JST

http://penerbit.uthm.edu.my/ojs/index.php/jst
ISSN : 2229-8460 e-ISSN : 2600-7924

Journal of Science and Technology

The Photocatalytic Activity of Green Zinc Oxide Nanoparticles in The Treatment of Aerobically Palm Oil Mill Effluent

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DOI: https://doi.org/10.30880/jst.2023.15.01.002
Received 17 February 2023; Accepted 17 May 2023; Available online 20 July 2023

Abstract: Traditional treatment of aerobically palm oil mill effluent (A-POME) is incapable of removing the colour and organic load that does not exceed the discharge standard limit to the stream channel. Green synthesis nanoparticles (NPs) provide a significant potential for substantial performance in the photocatalytic degradation of high-strength wastewater. Therefore, the current project's goal is to investigate the photocatalytic degradation performance of A-POME in the addition of green Zinc Oxide Cymbopogon Citratus (ZnO–CC) NPs in terms of chemical oxygen demand (COD), turbidity, and colour removal. The outcomes showed that pH 8 and a ZnO-CC NPs loading of 0.3g/L was ideal for the photocatalytic degradation of A-POME with a significant percentage reduction of turbidity (68.03%), colour (48.11%), and COD (75.4%). The equilibrium data revealed a better fit Langmuir-Hinshelwood models with higher R2 and K values of 0.9906 and 0.0225, respectively. Increased ZnO–CC NPs loading in alkaline medium aided in the breakdown of A-POME pollutants by increasing the surface area accessible for UV light adsorption during the photocatalytic process. Thus, the finding from this study can assist the palm oil mill sector in improving A-POME treatment to provide high-quality treated effluent.

Keywords: Zinc oxide, nanoparticles, photocatalytic, aerobically palm oil mill effluent

1. Introduction

Water quality has become a serious problem worldwide due to ignorance regarding the proper treatment of wastewater discharged from residences, workplaces, and agricultural areas. The primary environmental concern of the industry is wastewater, followed by other minor issues such as solid waste, safety, and health. Palm oil is one of the most important vegetable oils in the world. According to Subramaniam [1], Malaysia is the world's top producer, producing 80% of the world's palm oil. Palm oil mill effluent, also known as POME, is a brown viscous liquid waste with a strong odour and a high concentration of colloidal suspensions. It also has much biological material. It has a relatively low pH, making it very toxic. POME is another hazardous mixture of organic and inorganic waste. POME is a mixture of

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wastewaters produced and released during the operation of the crude oil process, including sterilizer condensate, hydro cyclone and clarifying unit. Pre-treated POME is frequently referred to as aerobically palm oil mill effluent (A-POME) because it has already undergone biological treatment. Although A-POME has undergone a number of treatment cycles, its characteristics still fail to meet the Department of Environment's criteria for discharge because its chemical oxygen demand (COD), biological oxygen demand (BOD), and colour intensity values are still high and deemed dangerous to be released, having a detrimental effect on the biological system, especially aquatic life [2].

Furthermore, A-POME is treatable using several methods, including an anaerobic-aerobic system, membrane filtration and reverse osmosis [3]. Unfortunately, there are many limitations to these treatments, including the fact that it requires high costs, the need for activation agents, ineffective removal, and the production of secondary pollutants. Additionally, A-POME can be treated via a photocatalytic treatment using ultraviolet (UV) light. For various wastewater treatment methods, many NPs such as tin dioxide (SnO_2), cadmium sulphide (CdS) and iron oxide (Fe_2O_3) have been employed in photocatalysis treatment. Among these NPs, ZnO has been regarded as the most effective photocatalyst. ZnO has been extensively researched for its potential as a photocatalyst due to its favourable features, such as high exciton binding energy, significant surface area, high reactivity, low toxicity, light sensitivity, and chemical resistance [3].

Commonly, chemical methods are used for synthesizing nanoparticle, which requires a high amount of chemical, produce toxic by-products, and involves a complex reaction. In a previous study, they used PEG as a capping agent for ZnO photocatalysts to enhance photocatalytic degradation performance [4]. Puasa [4] reported that the elimination of conventional pollutants, including COD, BOD and colour in A-POME, showed a considerable improvement via photocatalytic treatment in the presence of ZnO–PEG. The synthesis of NPs from green raw material received much attention due to its therapeutic uses and environmental benefits over traditional chemical methods. Green NPs open up new opportunities for NPs synthesis using plants and microorganisms to facilitate the size of the NPs. Sidik [5] has shown that ZnO-CC assisted membrane photocatalytic reactor (MPR) treatment of palm oil mill secondary effluent (POMSE) provides the best performance of colour removal efficiency at 99% of treated POMSE. Sidik [5] successfully showed the augmentation of ZnO performance in the MPR treatment process by using extracted CC as a capping agent. However, the main impediment to membrane deployment in wastewater treatment is the demand for regular membrane replacement, which may increase operating and maintenance costs. Interestingly, ZnO–CC NPs with a highly effective surface area might promote organic molecule adsorption and then will increase the photocatalytic activities. Therefore, this study aims to study the performance of ZnO–CC NPs in the photocatalytic process for A-POME treatment. Then, the mechanism of A-POME degradation was postulated using the Langmuir-Hinshelwood model to determine the maximum degradation in the variation of conditions [6,7]. These details are crucial for enhancing the performance of A-POME treatment by photocatalytic incorporation of ZnO–CC NPs, which was not discovered in the previous study.

