Ozone Plasma Nanobubble (OPN) Reactor Combined with Coagulation-Flocculation Process: A Promising Technology for Leachate Treatment

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Abstract: *According to World Bank data, approximately 2.01 billion tons of urban waste is produced annually, with approximately 33% of waste being improperly managed, leading to concentrated and toxic leachate. This poses a global challenge due to its varied characteristics influenced by climate, landfill age, and waste composition, resulting in groundwater and surface water pollution with severe impacts on human health, ecosystems, and biodiversity, necessitating stringent treatment measures. To address this, a study integrated coagulation-flocculation and advanced oxidation processes (AOPs) using a dielectric barrier discharge (DBD) ozone plasma nanobubble (OPN) reactor to degrade leachate. Gas flow rate, plasma voltage, and gas sources are variated. This research uses O_2 or air as a gas source that produces plasma. The leachate is fed into the DBD reactor, so the bubble will burst and produce further ROS. Optimal results were observed after 60 min, with oxygen gas feed reducing total suspended solids (TSS), chemical oxygen demand (COD), and biological oxygen demand (BOD) by 100, 93.93, and 74.12%, respectively, alongside a decrease in pH. This study indicates the promising potential of this technology for leachate treatment and demonstrates the potential for nitrate production using both types of gas feed.*

Keywords: *AOPs; plasma technology; DBD; ozone; leachate*

INTRODUCTION

With the continuous growth of the world's human population, the production of hazardous waste detrimental to the quality of life and health of humans and the environment is increasing [1]. The accumulated waste undergoes physicochemical changes, resulting in the formation of a liquid extract with a high concentration called leachate [2], which is toxic. This is because leachate contains high amounts of organic materials and heavy metals [3-5]. The coagulation-flocculation process is widely used in water treatment because it effectively reduces chemical oxygen demand (COD), total suspended solids (TSS), and fire-retardant compounds, and it is easy to operate [6]. Leachate processing in Indonesia still relies on conventional methods using pond systems, such as settling ponds, anaerobic ponds, aerobic ponds, stabilization ponds, and wetlands [7-10]. This method requires a large land area and a long processing time, usually 30 to 50 days [11]. The solution to overcome this limitation is to apply a combined process of coagulation-flocculation and advanced oxidation processes (AOPs).

Ozone-based AOP (as a strong oxidizer) in degrading liquid waste has several advantages, including reducing sludge and being able to remove organic contaminants in liquid waste because ozonation induces sludge dissolution, thereby reducing biomass yield [12-13]. Research on ozone-based AOP methods conducted by Kwarciak-Kozlowska [14] shows that the use of ozone (O_3) alone can reduce biological oxygen demand (BOD) and COD by 53 and 70%, respectively. In addition, research by Rahmayanti et al. [15] using the AOPs method with an O_3 generator achieved TSS removal levels of 67%, BOD 84.1%, and COD 88.41%.

In this research, leachate processing uses the AOPs method in a DBD O_3 plasma reactor with nanobubbles, which has previously been used in research for industrial water treatment and de-pollution [16]. Previous leachate processing using reactors with additional O_3 generators did not meet quality standards [15]. Apart from that, the high need for O_3 in the process and the high price of O_3 generators need to be considered when using ozone-based energy AOP. To overcome this problem, nanobubble technology in the DBD reactor system was included in this research.

Nanobubbles can last longer because of their good kinetic balance and the bubbles can withstand high internal pressure [17]. Unstable nanobubbles will burst during ozonation, releasing hydroxyl radicals (•OH) as an oxidizing agent [18]. Nanobubble technology was introduced into the DBD reactor to increase wastewater treatment efficiency because very small bubbles (nanobubbles) in the flow can ensure a larger cross-sectional area, indicating a larger contact area and a longer residence time. In addition, the integrated reactor system (integrated with an O_3 generator inside) is used in this research. This is an innovation in the treatment technology used. This research aims to degrade landfill leachate by observing the removal of COD, BOD, and TSS values in the combination of coagulation-flocculation processes with AOP in an O_3 plasma nanobubble reactor. Additionally, changes in pH and nitrate during the degradation process are also observed.

■ EXPERIMENTAL SECTION

Materials

The research materials used include sulfuric acid (H_2SO_4, 98% purity, Merck Millipore), potassium permanganate ($KMnO_4$ for analysis, Merck Millipore) 0.01 M, and sodium oxalate ($Na_2C_2O_4$ for analysis, Merck Millipore) 0.01 M for permanganometric titration, NaOH (Merck Millipore) 0.01 M for COD standard solution, ozone test kit (Merck Millipore 100607.0001) for reagents in O_3 solubility test, Nitra Ver 5 (Merck Millipore) for nitrate analysis reagent, alum ($Al_2(SO_4)\cdot 12H_2O$) as coagulant and flocculant, activated carbon from Merck Millipore for filtration, distilled water and leachate sample from one of the largest sanitary landfills in Indonesia.

Instrumentation

The quantification of •OH is conducted using the permanganometry method to determine the concentration of generated •OH and O_3 solubility with the ozone test kit reagent using UV-vis spectrophotometer (UV-M51). BOD concentration testing is performed using the Winkler method, COD with UV-vis spectrophotometer (UV-M51) at a wavelength of 605 nm, TSS with a colorimeter DR/890, TDS with a TDS meter, nitrate content testing using UV-vis spectrophotometry according to SK SNI M-48-1990-03, and pH value with a pH meter.

