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Degradation of organics in the mature and young landfill leachate by ozonation process

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ABSTRACT

The compound constitution of refractory organics in mature and young landfill leachate is very different, and the structure of dissolved organic matter can profoundly influence treatment performance. In this work, the treatment efficiency and transformation mechanism of mature and young landfill leachate in an ozonation process were studied. The reaction mechanism destroys the aromatic structure (benzene rings) and chromophore groups of macro-molecular humus and produces many small intermediates, which change the organic composition of landfill leachate and drastically improve its biodegradability. In mature leachate, ozone can remove macromolecular humus by rearranging the molecular structure; however, in young leachate, ozone can completely degrade small molecules. Therefore, the different compounds in mature and young leachate cause different organic reaction processes and rates. This work, by a comparative study, provides a better understanding of the organics degradation and removal mechanism of ozonation treating mature and young landfill leachate.

Keywords: Ozonation; Mature leachate; Young leachate; Comparative study; Humic substances

1. Introduction

With the rapid economic development and the gradual improvement of the living standards in China, the production of municipal solid waste (MSW) has increased over time [1–4]. The conventional MSW disposal and treatment methods include recycling, composting, incineration, and landfilling, among which sanitary landfilling is widely accepted and used because of its higher economic advantages in developing countries and underdeveloped areas [5–14]. Landfill leachate is inevitably generated due to microbial decomposition and natural precipitation during the process of landfill stabilization. Landfill leachate has a high organic matter concentration, complex composition, and high ammonia nitrogen concentration [15–21]. Therefore, leachate must be strictly treated before it is discharged into receiving water, and this is not an easy task.

The proper treatment of landfill leachate has raised significant international concerns. Coagulation–flocculation is widely used for landfill leachate pretreatment, but this method generates a large amount of organic–inorganic sludge [22–26]. Leachate recirculation has been applied to many landfills in China for economic reasons, but mature landfill leachate is not suitable for this process because it contains complex compounds and the dissolved organic matter (DOM) has high humidification [16,27–31]. Although incineration can be used to treat leachate with high organic matter concentration, the high water content of the leachate will affect the thermal condition and normal operation of treatment.

Advanced oxidation processes (AOPs) take advantage of different methods to activate and/or produce highly reactive radical species and are known for their ability to mineralize a wide range of organic compounds from industrial wastewater as well as landfill leachate [15,32–40]. In particular, the Fenton method has been used in practical applications, although it generates a secondary pollutant (i.e., iron-sludge) [41,42]. Ultraviolet (UV) radiation is widely used to degrade organic contaminants, but the high concentrations of UV-quenching substances (i.e., humic and fulvic acid) that exist in leachate affect light transmission and UV treatment effectiveness [43–45]. Consequently, the UV radiation method is ineffective and expensive for treating landfill leachate, especially mature leachate. Ozone is a selective oxidant and can quickly oxidize organics that have electron-rich moieties [16,43]. In addition, in the ozonation process, refractory substances are degraded or mineralized by ozone, and •OH is generated at very high rates. The application advantages of ozone oxidation in the pretreatment and advanced treatment of landfill leachate have been widely reported and include strong oxidizing ability, easy operation, and absence of sludge production.

Moreover, the chemical structure of DOM in leachate gradually becomes more complicated during the landfill stabilization process [16]. Previous studies reported that organic components in leachate could affect treatment efficiency during the wet oxidation process [46,47]. Meanwhile, the reaction rates of •OH with young and mature landfill leachate organics are 8.28×10^9 and 9.76×10^8/M/s, respectively [48]. Consequently, the different chemical molecular configurations of DOM in landfill leachate significantly affect redox activity. Yet, comparative studies on degradation or transformation of mature and young leachate in an ozone system are scarce. Furthermore, because of the existence of complex DOM compounds in leachate, it is very difficult to extract accurate molecular information about DOM in different leachates.

Spectral analysis technology plays an important role in describing DOM. Three-dimensional fluorescence spectroscopy is often used to identify the source and humus degree of DOM, and ultraviolet-visible spectroscopy can characterize the molecular weight and molecular condensation of DOM [34,49,50]. So, three-dimensional fluorescence spectroscopy combined with ultraviolet-visible spectroscopy can help to study the transformation of DOM in landfill leachate during the advanced ozone oxidation process. However, there are few comparative studies on refractory organics in leachate during ozone-based oxidation processes.

In this research, mature and young landfill leachates were treated using an ozonation process, and the degradation kinetics of organics were studied. The degradation mechanism during the ozonation of the two types of leachate was investigated by three-dimensional fluorescence spectroscopy and ultraviolet-visible spectroscopy. On this basis, the improvement in the biodegradability of the two leachates by the ozonation process was explained. The objectives of the study were (1) to explore the composition of DOM in mature and young landfill leachate and to describe its transformation in the ozonation process, and (2) to provide fundamental information for guiding the application of an ozone oxidation process for treating refractory landfill leachate.

