

PAPER 24 – APPLICATION OF MODIFIED HOLLOW PVDF-MEMBRANE SYSTEM FOR REMEDIATING PALM OIL MILL EFFLUENT

M. Abdulsalam*, I. B. Dalha, S. U. Yunusa

Department of Agricultural and Bio-resources Engineering, Faculty of Engineering, Ahmadu Bello University, Zaria.

*Email: m.abdulsalamim@gmail.com

ABSTRACT

The objective of this work was to introduce an advanced wastewater treatment technology; co-polymerized polyvinyl difluoride (PVDF)-polyethylene glycol (PEG) membrane system for anaerobically-pretreated palm oil mill effluent (POME) treatment. The co-polymerized hollow fibre membranes were fabricated using a wet spinning technique and then used to remediate POME as the feedstock. The physicochemical properties of the POME were analyzed before and after treatment with the hollow fibre. The analyzed parameters included chemical oxygen demand (COD), colour, total suspended solids (TSS), turbidity (TDS), and total nitrogen (TN). A preliminary test was carried out using distilled water before continuing with POME as a feed solution. The average permeate flux obtained by the PVDF-PEG membrane was 70 L/m².hr with a slight flux decline that is probably due to the attachment of foulants compounds on the membrane surface and pores. The synthesized modified membrane reduced the COD, colour, TSS, TDS and TN by 92.1, 86, 97.89, 99.98 and 80.26 %, respectively. In conclusion, it can be said that the modified PVDF-PEG membrane demonstrated excellent performance in treating the POME to produce a permeate with better qualities.

KEYWORDS: Nano-MgO, PVDF-PEG Membrane, POME, Filtration, Contaminants Removal

1 INTRODUCTION

The commonly applied nanoparticles to modified polymeric membranes includes ZnO, TiO₂, Ag₂O₃, Al₂O₃, graphene oxide, SiO₂ and CuO (Jhaveri & Murthy, 2016). Tan et al., (2017) enhanced the permeation and antifouling properties of a bared PVDF membrane by incorporating synthesized Zn-Fe oxide (ZIO) into the matrix structure. The nanocomposite membrane with 0.5 wt % ZIO loading demonstrated a significant increase in permeate flux to the magnitude of 25% raise compared to the bared PVDF membrane. Also, Shen et al., (2012) modified the matrix structure of polymeric membrane using ZnO nano-additive. The result showed that the additive had significant influence on the pores structure as well as the hydrophilicity of the membrane. Over 254% improvement in permeability flux was reported at the loading of 0.3 g ZnO nano-additive. Furthermore, the authors validated that the porosity of the modified composite membrane increased with the presence of the nano-additive, which ultimately justified the reported high flux. The Nano-ZnO has large surface area that expedite the formation of hydroxyl (–OH) functional group on the surface. The presence of –OH enhanced hydrophilicity of the PVDF polymeric membrane, thus mitigating fouling rate. Analogously, TiO₂, Ag₂O₃ and Al₂O₃ also exhibit similar features when incorporated into the matrix structure of polymeric membrane. (Subramaniam et al., 2017) synthesized titanate nanotubes using nano-TiO₂ as a precursor to modify the PVDF membrane. The results substantiated that under photo-catalytic condition, the involvement of TiO₂ in the dope formulation improved the permeation consistency (35.8 L/m²h) of the resultant nanocomposite membrane. Negligible fouling was observed at 0.5 wt % TNT loading throughout the 4 h continuous filtration. Another report has shown strong agreement with this observation, and the results indicated that the antifouling performance of TiO₂ was due to generated –OH under UV spectrum and its aptitude to exhibit self-cleaning. Also, attention has long drifted to the use of nano-Ag₂O₃ to modify polymeric membrane (Biswas & Bandyopadhyaya, 2017). The nano-additive released Ag ions to inhibit the metabolism of the microbial-foulants, thereby preventing the generation of the extracellular polymeric substance (EPS). Thus, this ultimately curtailed the organic and bio-fouling. Maximous et al., (2010) investigated the antifouling impact of Al₂O₃ and the results showed that at optimum 0.05 wt % loading, the modified composite polymeric membrane was less prone to fouling. Besides, the presence of Al₂O₃ in the matrix structure of a polymeric membrane not only reduces the fouling but also improves the flux consistency.

