

Short Communication

Treatment of landfill leachate by ozone-based advanced oxidation processes

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Abstract

In this study, laboratory experiments are conducted to compare the efficacy using several ozone-based advanced oxidation processes (AOPs), such as O_3 , O_3/H_2O_2 , and O_3/UV , to treat landfill leachate. Raw leachate was initially coagulated by ferric chloride ($FeCl_3$) at the experimental-determined optimal dosage of 900 mg l^{-1} , and the ozone-based AOPs were subsequently applied. Results indicate that all AOPs would result in a significant increase on the ratio of BOD_5/COD from 0.06 to 0.5 at the applied ozone dosage of 1.2 g l^{-1} . The increase on biodegradability for ozonated leachate indicates that these AOPs would be beneficial to the subsequent biological treatment process. To better explain the alteration of high organic molecules after oxidation, ultrafiltration was used to separate the leachate by several molecular weight cutoffs (MWCO). The COD distribution for coagulated leachate is 34% for MWCO > 10 kDa, 7% for MWCO between 5 and 10 kDa, 22% for MWCO between 1 and 5 kDa, and 37% for MWCO < 1 kDa. Following ozonation or AOPs, the predominant distribution of COD would be obviously shifted to the MWCO less than 1000 g mol^{-1} (72–85%) over the other MWCO ranges. In addition, Gel Permeation Chromatograph (GPC) analysis has showed a substantial agreement on the cleavage of larger organic compounds into smaller ones. O_3/UV was found to be the most effective approach among these ozone-based AOPs to enhancing the biodegradability and eliminating the color of leachate.

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1. Introduction

The fact for the serious contamination into the receiving water by the effluent of landfill leachate has increasingly attracted more concerns worldwide. Fortunately, the remarkable growth in economics and living standard has accelerated the development of water and wastewater purification technology. It is well acknowledged by the

fact that landfill leachate released by municipal wastes contains large quantities of non-biodegradable and toxic constituents including organic and inorganic substances and that several treatment steps must be adopted to achieve a satisfactory removal of hazardous pollutants. Landfill leachate is commonly generated as a result of water from precipitation, surface run-off, and infiltration or intrusion of groundwater percolating through the landfill (Tsai et al., 1997; Ince, 1998; öman and Rosqvist, 1999). Leachate characteristics are determined by the siting, the design and the means of operation of the landfill, and also depend on the condition of waste biodegradation through time. It is rather complicated that contaminants in the landfill leachate are released from the waste due to

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successive biological, chemical, and physical processes. Baig et al. (1999) classified landfill leachate into three types, such as young, intermediate, and stabilized, according to its different landfill ages.

Conventionally, Landfill leachate is treated by the biological processes to eliminate its organic loading in the effluent. Aerobic and anaerobic biological processes have been reported to remove a substantial fraction of biological oxygen demand (BOD), chemical oxygen demand (COD) and ammonia from old solid-waste landfill leachate (Dzombak et al., 1990). Although Nedwell and Reynolds (1996) indicated that the use of two-stage anaerobic processes involving methanogenic and sulfur-reducing digestions results in a steady state removal efficiency of COD up to 97%, the most difficult aspects for the old landfill site is the degradation of those recalcitrant organic compounds within a reasonable period by bio-treatment. In the past decade, advanced oxidation technologies including ozonation have been proposed and suggested as an auxiliary approach or alternative for the management of landfill leachate (Bigot et al., 1995). Although many of the previous researches using ozone or advanced oxidation processes (AOPs) have demonstrated the effectiveness in eliminating COD or total organic carbon (TOC) for the landfill leachate (Wable et al., 1993; Bigot et al., 1994; Kim et al., 1997; Steensen, 1997; Wenzel et al., 1999), most of them only used AOPs on the final stabilization prior to discharging into the receiving water body. Therefore, in this study we have attempted using ozone-based AOPs as pretreatment to decompose the recalcitrant organic matters and increase their biodegradation for the subsequent bio-associated treatment. Therefore, the objectives in this paper could be summarized as (1) to evaluate the feasibility of preoxidation of ozone-based AOPs to increase the biodegradability and (2) to compare the efficacy of different ozone-based AOPs on oxidizing the organic compounds.