2. Materials and Methods

2.1 Materials

The A-POME sample was taken from a neighboring palm oil plantation in Johor, Malaysia, and placed in a 10 L airtight container. Before usage, the A-POME samples were preserved in a chiller at 4°C. The ZnO–CC NPs was produced according to Sidik [5] through the precipitation process, as illustrated in Fig. 1. The suggested process, demonstrated in Fig. 1, supports the potential of plant extract in reducing ZnO–CC NPs for further usage in photocatalytic for treating A-POME. Hydrochloric acid (HCL), commercial grade ZnO (C–ZnO) (Sigma-Aldrich), and sodium hydroxide (NaOH) were purchased from BT Scientific in Malaysia.

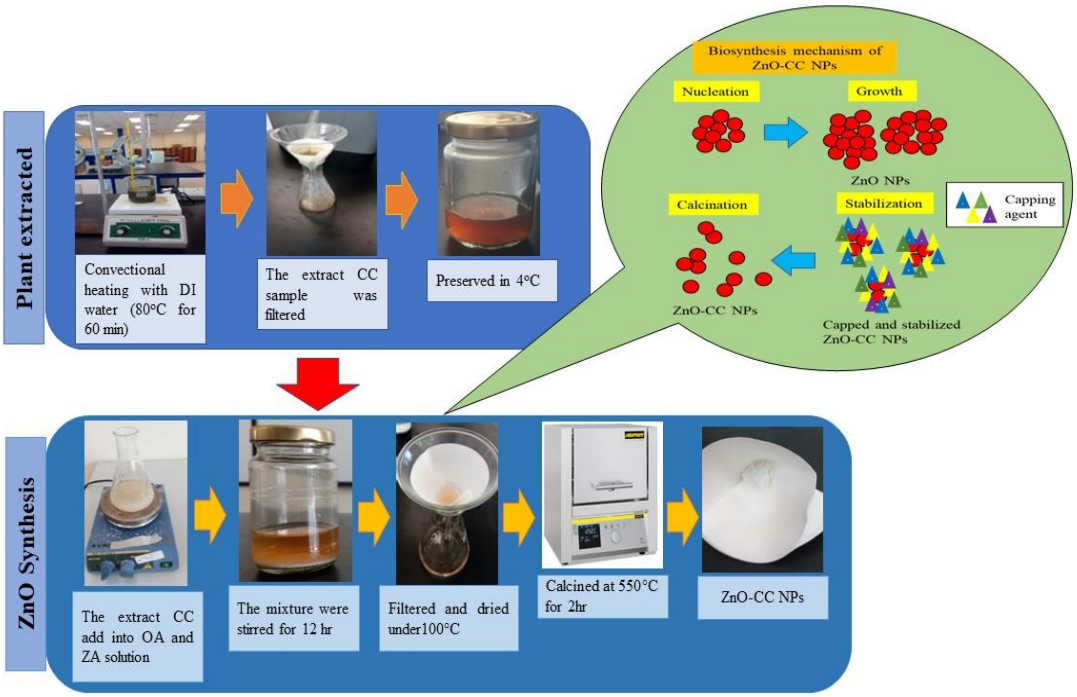

Fig. 1 - Schematic diagram of green synthesis ZnO–CC NPs

2.2 Photocatalytic Process for A-POME Treatment

During the photocatalytic treatment of A-POME, many parameters governing the photocatalytic activity of the ZnO–CC NPs were examined. The photocatalysis procedure was first carried out in a 2 L reactor with UV light, which has a defined power of 15 W and emits at 365 nm. Then, the experiment used 0.1 g/L ZnO–CC as a photocatalyst under various dosages (0.1, 0.3, and 0.5 g/L). Fig. 2 depicts a schematic diagram of the photocatalytic system used in this study at the laboratory scale. The mixture was vigorously stirred at 150 rpm using an impeller (PL111) with an overhead stirrer (WireStir HS30D) for 30 minutes in the dark before initiating the photocatalysis technique to obtain the adsorption-desorption equilibrium. The operation temperature was controlled at 25°C by recirculating cooling water through a water chiller. Prior to analysis, 5 mL of samples were collected every 10 minutes and separated for 20 minutes in a centrifuge (Gyrozen 1736R) at 8000 rpm at 4°C [4]. A similar procedure was followed for the photocatalytic performance of ZnO–CC NPs under various pH conditions (4, 6, and 8). After the photocatalytic treatment, the effluent was collected and kept at 4°C to prevent contamination.

