

A study on municipal leachate treatment through a combination of biological processes and ozonation

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Abstract. Landfill is the most commonly method of municipal solid waste disposal in many countries. This practice has great potential to produce highly polluted leachate in massive quantities, which can cause environmental contamination. Biological processes are known as a common method to treat municipal leachate however this process alone in is less effective, especially in reducing the concentration of organic pollutants (BOD₅/COD ratio). Leachate properties are site-specific and greatly influenced by landfill age. This study focuses on the investigation of treatment methods that can increase the extent of leachate biodegradability by applying an ozone concentration of 2.5 mg/L with up to 360 minutes of contact time. In this study, batch reactors were used and operated in anaerobic and aerobic conditions. The leachate used here represents both young and old leachate. Several treatment combinations were compared: Variation I (a combination of biologically aerobic and anaerobic process), Variation II (ozonation included as a pre-treatment process), and Variation III (ozonation was included as a post-treatment process). The results suggest that the BOD₅/COD ratios of young and old leachates were 0.58 and 0.21, respectively. The COD removal for a young and old leachate treatment by biological process alone was 96.8% and 50.8%, respectively. Meanwhile, a combination of anaerobic-ozonation-aerobic processes gave better COD removal. Ozonation had a significant effect on the old leachate treatment, where the COD removal rose from 50.8% to 75%. Ozonation is a type of technology that can be applied to a subsequence treatment of biological processes in order to elevate the COD removal efficiency.

1 Introduction

The rapid growth of the population and the global economy has led to an increasing generation of municipal solid waste (MSW) [1]. Currently, final MSW disposal in Indonesia is still hugely dependent on conventional landfilling due to the low operation and up-front costs, as well as maintenance needs [2, 3]. This operation is considered as a

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significant challenge facing Indonesia's government, as the landfill generates enormous volumes of leachate that should be properly treated. Otherwise, it can be potential sources of soil and water contamination.

MSW constitutes various types of pollutants that can be leached out by rainwater infiltration, groundwater percolation as well as the moisture that exists in waste itself [4]. Leachate mostly consists of principal pollutants that can be split into four main groups: inorganic substances, heavy metals, dissolved organic matter and xenobiotic substances. In excess concentration, each group has the potential to deteriorate the quality of groundwater and surface water. Leachates with parameter quality exceeding the standard must undergo further treatments before discharge to water bodies [5, 6]. In some developing countries, such as Indonesia, water pollution emerges as a serious concern as several landfill facilities are not equipped with a proper leachate collection and treatment systems. Meanwhile, developing an effective leachate treatment to reduce environmental burden is a challenge due to the complexity of leachates composition.

Landfill age is the most considerable factor that influences the effectivity of municipal leachate treatment. Concerning the amount of time the waste has been at the landfill, leachates are classified into young leachate (less than five years), medium age leachate (5-10 years), and old leachate (more than ten years) [7]. Generally, young leachate is mostly made up of organic fractions that are easily biodegradable with relatively lower molecular weights, indicated by the ratio of $BOD_5/COD > 0.6$. With the prolonged life of a landfill, organic fraction in older leachates tend to have persistent characteristics and contain humic and fulvic substances with higher molecular weights, indicated by BOD_5/COD ratios > 0.3 [8]. Also, old leachates primarily consist of refractory substances due to less fatty acids that are easy to volatilize, which in turn, may decrease the BOD_5/COD ratio [9]. Biological processes are the most commonly used method in leachate treatments: however, they become less effective because of the presence of biologically recalcitrant organics that are typically present in municipal leachate [3]. Considering these limitations of using biological processes, this study aims to investigate other treating methods for both young and old leachate.

Leachates generated from MSW consist of the high level of Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD) and ammonium. The amount of leachate generation and its composition vary with the composition of the deposited waste, weather patterns and the amount of time the waste has been at the landfill. Furthermore, leachate characteristics highly fluctuate. The combination of physical and chemical treatments has been widely used as a useful technology in treating the old leachate [2, 10]. Treatment with ozone is one of the robust chemical processes in leachate treatment, as it has oxidation potential in reducing the bio-recalcitrant organic fraction [11]. In this study, ozone is used both before and after anaerobic-aerobic biological processes to treat leachate.