2. Materials and methods

2.1. Leachate collection and characteristics

Raw leachate was collected from the wastewater treatment plant of Chen–Shi–Li municipal landfill located close to Tainan city in southern Taiwan. Upon collection, the leachate was stored at 4 °C to minimize any further change that might occur in its physicochemical and biological properties until the experiments and analyses were carried out within a week. The physicochemical characteristics of the raw leachate used in our study were analyzed and listed in Table 1. According to the characteristics of pH and biodegradability in the collected raw leachate, it is apparent that the raw leachate would fall into the category of stabi-

Table 1
Characteristics analysis of raw landfill leachate used in this study

Parameter	Mean value or concentration
pH	8.1 ^a
COD	6500 mg l ⁻¹
TOC	4000 mg l ⁻¹
BOD ₅	500 mg l ⁻¹
NH ₃ -N	5500 mg l ⁻¹
Cl ⁻	6000 mg l ⁻¹
Alkalinity	650 mg l ⁻¹ as CaCO ₃
True color	12 000 ADMI ^b

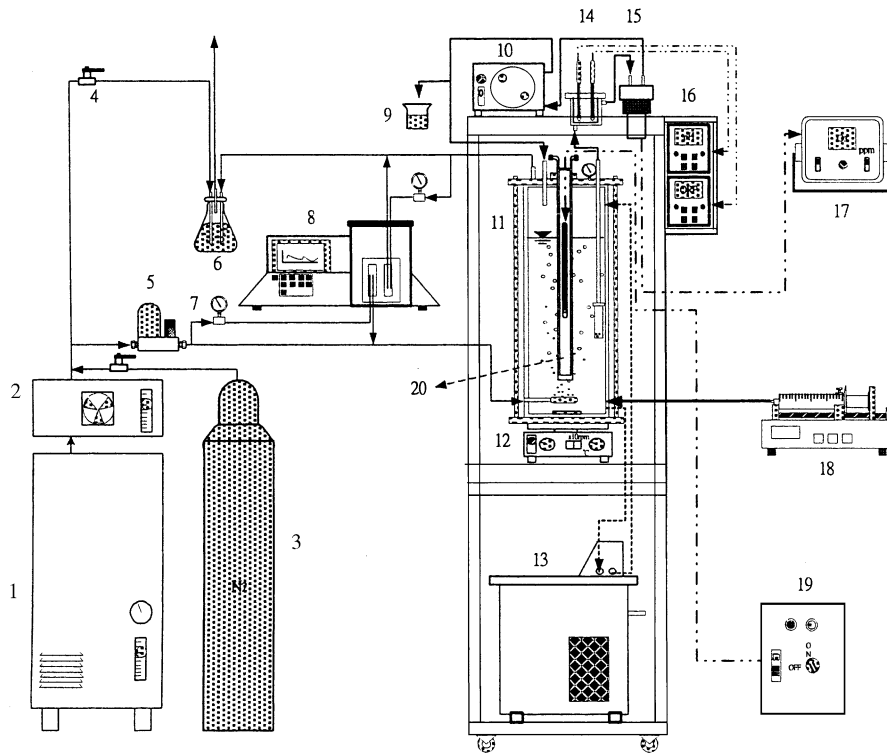
^a The median value.

^b American Dye Manufacturers Institute.

lized form as it has higher pH value (>7.5) and lower BOD₅/COD (<0.1) due to the slow release of refractory organic matter from the landfill site.

