Waste Technology (WasTech)
Journal homepage: http://ejournal.undip.ac.id/index.php/wastech
An International Journal

Enchanced Produced Water Treatment Using Zeolite Pretreatment and PVDF-TiO_2@UiO-66-NH_2 Membrane

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Abstract - Produced water contains complex mixtures of organic and inorganic contaminants that are difficult to remove using conventional treatment methods. This study proposes a hybrid treatment system combining zeolite adsorption as a pretreatment and a PVDF–TiO_2@UiO-66-NH_2 photocatalytic membrane for enhanced produced water purification. The zeolite adsorption process effectively reduced pollutant load prior to membrane filtration, with kinetic analysis indicating that NH_3–N removal followed the pseudo-second-order model ($R^2 \approx 0.977$), suggesting a chemisorption mechanism. Under light irradiation, the photocatalytic membrane demonstrated enhanced performance due to the generation of reactive oxidative species, resulfyting in improved contaminant degradation and flux stability. The optimal membrane (2 wt% TiO_2@UiO-66-NH_2) achieved removal efficiencies of approximately 36% for TDS, 62% for COD, and 80% for NH_3–N. The overall results demonstrate a strong synergistic effect between adsorption, photocatalysis, and membrane filtration, leading to improved treatment efficiency and reduced fouling potential. This integrated approach offers a promising and sustainable solution for produced water treatment.

Keywords *–Produced water; zeolite adsorption; photocatalytic membrane; PVDF; TiO_2@UiO-66-NH_2*
Doi: http://dx.doi.org/10.14710/wastech.14.1.1-7
[How to cite this article: Kusworo, T.D., Safitri, D.L., Puspa, M.B. (2026). Enchanced Produced Water Treatment Using Zeolite Pretreatment and PVDF-TiO_2@UiO-66-NH_2 Membrane, 14(1), 1-7 doi: http://dx.doi.org/10.14710/wastech.14.1.1-7]

1. Introduction

Produced water is the largest waste producted by the oil and gas industry, with global volume estimated at 250 million barrels per day and continue to increase as productions and well ages (Yousef, 2020). Approximately 60% of total fluid produced by oil and gas exploration and production activities is produced water, while nearly 30% world gas products come from offshore operations (Yacovitch, 2020). In the United States alone, produced water production reaches approximately 21.6 billion barrels per year, with 97% come from onshore operation and remainder from offshore, most of which discharged directly into nearby surface water. This large volume makes produced water makes it a crucial environment issue. Characteristically, produce water contains various hazardous organic and anorganic contaminants such as BTEX compounds (benzene, toluene, ethylbenzene, xylene), polycyclic aromatic hydrocarbons (PAH), phenol, heavy metals, and Total Dissolved Solids (TDS) in high concentration. The produced water TDS value can reach 300-400 g/L, significantly higher compare to sea water, which range around 30 g/L (Sakrabani, 2021). Produced water treatment generally involves initial, primary, secondary, and tertiary treatment. Physical methods such as gravity sedimentation, gas flotation, adsorption, and membrane separation are used to remove free oil and suspended solid. Meanwhile, chemical and biological processes applied to reduce dissolved organic particle, BOD, and COD (Jasim, 2020). However, the complex composition of produced water often limits conventional methods, particularly in remove dissolved contaminant and persistent organic compounds, so more effective and selective advanced technology is needed. Membrane technology has emerged as promising solution in produced water treatment due to its ability to separate contaminants based on pore size and chemical properties. Process as microfiltration, ultrafiltration, nano filtration, until reverse osmosis able to significantly increase water quality. Membrane material as polyvinylidene fluoride (PVDF) are widely used due to its good chemical and thermal stability, although they have disadvantages of being hydrophobic and susceptible to fouling. Therefore, membrane modification used hydrophilic and photocatalytic materials such as TiO_2 have become widely developed strategies to increase flux, selectivity, and fouling resistance. In addition, the intregration of advanced material such as Metal Organic

Framework (MOF), especially UiO-66-NH_2, with TiO_2 in a photocatalytic membrane system offers the potential to increase the efficiency of organic contaminant degradation through advanced oxidation mechanisms. This combination is able to increase charge separation, broaden lights response, and reduce electron-hole recombination, thereby improving photocatalytic performance. Thus, the development of zeolite pretreatment and PVDF-TiO_2@UiO-66-NH_2 composite membrane is an innovative and prospective approach in produced water treatment that is more effective, sustainable, and environmentally friendly.

