Palm Oil Wastewater Treatment (POME) Using ZnO Photocatalyst Biosynthesis with Plant Extracts as Stabilizers

Yuniar[1]*, Metta Wijayanti[2], Alif Adriani Puspitasari[1], Kana[1], Maharani Putri[1]

[1*] Department of Industrial Chemical Technology, [2] Department of Chemical Engineering,
Sriwijaya State Polytechnic, Jalan Srijaya Negara, Bukit Besar, Palembang, 30139 South Sumatra, Indonesia
yuniar@polsri.ac.id

ABSTRACT Palm oil plays a vital role in Indonesia's economy, with production reaching 45.58 million tons in 2022. However, the increase in palm oil production also leads to the generation of palm oil mill effluent (POME), which poses a potential environmental threat. POME contains high levels of chemical oxygen demand (COD), making its treatment crucial. Photocatalytic technology using zinc oxide (ZnO), produced through biosynthesis, offers a promising solution. This study aims to assess the impact of irradiation time and optimal ZnO weight on the reduction of COD levels in POME. The research involved varying the irradiation time between 15–75 minutes with a ZnO weight of 120 mg, alongside different plant-based photocatalysts, such as yellow pumpkin seeds, papaya leaves, and pineapple peels. The best results for POME photodegradation were achieved using ZnO derived from yellow pumpkin seeds, which resulted in a COD reduction to 469 mg/l after 75 minutes of irradiation.

Keywords: Photocatalytics, Plant extracts, POME, ZnO biosynthesis.

1. INTRODUCTION

Oil palm (*Elaeis guineensis Jacq.)* plays an important role in the Indonesian economy as one of the sources of non-oil and gas foreign exchange. In 2022, palm oil production in Indonesia reached 45.58 million tons, up 1.02% compared to the previous year. However, increased production also produces more waste, especially Palm Oil Mill Effluent (POME), which is an organic waste with a high potential to pollute the environment.

POME is a liquid waste of palm oil mills consisting of dissolved and suspended solids in the form of colloids containing 95-96% water, 0.6-0.7% oil and 4-5% fats and total solids. POME produced by the industry is brown with a discharge temperature between 80 $^{oC\text{ and }90\text{ }oC}$ with a pH value in the range of 3.5-4.0. The average POME contains BOD ranging from 8200-35000 mg/l and COD ranging from 15103-65100 mg/l which can be a pollutant if discharged directly into free waters (Palm & Mill, 2023) .

There are several methods that can be used in POME processing, one of which is by using photocatalytic technology. Photocatalytic technology is a renewable energy-

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based technology that utilizes light/light as an energy source to degrade organic waste through a reduction-oxidation reaction (Syahroni, 2015) which is assisted by catalysts. Catalysts used in photocatalytic processes are called photocatalysts.

The use of photocatalytic technology to process POME uses a ZnO photocatalyst that is biosynthetically synthesized with a bioreducer of plant extracts such as pineapple peel, papaya leaves, and yellow pumpkin seeds.

Biosynthesis has been developed as an alternative method by utilizing organic reducing agents as biological agents in the synthesis process so that it is more environmentally friendly (Wulandari et al., 2023). The functional group is suspected to act as a bioreducer and stabilizing agent. This photocatalytic technology is expected to be able to reduce the levels of Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), and Total Suspended Solids (TSS) in POME waste.

This study aims to biosynthesize ZnO photocatalysts using plant extracts, determine the optimal conditions for photocatalytic processes, include photocatalyst weight and irradiation time, evaluate the effectiveness of POME degradation with all three types of ZnO photocatalyst biosynthesis.

This research is expected to include more environmentally friendly palm oil waste treatment solutions and the application of ZnO photocatalysts in the palm oil processing industry.

2. RESEARCH METHODS

2.1. Materials

The ingredients used are yellow pumpkin seed extract, papaya leaf extract, pineapple peel extract. Zn(CH3COOH)2.2H2O, NaOH, POME, and aquifers.

2.2. Equipment

The equipment used includes 13 watt UV lamps, X-Ray Difraction (XRD Rigaku Miniflex 600), Fourier Transdform Infra Red (FTIR Thermo Nicolet iS10)

2.3. Method

Plant Extraction

Yellow pumpkin seeds, papaya leaves and pineapple peel are dried in the oven at 100 °C, then ground until smooth. A total of 10 g of plant powder is mixed with 100 ml of aquaades, heated at 100 °C for 25 minutes with stirring at 300 rpm, then filtered.