Procedure

Experimental setup

The experimental setup employed in this study is identical to that of previous experiments [16]. Two types of gas feed, O_2, and air, were used. Fig. 1 shows the configuration of this experiment. There are slide regulators to control plasma voltage variations, a compressor to flow the gas feed, a DBD reactor as the site of the leachate degradation process, a nanobubble nozzle to generate nano-sized bubbles, a pump to flow the leachate into the reactor, and a reservoir to contain the leachate. This system is also equipped with a voltmeter to measure voltage and a flowmeter to measure the gas feed rate.

The reactor used is the DBD-OPN equipped with a nanobubble nozzle at the bottom of the reactor as a large bubble breaker to produce bubbles with a diameter of 40–100 nm. This nanobubble plasma reactor injects air or pure O_2 into a prepared inlet hole on one side, where the gas is subsequently brought into contact with the plasma discharge formed at the positive electrode. The purpose is to observe the reaction phenomena occurring within the reactor. Waste is pumped into the reactor. The reaction that occurs when the gas contacts the plasma transforms O_2 gas into O_3 and other radicals in the outer part of the reactor, thus eliminating the need for an O_3 generator. This feature represents one of the innovations of this O_3 plasma nanobubble reactor, where

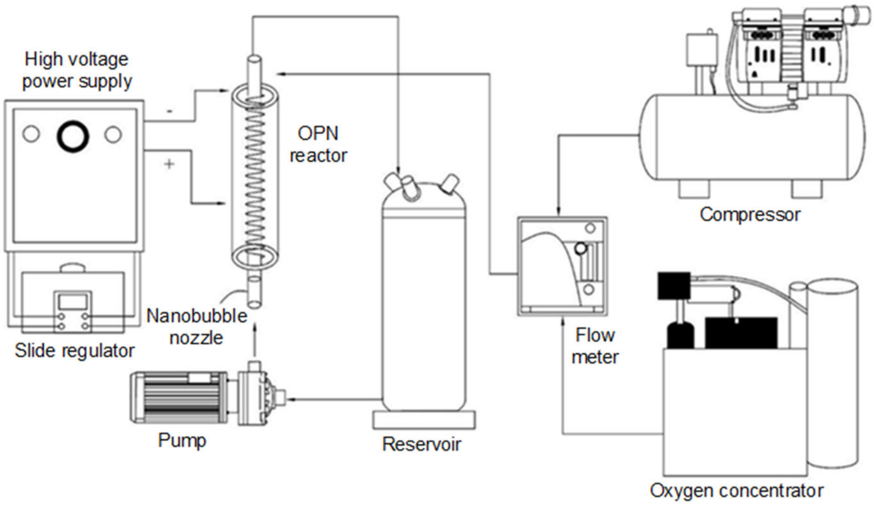

Fig 1. Configuration of leachate treatment

O_3 can be autonomously produced within a single reactor. This is the advantage of the OPN reactor, which demonstrates the self-production of O_3 within one system. The radical generated in this system is •OH, a strong oxidizer in the leachate degradation process.

Leachate preparation

The leachate sample obtained originates from one of the largest sanitary landfills in Indonesia. Prior to being introduced into the reactor system, pretreatment of the leachate is carried out through coagulation-flocculation using alum and filtration using activated carbon to reduce the impurity load in the leachate. The coagulation process is conducted at an agitation speed of 200 rpm for 2 min, followed by flocculation at an agitation speed of 40 rpm for 10 min. After agitation, the solution is allowed to settle for 30 min to allow the formed flocs to settle. Subsequently, the filtration process is performed by adding activated carbon into a funnel filled with cotton. The filtrate is transferred into the reservoir.

Leachate degradation

The gas flow rate is adjusted with 1, 3, and 5 LPM variations. The flow rate is used to determine the amount of gas entering the reactor. The larger gas input, the greater amount of reactive species produced. The slide regulator is adjusted to vary the voltage between 10 and 17 kV. The varied gas flow rate and voltage are intended to determine the optimal conditions for further application in leachate treatment. To ascertain these optimal conditions, tests are conducted on the •OH and O_3 solubility generated at each flow rate and voltage. After leachate preparation step, the leachate is pumped into the reactor. Leachate degradation is carried out using optimal gas flow rate and plasma voltage by varying the type of gas feed (air and O_2). The gas feed is injected into the reactor with the assistance of a compressor. The interaction between plasma and gas feed will generate reactive species with high oxidation potential, such as •OH and O_3, that can degrade leachate. The leachate treatment process is conducted cyclically for 60 min. Leachate samples from the treatment process are taken at 5, 10, 15, 30, 45, and 60 min for testing the changes in BOD, COD, TSS concentrations, nitrate, and pH.

■ RESULTS AND DISCUSSION

Quantification of •OH

The quantification test of •OH aims to assess the performance of DBD plasma in producing •OH. These radicals are generated from cold plasma and are strong oxidants with an oxidation potential of 2.8 V, which plays a significant role in the degradation process of organic compounds in liquid waste [19]. The •OH exhibits highly reactive properties in water but has a relatively short lifespan [16]. With the presence of plasma, •OH reacts with each other to form hydrogen peroxide (H_2O_2) through the following reaction shown in Eq. (1).