2. Materials and Methods

2.1 Materials

Produced water used in this study was collected from an oil and gas production site located in Cirebon, Indonesia. Zeolite, Polivynilidene fluoride (PVDF) were obtained from Solvay Advance Materials, USA, N-methyl-2pyrrolidone (NMP), Titanium dioxide (TiO_2), *Zincornium tertrachloride* ($ZrCl_4$), 2-aminotheraptelic acid, acetic acid, methanol, and dimetylformanide (DMF) were obtained from Sigma Aldrich, Singapore.

2.2 Pretreatment

The zeolite adsorption pretreatment was performed by introducing 30, 50, and 70 gram of zeolite into 1L of produced water effluent in a beaker. The zeolite and produced water was continuously stirred using a magnetic stirrer for three hours. In every 30 minutes of striring process, aliquots were collected for subsequent analysis. For allowing sedimentation, aliquots were left overnight. After that, the aliqouots were centrifuged for 10 minutes at 3500 rpm to separate zeolite from the supernatant. The liquids was then analysed using TDS meter, discrete analyzer and UV-Vis spectrophotometer to determine the concentration of residual contaminants.

The adsorption rate of the zeolite governs the removal of pollutants from produced water. To elucidate this process, several kinetic models were utilized, including pseudo-first-order, peudo-second-order, Elovich, and Bangham's models (Kusworo et al., 2024). These models offer important understanding of the mechanisms and key factors that govern pollutant adsorption, each presenting a different perspective on the dynamics of the process. The mathematical expressions for these models.

The pseudo-first-order model:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} - \frac{t}{Q_e}$$

The pseudo-second-order model:

$$Q_t = Q_{it}^{\frac{1}{2}} + C_i$$

The elovich model:

$$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$$

Bangham Pore Diffusion Model:

$$\log[\log\left(\frac{C_o}{C_o - mq_t}\right)] = \log\left(\frac{mK_b}{2.303\,V}\right) + \alpha \log t$$

Where Q_t and Q_e are the pollutant adsorption capacity at a equilibrium (mg/g). Parameters $K_{2,}K_b$, and C_i are the kinetic constants for various models, including pseudo-first-order (min^{-1}), pseudo-second-order ($g.mg^{-1}.min^{-1}$), Elovich ($g.mg^{-1}$), and Bangham's model ($L.g^{-1}$).

2.3 Fabrication of PVDF-TiO_2/UiO-66-NH_2 membrane

The UiO-66-NH_2 were produced from 0,2332 gram $ZrCl_4$, and 0,1812 gram 2-aminothereptalic acid was dispersed in 50 mL DMF, acetic acid was added for modulator. The aliquot were heated inside Teflon-lined stainless steel autoclave in 135°C for 24 hours. After cooled the aliquot were centrifuged to separate solid and aliqot. The solid product were heated in 60°C oven. The synthesis of TiO_2@UiO-66-NH_2 composite is obtained from dispersed 0,4 gram TiO_2 and 0,1 gram UiO-66-NH_2 with 50 mL DMF and sonicated for 30 minutes. The solution was stirred in 120°C overnight. The solid product that obtained from centrifugation were washed using methanol and dried in vacuum condition with temperature 120°C. PVDF-TiO_2@UiO-66-NH_2 membrane were prepared via dry wet phase inversion method. PVDF was dissolved in NMP under contious stirring at 60°C for 1 hour until homogen. Separately TiO_2@UiO-66-NH_2 composite was dispersed in NMP using ultrasonic for 30 min to ensure homogenous solution. The dispersed composite was incorporated into PVDF solution and stirred at 300 rpm at 50-60°C for 6 hours to obtained homogenous casting solution. The result dope solution was degassed at room temperature for 24 hours to eliminate entrapped air bubbles. Membrane casting was performed by spreading the solution onto a clean glass plate using a casting knife to control film thickness. The cast film was exposed to air for 1 min (dry step) prior to immersion in a deionized water coagulation bath at room temperature for 1 h to induce phase separation. The membrane was subsequently soaked in fresh deionized water for 24 h to ensure complete solvent removal. Finally, the membranes were dried at 30°C overnight before further characterization and performance evaluation. Table 1 shows the composition of membrane:

