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Performance of Membrane Photocatalytic Reactor on Palm Oil Mill Secondary Effluent using zinc oxide –*Cymbopogon citratus* (ZnO-CC)

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Abstract: Palm oil mill is one of the largest industries in Malaysia which could contribute for Malaysia's economy. However, palm oil mill secondary effluent (POMSE) from this industry has created major disposal problem which could not be discharged to the environment due to its high biochemical oxygen demand (BOD), chemical oxygen demand (COD) and turbidity. Thus this present study aim to identify the performance of Zinc oxide-*cymbopogon citratus* (ZnO-CC) as the photocatalyst in the photocatalytic degradation process for POMSE treatment using membrane photocatalytic reactor (MPR). The performance of three different ZnO-CC nanoparticles (3:1, 5:1 and 9:1) in treating POMSE were successfully being observed and compared with commercial ZnO. The treated wastewater were analysed after membrane filtration process in terms of its turbidity, pH, BOD andCOD . The membrane surface of fouling layer was characterized using Field Emission Scanning Electron Microscopy (FESEM). The result revealed that higher efficiency in removal of COD, BOD and turbidity in presence of ZnO-CC (3:1) (98-99%) of POMSE treatment using MPR. Thus, it is believed that this study have a potential on the improvement of MPR system and lead to an alternative methods for polishing process of POMSE.

Keywords: Zinc oxide *Cymbaphogon citrartus*, Palm Oil Mill Secondary Effluent, Field Emission Scanning Electron Microscopy, Membrane Photocatalytic Reactor

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1. Introduction

As industry of palm oil developed more rapidly parallel with technology, the pollution issues rises towards palm oil mill secondary effluent (POMSE) cannot be overlook. POMSE was produced from the secondary biological treatment of POME. It contains a high concentration of organic matter which harmful to the environment and human health [1]. Based on the process of oil extraction and the properties, POMSE exhibits brownish colour due to the multiple lignin and tannin complexes resulting from aerobic treatment of POME where can invoke environmental issues and pollution of water bodies [2]. Membrane photocatalytic reactor (MPR) is an alternative for the advanced treatment where the photocatalysis process was used for the decomposition of organic pollutant and coupled with membrane separation process to permits continuous operation system for the recovery of photocatalyst.

Recently, nanoparticles (NPs) have received a lot of attention due to their unique properties such as photoemission, antimicrobial activity, optical properties and catalytic activity [3]. NPs have the potential to be used in membrane technology, which significant for the applications in the wastewater treatment technology. Titanium Dioxide (TiO_2) have been commonly used as a photocatalyst due to its high activity, low price and nontoxicity. However, the extensive use of TiO_2 NPs shows that its photocatalytic activity is limited [4]. Previous study has been reported that ZnO-PVP NPs show the highest performance in MPR for industrial dye wastewater treatment, in terms of photocatalytic activity, flux decline and membrane fouling [5]. MPR has a several distinct features in comparison with conventional photocatalytic reactors, such as: (1) keeping the photocatalyst confined in the reaction environment through membrane technology; (2) realizing a continuous process with simultaneous separation of photocatalysts and products from the reaction environment; (3) separating the photocatalysts from the treated water [5].

Wastewater from palm oil mill industry is frequently rich in color, hard degradation materials and very high COD and BOD concentration. At the present moment, there are several limitations to wastewater treatment plant treating method – ultrafiltration, adsorption treatment, coagulation which hardly meets the discharge criterion of environmental quality [6,7].

Green synthesis is the synthesis of either nano- or macro-particles that is pollution free process and natural reserved which remain unaffected. In this project the green synthesis being used is *Cymbopogon citratus* extracted plant. This project shows the elaboration uses of ZnO NPs in MPR treatment of POMSE. It is eco-friendly, biodegradable and also very easy to prepare. This nanoparticle is also very economic because it is produce by *cymbopogon citratus*. *Cymbopogon citratus* is believed can act as capping agent to reduce the size of ZnO NPs which responsible to enhance the degradation rate in photocatalysis process and subsequently can improve the membrane fouling. Therefore, this research aimed to elucidate the performance of POMSE treatment using MPR in presence of ZnO-CC NPs at different concentration of extracted *Cymbopogon citratus* in terms of pH, COD, BOD and turbidity. In addition, it was to characterized membrane surface using FESEM.

2. Materials and Methods

2.1 Materials

The final effluent from an open pond that belong to a local palm oil mill located in, Johor, Malaysia. The ZnO-CC NPs used in this study were synthesised using precipitation method as reported in [1]. Hydrochloric acid (HCL) and sodium hydroxides (NaOH) were purchased from R&M Marketing. Polypiperazines-amides (PA) NF membrane (GE Osmonics, TrisepTS40, USA), was used in this study.