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \quad (1)$$

H_2O_2 compound has more stable properties in solution, thus having a longer lifespan and can be used to estimate the production level of •OH, where the higher the concentration of H_2O_2 in the solution, the higher the concentration of •OH in the solution.

The Influence of Gas Flow Rate to Quantification of •OH

From both types of working gases (air and O_2) in Fig. 2, it is observed that the higher the air flow rate used, the greater •OH formed. At a flow rate of 5 LPM, 0.281 mmol of •OH was generated at 30 min with air as the gas feed. This is because the greater the gas flow rate entering the reactor, the more reactants or compounds that react to form •OH [20]. Increasing the gas flow rate into the reactor will increase the amount of O_2 reacting to form O_3, and the O_3 produced will decompose into •OH. Eq. (2–10) show the O_3 decomposition reaction into •OH.

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (2)$$

$$O_3 + HO_2^- \rightarrow HO\bullet + 2O_2 \quad (3)$$

The flow rate of 5 LPM has a higher concentration of H_2O_2 compared to other variations. This illustrates that the higher production of •OH correlates with the increase in the oxygen flow rate. The amount of oxygen entering influences the production of •OH in various ways, including direct collision, O_3 decomposition, and reaction with reactive oxygen species (ROS), as shown in Eq. (4–10). Direct collision between electrons in the plasma with O_2 forms •OH, as shown in Eq. (4–5);

$$O_2 + e \rightarrow 2O \quad (4)$$

$$O + H_2O \rightarrow 2^{\bullet}OH \quad (5)$$

O_3 decomposition where plasma can produce O_3 through reactions involving O_2 as shown in Eq. (6);

$$O_3 + e \rightarrow O_2 + O \quad (6)$$

Reaction with ROS as shown in Eq. (7–9);

$$O_2^{\bullet 2-} + O_2 \rightarrow 2O_2^{\bullet -} \quad (7)$$

$$H_2O + O_2^{\bullet -} \rightarrow \bullet OH + HO_2^{\bullet} \quad (8)$$

$$HO_2^{\bullet} \rightarrow \bullet OH + \frac{1}{2}O_2 \quad (9)$$

The more O_2 is delivered to the reactor, the more O_2 reacts to form active species.

Active species and formed radicals can directly enter the liquid to oxidize or decompose organic material efficiently. In treating waste using the OPN reactor, •OH are active species that play a significant role in the degradation process of leachate. With O_2 gas feed, the highest H_2O_2 concentration is obtained at a flow rate of 5 LPM and 30 min with a concentration value of 0.319 mmol.

The Influence of Plasma Voltage on the Quantification of •OH

Fig. 3 shows that the greater the input electrical voltage provided to the plasma reactor, the greater the •OH formed. Using air as the gas feed, no significant