Table 1. Composition of Membrane

Code	PVDF (%m)	NMP (%m)	TiO_2 (%m)	TiO_2@UiO-66-NH_2 (%m)
M1	15	85	0	0
M2	15	85	0	1
M3	15	85	0	1,5
M4	15	85	0	2

2.4 Membrane Filtration

Filtration of PVDF-TiO_2@UiO-66-NH_2 membrane were conducted using a laboratory scale membrane filtration system in cross flow mode. The area of membrane was (x cm^2) and the operating pressure was maintained at (x bar). The filtration system were evaluated in zeolite pre treatment followed by membrane filtration. Permeate samples were analyzed for TDS, COD, and ammonia. Permetae flux (J) calculated using:

$$J = \frac{V}{A.t}$$

Where:

V = permeate volume (L)
A = effective membrane area (m^2)
t = filtration time (h)

Removal efficiency (%) was calculated using:

$$Removal\ (\%) = \frac{C_f - C_p}{C_f} x\ 100$$

Where:

C_f = feed concentration
C_p = feed concentration

3. Results and Discussion

3.1 Characterization of Produced Water

The characteristics of produced water were analyzed to determine the initial characteristics of produced water. Total dissolved solids (TDS) were measured with a TDS meter, Chemical Oxygen Demand (COD) was determined using a UV-Vis spectrophotometer in with SNI 6989.2:2019 method, and Ammonia were analyzed using Discrete Analyzer with SNI 19-6964.34-2004 Method. Table 2. Shows the initial characteristics of produced water

Table 2. Initial characteristics of produced water

No	Parameter	Unit	Value
1	TDS	ppm	25075
2	COD	ppm	370,658
3	Ammonia	ppm	54,18

The produced water contains very high concentration of pollutants based on the analysis results. It indicated the produced water can cause environmental pollution if discharged without adequate treatment.

3.2 Pretreatment

Various methods such as adsorption, membrane filtration advance oxidation, ion exchange, and reverse osmosis have been employed in water treatment with organic pollutant. The solid-state adsorption is the most effective for eliminating organic and inorganic pollutant than other methods (Dehmani et al., 2024). Natural zeolite is cost effective adsorbents that work primarily by ion-exchange process. This adsorption process can be improve by adding various metals such as TiO_2, Fe, Mn, Ag, and Na for increasing pollutants they can trap (Baskar et al., 2022). Figure 1(a), 1(b), and 1(c) shows the increasing trend in the percentage of TDS, COD, and NH_3-N rejection with increasing contact time in optimum dosage. Zeolite dosage of 50 grams/ 1L shows the most optimal for pollutants rejection.

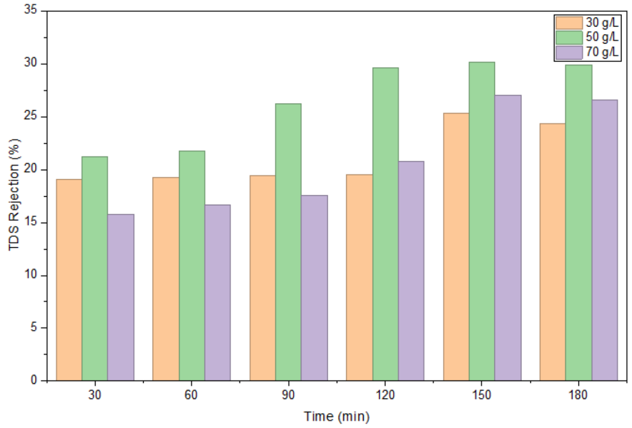

Figure 1(a). TDS Rejection (Pre Treatment)