Most of the widely used nanoparticles, particularly as mentioned above, are photo-catalytic driven to address the fouling issue. This implies that the presence of ultraviolet radiation is a prerequisite to precede the antifouling performance. More so, the issue continues releasing antifouling radicals and superoxide could seriously jeopardize the stability of the composite matrix structure. In line with this, Tan et al. (2017) reported that the structural instability of the modified nanocomposite PVDF-ZIO membrane was discernible after four filtration cycles due

to the collapse of the incorporated nanoparticles. This could significantly undermine the overall antifouling performance and also re-expose the modified membrane to inconsistencies in permeation flux along with frequent fouling challenges. Moreover, the nano- ZnO, TiO₂, Ag₂O₃, Al₂O₃ and CuO are relatively expensive and the running cost could be unsustainable for industrial applications (Jhaveri & Murthy, 2016).

Meanwhile, nano-MgO has remained one of the antimicrobial and super hydrophilic nanomaterials yet to be fully explored in improving filtration and antifouling performance of polymeric membrane (Parvizian et al., 2017). The nano-MgO has the ability to release reactive oxygen species (ROS) which directly extract lipid from the cells of the microbial-foulants. This ultimately disrupted the metabolic activities and hindered biofilm formation. More interestingly, the nano-MgO not only averts bio-fouling formation but, it is also capable of evincing self-cleaning mechanism. The nano-MgO precursor is readily available and comparably cheaper than other nanomaterials (such as TiO₂, Ag₂O₃, Al₂O₃, and ZnO). Therefore, MgO-nanoparticles intimate a promising additive capable of enhancing antifouling properties and permeation performance of polymeric membranes for industrial filtration purposes. Currently, application of a modified Nano-MgO (MGO) composite PVDF-PEG membrane for separation of color pigment from POME has not been reported.

In view of these, the present study focuses on modifying the structure of an in-house fabricated PVDF-PEG ultrafiltration membrane at various loadings of MGO. The impacts of the incorporated MGO were examined based on the morphological changes, hydrophilicity, the permeability flux and fouling resistance of the resultant membrane. Furthermore, the rejection and color separation efficiency were studied, and also the used membranes were characterized using Fourier transform infrared spectroscopy. The outcome of the study demonstrated that the involvement of the MGO in the dope formulation significantly improved the antifouling properties and the permeation performance, alongside with color separation from palm oil mill effluent (POME) via the synergy of surface deprotonation and pore size screening mechanism.

2 MATERIALS AND METHODS/METHODOLOGY/EXPERIMENTAL PROCEDURE

2.1. Materials

Nano-MgO (MGO: particles size (BET) < 50 nm; MW = 40.30 g/mol; purification 99.9%), Pellets PVDF (Kynar 740) and polyethylene glycol (PEG: 12,000 g/mol) were procured from Sigma Aldrich (M) Sdn Bhd, Selangor, Malaysia. The PVDF was applied as the major membrane matrix polymer, while the PEG as co-polymer to enhance pore formation. The N,N-dimethylformamide (DMF), ethanol and glycerol were also obtained from Sigma Aldrich (M) Sdn Bhd, Selangor, Malaysia, and respectively used as doping and post-treatment solvents without any further purification. LiCl₂.H₂O was purchased from Acros Organic Industry, Chemicals and Reagents, Semenyih, Selangor, Malaysia. Also, POME sample was collected from an Oil Palm Milling industry in Malaysia.

2.2. Synthesis of Nanocomposite PVDF/PEG-MGO

2.2. Dope Formulation

The dope formulation was preceded by adding nano-MgO into DMF and then subjected to sonication using digital ultrasonic water bath (VWR 142-0300) at 75 °C for a period of 20 min. Subsequently, LiCl₂.H₂O was added into the mixture with steady agitation of 350 rpm and 75 °C for a period of 24 h. Essentially, this procedure assists in dispersion of the MgO as well as ensuring good blending of the mixtures. The mixture was followed by adding the dehydrated PVDF pellets and the co-polymer, PEG. The combination was stirred continuously at 350 rpm and 100 °C for another 24 h using a hot-plate stirrer (Monotaro; C-MAG HS7, Malaysia) to achieve a homogenous solution. The amount of the MgO contained in the dope solutions were varied as contained in Table 1.

