

Efficiency of fenton oxidation and membrane hybrid processes for paracetamol removal in seawater

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Abstract. Traces of Paracetamol (PCT) as a micropollutant in the environment, particularly in seawater (SW), have become a global concern in recent years due to the toxicity effect on humans and environment. Due to special characteristics, conventional wastewater treatment plants are able to degrade PCT partially. Therefore, an alternative treatment was necessary to treat PCT substance. Homogeneous Fenton oxidation is an efficient process to degrade PCT at various levels. Nevertheless, separation of dissolved iron by-products in the effluent caused a problem. Combination of Fenton oxidation and ultrafiltration treatment presents a promising opportunity as one of the alternative treatments for PCT removal across aqueous matrices and removal of iron residue. Despite promising, information related to combine Fenton and membrane process was lacking. Therefore, this study aims to evaluate the efficiency of the hybrid processes to remove PCT, represented in Chemical Oxygen Demand (COD), for both distilled water (DW) and seawater. In this study, crucial parameter Fenton's reagent with $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio (w/w) was observed. In the DW matrix, optimal 1:0.5 ratio resulted 45% COD removal, whereas 1 :1 ratio exhibited 37% COD removal in SW. Flat sheet Polyethersulfone (PES) with pore size of 30 nm and 7 nm (50 kDa) membrane was employed with a constant flux of 120 L/m²·h. A lack of contribution of COD removal in DW and 37% in SW was observed during the ultrafiltration process, respectively. Furthermore, 54% and 92% removal of Fe^{2+} residue was observed during ultrafiltration at adjusted pH 8.5 in both water matrices using different membrane pore sizes, respectively.

1 Introduction

Micropollutants are currently gaining attention for further study due to their unregulated composition, and their presence in aquatic environments that can only degrade partially by conventional water treatment technologies. Various studies have been conducted to evaluate further the occurrence of diverse micropollutants in the environment. Previous various studies conducted on micro-pollutants in different countries, stating that the three main

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priorities for micro-pollutants are Pharmaceutical and Personal Care Products (PPCs), pesticides, and industrial waste chemicals [1], [2].

Paracetamol (PCT) is one of the predominant PPCs commonly encountered in various environment matrices. As a non-steroidal anti-inflammatory drug (NSAID) class, PCT functions predominantly as therapeutic agent for mild to moderate pain conditions such as headaches, menstrual pain, toothaches, and muscle aches and is available in various forms, such as tablets, syrups, drops, and infusions [3]. As a micropollutant, PCT in the aquatic environment is found in relatively low concentrations, and was reported that in seawater worldwide, PCT's concentration varies in range of 3.2 ng/L to 200 ng/L [4]. In 2021, Indonesian society was alarmed by the discovery of PCT in the coastal area of Jakarta, Ancol and Angke with a concentration of 420 ng/L and a concentration of 610 ng/L, respectively [5].

Nonetheless, this discovery has raised concerns among the public about the potential impact of PCT on human health. In accordance with another investigation, PCT has a high potential for toxicity, affecting both human and aquatic organisms. Its presence could lead to genetic code damage, lipid oxidation degradation, and protein denaturation within cells. This toxicity can range from low to moderate, depending on the duration of exposure to paracetamol itself [2].

The nature of PCT, which can only be partially degraded by conventional technologies, leads to the necessity for reliable tertiary technologies. Oxidation technology along with filtration are some of the most extensively researched technologies due to their effectiveness in pharmaceutical removal across water matrices [6]. One prominent type of oxidation is Advance Oxidation Process (AOP). AOP utilized the presence of hydroxyl radicals to degrade recalcitrant pollutants that can only be impaired partially by biological processes, making it suitable for removing PCT across water matrices. AOP comprises various types depending on the operational processes and catalysts used to accelerate the formation of hydroxyl radicals, such as Fenton, which utilizes iron as a catalyst.

A comprehensive study showed promising results in removing pharmaceutical substances through the Fenton processes [6]. These investigations conclude that the efficacy of pharmaceutical removal across diverse aqueous media fluctuates on the specific Fenton operational configuration, pollutant concentration, catalyst type and dosage, pH levels, and other pertinent parameters. Consequently, the removal efficiency under these operating conditions spans from 35% to 100% [6]. Fenton's ability to degrade pharmaceutical substances is as a result of hydroxyl radical exposure that formed through Fenton's reagent H_2O_2 and Fe^{2+} [7].

Conversely, a limitation of the Fenton process lies in the requirement for a significant amount of the chemicals and the need for effluent characterization due to the presence of the reagents used after the oxidation process [8]. This issue raises concerns because in Indonesia there are regulations for the allowable iron concentration in water matrices, that is should not be above 0.3 mg/L [9].

