

PAPER • OPEN ACCESS

Development of Polyvinylidene fluoride (PVDF)-ZIF-8 Membrane for Wastewater Treatment

To cite this article: N A Ibrahim et al 2018 *IOP Conf. Ser.: Earth Environ. Sci.* **140** 012021

View the [article online](#) for updates and enhancements.

Related content

- [Surface Modification of Polyvinylidene Fluoride \(PVDF\) Membranes by Low-Temperature Plasma with Grafting Styrene](#)
Chen Jian, Li Jiding and Chen Cuixian
- [Frequency dependence of electrical properties of polyvinylidene fluoride/graphite electrode waste/natural carbon black composite](#)
D R Insiyanda, N Indayaningsih, B Prihandoko et al.
- [Birefringence Change in Polyvinylidene Fluoride Induced by Electric Field](#)
Yutaka Ohmori, Katsumi Yoshino and Yoshio Inuishi



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Development of Polyvinylidene fluoride (PVDF)-ZIF-8 Membrane for Wastewater Treatment

N A Ibrahim, M D H Wirzal*, N A H Nordin and N S Abd Halim

Chemical Engineering Department, Faculty of Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

Email: mdzulhakim.wirzal@utp.edu.my

Abstract. Nowadays, the water shortage problem following the urbanization and increasing pollution of natural water source have increased the awareness to treat wastewater. Membrane filtration is often used in wastewater treatment plants to filter out more residual activated sludge from aeration process in the secondary stage. However, fouling is the main concern due to the fact it can happen to any membrane application. Antifouling properties in membrane can be improved by blending membranes with fillers or additives to make them more hydrophilic. This study aims to improve the antifouling properties in polyvinylidene fluoride (PVDF) membranes while optimizing the loading of Zeolitic imidazolate framework-8 (ZIF-8) fillers; at different loading (2.0 wt. %, 4.0 wt. %, 6.0 wt. %, 8.0 wt. % and 10.0 wt. %). Manual hand-casting of flat sheet membrane was done and the fabricated membranes were tested for their filterability against pure water and domestic wastewater. Both permeability tests showed that PVDF with 8% ZIF-8 membrane was the most permeable with a pure water and wastewater permeability of 150 L/m².h.bar and 94 L/m².h.bar, respectively. The pure water permeability of PVDF with 8% ZIF-8 membrane increases for about 130% compared to the pure PVDF membrane. The turbidity test of the initial feed and final permeate of wastewater, PVDF with 8% ZIF-8 membrane also gave out the highest reduction rate at 87%, which is 36% higher than that of pure PVDF membrane. It can be deduced that 8% of ZIF-8 is the ideal loading to PVDF in improving its antifouling properties to be used in domestic wastewater treatment.

1. Introduction

In the current fast moving global development, a huge amount of wastewater has been discharged into surface water such as lakes, rivers and seas [1, 2]. Presently, treating wastewater has a higher importance compared to a century ago since the world is facing a problem of water shortage due to population growth that led to pollution of natural water source [3, 4]. The application of membrane technology in wastewater treatment system is no longer a new thing. Membranes allow the removal of contaminants where other technologies are not capable of doing so. Membranes are competitive in the sense of producing a high standard water discharge and reduce environmental effect [5]. Nowadays, membranes are used as a secondary and tertiary treatment for water treatment [6]. Membranes are presently actively applied in the removal of suspended solids, protozoa and bacteria [7].

In wastewater treatment plants, membranes are often used in a membrane bioreactor (MBR). MBR is basically a combination of biological treatment and membrane separation. Secondary wastewater will be undergoing treatment biologically which is the activated sludge process and later the membrane separation process, either microfiltration or ultrafiltration. The conventional way of treating wastewater



at this stage is by using clarifier after the activated sludge process [8]. However, clarifier tanks require bigger footprints compared to an MBR. A clarifier is not sufficient to produce disinfected effluent. Hence, more footprint is required for tertiary treatment to disinfect the effluent. Other than smaller areas needed, MBR is an attractive alternative because of it is capable of producing disinfected effluent with higher quality [9, 10].