2 Materials and method

This study is conducted to examine the treatability of old and young leachate in the laboratory. The combination of treatments tested in this study are as follows:

1. Variation-I is the configuration of anaerobic-aerobic treatment.
2. Variation-II is analogous to the Variation-I, but includes ozonation as the pre-treatment.
3. Variation-III is analogous to the Variation-I, but includes ozonation as the post-treatment.

2.1 Source of leachate

In this study, artificial leachate was made in the laboratory to mimic the characteristics of young leachate. MSW was collected from one of the waste transfer stations in Bandung, Indonesia, which was then immersed in demineralized water. The waste samples were immersed in plastic reactors (50 cm diameter and 81 cm height) until saturation. Leachate was collected from the sampling port after one week. Before the samples were immersed, the waste sample was segregated and shredded, thus, the only biodegradable fraction that was processed. The waste samples weighed 51.86 kg and were composed of food waste, yard waste, and paper. They also had a moisture content of 69.05% and volatile content of 78.72% (in weight basis). The old leachate was from the Sarimukti landfill site that has operated since 2007. It receives MSW from Bandung city and the surrounding areas, such as Cimahi city and West Bandung district. The existing leachate treatment in Sarimukti landfill includes equalization, anaerobic, aerobic, and sedimentation pond as well as wetland and effluent tank. The leachate used was fresh leachate taken from the inlet of a leachate treatment plant.

2.2. Laboratory scale reactor

The test on Var-I used anaerobic and aerobic reactors. The reactors were 58 cm tall with a 19 cm diameter. The anaerobic reactor was equipped with a submersible pump to recirculate the leachate, providing efficient mixing and a homogenous distribution. Nitrogen gas was injected to replace oxygen in the anaerobic reactor. The aerobic reactor was equipped with an aeration system to provide adequate oxygen inside the reactor. The schematic of the Var-I reactor combination is shown in Fig. 1 (a).

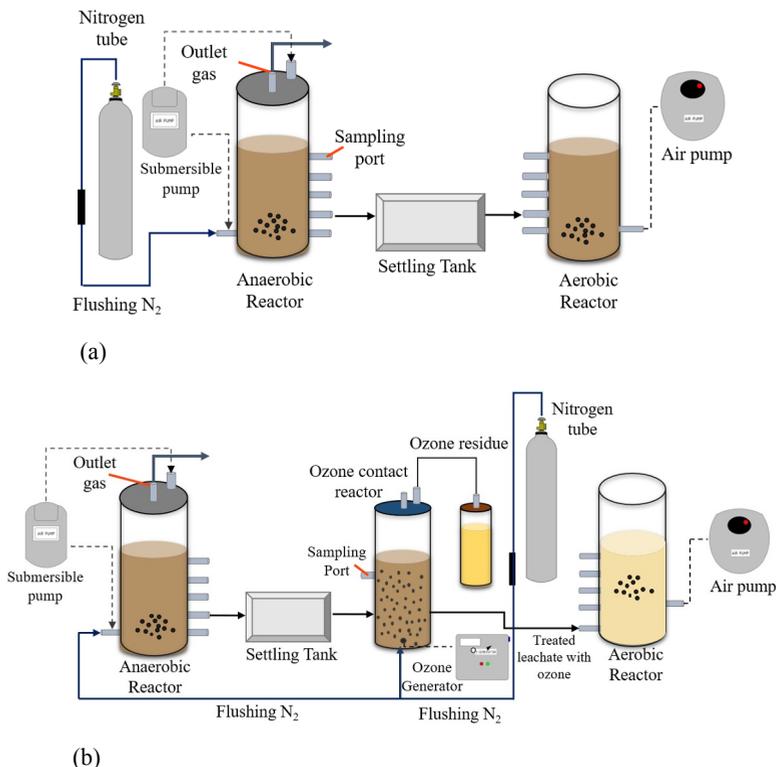


Fig. 1. Schematic diagram of reactors for (a) Var-I, and (b) Var-II.

The test on Var-II and Var-III used the same reactors as in Var-I, but ozone contact reactor was also used in these variations. In Var-II, the ozone contact reactor was placed before the anaerobic reactor (Fig. 1b) and placed after the aerobic reactor on Var-III. The ozone contact reactor held a working volume of 9 L, with 53 cm height and 15 cm width. It is equipped with the Resun-RSO₂₅ ozone generator that can provide an ozone flow rate of 0.25 g/hour in the frequency of 50/60 Hz, providing an ozone flow rate reaching 1.4 L/minute after calibration. The pH of the sample in the reactors was maintained neutral. The hydraulic retention time of the ozone reactor in Var-II was 180 minutes for young leachate and 300 minutes for old leachate. The ozonation time in Var-III was 360 minutes. Samples were collected at 30-minute intervals to monitor the decrease in the COD.