2.2. Ozone and AOPs experiments

Ozone was generated from dried pure oxygen by corona discharge using an ozone generator (Ozononia RXO-5), which can produce 6% ozone concentration (w/w) in the oxygen enriched gas stream. To better maintain the performance of the ozone system, the oxygen was dried using a molecular sieve before entering into the ozone generator. A 4-l semi-batch reactor, which was made of pyrex glass with the dimensions of 12 cm diameter and 50 cm tall, was used to facilitate the operation of all ozone-based oxidation processes (Fig. 1). Ozone was introduced through a porous fritted diffuser that can produce fairly fine bubbles with diameter less than 1 mm, which had been determined using camera with close-up lens and image analysis software Matrox Inspector 2.0 (Chang, 2001). The gas flowrate was regulated at 1 l min⁻¹ by a mass flow controller (Brooks 5850E). The gaseous ozone concentrations in the inlet and outlet stream were determined spectrophotometrically by the absorbance of ozone measured in a 2-mm flow-through quartz cuvette at the wavelength 258 nm. An extinction coefficient of 3000 M⁻¹ cm⁻¹ was used to convert absorbances into concentration units (Nowell and Hoigné, 1988). The inlet and outlet gaseous ozone concentrations in this study were calculated as 40 and 0 mg l⁻¹, respectively. Since ozone dosage is typically defined as the product of gas flowrate, ozone concentration, and ozonation period, divided by the reactor volume, the desired dosage of 1.2 g l⁻¹ would take 30 min to achieve. To reduce foaming caused by the bubbling of ozone into the leachate, 5 ml of anti-foaming agent, Anti-foam 289 (Sigma Co.) was added to the leachate prior to ozonation. All experiments were operated at 25 °C using a water jacket around the reactor. During the experimental period, the leachate in



- | | |
|-------------------------|-------------------------------------|
| 1. Oxygen generator | 11. Reactor |
| 2. Ozone generator | 12. Magnetic stirrer |
| 3. Nitrogen | 13. Circulating bath |
| 4. Needle valve | 14. Chamber for pH measurement |
| 5. Mass flow controller | 15. Dissolved O ₃ probe |
| 6. Trap solution (KI) | 16. pH monitor |
| 7. Pressure gauge | 17. Dissolve O ₃ monitor |
| 8. UV Spectrophotometer | 18. Syringe pump |
| 9. Sampling port | 19. UV power supplier |
| 10. Peristaltic pump | 20. UV lamp |

Fig. 1. System setup for ozone-based advanced oxidation processes.

the reactor was pumped continuously through a closed loop equipped with a chamber where all sensors of pH and dissolved ozone monitor were placed and with a sampling port where the leachate could be withdrawn for chemical analyses. The hydrogen peroxide (30%) injection system was initiated using a syringe pump to deliver a fixed flowrate, depending on the ratio to the applied ozone dosage, into the reactor. The input ratio of H₂O₂ to ozone by weight was controlled at 1.0 g g⁻¹, which had been previously determined to be the optimal ratio (Chang, 2001). In addition, a high-pressure mercury UV lamp (Hanovia Co.) with an input energy of 200 W and output intensity of 5.1 mW cm⁻² was placed at the center of the reactor and shielded by a vertically immersed quartz jacket which was circulated with cold

water to avoid heat accumulation. A black box placed outside the reactor was employed to minimize any penetration of UV light when UV-enhanced facility was operated.

2.3. Analytical methods

The characteristic analyses of the raw and oxidized leachate including BOD₅, COD, and ammonia nitrogen, were performed according to Standard Methods (APHA, 1998). Chloride ions and TOC were measured using ion chromatography (Dionex, DX-100) and TOC analyzer (Tekmar Dohrmann, Apollo 9000), respectively. Color was determined according to the ADMI method proposed by American Dye Manufactures Institute using

three different wavelengths, including 438, 540, and 590 nm. To better understand the change of molecular weight distribution after oxidation, both gel permeation chromatograph (GPC) and ultrafiltration membrane separation were employed. GPC was performed using a HPLC system (Shimadzu LC-10) and a refractive-index detector. The TSKgel G3000PW_{XL} column (TOSOH Co.), which is especially suitable for the analysis of molecular weight within the range of 1–8.5 kDa, was used to separate the organics in the leachate into several groups. The pump flowrate was set at 0.6 ml min⁻¹. The average molecular weight determined by GPC chromatography could be expressed as below (Dickenson and Amy, 2000).

$$M_n = \sum C_i M_i / C_i$$

$$M_w = \sum C_i M_i^2 / \sum C_i M_i$$

$$D = M_w / M_n$$

where M_n is the average molecular weight based on the calculation by molecule number; M_w is the average molecular weight based on the calculation by weight composition of molecules; C_i is the area or number of specific molecular weight (M_i) from GPC chromatography; M_i is the molecular weight; D is the distribution coefficient of average molecular weight and $D \geq 1$. The UF system (Amicon Co.) was utilized to separate organics by passing leachate sample through the ultracel PL membranes with several molecular weight cutoffs (MWCO) of 1, 5, and 10 kDa. Furthermore, the fourier transform infrared spectroscopy (FTIR-8201, Shimadzu Co.) was also used to characterize and observe the change of functional groups in the leachate.