Despite the highly efficient of membrane applications in treating wastewater, its performance is always at constant threat of fouling. The widespread of this application is somehow limited due to this issue. Fouling causes a loss in water flux and quality, reducing efficiency, lost service time, premature membrane replacement and higher operating cost [11, 12]. Fouling in membranes can result in many undesirable consequences such as a rise in operational cost due to membrane cleaning and replacement. Fouling in membrane is basically the deposition of particles, colloids, macromolecules of the feed on the membrane surface and in the membrane pores. In simpler words, membranes are fouled when they are blocked. This phenomenon then leads to a declination in flux [13]. Fouling is ought to happen more in hydrophobic membranes due to the reason that hydrophobic molecules are more attracted to the surface of membranes, which then can cause the membranes to be congested [14]. To overcome this problem, composite membranes are used instead of pure polymer membranes [15]. Composite membranes can be synthesized by blending the base membrane which is of the water-hating properties with hydrophilic additives which would then improve the wetting-resistance [16].

Zeolitic imidazolate framework-8 (ZIF-8) are porous materials that are used as adsorbents which have great prospective as a means for hydrogen storage, carbon dioxide adsorption, alkane/alkene separation and heterogeneous catalysis. The materials are flexible in pore sizes and surface functionality [17]. Although ZIF-8 is widely used in gaseous separation, there are growing researches intending to extend the applications of ZIF-8 membrane to liquid separation processes such as organic solvent separation and aqueous mixture separation [18]. It is reported by Fan et.al [19] where polyvinyl alcohol (PVA) membrane incorporated with ZIF-8 gave better adsorption performance in removing dye for wastewater treatment. ZIF-8 is a filler or additive that has a potential to improve the performance of polyvinylidene fluoride (PVDF) membrane in water treatment. However, the addition of ZIF-8 to polymer is still rarely investigated. ZIF-8 are porous materials and known to have rather high chemical and thermal stability [20]. ZIF-8 has the potential to improve the quality of wastewater due to its high surface area which is up to 1000 m²/g [21].

The proposed hypothesis for this study is that the addition of ZIF-8 to PVDF solution would improve its antifouling properties in the sense that it increases the viscosity of the solution, thus promotes the formation of higher number of pores on the membrane surface. With higher number of pores, the membranes' performance is expected to increase. Therefore, investigating the ZIF-8 loading on membrane properties and performance is very crucial.

2. Materials and Method

2.1. Materials

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) was purchased from Alfa Aesar Chemicals. 2-Methylimidazole (2-MeIM), triethylamine (TEA) and Dimethylformamide (DMF) were obtained from Sigma Aldrich.

2.2. ZIF-8 Analysis

ZIF-8 (Zn (NO₃)₂: 2-MeIM: H₂O) with ratio of 1:6:500 was prepared as follows; a metal salt solution was prepared by dissolving 2 g of Zn (NO₃)₂ (6.72 mmol) in 12.11 g of deionized water (20 % of total deionized water). Zinc nitrate (10g) was dissolved into deionized water (100g) while H-MeIM (16.56g) was dissolve into TEA (10ml) in 400g of deionized water [21]. Zinc nitrate solution was added to the H-MeIM solution and cloudy solution formed upon mixing the solutions. The solution was stirred continuously for 30 minutes. The solution was centrifuge to remove separate the mixture and washed

with deionized water several times to remove reactants. The solution was dried in oven at 60°C overnight. The powder formed was collected and weighted to calculate mass yield.

2.3. Asymmetric Flat Sheet Membrane Preparation

An asymmetric flat sheet MMM was prepared from the solution consisting of PVDF (17.5), dimethylformamide (DMF) (82.5) and ZIF-8 loading (2.0 wt. %, 4.0 wt. %, 6.0 wt. %, 8.0 wt. % and 10.0 wt. %). First, ZIF-8 powder of different loadings were added to 5 different Schott bottles with 24.75 g of DMF and the mixtures were sonicated for thirty minutes. Next, 10% of total PVDF (total PVDF = 5.25 g) was added to the mixtures and stirred until completely dissolved. Once the polymer dissolved, remaining PVDF was added to the solutions and stirred. After 24 hours of stirring at 160 rpm and 60 °C, the polymer solutions were ready to be casted. For pure PVDF solution, the same steps were carried out except the sonification of ZIF-8 powder with DMF. Table 1 shows the ZIF-8 loadings that will be tested upon in this research. Flat sheet membranes were made from the polymer solutions by using manual hand-casting method. Each membrane was casted on a non-woven sheet as a support. The membranes were casted at a thickness of around 230 µm. The membranes were let to be cooled for a minute before being immersed in water bath at room temperature for 10 minutes.

