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Eggshell/TiO_2 Composite for Palm Oil Mill Secondary Effluent Treatment

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Abstract: The integration of eggshell and titanium dioxide composite for treating palm oil mill secondary effluent (POMSE) was studied. This study is focusing on the effectiveness of the eggshell/titanium dioxide (ES/TiO_2) composite for adsorption capacity and photocatalytic process. Five samples of ES/TiO_2 composite were synthesized and compared with two control samples which are 100% TiO_2 and eggshell. The amount of TiO_2 catalyst loading was investigated, followed by the different ratios of ES/TiO_2 for photocatalytic degradation of POMSE. The result showed 1 g/mL of TiO_2 loading gives the higher performance of adsorption and photocatalytic performance compared to others. Referring to this loading, the optimum integration ratio of ES/TiO_2 composite was at 6:4 where the adsorption and photocatalytic performance was achieved 90%. It is believed that this integrated approach can be implemented in the industry in order to achieve a discharged standard of POMSE and helps to save the nature and environment so as not to be contaminated in the future.

Keywords: Eggshell, Titanium Dioxide, Adsorbent, Photocatalytic, POMSE

1. Introduction

The pre-treated palm oil mill effluent (POME) is also known as palm oil mill secondary effluent (POMSE) as they have been treated at the first stage [1]. Even though the POMSE has been treated in several series of treatment, the values of chemical oxygen demand (COD), biochemical oxygen demand

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(BOD) and color intensity are still at a high level which not fulfill the requirements as stated by the Department of Environment (DOE) to be discharged to water body [2]. In general, POME has a high organic load where around 45,500- 65,000 mg/L of COD, 21,500-28,500 mg/L of BOD which is detrimental to aquatic life [3]. POMSE has a high color intensity, turbidity, and organic load of BOD, which still has not achieved the discharged requirement by the DOE. Therefore, the researchers suggest several alternative treatments for POMSE and photocatalytic degradation process have been selected as the best method.

Recently, the utilization of self- synthesized zinc oxide nanoparticles in the presence of polyethylene glycol as a capping agent (ZnO-PEG) was synthesized for POMSE treatment using a photocatalytic degradation process [3]. The illumination of UV has generated hydroxyl radicals (•OH) from ZnO catalyst for photocatalytic degradation to take place [4]. These radicals then attacked the organic compounds in the bulk solution and consequently result in the degradation of the POMSE [5]. TiO_2 nanoparticles are also widely used as the photocatalyst to remove pollutants in the wastewater. Until now, there is no research has been done by using TiO_2 as a photocatalyst for POMSE treatment. However, the effectiveness of TiO_2 as a photocatalyst in POMSE treatment needs to be enhanced by integration with other materials due to the presence of oils and grease in wastewater.

Eggshell is a solid waste and is also considered agricultural wastes. It is produced several tons per day as only the inside of the egg is used from all over the world. Therefore, industries dispose of the eggshell residue at landfills, and it causes organic pollution. Eggshell has been just 9%–12% of the total egg weight and is a natural, porous bioceramic. Eggshell can be used as an adsorbent to remove methyl violet and mercury ions from wastewater [6]. Eggshell is made up of 2% water and 98% dry matter such as ash and crude protein. The eggshell itself contains 94% calcium carbonate, 1% calcium phosphate, 1% magnesium carbonate, and 4% of other organic substances [7]. Due to the high content of calcium carbonate in eggshell, researchers nowadays make some initiatives not to waste it and instead use it as a biomaterial [7].

Some studies have shown that the eggshell can be used and utilized for something that has benefits to us like the uses of eggshell waste as a catalyst employed in synthesis biodiesel, hydrogen/syngas, dimethyl carbonate (DMC), bioactive compounds, and wastewater treatment [8]. Besides, it proved that the use of eggshells helps reactions to reach maximum efficiency while reducing the cost process [9]. The researchers used calcined waste eggshell because it has the highest adsorption capacity to react. Also, eggshells are valuable environmental and economic adsorbents to their abundance and ability to remove harmful and dangerous components of all adsorbents.

In a previous study, the eggshell can be integrated with other materials to form a composite to enhance the photocatalytic process. The potential of eggshell powder as an adsorbent for methylene blue (MB) removal has been proved by Henry et al. in 2019 [10]. Besides, a review by Habeeb, Yasin, and Danhassan showed, the adsorption of cationic MB from aqueous solution onto the eggshell powder was carried out by varying the operating parameters which were contact time, pH, the dosage of eggshell powder, and temperature to study their effect in adsorption capacity of eggshell powder [11]. Several studies show that eggshells and eggshell membrane may be used as an adsorbent for iron, chromium, and reactive dye [12].