2.2 Cross-flow process in Membrane Photocatalytic Reactor

A schematic of the laboratory scale MPR used in this study is present in Figure 1. A 2L of photocatalytic reactor with UV lamp (253.7 nm, 18W, USA) was used to activate the photocatalyst. In order to avoid compaction of membrane, MPR was wetted with RO water. Before photocatalysis process was started, the mixture was well agitated at 300 rpm using WireStir impeller (Model PL111) for 30 min without UV lamp. Then, the UV lamp was switched on for 20 min. Retentate effluent was flowed into bypass flow in which the temperature was maintained at 25°C by recirculating of the water chiller. The effluent was charged into stainless steel flat sheet membrane module. The permeated effluent was collected and stored at 4ºC for water quality analysis [1].

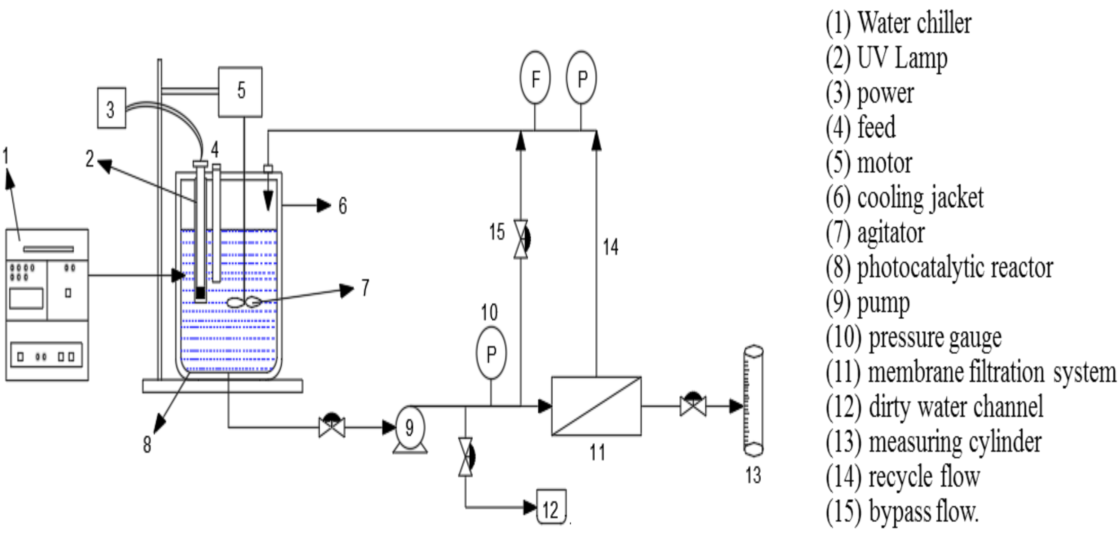

Figure 1: The cross-flow process in Membrane Photocatalytic Reactor

2.3 Analytical Method

POMSE samples had been analyzed in triplicate with quality parameter including pH, turbidity, COD and BOD as per standard method APHA (2012). The pH of fresh and treated POMSE was analyzed using benchtop meter pH (Oakton pH 700) and turbidity was recorded using spectrometer (UV-Vis Hach, USA). Then the COD result were obtain using POME is incubated with a strong chemical oxidant under specific conditions of temperature and for a particular period of time and the DO data were obtain using meters and probes.

The percentage removal (COD, BOD and turbidity) of contaminants was calculated using Eq. 1

$$R = \frac{C_o - C_t}{C_o} x100\% \qquad \text{Eq. 1}$$

where R is the percentage removal, C_o (mg/L) is the initial water quality index of POMSE, and C_t is the water quality index at reaction time, t (treated POMSE after MPR process).

The surface morphology of all membranes were characterized using FESEM (JSM-7800F) analysis. Prior to FESEM examination the membrane were sputter coated with platinum using a Q150R Sputter Coater. The accelerating voltage was set at 5kV during the analysis [8].

3. Results and Discussion

There are several discharge standard of parameters outlined by the Department of Environment (DOE) that need to be monitored before the wastewater is discharged such as pH, COD, BOD and turbidity as tabulated in Table 1. The pH value for pure POMSE is in the range of discharged standard whereas the COD, BOD and turbidity values exceed the discharged standard.