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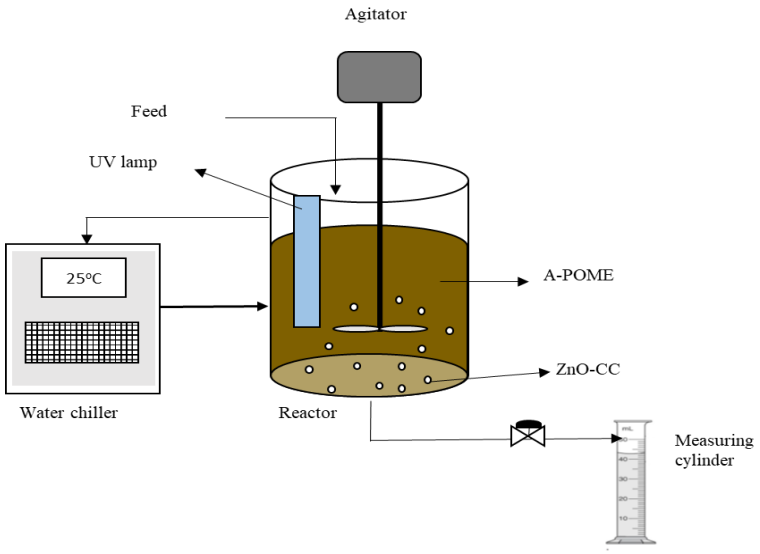


Fig. 2 - The photocatalytic reactor system schematic diagram

2.3 Wastewater Analytical Procedures

Color intensity, turbidity, pH and chemical oxygen demand (COD) were determined for the fresh and treated effluent. The colour intensity was measured using a DR6000 UV-Vis Laboratory Spectrophotometer (Hach) following the ADMI standard technique (programme: 97 Color ADMI 1 inch). The treated A-POME was added into COD digestion reagent vials before being further preheated using DRB200 (Hach, Germany) reactor for 2 h at 150°C [4,5]. The material was then cooled to room temperature and analyzed using a DR6000 Spectrophotometer. A portable turbidity meter (Cole Parmer Oakton) was used to measure the turbidity of each sample. Finally, the pH of the effluent was measured using a portable pH meter (Milwaukee).

Equation (1) was used to calculate the removal efficiency of treated A-POME utilizing the photocatalytic technique,

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where R represents removal efficiency, C_0 represents the starting concentration and C_e represents equilibrium concentration after photocatalytic treatment [4].

2.4 Kinetic Study

The photocatalytic activity of A-POME has been identified using a pseudo-first-order kinetic model based on the Langmuir-Hinshelwood (L-H) rate law which can be expressed as Equation (2),

$$Ln\left(\frac{C_{Ao}}{C_A}\right) = kt \quad (2)$$

where C_{AO} denotes the initial concentration of COD (mg/L), C_A denotes the concentration of COD at time *t* (mg/L), *t* denotes time in minutes, and *k* denotes the apparent rate constant of COD at specific reaction time (min^{-1}) after the photocatalytic process. The particular reaction time, *k*, and R^2 values for each experiment were established by plotting a graph of $Ln\left(\frac{C_{Ao}}{C_A}\right)$ versus time [6,7].

3 Results and Discussion

3.1 Photocatalytic Degradation of A-POME Under Various Photocatalyst

It is essential to investigate the ideal type of photocatalyst to enhance photocatalytic performance, which is also a vital factor from an economic perspective. This study produces lower colour intensity, turbidity, and COD due to the ZnO–CC NPs' ability to breakdown the organic compounds in A-POME during the photocatalytic process. Table 1 shows the characteristics of A-POME before and after photocatalytic treatment for several types of ZnO. It was discovered that ZnO–CC produced the best results after 60 min of treatment compared to Commercial ZnO (Comm-ZnO) and without ZnO (No–ZnO).