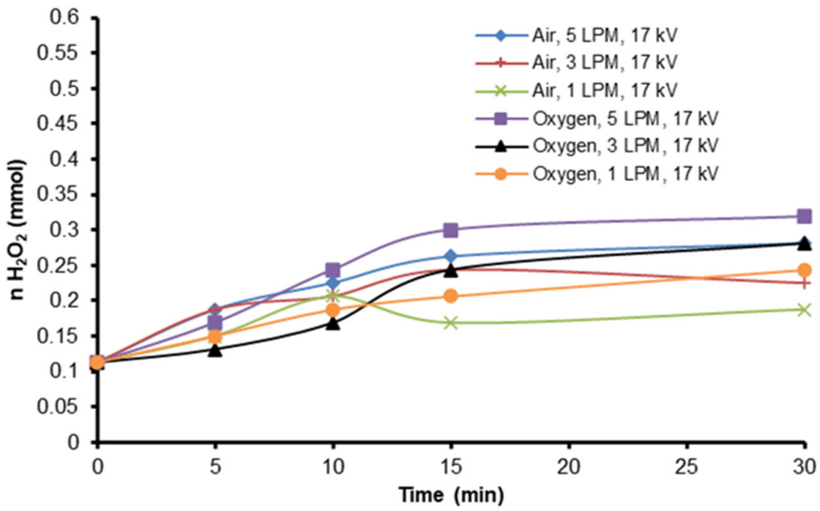

Fig 2. The influence of gas flow rate on •OH formation

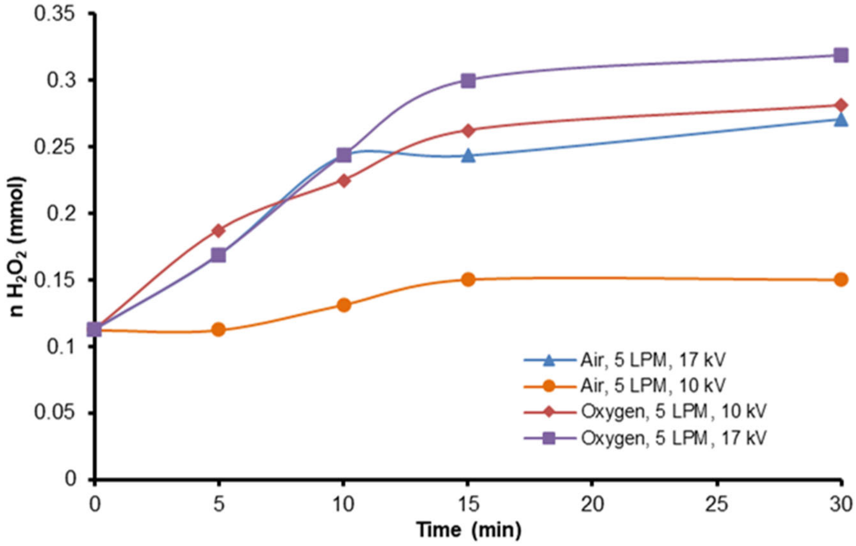

Fig 3. The influence of plasma voltage on •OH formation

difference was observed in the application of plasma voltages at 10 and 17 kV. However, a difference was observed when O_2 was used as the gas feed with varying plasma voltages (10 and 17 kV). O_2 with high plasma voltage can generate a significant amount of •OH because the high plasma voltage increases the energy within the system.

The increase in input voltage causes the flow of current and charge to become high, increasing plasma formation. The voltage increase also affects active species formation, which increases further. This occurs because the charge formed in the reactor increases [21]. High current and charge cause an increase in the electric field between the two electrodes, producing more •OH through the interaction between O_2 gas or air, which becomes plasma and interacts with liquid leachate. The gas fluid flowing between the electrode gaps reacts with the electrode surface, and electrode polarization causes gas molecules to undergo ionization or gain or lose charge on the molecules. Electrons will move from the cathode to the anode, and electrons will collide with gas particles. The higher electric field intensity, the greater the number of particles and electrons produced, resulting in more collisions [22].

Dissolved O_3

O_3 plasma nanobubble reactor produces O_3, which will later decompose into •OH. Besides •OH, O_3 is also one of the strong oxidants in the degradation process of leachate, with an oxidation potential of 2.07 V [23]. The O_3 gas formed will diffuse in water. O_3 solubility is a parameter used to identify the presence of O_3 in a liquid fluid. Fig. 4 shows that the higher the gas flow rate, the greater the dissolved O_3. This is because more O_2 enters the reactor, resulting in more O_2 reacting to produce O_3. The reaction in electrical discharge (plasma) is shown in Eq. (10) [24].

$$O_2 + \text{electric spark} \rightarrow 2O^{\bullet} \quad (10)$$

The oxygen atom ($O^{\bullet}$) will collide with O_2 molecule to form O_3 is shown in Eq. (11).

$$O_2 + O^{\bullet} \rightarrow O_3 \quad (11)$$

O_2 from the oxygen concentrator is dry, as the concentrator contains an absorbent system to absorb moisture from the incoming air. Meanwhile, the amount of O_3 produced by the reactor using O_2 injection is higher than that of free air injection, significantly affecting the O_3 production value. The presence of H_2O content in the air is suspected to also play a role in increasing •OH production, which results in minimal O_3 production from air due to the higher ROS content from the O_2 feed. In contrast, in the case of air feed, the reactive oxygen content is lower and reacts with reactive nitrogen to form nitrate. It can be seen in Fig. 4 that using O_2 gas feed results in higher dissolved O_3 compared to using air.

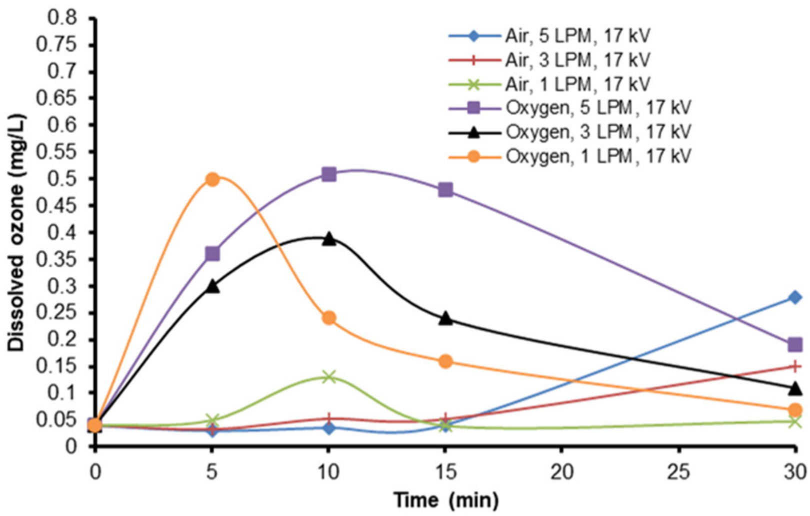

Fig 4. The influence of gas flow rate on dissolved O_3

When using O_2 gas feed, the composition of O_2 gas entering is greater than nitrogen gas, so O• radicals are formed less than •N_2. These formed O• will then react with the O_2 feed to produce O_3, leading to higher O_3 concentrations in the solution. The maximum O_3 concentration can be obtained in a shorter time, typically 5 to 10 min. However, as the operating time increases, the dissolved O_3 decreases. This can happen because the heat in the reactor increases. With higher temperatures, the solubility of O_3 in water decreases, resulting in a decrease in dissolved O_3 concentration [25]. High temperatures also affect the stability of O_3. O_3 at high temperatures will degrade into O_2 more rapidly [26]. The heat energy generated can destroy O_3 and break it into O_2 ($2O_3 \rightarrow 3O_2$), known as the thermal decomposition process. The choice of gas source injected into the reactor affects O_3's solubility and the resulting radicals' formation. Using ambient air injected into the reactor, more •OH and •N_2 are produced considering the assumed composition of air, which is 21% O_2 by weight and 79% nitrogen by weight. Meanwhile, an oxygen concentrator yields a greater amount of •OH.

