The effect of Ozonation on the chemical structure of microplastics

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Abstract. Microplastics are not susceptible to microbial degradation, thus often end up in aquatic ecosystem. Moreover, microplastics cause danger to aquatic biota and human. Effective technological solutions to degrade microplastics in wastewater treatment plants are desirable. Biodegradation is one of the most applied techniques, but takes a long time. This study evaluates the ozonation as pre-treatment to transform the chemical structure of polyethylene microplastics into more susceptible to biodegradation. The process was done by using a corona-discharge ozonator and batch reactor, varied pH value (6, 7, 8, 10, 12), ozone flowrate (1, 3, 5 L/min), and contact duration (1, 2, 3 hours). The study was begun by quantification of OH radicals and dissolved ozone, ozonation of microplastics, evaluation of ozonation by gravimetric weight loss including the change of microplastics chemical structure through FT-IR (Fourier Transform Infrared). The results revealed chemical structure changes of polyethylene after ozonation confirmed by the appearance of carbonyl bonds and the loss of weight. The optimum operating condition appeared at pH 12 with 5 L/min ozone flowrate, resulted in 0.0482% weight loss and carbonyl bond intensity reached 104.556% after 3 hours ozonation.

Keywords: Biodegradation, microplastics, ozone, ozonation, polyethylene

1. Introduction

Nowadays plastics have transformed human daily life. The high rising production of plastics in line with the waste generation. Often plastics waste ends up in aquatic ecosystems. It has been revealed that Indonesia is the second country with the highest amount of plastics waste in the oceans [1]. Plastic debris may be broken down and become microplastics (MPs) in the size range of 0.001 - 5 mm [2]. Microplastics originate from two sources, primary and secondary. Primary MPs are intentionally manufactured, usually for toothpaste, exfoliating facial scrubs, resin pellets, etc. Secondary MPs are formed from the breakdown of larger plastics, come from household appliances, plastic bags, etc. Microplastics are not easily removed owing to the recalcitrance to microbial degradation. Moreover, microplastics have the potential to transfer chemicals and endanger aquatic biota and human, resulting from ingestion.

One of the solutions to reduce the microplastics contaminants in aquatic ecosystems is through Wastewater treatment plants (WWTPs). However, the technologies in WWTPs have not been able to completely remove microplastics [3]. Biodegradation is the most widely applied treatment for organic compounds waste. However, it takes longer time than physical or chemical methods. Therefore, to
increase the efficiency of biodegradation, pre-treatment of abiotic degradation is necessary [4]. Ozonation as pre-treatment allows the reaction not merely between microplastics and ozone (direct reaction), however reaction between microplastics with OH radicals as a result of ozone decomposition in water also occurs (indirect reaction). Tian, et al. (2017) revealed ozonized polystyrene (β-14C) before incubation with *Penicillium variabile* degraded microplastics higher than the non-ozonized [5]. The result suggested ozone pre-treatment ability to change the polymer chemical structure into shorter chains, thus more susceptible to biodegradation [6].

In the present study, we evaluated the potential of ozonation pre-treatment to transform the chemical structure of polyethylene (PE) microplastics into more susceptible to biodegradation. PE was known as the most commonly found non-biodegradable solid waste [7]. Pratama obtained the optimal reduction of oil content was at the highest ozone dose, namely 0.53 g/hour and the highest pH, namely pH 8, suggesting the effect of pH and ozon dosage variation [8]. This study was varied on the initial pH value (6, 7, 8, 10, 12), ozone flow rate (1, 3, 5 L/min), and contact duration among ozone and microplastics (1, 2, 3 hours). Result parameters were seen based on the gravimetric weight loss, associated with the changes in the chemical structure which will be analyzed by FT-IR (Fourier Transform Infrared), and pH changes.

2. Materials and Methods

2.1 Microplastics

Microplastics used were commercial polyethylene powder with white color and a size of 20 mesh. The microplastic was weight for 0.5000 g and mixed with 200 mL aquadest.