Therefore, in this study, the potential of eggshell as an adsorbent was carried out by integrating with titanium dioxide (TiO_2) to form composite in different ratios. Then, the effectiveness of eggshell/titanium dioxide (ES/TiO_2) composite was explored as a photocatalyst for treating POMSE in percentage photocatalytic degradation.

2. Materials and Methods

2.1 Materials

In this study, eggshell powder with 45 µm particle sizes and ethanol (QRec, 95% denatured) was used without purification. Titanium dioxide, TiO_2 from Sigma-Aldrich with 21 nm of particle sizes was used as a photocatalyst in the photocatalytic degradation of POMSE treatment. Raw POMSE samples were directly collected from the polishing pond of the ponding treatment system of palm oil located in Pagoh. The samples were transported to the laboratory in 5L sample bottles.

2.2 Methods

The preparation of a composite photocatalyst was carried out by the solid-state dispersion (SSD) method on a 10 g basis. The eggshell/TiO_2 composite photocatalyst was prepared according to Henry et al. in 2019 [10]. All samples were prepared with different ratios and labeled as stated in **Table 1**.

Table 1: Composite photocatalyst preparation with different ratios

The ratio of Eggshell/TiO_2 composite	Composite identification code
10:0	100% Eggshell
9:1	ES/TiO_2 (9:1)
8:2	ES/TiO_2 (8:2)
7:3	ES/TiO_2 (7:3)
6:4	ES/TiO_2 (6:4)
5:5	ES/TiO_2 (5:5)
0:10	100% TiO_2

The adsorption and photocatalytic degradation of POMSE was carried out in a suspension system by placing a UV lamp at 10 cm from the beaker. 50% dilution of POMSE was used as a feed solution and stirred using a magnetic stirrer in the dark conditions for 30 min for adsorption equilibrium. Then, the UV lamp was turned on for photocatalytic activity testing. The experiment was conducted for 120 min and at each 20 min interval, 2 mL aliquot sample was taken and centrifuged at 6000rpm for 10 min. The aliquot samples were analyzed by a UV-Vis Spectrophotometer (HITACHI U-3900H) with a wavelength of 600 nm. After the aliquot sample was analyzed, the percentage of color degradation was calculated using the formula stated in Eq.1:

$$\%\, degradation = \frac{C_i - C}{C_i} \times 100\% \qquad \textbf{Eq. 1}$$

where c_i is the initial concentration and C is the retained concentration of POMSE solution. First and foremost, the photocatalytic process was conducted by adding the different loadings of 100% TiO_2 photocatalyst which 0.5 g/L, 1.0 g/L, and 1.5 g/L to get the maximum performance of POMSE treatment. Next, the experiments were carried out by using different ratios of ES/TiO_2 composite photocatalyst with 1.0 g/L of loading.

3. Results and Discussion

The morphological structures of TiO_2, eggshells and ES/TiO_2 (7:3) were investigated by SEM as shown in **Figure 1**. TiO_2 appeared as fine particles (**Figure 1a**) whereas the eggshell is bigger due to the microsized particles and exhibits irregular shape and size (**Figure 1b**).

Figure 1c shows the distribution of TiO_2 on the surface of the eggshell, where the fine particle of TiO_2 is dispersed on the surface of the eggshell. The distribution of eggshell particles is more clearly observed compared to TiO_2 nanoparticles in the SEM images due to the high loading of eggshell (70%).

As depicted in **Figure 1c,** it is confirmed that the TiO_2 and eggshell particles bonded and formed a composite photocatalyst after the calcination process.

Figure 1d shows the percentage distribution of the elements on the composites using SEM–EDX where the dispersion of TiO_2 covering the surface of eggshell and all the elements of $CaCO_3$ and TiO_2 were detected. This proves that the TiO_2/eggshell composite photocatalyst was successfully formed through the SSD method.

