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Research Article

Effect of ultrasound-advanced oxidation processes for pretreatment of oil palm mesocarp fiber for cellulose extraction

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Abstract. Palm mesocarp fiber, a by-product of the palm oil industry, holds significant potential as a cellulose source for biofuel, biopolymer, and biocomposite production. However, its utilization is hampered due to the presence of lignin, which covers the cellulose. The use of ozone promotes a high level of lignin degradation, making it efficient in breaking down lignin bonds in lignocellulose. However, the ozonation method has low ozone mass transfer. This deficiency can be overcome with ultrasonic waves because of the cavitation phenomenon that can expand the contact surface of ozone and lignocellulose. The ozonation-ultrasonic hybrid method is used to remove lignin. This research investigates the use of a hybrid ozonation-ultrasonic method with the effect of reaction time and pH under acidic conditions on the pretreatment of palm oil mesocarp fiber. This process was carried out at reaction times (70, 80, and 90 minutes) and solution pH (4, 5, and 6) with an ozone flow rate of 2 L min^{-1}. The cellulose content was analyzed using the Chesson method. The results showed a decrease in lignin and an increase in cellulose, which was confirmed by Fourier Transform Infrared Spectroscopy (FTIR) analysis shows a decrease in the lignin absorption peak at 1635 cm^{-1} and 1420 cm^{-1}. XRD analysis showed an increase in crystallinity after pretreatment, with lignin degradation observed at 6.35%. SEM Morphological showed a more friable, stable, and porous surface after pretreatment, indicating the presence of perforations in the cell walls and the damage to the lignin structure. Therefore, this research succeeded in reducing the use of chemicals in the biomass waste delignification process. The ozonation-ultrasonic hybrid pretreatment process, which aims to degrade lignin in palm fiber biomass, shows promising results, producing high cellulose content in palm fiber by reducing the amount of chemicals as mostly used in conventional processes.

Keywords: Oil Palm Fiber, Lignin, Cellulose, Ozonation, Ultrasonic

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1. Introduction

Indonesia is the largest producer of palm oil in the world. Indonesia's palm oil production continues to increase, approaching 50 million tons in 2021 (Directorate General of Plantations, 2021). In general, each palm oil mill produces 25%–30% of the main products in the form of CPO (20%–23%) and palm kernel (5%–7%), while the remaining 70%–75% is solid waste from processing. Solid waste from palm oil processing includes empty fruit bunches (20%–30%), fiber (10%–20%), and shells (7%–9%) (Ni'mah *et al*., 2017). Oil palm fruit fiber comprises approximately 13% of the fruit weight, generating a waste volume of 4,023,361 tons in 2016 and 4,319,820 tons in 2017 (Rosdiana *et al*., 2021).

Oil palm fruit fiber, a by-product of milling, is rich in lignocellulose; it primarily comprises cellulose (33.9%), lignin (27.7%), and hemicellulose (26.1%) (Kurniawan, 2020). Cellulose, the principal constituent of plant cell walls, is a glucose polymer with ß-1,4 glucoside bonds forming straight chains. Its natural binding with hemicellulose and protection by lignin necessitate the pretreatment of lignocellulose to obtain pure cellulose.

The pretreatment of lignocellulose is a crucial step in cellulose utilization; it involves the conversion of complex lignocellulose into cellulose, hemicellulose, and lignin. This process also entails removing lignin and reducing cellulose crystallinity (Kumari & Singh, 2018). Further, lignocellulosic pretreatment methods can be classified into four types: physical, chemical, physico-chemical, and biological. Physical pretreatment aims to reduce the particle size of raw materials, often accomplished through ultrasound treatment. Ultrasound waves lead to morphological changes in lignocellulosic biomass by generating small cavitation bubbles that break down cellulose and hemicellulose fractions. Biological process shows a potential result of cellulose degradation despite of its slow process (Abdullah *et al* 2018). Chemical pretreatment, on the other hand, focuses on enhancing cellulose biodegradation. This method can be carried out with acidic, alkaline, oxidative, organosolv, and ionic liquid, as well as ozonation pretreatment. Moreover, chemical pretreatment method is found to be more expensive as a large amount of chemicals is used for pretreating the lignocellulosic substrate. Ozonation, as one such method, involves reducing lignin content in lignocellulosic biomass by introducing a specific amount of ozone gas while monitoring the biomass's moisture content (Kumar & Sharma, 2017).

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Numerous studies have been conducted to extract cellulose from oil palm fiber. For instance, Laghari *et al.* (2016) employed microwave-assisted delignification with various chemical solutions, resulting in a cellulose increase from 35.41% to 56.69%. Similarly, Taharuddin *et al.* (2018) utilized ethanol and NaOH, leading to a cellulose increase from 39.50%–50.77%. Fuertez-Córdoba *et al.* (2021) also investigated alkaline delignification methods on lignocellulosic biomass from African palm fiber, yielding 54.3% cellulose.

