Progress in Engineering Application and Technology Vol. 4 No. 1 (2023) 841-849

PEAT

Homepage: http://publisher.uthm.edu.my/periodicals/index.php/peat
e-ISSN : 2773-5303

Performance of ZnO-Kaolin for Palm Oil Mill Secondary Effluent (POMSE) Treatment via Photocatalytic Reactor

Nuramira Aliah Sahilan[1], Zarizi Awang[1*], Nur Hanis Hayati Hairom[1]

[1]Department of Civil Engineering Technology, Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, 84600 Pagoh, Johor, MALAYSIA

*Corresponding Author Designation

DOI: https://doi.org/10.30880/peat.2023.04.01.087
Received 14 January 2023; Accepted 1 February 2023; Available online 1 February 2023

Abstract: Palm oil mill secondary effluent (POMSE) is one of the biggest byproducts produce in every palm oil mill and its contribute to a conflict for environment when this effluent property does not achieve the discharge requirement by Department of Environment (DOE). Hence, this study wanted to show that there is an advance technology called photocatalytic process via photocatalytic reactor can settle this problem more effective rather than traditional method in order to solve it. However, this photocatalytic process for POMSE treatment in this study have been used ZnO nanoparticles with the presence of natural clay, Kaolin as photocatalyst. Kaolin powder used is categorized as low grade to equate with the natural kaolin properties and made this study differ from others. ZnO-Kaolin have been synthesized under different ratios such as 1:3, 1:4 and 1:5 and the optimum ratio of photocatalyst for POMSE treatment determined. Besides, the performance of ZnO-Kaolin been observed by its parameters (turbidity, COD, BOD, color and pH). Then, after having all the data, the performance of ZnO-Kaolin (low grade) and ZnO-Kaolin (high grade) will be compared and conclude. From the data obtained, it shows that the ZnO-Kaolin (low grade) for the ratio 1:5 parameters of BOD, COD, and color percentage removal is higher than ZnO-Kaolin (high grade). Percentage removal for turbidity only showed that ZnO-Kaolin (high grade) is higher than ZnO-Kaolin (low grade). This indicate that ZnO-Kaolin (low grade) 1:5 is the optimum ratio that can effectively treat POMSE by photocatalytic process.

Keywords: POMSE, Ratios, Photocatalytic, Photocatalyst, Optimum, Performance, Membrane Photocatalytic Reactor (MPR), Kaolin

1. Introduction

Malaysia is the one of the biggest producer of palm oil with the high demand through years. While the oil palm sector has been lauded for its role in economic development, it also has generated and contribute a huge parts of contaminant through our environment. POME is a viscous liquid with a

**Corresponding author: azarizi@uthm.edu.my*

brownish appearance that is created as a byproduct of the palm oil manufacturing process. Furthermore, POME has a foul odor and is high in colloidal suspension. It also has a high biological demand (BOD) and a high chemical oxygen requirement (COD). As a result, it is not safe to release POME into a water stream because it is a particularly dangerous contaminant to aquatic life [1]. But, nowadays there are a lots of cases happened with palm oil mill effluent contaminated the rivers nearby. These cases mostly same things happened by discharge the POME through water stream but at different time. As example the case happened at Kluang, Johor one of the palm oil premise ordered to stop their operation immediately Johor Department of Environment have detected a high level of ammonia and some other harmful organic pollutant in the river nearby. This is the proven that the treatment of palm oil effluent is not easy to handle and consume a lot of time [5]. This study have approach an advanced method to treat this effluent with less time consuming, low cost, efficient and environmental friendly by using photocatalytic process with added photocatalyst which is ZnO-Kaolin. Kaolin used in this study are categories as low grade which is the kaolin itself have not gone through a lot of process and not added any kind of chemical substances from manufacture state. Besides, the high grade kaolin is the type of kaolin been used commercially; for laboratory work, house work, construction and more. The main objectives for this study are to synthesize ZnO-kaolin clay under different ratios via precipation method, to explore the performance of ZnO-kaolin for POMSE treatment via MPR by pH, COD, BOD, turbidity and colour. ZnO synthesize with kaolin clay as its catalyst within then provided/set up ratios in this research. ZnO-kaolin clay will be synthesized under different ratios, which are 1:3, 1:4, and 1:5. The specific field for this study is for palm oil mill secondary effluent to be treated using POMSE treatment using Membrane Photocatalytic Reactor (MPR) but more focused only on photocatalytic process. Problem statement for this study is how to manage the cost consuming in treating POMSE, so low grade clay which is kaolin will be used in the experimental stage rather than commercial kaolin. Then, the comparison of performance of ZnO-kaolin (low grade) and ZnO-kaolin (hign grade) to see the differences