Table 1: dope formulation

Description	PVDF:PEG g	Nano-MgO	LiCl ₂ .H ₂ O	DMF
Neat Sample	30:10	0.0	2	158
Modified Sample	30:10	0.5	2	158

2.3. Spinning of Nano-Hybrid PVDF/PEG-MGO Hollow Membrane

It is important to note that same spinning parameters were applied for all of the samples. The dopes were spun through dry-jet wet swirling technique employing an annular spinneret. The inner and outside diameter of annular spinneret was 0.55 and 1.15 mm, respectively. During the fabrication of the membrane, tap water and distilled water was used as the external and internal coagulant. In addition, the pick speed control, collecting drum speed, extrusion rate, air gap, external coagulant temperature, room temperature and room humidity remains constant at 7 rpm, 11 rpm, 5 mL/min, 10 cm, 25 °C, 29.5 °C and 72.7%, respectively. The spun fibers were drench in a continues flow water-bath at least for a period of 24 h to dislodge solvent remnants. In order to minimize shrinkage, post-treatments were applied on the fibers by immersing in ethanol for 12 h, then followed by drenching in glycerol for 5 h, respectively. The post-treated fibers were air-dried for at least 24 h to ensure complete dehydration.

2.4. Morphology Characterization

The cross section and surface morphology of the synthesized Nano-hybrid fiber were examined using scanning-electron-microscope, (SEM: S-3400N). The composite fibers were immersed into liquid nitrogen for 5 min to ensure sharp breaking of the fiber to reveal the cross-sectional structure. Then, the fractured samples were sputtered coated with gold thin layer, and the voltage acceleration was maintained constant at 20 kV during the image capturing.

2.5. Flux analysis

The filtration performance was examined using a fabricated dead-end permeation system, equipped with membrane module cell and a peristaltic pump to provide the required suction pressure. Each of the modules comprises of 10 units of the membrane with equal length of 20 cm. initially, the membrane was compacted at a pressure of 0.4 MPa for a period of 30 min to ensure steady flux, while the subsequent filtration operations were performed at lower pressure of 0.3 MPa. The DI water (J_w) and permeate flux (J_p) were determined using Equation (1):

$$J = \frac{V_p}{A_s \Delta t} \quad (1)$$

where J denotes the flux in $L/m^2 \cdot h$, V is the volume of permeate (L), A_s is membrane surface area (m^2) and Δt is filtration time in h.

2.6. POME Remediation

The membrane fibers were subjected to filtration of diluted POME with 4285 ADMI color concentration using same set-up as applied when pure water was used as feed. Initially, the membranes fibers were submerged in the POME solution for 90 min to initiate adhesion of thin layer color pigments on the fibers. This procedure assists in achieving accurate color rejection performances of the fibers (Subramaniam et al. 2017). The apparent color content of the feed POME and permeate were analyzed in ADMI using UV-spectrophotometer (DR4000U, HACH) at an absorbance wavelength of 400 nm. The POME decolorization efficiency was determined using Equation (2):

$$\%C_{removal} = \left(1 - \frac{C_p}{C_{POME}}\right) \times 100 \quad (2)$$

2.7. Analytical Methods

The chemical oxygen demand (COD), ammonia nitrogen (AN), total suspended solids (TSS), turbidity (TDS), and colour removal were analyzed using recommended standard procedures (APHA, 2005).

3. RESULTS AND DISCUSSION

3.1. Membrane Morphology

Figure 1a presents the scanning electron microscope (SEM) images of cross-sectional view of the neat and modified hybrid nano-MgO (MGO) PVDF-PEG membranes. It is obvious that the neat fiber had 3 layers. The middle layer constitutes majorly of sandwich-like morphology containing short finger-like pores at both sides toward the ultra-thin layers. However, different scenarios were observed with the modified nanocomposite membranes. A finger-like pore became longer and the number of the micro-pores structure increased considerably

Figure 1b (Shen et al. 2012) . In addition, some spongy macro-voids were also noticed towards the inner ultra-thin layer. This observation is in agreement with previous studies reported (Shen et al. 2012). From Figure 1b, it can be deduced that the 0.5g MgO loading was successfully and homogenously dispersed within the matrix structure. This also show good compartment at this loading.