Table 1 - **Characteristics of untreated and treated A-POME under various photocatalysts**

Parameter	Unit	Types of ZnO					
		ZnO–CC	**Removal (%)**	**Comm–ZnO**	**Removal (%)**	**No–ZnO**	**Removal (%)**
COD	mg/L	168.00 ± 0	75.40 ± 0	200.60 ± 0.58	70.62 ± 0.09	187.00 ± 0	72.62 ± 0
Colour	ADMi	606.00 ± 0	48.12 ± 0	607.30 ± 0.58	48.00 ± 0.05	601.30 ± 0.58	48.52 ± 0.05
Turbidity	NTU	9.33 ± 0.41	68.04 ± 1.40	14.653 ± 0.17	49.82 ± 0.57	8.94 ± 0.03	69.37 ± 0.09

Fig. 3 demonstrates the significance of wastewater parameters such as COD, colour, and turbidity of A-POME upon photocatalytic treatment with ZnO–CC NPs, Comm–ZnO, and No–ZnO. Notably, A-POME showed the maximum percentage of turbidity elimination in the absence of ZnO (69.37%), followed by ZnO–CC NPs (68.09%), and the lowest was shown for the Comm–ZnO (49.81%). The efficiency of A-POME turbidity rejection No–ZnO and with ZnO–CC NPs is less substantial. This result demonstrated that the inclusion of ZnO–CC NPs could boost removal efficiency when compared to Comm–ZnO, which correlates with the photocatalyst's characteristics. The photoactivity of ZnO–CC NPs was higher than that of Comm–ZnO, showing that incorporating CC into ZnO facilitated charge carrier separation and increased the photocatalytic degradation efficacy of A-POME. On the other hand, the rapid electron-hole pair recombination might be responsible for Comm–ZnO's limited photocatalytic performance [3]. The use of ZnO–CC NPs in A-POME treatment via photocatalytic can enhance the A-POME characteristics prior to discharge, as demonstrated in

this study. The COD removal rate in the absence of ZnO is lower (72.62%) than when ZnO–CC presents (75.40%). Considering that there is no degradation without ZnO, this behavior could be caused by the presence of bigger organic materials and suspended matter from A-POME during the process. This result confirmed that photocatalytic processes could increase A-POME treatment performance by reducing the particle size of larger compounds in A-POME pollutants. This scenario demonstrates that when compared to the absence of ZnO and the presence of commercial ZnO, the inclusion of ZnO–CC NPs created through green synthesis is an important technique to consider.

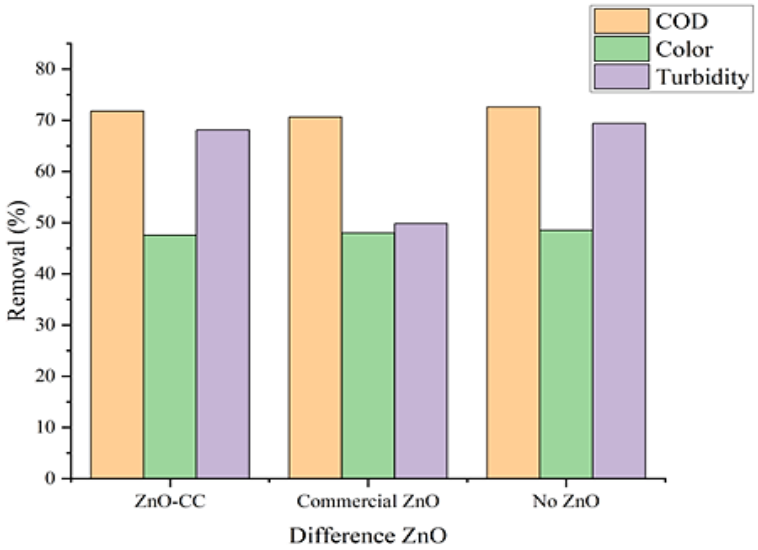


Fig. 3 - Percentage removal of treated A-POME under various photocatalysts

3.2 Photocatalytic Degradation of A-POME Under Various ZnO–CC NPs Loading

Table 2 shows the treated A-POME from various ZnO–CC loadings (0.1, 0.3, and 0.5 g/L) after photocatalytic treatment. After 60 min of treatment, it was discovered that ZnO–CC with a loading of 0.3 g/L produced the best results of COD, which is below the acceptable range of the DOE's discharge limit into the water body (Table 2).

Table 2 - Characteristics of the treated A-POME under various ZnO–CC loading

Parameter	Unit	Different Loading			Untreated A-POME	Standard DOE Value [8]
		0.1	0.3	0.5		
COD	mg/L	192.60 ± 0.58	168.00 ± 0	199.00 ± 0	683	200
Colour	ADMI	612.60 ± 0.58	606.00 ± 0	596.00 ± 0	1168	50
Turbidity	NTU	9.32 ± 0.10	9.33 ± 0.41	9.25 ± 0.10	29.2	NA