2. Materials and Methods

2.1 Materials

For this study, the materials used are palm oil mill effluent that been collected the sample from Kian Hoe Plantations Berhad, Kluang, Johor and kaolin powder (type S300) purchased directly from supplier, Kaolin Malaysia Sdn. Bhd. Besides, the chemical substances such as zinc acetate-2-hydrate and oxalic acid dehydrate also used for experimental process and have been provide by laboratory. These two chemical substances is needed for synthesis zinc oxide solution by precipitation method and it been produced based on the amount needed in order to complete three ratio samples. Then, the solution processed until it becomes powder form and mixed with kaolin powder for photocatalytic process treatment.

Figure 1: Palm oil mill effluent pond

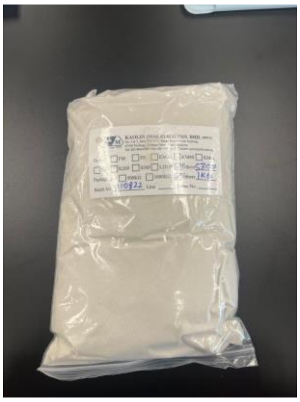

Figure 2: Kaolin powder

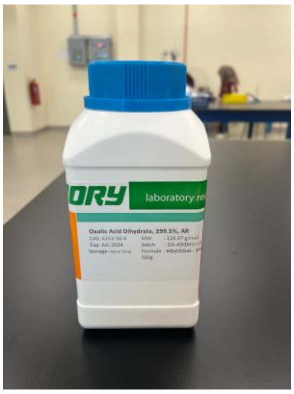

Figure 3: Oxalic acid dehydrate

Figure 4: Zinc acetate-2-hydrate

2.2 Methods

Before having photocatalytic process, ZnO have to synthesize first by precipitation method. Precipitation method is the process of conversion of a solution into solid by converting the substance into insoluble form or by making the solution a super saturated one [9]. The flowchart below **(Figure 5)** summarized the method of synthesis of ZnO-Kaolin. 150 ml of a mixture containing 0.1 M of zinc acetate and 0.15 M of oxalic acid were combined using a magnetic stirrer to create ZnO-Clay in a 1:3 ratio. The mixed solution was added 10 g of Kaolin power and heated to 55°C after being magnetically agitated for 5 minutes. At room temperature, the ZnO-Kaolin composite powder was then continuously agitated for 12 hours[10]. It was ready to be decanted and repeatedly cleaned with distilled water as a result of the reaction, which produced a precipitate product. The ZnO-Kaolin precipitate was then dried in an oven for one hour at under 100°C to eliminate the water content. The precipitates were then heated to 550°C for three hours in a furnace to eliminate the impurities[10]. Then, the steps be repeated for 1:4 and 1:5 ratio.