2.2 Preparation Stage

The preparation stage was divided into the ozonator productivity test using Iodometric titration method, ozone flow rate calibration, hydroxyl (OH) radical quantification through permanganate titration method, and ozone solubility test in water. The ozone dissolved was carried out using Merck Ozone Reagent Test Kit No. 100607 and the UV VIS Spectrophotometer.

2.3 Microplastics Ozonation

Process was done in batch system. The equipment used at this phase was ozonator HYPRO GJ-8002K and Erlenmeyer Pyrex 250 mL as batch reactor. The equipment was arranged according the following scheme.

![Figure 1. Schematic tool of the ozonation process](image-url)
2.4 Determination of Weight Loss of PE Microplastics

The procedure was validated based on research by Auta, et al. (2018) [9]. The ozonized microplastics in aquadest were filtered by Whatman grade 41 filter paper and dried in a hot-air oven BIOBASE BOV-T50F at 105 °C for 4 hours. The residual polymer weight measured to determine the weight loss using the AND GR-200 analytical balance with a readability of 0.0001 g. The weight loss of the PE microplastics in percentage was determined using Eq. 1:

\[ \%W = \frac{W_0 - W_x}{W_0} \times 100\% \]  

where \( W_0 \) is the initial weight of the microplastics (g) and \( W_x \) is the weight of microplastics after ozonation (g).

2.5 Fourier transform infrared (FTIR) analysis of Microplastics

The changes in the chemical structure of the microplastics were analyzed using Nicolet iS 5 FT-IR (Fourier Transform Infrared) Spectrometer in the frequency range of 4000–450 cm\(^{-1}\).

2.6 pH Change Measurement

pH after ozonation was a key factor of microorganisms’ activity in the next biodegradation process [8]. The pH change was calculated by subtracting the final pH of the ozonized microplastic solution with initial condition using pH meter ST 20. The result then was analysed to recommend the optimal condition since most of the bacteria living in soil or aquatic ecosystems grow and work optimally in a pH range of 6-8 [10].

3. Result and Discussion

3.1 Preparation Stage

The ozonator HYPRO GJ-8002K has an average of 262.4 mg/h productivity. Due to the incremental of flow rate, the production rate of ozone increased, namely 64.8 mg/h, 118.8 mg/h, and 248.4 for 1, 3, 5 L/min respectively. Furthermore, the longer contact duration resulted lower productivity. The ozonation procedure was firstly varied by initial pH solution during 1, 2, 3 hours with constant flowrate of 3 L/min.

Then the ozonized microplastics were observed by final pH condition to determine the constant value of pH in ozone flowrate variation. pH 12 was selected due to the lowest pH changes in the range of base. The quantification of OH radical increased along with the high pH, ozone flowrate, and contact duration. As for dissolved ozone concentration tended to be unstable. However, on average, the concentration in alkaline was less than acidic and neutral conditions. Higher ozone flowrate resulted greater dissolved ozone in the solution.

3.2 Weight loss of PE microplastics

The weight loss of the PE microplastics results are presented in Fig 2.

![Figure 2. Effect of pH (a) and ozone flowrate (b) on weight loss of microplastics](image)

The graphics showed the effect of pH, ozone flowrate, and contact duration. As pH value increased, the weight loss of microplastics increased as a result of higher number of OH radicals. Likewise, higher ozone flowrate and longer contact duration resulted higher weight loss percentage. Even so, fluctuated
results occurred due to the decreasing of ozonator productivity and the possibility for sample to contact with air during gravimetric procedure.

In different study, Auta, et al. (2018) obtained the highest weight loss reached 6.40% in granular polypropylene after UV pre-treatment and 40 days of incubation with Rhodococcus sp. strain 36 [9]. Middleton, et al. (2013) showed ozonation process reduce the weight of polymers up to 0.30% after 28 days of ozone injection [11]. In the present study, the highest weight loss of PE microplastics was 0.53%. The lower yields compared to previous studies were due to differences in the variation in the duration of contact with the degrading agent.