2. Materials and methods

2.1. Materials

The mature (1#) and young (2#) leachates were collected from two large-scale traditional sanitary landfills in southwest China. The landfill 1# had been operated for 26 y and were closed in 2017. The mature landfill leachate had a chemical oxygen demand (COD) of 5,000–6,000 mg/L, ammonia nitrogen concentration of 1,000–2,000 mg/L, and weakly alkaline pH. The landfill 2# had been in operation for 5 y and its young landfill leachate had COD concentrations ranging from 25,000 to 30,000 mg/L, ammonia nitrogen concentrations ranging from 4,000 to 6,000 mg/L, and weakly acid pH. Both mature and young leachates were immediately sealed after collection and were stored at 4°C.

2.2. Experimental procedure

First, both mature and young landfill leachates were diluted to approximately 1,000 mg COD/L. Secondly, the pH of diluted samples (2 L) was adjusted to 7.80 ± 0.02 using NaOH and H_2SO_4. Then, samples of pH-adjusted mature and young landfill leachates having the same COD concentration were respectively treated by an ozonation process in a reactor. The experimental setup and reactor are shown in Fig. 1. The reactor had a height = 1 m, total volume = 3 L, and a sampling port set at the height of 0.5 m. Oxygen was supplied by an oxygen tank (purity = 99.99%) and flowed into the ozone generator (KT-OZ-15G CONT, USA) at a controlled flow rate. Sequentially, ozone was dispersed uniformly into the reactor through a micro-porous titanium diffuser. The treatment time was controlled to be 20 min, and samples with a volume of 15 mL were collected at reaction times of 2, 4, 6, 8, 10, 12, 15, and 20 min. In any given experiment, the accumulated sample volume was approximately 5% of the treated volume; therefore, the effect of sampling on treatment efficacy was assumed to be negligible. Each sample was immediately put in a constant temperature water bath (75°C ± 0.5°C) for 5 min to eliminate residual ozone. Then the pH was detected and each sample was filtered through a 0.45 μm glass fiber membrane. The filtered and diluted samples were analyzed as described in section 2.3 (Analytical methods).

2.3. Analytical methods

The COD concentrations of mature and young leachates were determined using the microwave digestion-titration method according to a standard method (HJ 828-2017) [51]. The color number (CN) was calculated according to the Eq. (1):

$$\mathrm{CN} = \frac{A_{436}^2 + A_{525}^2 + A_{620}^2}{A_{436} + A_{525} + A_{620}} \tag{1}$$

in which A_{436}, A_{525}, and A_{620} represent the absorbance at wavelengths of 436, 525, and 620 nm, respectively [52].

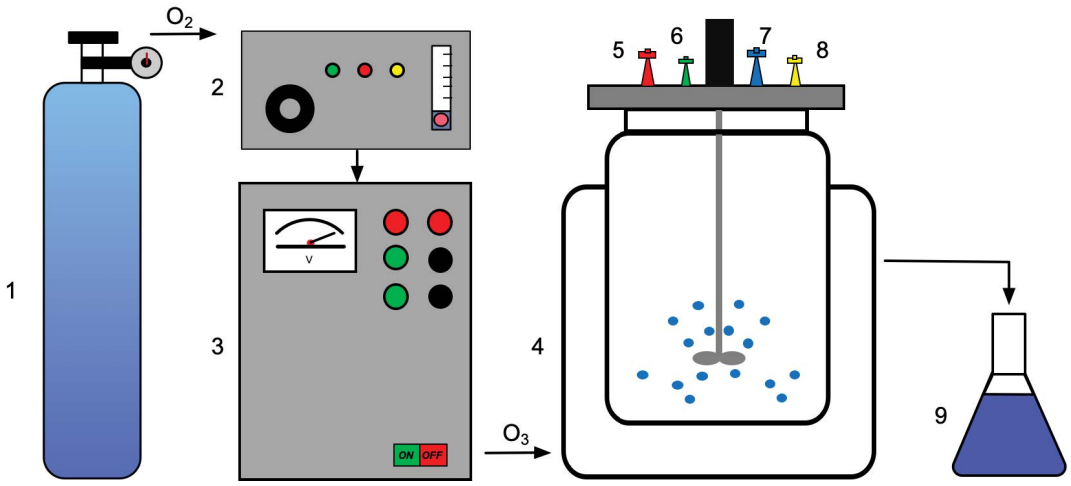

Fig. 1. Experimental set-up of ozone process. (1) Oxygen bottle, (2) ozone flow rate meter, (3) gas generator, (4) reactor, (5) pH adjustment port, (6) pH determination port, (7) sample in, (8) sample out, and (9) KI solution.