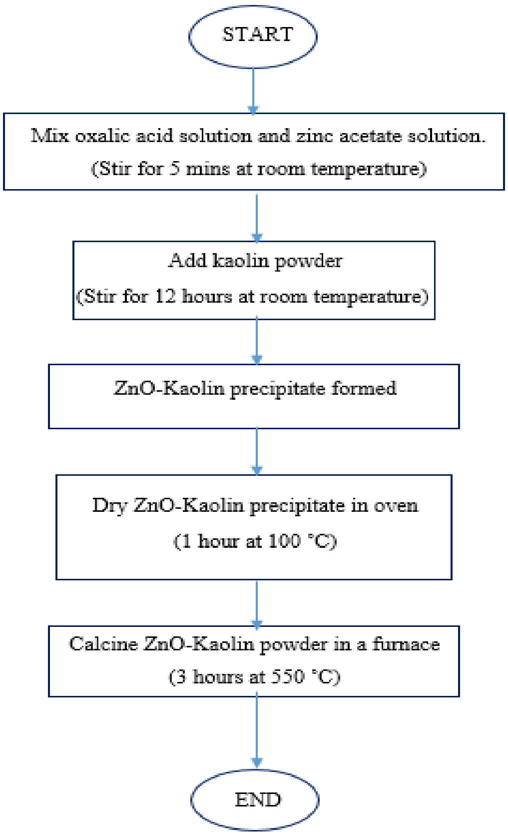

Figure 5: Synthesis of ZnO-Kaolin

The flowchart below **(Figure 6)** discussed about the whole process of the study flow. Firstly, the flow started with synthesis ZnO and mixed it with Kaolin by different ratios such as 1:3, 1:4 and 1:5. These ratios refers to one portion of ZnO to three portion of kaolin powder for 1:3 ratios. Then, the precipitate been mixed with POMSE in order to gone through photocatalytic process via membrane photocatalytic reactor (MPR). early 30 minutes, agitation process take over the solution by stirring it continuously in order to ensure the solution and precipitate blend together at optimum level. It continues with photocatalytic process under uv light within 20 minutes. Then, stop the MPR and water sample collected for the analysis part. Analysis of samples water handled to determine the characteristics of the treated POMSE water with ZnO-Kaolin by its physical, chemical and biological properties. A few tests were necessary, including those for pH, turbidity, chemical oxygen demand (COD), colour, and biological oxygen demand (BOD).

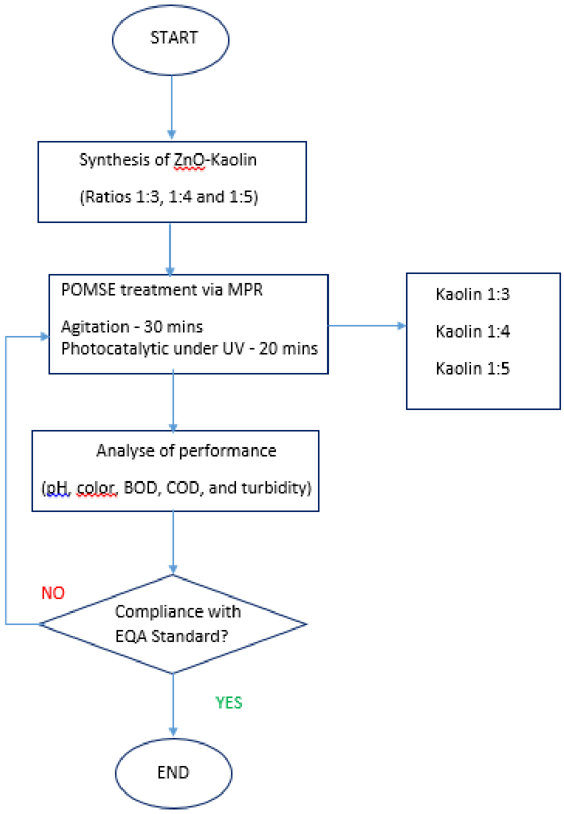

Figure 6: Flow chart of the experimental procedure

Figure 7: Membrane photocatalytic reactor (MPR)

2.3 Analysis of treated POMSE quality

The analysis of treated POMSE quality is based on these 5 parameters which are pH, color, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and turbidity. This research use pH meter to test pH value by dipping it into samples. A high pH value indicates that the water is polluted [4]. For colour parameter, POMSE products been measured by DR6000^{TM} UV-vis spectrophotometer (Hach) with program 97 color DMI 1 inch. An environmental method that is frequently used to assess how much oxygen can support microbiological life in a sample is called biochemical oxygen demand (BOD)[8]. When 300ml of three BOD is combined with water sample and dilution water, three samples are used. Two bottles for the water sample, one bottle for the blank sample. Each bottle's initial dissolve oxygen (DO) value was determined and recorded before being stored in a dark incubator at 20°C for five days. To track the DO depletion after five days, the final DO concentration was calculated. The reduction may, in theory, take place. The COD test was performed using a DR6000^{TM} UV-vis spectrophotometer (Hach) in accordance with Hach's established procedures. Water and wastewater quality is evaluated using chemical oxygen demand (COD). The efficacy of water treatment facilities is frequently assessed using the COD test. Lastly, turbidity of the samples was measured using a turbidity meter (Hach, H280 G) in this experiment. Water turbidity is measured to determine whether suspended particles like sludge, limestone, yeast, or bacteria are present. There are many ways to quantify turbidity, including as the standard turbidity unit (mg/l), the Jackson turbidity unit (J.T.U), and nephelometric turbidity (N.T.U).