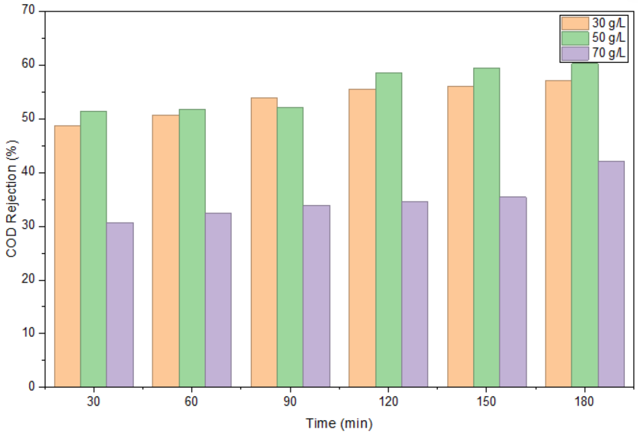

Figure 1(b). COD Rejection (Pre Treatment)

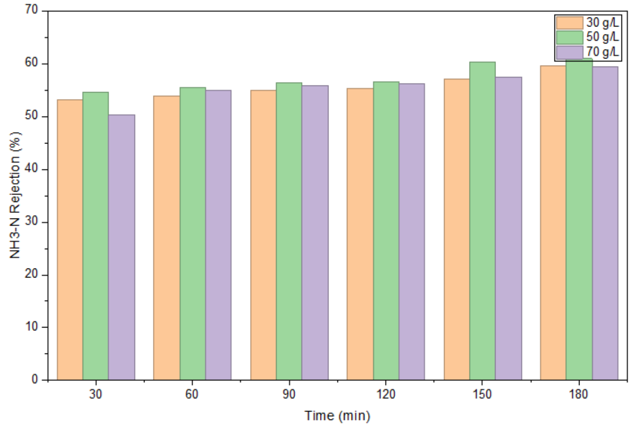

Figure 1(c). NH_3-N Rejection (Pre Treatment)

The adsorption kinetic of NH_3-N on zeolite were evaluated using various kinetic models to know the mechanism steps involved in the process. The models are pseudo-first order, pseudo-second order, elovich, and bangham pore diffusion. The pseudo-first order model

The pseudo-first order model, which assumes that the adsorption rate is proportional to the difference between the equilibrium adsorption capacity and the amount adsorbed at a given time, showed a relatively low coefficient of determination (R^2 = 0.9303) (Revellame et al., 2020).. This suggests that NH_3-N adsorption onto zeolite does not follow a simple physisorption mechanism and may involve more complex interactions between adsorbate and adsorbent, particularly in porous materials with heterogeneous active sites. In contrast, the pseudo-second order model provided an excellent fit to the experimental data, with higher correlation coefficient (R^2 = 0.9987). This model assumes that adsorption is governed by chemisorption involving valence forces through sharing or exchange of electrons between the adsorber and the adsorbent surface. The calculated adsorption capacity (q_e = 1,467 mg/g) further indicates the strong affinity of zeolite for NH_3-N removal. The high agreement between experimental and model data confirms that the adsorption process is predominantly controlled by chemisorption (J. Wang & Guo, 2020). The Elovich model, which is commonly used to describe adsorption on heterogeneous surfaces, showed a relatively lower correlation coefficient (R^2 = 0.8808), indicating a less satisfactory fit compared to the pseudo-second order model. However, the relatively high initial adsorption rate constant suggests that adsorption occurs rapidly at the initial stage due to the abundance of active sites on the zeolite surface. Despite this, the overall poor fitting implies that surface heterogeneity is not the primary factor controlling the adsorption kinetics, although it still contributes to the overall adsorption behavior. Furthermore, the Bangham pore diffusion model was applied to evaluate the contribution of intraparticle diffusion in the adsorption process. The model yielded a moderate correlation coefficient (R^2 = 0.8820), indicating that pore diffusion is not the sole rate-limiting step. Although diffusion into the pores of the zeolite contributes to the overall adsorption mechanism, it does not dominate the adsorption rate. This suggests that the adsorption process involves multiple steps, including external mass transfer, pore diffusion, and surface interaction, which is a common phenomenon in porous adsorbents. In conclusion, among all the evaluated kinetic models, the pseudo-second order model provided the best fit, indicating that chemisorption is the dominant mechanism governing NH_3-N adsorption onto zeolite. While intraparticle diffusion and surface heterogeneity contribute to the overall process, they are not the primary controlling factors. These findings confirm that zeolite is an effective adsorbent for NH_3-N removal due to its strong interaction with organic pollutants and well-developed porous structure.