Table 1: Wastewater parameter's characteristic for pure POMSE and the discharged standard

Parameter	Units	Pure POMSE	Discharge standard (DoE)
pH	-	7.53	5 – 9
COD	mg/l	1443.34	50
BOD	mg/l	807.69	100
Turbidity	NTU	653	NA

Based on the experimental result, there were significant differences in each parameters between the pure POMSE, and treated POME (3:1, 5:1, 9:1, commercial and without ZnO). This study showed that the characteristics of treated POMSE were improved after MPR system. Figure 2 demonstrated the water quality shows the higher removal for each water parameter at ZnO-CC (3:1). This treatment with ZnO-CC (3:1) successfully reduces COD, BOD, and turbidity up to 99.3%, 98.1% and 99.78% respectively (Figure 2). This phenomena might be due to the efficiency of the ZnO-CC (3:1) NPs in the degradation of POMSE pollutant during the treatment process.

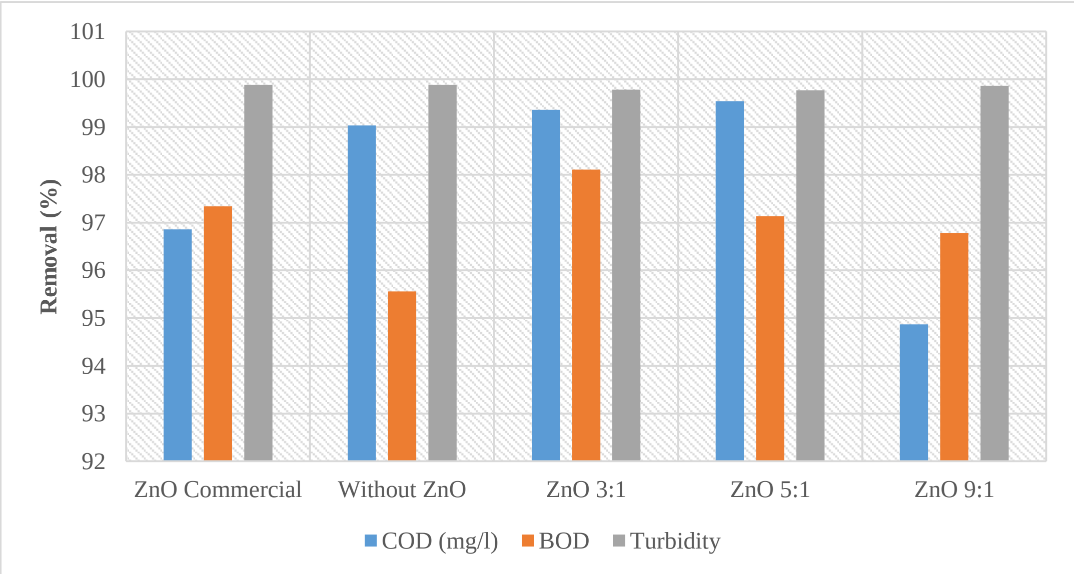

Figure 2: POMSE parameter removal value for different types of photocatalyst

The pH value was at 8.66 which indicate the best value for treated POMSE (alkaline) as shown in Table 2. With the lowest COD recorded which is 9.3 mg/l this indicates that it consumed the least amount of oxygen to degrade the pollutants. Though the value for turbidity was in one of the highest, but still it was in an acceptable value compared to pure POMSE which is 615. In addition, the higher efficiency of treated POMSE quality parameter also correlated with the mitigation of membrane fouling with the presence of ZnO-CC NPs. Thus, the outcomes from this study implicated that the MPR system of treatment POMSE using ZnO-CC (3:1) was significant for the enhancement of treated POMSE quality to comply with the standard discharge requirement according to Environmental Quality Act 1974 (Act 127).

Table 2: POMSE parameter value in pH, COD, BOD and Turbidity after MPR system

Parameter Membrane	pH	COD (mg/l)	BOD	Turbidity
ZnO Commercial	6.61	45.3	21.45	0.794
Without ZnO	7.58	14	35.85	0.802
ZnO 3:1	8.66	9.3	15.3	1.43
ZnO 5:1	6.70	45.2	23.17	1.47
ZnO 9:1	6.75	74	25.98	0.940

3.1 Membrane Characterization

FESEM shows the topographical information of membrane surface before and after filtration of POMSE in MPR system. Comparison of the surface membrane with the presence and without ZnO-CC causes a marked change in the surface texture from the FESEM image as indicated in Figure 3. It is clearly demonstrating that before filtration, NF membrane had smooth and clean surface without contamination (Figure 3 a).