ZnO biosynthesis

A total of 10 ml of plant extract is mixed with 90 ml of $Zn(CH3COOH)_2$ solution.2H2O 0.15 M, heated at 70 °C for 10 minutes, then added NaOH until the pH reaches 8. The mixture is stirred for 1 hour, the sediment is separated, washed, and dried in the oven at 100 °C, then analyzed using FTIR and XRD.

Characterization

Photocatalysts of ZnO-yellow pumpkin seed extract, ZnO-papaya leaf extract and ZnO-pineapple peel extract were characterized by X-Ray Difraction to see the surface morphological structure and particle size. Meanwhile, FTIR analysis is carried out to determine the functional groups in a compound.

Applications on POME

ZnO photocatalyst is applied to diluted POME waste, with a catalyst weight of 120 mg. Irradiation is carried out with UV lamps with time variations of 15, 30, 45, 60 and 75 minutes. The analysis parameter is COD

3. RESULTS AND DISCUSSION

3.1 Initial POME Analysis

The analysis of the initial POME sample was carried out to determine the content of COD, BOD, TSS, and initial pH values before the photocatalytic process was carried out in the treatment of POME waste. The characteristics of POME waste can be seen in table 3.1. Table 3.1 shows that the COD, TSS, and pH values are still far from the wastewater quality standards, while the BOD has met the wastewater quality standards. After obtaining these results, a photocatalytic process was carried out on POME waste using a biosynthesized ZnO photocatalyst from papaya leaves, pineapple peel extract and yellow pumpkin seed extract to reduce COD, pH and TSS values in table 3.1.

Table 3.1 Results of Initial POME Analysis

Examination	Result
COD	762,107 (mg/l)
BOD	11,000 (mg/l)
TSS	62650,000 (mg/l)
Ph	4,2
Oils and Fats	576,500 (mg/l)

3.2 ZnO Characterization

ZnO Characterization Results Using XRD Test

ZnO photocatalyst characterization is carried out to determine the crystallinity phase of the synthesized ZnO so that the particle size and crystal structure can be known. The analysis of ZnO-papaya leaves, ZnO-pineapple peel and ZnO-yellow pumpkin samples using XRD tests can be seen in figure 3.1.

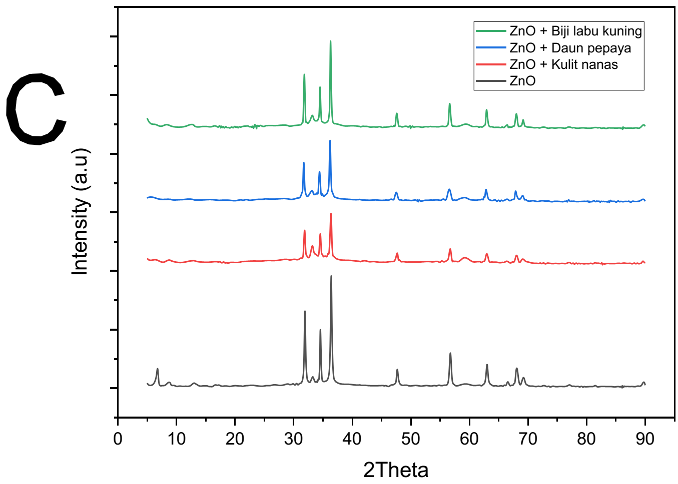


Fig 3. 1 XRD Results of ZnO, ZnO-Yellow Pumpkin Seeds, ZnO-Papaya Leaves and ZnO-Pineapple Peel

It was found that all samples had peak angular values (2□). The XRD results of ZnO papaya leaves showed a peak of diffraction at 31.70o; 32.89o; 34.37o, 36.19o; 47.47o; 56.48o; 62.76o; 67.83o; 69.04o. . . The ZnO photocatalyst of pineapple peel shows a peak of diffraction at 31.88o; 33.16o ; 34.54o ; 47.66o ; 56.72o; 59.22o; 59.22o; 62.98o; 68.12o ; 69.14 and Yellow pumpkin ZnO photocatalyst shows a peak of diffraction at 12.23 °, 31, 82 °, 33,00 °, 34,49 °r, 36,26 °r, 47,54 °r, 56,61 °r, 62.88o, 67.94o, 69.12o. These peaks are identified as characteristic of ZnO. The resulting diffraction peak is almost the same as the ZnO peak from JCPDS standard data No.36-1451 (Adeleke et al., 2018). There were no other diffraction peaks indicating the presence of contaminants, indicating that the resulting nanoparticles were of high purity. It can be seen in Figure 3.1 that all samples have shown the presence of ZnO crystal structure *wurtzite* with crystal form *hexagonal* (Chandel et al., 2020). The crystal size of the biosynthesized ZnO nanoparticles is calculated by Debye Scherrer's equation (Kefeni & Mamba, 2020) et al., 2020).