Pre-treatment of the Leachate

Pretreatment of the leachate is carried out through coagulation-flocculation using alum to reduce the impurity load in the leachate. The alum dosage utilized in this process is 50 mg/L; as per the study conducted by [27], the application of alum at this dosage is found to be the most effective in reducing COD values in wastewater. In Table 1, the influence of the coagulation-flocculation process using alum on landfill leachate samples can be observed. The initial pH value of the leachate before pretreatment using the coagulation and flocculation process is 8.19, and after pretreatment, it is 4.22. The decrease in pH occurs naturally and is not conditioned. This decrease in pH can occur because alum has acidic properties. Alum can lower the pH when added to a solution due to its acidic nature. When dissolved in water, alum undergoes hydrolysis, reacting with water molecules to release hydrogen ions (H^+). The increase in H^+ concentration leads to a decrease in pH. The hydrolysis reaction of alum can be described by the following reaction in Eq. (12).

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4 \quad (12)$$

Table 1. Characteristics of leachate after coagulation-flocculation

Parameter	Initial	Coagulation-flocculation process
pH	8.19	4.22
COD (mg/L)	12324.5	5591.4
TSS (mg/L)	1190	760
BOD (mg/L)	1753.16	1753.16

Under these pH conditions, $Al_2(SO_4)_3$ has the capability to generate $Al(OH)_3$ precipitates, which bind to suspended particles and contaminants. These precipitates aid in creating larger and denser flocs, facilitating their removal from the water and reducing TSS value after filtration [28]. Also, the OH^- formed in Eq. (12), causing it to adsorb onto the surface of organic anionic particles and become insoluble. This phenomenon can lead to a decrease in COD [29].

pH of Treated Leachate

The pH of the landfill leachate entering the nanobubble plasma O_3 reactor is not conditioned, considering that this would require additional chemical substances, thereby increasing the practical application costs. The pH test results on the leachate can be seen in Fig. 5. The initial pH value of the leachate before the pretreatment process is 8.19, and after pretreatment, it is 4.22. The decrease in pH during wastewater treatment using the DBD reactor is relatively small using both types of gas. Key reactive species with high reactivity, such as •OH, H, O_3, NO, and N_2, are responsible for the dominant changes in the sample [30].

The ozonation process is thought to reduce the pH value because carboxylic acid is produced in this process [31]. A decrease in pH also occurs because the formation of certain reactive species, such as nitrogen dioxide (NO_2) or nitrogen trioxide (NO_3), in plasma can modify the sample pH towards acidity. This species can react with water, causing the formation of nitric acid (HNO_3) or nitrous acid (HNO_2), resulting in a decrease in pH [32]. On the other hand, the formation of •OH in plasma can contribute to the modification of the sample pH towards alkalinity. The •OH can react with water to produce hydroxide ions (OH^-), which can increase the pH of the sample [33]. Therefore, the simultaneous formation of acid compounds and OH^- causes subtle changes in pH.

The pH obtained using air and O_2 as ozonator feed gas is 4.2 and 3.3, respectively. Using O_2 as a feed gas produces a slightly lower pH than using air as a feed gas. This does not seem to be in accordance with existing theory, but it can be explained that the abundant •OH produced may have been utilized in the oxidation process to break down complex bonds in waste to form light acids. Light acid compounds that can be formed during the oxidation process include acetic acid, formic acid, and propionic acid [34]. The formation of these acids causes a decrease of pH.

COD Removal of Treated Leachate

Leachate contains a significant amount of organic matter (both biodegradable and refractory organics), which are the main contributor to its high COD value. COD removal from leachate can occur because the formation of •OH can degrade refractory organics such as aromatic compounds, chlorinated compounds, and phenolics [35]. When O_3 is absorbed into a solution containing target organic compound B, several reactions may occur in the leachate during this oxidation process, such as:

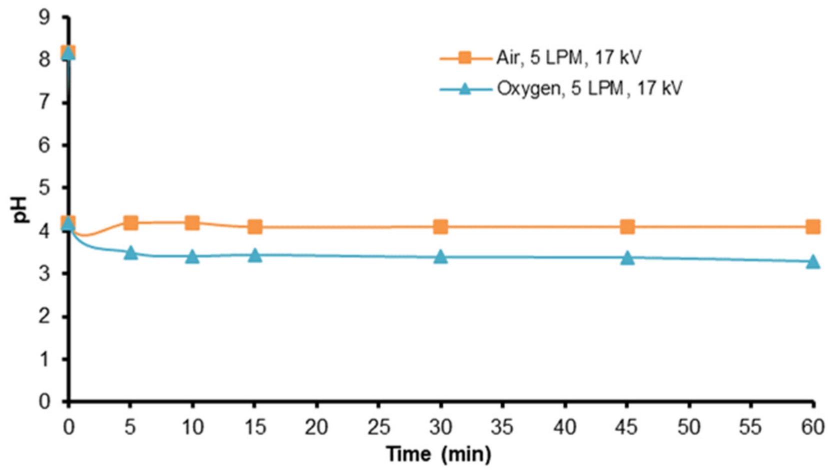

Fig 5. Changes in the pH of leachate

Direct oxidation reaction of O_3 with organic compound B is shown in Eq. (13);

$$O_3 + zB \rightarrow Product \quad (13)$$

Indirect oxidation reaction of •OH with organic compound B is shown in Eq. (14);

$$\bullet OH + B \rightarrow Product \quad (14)$$

The greater amount of O_3 dissolved in a solution, the greater the performance in direct oxidation processes.