Table 1. ZIF-8 Loading for PVDF Membrane

Solution	(ZIF-8)		Polymer (PVDF), g	Solvent (DMF), g	Total Weight, g
	wt. %	g			
1	0	0			30.000
2	2	0.107			30.107
3	4	0.219			30.219
4	6	0.335	5.25	24.75	30.335
5	8	0.457			30.457
6	10	0.583			30.583

2.4. Characterization of Membrane

Contact angle (CA) is a measurement of the hydrophilicity of the membrane. CA measuring was used to measure the angle between the surfaces of the membrane with the meniscus formed by the water. An average of 10 readings were taken at different location of the membrane sample and the average reading was recorded. Scanning Electron Microscopy (SEM) was used to study the topography and microscopic observation of the membrane. ImageJ software was used alongside with SEM images to measure pore size and pore density. Porosity is a measure of the empty spaces in the membrane (pores). Porosity was calculated by measuring the volume of water retained in the membrane after drying and comparing it with the initial weight of the membrane.

2.5. Filterability Test

The permeability (L) of the membrane was calculated as:

$$L = \frac{V}{A \cdot t \cdot TMP} \text{ (L/ (m}^2\text{h bar))} \quad (1)$$

where in equation 1, V is permeate volume (L), A is effective filtration area (m²), t time (h) and TMP trans-membrane pressure (bar). Filtration was done by using a membrane cross-flow unit. The volume of filtered water was collected every 10 minutes continuously until steady state is achieved. The permeability of the membrane against time was tested using pure water and secondary wastewater. Membrane cuts were replaced for every run.

2.6. Filtration of Domestic Wastewater

The membranes were then evaluated for the flux and permeability of wastewater. For this test, the wastewater drawn was secondary effluent from the sewage treatment plant in Universiti Teknologi PETRONAS (UTP). Other than the permeability, the wastewater was also tested for its initial and final turbidity. The turbidity reading before and after filtration was measured using a turbidity meter and the readings were used to calculate the removal rate using the equation 2.

$$\text{Removal rate of turbidity \%} = \frac{c_0 - c_f}{c_0} \times 100\% \quad (2)$$

where;

C_0 = initial concentration of constituents ($\mu\text{g/L}$)

C_f = final concentration of constituents ($\mu\text{g/L}$)

3. Results and Discussion

3.1. Membrane Characteristics

From characterization analysis that has been done, the summary of membrane properties is tabulated in Table 1. It can be seen that the thickness of all membranes fabricated is ranging between 220 to 240 μm . From the porosity test, the result obtained showed that PVDF membrane with 6% ZIF-8 has the highest value at 49.3%. However, the difference in porosity of M-0 to M-8 was minimal, almost insignificant as the value maintained around 46 to 49%. Though, there is a clear reduction in porosity for M-10. This is most likely due to the reason that the solution with 10 wt% ZIF-8 is too viscous that the formation of pores is underdeveloped, hence lower overall porosity [22].

Contact angle (CA) is a measure of hydrophilicity of a membrane. A membrane with lower CA indicates it has a higher hydrophilicity. Initial hypothesis made was that the addition of ZIF-8 would increase the hydrophilicity. However, from the result obtained, M-0 which is the pure PVDF membrane has the lowest CA. Furthermore, as the amount of ZIF-8 increases, there is no clear trend on the CA measurement, either it is increasing or decreasing. Thus, no conclusion can be made with this measurement.