Next in line is the physical removal technology, known as filtration, which is commonly executed utilizing membrane-based systems. Membranes are a treatment system that utilizes the separation of contaminants in water based on Molecular Weight Cut-OFF (MWCO). The very small particle size of paracetamol can be separated by this membrane system [3]. On the other hand, the drawback of this system is its high energy requirement and susceptibility to fouling phenomena.

Each treatment technology has its own set of dis- and advantages. Hybrid technology is employed to achieve the desired treatment results while minimizing the shortcomings of the technology used. In this study, the removal of paracetamol was evaluated using a hybrid technology combining Fenton oxidation and membrane filtration, as well as how the membrane removes residual iron from the AOP reactor effluent.

2 Material and methods

Paracetamol ($C_8H_9NO_2$) with purity of more than 98% obtained for research purposes. Paracetamol solutions were prepared by dissolving predetermined amount of PCT in ultrapure water. Homogenous Fenton reagent, H_2O_2 30% w/w and $FeSO_4 \cdot 7H_2O$ was used as a source of Fe^{2+} . $H_2SO_4 \cdot 7H_2O$ 1M was used to adjust the solution pH to 3. Ultrafiltration Polyethersulfone (PES) membranes with average Molecular Weight Cut-off 30 nm from Sterlitech corporation and 7 nm (50 kDa) developed membrane prototype were employed.

Paracetamol degradation experiments by Fenton oxidation and membrane filtration were performed in a lab scale reactor at batch operation mode for both DW and SW (Figure.1). The Fenton experiments were carried out in a 1000 mL glass reactor filled with 500 mL of PCT solution at concentration of 100 mg/L with a constant ratio of COD/ H_2O_2 1:1. The solution pH was adjusted to 3 by adding H_2SO_4 1M. Then, various $FeSO_4 \cdot 7H_2O$ dosage and H_2O_2 (30% w/w) were added to the reactor by the ratio mentioned above. The reactor placed on a stirrer and agitated at 150 rpm at room temperature (30°C) for 60 minutes. After the reaction time, samples were collected to be measured for iron residue as well as COD. After sample collected from the Fenton reactor, the rest of the effluent then filtered through the flat sheet PES membrane that vary in MWCO (30 nm and 50 kDa) with surface area of 1,735.64 mm^2 . Membrane filtration process was operated at constant flux of 120 $L/m^2 \cdot h$. Simultaneously, water permeate were also collected to test for iron residue and COD.

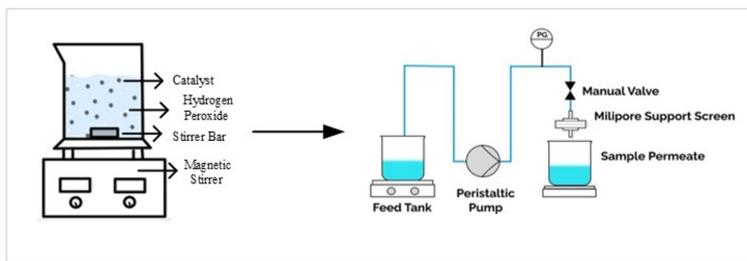


Fig. 1. Experimental set-up

The effect of catalyst dosage was investigated by applying a constant dose of H_2O_2 , obtained through a ratio of COD/ H_2O_2 1:1 for both DW and SW after the addition of 100 mg/L PCT. Therefore, different matrix resulted for different additional concentration of H_2O_2 , such as 198 mg/L and 818 mg/L for DW and SW, respectively. The variation in the H_2O_2/Fe^{2+} ratios were as follows: 1:0.33; 1:0.5; 1:1; 1:2, or equivalent to Fe^{2+} of 66 -396 mg/L for DW and 273-1,636 mg/L for SW.

PCT's concentration was characterized by employing chemical oxygen demand (COD) according to HACH Method No. 8000. Removal of PCT in Fenton oxidation was measured by comparing COD concentration after the addition of H_2O_2 and COD concentration after 60 minutes reaction. Whereas the removal measurement from ultrafiltration was done by comparing the feed and membranes permeate COD. The pH solution was determined by pH meter. Post filtration PES membrane's characterization was done through scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS) and fourier transform infrared (FTIR).

3 Result and discussion

This section discussed the performance of the hybrid processes to treat PCT from the perspective of Fenton oxidation and membrane separation process.