The ozone dosage was determined by the iodometric method, according to the Standard Methods No 2350 E procedure. The processes in the reactor were run in a thoroughly mixed condition and batch mode. The air was pumped through the ozone generator, where molecular oxygen was converted to ozone. Ozone molecules were then injected into the reactor, thoroughly mixing the bubbles and leachate due to the turbulence inside the reactor.

2.3 Seeding preparation and acclimatization

The inoculum for seeding material for the anaerobic process came from an anaerobic sludge pond in a domestic wastewater treatment plant in Bandung, namely Bojosoang. Meanwhile, for the aerobic processes, it was from the aerobic pond. Approximately three-parts of the sludge volume from either anaerobic or aerobic pond were mixed with a two-part volume of nutrient solution. The nutrient solution was a mixture of glucose (C₆H₁₂O₆), which served as the carbon source, an ammonium sulfate powder (NH₄)₂SO₄, which served as the nitrogen source and potassium dihydrogen phosphate (KH₂PO₄), which served as the phosphorous source. The required C:N:P ratio is 250:5:1 for these experiments [12], which can be achieved by adding distilled water to these mixtures.

Artificial leachate was used as a substrate in the acclimatization stage. The leachate COD concentration was 51,750 mg/L. During the first week, the feeding contained only 10% volume of leachate. The leachate volume was increased gradually until it reached 100% in the fourth week. The solutions were characterized regarding temperature, pH, dissolved oxygen (DO) for the aerobic reactor and mixed liquor volatile suspended solids (MLVSS) concentration.

The acclimation phase is considered successful and ready for the testing when the following conditions can be achieved:

1. MLVSS concentrations in the reactor are no less than 2000 mg/L for aerobic process and 4000 mg/L for the anaerobic process.
2. pH, MLVSS, temperature, and organic removal efficiency was constant, with fluctuation rates below 10%.
3. COD removal reached 80%, establishing a steady-state condition.
4. Biomass color becomes darker (dark brown).

2.4 Experimental procedure

The main parameters measured were the BOD₅/COD ratio of the old and young leachate from each trial variation. The anaerobic reactor was periodically flushed with nitrogen gas to eliminate any presence of oxygen, while the oxygen supply was maintained within the aerobic reactor. The environmental conditions in both reactors were kept at an optimum pH of 6-9 and a temperature of 23-25°C:

1. Var-I: after the steady-state condition at the acclimatization stage was reached, the aerobic process was continued until COD removal reached a steady state.

2. Var-II and Var-III: The treated leachate from the anaerobic reactor was then treated further in the sedimentation tank to separate biomass and leachate before introduction into the ozone reactor. When the optimum ozone flow was reached, the ozonation process was performed as a leachate pre-treatment before entering the aerobic reactor (Var-II), or post-treatment, as in Var-III.

2.5 Sampling and analysis

The leachate properties were analyzed for the following elements: BOD₅, COD, total suspended solids (TSS), volatile suspended solids (VSS), total phosphates, total kjeldahl nitrogen (TKN), as defined in the Standard Method reference. Environmental factors like pH, DO, temperature and conductivity were also measured. The BOD₅ and COD were used to express the leachate biodegradability level. All the parameters were analyzed based on the procedure included BOD₅ [13], COD [14], TSS, and VSS [15,16], total phosphates and total kjeldahl nitrogen [17,18]. The DO, conductivity, and pH values were determined by using DO meter (DO-5512SD) and pH meter (3200P), respectively.

3 Result and discussion

3.1 Leachate characteristics

The comparison of initial physical-chemical properties of young and old leachate is presented in Table 1.

Table 1. A comparison of initial characteristics of the young and old leachate tested in this study.