The absorbance of samples at wavelengths from 220 to 700 was measured using ultraviolet-visible (UV-vis) spectroscopy (Lambda 950, Perkin-Elmer, Inc., Waltham, MA, USA) with a scanning interval of 1 nm. Changes in humic substances under different ozone concentrations were determined using synchronous three-dimensional excitation emission matrix (3D-EEM) spectroscopy (Aqualog-UV-800C, HORIBA Scientific, Inc., Edison, NJ, USA).

Energy in the ozone process is mainly consumed by the ozone generator. To investigate the energy utilization efficiency, E (the required electric energy) was determined as the amount of electrical energy (kWh) required to reduce one order of magnitude of pollutant concentration in 1 m^3 of contaminated water. The E (kWh/m^3) was calculated using the following equation:

$$E = \frac{P \times t \times 10^3}{V \times 60 \times \log\left(C_i / C_f\right)} \tag{2}$$

in which P is the power (kW) of the ozone generator; t is the reaction time (min) since ozone started being produced until the reaction ends; V is the volume (L) of treated wastewater sample; and C_i and C_f are the initial and final COD concentrations, respectively, of a treated sample. The constant "60" converts min to h.

3. Results and discussion

3.1. Degradation characteristics of mature and young landfill leachates treated by the ozonation process

As depicted in Fig. 2, the light absorbance values at 254 nm (UV_{254}) of mature and young landfill leachate were 7.03 and 1.04 cm^{-1}, respectively, for the same COD concentration (1,000 mg/L). The color number (CN) values of mature and young landfill leachates were 0.2341 and 0.0822, respectively. During landfilling or composting, the humidification process can be explained by the transformation in which simple organics are gradually transformed to complex organics [16,30,53]. Therefore, at a given COD concentration, the content of aromatic substances as well as those containing chromophore groups in mature landfill leachate was far more abundant than in young landfill leachate. The difference in the content of aromatic substances also showed that that the stabilization process in a landfill was accompanied by humic substances that complicated the characteristics of DOM.

To investigate the treatment efficacy of mature and young leachates by the ozone process, the COD concentrations of the two types of leachates were diluted to the same COD concentration (1,000 mg/L). A comparison study then was carried out under the same initial pH value and ozone dose. As depicted in Fig. 2a, a greater decrease in pH occurred in young leachate than in mature leachate. This was explained from two perspectives. On the one hand, the mature leachate contained more micro-molecular organic substances, which had a great buffering effect on pH changes. On the other hand, many acidic substances were produced in the landfill leachate during ozonation [54,55]. Hence, the lower buffering capacity in young leachate coupled with the organic acids produced during ozonation led to a faster pH decrease in the young leachate.

The efficacy of treating landfill leachate by ozone can be reflected by COD, UV_{254}, and CN removals. As shown in Figs. 3b–d, the values of COD, UV_{254}, and CN all showed a decreasing trend as the reaction time increased. After first-order-kinetic fitting, the rate constant k_{obs} of COD, UV_{254}, and CN were determined to be 0.0208, 0.0542, and 0.0685, respectively (for mature leachate), and 0.0411, 0.0904, and 0.1503, respectively (for young leachate). These results showed that for young leachate the rate of organic degradation in the ozone process was faster than for mature leachate. Moreover, organic substances in both mature and young leachates were degraded by ozone, and the removal efficiency order was CN > UV_{254} > COD. The results suggested that chromophore and auxochrome groups in organic matter were first degraded by ozone, after which the organic substances were degraded into smaller organics and even mineralized.

