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The Performance of POMSE Treatment using Different Synthesized Green Zinc Oxide-*Cymbopogon Nardus* (ZnO-CN) using Photocatalytic Reactor

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Abstract: Palm oil production is essential in Malaysia since it impacts to the economic growth. However, palm oil mill secondary effluent (POMSE) has a high color intensity that could be detrimental to aquatic life. Membrane photocatalytic reactor (MPR) have emerged as one of the most promising technologies for treating palm oil mill secondary effluent (POMSE). This study intended to treat POMSE with the presence of utilising several kinds of zinc oxide (ZnO) nanoparticles in MPR, including ZnO-cymbopogon nardus (ZnO-CN) at varying concentrations (1%, 4%, and 8%), ZnO commercial, and non-synthesized green ZnO. The sampling of the sample was carried out at 10 minutes interval for 3 hours. Then, the treated sample was tested in terms of their color using Hach DR 6000. It had been found that ZnO-CN8 yields the highest performance in the color reduction of POMSE (23.63%). Thus, it can be inferred that this study influences the efficacy of the MPR system in the treatment of POMSE with the presence of green photocatalysts.

Keywords: Color, Photocatalytic, POMSE, Zinc Oxide

1. Introduction

Malaysia is presently regarded as the second largest producer of palm oil mill after Indonesia, owing to its tropical environment and plenty of natural resources. As the oil palm sector has been acknowledged for its impact on economic growth [1], it has also negatively contributed to environmental contamination as a result of the generation of massive quantities of byproduct from the oil extraction process. The manufacture of palm oil essentially created the palm oil mill effluent (POME), which is a viscous liquid with a brownish color. Furthermore, POME high in colloidal suspension and has a disagreeable odour. It also has a high biological demand (BOD) and a chemical oxygen requirement (COD). As a result, it is not safe to dispose POME into a water stream since it is a very toxic pollutant to aquatic life, resulting in a pre-treated POME occur known as palm oil mill

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secondary effluent POMSE before being released into a water stream [2]. Several biological, physical, and chemical strategies have been published as therapeutic methods during the last two decades and few have been implemented by the industries. Integrated systems of anaerobic-aerobic bioreactors (IAAB) are among the many and most recent alternative treatment options [3]. Several approaches have recently been researched in order to provide less expensive and more effective treatment solutions. Photocatalytic degradation employing a membrane photocatalytic reactor (MPR), in which photocatalysts play an important part in the photocatalytic process, is an approach for enhanced POMSE treatment. UV or solar radiation can be employed to generate photocatalysis reactions in photocatalytic reactors. The presence of photocatalysts in the process has drawn significance due to their unique qualities such as optical properties, antibacterial activaty, catalytic activity and photoemission [4]. Previous research has shown that ZnO-PVP NPs work well in MPR for industrial dye wastewater treatment in terms of photocatalytic activity, membrane fouling, and flux decrease [5]. This paper focuses on the ZnO nanoparticles for wastewater treatment derived from Cymbogopogon Nardus extract. In Malaysia, Cymbopogon nardus has been widely grown for the production of essential oil. Cymbopogon citratus and Cymbopogon nardus have recently proven the potential to be used in the green synthesis of photocatalyst for wastewater treatment, which can increase the rate of degradation in the photocatalysis process. It is biodegradable, environmentally friendly, and cost-effective [6]. Therefore, this study aimed to evaluate the performance of POMSE treatment in terms of color removal utilising MPR in the presence of ZnO-CN NPs at varied concentrations of extracted Cymbopogon nardus.

2. Materials and Methods

2.1 Materials

The samples were prepared by mixing 25% Palm Oil Mill Secondary Effluent (POMSE) from the Palm Oil Mill Industry in Kluang, Johor and 75% river water from the Sembrong River in Batu Pahat, Johor. The ZnO commercial was obtained from R&M Marketing in Essex, UK, and the ZnO-CN utilised in this experiment was synthesized in the lab at varied concentrations (1%, 4%, and 8%).

2.2 Polluted river water treatment process

This experiment used a 2-L photocatalytic reactor without passing through the membrane filtration to treat polluted river water. **Figure 1** depicts the reactor's schematic configuration. To activate the photocatalyst, a UV light (253.7 nm, 18 W) was put within the reactor. In a photocatalytic reactor with a loading of 0.09 g/L each of different photocatalysts, contaminated river water was treated. The contaminated river water and photocatalyst mixture was rapidly agitated at 150 rpm in the dark for 30 minutes before starting the photocatalysis method to achieve photocatalyst equilibrium. The operating system's temperature was kept constant at ambient temperature (25°C). After 10 minutes of photocatalysis, 20 mL of polluted river water was collected, and the process was repeated for 3 hours. To avoid contamination, the treated polluted river water was collected and stored at 4°C prior to analysis. The treated samples were then centrifuged at 3200 rpm for 20 minutes to separate the suspended particles in the treated sample. Finally, the color intensity of the treated river water was evaluated.