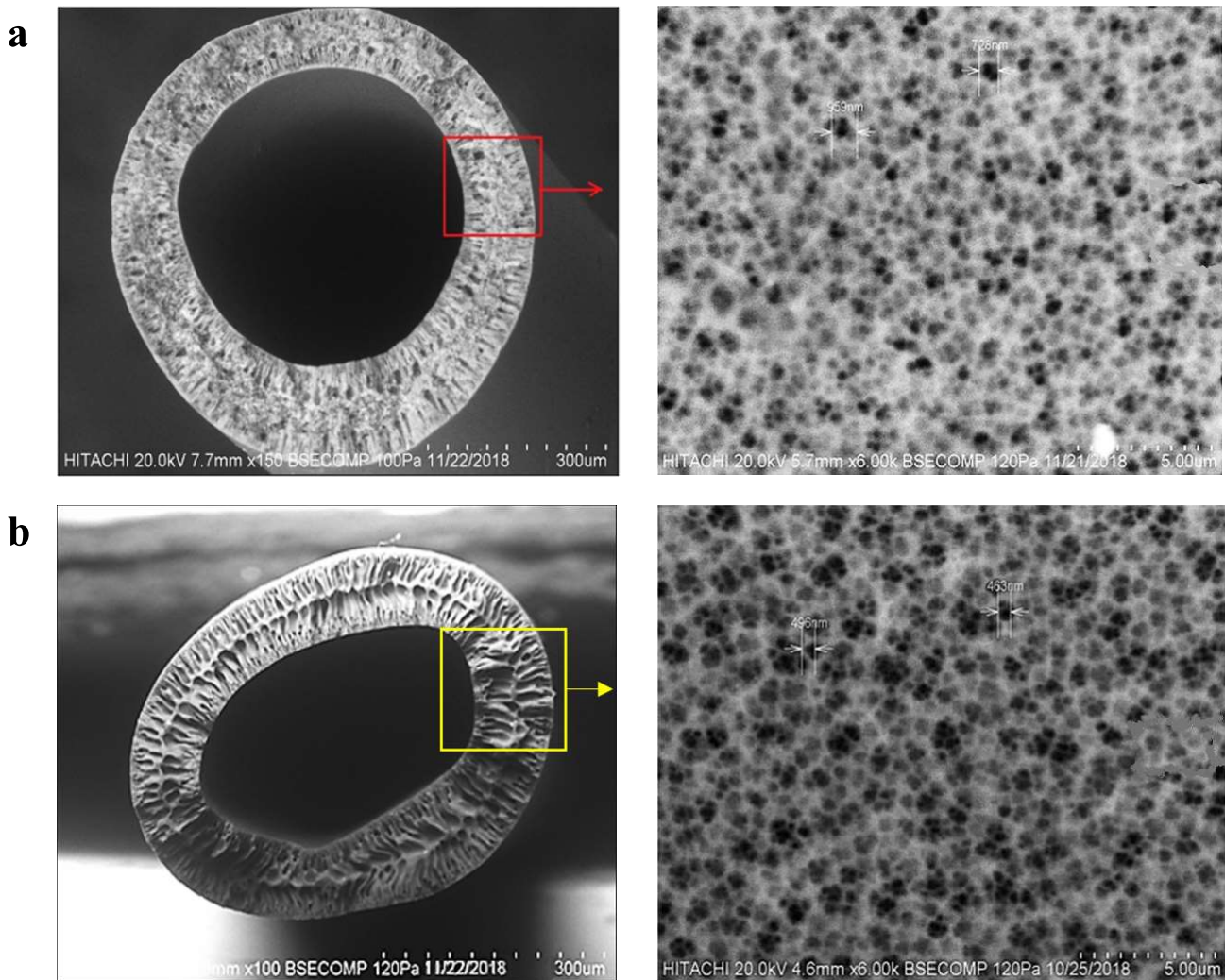


Figure 1: Cross-section and surface view of the SEM analysis of the (a) neat and (b) modified membrane with MgO

3.2. Flux performance

The modified membranes presents higher flux of 70 L/m²·h, as against 48.59 L/m²h for the neat membrane. Collectively, the magnitude of the fluxes in POME filtration were noticeably lower compared to the pure water filtration. This could be due to the presence of contaminants, such as suspended solids, color pigments, organic and inorganic substances) in the POME, which apparently restrict the free flow of permeate through the membranes. Basically, the selectivity and rejection of the contaminants is based on size differences in the pores as well as the surface zeta potential of the membrane (Tan et al. 2017).