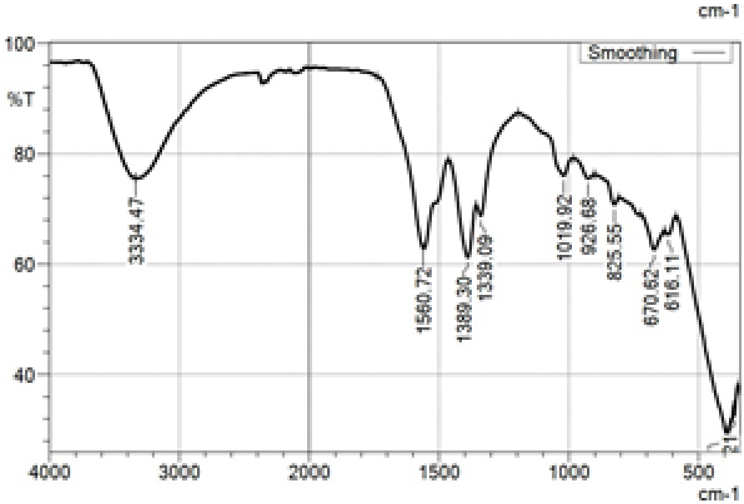
$$D = \frac{k \times \lambda}{\beta \cos \theta} \qquad (1)$$

D = crystal size (nm)
k = constant i.e. 0.9,
λ = X-ray wavelength i.e. 0.15406
β = FWHM
θ = Bragg Angle
P = (0,154)

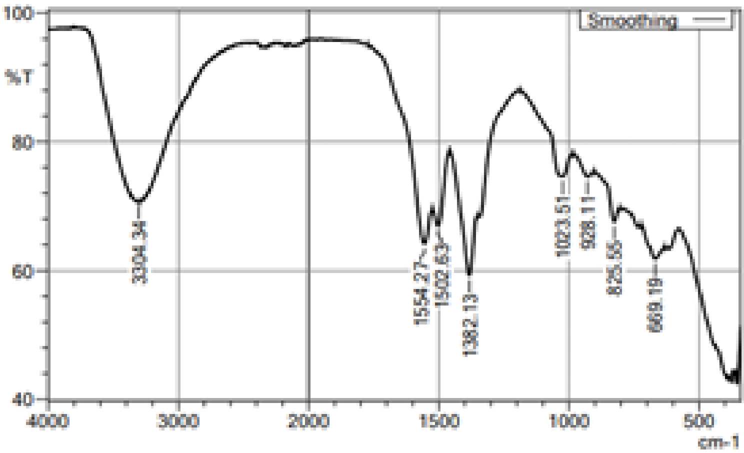
From the equation above, calculations were carried out and the results obtained that the average crystal size was 33.451 nm (ZnO - papaya leaves), 25.95 nm (ZnO - pineapple peel) and 37.58 nm (ZnO - yellow pumpkin seeds), which means that it includes the size of nanoparticles. It can be seen in Figure 3.1 that all samples have shown the presence of ZnO crystal structure *wurtzite* with crystal form *hexagonal* (Etape et al., 2018).

ZnO Characterization Results Using FTIR Test

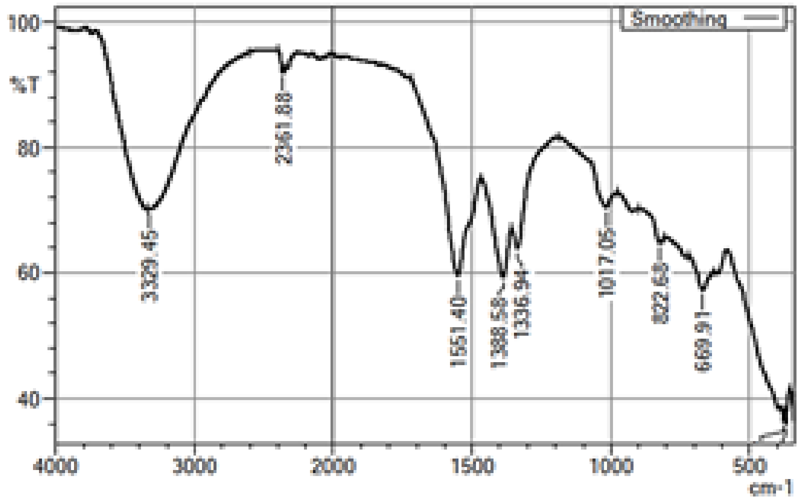
The analysis of the compound functional group was carried out using an FTIR spectrophotometer. The results of the FTIR spectrum for ZnO of papaya leaves, ZnO of pineapple peel and ZnO of yellow pumpkin can be seen in Figure 3.2.