3. Results and Discussion

Results stated below are based on all the analysis have been done. All studies based on the physical, chemical, and biological properties are completed in order to measure the features of treated POMSE with ZnO-Kaolin. pH, color and turbidity are physical parameters, COD is a chemical parameter, and BOD_5 is a biological parameter.

3.1 Data analysis

The result obtained from the study by parameters in the Table 1. The parameters consist of percentage removal of color, BOD, COD, and turbidity.

Table 1: Percentage removal of water quality analysis

SAMPLE	Colour, %	BOD,%	COD, %	Turbidity, %	pH
POMSE treated 1:3	20.5	20.6	14.2	45.4	8.80
POMSE treated 1:4	31.1	16.5	8.1	38.1	8.79
POMSE treated 1:5	31.4	30.9	10	44.2	8.79

3.2 Discussions

According to Desa et al., 2019, the conclusion for this study can be drawn that the percentage removal of ZnO- Kaolin in turbidity increased from ratio 1:3 to 1:4 and abruptly reduced for ZnO-Kaolin 1:5 because the loading of clay is higher. Additionally, the surface area of ZnO decreases when the loading of kaolin is excessively high [7], as was the case with a ZnO-Kaolin 1:5 ratio. For this results, optimum loading of clay for the ratio is from 1:3 to 1:4 due to clay's ability to boost ZnO's surface area when loaded to its optimal level. Then, the data proven that 1:4 ratio is the optimum loading of clay need in order to improve POMSE treatment by adsorption and degradation activity. This proven that when compared to naked ZnO, the combination ZnO/Clay exhibits better adsorption and photocatalytic degradation efficiency. The rate of photocatalytic degradation, on the other hand, can also rise as the number of active sites rises and is able to lower the higher turbidity reading.

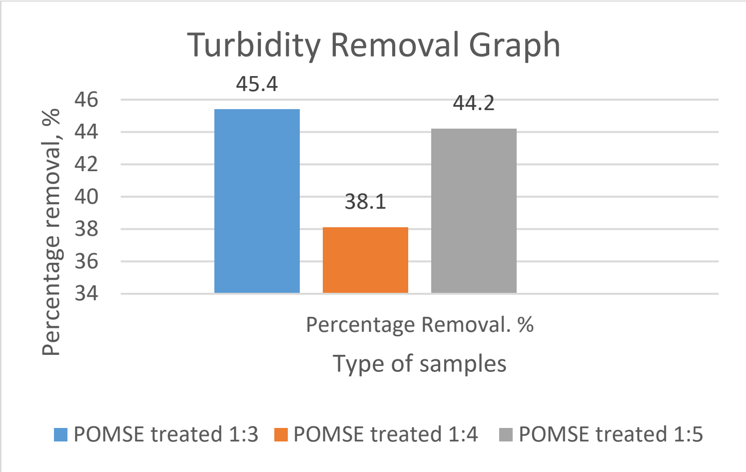

Figure 8: Graph of percentage removal of turbidity

Colour removal parameter discuss that the data proven **(Figure 9)** maximum loading of clay give the maximum adsorption capacity of colour since the reading of ZnO-Kaolin, 1:5 was slightly different with 1:4 ratio. This occurred as a result of the dense, rigid structure that developed on the membrane's surface, which increased membrane fouling and the percentage of colour rejection. Since it took into consideration the potential of the membrane to remove the organic impurities and solid particles from POMSE, type and pore size of the membrane employed were also important to obtain the excellent value of colour after treatment [2].