The ozonolysis method is widely recognized as an effective pretreatment process for lignocellulose. It utilizes hydroxyl radicals (•OH) as non-selective oxidizers with high oxidation potential, making them ideal for lignocellulose pretreatment. Ozonolysis operates through two mechanisms: direct and indirect, each of which is dependent on the solution's pH. Direct ozonolysis occurs under acidic conditions (pH < 5), where ozone molecules drive oxidation. Indirect ozonolysis, on the other hand, employs hydroxyl radicals for oxidation and is effective under alkaline conditions (pH > 8). This method offers several advantages, including strong oxidation potential and the ability of ozone to readily react with complex compounds containing conjugated double bonds and high-density functional groups, facilitating the oxidation of lignin, which contains high C=C bonds (Anggoro *et al*., 2023).

Various studies have explored the ozonolysis method for lignocellulose reduction. Wu *et al.* (2013) investigated pretreating wheat straw with ozone, observing a decrease in lignin content to 11.9% with increased ozonolysis time and hydrogen production. Similarly, Travaini *et al.* (2013) studied bagasse pretreatment and reported up to 55% lignin degradation with ozone treatment.

In recent years, the ozonolysis method has been enhanced by combining it with ultrasound, forming the ozonation-ultrasonic method. In ozonolysis processes, ozone efficiency is hindered by low mass transfer due to ozone's low solubility and stability in liquid. Ultrasound enhances mass transfer by inducing cavitation, generating microbubbles that increase the gas-liquid contact area. Acoustic cavitation reduces ozone mass transfer resistance by creating turbulence and microcirculation around cavitation bubbles, thereby favoring ozone dissolution (Boczkaj *et al*., 2018). Under ultrasound, ozone decomposes into oxygen molecules and atoms, forming radical compounds (•OH) via reactions with water molecules (Kıdak & Doğan, 2018).

Shen *et al.* (2017) examined the simultaneous use of ozonolysis and ultrasound processes in degrading reactive red X-3B, demonstrating a degradation effect of up to 99.2%. Additionally, Xiong *et al.* (2019) reported that the ultrasonic catalytic micro-bubble ozonation process could enhance the mass transfer of ozone and the conversion of ozone to hydroxyl radicals, resulting in the improved degradation of recalcitrant contaminants in bulk solutions. Therefore, combining ozonolysis with ultrasound shows significant potential for enhancing the degradation efficiency of complex compounds like lignocellulosic biomass. In this study, a hybrid ozonation-ultrasonic method was employed as a pretreatment for palm fiber lignocellulose, with operating variables such as initial pH and treatment duration optimized to determine the most effective conditions for pretreatment.

2. Materials and methods

The palm fiber utilized in this study was sourced from waste generated by oil palm companies in Central Kalimantan, Indonesia. The raw material, palm fiber waste, was initially purified by washing it with distilled water and subsequently drying it in an oven at 105°C until it reached a constant weight. Afterward, the fiber was chopped, sieved through a size of 40 mesh, and stored in a sealed container at room temperature. Chemicals employed in the research included H2SO4 with a purity of 95%–97% (E. Merck Cat. No. 100731) and NaOH with a purity of 99% (E. Merck Cat. No. 106498). Ozone gas was generated from an ozone generator (Dipo Technology Indonesia), and ultrasonic irradiation was conducted using an ultrasonic bath type KLS 303365 equipped with a thermostatic water bath operating at a frequency of 42 kHz.

2.1 Ozonation-Ultrasonic Pretreatment

For pretreatment, 15 g of palm fiber was placed into a three-neck flask and mixed with 225 mL of distilled water. Subsequently, ultrasonic ozonation was conducted with an ozone flow rate of 2 L/min at 30°C for durations of 70, 80, and 90 minutes under solution pH conditions of 4, 5, and 6, adjusted by adding either 0.1 M NaOH or 0.1 M H2SO4 to the solution. Following treatment, the residue was filtered, washed with distilled water, and dried in an oven at 100°C (Anggoro *et al*., 2022).

2.2 Extraction of α-Cellulose

The delignified palm fiber underwent soaking in a 5% H2O2 solution at 80°C for 1 hour. Subsequently, the fiber was filtered, washed to neutrality, and dried. Next, the fiber waste was soaked in a 17.5% (w/v) NaOH solution for 45 minutes at 80°C. The resulting mixture was filtered and washed with distilled water until reaching a neutral pH. The obtained residue (cellulose) was dried in an oven at 105°C until it reached a constant weight; subsequently, an analysis was conducted to determine cellulose, hemicellulose, and lignin levels in the palm fiber.

2.3 Characterization of Oil Palm Fiber

Characterization of the cellulose, hemicellulose, and lignin content of oil palm fiber was conducted using the Chesson-Datta method (Lismeri *et al.,* 2016). The analysis involved the following steps: 1 g of oil palm mesocarp fiber (weight a) was placed into a glass beaker and mixed with 150 ml of distilled water, then heated at 100°C for 1 hour. The mixture was subsequently filtered, and the residue was washed with distilled water until the filtrate volume reached 300 ml, after which the residue was dried in an oven at 105°C until a constant weight was achieved (weight b). The residue was then transferred to an Erlenmeyer flask and mixed with 150 ml of 1 N H2SO4, heated at 100°C for 1 hour, filtered, and washed with distilled water until the filtrate volume reached 300 ml. The residue was then dried in an oven at 105°C until a constant weight was achieved (weight c). Subsequently, the residue was treated with 10 ml of 72% v/v H2SO4 and soaked at room temperature for 4 hours, followed by the addition of 150 ml of 1 N H2SO4 and heating at 100°C for 1 hour. After filtration and washing with distilled water until the filtrate volume reached 400 ml, the residue was dried, weighed until a constant weight was reached (weight d), and ignited (weight e).

