.100833

[21] Karimi, Atefeh, Alireza Khataee, Ali Ghadimi, and Vahid Vatanpour. "Ball-milled Cu2S nanoparticles as an efficient additive for modification of the PVDF ultrafiltration membranes: Application to separation of protein and dyes." *Journal of Environmental Chemical Engineering* 9, no. 2 (2021): 105115. https://doi.org/10.1016/j.jece.2021.105115

[22] Khashi'Ie, Najiyah Safwa, and Khairum Hamzah. "Mechanical properties of jute fiber polyester hybrid composite filled with eggshell." *Semarak Eng J* 6, no. 1 (2024): 20-8. https://doi.org/10.37934/sej.6.1.2028

[23] Zaman, Haydar. "Physico-Mechanical Behaviors of Chemically Treated Natural Fibers Reinforced Hybrid Polypropylene Composites." *Malaysian Journal on Composites Science and Manufacturing* 15, no. 1 (2024): 25-40. https://doi.org/10.37934/mjcsm.15.1.2540