The weight loss was a result of polymer molecules attacked by ozone and the loss of certain properties, hence hinting at the physical breakdown and degradation of polymers [12]. FT-IR analysed the presence of missing groups. In all samples varied by pH, absorption peaks were disappeared at 1059.73; 1135.61; 1182.29; and 1212.96 cm⁻¹, were attributed to the C-O group. The S = O and C = C groups assigned 1400.05 and 1635.61 cm⁻¹ were also disappeared. At flowrates of 1 and 3 L / minute, the presence of missing C-O groups was marked at 1059.73; 1135.61; 1212.96 cm⁻¹. The S = O and C = C groups assigned 1400.05 and 1635.61 cm⁻¹ were also disappeared in all samples varied by flowrate.

In addition to the FT-IR, the cause of weight loss has observed by the Olympus CX41 microscope with the finding of cavity in microplastics surface. Tian, et al. (2015) supported the results of the rough and hollow of Polystyrene through SEM (Scanning Electron Microscopy), followed by the reduction of molecular weight using GPC (Gel Permeation Chromatography), indicates chain cutting [13] and polymer degradation after ozonation and biodegradation.

3.3 Fourier transform infrared (FTIR) analysis of Microplastics

The infrared bands of polyethylene were the CH₂ asymmetric and symmetric appear at 2917 and 2852 cm⁻¹, respectively. CH₂ scissoring vibration at 1468 cm⁻¹ and rocking vibration at 718 cm⁻¹ [14]. The reactions of ozone and polyethylene explained by Kefeli, et al. (1971) [15]:

\[
\begin{align*}
RH + O_3 & \rightarrow RO\cdot + OH^* \\
RO\cdot + RH & \rightarrow ROOH + R^* \\
R^* + O_2 & \rightarrow ROO^* \\
ROOH + O_3 & \rightarrow RO\cdot + O_2 + OH^* \\
RO\cdot & \rightarrow \text{product} + \cdot R \\
2\cdot R & \rightarrow \text{product}
\end{align*}
\]

Based on the above reaction, the peroxide radical (RO•₂) was generated as a result of the interaction of polyethylene with ozone then led to the formation of carbonyl, carboxyl, and hydro peroxide. Below FT-IR spectrum was presented based on the position of new carbonyl, suggested by Tian, et al. (2015) as the evidence of polymer degradation. The carbonyl (C = O) were identified at wavenumbers 1650-1818 cm⁻¹. Figure 3 shows the effect of pH on the appearance of carbonyl groups after 3 hours ozonation.

![Figure 3. Effect of pH on the appearance of carbonyl groups in the FT-IR spectrum (Flowrate = 3 L/min; contact duration = 3 hours)](image-url)
The FT-IR spectra showed the presence of a carbonyl absorption band at pH 6, 10, and 12, specifically ketones, aldehyde, and carboxylic acid, respectively. pH 10 as the second highest number of OH radical and dissolved ozone, had the highest carbonyl intensity with 107.77% of transmittance. The addition of a new group was formed at 3200 - 3700 cm\(^{-1}\), was assigned to the OH stretching band on samples varied by pH. Although pH 7 and 8 had no carbonyl found, evidence of PE changes could be seen from the new O-H bands. Compared with control sample, the transmittance of the CH\(_2\) group stretching at pH 6, 7, 8, and 12 decreased, indicates the increase of CH\(_2\) intensity, corresponding with Vimala & Mathew [16]. On the contrary, CH\(_2\) stretching vibration at pH 10 was higher than control sample. This likely due to the formation of carbonyl bonds with the highest intensity. Figure 4 shows the effect of ozone flowrate on the appearance of carbonyl groups after 3 hours ozonation.

![Figure 4](image1.png)

**Figure 4.** Effect of flowrate on the appearance of carbonyl groups in the FT-IR spectrum (pH = 12, contact duration = 3 hours)

The carbonyl group was formed in flowrate of 3 and 5 L/min, specifically ketones and aldehyde, respectively. The flowrate of 5 L/min with second highest number of OH radicals and highest dissolved ozone has the greatest carbonyl intensity. Even so, the flowrate of 1 L/min with no carbonyl found, has the highest C-H groups reduction. Samples with 5 L/min had the most frequent O-H stretching groups appearance, followed by 3 L/min and 1 L/min. Another new group is C = C (alkene) at 1 and 5 L/min. Figure 5 shows the effect of contact duration on the appearance of carbonyl groups at pH 12 and 5 L/min ozone flowrate.