The results of COD removal in the DBD reactor can be seen in Fig. 6. The trend of decreasing COD is caused by the active species in the reactor oxidizing the organic components in the sample. Mineralization and degradation occur due to the oxidation of these organic components. O_3 breaks down organic compounds into smaller molecules, potentially converting them into CO_2, H_2O, and inorganic by-products. The mineralization process leads to a decrease in COD levels [36]. With the presence of O_3, the biodegradability of organic compounds is higher.

The increase in COD in the graph may be due to the leachate solution containing various types of compounds. This leads to a high likelihood of these compounds transforming or breaking down into intermediate compounds. O_3 treatment of organic matter leads to the formation of intermediate compounds with low molecular weights. Complex compounds have a significant potential not to degrade or mineralize directly. Due to their complex structure, the chance of breaking down into intermediate compounds or transforming is greater than direct degradation into simple compounds. Some intermediate compounds that may be formed during the leachate degradation include aldehydes, ketones, light organic acids, hydroxylamine and other organic nitrogen compounds, aromatic compounds, and sulfur compounds [37].

COD value of raw leachate is 12324.5 mg/L, and after pretreatment is 5591.4 mg/L. After processing in the OPN reactor with air as the gas feed, the final COD removal of 1044.8 mg/L was achieved, while O_2 was used to achieve 748.04 mg/L. The percentage of COD removal obtained using air and O_2 was 91.52 and 93.93%, respectively. The COD removal results with O_2 feed were more remarkable compared to air, which is attributed to the higher solubility of •OH and O_3.

Furthermore, the decrease in COD values using air as the gas feed occurred more rapidly due to the leachate's higher pH than when using O_2, as indicated in Fig. 5. At higher pH levels, the reaction mechanism follows the radical pathway, generating more •OH. In contrast, it follows the selective direct reaction pathway at lower pH levels. Therefore, a higher solution pH is recommended to enhance O_3 decomposition into •OH, thereby increasing the degradation of refractory organics [38]. The DBD reactor system equipped with OPN applied in this research can contribute to the reduction of COD values. The relation between COD removal and O_3 nanobubbles in wastewater treatment processes is significant. It stems from the oxidative properties of O_3

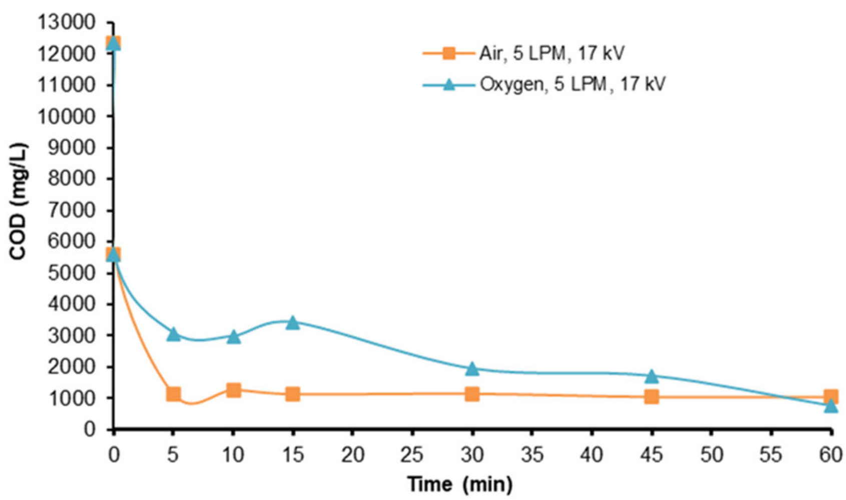

Fig 6. COD removal

and its efficient delivery in nanobubble form. O_3 is a powerful oxidizing agent commonly used in wastewater treatment to degrade organic pollutants. When O_3 is delivered as nanobubbles, it increases the surface area-to-volume ratio, enhancing its contact efficiency with organic compounds in the wastewater. This heightened oxidative capacity allows O_3 nanobubbles to effectively target and reduce COD in the wastewater.

Due to their small size and high surface area, nanobubbles exhibit enhanced mass transfer properties. When O_3 is encapsulated within nanobubbles, it facilitates its transport and dispersion in the aqueous phase of the wastewater. This enhanced mass transfer ensures better contact between O_3 and organic pollutants, improving COD removal. The high O_3 reactivity with organic compounds leads to rapid oxidation reactions, breaking complex organic molecules into simpler, less harmful byproducts. O_3 nanobubbles promote faster reaction kinetics by maximizing the contact time between O_3 and organic pollutants, thereby accelerating COD removal.