Table 2 . Parameters of kinetic model for NH_3-N

Kinetic Models	Parameter	Value
Pseudo-first order	K_1 (min^{-1})	0,0124
	Q_e (mg/g)	0,1681
	R^2	0,9303
Pseudo-second order	K^2	0,0439
	Q_e (mg/g)	1,4670
	R^2	0,9987
Elovich	R^2	0,8808
Bangham's	K_i (L/g)	0,5328
	R^2	0,8802

3.3 Membrane Performance

3.3.1 SEM

The surface morphology and structural integrity of the synthesized TiO_2@UiO-66-NH_2 composite were investigated using Scanning Electron Microscope (SEM), as presented in Figure 2. At magification 15000x. The UiO-66-NH_2 particles exhibit a well defined, sharp-eged cubic or octahedral geometry, which is a hallmark of high crystallinity in Metal organic frameworks (MOFs). The TiO_2 parcticles are appear as smaller. The uniform distribution of TiO_2 and uiO-66-NH_2 matrix indicates a succesful hybridization process.

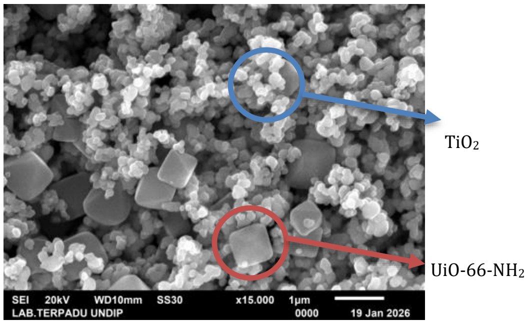

Figure 2. SEM TiO_2@UiO-66-NH_2 Composite

The morphology on the surface of PVDF-TiO_2@UiO-66-NH_2 2% membrane was tested using Scanning Electron Microscope (SEM). The successful integration of TiO_2@UiO-66-NH_2 material into the structure of the PVDF membrane has provide by the SEM analysis. Bright regions observed on the membrane surface correspond to the presence of inorganic particle TiO_2 and UiO-66-NH_2 particles, which appear due to their higher electron density compared to the PVDF matrix. Hoewever, the particle distribution is not entirely uniform, the aglomeration is still evident at the micrometer scale, as indicated by the 5 μm scale bar. From a functional perspective, TiO_2 enchance membrane hydrophilicity, contributing to improved water flux. Meanwhile, UiO-66-NH_2 enchances selectivity through adsorption mechanisms. However, particle agglomeration may reduce the effective surface area, limiting overall performance improvement. In conclution, although the PVDF-TiO_2@uiO-66-NH_2 membrane was succesfully fabricated with a good structural morphology, further optimization in filler dispersion is requires to achieve a more uniform distribution and enchance membrane performance. Figure 2. Shows membrane morphology:

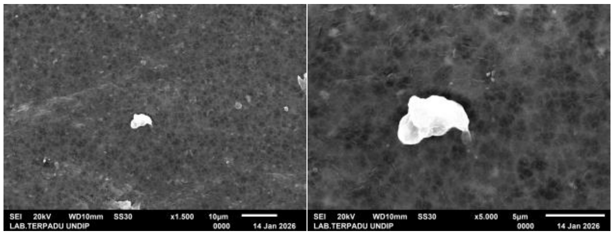

Figure 3. (a) SEM Image 500x (b) SEM Image 5000x

3.3.2 Water Contact Angle

Water contact angle (WCA) is a parameter for evaluating membrane surface wettability, which affects water permeability of membrane. Figure 3 shows the contact angle of membrane. The PVDF membrane exhibited a contact angle of 71,7°, indicating a moderately hydrophilic surface. After modification with TiO_2@UiO-66-NH_2 2%, the contact angle decreased to 68,2°, indicating enhanced hydrophilicity. This improvement can be attributed to the incorporation of hydrophilic functional groups such as hydroxyl (–OH) from TiO_2 and amino (–NH_2) groups from UiO-66-NH_2, which increase surface energy and give a stronger interaction with water molecules. Similar studies have reported that the incorporation of TiO_2 and MOF-based materials effectively enhances membrane wettability due to the introduction of polar functional groups and improved surface properties (Zhang et al., 2022; Li et al., 2023). However, the relatively small decrease in contact angle suggests that the modification effect is moderate, which may be due to limited dispersion or partial embedding of TiO_2@UiO-66-NH_2 within the PVDF matrix. Nevertheless, even a slight increase in hydrophilicity can improve membrane performance by facilitating water transport and forming a hydration layer that reduces foulant adhesion (Chen et al., 2025).

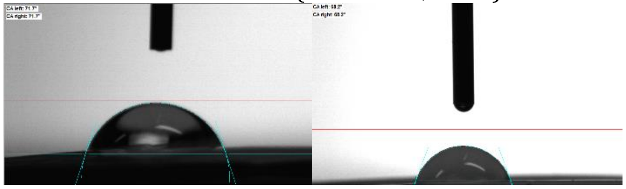

Figure 4. (a) WCA of M1, (b) WCA of M4

3.4 Membrane Performance

The PVDF-TiO2@UiO-66-NH2 membrane's flux was analyzed using filtration process conducted over 3 hours, with taken at 30 minute intervals to measure the volume of filtrate. Variation concentration of membrane were systematically executed to investigate the influence of the composite. The normalized flux and permeate performance of the PVDF-TiO_2@UiO-66-NH_2 membrane are illustrated in Figure 5. Among the studied variations, the M4 membrane exhibited the highest flux, indicating the optimal balance between hydrophilisity, porosity, and structural integrity. Overall, optimum filler concentration significantly improves the rejection performance for TDS, COD, and NH_3–N due to enhanced surface functionality, improved pore structure, and stronger adsorption interactions within the mixed matrix membrane (Zhang et al., 2021; Li et al., 2022).