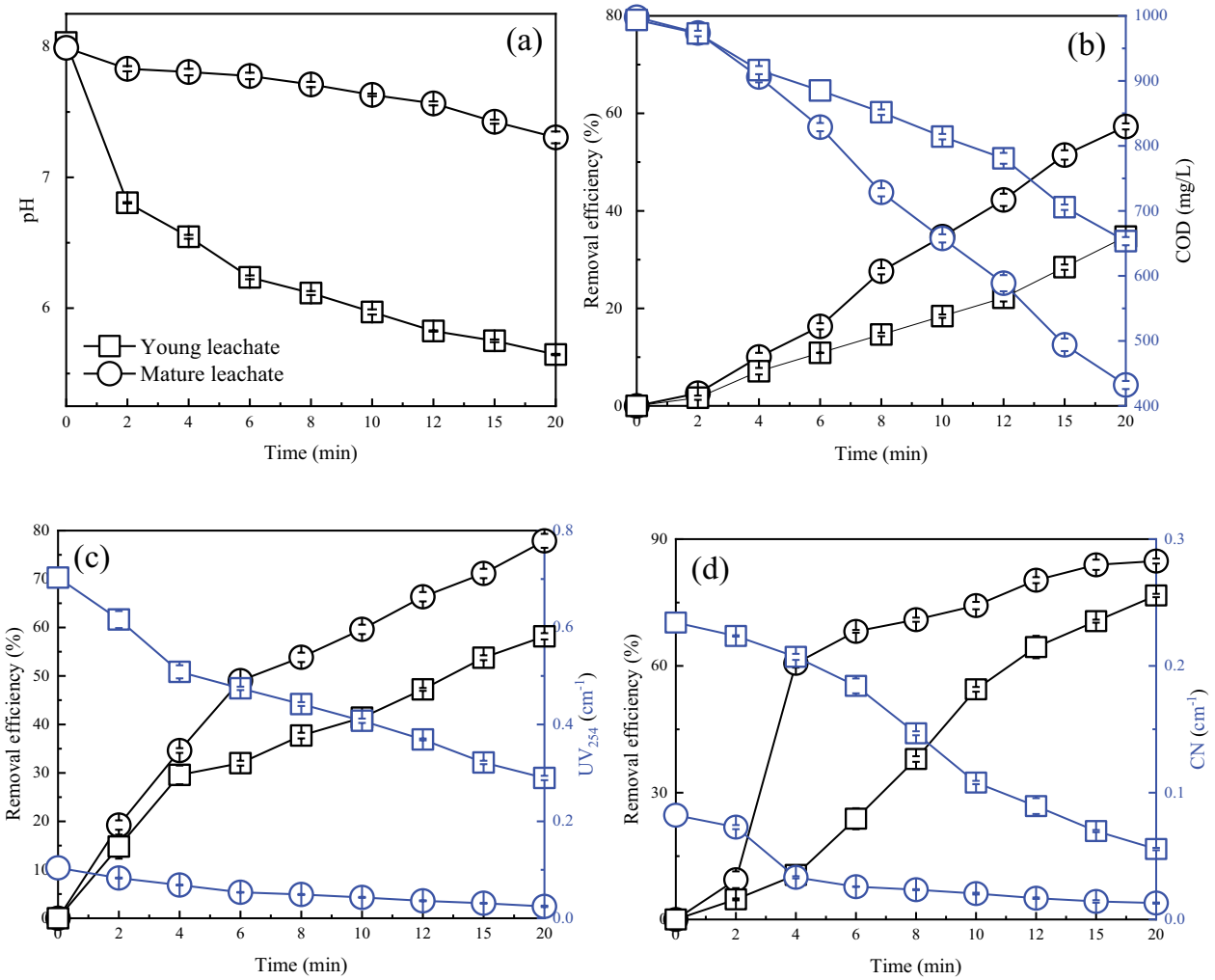

Fig. 2. Treatment efficiency of ozone process on mature and young leachates: (a) effluent pH, (b) chemical oxygen demand (COD) removal efficiency, (c) absorbance at 254 nm (UV_{254}) removal efficiency, and (d) color number (CN) removal efficiency (oxygen flow rate = 9.80 mg/min).

Notably, the efficiencies of removing UV_{254} and CN from mature leachate by the ozone process were much higher than those for young leachate, while the COD removal efficiency from mature leachate was much lower than that from young leachate. These results showed that ozone can effectively mineralize organic substances. With regard to humic substances, ozone mainly changed their aromatic degree and destroyed the chromophores. Ozone especially showed its advantage in degrading organics in mature leachate, which has a higher aromatic degree than young leachate.

3.2. Analysis of changes in COD vs. changes in UV_{254} and CN

To further investigate the treatment efficiency of ozonation in removing DOM from mature and young landfill leachates, the removed amount of CN (ΔCN) and removed UV_{254} (ΔUV_{254}) were compared with removed COD (ΔCOD). Linear regression was used to describe the relationships (shown in Fig. 3).

The ratios $\Delta UV_{254}/\Delta COD$ and $\Delta CN/\Delta COD$ represented the amounts of removed UV_{254} and CN amount when 1 mg/L COD was removed. Ozone, as a selective oxidant, will attack electron-rich moieties to degrade hydrophobic humic acid and/or fulvic acid, both of which are highly and linearly related to UV_{254}. As shown by the coefficients of the regression equations in Figs. 3a and b, for any given COD reduction, the UV_{254} reduction of mature leachate was much higher than that of young leachate (i.e., $6.2511 \times 10^{-4} > 3.3022 \times 10^{-4}$). This difference suggested that in mature leachate that has been subjected to long-term stabilization, the small molecular organics that were present in the early stage of stabilization were transformed into recalcitrant macromolecular organics. This result confirmed that hydrophilic substances in young leachate are resistant to reaction with ozone.