3.1 Fenton oxidation: effect of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio

As shown in Figure 2, the removal efficiency did not increase proportionally with increasing catalyst dosage. It can be seen through when the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ COD ratio was at the highest, 1:2, the COD removal efficiency achieved was only 27.5% and 19.7% for DW and SW respectively. On the other hand, at lowest dosage, a comparable removal of COD with 28.5% in DW and 20.7% in SW was observed. A similar report also indicated that the highest dosage of Fe^{2+} resulted in lowest COD removal of PCT within 60 minutes of Fenton reaction in DW matrix, whereas highest dosage of catalyst was achieved through $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio 1:3 that was equal to 300 mg/L Fe^{2+} with a 33% COD removal [10]. The phenomenon that was observed in both matrices can be explained through the presence of the hydroxyl radical. When the Fe^{2+} was at a low concentration, insufficient Fe^{2+} resulted in low formation of $\text{OH}\cdot$. Moreover, theoretically, the addition of Fe^{2+} will boost the chances of the formation of hydroxyl radicals to oxidize pollutants into CO_2 and H_2O [11]. Nevertheless, excess amounts of Fe^{2+} can result in $\text{OH}\cdot$ scavenging, that is when $\text{OH}\cdot$ react with Fe^{2+} and lead to the formation of less destructive products [7].

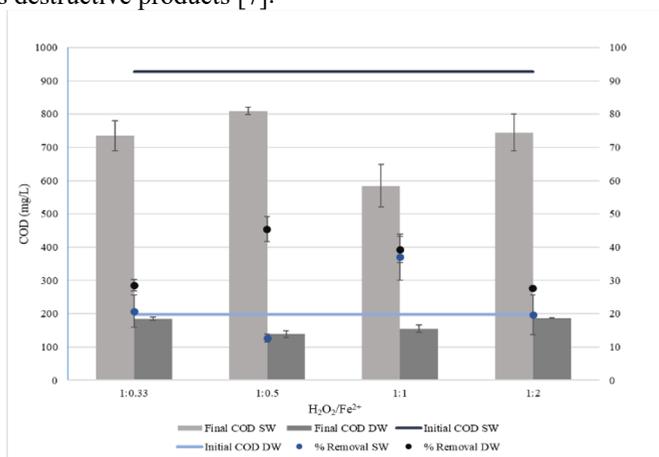


Fig. 2. PCT's degradation at various $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ DW matrix

Consequently, the optimal $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ was identified for both matrices. In DW, 1:0.5 $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio yielded the highest COD removal of 45.4%. Whereas in SW, 1:1 $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio resulted in 37% COD removal. The difference in the optimal $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio and the lower removal percentage in SW, compared to DW matrix was due to the salinity of seawater. Seawater naturally contained NaCl, and it can lead to the decrease of Fenton process efficiency. This was caused by the Cl^- anions reacting with hydroxyl radicals as shown by equations 4 and 5 [12].

A comparative experiment was also conducted in SW without the addition of paracetamol. The experiment was done with a ratio of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ 1:1, which showed that Fenton oxidation can reduce COD up to 55%. This indicated that the reduction of COD in SW with the addition of paracetamol, conceivably from the reduction of seawater pollutants. Therefore, specific tests are needed to detect the actual content of paracetamol, such as high performance liquid chromatography (HPLC), to determine the reduction of paracetamol. Furthermore, HPLC could also detect PCT intermediate by-products formed during the destruction of complex PCT molecules due to the presence of hydroxyl radicals from Fenton reaction. These subject molecules include aromatic derivatives and carboxylic acids, as reported in [13]. Given the characteristics of these by-products, the possibility that the COD

level of the Fenton's effluent in DW and SW consisted of them, rather than the original PCT, cannot be ruled out.

3.2 Membrane performance

A further process employing membrane was performed as a post treatment of Fenton oxidation for respective catalyst dosage applied for both DW and SW. Moreover, the removal of paracetamol and iron in both matrices was discussed.

3.2.1 PCT removal of varied catalyst dosage

As shown in Figure 3, initial COD for both DW and SW varied for every $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio. It could be explained due to contribution of the feed originated from Fenton's effluent that has different COD concentration (Figure 2). For DW's lowest $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio, 1:0.33, permeate's COD was 176 mg/L, or equivalent to a COD removal of 4.6%. In parallel, Comparable results was observed at higher $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio with insignificant COD Removal. On the other hand, membrane PES 30 nm retention showed better performance in SW's COD retention. The COD removal result was approximately similar, in the range of 20-30% for each $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio. Generally, different $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio revealed ineffective on membrane performance of PCT removal. The retention for all variations of catalyst resulted in the same trend for both DW (<4.6% removal) and SW (21-33.4%), respectively. These findings correspond to a prior study that concluded ultrafiltration membrane was unable to remove PCT. The rejection of PCT from the ultrafiltration process was ranged between 3.54 and 8.79% [14]. The phenomenon can be explained through the membranes pore diameter that was larger than the size of paracetamol molecules. Pollutant removal by membranes is based on pore size, with the goal of separating molecules of different sizes based on their molecular weight cut-off (MWCO). Micropollutants typically have an MWCO of less than 1 kDa, which is a unit of atomic mass units [15]. The MWCO of PCT is ranged from 0.1 to 0.3 kDa and membrane PES 30 nm has a MWCO of 30 nm (600 kDa) [14]. Therefore, the PES 30 nm membrane is unable to remove paracetamol because the paracetamol molecules were microscopic to be retained by the membrane pores.