3. Results and discussion

3.1 Characterization of Oil Palm Fiber Before Ozonation-Ultrasound Pretreatment

Palm fiber was characterized on samples without delignification treatment to determine the lignocellulose components present.

Table 1
Components of Oil Palm Fiber Before Pretreatment

Material	Compound (%)				Ref
	C	HC	Lig	Ash	
Mesocarp Fiber	36.8	31.2	15.1	3.6	This Research
	33.9	26.1	27.7	3.5	Kong *et al.* (2014)
	39.5	9.8	32.8	9.3	Saka *et al.* (2008)

C = Cellulose; HC = Hemicellulose; Lig = Lignin

The characterization employed the Chesson-Datta method on a 40-mesh sample, and the results are presented in Table 1.

The characterization of untreated palm fiber revealed cellulose content of 36.8%, 31.2% hemicellulose, and 15.1% lignin. Palm fiber, with its high cellulose content, is potentially valuable for bioenergy development. However, the significant presence of 15.1% lignin could impede cellulose accessibility. Therefore, lignin removal through a pretreatment process was deemed necessary.

Variations in results across different studies on palm fiber could be attributed to various factors such as plant growth, age, soil conditions, and climatic influences in the environment where oil palm was planted (Asyraf *et al*., 2022). This research obtained oil palm from Central Kalimantan, Indonesia, whereas oil palm studied by Kong *et al.* (2014) and Saka et al. (2008) originated from Malaysia. Different growing locations certainly cause differences in components, as the nutritional content of the soil varies. Additionally, even though the research by Saka and Kong was conducted in the same country, their studies were conducted at different times, resulting in different growing conditions. This variation can affect the lignocellulose content in the palm fiber. Despite differences in component amounts, cellulose remained the primary constituent of lignocellulose in oil palm fiber.

3.2 Effect of Ozonation-Ultrasound Pretreatment Time on Cellulose Content in Oil Palm Fiber

The duration of the pretreatment process significantly affected the cellulose yield. In this study, pretreatment was conducted at 30°C with an ozone flow rate of 2 L/min at pH 4, 5, and 6 for durations of 70, 80, and 90 minutes. The resulting cellulose percentages with varying pretreatment times are illustrated in Figure 1.

Pretreatment duration impacts cellulose yield, with longer durations generally leading to increased yields until a certain maximum level is reached. The reaction time significantly influences the cellulose yield; thus, at a certain point, the maximum cellulose yield will be achieved. This phenomenon occurs because the longer reaction time allows for greater particle contact, resulting in a larger quantity of cellulose produced. During the pretreatment process, bonds within the lignocellulose structure are broken, leading to the degradation and dissolution of lignin, while the cellulose content increases.

However, excessively long durations beyond the point of maximum cellulose yield can lead to reduced cellulose due to increased dissolution of substances during the process, potentially damaging the cellulose chain (Rahayu *et al.,* 2022). Omar and Amin (2016) noted a similar phenomenon, stating that prolonged ozonation-ultrasound times could lead to excessive lignin degradation, followed by potential degradation of hemicellulose and cellulose.

In this study, longer pretreatment times with the hybrid ozonation-ultrasonic method resulted in higher percentages of lignin degradation. The highest cellulose yield was achieved at pH 6 for 90 minutes, reaching 55.2%. This was followed by cellulose yields of 54.7% and 50.9% at pH 5 and pH 4, respectively, for the same duration.

3.3 Effect of pH of Ozonation-Ultrasound Pretreatment on Cellulose Content in Oil Palm Fiber

The pretreatment process aimed at obtaining cellulose was significantly influenced by the solution pH, which had to be adjusted to facilitate effective lignin degradation. Based on previous research conducted by Anggoro (2022), utilizing Ultrasound-Advanced Oxidation Processes on palm oil fibers, the optimum time was found to be 60 minutes, at a pH of 9–10. However, in this study, it was carried out at pH 4, 5, and 6 with a duration of 70, 80, and 90 minutes, respectively. To examine the effect of solution pH, the pretreatment process was conducted at 30°C with an ozone flow rate of 2 L/min. The effect of solution pH on the resulting cellulose percentage is illustrated in Figure 2.

This study demonstrated that the hybrid ozonation-ultrasonic method yielded an increasing percentage of cellulose with higher solution pH values. Figure 1. indicates the highest cellulose percentage at pH 6, with a processing time of 90 minutes. As the solution became more alkaline, signifying a higher pH, lignin degradation intensified, thereby enhancing cellulose yield.