Table 2. Summary of membrane characteristics

Membrane code	ZIF-8 content (%)	Thickness (μm)	Overall porosity (%)	Contact angle ($^\circ$)	Pore Size (μm) ^a	Pore density (pore/ nm^2) _a
M-0	0	220	47.9 ± 0.6	80.5 ± 0.7	0.06	307.83
M-2	2	240	46.7 ± 1.3	85.5 ± 0.6	0.09	158.07
M-4	4	220	47.8 ± 1.3	83.6 ± 0.1	0.09	143.74
M-6	6	220	49.3 ± 0.8	87.9 ± 0.4	0.10	123.44
M-8	8	220	46.6 ± 0.7	87.7 ± 0.5	0.08	185.97
M-10	10	230	41.7 ± 1.0	82.1 ± 4.0	0.10	119.47

^a. Measured from series of SEM images

The SEM images on pore distribution are shown in figure 1. From the images, it can be seen that the pore size of M-2, M-4, M-6 and M-10 are bigger than those of M-0 and M-8. Pore size is related to the particle size that can be rejected by the membranes. Since the membranes are used to filter secondary effluent, smaller pore size is desirable so that the tiny particles left in the feed can be rejected.

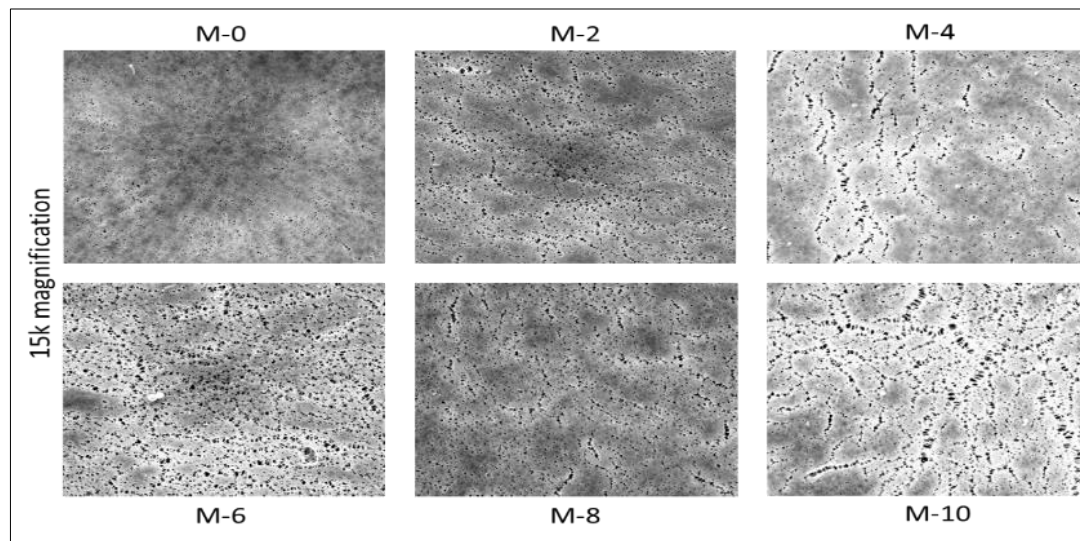


Figure 1. SEM images of the membrane samples

3.2. Membrane Performance

The filterability test of each membrane was done under a pressure of 1 bar, after being compacted at 4 bar for the first ten minutes. In Figure 2a, the pure water permeability, it can be seen that PVDF with 8% of ZIF-8 gave out the highest permeability and took the longest time to reach a steady state while the pure PVDF membrane had the lowest permeability and was the fastest to reach steady state. The same pattern was observed in Figure 2b, which is the wastewater permeability. This indicates that pure PVDF membrane is hydrophobic compared to PVDF/ZIF-8 membranes since it fouled faster with a significantly lower permeability. It is correlate with research made by Wang et.al [23] where the polyamide co-operated with ZIF-8 gave better membrane permeability and selectivity compared with the pure polyamide membrane.

In Figure 2c, the comparison of final permeability, it can be seen that PVDF with 8% ZIF-8 had the highest permeability for both pure water and wastewater. The permeability of pure and wastewater had a clear trend in which it increased with increasing ZIF-8 loading. However, at 10% of ZIF-8 loading, the permeability for pure water and wastewater decreased. The reason to this decrement is probably to the swelling in membrane pores, which subsequently reduce the effective area for permeability [24].