CN is the true color of a wastewater, and is generally imparted by auxochrome groups and chromophores in DOM. As shown in Figs. 3c and d, for the same COD reduction in the early stage of ozonation, the reduction in the CN value of young landfill leachate was slightly higher than that of mature leachate. However, late in the ozonation reaction, for the same COD removal, reductions in the

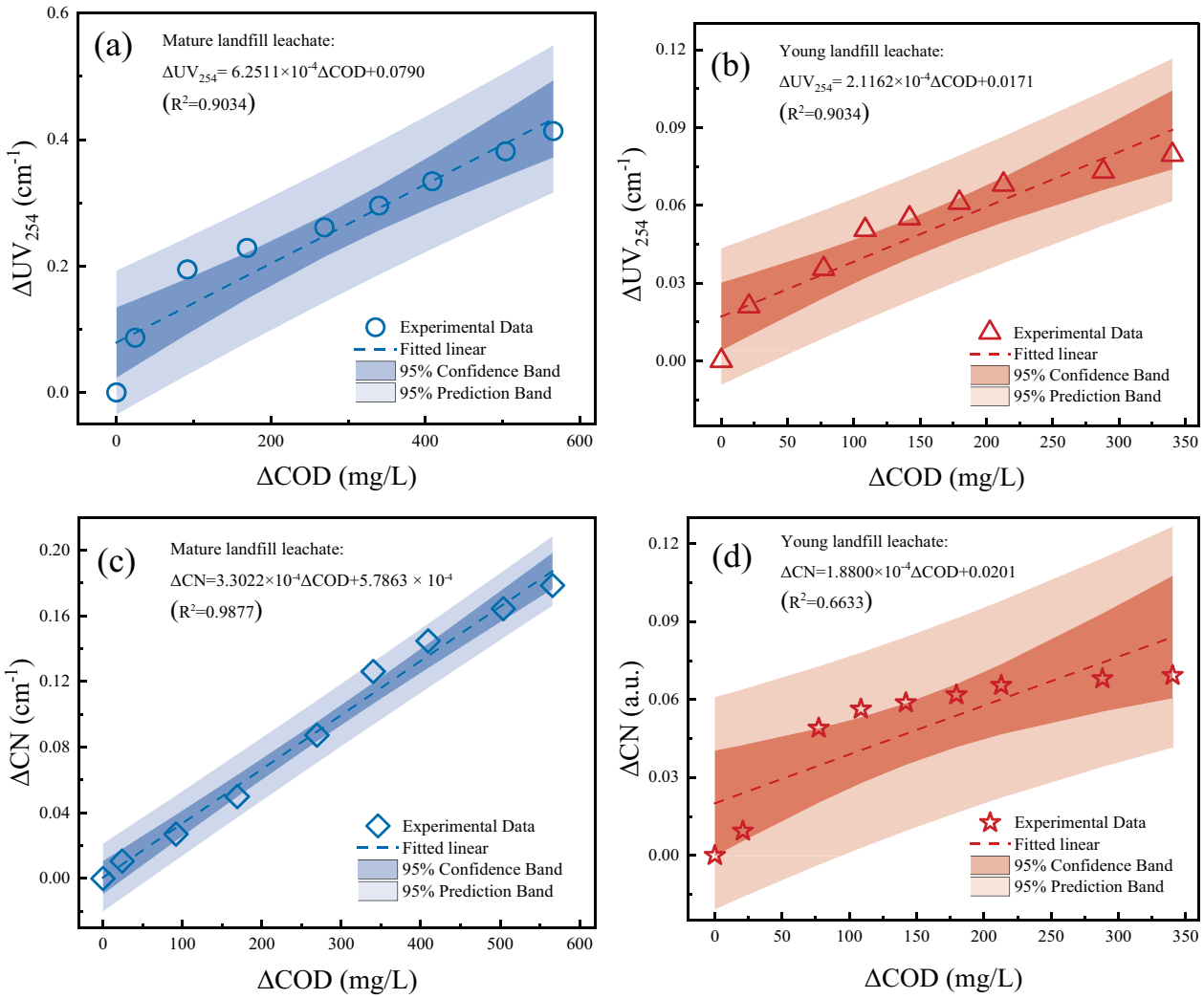

Fig. 3. Analysis on ΔCOD vs. ΔUV_{254} and ΔCN relationships (a and c) mature and (b and d) young landfill leachate.