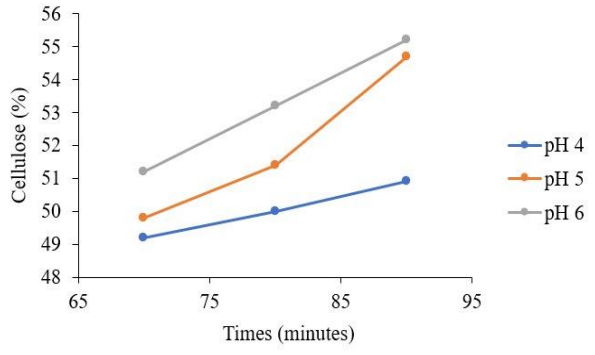

Fig 1. Effect of ozonation-ultrasonic pretreatment time on cellulose percentage

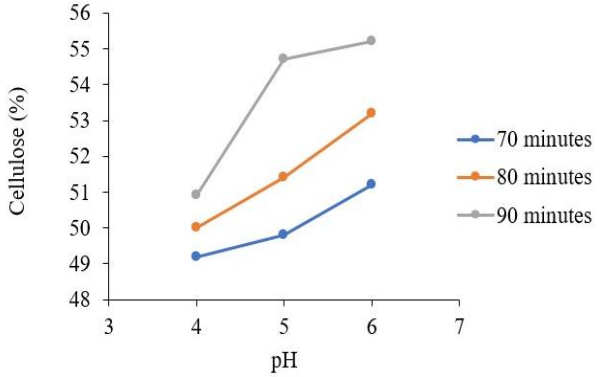

Fig 2. Effect of pH of ozonation-ultrasonic pretreatment on cellulose percentage

In the degradation of complex compounds, ozone-based advanced oxidation methods operate through direct and indirect mechanisms contingent upon the solution's pH (Pratiwi *et al,* 2024). Direct oxidation involves ozone molecules facilitating oxidation, primarily effective in acidic conditions (pH < 5). Conversely, indirect oxidation relies on hydroxyl radicals (•OH) generated from ozone decomposition that are effective in alkaline conditions (>7 pH) (Anggoro *et al*., 2023). Solution pH is pivotal in ozonation-ultrasound pretreatment, regulating mass transfer and O3 decomposition (Rekhate & Srivastava, 2020). Lower pH levels promote ozone stability and prolong ozone half-life, favoring direct oxidation utilizing ozone molecules in lignin degradation within lignocellulosic biomass (Hirahara *et al*., 2019). However, low pH conditions may lead to glycoside bond cleavage, resulting in holocellulose component degradation, thus reducing cellulose yield (Maqsood *et al*., 2017). Furthermore, higher solution pH values diminish ozone half-life, necessitating a certain duration to achieve the oxidation effect. Alkaline conditions foster hydroxyl radicals (•OH) formation, facilitating indirect oxidation primarily through hydroxyl radicals in lignin degradation within lignocellulosic biomass (Galdeano *et al*., 2018).

In this study, elevated pH conditions in the hybrid ozonation-ultrasonic method correlated with increased lignin degradation percentages, as the oxidation process predominantly relied on hydroxyl radical compounds (•OH) generated from ozone decomposition, exhibiting a greater oxidation potential (2.80 eV) than ozone (2.07 eV). Consequently, delignification under high pH conditions (indicative of alkalinity) resulted in enhanced lignin degradation percentages and increased cellulose yield with increasing solution pH (Palomares-Reyna *et al.,* 2022). Thus, solution pH emerged as a crucial determinant, influencing the reaction pathway in ozone-based advanced oxidation methods and ultimately affecting the cellulose percentage in the obtained product.

3.4 FTIR Analysis of Cellulose and Palm Fiber

FTIR analysis was conducted on commercial cellulose products and palm fiber subjected to ozonation-ultrasonic hybrid pretreatment to observe the functional groups in the lignocellulosic biomass. The functional group analysis was performed by interpreting the absorption peaks within the infrared spectrum. The results of the FTIR analysis are presented in the Figure.3

The FTIR analysis revealed that the hybrid ozonation-ultrasonic pretreated palm fiber and the commercial cellulose products exhibited relatively similar absorption peaks, indicative of similar functional group compositions. However, discernible differences in the absorption peaks were observed between the materials, particularly in minor absorption peaks at certain wavenumbers. Additionally, the FTIR analysis demonstrated the presence of cellulose functional groups, including -OH, C-H, C=O, C=C, and C-O-C bonds (Pratama *et al*., 2019).

The FTIR analysis of palm fiber subjected to hybrid ozonation-ultrasonic pretreatment revealed distinctive peaks corresponding to various functional groups. Specifically, O-H bonds were identified at a wave number of 3332.22 cm^{-1}, C-H bonds at 2890.80 cm^{-1}, C=O bonds at 1408.04 cm^{-1}, C=C bonds at 1593.55 cm^{-1}, and C-O-C bonds at 1028.27 cm^{-1}. The presence of O-H bonds was further evidenced by broad absorption peaks between wave numbers 3200 cm^{-1} and 3400 cm^{-1}, indicating the presence of O-H bonds. This characteristic feature was observed as a broad peak absorption at the wave number of 3332.22 cm^{-1}, corresponding to cellulose hydroxyl groups. The presence of these hydroxyl groups in cellulose led to intramolecular shifts due to hydrogen bonding. Additionally, the C-H group was identified at a peak wave of 2890.80 cm^{-1}, representing an aldehyde C-H group typically observed within the range of 2800 cm^{-1} and 2900 cm^{-1} (Salimi *et al.,* 2021).

The FTIR analysis also revealed two absorption peaks between 1400 cm^{-1} and 1600 cm^{-1}. The peak at 1593.55 cm^{-1} indicated the presence of C=C groups within the aromatic ring of lignin, suggesting the presence of lignin residues within the cellulose structure. Additionally, the peak at 1408.04 cm^{-1} indicated the presence of C=O groups associated with hemicellulose (Nurjannah *et al.,* 2019). This finding suggested that the ozonation-ultrasonic pretreatment might not have optimally degraded lignin, particularly under acidic conditions. Furthermore, the absorption peak of 1028.27 cm^{-1} indicated stretching within the C-O-C pyranose ring, suggesting an increase in the crystalline value of cellulose (Adha & Dewi, 2022).