Fig. 4 depicts the significance of wastewater characteristics such as COD, colour, and turbidity derived from the examination of various sample loadings (0.1, 0.3, and 0.5 g/L) taken at 60 minutes following the photocatalytic treatment process. The A-POME concentration was fixed at 50% dilution with distilled water. Notably, loading at 0.3 g/L has the best COD removal trend (75.4%), which is higher than loading at 0.1 g/L (71.79%) and 0.5 g/L (70.86%). Meanwhile, as the loading increased, the COD removal of the treated A-POME reduced significantly (0.3 g/L and 0.5 g/L). One possible explanation is that the smaller size of ZnO–CC NPs gives more surface area for UV light absorption. As a result, less catalyst is recommended to allow light to penetrate and breakdown the organic molecules in A-POME, leading to increased COD removal [8]. There is a relatively small difference in the percentage of A-POME for color removal after the photocatalytic process. The poor percentage removal for colour can be due to the complex composition of A-POME, which may have caused adsorption to be particularly slow in the dark phase. In addition, the increased loading of the catalyst increases photocatalytic activity. However, once a saturation phase is reached, the increased loading of the catalyst creates cloudiness in the treated A-POME. In addition, the trend of the turbidity removal percentage is similar to the colour removal as indicated in Fig. 4. The removal percentage of turbidity in ZnO–CC loading of 0.3g/L is 28.37% while loading of 0.1g/L and 0.5g/L is 28.49% and 29.01%, respectively.

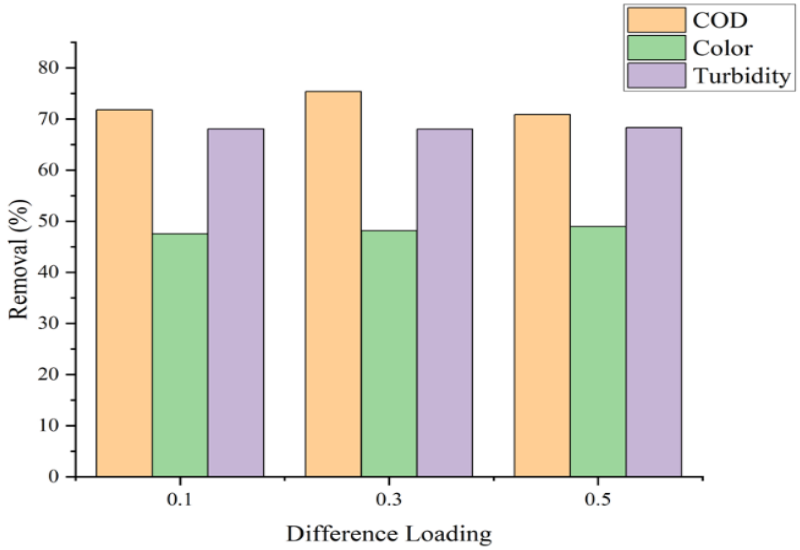


Fig. 4 - Percentage removal of treated A-POME under various ZnO–CC NPs loadings

3.3 Photocatalytic Degradation of A-POME Under Various pH

The influence of pH on photocatalytic degradation performance in the heterogeneous photocatalytic process is substantial. In this investigation, the pH of the A-POME sample was 4, 6, and 8. HCl and NaOH were used to adjust the pH of the sample. Table 3 shows the characteristics of A-POME after 60 minutes of photocatalytic treatment for various pH levels.

Table 3 - Characteristics of treated A-POME with loading 0.3g/L under different pH

Parameter	Unit	Different pH			Untreated A-POME	Standard DOE Value [8]
		4	6	8		
COD	mg/L	263.60 ± 10.12	200.30 ± 2.31	168.00 ± 0	683	200
Colour	ADMi	541.00 ± 0	537.00 ± 0	606.00 ± 0	1168	50
Turbidity	NTU	3.43 ± 0.14	3.89 ± 0.16	9.33 ± 0.41	29.2	NA

Fig. 5 shows the course of the A-POME's COD removal, colour degradation, and turbidity decrease over 60 minutes at various pH levels. Based on the results, the photocatalysis process under pH 8 showed the largest percentage of COD removal, which was 75.4%, compared to pH 4 and pH 6. Moreover, pH 4 shows the most turbidity reduction at 88.3%, and pH 6 shows the highest colour removal (54.02%). This result shows that pH 8 was preferred for the photocatalytic breakdown of A-POME compared to an acidic solution (pH 4 and pH 6). The findings revealed that pH has a substantial impact on degradation efficiency. Alkaline environments have slowed photocatalytic degradation in general. This effect could be explained by the proclivity of hydroxyl free radicals to develop easily in an alkaline environment, which contributes to an increase in active surface for photocatalytic degradation. As a result, pH 8 is the optimal condition for COD removal since it shows the highest percentage of COD elimination [9].