CN value of mature leachate were much greater than the reductions in young leachate. These results occurred for two reasons. First, the hydroxyl radical exists in the ozonation process, and can non-selectively degrade both hydrophobic and hydrophilic substances via H atom extraction, electron addition, and electron transfer. Therefore, the chromophores of DOM in young landfill leachate will be attacked early in the reaction, and the CN value reduction of young leachate exceeds that of mature leachate. Second, owing to the hydrophilicity increase of young leachate later in the ozonation reaction, the primary oxidant (ozone) reacts slowly with DOM. Additionally, mature leachate mainly contains hydrophobic DOM that reacts rapidly with ozone. As a result, in the late stage of ozonation, CN reduction in mature leachate was much higher than in young leachate.

3.3. DOM identification and removal characteristics in mature and young leachates

3D-EEM often is used to analyze aromatic organics that have π–π* conjugated double bonds in humic substances [17]. To investigate the transformation characteristic of different molecular weight organics in the ozonation process, 3D-EEM was applied in this study to characterize the fluorescence of DOM in mature and young leachates during the ozonation process.

As shown in Fig. 4, two fluorescent peaks were observed in young leachate. According to previous studies [34,56–58], these peaks were marked. Fluorescent peak 1 (Y-P1) represented fulvic-like peaks in the ultraviolet light region. Fluorescent peak 2 (Y-P2) represented tryptophan, which has a high excitation wavelength in the ultraviolet light region [59,60]. In addition, four fluorescent peaks were observed in mature leachate. Fluorescent peak 1 (M-P1) was fulvic-like peaks in the ultraviolet light region. Fluorescent peak 2 (M-P2) represented humic-like peaks in this region. Fluorescent peak 3 (M-P3) represented tryptophan, which has a high excitation wavelength. Fluorescent peak 4 (M-P4) represented fulvic-like peaks in the visible light region. Fulvic-like substances in the ultraviolet light region mainly contained organic substances with low molecular weight and high fluorescent degrees. Tryptophan, a protein, is easy