3.5 XRD Analysis of Cellulose and Palm Fiber

XRD analysis assessed the crystallinity of cellulose derived from oil palm fiber subjected to ultrasonic ozonation treatment. Crystallinity, typically assessed using the crystallinity index, was

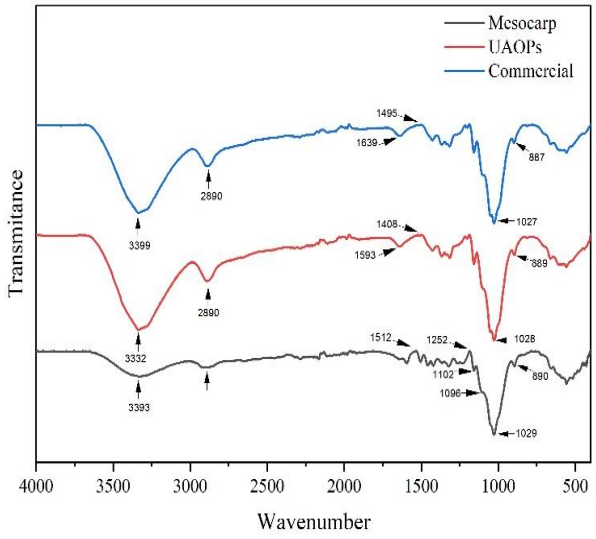

Fig 3. FTIR analysis results

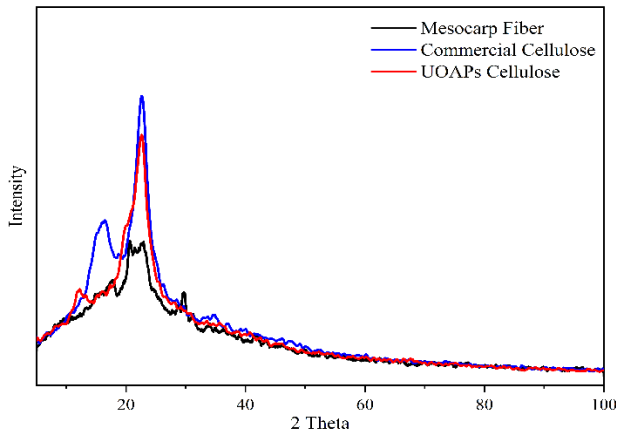

Fig 4. XRD analysis results

employed to determine the degree of crystallinity in the cellulose samples. The XRD analysis results for palm fiber cellulose are presented in Figure 4.

As depicted in Figure 4, the XRD pattern exhibits prominent peaks at 2θ angles, particularly around 17° and 23°, corresponding to amorphous and crystalline regions, respectively. Notably, at 2θ = 23°, untreated palm fiber demonstrates broader and more sloping peaks, whereas treated palm fiber exhibits sharper and narrower peaks. Commercial cellulose also displays sharper peaks, indicating a higher crystallinity level in commercial cellulose and ultrasonically ozonated palm fiber (Nordin *et al.,* 2013).

The crystallinity index of untreated palm fiber was measured at 5.48, which increased to 6.35 after ultrasonic ozonation pretreatment. The low crystallinity of untreated palm fiber could be attributed to high levels of hemicellulose and lignin, which bind to cellulose. The observed increase in crystallinity index in untreated palm fiber was attributed to the removal of hemicellulose and lignin, facilitating cellulose rearrangement (Yasim-Anuar *et al*., 2017). However, the low increase in cellulose crystallinity was attributed to the suboptimal conditions of the ozonation-ultrasonic pretreatment process carried out under acidic conditions, limiting optimal lignin degradation.

3.6 SEM Analysis of Cellulose and Palm Fiber

Scanning Electron Microscope (SEM) analysis was employed to examine the surface morphology of palm fiber samples. In Figure 5 (A), the palm fiber biomass exhibits a dense, smooth, and regular structure without apparent breakage, indicating the presence of lignin, hemicellulose, and other binding components within the cellulose (Ni'mah *et al.,* 2015). Conversely, Figures 5 (B) and 5 (C) reveal perforations in the cell wall, signifying lignin degradation resulting from the pretreatment process involving ozonation and ultrasonic methods. The ultrasonic method facilitated lignin degradation by increasing mass transfer and inducing cavitation, where bubbles rapidly formed, expanded, and burst, generating localized hotspots that disrupted the biomass structure (Lee *et al*., 2022).