3. Results and discussion

3.1. Coagulation by ferric chloride

Raw leachate collected from the landfill site was initially coagulated by ferric chloride before all ozone-based advanced oxidation processes were applied. According to the evaluation of jar tests in the laboratory, the most optimal coagulant dosage for COD removal of the raw leachate was determined to be 900 mg l⁻¹. Under this circumstance the total COD decreased approximately 60% (from 6500 to 2500 mg l⁻¹). Similarly, the significant change on the percentage distributions of COD at different MWCOs was observed from 53% to 34% for the molecular weight range greater than 10 kDa (Fig. 2), indicating that coagulation mechanism would result in the substantial removal of larger organic molecules. The average molecular weight (M_w) based upon the calculation of its weight composition in GPC chromatography was also found to de-

crease significantly from 75 to 11 kDa. It appears that larger molecule portions of raw leachate can be effectively removed by ferric chloride coagulation. However, the ratio of BOD₅/COD, a traditional indicator of biodegradability, of the leachate after coagulation is still below 0.1. It can be predicted that the difficulty would take place if the subsequent biological treatment process is directly applied to decompose these residual organic matters in the effluent of coagulation treatment. Therefore, the ozone-based oxidation processes is proposed in the following session on highlighting the enhancement of biodegradability of landfill leachate and removal of color.

3.2. Ozone-based advanced oxidation processes

In this study, three kinds of oxidation processes including ozone, ozone/UV, and ozone/hydrogen peroxide were provided to treat the landfill leachate after coagulation. It is apparent that all of the ratios of BOD₅ to COD in Fig. 3(a) were observed to increase from 0.1 to 0.5 during the period of applying 1.2 g l⁻¹ ozone dosage regardless of the combination with UV or hydrogen peroxide. This result indicates that the biodegradability of the leachate has been substantially improved after oxidation reaction. Nevertheless, ozone/UV could be figured out to have a better oxidation ability at the initial oxidation period by comparing with the other two processes in Fig. 3(a). The hydroxyl radicals, induced from the decomposition of ozone or either from the initiation of hydrogen peroxide or UV lamp, are unable to further accelerate the degradation of non-biodegradable organics primarily due to the presence of greater alkalinity, such as bicarbonate and carbonate, acting as the OH radical scavenger (Langlais et al., 1991; Masten et al., 1996) in the leachate. Moreover, the effect of pH values was found to increase approximately from 8.1 to 8.6 for all ozone-based AOPs used in this study. The increase in pH upon sparging with ozone is thought to be due to the stripping of carbon dioxide and volatile fatty acids (Wu et al., 1998a).

Considering the influence of oxidation on molecular weight distribution, Fig. 2 using UF separation shows that COD distribution of the coagulated leachate is 34% for MWCO > 10 kDa, 7% for MWCO between 5 and 10 kDa, 22% for MWCO between 1 and 5 kDa, and 37% for MWCO < 1 kDa. After applying ozonation process alone, the predominant COD distribution would be significantly shifted to the MWCO less than 1 kDa (72%), which appears that the organic compounds with larger molecular weight has been oxidized into smaller ones. As such, ozone/UV behaves much further destruction for the large organic compounds into small pieces with the 85% portion in COD distribution less than 1 kDa. Similarly, the use of GPC separation also gives a clear evidence (Table 2) that average molecular weight