O_3 nanobubbles minimize O_3 losses through dissolution and off-gassing, providing a protective shell encapsulating the O_3 gas. This minimization of O_3 losses ensures higher O_3 concentrations are maintained in the wastewater, promoting efficient COD removal. The combined action of O_3 nanobubbles with other reactive species, such as •OH generated during the ozonation process, can lead to synergistic effects, further enhancing COD reduction. The oxidative potential of O_3 and •OH contributes to the degradation of a wide range of organic pollutants in the wastewater.

TSS Removal of Treated Leachate

TSS removal in leachate processing using a DBD reactor is presented in Fig. 7. Achievement of 100% removal efficiency was observed using both types of gas feed. The primary mechanism of TSS removal in plasma reactors does not appear to involve direct degradation. In DBD plasma reactors, high-voltage electrical discharge generates various reactive species, including O_3 and •OH, as well as other reactive species originating from nitrogen and oxygen. These reactive species have strong oxidation capabilities. Organic compounds such as suspended particles, colloids, and organic substances are often present as TSS in wastewater. The reactive species generated in the plasma can oxidize and reduce these organic components, leading to a decrease in TSS levels.

The energy released in the plasma can break down large particles or aggregates in suspended solids. This fragmentation breaks down solid particles into smaller fragments, facilitating further degradation. The degradation of organic matter and fragmentation of TSS can accelerate sedimentation and separation processes. More effective solid-liquid separation techniques, such as sedimentation or filtration, can be applied because smaller fragmented particles or solids are more likely to settle and separate from the liquid phase.

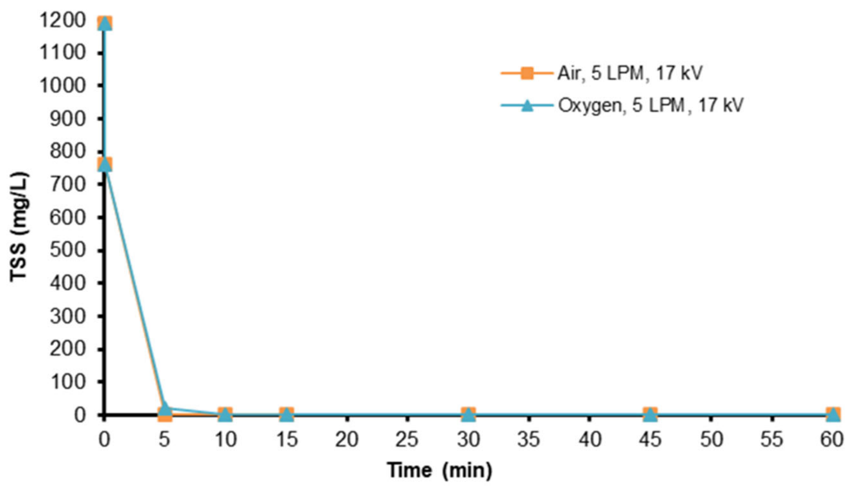

Fig 7. TSS removal

BOD Removal of Treated Leachate

The coagulation and flocculation processes cannot reduce the BOD value. The BOD removal occurs in the OPN reactor. The results can be observed in Fig. 8. Using both types of gas feed for 60 min resulted in a significant decrease in BOD. This can occur because ozonation generates a higher availability of partially oxidized products for further biological processes, such as microbial energy sources for aerobic respiration, which are measured by the BOD parameter [39]. The percentage of BOD removal using air and O_2 sequentially is 71.50 and 74.12%, respectively. When nanobubbles interact with wastewater containing dissolved organic matter, they can carry O_2 into the solution and enhance the oxygen transfer to the organic matter. The available oxygen is then utilized in the oxidation process of organic matter by aerobic microorganisms in the wastewater. The BOD removal using oxygen gas feed is higher than that using air due to the higher solubility of O_3 and •OH produced. These generated O_3 and •OH can break down large organic molecules into smaller, more easily biodegradable forms [40]. This indicates that the DBD plasma O_3 nanobubble reactor effectively reduces the BOD value in leachate.

The obtained results are compared with the leachate quality standards outlined in Regulation of the Minister of Environment and Forestry Number 59/2016. Additionally, a comparison of leachate degradation results using the nanobubble plasma O_3 reactor with air and O_2 feeds is presented in Table 2.

Table 2 shows that using O_2 feed generally yields better COD, BOD, and TSS removal values than using air feed under a gas flow rate of 5 LPM and plasma voltage of 17 kV for 60 min. From the elaboration on the removal of COD, BOD, and TSS parameters conducted in the degradation of leachate, it can be understood that in wastewater treatment using an OPN reactor, •OH and O_3 are the active species that play a significant role in the waste degradation process. The formation of •OH requires sufficient amounts of O_2 and H_2O gas, where electrons flow through the gas and dissipate energy into it, resulting in a temperature increase. The gas particles then undergo collisions with surrounding particles and dissociate into active species, including •OH. As the process time progresses, the quantity of gas decreases while the amount of •OH increases, leading to higher pollutant degradation.