(a)



(b)



(c)

Fig. 3.2. (a) ZnO-ekstrak daun pepaya ; (b) ZnO-ekstrak kulit nanas; (c) ZnO ekstrak biji labu kuning

Figure 3.2. (a) Photocatalyst ZnO papaya leaves shows that the FTIR test results of the main peak are, 3334.47 m^{-1}; 1560,72 m^{-1}; 1389,30 m^{-1}; 1339,09 m^{-1}; 1019,92 m^{-1}; 926,68 m^{-1}; 825,55 m^{-1}, 670,62 m^{-1}, and 616.11 m^{-1}. The functional cluster is at the peak of 3334.47 m^{-1} obtaining the presence of an OH functional group indicates the presence of compounds containing hydroxyl groups, such as alcohol or carboxylic acid according to the results of the study (Boutra et al., 2020). Then at the peak of 825.55 is the functional group of Zn according to the results (Shoueir et al., 2018). And the functional cluster at the top of 616.11 m^{-1} in accordance with the results of the study (Shoueir et al., 2018) get the ZnO functional group.

Figure 3.2(b) can be seen the main peak result is found at 3304.34cm^{-1} ; 82 5.22cm^{-1} ; 928.11cm^{-1} ; 1023.51 cm^{-1}; 1382.13 cm^{-1}; 1502.63cm^{-1} 1554.24 cm^{-1}. The functional clusters are at a peak of 3304.34 cm^{-1} indicates the presence of an OH group^{-} shows the presence of alcohol and carboxylic acid bonds and absorption by ZnO, this result is in accordance with the result reference (Rohmawati et al., 2024), then at the peak of absorption 825.55 detection is the functional group of Zn according to the reference results (Długosz et al., 2020), while the ZnO function group is found at the peak of the wave of 669.19 cm^{-1}. In his research, it was stated that the ZnO functional group was formed at a wave number of 800-400 cm^{-1} (Lee et al., 2016).

Figure 3.2(c) can be seen the main peak result at 3329.45cm^{-1} ; 82 2.68cm^{-1} ; 1017.05 cm^{-1} ; 1336.94 cm^{-1}; 1388.58 cm^{-1}; 1551.40 cm^{-1}. The functional clusters are at the peak of 3329.45 cm^{-1} indicates the presence of an OH group^{-} showed the presence of alcohol and carboxylic acid bonds and absorption by ZnO. Then at the peak of absorption 822.68 detection is a functional group of Zn according to the reference results (Lee et al., 2016), while the ZnO function group is found at the peak of the wave of 669.19 cm^{-1} (Ong et al., 2018). In his research, it was stated that the ZnO functional group was formed at a wave number of 800-400 cm^{-1} .

3. 3 Photocatalyst Application with POME

After the initial characteristic analysis of POME, it was followed by the ZnO biosynthesis process with the help of yellow pumpkin seed extract and its application to POME.

Chemical oxygen demand (COD) is a parameter used to measure the amount of oxygen needed to oxidize organic matter in the air. A decrease in COD in a system indicates that organic matter has degraded into simpler or oxidized compounds.

The COD value is used to measure the amount of organic pollutants in the water and assess the efficiency of waste treatment. The higher the COD value, the greater the level of pollution in the water or waste, because more oxygen is needed to oxidize the organic compound. This will reduce the amount of oxygen available to microorganisms in the aquatic ecosystem. The characteristics of POME results after the application of the ZnO catalyst are shown in Figure 3.3.

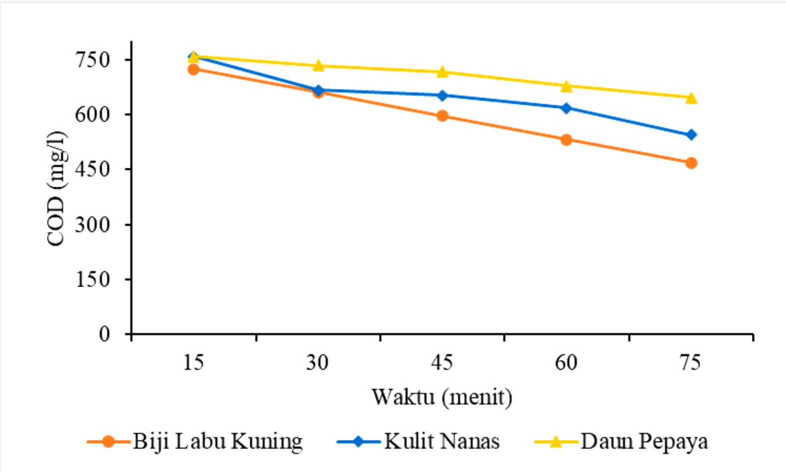


Fig 3. 3 COD Results of ZnO-Yellow Pumpkin Seeds, ZnO-Papaya Leaves and ZnO-Pineapple Peel