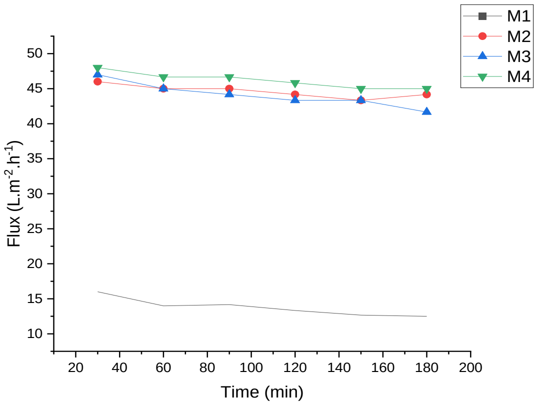

Figure 5 (a). Effect of Concentration in Permeate Flux

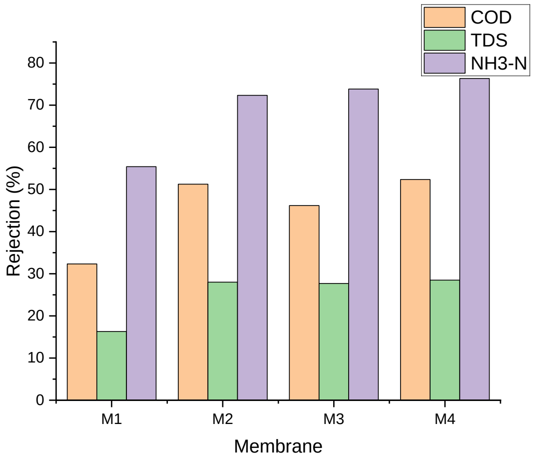

Figure 5 (b). Effect of Concentration in Membrane Rejection

Pre treatment give a crucial role in reducing suspended solids and organic matter in water treatment process. With a focus to mitigate membrane fouling. The application of zeolite adsorption pretreatment using 50g/L zeolite give effectiveness in water treatment process. Zeolite pretreatment reduces the pollutant load entering the membrane system. Figure 6 shows that the permeate flux and rejection of membrane increase by giving zeolite adsoption treatment.

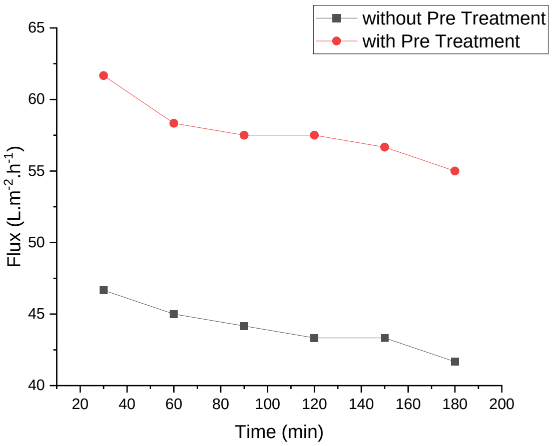

Figure 6 (a). Effect of Pre Treatment in Permeate Flux

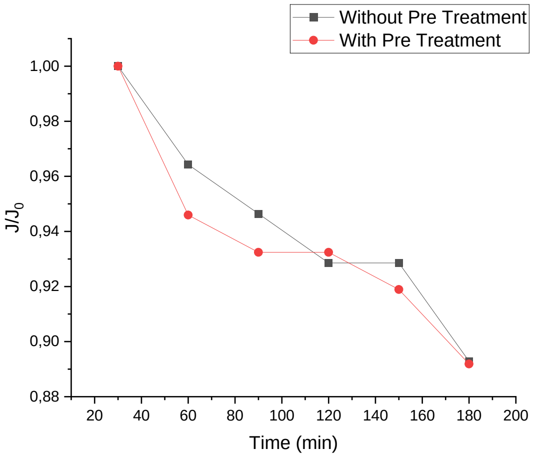

Figure 6 (a). Effect of Pre Treatment in Normalize Flux

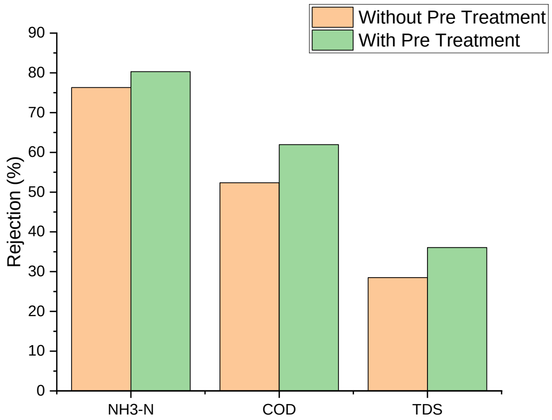

Figure 6 (a). Effect of Pre Treatment in Rejection

The membrane was exposed to visible light and dark condition. Under dark conditions, the removal efficiencies remain lower compared to light-assisted conditions because photocatalytic reactions are not activated. When light irradiation is applied, the membrane performance improves further as the TiO_2 component in the TiO_2@UiO-66-NH_2 composite generates reactive oxidative species such as hydroxyl radicals (•OH), which facilitate the degradation of organic contaminants (Wang et al., 2020; Chen et al., 2023).This enhancement is attributed to the function of the photocatalyst in increasing hydrophilicity and porosity of membrane. In addition, pollutant rejection increase under visible light. The rejection increased from 76,31% to 80,31% for NH_3-N, 52,36% to 61,96% for COD, and 28,49% to 36,06% for TDS. . Flux and rejection performance of the PVDF-TiO_2@UiO-66-NH_2 membrane in dark and light condition are illustrated in Figure 7. Photocatalytic activity influences hydrodynamic behavior by increasing the hydrodynamic radius, affecting particle size distribution and promoting size based separation.