It is observed that the variation of fragments formed on the surface of membrane, size of fragments increased gradually with the ZnO-CC as indicate in Figure 3. The dense fine structure of contaminant shown in Figure 3 (b), (c), (d) and (e) with presence of ZnO-CC might be due to the foulant and nanoparticles were trapped on the membrane surface. Thus resulting the formation of uniform smaller particles compare with commercial and without ZnO as in Figure 3 (e) and (f) respectively.

As seen in the Figure 3 (d), ZnO-CC (9:1) has the roughest surface compared to others. The ZnO-CC (3:1) shows FESEM image of neat and most organised films as in figure 3 (b). As for ZnO-CC (5:1), the thickness and the sharpness of the top skin layer was increased in comparison with the pure NF membrane (Figure 3 (c)). The surface of the membrane is bumpy and stony other than it is more regular than those of the pure one.

This can be relate with the performance of POMSE water quality as indicated in Table 2 which resulting lower turbidity, COD and BOD reduction of ZnO-CC (9:1) compared to ZnO-CC (5:1) and 3:1. This phenomenon might be due to the size of nanoparticles which indicate larger size of ZnO-CC (9:1) (41.36 nm) followed by ZnO-CC (5:1) (32.25 nm) and ZnO-CC (3:1) (23.3 nm). The increment of nanoparticle size might contribute to the reduction of photocatalytic activity for ZnO-CC (9:1) and ZnO-CC (5:1). Indeed, greater size of nanoparticles will result in lower specific surface area for the adsorption process between contaminant and photocatalyst in MPR treatment of POMSE. Thus, promote more particles to penetrate on the membrane surface.

On the opposite, the structure of fouling layer ZnO in Figure 3 (f) exhibit inhomogenous porous particles on the membrane surface. This probably due to the interaction of photocatalyst and contaminants on the surface of membrane. Without ZnO, the surface density of contaminant molecules were larger and more foulant deposited on the membrane surface.