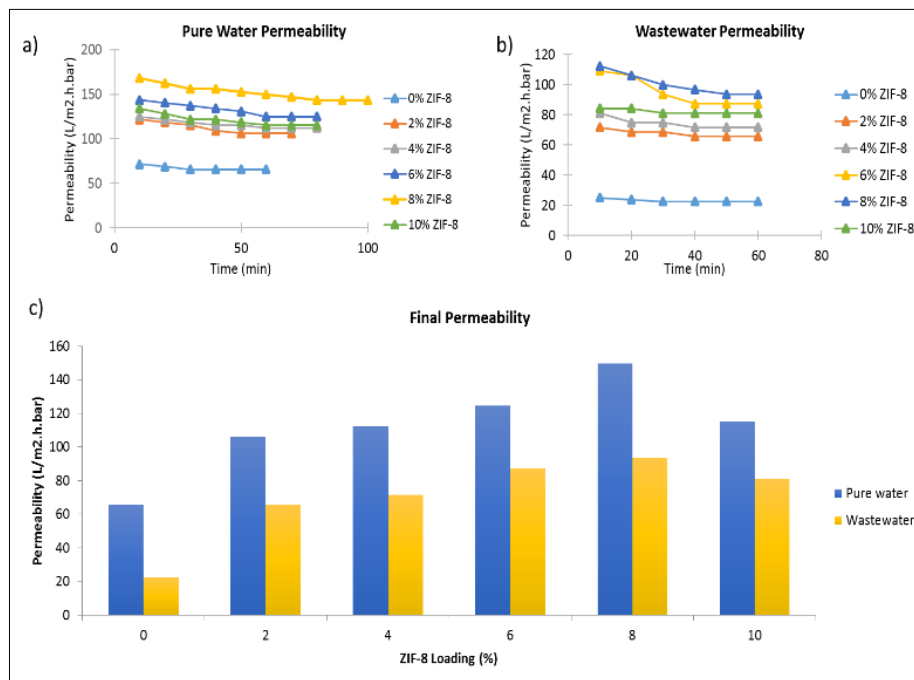


Figure 2. Membrane performance for different feed using a) pure water and b) secondary effluent; c) comparison of final permeability for both feed

Before the filtration of wastewater, some of the sample was kept for initial turbidity measurement. Once the permeability had reached a steady state, the filtrate was collected for final turbidity measurement. Figure 3 shows the initial and final turbidity readings of the samples and their removal or reduction rate. From the data, the trend observed was similar to that of the final permeability in which the reduction rate increases as the ZIF-8 loading increases and started to decline at 10% ZIF-8 loading. Moreover, the highest removal was at 8% ZIF-8 loading where the turbidity was measured from 2.00 NTU to 0.02 NTU. It is believed that the ZIF-8 particles reduce the size of the pores and increase the selectivity of the membrane.

From the permeability and turbidity data, it can be deduced that the addition of ZIF-8 has a positive impact on the membrane performance and improving its antifouling properties. However, excessive loading of ZIF-8 can cause a declination in its performance. From this study, the conclusion arrived was that 8% of ZIF-8 is the ideal loading to PVDF in treating wastewater in terms of turbidity reduction.