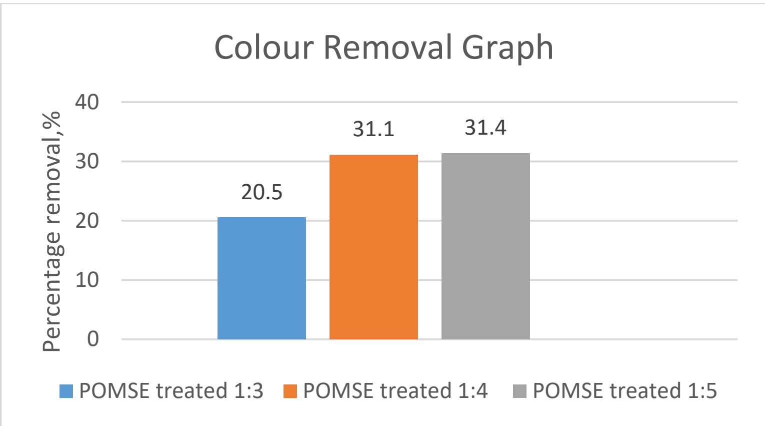

Figure 9: Graph of percentage removal of colour

PH reading of the four samples that have been analyse and some of the samples have been through MPR system. All the sample results obtained the same pH value and rather differ a bit from another but not in a big different. In addition, it can be claimed that the pH situation is unaffected by the treatment when POMSE is being treated in MPR. The pH value stayed in range 8.74 until 8.80 and it continues to adhere to the DOE's 2015 future standard discharge limit for palm oil mill effluent, which is established at a range of 5.0 to 9.0 [3]

Referring to **Figure 10**, it was found that the quality of COD exhibited a removal efficiency range of 8.1% to 14.2%. The observation have been arrowed to the maximum loading of clay amount that somehow will effect the COD reading as proven the greater amount of clay, resulting the lowest value of percentage for COD removal [6]. COD estimates the quantity of oxygen required to decompose the organic contaminants in water. A sample with a higher COD has more oxidizable stuff in it. If this is the case, the water's dissolved oxygen content will have decreased. Higher aquatic lifeforms may suffer environmental harm where this occurs. Therefore, lowering the levels of COD in water is the goal of wastewater treatment.

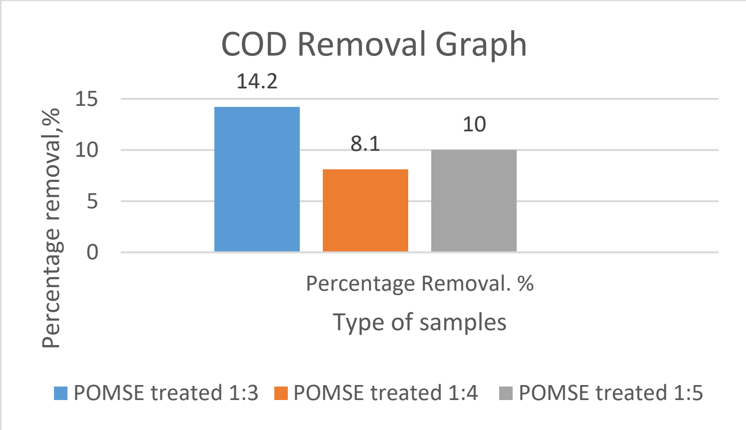

Figure 10: Graph of percentage removal of COD

For measuring the quality of water, the BOD is a crucial factor. In order to oxidise organic compounds, aerobic biological organisms consume a certain amount of oxygen per litre (mg O2 L 1). The mortality of some organisms may result from wastewater effluent with high BOD because it can reduce the oxygen in receiving waters. Table 4.6 shown that the lowest BOD value gained from ZnO-Kaolin with the ratio 1:4 (16.5%) while the highest value of BOD obtained from ZnO-Kaolin 1:5 ratio (30.9%). To support those data, the study from [5] have proven that the type and quantity of the adsorbent affect how well metal ions are scavenged. COD, BOD, chloride, and heavy metal removal as a result of adsorbent dose. It is implied that there was a rise in the adsorption of pollutants for kaolin and kaolin/ZnO nanocomposites since the removal efficiency of metal ions, COD, BOD, and chloride improved with increase in adsorbent dosage. Larger surface functionality, greater availability of more active or exchangeable sites, and increased surface area of the adsorbents can all be used to explain the concurrent increase in metal ion uptake and other indicator measures (COD, BOD, and chloride) with dosage increase. Thus, it can be conclude that the high loading of clay in this composite, the more BOD removal percentage can be obtained.