Parameter	Units	Young Leachate	Old Leachate	Government Regulation
pH	-	4.3	8.8	6.0-9.0
Temperature	°C	25.1	24.3	-
Conductivity	mS/cm	7.96	19.33	-
COD	mg/L	51,750	5200	300
BOD ₅	mg/L	29,402	1071	150
BOD ₅ /COD	-	0.58	0.21	-
TKN	mg/L	483	1757	60
Total Phosphate	mg/L	20.3	2.78	-
VSS	mg/L	1376	936	-
TSS	mg/L	1822	1.95	100
TDS	mg/L	4760	11.60	-
C:N:P		2549:14.8:1	206:3.9:1	-

The young leachates, which are artificial, possess a pH 4.3, this value indicates that the organic decomposition has reached acidogenesis and acetogenesis phase. The presence of dissolved organic matter in the leachate can result in the formation of volatile fatty acids that lowers the pH. At the same time, hydrolysis of organic matter may decline the pH and dissolve some minerals. The quality of both the young and old leachate has not been fulfilled by the effluent standard set by government regulation (Table 1).

The old leachate from Sarimukti landfill has a pH 8.8. This value indicates that organic decomposition has reached the methanogenic phase; the increase in alkalinity has to result in a higher pH, and the existing volatile fatty acids have been converted into methane gas and CO₂ by methanogens [19]. The young and old leachate acidity are 1575 mg/L and 4925 mg/L, respectively. The alkalinity is caused by the presence of bicarbonate ions, carbonates, and hydroxyl ions. Young leachate has a higher BOD₅/COD ratio (0.58) than the old leachate (0.21). The higher value suggests that there are more biodegradable organic fractions contained in the young leachate. The existence of humic and fulvic acids in the old leachate is the primary reason it becomes more resistant to degradation than the young leachate [20]. The electrical conductivity of young leachate varies between 4-10 mS/cm. At low pH values, mineral and anionic cations metals are dissolved, increasing electrical conductivity [21]. Old leachates also contain TKN and NH₃-N concentrations of 2,324 mg/L and 1,659 mg/L, respectively. In these conditions, ammonium accumulates due to its stability under anaerobic environments: this accumulation is also reflected in the leachates in a landfill. Inorganic phosphates are produced from proteins and amino acids that decompose in the solid waste, whereas the polyphosphates are generated from soap/detergent [22].

3.2 Inoculum sludge characteristics

Table 2. Initial characteristics of sludge from domestic wastewater.

Parameter	Units	Anaerobic sludge	Aerobic sludge
pH	-	6.62	6.62
Temperature	°C	25.5	25.5
VSS	mg/L	36,161	36,959
COD	mg/L	55,040	55,070
Total Phosphate	mg/L	32.75	30.00
TKN	mg/L	2254	2300

Table 2 shows the initial physicochemical properties of sludge used as an inoculum. These sludges were obtained from the aerobic and anaerobic pond in the domestic wastewater plant. The sludge contains a high level of organic COD, TKN, and total phosphates, as it is originated from domestic wastewater that will be subject to further biological treatments.

3.3 Comparison of inoculum sludge and leachate characteristics

The comparison between COD concentration in the sludge and leachate in anaerobic and aerobic process was 0.35:1 and 4.54:1, respectively. Furthermore, the VSS concentration in the sludge compared to that in leachate for anaerobic and aerobic processes was 6.58:1 and

6.76:1, respectively. From these results, it is clear that microorganisms contribute more to the sludge than the leachates.

3.4 Seeding and acclimatization

The seeding process aims to multiply the population of microorganism. Acclimatization is the first step in the seeding process, to allow a given microorganism to adapt to its changing circumstance; in this case, this circumstance is the leachates. The acclimatization process in both reactors resulted in a decrease of COD concentration at $t = 0$ and $t = 30$ days, where it achieved 88.4% and 76.25% removal efficiency for anaerobic and aerobic conditions, respectively. Meanwhile, the VSS concentration rose from 36,161 mg/L to 40,960 mg/L in anaerobic conditions and from 36,959 mg/L to 40,150 mg/L in aerobic conditions. These results imply that microorganisms can adapt to the leachate characteristics.