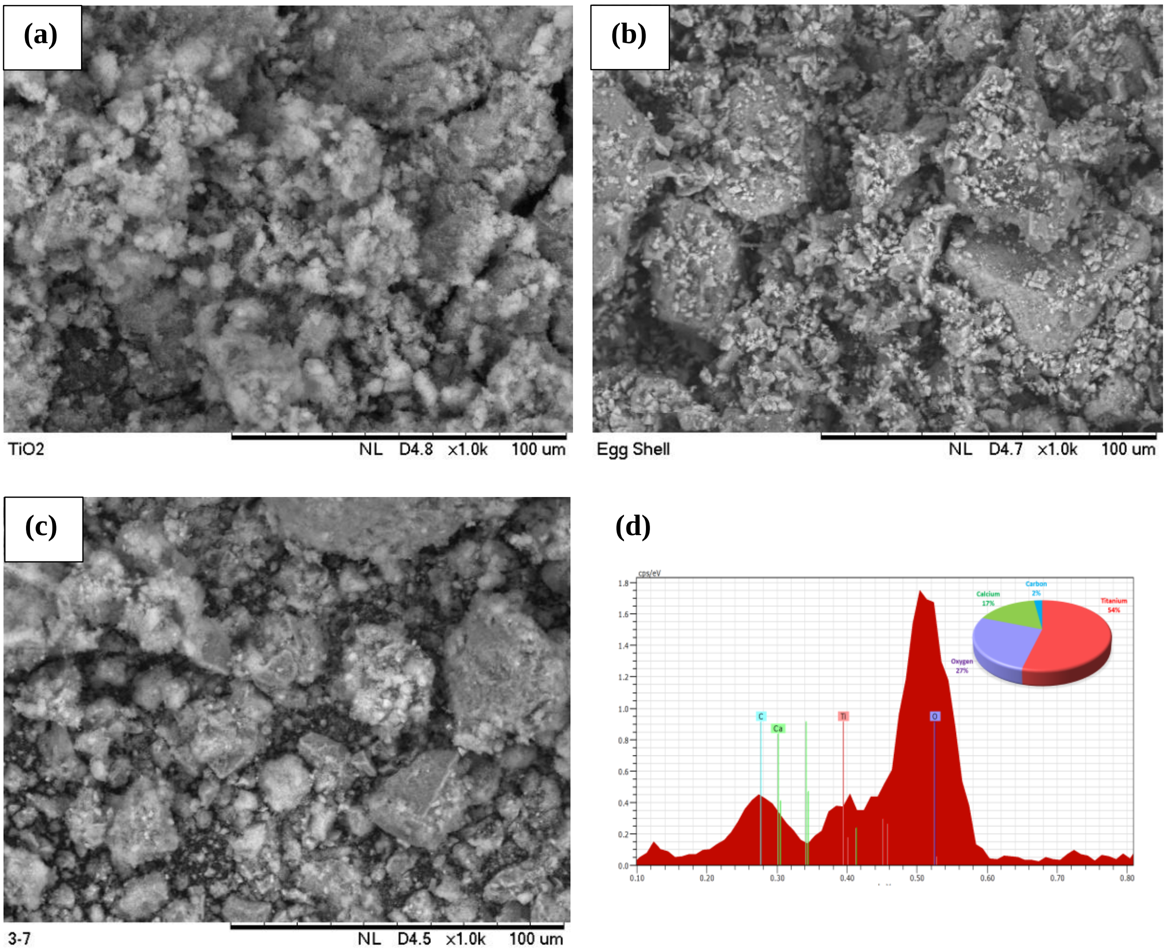

Figure 1: SEM images (a) TiO_2, (b) eggshells, (c) TiO_2/eggshell (3:7) and (d) EDX mapping for percentage element of TiO_2/eggshell (3:7)

The absorption and photocatalytic efficiency of photocatalyst in POMSE treatment was measured by varying the loadings of photocatalyst for 30 and 60 minutes, respectively. Referring to Henry et al., 2019 [10], they were used 0.004 g/L of eggshell/TiO_2 composite loadings for MB removal where 100% TiO_2 shows the highest performance due to the size of TiO_2 is in nanoparticles. Therefore, this study was started by varying the loadings of TiO_2 nanoparticles for POMSE treatment. As clearly shown in **Figure 2**, 1 g/L loading of TiO_2 nanoparticles shows the highest adsorption capacity and subsequently enhanced the photocatalytic performances. It is interesting to note that the TiO_2 loadings for POMSE treatment achieved a threshold limit at 1 g/L where exceed 1g/L loading, as a result, the adsorption and photocatalytic performance was decreased.