Nonetheless, the removal of pollutants with MWCO smaller than the membrane's own MWCO is still possible. This is explained by the electrostatic interaction mechanism. Various studies have shown that most polymer membranes have a negative charge. This is measured using the zeta potential parameter and varies in value from membrane to membrane and is highly dependent on the chemical bonding with the feed water. Studies that examine the electrostatic interaction between the membrane surface and negatively charged pharmaceutical pollutants demonstrate good rejection results. This rejection can be explained by electrostatic repulsion between the membrane and negatively charged pollutants [7]. PCT solution has been identified as negatively charged [16], therefore the filtration process allows rejection due to this electrostatic interaction. However, the MWCO of paracetamol (0.1-0.3 kDa) which is 6,000 times smaller than the PES 30 nm membrane (600 kDa) is the main factor that prevents paracetamol from being retained by the membrane.

In addition to the MWCO rejection mechanism, the low rejection of paracetamol by ultrafiltration membranes can also be caused by adsorption from the membrane surface. This adsorption mechanism is influenced by the octanol/water partition coefficient (Log Kow) of the pollutant [7]. The partition coefficient of PCT is 0.46 [13], which indicates that paracetamol has a very low Log Kow because it is below 2.6. The low Log Kow makes paracetamol very hydrophilic, so there was no adsorption on the membrane surface, which resulted in minimal COD rejection in this study.

Nevertheless, in SW with 100 mg/L PCT, up to 33.4% COD retention was observed. a comparison of filtration experiment was also carried out from the Fenton oxidation effluent with a seawater matrix without the addition of PCT. Seawater that has undergone the Fenton oxidation process, initially had a COD value of 285 mg/L, after undergoing the filtration process the COD value decrease to 130 mg/L or equivalent to 54% COD removal. COD removal by ultrafiltration process in seawater matrix is in accordance with study that conclude ultrafiltration membranes in processing seawater was able to reject COD of 35%[17]. This comparison experiment result can be an indication that in the removal of COD in seawater with the addition of PCT, the removed organic substances was contributed from seawater pollutants instead of PCT. Therefore, specific tests are needed to detect the actual content of paracetamol, such as HPLC, to determine the removal precisely.

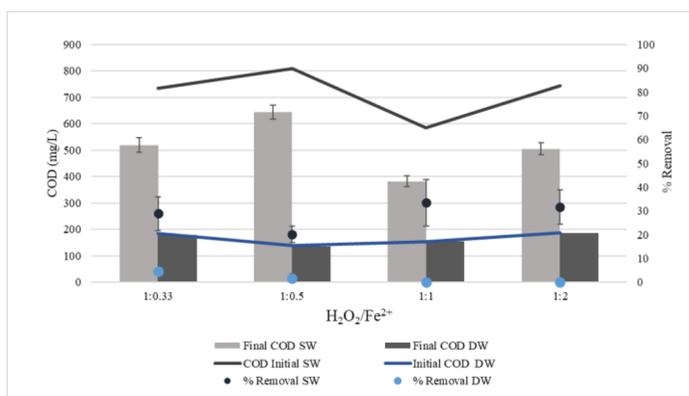


Fig. 3. PCT's retention of membrane filtration process at different H_2O_2/Fe^{2+} Ratio

As for the PES 7 nm (50 kDa) membrane, it exhibited a different trend in COD removal compared to the PES 30 nm membrane. At the same H_2O_2/Fe^{2+} ratio, the COD concentration in the permeate was consistently higher than the feed, up to 3 times higher. This might be explained due to degradation of PES 7 nm (50 kDa) membrane during the filtration, resulting in an increase in COD value. The degradation was due to the presence of hydroxyl radicals generated by the Fenton reaction. The hydroxyl radical's abstract hydrogen atoms from the PES membrane, causing it to break down [18]. In addition to the presence of hydroxyl radicals, H_2O_2 can also be attributed to membrane degradation. This is because H_2O_2 is a strong oxidizing agent (oxidation potential = 1.8 Volts). Membrane degradation due to H_2O_2 is caused by the loss of the S=O chain, such as the conversion of the $-SO_2$ group to $-SO_3$, [18].

3.2.2 Catalyst retention effect of pH adjustment

The evaluation of the performance of membrane as a post-treatment for Fenton oxidation was conducted not only to investigate the removal of PCT, but also the performance of the membrane in removing iron from $FeSO_4 \cdot 7H_2O$ used as a catalyst. Analysis of iron content in the permeation of a PES membrane with pore sizes of 30 nm and 7 nm (50kDa) showed that the quantity of catalyst added was proportional to the iron remaining in the permeate of both membrane variations when the pH was not adjusted in DW (Figure 4). Both membranes showed removal at a threshold of 15%.