2.3 Analytical Method

The treated samples were tested in triplicate with quality parameter in terms of color. The color of fresh treated sample was analyzed using Hach DR6000 spectrophotometer (program: 97 Color ADMI 1 inch). The percentage removal of contaminants was calculated using **Eq. 1:**

$$R = \frac{C_0 - C_1}{C_0} \times 100\%, \qquad \textbf{Eq. 1}$$

where R is the percentage of pollutants removed, C_o (mg/L) is the untreated samples' starting color intensity (ADMI) value and C_1 (mg/l) is the treated samples' color intensity (ADMI) value at reaction time, t (min).

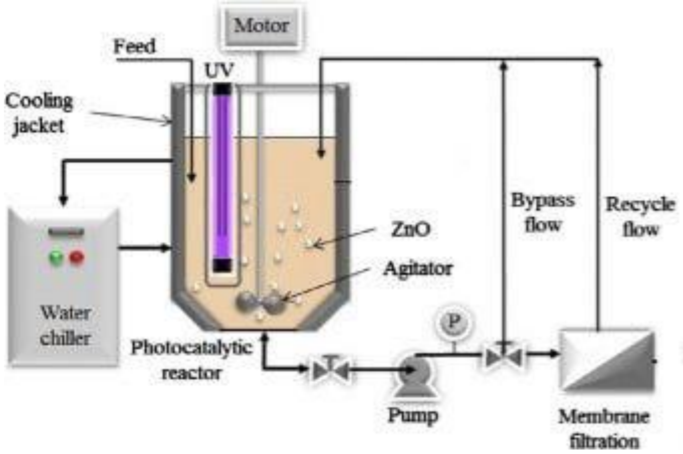

Figure 1: Schematic set up for reactor.

3. Results and Discussion

The initial ADMI value of the wastewater color was 402 ADMI, indicating that the characteristic of the wastewater was improved after the photocatalytic process.

Table 1: Wastewater color removal value (ADMI) for using different types of photocatalyst

Time, min	Without ZnO	ZnO	ZnO-C	ZnO-CN1	ZnO-CN4	ZnO-CN8
0	382.33	308.00	302.00	63.33	300.00	304.00
10	349.00	309.33	308.33	245.33	303.00	303.00
20	345.33	308.00	310.00	312.33	299.00	304.67
30	354.33	313.33	313.33	324.00	305.00	307.00
40	355.00	304.67	312.33	312.67	306.33	310.33
50	358.33	314.00	310.67	327.00	306.00	313.33
60	354.33	318.00	312.33	324.00	308.00	307.00

According to the data in **Table 1**, there were significant differences in the ADMI value of the wastewater color for each photocatalyst used in the photocatalytic process.

3.1 Percentage of Color Removal For Different Photocatalyst

Figure 1 depicts the percentage value for color removal for each type of photocatalyst. Based on the highest value of color removal percentage, 23.63%, the photocatalytic process that used ZnO-CN8 as a photocatalyst was proven to be the most suitable photocatalyst. This result could be attributed to the ZnO-CN8 nanoparticles' efficiency in degrading wastewater pollutants during the treatment process. The presence of ZnO-CN8 as a photocatalyst in photocatalytic activity resulted in the highest percentage of color removal of wastewater (23.63%, ADMI 307), followed by ZnO-CN4 (23.38%, ADMI 308), and the lowest was 11.86% (ADMI 354.33) when ZnO nanoparticles were not present. However, some inconsistencies occurred during the sampling of ZnO-CN1, resulting in inaccurate results at zero time intake. Hence, it has been demonstrated that using ZnO-CN nanoparticles as a photocatalyst in wastewater treatment can improve the characteristics of the wastewater prior to discharge.