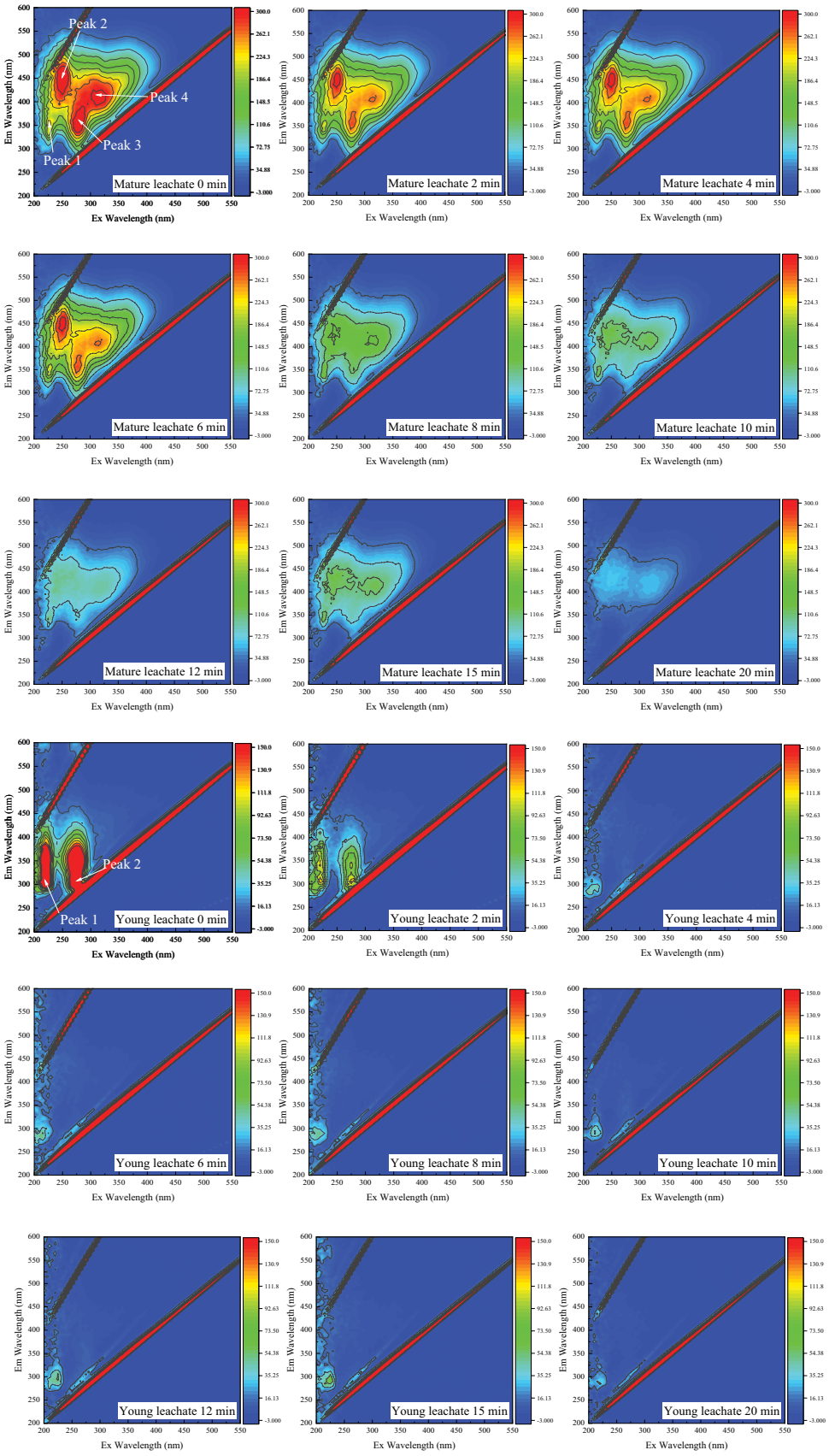

Fig. 4. Three-dimensional emission and excitation spectra of mature and young leachates in ozone process over time.

to biodegrade. The components of fulvic-like substances in the visible light region were relatively stable macro-molecular weight aromatic organic substances. The humic-like substances were resistant to bio-degradation.

As illustrated in Table S1, fluorescent peaks in both mature and young landfill leachates showed a significant decrease as the ozonation reaction time increased. Results showed that fulvic-like substances in the ultraviolet region and tryptophan (with high excitation wavelength) were easily degraded by ozone. The peak value significantly decreased at reaction time of 6 min and the removal efficiency was nearly 100%. Previous study [61] reported that the removal of micro-molecular weight organics in an oxidation system mainly was through mineralization. In addition, removal efficiencies of M-P1, M-P2, M-P3, and M-P4 from mature leachate were 82.31%, 83.30%, 89.63%, and 81.05%, respectively, after an ozone reaction time of 20 min. Furthermore, in mature leachate after ozonation the position of the spectral peak exhibited a blue-shift, demonstrating that the organic content of the leachate was dramatically reduced, and the molecular weight and humidification degree of organics also decreased to some extent.

Fig. S1 shows that pseudo-first-order kinetic equations developed using fluorescent peak decrement data of mature and young leachates described the observed data well. In young leachate, the k_{obs} values of Y-P1 and Y-P2 were 0.3712 and 0.4810, respectively. In mature leachate, the k_{obs} values of M-P1, M-P2, M-P3, and M-P4 were 0.0607, 0.1010, 0.1186, and 0.0874, respectively.

In conclusion, organic substances in young landfill leachate reacted with ozone faster than those in mature leachate (owing to a simpler chemical structure) and were removed through mineralization. However, mature leachate had more macromolecular weight organics than young leachate and these were more complex in composition; therefore, their reaction rate with ozone was much slower. Hence, the ozonation process could effectively degrade macromolecular organics in landfill leachate. The results of 3D-EEM analysis were consistent with COD, UV_{254}, and CN removal.

3.4. DOM transformation of mature and young leachates in the ozonation process

UV-vis spectra were used to study the DOM transformation of mature and young leachate in the ozonation process. The complexity of chemical structure and aromatic degree of these organics can be reflected by the absorbance value in ultraviolet region at wavelengths from 200 to 400 nm.

As shown in Fig. 5, no obvious absorbance peak was observed in either mature or young landfill leachate, indicating that the leachates contained many types of organic substances in high concentrations [33,34]. The absorbance value of mature leachate was significantly higher than that of young leachate in the UV light region, demonstrating that the organic chemical structure became more complex (i.e., showed a great increase in humidification degree) in the long-time stabilization process [62]. The results are consistent with those of a previous study [16].

The absorbance of young leachate showed a slight overall decline as the ozonation reaction time increased; however, the decline of absorbance of mature leachate was much more significant. These results illustrated that the organic substances in mature and young leachates were oxidized by ozone; therefore, the organic concentration decreased and the aromatic degree (as well as conjugation degree) greatly declined. Notably, the absorbance reductions in mature leachate were much larger than in young leachate. The relatively greater decrease of absorbance by mature leachate could be attributed to two effects. First, compared to mature leachate, young leachate is less stabilized and has more aromatic organic acids that have a low humidification degree. Furthermore, ozone preferentially reacts with hydrophobic substances and has a low reaction rate with hydrophilic substances. Thus, after ozonation, the absorbance decrease of young leachate is lower than