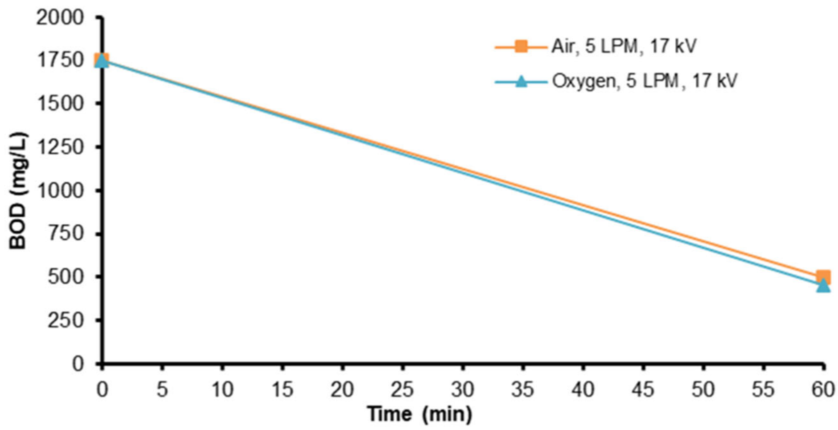

Fig 8. BOD removal

Table 2. Characteristics of leachate

Parameter	Standard quality	Initial	Air	Oxygen
pH	6–9	8.19	4.20	3.30
COD (mg/L)	300	12324.5	1044.8	748.0
TSS (mg/L)	100	1190	0	0
BOD (mg/L)	150	1753.16	499.63	453.73

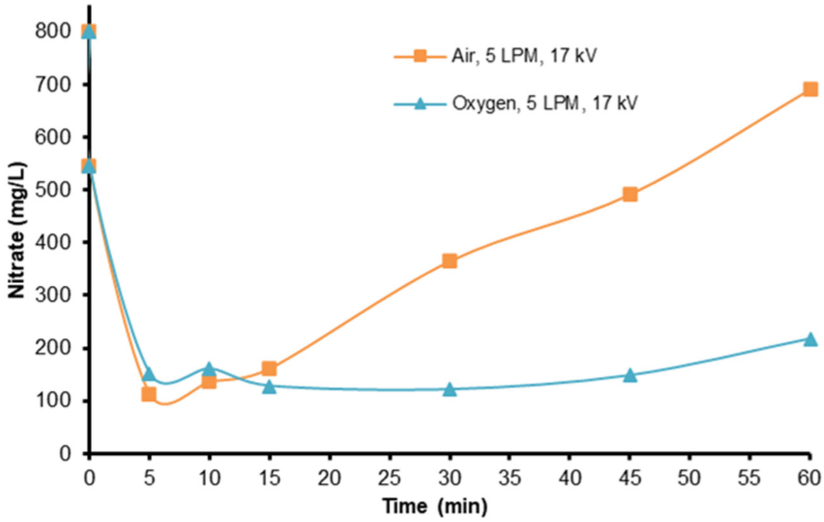

Fig 9. Nitrate concentration of leachate

Nitrate Concentration of Treated Leachate

Apart from removing the leachate's parameter values (presence), the leachate processing process using a DBD reactor produces products that are then analyzed further. The products produced include acidic nitrate compounds (NO_3^-). In this study, the NO_3^- in the processed leachate was crucially analyzed to determine the potential of the leachate as a liquid fertilizer to become a value-added product. The amount of nitrate in the processed leachate was analyzed using spectrophotometric methods. In Fig. 9, an increase in NO_3^- concentration within the sample can be observed. NO_3^- can be produced during this process because if nitrite ions (NO_2^-) are present in the sample content, O_3 and ROS in the reactor can oxidize NO_2^- into NO_3^- [41]. The nitrate formation reaction can be seen in Eq. (15–21) [42].

$$\bullet N_2 + \bullet O \rightarrow 2NO \quad (15)$$

$$NO + \bullet O \rightarrow NO_2 \quad (16)$$

$$3NO_2 + H_2O \rightarrow 2H^+ + 2NO_3^- + NO \quad (17)$$

$$2NO_2 + N_2O_4 + 2H_2O \rightarrow 2HNO_3 + 2HNO_2 \quad (18)$$

$$NO_2 + NO + H_2O \rightarrow 2HNO_2 \quad (19)$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \quad (20)$$

The NO compound formed in the reaction can be oxidized into NO_2 when using air, thus causing an increase in the concentration of formed NO_3^-. The reaction between NO_2 and •OH leading to the formation of nitric acid is shown in Eq. (20) [43].

$$NO_2 + \bullet OH \rightarrow HNO_3 \quad (22)$$

This is evidenced by the greater amount of NO_3^- produced with air than O_2 feed gas. The NO_3^- produced with air and O_2 feeds is 690.6 and 218 mg/L.

■ CONCLUSION

The AOPs method for leachate degradation applied in OPN reactors shows promising potential in removing parameters such as COD, BOD, and TSS. The best leachate processing results are obtained by increasing the feed gas flow rate and plasma voltage. In this study, the effectiveness of leachate processing was observed at a gas flow rate of 5 LPM and a voltage of 17 kV for 60 min. It was found that the type of gas feed significantly influenced the parameters of the treated leachate due to its impact on the quantification of •OH and the solubility of the resulting O_3. The use of high concentration O_2 feed (93%) resulted in higher COD and BOD removal compared to air gas feed.

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■ CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

■ AUTHOR CONTRIBUTIONS

Ken Azzahra and Azizka Inneke Putri: conducted the experiment. Habiibatuz Zahra: writing-original draft preparation, analysis, investigation, and editing. Veny Luvita: methodology, conceptualization, validation, and supervision. Setijo Bismo: discuss the experimental result, provide guidance, and provide assistance in writing.

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