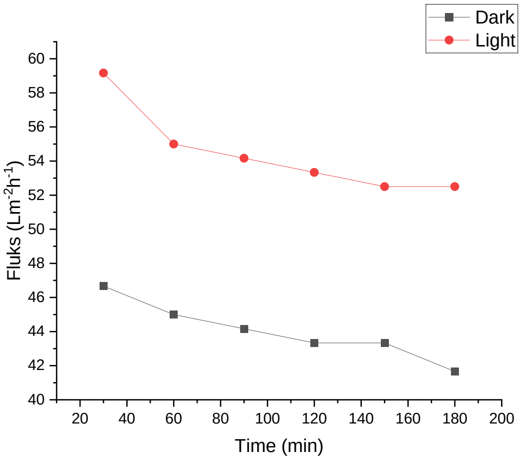

Figure 7 (a). Effect of Radiation in Permeate Flux

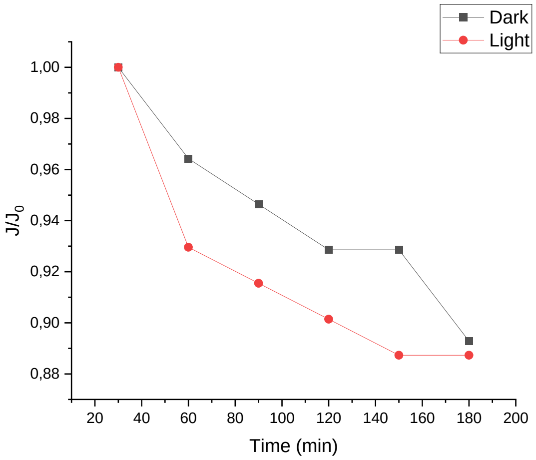

Figure 7 (b). Effect of Radiation in Normalized Flux

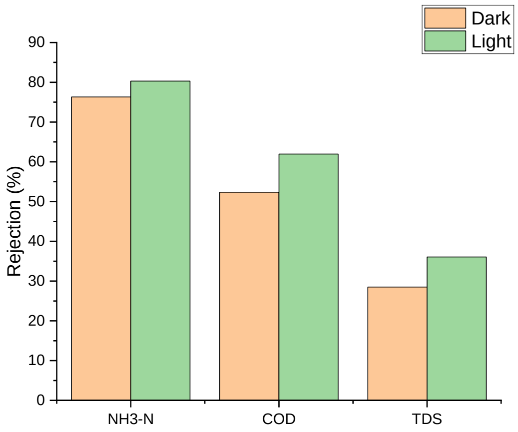

Figure 7 (c). Effect of Radiation in Rejection

4. Conclusions

This study successfully enhanced the developed of water treatment system by integrating zeolite adsorption pretreatment and PVDF-TiO$_2$@UiO-66-NH$_2$ membrane filtration for produced water treatment. Zeolite pre treatment increased membrane flux and rejection with the optimum dosage of zeolite is 50 g/L. Membrane M2 is the most the optimum concentration of PVDF-TiO$_2$@UiO-66-NH$_2$ give highest flux and rejection pollutant rejection performance. The addition of nano photocatalyst not oly improves membrane performance but also membrane characteristics compared to PVDF- neat membrane. Specifically, the PVDF-TiO$_2$@UiO-66-NH$_2$ 2% (M2) membrane demonstrates superiof performance in both pollutant rejection and flux value. This study has the potential to contribute in membrane application for produced water treatment.

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