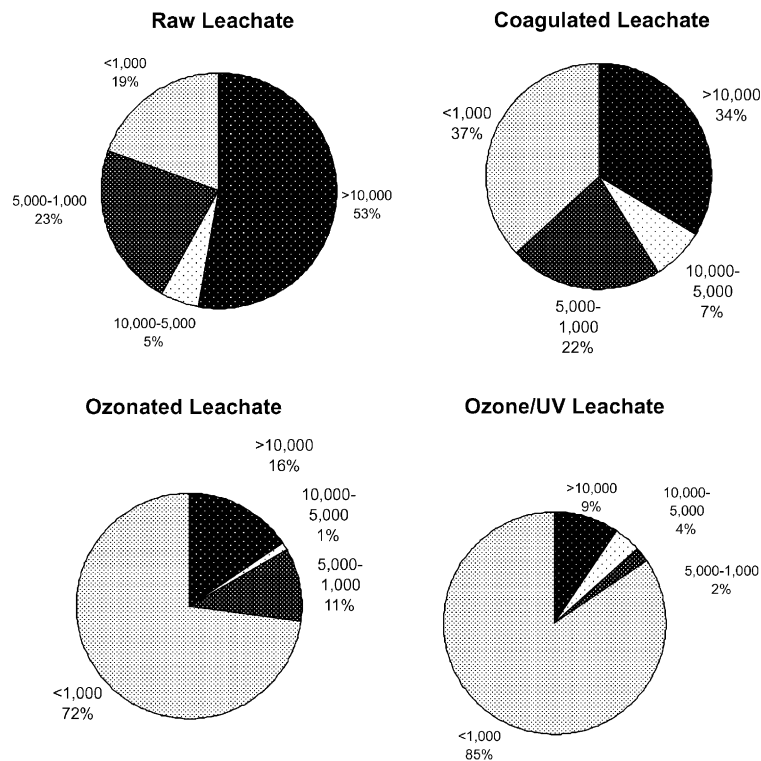


Fig. 2. Percentage distribution of COD on leachate using UF separation at different MWCOs.

(M_w) of the organic compounds in the leachate decreases from $10\,800\text{ g mol}^{-1}$ to 7170 g mol^{-1} by ozonation alone, to 7800 g mol^{-1} by ozone/UV, and to 6080 g mol^{-1} by ozone/hydrogen peroxide. Another critical parameter, distribution coefficient defined by $D = M_w/M_n$, was used to assess the distribution range of molecular weights. The larger D value means more broadened distribution of molecular weights would be perceived. Table 2 indicates the d value was observed to decrease from 3.4 to 2.2 by the ozone-based oxidation processes. Thus, the trend of becoming into smaller molecules from larger organic compound by chemical oxidation processes would be closely related to the enhancement of biodegradability. Vogel et al. (2000) presented a useful parameter for characterizing oxidation process by using the mean oxidation number of carbon (MOC):

$$\text{MOC}_s = 4 - 1.5(\text{COD}/\text{TOC})$$

The changes of MOC during the course of oxidation reaction were observed in Fig. 3(b). Ozone/UV leads to the most rapid increase in the oxidation state of carbonaceous compounds than the other two processes. It is essentially consistent to the observation for the change of BOD_5/COD . Nevertheless, the oxidation states finally achieve a stable level after ozone dosage greater than 0.6 g l^{-1} for all of three oxidation approaches.

For the removal of organic parameters such as TOC, it can be found in Fig. 3(c) that ozonation process alone has the least efficiency in reducing TOC (15% removal), which can be attributed to the destruction mechanisms partially governed by direct reaction of ozone molecules, which are known to react slowly and to end up in carboxylic acids, aldehydes, and ketones, rather than CO_2 . Although the ozone process alone has the ability to produce hydroxyl radicals via the decomposition pathway of radical-type chained reactions (Langlais et al., 1991), the net production efficiency of free radicals is still less than the other ozone-based AOPs used in this research. Since the ozone-based AOPs could not decompose appreciable amount of organic components in the leachate at the ozone dosage used in this experiment, a biological process would be recommended to operate after the oxidation treatment by degrading the residual organic intermediates into final stable products, such as carbon dioxide and water. Typically, color of leachate is another environmentally concerned issue. As ozone has been widely utilized as a reliable technique and alternative for decolorizing effluent of the dyeing industry (Wu et al., 1998b), the removal of color of leachate is also included in this session. Color of leachate has been measured to decrease significantly with the increase of ozone dosage as seen in Fig. 3(d). Since most colors are