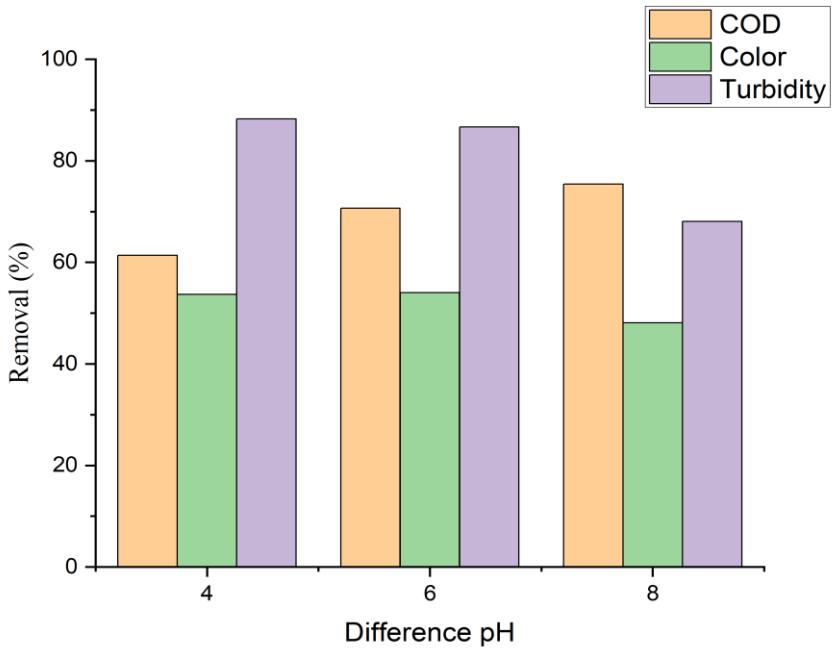
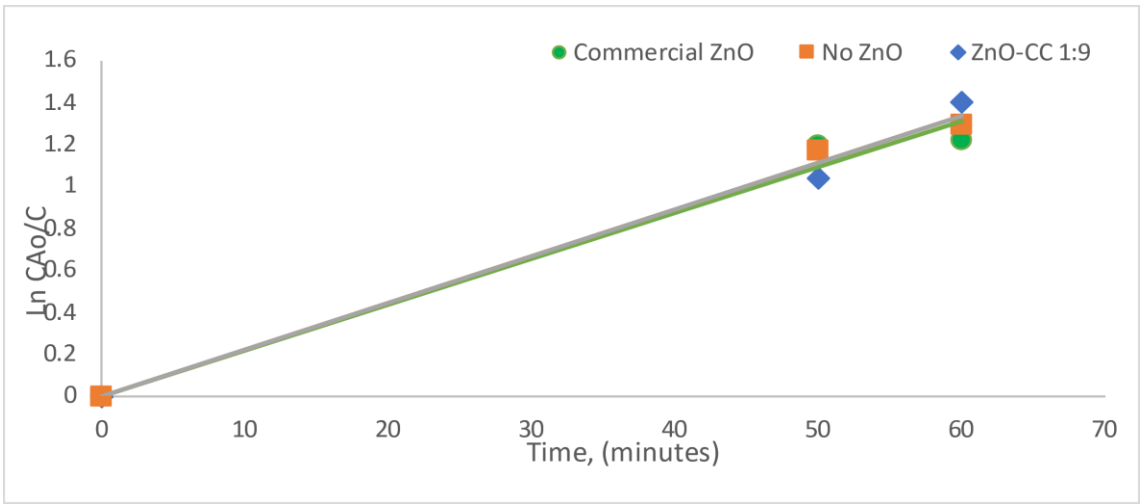


Fig. 5 - Percentage removal of treated A-POME under various pH

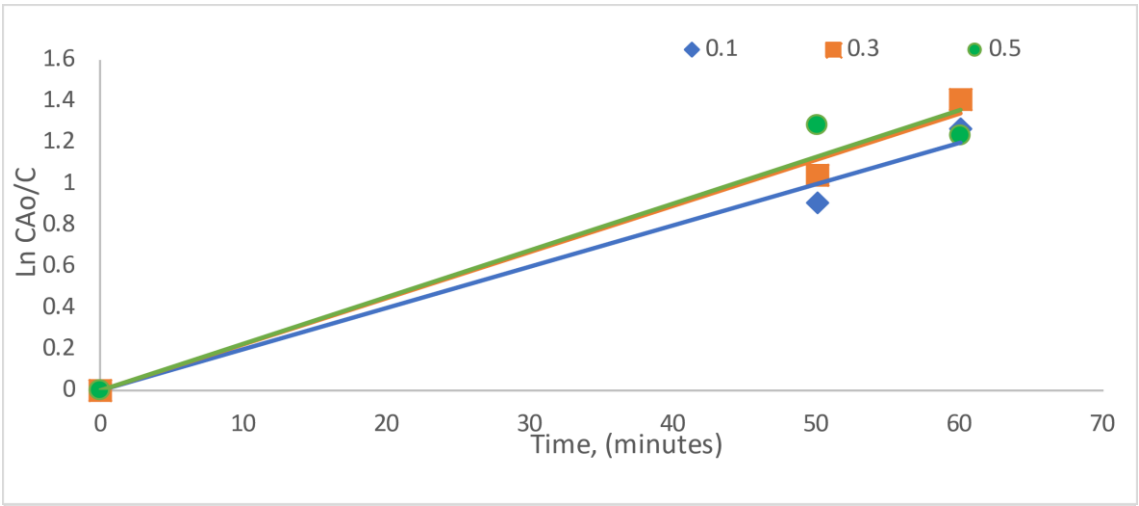
3.4 Kinetic Study of Photocatalytic Degradation of A-POME