3.5 Leachate treatment in Variation-I

Fig. 2 presents the COD removal trendline during 40 days of observations for the anaerobic and aerobic treatments of young and old leachate. The old and young leachates have COD concentrations of 5200 mg/L and 51,750 mg/L, respectively. Regarding these concentration levels, the leachates were then subjected to a treatment in an anaerobic environment, as the anaerobic treatment is more suitable for waste with COD concentrations ranging from 3000 to 60,000 mg/L [23]. The initial COD concentration of young leachate at $t = 0$ days and $t = 26$ days is 37,440 mg/L and 3120 mg/L, respectively, with a COD removal efficiency of roughly 90.9%. From these results, there was an alteration of COD concentration at 24-26 days, with fluctuations no more than 10%.

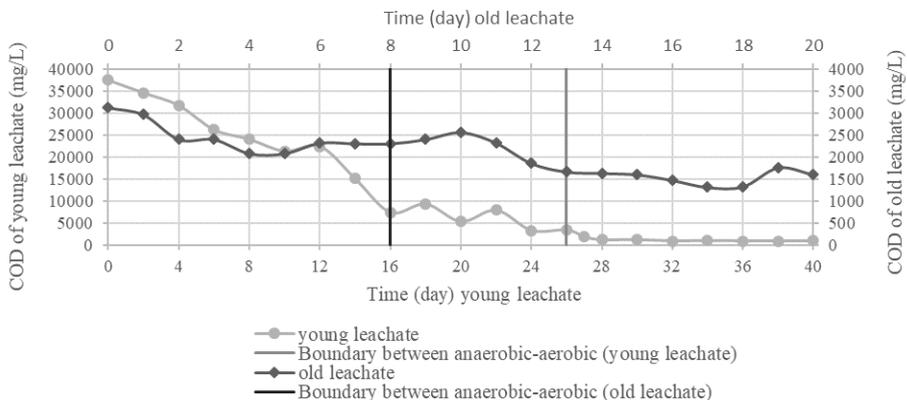


Fig. 1. COD young and old leachate removal Var-I.

Furthermore, in the aerobic experiment, the inlet COD concentration was 3000 mg/L and at $t = 14$ days was 1056 mg/L with a COD removal efficiency of 64.8%. The total COD efficiency of the anaerobic-aerobic process was 97.18% during the 40 day detention time. On the other hand, the COD concentrations of the old leachate at $t = 0$ and $t = 8$ days were 3120 mg/L and 2304 mg/L, respectively, with a COD removal efficiency of 26.15% in the anaerobic process. Furthermore, in the aerobic process, the inlet COD concentration was 2400 mg/L and at $t = 11$ days was 1600 mg/L with removal efficiency of 33.33%. The total COD efficiency of the anaerobic-aerobic process combination was 48.72% during the 20 day detention time. This result reveals that organic matter in the young leachate is easier to biologically degrade, as the BOD_5/COD ratio is 0.58, than the old leachate, which holds a

BOD₅/COD ratio of 0.21. The lower BOD₅/COD ratio in the latter is primarily caused by the organic, biologically recalcitrant fraction that is contained in the leachate.

The VSS formation during the young and old leachate treatment on Var-I also exhibited a trend (Fig. 3).

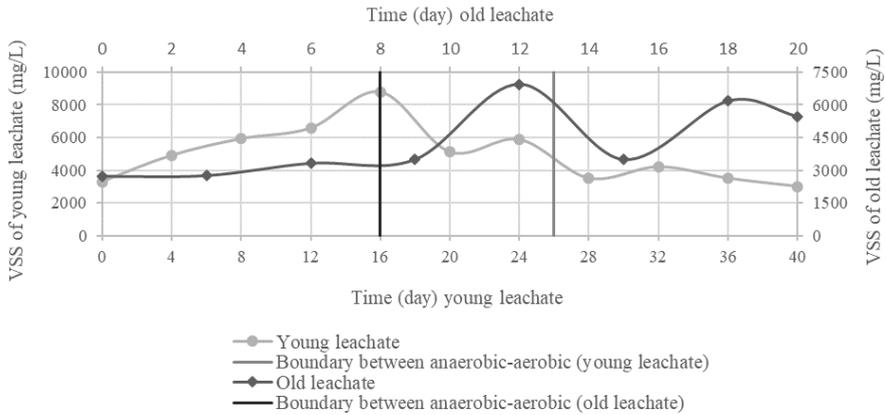


Fig. 2. VSS in young and old leachate in Var-I.

The VSS concentrations tended to fluctuate but became constant once the ranged exceeded 5000 mg/L for anaerobic process and between 2000 to 3000 mg/L for aerobic process. The changes in the amount of biomass occurred as the biomass in the system adapted to the given organic substances.