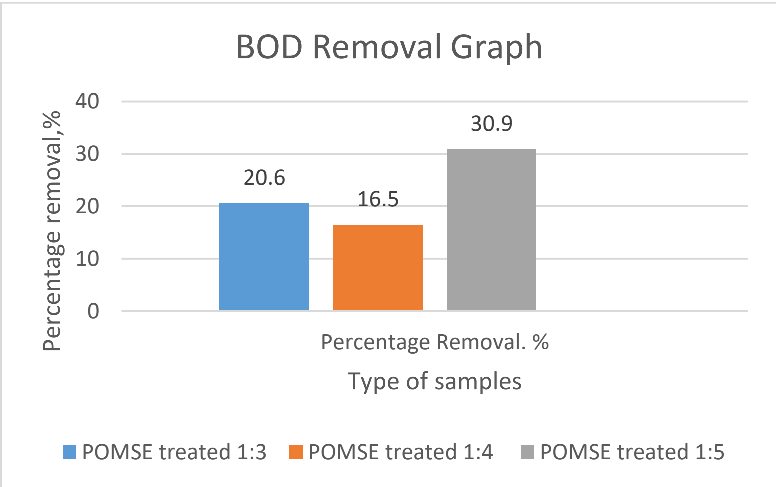

Figure 11: Graph of percentage removal of BOD

3.3 Comparison between ZnO-Kaolin (low grade) and ZnO-Kaolin (high grade)

As mentioned in objective, this study aims to compare the uses of kaolin from different grade which are low grade and high grade (commercial) in order to explore on how the low grade kaolin function and can it be replace with high grade kaolin to reduce cost when using it in a huge quantity for industry. Referring from the previous study data in **Table 2 and 3** it showed that the results achieve were not differ from the ZnO-Kaolin (low grade) data obtained. The higher value of percentage removal of turbidity can be seen on high grade kaolin while for percentage removal of colour, BOD and COD were higher than high grade kaolin.

Table 2: Percentage removal results for various ratios of ZnO-Kaolin (low grade)

SAMPLE	Colour, %	BOD,%	COD ,%	Turbidity,%	pH
POMSE treated 1:3	20.5	20.6	14.2	45.4	8.8
POMSE treated 1:4	31.1	16.5	8.1	38.1	8.79
POMSE treated 1:5	31.4	30.9	10	44.2	8.79

Table 3: Percentage removal results for various ratios of ZnO-Kaolin (high grade)

SAMPLE	Colour, %	BOD,%	COD, %	Turbidity,%	pH
POMSE treated 1:3	15.2	14.1	-30.8	60	8.0
POMSE treated 1:4	24.6	14.5	22.2	70.9	8.0
POMSE treated 1:5	10.9	2.7	11.5	41.9	8.0

4. Conclusion

In conclusion, all of the objectives study have been achieved by having ZnO-Kaolin synthesized under different ratios which are 1:3, 1:4 and 1:5 and it proven that photocatalyst with ratio of 1:5 is the optimum ratio for POMSE treatment by photocatalytic process. Then, parameters of samples treated POMSE also shown the performance of ZnO-Kaolin 1:5 much better than other ratios by their percentage removal results. Besides, the comparison between the performance of ZnO-Kaolin (low grade) and ZnO-Kaolin (high grade) also proven that low grade kaolin can compete with the commercial kaolin in treating palm oil mill effluent because its more efficient, less cost needed and environmental friendly. ZnO-Kaolin (low grade) performance results can be presentable as ZnO-Kaolin (high grade) and can be even better in aspects of low cost semiconductor and non-toxic nature. As a result, industry must approach this kind of wastewater treatment for advance steps to treat their POME within short period as our environment will be protected.

Acknowledgement

The authors would also like to thank her family, supervisor and fellow friends, the Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia for its support.

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