It is challenging to create a model for the dependence of the photocatalytic degradation rate on the experimental parameters for the whole treatment time due to the complicated mechanism of reactions. As a result, photocatalytic kinetic modelling is often restricted in examining the early rate of photocatalytic degradation. This study employed the pseudo-first-order kinetic models to describe the photocatalytic degradation of A-POME under various conditions. Fig.. 6 shows a linear relationship derived from the graph of $Ln\left(\frac{C_{Ao}}{C_A}\right)$ versus time.

a)



b)



c)

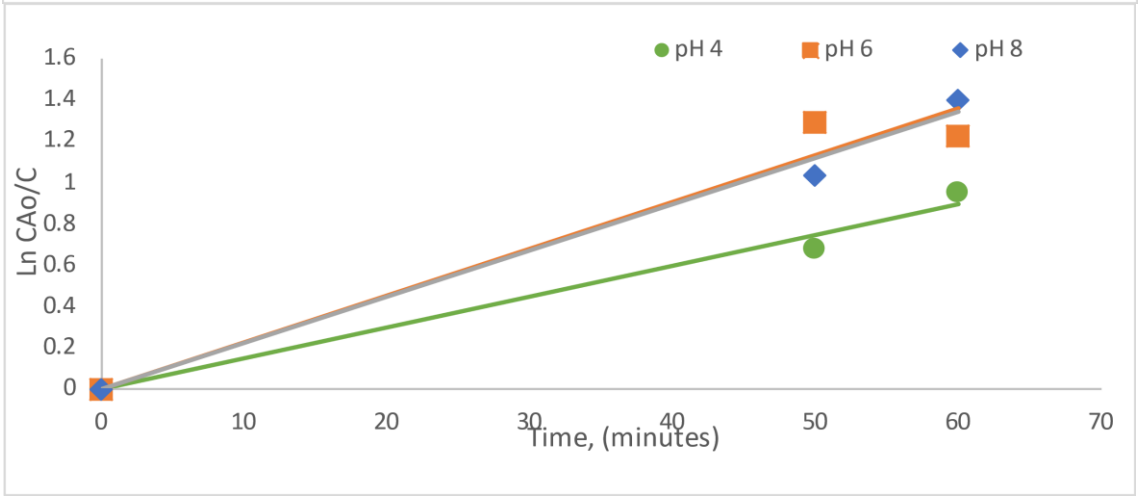


Fig. 6 - Kinetic study - the Langmuir–Hinshelwood model evaluation for the degradation of A-POME under various (a) types of photocatalyst; (b) ZnO–CC NPs loading, and; (c) pH of A-POME

Table 3 summarizes the photocatalytic degradation kinetic characteristics, including pseudo-first-order rate constant (*k*) and coefficient of correlation (R^2) for A-POME treatment under various conditions. The experimental results significantly suited the pseudo-first-order kinetic model for each condition since the R^2 value was in the 0.96–0.99 range.

Table 3 - The rate constant values (k) and the correlation of coefficient (R^2) of the Langmuir–Hinshelwood model under various (a) types of photocatalyst, (b) ZnO–CC NPs loading, and (c) pH of A-POME

Condition		Value	
		R^2	K
Different photocatalyst	ZnO–CC	0.9906	0.0250
	Comm–ZnO	0.9822	0.0215
	No–ZnO	0.9955	0.0222
Different loading, g/L	0.1	0.9856	0.0202
	0.3	0.9906	0.0225
	0.5	0.965	0.0222
Different pH	4	0.984	0.0151
	6	0.9615	0.0221
	8	0.9906	0.0225

The constant value (K) for different photocatalysts demonstrates that ZnO–CC NPs degrade faster than Comm–ZnO and No–ZnO conditions, indicating increased photocatalytic activity, as supported by the photocatalytic degradation results in Section 3.1. The rate constant K value has the largest value at 0.3 g/L loading of ZnO–CC NPs, which is 0.025, and it decreases at 0.1 g/L and 0.5 g/L loading of ZnO–CC NPs. The A-POME degradation efficiency diminishes with

increased loading, possibly due to the lack of a binding site in the ZnO–CC NPs. The best loading of ZnO–CC NPs 0.3g/L was selected to evaluate future experimental approaches in large-scale applications to treat A-POME. Finally, pH 8 has the highest value of K compared to pH 6 and pH 4, where both are acidic. This is because ZnO–CC NPs tend to aggregate in acidic conditions, which impacts the reaction's availability of ZnO-CC NPs binding sites [7]. The result acquired is sufficient evidence of the synthesized ZnO–CC NPs' effective photocatalytic activity.