Figure 3.3 shows that the relationship between time and weight of ZnO to COD values is inversely proportional. The longer the UV irradiation time and the greater the weight of ZnO, the lower the COD value. This shows that the presence of ZnO catalysts plays a sufficient role in degrading the organic content of POME.

From the data, it can be concluded that the longer the UV irradiation time, the COD decreases, the decrease in COD is quite significant at 45 minutes compared to other minutes, this shows that the active time of the ZnO catalyst works in the range of 20-40 minutes of operation time. Photo degradation will increase with increasing time. Directly increasing the amount of contact time of the photocatalyst surface thereby causing an increase in the formation of a number of OH radicals that can degrade organic pollutants in POME. The most significant decrease in COD value occurred at 75 minutes of UV irradiation with a result of 469 mgO2/l.

Figure 3.3 shows that the COD value in yellow squash shows a steady decrease over time, ranging from 725 mg/l at 15 minutes to 469 mg/l at 75 minutes. This consistent decline reflects the effectiveness of the degradation process of organic matter contained in yellow pumpkin compared to pineapple peel and papaya leaves. The synthesis of nanoparticles is affected by the concentration of extracts of natural ingredients. Higher extract types and concentrations can increase particle size as the solution forms aggregations (Acs et al., 2008). The results of the analysis of the size distribution show in general that the size of the ZnO-plant extract nanoparticles produced is heterogeneous or diverse.

Plant extracts (yellow pumpkin seeds, papaya leaves or pineapple peels) have been shown to be effective as a stabilizer (capping agent) that can control the size and shape of the ZnO nanoparticles produced. The average size of the nanoparticles ZnO-plant extract is 37.58 nm, 33.451 nm and 25.95 nm. The role of capping agents is very important in regulating the size of ZnO nanoparticles and preventing agglomeration, especially during the calcination process. Research conducted by Basnet and Chatterjee (2020) Using surfactants, polymers, amino acids, polysaccharides and bio-extracts as capping agents, they found that each of these compounds produced ZnO nanoparticles with different size and shape characteristics.

The results showed that ZnO nanoparticles had the activity of lowering COD values as shown in Figure 3.3 with ZnO-yellow pumpkin seed extract which was the best in lowering COD of POME waste with a contact time of 75 minutes.

Additionally, capping agents serve as structure-directing agents, playing a crucial role in the formation of various ZnO nanostructures. However, understanding the kinetics of particle growth is essential for effectively controlling the morphology of ZnO. ZnO particles are nucleated in solution, and over time, they aggregate and increase in size. By monitoring the growth kinetics at critical concentrations, it is possible to ensure controlled growth during the sedimentation process. To prevent the growth of specific facets and achieve ZnO with a desired morphology, capping agents can be employed to selectively inhibit certain facets. ZnO with a variety of morphologies and nanostructures can be synthesized due to its chemically active polar and nonpolar inert sides (Basnet & Chatterjee, 2020). The most stable structure of ZnO is the hexagonal form of wurtzite, which consists of two polar sides and six side sides, where: (001), (001) is the chemically active polar field, (010), (100) and (110) are chemically stable non-polar fields and (100) is the most stable chemically inert field. The growth rate of these sides can be controlled through a capping mechanism to form various ZnO nanostructures. Although different capping agents direct particle orientation in different ways, the type of synthesis involved is one of the important factors that equally regulate the final morphology, microstructure, and size of ZnO.

4. CONCLUSION

For ZnO photocatalysts synthesized from Zn-Acetate and Sodium hydroxide, plant extracts are used as stabilizers during synthesis, namely papaya leaf extract, pineapple peel extract or yellow pumpkin seed extract. The structure and functional cluster of the analysis confirmed the formation of the ZnO photocatalyst. Photocatalytic activity, i.e. irradiation time, is the most efficient to lower COD is 60 minutes and above because the longer the photocatalyst time, the more compounds will be decomposed.

Of the three plants that are used as the best stabilizer, yellow pumpkin is because it consistently reduces COD from 762.107 mg/l to 469 mg/l or a decrease of 62%.

Therefore, this ZnO biosynthesis has great potential if used for the degradation of POME waste under UV light.

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