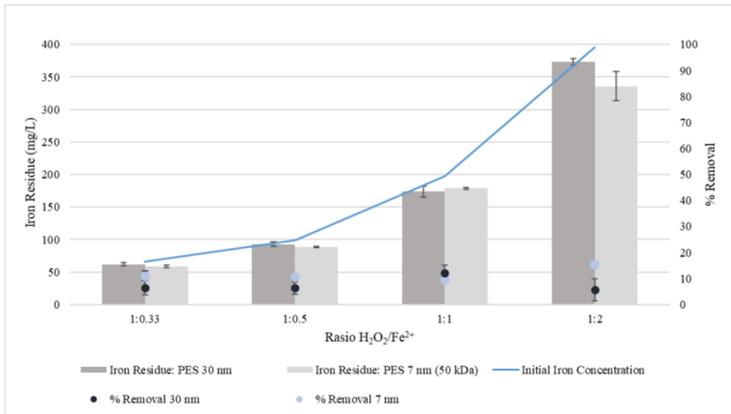


Fig. 4. Iron removal at unadjusted pH

Less than 15% of iron removal occurred due to the membrane mechanism in removing pollutants. Iron catalysts in Fenton oxidation are transformed into dissolved iron [13]. In general, metallic elements in the dissolved phase have a molecular weight cutoff (MWCO) of 10^{-10} to 10^{-9} meters or equivalent to 1 nm [19]. The membrane MWCO used in this study was 7 nm (50 kDa) and 30 nm. The larger MWCO of the membrane than the MWCO of iron is what makes iron particles unable to be removed by more than 15%.

Moreover, pH adjustment was conducted for further evaluation of membrane performance in DW. This was carried out on the effluent of the Fenton oxidation process with the optimal catalyst dosage to remove PCT, which had been obtained from previous experiment (Figure 2). The effluent, which initially had a pH of 3, was adjusted to pH 3; 5; 6.5; and 8.5 by adding NaOH 1M. As shown in Figure 5, pH that has been adjusted to 8.5 yielded the highest iron removal of 58.1% and 92.7%. This corresponded to the theory of the smaller MWCO membrane resulted in better rejection [20].

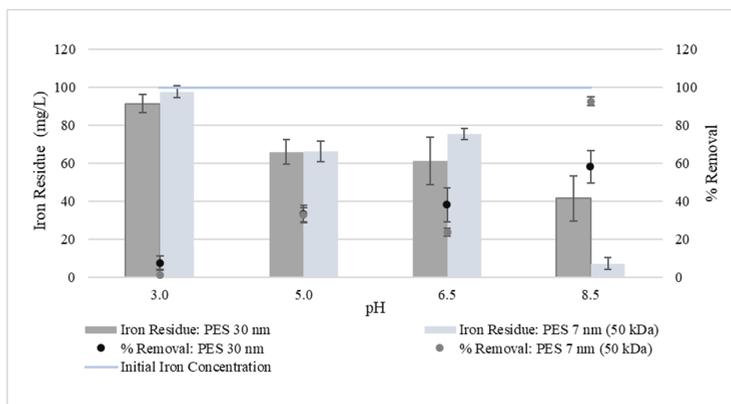


Fig. 5. Iron removal at adjusted pH

The mechanism of iron removal when adjustment of pH applied was due to the oxidation precipitation process of dissolved iron. This was observed in a study that investigated the mechanism of iron precipitation from $FeSO_4 \cdot 7H_2O$ at pH 6 and 9. The first stage of the process was a rapid initial oxidation rate of Fe^{2+} and the instantaneous formation of primary particles (nucleation) of Fe^{3+} known as polynuclear cationic species. The size of these particles increased through a condensation mechanism, resulting in the removal of hydrogen ions. The removal rate of this process tended to have a linear correlation with the pH increase.

The increment of pH resulted for formed particles reacted back with Fe^{2+} and through an adsorption mechanism formed flocs. When the pH was in a higher range, the reaction kinetics became faster so that the precipitation formed occurred in a short time. The last phase of the process was the aggregation of the formed particles. In this phase, the Ferrihydrite particles consumed traces of supersaturation through an aggregative mechanism at pH 6 and through crystalline phase transformation at pH 9. The aggregates formed at pH 9 had smaller particle sizes due to the higher nucleation rate at the beginning. Although they had smaller particle sizes, the stability of the precipitate produced was better than at pH 6 [21].

As for SW experiment, the iron retention rate was in the range of 41% to 53%, with the remaining iron concentration ranging from 129 to 750 mg/L at pH adjusted to 8.5. These results were similar to the results of iron removal in synthetic water, which with a pH of 8.5 was able to remove iron up to 58%. This indicated that there was no significant difference in iron removal by the membrane on different water matrices. All in all, ultrafiltration was most effective to retain iron when the feed's pH is adjusted to 8.5 for both in DW and SW.