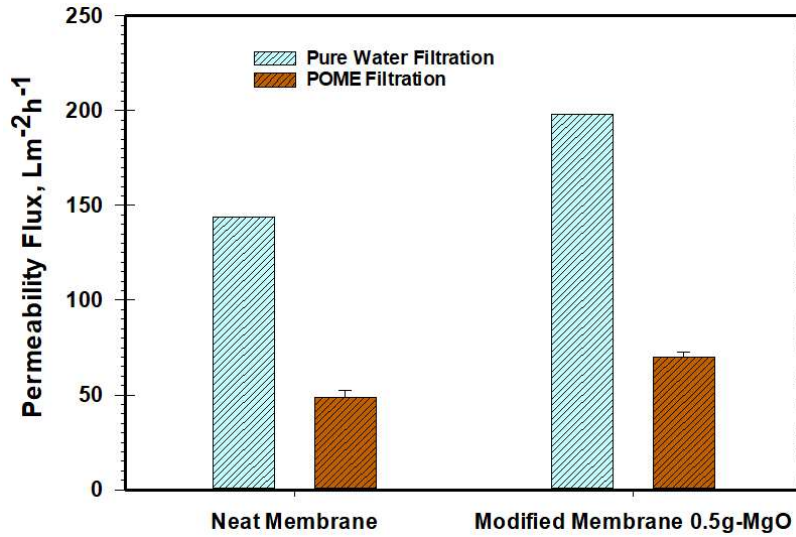


Figure 2: Pure water and POME Permeability flux for the Neat and Modified Membrane

3.3. POME Remediation Performance

Figure 3 present the remediation performance of both the neat and modified membrane. The neat membrane successfully reduced the COD, colour, TDS, TSS and TN concentration in the POME by 80.15, 67.5, 83.6, 87.01 and 70 %, respectively. However, under same conditions of operations, the modified membrane presented a superior performance with an upturn of 92.1, 86, 97.89, 99.98 and 80.26%, respectively. The better separation performance of the modified membrane may be due to the incorporated nano-MgO. The blended nanoparticles serve as filler which is capable of reducing the pore sizes and thus improve the selectivity (Nunes-Pereira et al., 2017). More so, nano-MgO introduces hydroxyl functional group (OH⁻) into the matrix structure, and this enhances waterlike characteristic of the polymeric membrane, thus the permeability flux (Khamkongkao et al., 2017).

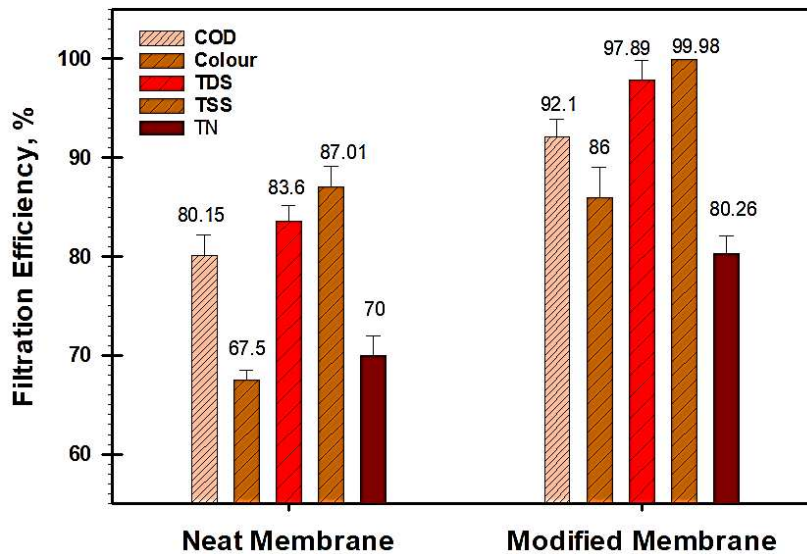


Figure 3: Filtration Efficacy: COD, Colour, TDS, TSS and TN Separation

4. CONCLUSION

Hybrid PVDF-PEG hollow fibers blended with nano-MgO was fabricated using phase inversion technique. The loading at 0.50 g-MGO presented auspicious performance with 198.35 and 70 L/m²h of pure water and POME