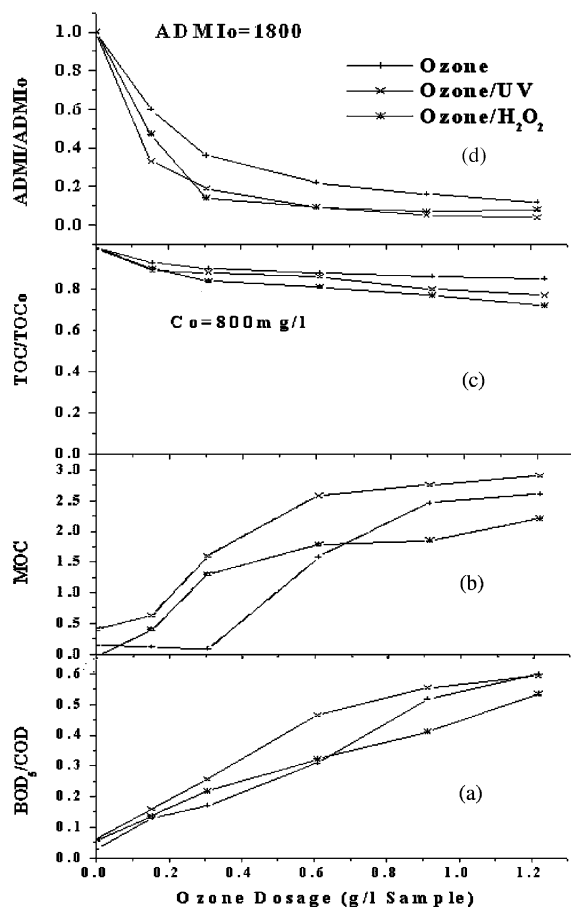


Fig. 3. (a) BOD_5/COD change, (b) MOC change, (c) percentage change of TOC, and (d) percentage change of color (ADMI) of leachate at different ozone-base AOPs and ozone dosage.

Table 2
Calculation of average molecular weight on GPC separation

	M_n	M_w	$d(M_w/M_n)$
After coagulation	3190	10 800	3.4
O_3	3070	7170	2.4
O_3/UV	3010	7800	2.6
H_2O_2/O_3	2810	6080	2.2

mainly originated from the unsaturated bonds and specific functional groups, ozone and hydroxyl radicals would be very attractive on specifically attacking the conjugated chains that impart color to the organic molecules.

Fourier transform infrared spectroscopy (FTIR) has been frequently utilized in characterizing the functional groups of the organics for many environmental analyses. In Fig. 4, it is apparent that the hydroxyl group intensity

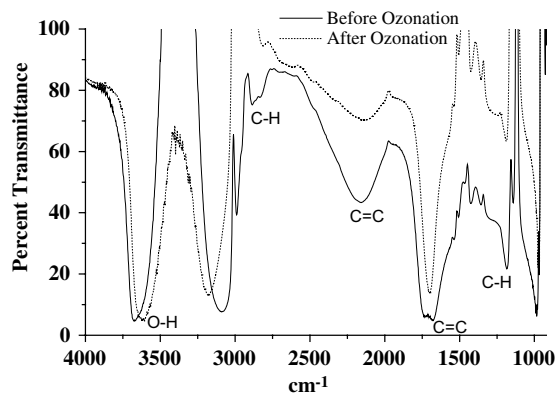


Fig. 4. FTIR spectra of leachate before and after ozonation process.

increases after ozone oxidation, which results in the substitution of functional groups of the organic intermediates associated with the electrophilic reaction by adding into the oxygen atoms. In contrast, the intensity representing the specific stretch wavenumbers of double or triple bond between carbons has been observed to diminish after ozonation mainly due to the mechanism of cyclo addition (Langlais et al., 1991).

4. Conclusion

This research can lead to several conclusions summarized as below:

1. Coagulation pretreatment can effectively remove varieties of large molecules in the raw landfill leachate and aid on the subsequent treatment of ozone-based advanced oxidation processes.
2. Biodegradability indicated by BOD_5/COD of landfill leachate can be significantly enhanced when applied ozone dosage till 1.2 g l^{-1} . Ozone/UV is found to be the best oxidation approach among the three types of selected processes. Leachate separated by UF membrane and GPC has demonstrated the composition shifting from larger molecules into smaller ones. Thus, it is thought to have a direct relationship with the increase of leachate biodegradability.
3. The ozone-based advanced processes are demonstrated to decolorize the leachate for 90% removal. Nevertheless, the removal of TOC is potentially limited even though rather high dosage of ozone is applied. This result implies that ozone-based AOPs should be an excellent alternative prior to using biological treatment process.
4. The FTIR analysis provides useful information in characterizing the change of functional groups of leachate after ozonation reaction.

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