3.2.3 Membrane Characterization

Membrane characterization was done for both variation through SEM-EDS to identify membrane's surface morphology and FTIR to analyze membrane's surface functional groups after the filtration of DW. As shown in Figure 6.1, the membrane PES 30 nm that has been used has particles build up on its surface compared to the pristine membrane. Whereas membrane PES 7 nm (50 kDa) showed different result for pristine and used membrane (Figure 6.2). As shown in Figure. 6.2b, after filtration membrane has a significant number of smaller pores compared to the pristine condition. This can be a supporting evidence to membrane degradation, which potentially caused by the presence of hydroxyl radical as explained in sec 3.2.1.

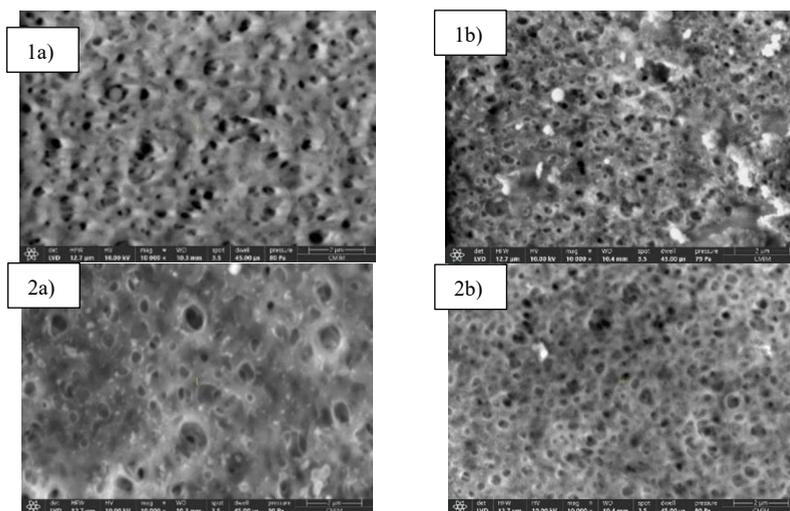


Fig. 6. SEM-EDS images 1) membrane PES 30 nm 2) membrane PES 7 nm a) Pristine membrane; b) used membrane

FTIR result of pristine and used membrane PES 30 nm is shown in Figure 7. The FTIR spectra of the two membranes were identical, indicating that the functional groups on the surface of the membrane were not affected by the filtration process. Both spectra exhibited peaks at $3.362\text{--}3.385\text{ cm}^{-1}$, corresponding to N-H stretch vibrations. Additionally, peaks at

1.638 cm^{-1} and 1.485 cm^{-1} were assigned to C=O and C-N stretching vibrations, respectively, which corresponded with studies done before [22] [23]. The same result was also shown by membrane PES 7 nm (50 kDa), where there was no significant difference observed from the wavelength before and after filtration. Based on these results also, it can be shown that neither PCT nor its intermediate by-products were detected on the surface of the used membrane. As mentioned before, this phenomenon was potentially caused by MWCO rejection mechanism and adsorption mechanism that did not occur.

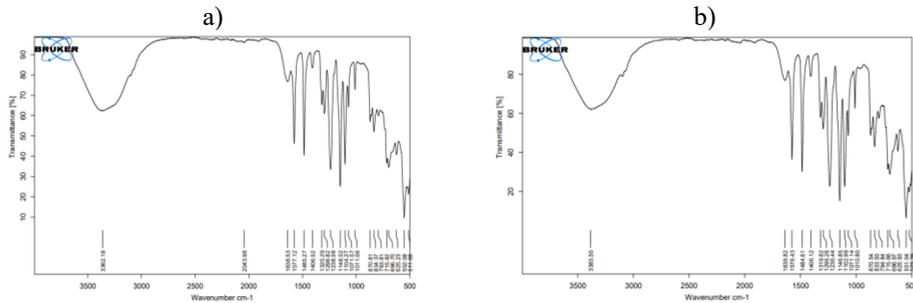


Fig. 7. FTIR result used membrane PES 30 nm a) pristine membrane; b) used membrane

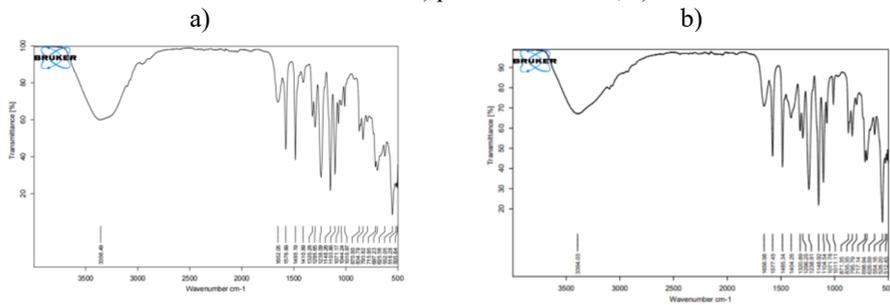


Fig. 8. FTIR result used membrane PES 7 nm (50 kDa) a) pristine membrane; b) used membrane