filtration flux, respectively. Also, the synthesized modified membrane reduced the COD, colour, TSS, TDS and TN by 92.1, 86, 97.89, 99.98 and 80.26 %, respectively. As against 80.15, 67.5, 83.6, 87.01 and 70 %, respectively for the neat membrane. Therefore, it can be deduced that nano MgO-hybrid PVDF-PEG membrane with 0.50 g-MgO loading presents a better permeate flux and separation performance compared to the neat membrane.

ACKNOWLEDGEMENT

The Authors wish to acknowledged the support of Universiti Putra Malaysia

REFERENCES

- Biswas, P., & Bandyopadhyaya, R. (2017). Biofouling prevention using silver nanoparticle impregnated polyethersulfone (PES) membrane: E. coli cell-killing in a continuous cross-flow membrane module. *Journal of Colloid and Interface Science*, *491*, 13–26. <https://doi.org/10.1016/j.jcis.2016.11.060>
- Jhaveri, J. H., & Murthy, Z. V. P. (2016). A comprehensive review on anti-fouling nanocomposite membranes for pressure driven membrane separation processes. *Desalination*, *379*, 137–154. <https://doi.org/10.1016/j.desal.2015.11.009>
- Khamkongkao, A., Mothaneeyachart, N., Sriwattana, P., Boonchuduang, T., Phetrattanarangsi, T., Thongchai, C., Sakkomolsri, B., Pimsawat, A., Daengsakul, S., Phumying, S., Chanlek, N., Kidkhunthod, P., & Lohwongwatana, B. (2017). Ferromagnetism and diamagnetism behaviors of MgO synthesized via thermal decomposition method. *Journal of Alloys and Compounds*, *705*, 668–674. <https://doi.org/10.1016/j.jallcom.2017.02.170>
- Maximous, N., Nakhla, G., Wong, K., & Wan, W. (2010). Optimization of Al₂O₃/PES membranes for wastewater filtration. *Separation and Purification Technology*, *73*(2), 294–301. <https://doi.org/10.1016/j.seppur.2010.04.016>
- Nunes-Pereira, J., Silva, A. R., Ribeiro, C., Carabineiro, S. A. C., Buijnsters, J. G., & Lanceros-Méndez, S. (2017). Nanodiamonds/poly(vinylidene fluoride) composites for tissue engineering applications. *Composites Part B: Engineering*, *111*, 37–44. <https://doi.org/10.1016/j.compositesb.2016.12.014>
- Parvizian, F., Sadeghi, Z., & Hosseini, S. M. (2017). PVC Based Ion-Exchange Membrane Blended with Magnesium Oxide Nanoparticles for Desalination: Fabrication, Characterization and Performance. *Journal of Applied Membrane Science & Technology*, *21*(1), 11–24. <https://doi.org/10.11113/amst.v21i1.105>
- Shen, L., Bian, X., Lu, X., Shi, L., Liu, Z., Chen, L., Hou, Z., & Fan, K. (2012). Preparation and characterization of ZnO/polyethersulfone (PES) hybrid membranes. *Desalination*, *293*(2012), 21–29. <https://doi.org/10.1016/j.desal.2012.02.019>
- Subramaniam, M. N., Goh, P. S., Lau, W. J., Tan, Y. H., Ng, B. C., & Ismail, A. F. (2017). Hydrophilic hollow fiber PVDF ultrafiltration membrane incorporated with titanate nanotubes for decolourization of aerobically-treated palm oil mill effluent. *Chemical Engineering Journal*, *316*, 101–110. <https://doi.org/10.1016/j.cej.2017.01.088>
- Tan, Y. H., Goh, P. S., Ismail, A. F., Ng, B. C., & Lai, G. S. (2017). Decolourization of aerobically treated palm oil mill effluent (AT-POME) using polyvinylidene fluoride (PVDF) ultrafiltration membrane incorporated with coupled zinc-iron oxide nanoparticles. *Chemical Engineering Journal*, *308*, 359–369. <https://doi.org/10.1016/j.cej.2016.09.092>