![Figure 5](image2.png)

**Figure 5.** Effect of contact duration on the appearance of carbonyl groups in the FT-IR spectrum (pH = 12, flowrate = 5 L/min)
Carbonyl groups were only formed after 3 hours ozonation. Furthermore, the intensity of the CH₂ rocking, scissoring, and stretching increased with the longer contact duration.

3.4 pH Changes Measurement
Based on research, the ozonation process resulted in a decrease of pH, indicated the intermediate product formed. All samples in the study obtained acidic conditions, except sample at pH 12. ΔpH at pH 12 was the smallest in the range 0.21-2.63 after 3 hours ozonation. The highest ΔpH was 7.10 which occurred at pH 10. Therefore, based on the pH final condition value and high carbonyl intensity, the optimal condition concluded at pH 12 with a flowrate of 5 L/min during 3 hours ozonation. In this condition, if the ozone level to be enlarged, the final pH possibly obtained are just in the range 6-8, namely the optimum pH range for bacteria to live in biodegradation process.

4. Conclusion
The ozonation process has been shown to showed changes of the chemical structure of polyethylene microplastics along with the influence on pH, ozone flow rate and contact duration among ozone and microplastics. Result study obtained the escalation in the weight loss and the structural changes of polyethylene microplastics using FT-IR, confirmed by the disappearance of certain groups and carbonyl groups (ketone, aldehyde, alcohol, and carboxylic acid) appearance. These changes pointed to the ability of the polymer fragment resulted from ozonation to be more accessible to biodegradation process. Based on the pH final condition and high carbonyl intensity formed, the optimal conditions occurred at pH 12 with a flowrate of 5 L/min during 3 hours ozonation. This condition was obtained pH range 6-8, namely the optimum pH range for bacteria to live in biodegradation process.

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References
[1] Jambeck J, Geyer R, Wilcox C, Siegler T, Perryman M, Andrady A, Narayan R and Law K 2015 Science 347 768–71
[2] Shim W J, Hong S H and Eo S 2018 Microplastic Contamination in Aquatic Environments 1–26
[3] Talvitie J, Mikola A, Koistinen A and Setälä O 2017 Water Research 123 401–7
[4] Onodera K, Mukamoto H, Katsuyaya Y, Saiganji A, Tani Y 2001 Polym Degrad Stabil 72 323–327
[5] Tian L., Kolvenbach B, Corvini N, Wang S, Tavanaie N, Wang L and Ji R 2017 New Biotechnology 38 101–5
[6] Cortez S, Teixeira P, Oliveira R and Mota M 2011 Journal of Environmental Management 92 749–755
[7] Harshvardhan K and Jha B 2013 Marine Pollution Bulletin 77 100–6
[8] Pratama F A M 2013 Tesis Fakultas Teknik Universitas Indonesia
[9] Auta H, Emikenie C, Jayanthi B and Fauzia S 2018 Marine Pollution Bulletin 12715-21
[10] Yani R B 2016 Skripsi Universitas Andalas
[11] Middleton J, Burks B, Wells T, Setters A M, Jasiuk I, Predecki P, Hoffman J and Kumosa M 2013 Polymer Degradation and Stability 98 436-45
[12] NIIR Board of Consultants & Engineers 2006 Asia Pacific Business Press, Delhi
[13] Raddadi N and Fava F 2019 Science of The Total Environment
[14] Bonifazi G and Serranti S 2010 The Open Waste Management Journal 3 35–45
[15] Kefeli A A, Razumovskii S D and Zaikov G Y 1971 U.S.S.R 13 904–11
[16] Vimala P P and Mathew L 2016 Procedia Technology 24 232–239.