4 Conclusion

1. The highest paracetamol removal was found to be 45% and 37% represented in COD at $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ 1:0.5 and 1:1 for DW and SW, respectively. The presence of Hydroxyl radicals and salt contributed the most to the result obtained.
2. Ultrafiltration PES 30 nm and 7 nm (50 kDa) membranes were insignificant to retain PCT as a post treatment to Fenton oxidation. Membrane PES 30 nm resulted in less than 5% and maximum 30% of removal of COD in DW and SW respectively. Membrane PES 7 nm (50 kDa) resulted in twice the amount of COD feed in its permeate due to the potential of the degradation of the membrane caused by the presence of hydroxyl radical and H_2O_2 .
3. Alkaline condition of pH 8.5 was found as the optimal pH in order to yield the highest iron retention. In DW, membrane PES 30 nm resulted in iron removal up to 58.1% and the PES 7 nm (50 kDa) membrane was able to remove 92%. Whereas in SW, membrane PES 30 nm was able to remove iron up to 53%. This was caused by the iron precipitation phenomenon at high pH.

This study offers an alternative approach to understanding and managing PCT pollution, opening exciting avenues for further exploration. The Fenton process was proven to be effective in degrading PCT across various water matrices. Future research can delve deeper

into its mechanistic details within diverse environments, such as real industrial or hospital wastewater. Additionally, HPLC-based approaches can refine PCT identification for enhanced accuracy. While UF demonstrably retained the iron catalyst through pH adjustment, exploring the efficacy of nanofiltration or reverse osmosis processes within hybrid Fenton-membrane systems could lead to improved PCT removal. Furthermore, ecotoxicological studies on byproducts, investigations into their environmental fate, economic feasibility assessments, and potential large-scale implementation can solidify the process's practical contribution to sustainable PCT removal from various water matrices.

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References

1. Y. Yang *et al.*, “Which Micropollutants in Water Environments Deserve More Attention Globally?,” *Environ Sci Technol*, vol. 56, no. 1, pp. 13–29, Jan. 2022, doi: 10.1021/acs.est.1c04250.
2. H. N. Phong Vo *et al.*, “Acetaminophen micropollutant: Historical and current occurrences, toxicity, removal strategies and transformation pathways in different environments,” *Chemosphere*, vol. 236, p. 124391, Dec. 2019, doi: 10.1016/j.chemosphere.2019.124391.
3. N. Rosman, W. N. W. Salleh, M. A. Mohamed, J. Jaafar, A. F. Ismail, and Z. Harun, “Hybrid membrane filtration-advanced oxidation processes for removal of pharmaceutical residue,” *J Colloid Interface Sci*, vol. 532, pp. 236–260, Dec. 2018, doi: 10.1016/j.jcis.2018.07.118.
4. W. Koagouw, N. A. Stewart, and C. Ciocan, “Long-term exposure of marine mussels to paracetamol: is time a healer or a killer?,” *Environmental Science and Pollution Research*, vol. 28, no. 35, pp. 48823–48836, Sep. 2021, doi: 10.1007/s11356-021-14136-6.
5. W. Koagouw, Z. Arifin, G. W. J. Olivier, and C. Ciocan, “High concentrations of paracetamol in effluent dominated waters of Jakarta Bay, Indonesia,” *Mar Pollut Bull*, vol. 169, p. 112558, Aug. 2021, doi: 10.1016/j.marpolbul.2021.112558.
6. I. Alessandretti, C. V. T. Rigueto, M. T. Nazari, M. Rosseto, and A. Dettmer, “Removal of diclofenac from wastewater: A comprehensive review of detection, characteristics and tertiary treatment techniques,” *J Environ Chem Eng*, vol. 9, no. 6, p. 106743, Dec. 2021, doi: 10.1016/j.jece.2021.106743.
7. S. O. Ganiyu, E. D. van Hullebusch, M. Cretin, G. Esposito, and M. A. Oturan, “Coupling of membrane filtration and advanced oxidation processes for removal of pharmaceutical residues: A critical review,” *Sep Purif Technol*, vol. 156, pp. 891–914, Dec. 2015, doi: 10.1016/j.seppur.2015.09.059.
8. S. Ziembowicz and M. Kida, “Limitations and future directions of application of the Fenton-like process in micropollutants degradation in water and wastewater treatment: A critical review,” *Chemosphere*, vol. 296, p. 134041, Jun. 2022, doi: 10.1016/j.chemosphere.2022.134041.
9. “Peraturan Pemerintah Republik Indonesia Nomor 22 Tahun 2021 .”
10. H. T. Van *et al.*, “Heterogeneous Fenton oxidation of paracetamol in aqueous solution using iron slag as a catalyst: Degradation mechanisms and kinetics,” *Environ Technol Innov*, vol. 18, p. 100670, May 2020, doi: 10.1016/j.eti.2020.100670.
11. S. Adityosulindro, “Activation of homogeneous and heterogeneous Fenton processes by ultrasound and ultraviolet/visible irradiations for the removal of