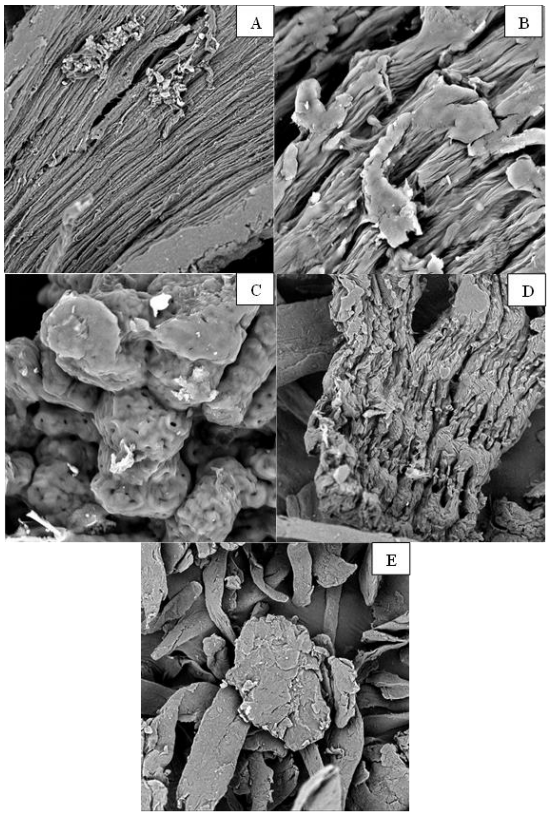

Fig 5. SEM analysis results of (A) Oil palm fiber, (B) Ozonated cellulose, (C) Ultrasonic cellulose, (D) Ultrasonic/ozonated cellulose, and (E) Commercial cellulose

Similarly, ozonation involved using ozone molecules or hydroxyl radicals (•OH) to oxidize lignin compounds. Figure 5 (D) illustrates the damaged biomass structure of oil palm fiber following hybrid ozonation-ultrasonic treatment, which closely resembles the morphology of commercial cellulose depicted in Figure 5 (E). The lignocellulosic structure experienced many perforations and damage due to lignin degradation after the delignification process using the ozonation-ultrasonic hybrid method. The hybrid ozonation-ultrasonic method appears to have a better effect on the damage of the structure of lignocellulosic biomass, compared with the ozonation and ultrasonic processes alone. This indicates that the hybrid treatment method effectively degraded lignin, resulting in an improved biomass fiber structure compared to individual ultrasonic or ozonation methods. Overall, the hybrid ozonation-ultrasonic method demonstrated enhanced efficacy in lignin degradation, as evidenced by SEM analysis.

4. Conclusion

The hybrid ozonation-ultrasonic pretreatment process aimed at degrading lignin in oil palm fiber biomass demonstrated promising outcomes, resulting in a high cellulose content in the palm fiber. This underscores the potential applicability of the ozonation-ultrasonic hybrid method. Optimal conditions were identified with a solution pH of 6 and a processing time of 90 minutes, yielding a cellulose content of 55.2% processed using the Chesson-Datta method. Solution pH emerged as a crucial factor, with superior results observed under higher pH conditions. FTIR analysis revealed two absorption peaks, indicating the presence of the C=C group on the aromatic ring of lignin, suggesting its residual presence within the cellulose. Additionally, an absorption peak corresponding to the C=O group indicated the existence of hemicellulose. These findings suggest that the ozonation-ultrasonic pretreatment process under acidic solution conditions was suboptimal, as complete lignin degradation was not achieved. This is further supported by the low increase in cellulose crystallinity, attributed to the less-than-optimal ozonation-ultrasonic pretreatment conducted under acidic conditions, hindering optimal lignin degradation. However, significant changes in the surface structure of lignocellulosic biomass were evident through SEM analysis, demonstrating the efficacy of the ozonation-ultrasonic hybrid method. Therefore, this research serves as a reference, highlighting the limitations of acidic solution conditions for the hybrid ozonation-ultrasonic method in achieving significant lignin degradation and cellulose content.

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References

Abdullah, A., Hamid, H., Christwardana, M., & Hadiyanto, H. (2018). Optimization of Cellulase Production by Aspergillus niger ITBCC L74 with Bagasse as Substrate using Response Surface Methodology. *HAYATI Journal of Biosciences*, 25(3), 115. https://doi.org/10.4308/hjb.25.3.115

Anggoro, D. D., Dewi, I. K., & Prasetyaningrum, L. B. A. (2023). Parametric Optimization Of Oil Palm Mesocarp Fiber Valorization With Hybrid Ozonation-Ultrasonic Pretreatment Method. *Ium Engineering Journal*, *24*(2), 45–66. https://doi.org/10.31436/iiumej.v24i2.2717

Anggoro, D.D, Buchori, L., Kusuma Dewi, I., & Prasetyaningrum, A. (2022). The Effect Of Ozonation, Ultrasonic, And Hybrid Ozonation-Ultrasonic Pretreatment Methods On The Delignification Of Oil Palm Mesocarp Fibers. *International Journal of Advanced Research*, *10*(12), 194–204. https://doi.org/10.21474/IJAR01/15827

Asyraf, M. R. M., Ishak, M. R., Syamsir, A., Nurazzi, N. M., Sabaruddin, F. A., Shazleen, S. S., Norrrahim, M. N. F., Rafidah, M., Ilyas, R. A., Rashid, M. Z. A., & Razman, M. R. (2022). Mechanical properties of oil palm fibre-reinforced polymer composites: a review. In *Journal of Materials Research and Technology*, 17, 33–65. https://doi.org/10.1016/j.jmrt.2021.12.122

Boczkaj, G., Gągol, M., Klein, M., & Przyjazny, A. (2018). Effective method of treatment of effluents from production of bitumens under basic pH conditions using hydrodynamic cavitation aided by external oxidants. *Ultrasonics Sonochemistry*, *40*(August 2017), 969–979. https://doi.org/10.1016/j.ultsonch.2017.08.032