The change of BOD₅/COD ratio at a combination of biological process and ozone as pre-treatment is presented in Fig. 4.

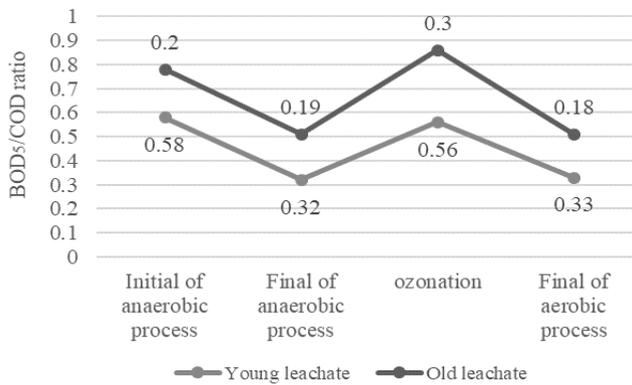


Fig. 4. BOD₅/COD ratio of young and old leachate.

The decreasing BOD₅/COD ratio occurred at the end of the anaerobic process (before ozonation as pre-treatment), and the final aerobic process (Fig. 5). This decrease indicates that the biodegradation of an organic compound in leachate during the biological process would decrease the BOD₅/COD ratio. Therefore, ozonation as a pre-treatment increased BOD₅/COD ratio before doing the biological aerobic process.

3.6 Leachate treatment in Variation-II

The total efficiency for COD removal in the combined anaerobic-ozonation-aerobic experiment for the young leachate was 97.1%, which is only slightly different than without

ozonation, which is 96.8%. The ozone treatment was conducted for 30 minutes; during that time, the BOD₅/COD ratio increased from 0.32 to 0.56. The extent of biodegradability increased when the BOD₅/COD ratio was higher than 0.4, which is the minimum value to achieve an efficient biological degradation process [23].

The ozone treatment for the old leachate took place for 240 minutes, in which the BOD₅/COD ratio rose from 0.2 to 0.3. The duration of ozone contact time does not result in significant changes in the ratio of BOD₅/COD regarding old leachate. During the 300 minutes ozone contact time, the COD removal efficiency only reached 35.3% with an increase in BOD₅ concentration from 891 mg/L to 959 mg/L. This result is because the concentration of COD of old leachate contains humic and fulvic acids, which are biologically recalcitrant. Ozonation is an oxidation method that relies on hydroxyl radicals to remove recalcitrant organic pollutants that are difficult to treat by conventional methods due to their high chemical stability or low biodegradability [24].

Ozonation as a pre-treatment for young leachate can increase the extent of biodegradability in the BOD₅/COD ratio from 0.32 to 0.56 at an ozone concentration of 2.51 mg/L, with an ozone drainage time of 30 minutes. As a result, the COD removal efficiency after ozonation pre-treatment can achieve 75%, whereas the process without ozonation only reaches 50.8% of COD removal efficiency.

3.7 Leachate treatment in Variation-III

Ozonation was used to eliminate pollutants that cannot be entirely removed by the biological processes. The ozonation process as a post-treatment was able to raise the BOD₅/COD ratio in the young and old leachate treatment from 0.27 to 0.51 and from 0.1 to 0.2, respectively. The post-treatment using ozone, however, did not significantly increase the COD removal efficiency on the young leachate. The COD removal in the young leachate treatment was 97.5%, which is only slightly above the value from the treatment without ozonation (96.8%). Regardless, ozonation has a significant effect on the old leachate treatment, where the COD removal rose from 50.8% to 65%.

4 Conclusions

The combination of biologically anaerobic-aerobic processes reduces the COD concentration of 96.8% in a young leachate treatment. The COD concentration in the young leachate, however, is still above the discharge standard in conformance with the Indonesian regulation. Ozonation is one of the technologies that can be applied as a treatment after the biological process to elevate the COD removal efficiency further. Concerning young leachate, the treatment using a combine anaerobic-ozonation-aerobic showed only slight differences than that without ozonation, where the COD removal efficiency just rose to 97.1%. On the other hand, ozonation had a significant effect on the old leachate treatment, where the COD removal rose from 50.8% to 75%. This increased value was obtained when the leachate was in contact with ozone for 360 minutes.

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