- ibuprofen in water,” Institut National Polytechnique de Toulouse (INP Toulouse), Toulouse, 2017. [Online]. Available: <https://oatao.univ-toulouse.fr/17913/7/aditosulindro-sandyanto.pdf>
12. A. Mirzaei, Z. Chen, F. Haghghat, and L. Yerushalmi, “Removal of pharmaceuticals from water by homo/heterogonous Fenton-type processes – A review,” *Chemosphere*, vol. 174, pp. 665–688, May 2017, doi: 10.1016/j.chemosphere.2017.02.019.
 13. M. Pacheco-Álvarez, R. Picos Benítez, O. M. Rodríguez-Narváez, E. Brillas, and J. M. Peralta-Hernández, “A critical review on paracetamol removal from different aqueous matrices by Fenton and Fenton-based processes, and their combined methods,” *Chemosphere*, vol. 303. Elsevier Ltd, Sep. 01, 2022. doi: 10.1016/j.chemosphere.2022.134883.
 14. M. Nadour, F. Boukraa, and A. Benaboura, “Removal of Diclofenac, Paracetamol and Metronidazole using a carbon-polymeric membrane,” *J Environ Chem Eng*, vol. 7, no. 3, p. 103080, Jun. 2019, doi: 10.1016/j.jece.2019.103080.
 15. N. Nasrollahi, V. Vatanpour, and A. Khataee, “Removal of antibiotics from wastewaters by membrane technology: Limitations, successes, and future improvements,” *Science of The Total Environment*, vol. 838, p. 156010, Sep. 2022, doi: 10.1016/j.scitotenv.2022.156010.
 16. N. Jallouli, K. Elghniji, H. Trabelsi, and M. Ksibi, “Photocatalytic degradation of paracetamol on TiO₂ nanoparticles and TiO₂/cellulosic fiber under UV and sunlight irradiation,” *Arabian Journal of Chemistry*, vol. 10, pp. S3640–S3645, May 2017, doi: 10.1016/j.arabcj.2014.03.014.
 17. X. Li, L. Jiang, and H. Li, “Application of Ultrafiltration Technology in Water Treatment,” *IOP Conf Ser Earth Environ Sci*, vol. 186, p. 012009, Oct. 2018, doi: 10.1088/1755-1315/186/3/012009.
 18. M. T. Tshaye, S. Velizarov, and B. Van der Bruggen, “Stability of polyethersulfone membranes to oxidative agents: A review,” *Polym Degrad Stab*, vol. 157, pp. 15–33, Nov. 2018, doi: 10.1016/j.polymdegradstab.2018.09.004.
 19. Y. Li, X. Gong, Y. Sun, Y. Shu, D. Niu, and H. Ye, “High molecular weight fractions of dissolved organic matter (DOM) determined the adsorption and electron transfer capacity of DOM on iron minerals,” *Chem Geol*, vol. 604, p. 120907, Aug. 2022, doi: 10.1016/j.chemgeo.2022.120907.
 20. S. Laksono, “Mini-plant and bench-scale studies on the fouling mechanisms as well as the responsible organic foulants during direct filtration of algal-containing waters using hollow-fiber membranes,” University of Duisburg-Essen, 2021.
 21. M. Hove, R. P. van Hille, and A. E. Lewis, “Mechanisms of formation of iron precipitates from ferrous solutions at high and low pH,” *Chem Eng Sci*, vol. 63, no. 6, pp. 1626–1635, Mar. 2008, doi: 10.1016/j.ces.2007.11.016.
 22. A. B. D. Nandiyanto, R. Oktiani, and R. Ragadhita, “How to Read and Interpret FTIR Spectroscopy of Organic Material,” *Indonesian Journal of Science and Technology*, vol. 4, no. 1, p. 97, Mar. 2019, doi: 10.17509/ijost.v4i1.15806.
 23. J. Kuttiani Ali, M. Abi Jaoude, and E. Alhseinat, “Polyimide ultrafiltration membrane embedded with reline-functionalized nanosilica for the remediation of pharmaceuticals in water,” *Sep Purif Technol*, vol. 266, p. 118585, Jul. 2021, doi: 10.1016/j.seppur.2021.118585.