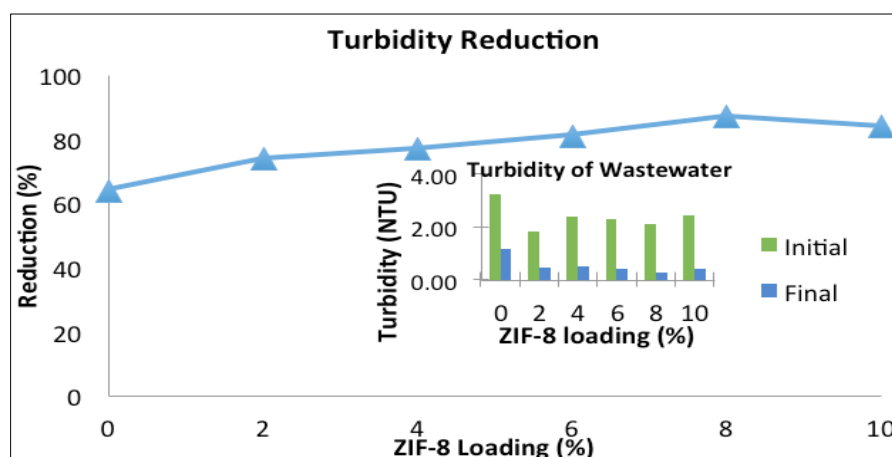


Figure 3. Reduction of turbidity before and after pure PVDF membrane and PVDF/ZIF-8 composite membranes filtration

4. Conclusion

In this study, the loading of ZIF-8 to PVDF in improving membrane antifouling properties and treating wastewater was investigated. Nevertheless, excessive loading of ZIF-8 can reduce the membrane performance. The most ideal loading of ZIF-8 to PVDF obtained from this study was 8% since it gives out the highest permeability at 150 L/m².h.bar for pure water and 94 L/m².h.bar for wastewater. The pure water permeability of PVDF with 8% ZIF-8 membrane increases for about 130% while the wastewater permeability increases approximately 32% compared to the pure PVDF membrane. In addition, PVDF with 8% ZIF-8 membrane also shows the highest reduction in wastewater turbidity at 87%, which is 36% higher than that of pure PVDF membrane. Therefore, it can be concluded that adding ZIF-8 to PVDF is advantageous in improving membranes performance. In the future, further research can be carried out to study the effect of ZIF-8 loading to PVDF in rejecting the chemical oxygen demand (COD) and biological oxygen demand (BOD) content in wastewater.

Acknowledgement

We acknowledge Universiti Teknologi PETRONAS for providing grants (grant number: 0153AA-F58) and facilities for conducting the research activities.

References

- [1] S. Hanchang, "Industrial wastewater-types, amounts and effects," Point Sources of Pollution: Local Effects and their Control-Volume II, p. 191, 2009.
- [2] M. D. H. Wirzal, A. R. Mohd Yusoff, J. Zima, and J. Barek, "Degradation of Ampicillin and Penicillin G using AnodicOxidation," Int. J. Electrochem. Sci., vol. 8, pp. 8978–8988, Jul. 2013.
- [3] T. Asano, "Water from (waste) water—the dependable water resource (The 2001 Stockholm Water Prize Laureate Lecture)," Water science and technology, vol. 45, pp. 23-33, 2002.
- [4] M. D. H. Wirzal, A. R. Mohd Yusoff, J. Zima, and J. Barek, "Voltammetric Determination of Nifedipine at a Hanging Mercury Drop Electrode and a Mercury Meniscus Modified Silver Amalgam Electrode," Int. J. Electrochem. Sci., vol. 10, pp. 4571–4584, Apr. 2015.
- [5] Owen, G., Bandi, M., Howell, J. A., & Churchouse, S. J. (1995). Economic assessment of membrane processes for water and waste water treatment. Journal of Membrane Science, 102, 77-91.
- [6] Nicolaisen, B. (2003). Developments in membrane technology for water treatment. Desalination, 153(1), 355-360.
- [7] Pendergast, M. M., & Hoek, E. M. (2011). A review of water treatment membrane nanotechnologies. Energy & Environmental Science, 4(6), 1946-1971.
- [8] Li, Q., Xu, Z., & Pinnau, I. (2007). Fouling of reverse osmosis membranes by biopolymers in wastewater secondary effluent: Role of membrane surface properties and initial permeate flux. Journal of Membrane Science, 290(1–2), 173-181.
- [9] Fraga, F. A., García, H. A., Hooijmans, C. M., Míguez, D., & Brdjanovic, D. (2017). Evaluation of a membrane bioreactor on dairy wastewater treatment and reuse in Uruguay. International Biodeterioration & Biodegradation, 119, 552-564.
- [10] A. S. Azizo, M. D. H. Wirzal, M. R. Bilad, and A. R. M. Yusoff, "Assessment of nylon 6, 6 nanofibre membrane for microalgae harvesting," AIP Conf. Proc., vol. 1891, no. 1, p. 020032, Oct. 2017.
- [11] Zularisam, A. W., Ismail, A. F., & Salim, R. (2006). Behaviours of natural organic matter in membrane filtration for surface water treatment — a review. Desalination, 194(1), 211-231.
- [12] A. Eliseus, M. R. Bilad, N. A. H. M. Nordin, Z. A. Putra, and M. D. H. Wirzal, "Tilted membrane panel: A new module concept to maximize the impact of air bubbles for membrane fouling