Fuertez-Córdoba, J. M., Acosta-Pavas, J. C., & Ruiz-Colorado, Á. A. (2021). Alkaline delignification of lignocellulosic biomass for the production of fermentable sugar syrups. *DYNA (Colombia)*, *88*(218), 168–177. https://doi.org/10.15446/dyna.v88n218.92055

Galdeano, M. C., Wilhelm, A. E., Goulart, I. B., Tonon, R. V., Freitas-Silva, O., Germani, R., & Chávez, D. W. H. (2018). Effect of water temperature and pH on the concentration and time of ozone saturation. *Brazilian Journal of Food Technology*, *21*. https://doi.org/10.1590/1981-6723.15617

Hirahara, Y., Iwata, K., & Nakamuro, K. (2019). Effect of Citric Acid on Prolonging the Half-life of Dissolved Ozone in Water. *Food Safety*, *7*(4), 90–94. https://doi.org/10.14252/foodsafetyfscj.d-19-00005

Ikhwanul Adha, M., & Dewi, R. (2022). Jurnal Iptek Media Komunikasi Teknologi Experimental Study Of Cellulose Extraction From Oil Palm Empty Fruits Bunches. *Jurnal IPTEK*, *26*(1). https://doi.org/10.31284/j.iptek.2022.v26i1.2

Kıdak, R., & Doğan, Ş. (2018). Medium-high frequency ultrasound and ozone based advanced oxidation for amoxicillin removal in water. *Ultrasonics Sonochemistry*, *40*, 131–139. https://doi.org/10.1016/j.ultsonch.2017.01.033

Kong, S. H., Loh, S. K., Bachmann, R. T., Rahim, S. A., & Salimon, J. (2014). Biochar from oil palm biomass: A review of its potential and challenges. *Renewable and Sustainable Energy Reviews*, *39*, 729–739. https://doi.org/10.1016/J.RSER.2014.07.107

Kumar, A. K., & Sharma, S. (2017). Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. In *Bioresources and Bioprocessing*, 4(1).. https://doi.org/10.1186/s40643-017-0137-9

Kumari, D., & Singh, R. (2018). Pretreatment of lignocellulosic wastes for biofuel production : A critical review. *Renewable and Sustainable Energy Reviews*, *90*(March), 877–891. https://doi.org/10.1016/j.rser.2018.03.111

Kurniawan, E. W. (2020). Proses Optimasi Produksi Bioetanol dari Limbah Serat Buah Sawit dengan Metode SHF. *Buletin Loupe*, *16*(01), 60–67. https://doi.org/10.51967/buletinloupe.v16i01.77

Laghari, S. M., Hasnain Isa, M., & Jabbar Laghari, A. (2016). Delignification Of Palm Fiber By Microwave Assisted Chemical Pretreatment For Improving Energy Efficiency. In *Malaysian Journal of Science* 35(1), 8-14. https://doi.org/10.22452/mjs.vol35no1.2

Lee, K. M., Quek, J. D., Tey, W. Y., Lim, S., Kang, H. S., Quen, L. K., Mahmood, W. A. W., Jamaludin, S. I. S., Teng, K. H., & Khoo, K. S. (2022). Biomass valorization by integrating ultrasonication and deep eutectic solvents: Delignification, cellulose digestibility and solvent reuse. *Biochemical Engineering Journal*, *187*. https://doi.org/10.1016/j.bej.2022.108587

Lismeri, L., Zari, P. M., Novarani, T., & Darni, Y. (2016). Sintesis Selulosa Asetat dari Limbah Batang Ubi Kayu. *Jurnal Rekayasa Kimia & Lingkungan*, *11*(2), 82. https://doi.org/10.23955/rkl.v11i2.5407

Maqsood, H. S., Bashir, U., Wiener, J., Puchalski, M., Sztajnowski, S., & Militky, J. (2017). Ozone treatment of jute fibers. *Cellulose*, *24*(3), 1543–1553. https://doi.org/10.1007/s10570-016-1164-y

Ni'mah, L., Ardiyanto, A., & Zainuddin, M. (2015). Pembuatan Bioetanol Dari Limbah Serat Kelapa Sawit Melalui Proses Pretreatment, Hidrolisis Asam Dan Fermentasi Menggunakan Ragi Tape. *INFOTEKNIK: Jurnal Keilmuan dan Aplikasi Teknik*,16(2), 227-242. http://dx.doi.org/10.20527/infotek.v16i2.206

Nordin, N. I. A. A., Ariffin, H., Andou, Y., Hassan, M. A., Shirai, Y., Nishida, H., Yunus, W. M. Z. W., Karuppuchamy, S., & Ibrahim, N. A. (2013). Modification of oil palm mesocarp fiber characteristics using superheated steam treatment. *Molecules*, *18*(8), 9132–9146. https://doi.org/10.3390/molecules18089132

Omar, W.N.N. and Amin, N.A.S. (2016). Multi Response Optimization of Oil Palm Frond Pretreatment By Ozonolysis. *Industrial Crops and Products*, 85, 389–402. https://doi.org/10.1016/j.indcrop.2016.01.027