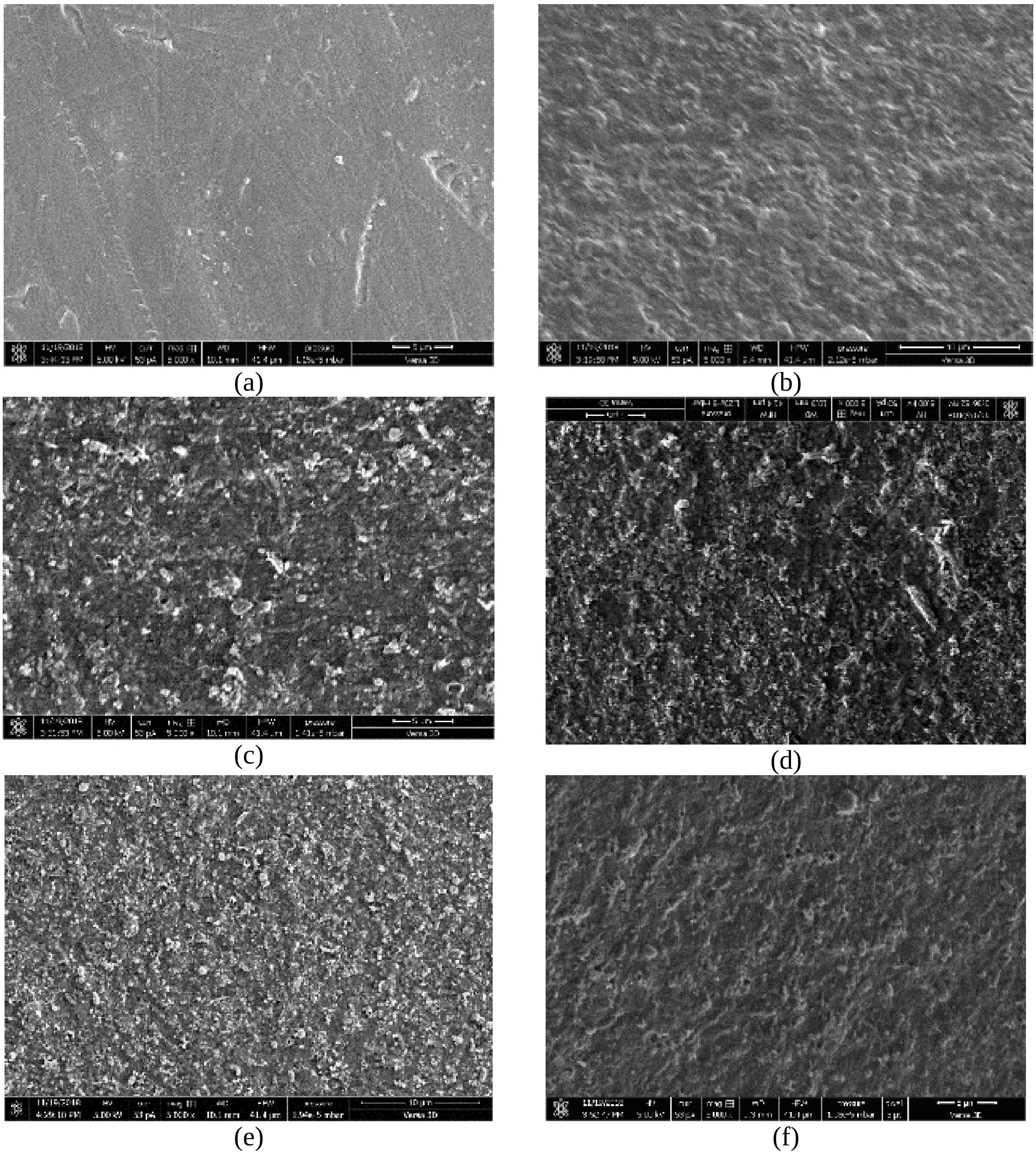

Figure 3: FESEM image of (a) fresh and fouled membrane b) in presence of ZnO-CC 3:1 NPs, c) in presence of ZnO-CC 5:1 NPs, d) in presence of ZnO-CC 9:1 NPs, e) in presence of commercial ZnO NPs, and f) in the absence of ZnO NPs

4. Conclusion

Palm oil mill secondary effluent (POMSE) is indeed need to be treated before discharge due to its visible brownish color primarily, and other unstandardized parameter with Department of Environment (DoE). The green synthesis ZnO-CC (3:1) showed the best overall performance in terms of wastewater quality after POMSE treatment via MPR. It has higher degradation rate of foulants than other ratio of ZnO-CC (5:1 and 9:1). Treated POMSE with ZnO-CC (3:1) has pH 8.66 (alkaline) which is desirable since the wastewater would cycled back through underground water system and neutralized rain that is acidic. With COD and BOD (9.3 mg/l and 15.3 mg/l respectively) is the lowest measured value and turbidity (1.43 NTU), ZnO-CC (3:1) is considered the best because all of these parameter meet the discharged quality requirements. The membrane characterization results of FESEM was affirmatively supporting the efficiency of water quality of treated POMSE using MPR assisted with ZnO-CC NPs.

Thus, ZnO-CC (3:1) was proven as a best photocatalyst able to improve the quality of POMSE performance in MPR system.

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References

[1] D.A.B. Sidik et al., "Performance of membrane photocatalytic reactor incorporated with ZnO-Cymbopogon citratus in treating palm oil mill secondary effluent," Process Saf. Environ. Prot., vol. 143, pp. 273–284, 2020, doi: 10.1016/j.psep.2020.06.038.

[2] M.N. Subramaniam et al., "Hydrophilic hollow fiber PVDF ultrafiltration membrane incorporated with titanate nanotubes for decolourization of aerobically-treated palm oil mill effluent," Chem. Eng. J. vol. 316, pp. 101–110, 2017, doi:10.1016/j.cej.2017.01.088.

[3] C. Hao et al., "Anionic surfactants-assisted solution-phase synthesis of ZnO with improved photocatalytic performance," J. Photoch Photobio A. vol. 332, pp. 384-390, 2017, doi: 10.1016/j.jphotochem.2016.09.013.

[4] H. Dong et al., "An overview on limitations of TiO2-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures," Water Res. vol. 79, pp. 128–146, 2015, doi: 10.1016/j.watres.2015.04.038.

[5] N.H.H. Hairom et al., "Influence of zinc oxidenanoparticles in the nanofiltration of hazardous Congo red dyes," Chem. Eng. J. vol. 260, pp. 907–915, 2015, doi:10.1016/j.cej.2014.08.068.

[6] E.U. Deveci et al., "Integrated process of fungal membrane bioreactor and photocaytalytic membrane reactor for the treatment of industrial textile wastewater," Biochem. Eng. J. vol. 105, pp. 420–427, 2016, doi: 10.1016/j.bej.2015.10.016.

[7] M. S. Sajab et al., "Cationic and anionic modifications of oil palm empty fruit bunch fibers for the removal of dyes from aqueous solutions," Bioresour. Technol, vol. 128, pp. 571–577, 2013, doi: 10.1016/j.biortech.2012.11.010.

[8] M.N. Subramaniam et al., "AT-POMEcolour removal through photocatalytic submerged filtration using antifoulingPVDF-TNT nanocomposite membrane," Sep. Purif. Technol. Vol. 191, pp. 266–275, 2018, doi:10.1016/j.seppur.2017.09.042.