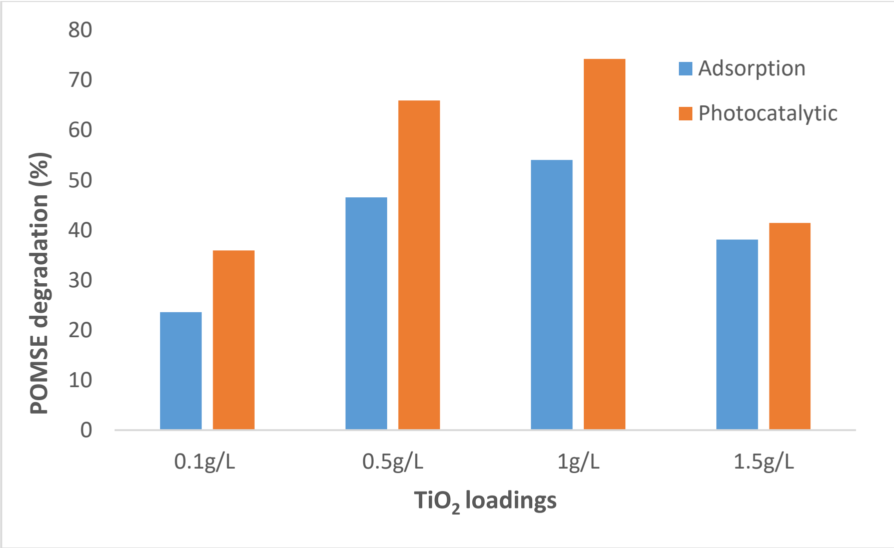

Figure 2: Adsorption and photocatalytic performance by using 100% TiO_2 nanoparticles

The efficiency of different ratios of eggshell/TiO_2 composite with 1 g/L for POMSE treatment is depicted in **Figure 3.** Distinctly, 100% eggshell shows the lowest capacity for absorption and photocatalytic performance. Nevertheless, the integration of TiO_2 nanoparticles with eggshell shows significant increment performances and reaches the highest performance for POMSE treatment at ratio 6:4 ES/TiO_2 composites. Surprisingly, the efficiency of the 6:4 ES/TiO_2 composite was higher compared to 100% TiO_2 nanoparticles as a control sample. It is noteworthy that the eggshell/TiO_2 composites are the most efficient for POMSE treatment compared to others due to the synergistic effect between eggshell and TiO_2 nanoparticles.

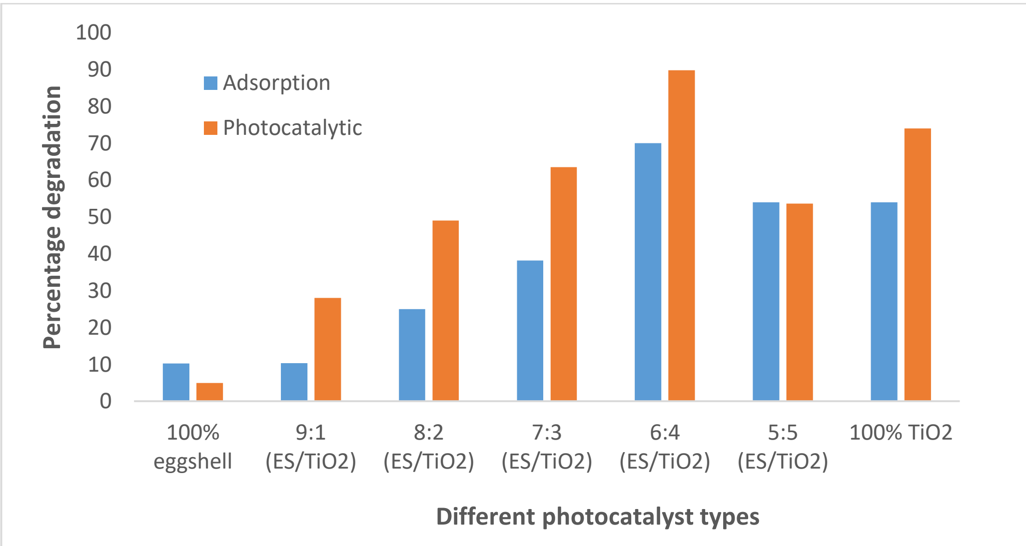

Figure 3: Adsorption and photocatalytic performance by using a different type of photocatalyst

Table 2: Comparison of different catalyst integrated with other materials for POMSE treatment

Catalyst	Process	Period of reaction time	Result	References
Commercial ZnO ZnO-PEG	Adsorption	30 min	ZnO-PEG is the most effective photocatalyst to degrade the POMSE color which achieved 73% of color removal.	[1]
ZnO-PEG ZnO-CC	Catalytic degradation	15 min	0.5 g/L loading of ZnO-PEG nanoparticles after 15 min treatment shows the highest percentage of color removal for POMSE via photocatalytic degradation process which is 70.75 %. Meanwhile, 0.5 g/L loading of ZnO-CC nanoparticles after 5 min shows the highest percentage of color removal of POMSE which is 59.47 %.	[3]
Commercial ZnO ZnO-CC	Membrane catalytic degradation	20 min	ZnO-CC nanoparticles showed the highest percentage of color rejection of POMSE (99.84%, 3.33 PtCo), followed by commercial ZnO (99.44%,11.67 PtCo) and the lowest was 99.24% (16 PtCo) indicating the absence of ZnO nanoparticles.	[4]
ZnO-CC NF-TS UF-UA MF-PVDF MF-PES	Photocatalytic membrane reactor	3 hour	NF-TS 40 membrane was able to remove almost 99.84% of POMSE color, followed by UF-UA 60 (99.28%), MF-PES (87.23%), and MF-PVDF (80.04%) membranes.	[5]