Palomares-Reyna, D., Carrera-Crespo, J. E., Sosa-Rodríguez, F. S., García-Pérez, U. M., Fuentes-Camargo, I., Lartundo-Rojas, L., & Vazquez-Arenas, J. (2022). Photo-electrochemical and ozonation process to degrade ciprofloxacin in synthetic municipal wastewater, using C, N-codoped TiO2with high visible-light absorption. *Journal of Environmental Chemical Engineering*, *10*(3). https://doi.org/10.1016/j.jece.2022.107380

Pratama, J. H., Rohmah, R. L., Amalia, A., & Saraswati, T. E. (2019). Isolasi Mikroselulosa dari Limbah Eceng Gondok (Eichornia crassipes) dengan Metode Bleaching-Alkalinasi. *ALCHEMY Jurnal Penelitian Kimia*, *15*(2), 239. https://doi.org/10.20961/alchemy.15.2.30862.239-250

Pratiwi, W.Z., Hadiyanto, H., Widayat, W. (2024). Response surface optimization of UV/H2O2-based photo-oxidative degradation of amoxicillin. *Results in Engineering*, 21, 101836, https://doi.org/10.1016/j.rineng.2024.101836

Rahayu, A., Hanum, F. F., Amrillah, N. A. Z., Lim, L. W., & Salamah, S. (2022). Cellulose Extraction from Coconut Coir with Alkaline Delignification Process. *Journal of Fibers and Polymer Composites*, *1*(2), 106–116. https://doi.org/10.55043/jfpc.v1i2.51

Rekhate, C. V., & Srivastava, J. K. (2020). Recent advances in ozone-based advanced oxidation processes for treatment of wastewater- A review. In *Chemical Engineering Journal Advances*, 3. https://doi.org/10.1016/j.ceja.2020.100031

Rita Nurjannah, N., Sudiarti, T., Lena Rahmidar, D., Kimia, J., Sains dan Teknologi, F., & Sunana Gunung Djati Bandung, U. (2019). Sintesis Dan Karakterisasi Selulosa Termetilasi Sebagai Biokomposit Hidrogel. *Al Kimiya: Jurnal Ilmu Kimia dan Terapan*, 7 (1), 19-27. https://doi.org/10.15575/ak.v7i1.6490

Rosdiana, R., Apriyanto, E., Santika, A. (2021). Potensi serat limbah buah sawit sebagai media tanam untuk pertumbuhan dan produksi tanaman pakcoy (Barassica rapa L.). *Jurnal agrosains dan teknologi*, 6(2). https://jurnal.umj.ac.id/index.php/ftan/article/download/9971/6361

Saka, M., Munusamy, M., Shibata, Y., Tono, & Miyafuji, H. (2008). Chemical constituents of the different anatomical parts of the oil palm (Elaeis guineensis) for theis sustainable utilization. *Natural Resources and Energy Environtment, JSPS-VCC Program on Environmental Science, Engineering and Ethics (Group IX)*, 19–34.

Salimi, Y. K., Hasan, A. S., & Botutihe, D. N. (2021). Sintesis dan Karakterisasi Carboxymethyl Cellulose Sodium (Na-CMC) dari Selulosa Eceng Gondok (Eichhornia crassipes) dengan Media Reaksi Etanol-Isobutanol. *Jambura Journal of Chemistry*, *3*(1), 1–11. https://doi.org/10.34312/jambchem.v3i1.9288

Shen, Y., Xu, Q., Wei, R., Ma, J., & Wang, Y. (2017). Mechanism and dynamic study of reactive red X-3B dye degradation by ultrasonic-assisted ozone oxidation process. *Ultrasonics Sonochemistry*, *38*, 681–692. https://doi.org/10.1016/j.ultsonch.2016.08.006

Taharuddin, T., Iryani, D. A., & Eka Wahyu, M. (2018). Influence of Oil Content on Solution Load Ethanol-Soda Delignification of Oil

Palm Mesocarp Fiber. *Jurnal Rekayasa Kimia & Lingkungan*, *13*(2), 200–208. https://doi.org/10.23955/rkl.v13i2.11145

Travaini, R., Otero, M. D. M., Coca, M., Da-Silva, R., & Bolado, S. (2013). Sugarcane bagasse ozonolysis pretreatment: Effect on enzymatic digestibility and inhibitory compound formation. *Bioresource Technology*, *133*, 332–339. https://doi.org/10.1016/j.biortech.2013.01.133

Wu, J., Upreti, S., & Ein-Mozaffari, F. (2013). Ozone pretreatment of wheat straw for enhanced biohydrogen production. *International Journal of Hydrogen Energy*, *38*(25), 10270–10276. https://doi.org/10.1016/j.ijhydene.2013.06.063

Xiong, X., Wang, B., Zhu, W., Tian, K., & Zhang, H. (2019). A review on ultrasonic catalytic microbubbles ozonation processes: Properties, hydroxyl radicals generation pathway and potential in application. In *Catalysts*, 9,(1). https://doi.org/10.3390/catal9010010

Yasim-Anuar, T. A. T., Ariffin, H., Norrrahim, M. N. F., & Hassan, M. A. (2017). Factors affecting spinnability of oil palm mesocarp fiber cellulose solution for the production of microfiber. *BioResources*, *12*(1), 715–734. https://doi.org/10.15376/biores.12.1.715-734