4 Conclusion

The photocatalytic performance in the addition of ZnO–CC NPs for treating A-POME revealed better COD removal efficiency (75.4%) under pH 8, 0.3 g/L ZnO-CC NPs loading, and 50% initial A-POME concentration, compared to No–ZnO and with Comm-ZnO. The efficiency of A-POME in removing COD varies slightly depending on the circumstance. It was discovered that removing color, COD, and turbidity from A-POME with the photocatalytic treatment was remarkably successful, with respective removal rates of 48.12%, 75.40%, and 68.04%. In order to meet with legal A-POME discharge restrictions, photocatalytic technology in the palm oil business offers another fascinating treatment method. In addition, photocatalysis is both ecologically beneficial and cost-effective. As a consequence, A-POME treatment employing photocatalytic process assisted ZnO-CC NPs at ideal conditions might be considered an alternative technique to treating A-POME. Further research will be needed to improve the performance of ZnO–CC NPs as a good potential photocatalyst by considering large-scale production for industrial usage to replace existing photocatalysts. The finding from this present study will be the basis of our future research.

Acknowledgement

The Universiti Tun Hussein Onn Malaysia funded this research through Tier 1 grant number Q439. The Centre for Diploma Studies at Universiti Tun Hussein Onn Malaysia is also acknowledged by the writers for its support.

References

[1] Subramaniam, M. N., Goh, P. S., Lau, W. J., Ng, B. C., & Ismail, A. F. (2018). AT-POME colour removal through photocatalytic submerged filtration using antifouling PVDF-TNT nanocomposite membrane. Separation and Purification Technology, 191, 266–275.

[2] Ng, K. H., Cheng, Y. W. Khan, M. R. & Cheng, C. K. (2016). Optimization of photocatalytic degradation of palm oil mill effluent in UV/ZnO system based on response surface methodology. Journal of Environmental Management, 184, 487–493.

[3] Chin, Y-H., Sin, J-C., Lam, S-M., Zeng, H., Lin, H., Li, H., Mohamed, A. R. (2022). 0-D/3-D heterojunction composite constructed by decorating transition metal oxide nanoparticle on peony-like ZnO hierarchical microstructure for improved photodegradation of palm oil mill effluent. Optik - International Journal for Light and Electron Optics. 260,169098.

[4] Puasa, N. A., Hairom, N. H. H., Dzinun, H., Madon, R. H., Ahmad, N. S., Sidik, D. A. B., Azmi, A. A. A. R. (2021). Photocatalytic degradation of palm oil mill secondary effluent in presence of zinc oxide nanoparticles," Environmental Nanotechnology, Monitoring and Management. 15, 100413.

[5] Sidik, D. A. B., Hairom, N. H. H. Mohammad, A. W., Halim, N. A., Ahmad, M. K., Hamzah, S., Sulaiman, N. (2020). 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 162, 12–27.

[6] Zangeneh, H., Zinatizadeh, A.A., Zinadini, S., Nazari, S., Sibali, L., & McKay, T. (2022). Visible light-driven photoactive L-Methionine (CNS tripledoped)-TiO2/ZnO nanocomposite aiming for highly efficient photodegradation of xenobiotic compounds in wastewater. Materials Research Bulletin 150, 111783.

[7] Sekaran, C., Vishnu, D., Dhandapani, B., Alagesan, T., & Balaji, G. (2022). Facile synthesis of zinc oxide nanoparticles using glycerol as cross-linker and the kinetic studies for the photocatalytic degradation of acid blue 113 dye. Results in Chemistry 4,100377.

[8] Sidik, D. A. B. Hairom, N. H. H., Ahmad, M. K., Madon, R. H., Mohammad, A. W. (2020). Performance of membrane photocatalytic reactor incorporated with ZnO-Cymbopogon citratus in treating palm oil mill secondary effluent. Process Safety and Environmental Protection. 143, 273-284.

[9] Zainuri, N. Z., Hairom, N. H. H., Sidik, D. A. B., Desa, A. L., Misdan, N., Yusof, N., Mohammad, A. W. (2018). Palm oil mill secondary effluent (POMSE) treatment via photocatalysis process in presence of ZnO-PEG nanoparticles. Journal of Water Process Engineering. 26,10-16.