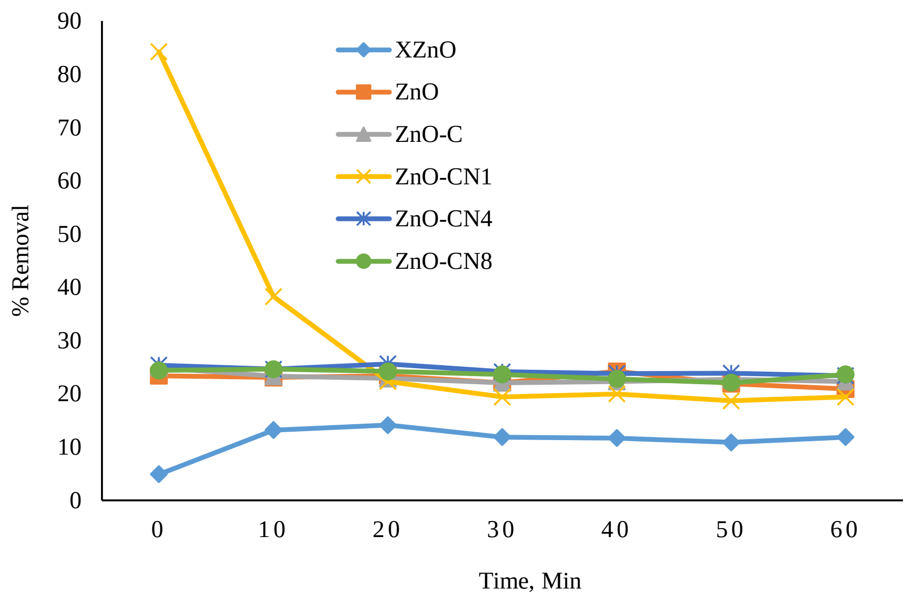

Figure 2: Percentage color removal for different photocatalyst.

3.2 Analysis on The Performance of Photocatalytic Activity by ZnO-CN Nanoparticles

The wastewater sample for this study had been prepared by combining 25% POMSE and 75% river water. This is related to the nature of the organic pollutant concentration, where the presence of more organic pollutants causes the catalyst to deactivate. The treatment can then be concluded to have the greatest degradation at the lowest concentration of POMSE used [7]. Aside from that, fresh POMSE contains a higher number of pigment molecules, which can reduce UV light photon penetration for photocatalytic activity [8], so dilution of POMSE in wastewater sample was an important step to consider before sample preparation.

Aside from that, the smaller size of ZnO-CN nanoparticles may result in an enhanced wastewater degradation rate [9]. It is well known that the morphology, surface area, and crystallinity of a material are primarily responsible for its photocatalytic activity; therefore, improving all of these factors will improve the photocatalytic activity [10]. A higher surface-to-volume ratio of a photocatalyst would aid in better photocatalytic activity; therefore, it is critical to control the size of ZnO nanoparticles during their synthesis in order to produce a higher surface-to-volume ratio [7]. Based on the experimental results, it is possible that this is because the surface area of ZnO-CN8 is the largest of the photocatalysts used. This is related because the photocatalytic reaction occurs on the surface of ZnO-CN8 nanoparticles in the presence of UV radiation, and smaller nanoparticle sizes improved photocatalytic performance by providing more specific surface area favourable to UV light adsorption and holding pollutant molecules in wastewater [9].

3.3 Comparison of Various Study for ZnO nanoparticles as a Photocatalyst

First and foremost, ZnO is the most powerful photocatalyst, and its presence also decreased agglomeration since it has the ability to undergo photocatalytic activity [2]. Next, it has been found that employing zinc oxide-polyethylene glycol (ZnO-PEG) nanoparticles rather than zinc-oxide-cymbopogon citratus (ZnO-CC) nanoparticles as a photocatalyst is much more effective at eliminating the color of POMSE, according to research by Puasa et al. This might be because the nanoparticles are more effectively stabilised by polymer capping, which also passivates the surface to decrease oxygen vacancy sites. In addition, ZnO-PEG has a large surface area, which allows for more UV light penetration. As UV photons will stimulate ZnO, which subsequently combines with water molecules or hydroxide ions to form hydroxyl radicals, it is crucial to allow UV light to pass through it [11].

Following that, a study was conducted using zinc oxide-polyvinylpyrrolidone (ZnO-PVP) nanoparticles as a photocatalyst to treat industrial dye wastewater. According to the experimental results, the changes in dye degradation have grown rapidly after 5 minutes of experimentation. However, it is possible that this is due to the use of PVP as a capping agent in ZnO nanoparticles. Aside from that, ZnO-PVP has good morphology and the smallest particle sizes, which can result in a faster degradation rate of dye wastewater. As a result, photocatalytic degradation has the ability to efficiently remove dyeing effluent colors [11].

4. Conclusion

The findings of this experiment demonstrated that the objectives were partially accomplished. The inclusion of ZnO nanoparticles with a green capping agent such as CN in MPR methods is effective in treating POMSE in terms of its visible brownish color as the color reduction decreases from the initial value. However, there are some limitations in this current work where the treated POMSE is not readily discharged into the river because it is only treated for one parameter which is color and does not achieve the effluent standard according to Department of Environment (DoE), which require a discharge limit of less than 200 ADMI. In accordance with that, treating POMSE passing through the membrane filtration is recommended to achieve a higher performance of treatment. Following that, the proportion of POMSE in the water sample should be increased by more than 25% in order to obtain a greater and clearer percentage of removal results. Following MPR treatment, water quality analysis revealed that green ZnO-CN8 had the best overall effectiveness in color reduction (23.63%) of POMSE. The rate of degradation in photocatalysis is related to the presence of UV and radical activity. As a result, additional study into employing ZnO with a green capping agent for treating polluted river water should be conducted in the future in order to raise awareness towards green chemistry and the use of the green route for the production of metal nanoparticles as it develops environmentally friendly procedures.Thus, it is anticipated that this research has a significant potential for use in the palm oil mill sector.

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