- control in microalgae harvesting," *Bioresour. Technol.*, vol. 241, no. Supplement C, pp. 661–668, Oct. 2017.
- [13] I.-S. Chang, P. Le Clech, B. Jefferson, and S. Judd, "Membrane fouling in membrane bioreactors for wastewater treatment," *Journal of environmental engineering*, vol. 128, pp. 1018-1029, 2002.
 - [14] D. Rana and T. Matsuura, "Surface modifications for antifouling membranes," *Chemical reviews*, vol. 110, pp. 2448-2471, 2010.
 - [15] M. S. Muhamad, M. {Citation} R. Salim, W. J. Lau, T. Hadibarata, and Z. Yusop, "Removal of bisphenol A by adsorption mechanism using PES–SiO₂ composite membranes," *Environmental Technology*, vol. 37, pp. 1959-1969, 2016/08/02 2016.
 - [16] S. Liang, Y. Kang, A. Tiraferri, E. P. Giannelis, X. Huang, and M. Elimelech, "Highly hydrophilic polyvinylidene fluoride (PVDF) ultrafiltration membranes via postfabrication grafting of surface-tailored silica nanoparticles," *ACS applied materials & interfaces*, vol. 5, pp. 6694-6703, 2013.
 - [17] Y.-R. Lee, M.-S. Jang, H.-Y. Cho, H.-J. Kwon, S. Kim, and W.-S. Ahn, "ZIF-8: A comparison of synthesis methods," *Chemical Engineering Journal*, vol. 271, pp. 276-280, 7/1/ 2015.
 - [18] H. Zhang, J. James, M. Zhao, Y. Yao, Y. Zhang, B. Zhang, et al., "Improving hydrostability of ZIF-8 membranes via surface ligand exchange," *Journal of Membrane Science*, vol. 532, pp. 1-8, 6/15/ 2017.
 - [19] X. Fan et al., "Characterization and application of zeolitic imidazolate framework-8@polyvinyl alcohol nanofiber mats prepared by electrospinning," *IOP Publ. LTD*, Feb. 2017.
 - [20] Ordoñez, M. J. C., Balkus Jr, K. J., Ferraris, J. P., & Musselman, I. H. (2010). Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes. *Journal of Membrane Science*, 361(1–2), 28-37.
 - [21] Nordin, N. A. H. M., Ismail, A. F., Mustafa, A., Murali, R. S., & Matsuura, T. (2015). Utilizing low ZIF-8 loading for an asymmetric PSf/ZIF-8 mixed matrix membrane for CO₂/CH₄ separation. *RSC Advances*, 5(38), 30206-30215.
 - [22] J. S. Taurozzi, H. Arul, V. Z. Bosak, A. F. Burban, T. C. Voice, M. L. Bruening, et al., "Effect of filler incorporation route on the properties of polysulfone–silver nanocomposite membranes of different porosities," *Journal of Membrane Science*, vol. 325, pp. 58-68, 11/15/ 2008.
 - [23] L. Wang, M. Fang, J. Liu, J. He, J. Li, and J. Lei, "Layer-by-Layer Fabrication of High-Performance Polyamide/ZIF-8 Nanocomposite Membrane for Nanofiltration Applications," *ACS Appl. Mater. Interfaces*, vol. 7, no. 43, pp. 24082–24093, Nov. 2015.
 - [24] A. Escoda, P. Fievet, S. Lakard, A. Szymczyk, and S. Déon, "Influence of salts on the rejection of polyethyleneglycol by an NF organic membrane: Pore swelling and salting-out effects," *Journal of Membrane Science*, vol. 347, pp. 174-182, 2/1/ 2010.