Comparison of different catalysts integrated with other materials for POMSE from other researchers was observed in **Table 2**. All the researchers used zinc oxide (ZnO) as a main photocatalyst and TiO_2 was not yet reported for POMSE treatment. Even though TiO_2 photocatalyst cannot be achieved as ZnO performances, but TiO_2 shows high potential for POMSE treatment once integrated with eggshell which acts as an adsorbent.

4. Conclusion

In conclusion, the integration of eggshell and titanium dioxide to produce ES/TiO_2 composite was successfully synthesized via solid-state dispersion method with the different ratios. The percentage of POMSE photocatalytic degradation achieved 90% at a 6:4 ratio with 1g/mL composite loading within 120 min under UV irradiation. Even though the eggshell used in microsize, the effectiveness of eggshell in composite photocatalyst for adsorption and highly potential as supported material to TiO_2. Overall, it can be concluded that eggshell can be employed as a useful material due to its high adsorption capacity and subsequently increased photocatalytic performance.

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References

[1] N. Z. Zainuri, "Palm oil mill secondary effluent (POMSE) treatment via photocatalysis process in presence of ZnO-PEG nanoparticles." Journal of Water Process Engineering, vol. 26, pp. 10-16, 2018.

[2] X. Huang, B. Gao, Q. Yue, Y. Zhang, and S. Sun, "Compound bioflocculant used as a coagulation aid in synthetic dye wastewater treatment: The effect of solution pH." Separation and Purification Technology, vol. 154, pp. 108-114, 2015.

[3] N. A. Puasa, "Photocatalytic degradation of palm oil mill secondary effluent in presence of zinc oxide nanoparticles." Environmental Nanotechnology, Monitoring & Management, vol. 15, p. 100413, 2021.

[4] D. A. B. Sidik, "The potential control strategies of membrane fouling and performance in membrane photocatalytic reactor (MPR) for treating palm oil mill secondary effluent (POMSE)." Chemical Engineering Research and Design, vol. 162, pp. 12-27, 2020.

[5] D. A. B. Sidik, N. H. H. Hairom, and A. W. Mohammad, "Performance and fouling assessment of different membrane types in a hybrid photocatalytic membrane reactor (PMR) for palm oil mill secondary effluent (POMSE) treatment." Process Safety and Environmental Protection, vol. 130, pp. 265-274, 2019.

[6] N. Ngadi, C. Chiek Ee, and N. A. Yusoff, "Removal of Methylene Blue Dye by Using Eggshell Powder." Jurnal Teknologi, vol. 65, no. 1, 2013, doi: 10.11113/jt.v65.1648.

[7] M. Waheed *et al.*, "Eggshell calcium: A cheap alternative to expensive supplements," *Trends Food Sci. Technol.*, vol. 91, no. July, pp. 219–230, 2019.

[8] A. Laca, A. Laca, and M. Díaz, "Eggshell waste as catalyst: A review," *J. Environ. Manage.*, vol. 197, pp. 351–359, 2017.

[9] X. Chen *et al.*, "Investigation on solar photocatalytic activity of TiO2 loaded composite: TiO2/Eggshell, TiO2/Clamshell and TiO2/CaCO3," *Mater. Lett.*, vol. 64, no. 13, pp. 1437–1440, 2010.

[10] Henry, C., Borhan, M., & Mustafa Kamal, M. (2019). *TiO_2/Eggshell Composite Photocatalyst for Methylene Blue Removal.* Universiti Tun Hussein Onn Malaysia.

[11] O. A. Habeeb, F. M. Yasin, and U. A. Danhassan, "Characterization and application of chicken eggshell as green adsorbents for removal of H2S from wastewaters," *IOSR J. Environ. Sci. Toxicol. Food Technol.*, vol. 8, no. 11, pp. 07–12, 2014.

[12] Alok Mittal et al., "Applications of egg shell and egg shell membrane as adsorbents: A Review" Journal of Molecular Liquids,vol 223,pp. 376-387, 2016.