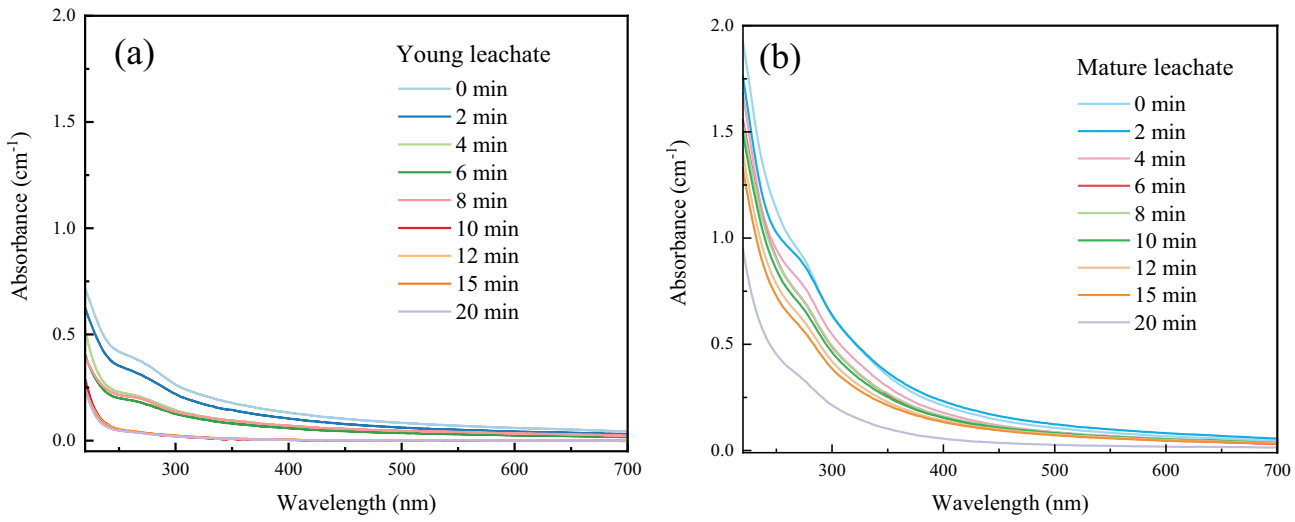

Fig. 5. Ultraviolet-visible spectra of (a) young and (b) mature leachates in ozone process over time.

that of mature leachate [16]. Second, mature leachate contains a large amount of hydrophobic humic-like substances, which can be degraded effectively by ozone to produce smaller molecular organics. In addition, the micromolecular organics that have a low aromatic degree and humidification degree will be nonselectively oxidized by the hydroxyl radical; therefore, a substantial decrease of absorbance in mature leachate was observed.

After 20 min of ozonation, the overall absorbance in mature leachate was still much higher than that of young leachate. This occurred because at the same initial COD concentration, macromolecular organics constituted a higher proportion of organic substances in mature leachate than in young leachate, and these were more complex in chemical structure. Hence, after the same oxidation conditions, the absorbance of mature landfill leachate was overall higher than that of young leachate.

UV-vis spectra can specifically show the characteristics of organic substances by absorbance values at specific wavelengths. The absorbance values of landfill leachate at specific wavelengths before and after ozonation are given in Table S2 and illustrate the transformation of organic substances in mature and young leachates during ozonation. Specifically, $A_{226-400}$ (the integral area of absorbance at a wavelength from 226 to 400 nm) indicates the concentration changes of benzene-ring substances. Results showed that the aromatic degree, molecular weight, and condensation degree all decreased in both mature and young leachates. As reaction time increased, $A_{226-400}$ of mature and young leachates declined from 114.8723 to 41.6642 (mature) and from 47.7388 to 4.4971 (young), suggesting that the concentration of benzene-ring substances considerably decreased. E_{280} (absorbance at 280 nm) and E_{254} (absorbance at 254 nm) represented the aromaticity and hydrophobicity, respectively, of organic substances. Both E_{280} and E_{254} decreased in mature and young leachate, but E_{280} of young leachate especially declined (by an order of magnitude). These results revealed that ozonation can effectively decrease the aromatic degree and the hydrophobicity of landfill leachate, and illustrated that the process had a significant treatment efficacy for landfill leachate (and other contaminated wastewater) with relatively low organic concentration.

3.5. Improvement of biodegradability in mature and young leachates

Fig. 6 shows that differences in landfill leachate age, organic constituents, and the organic concentration led to a dramatic difference in biodegradability of mature and young leachates. Owing to its short landfilling age, young landfill leachate contains many more small molecular organic substances than mature leachate; therefore, its biodegradability is higher (0.322). However, as the age of a landfill increases, the duration of anaerobic conditions also increases and many biodegradable organics will be decomposed by anaerobic microorganisms, leaving a large amount of residuals, or by-products that are extremely difficult to biodegrade. Hence, the biodegradability of mature landfill leachate is low (0.068).

Overall, the biodegradability of both mature and young landfill leachates increased after ozonation. The

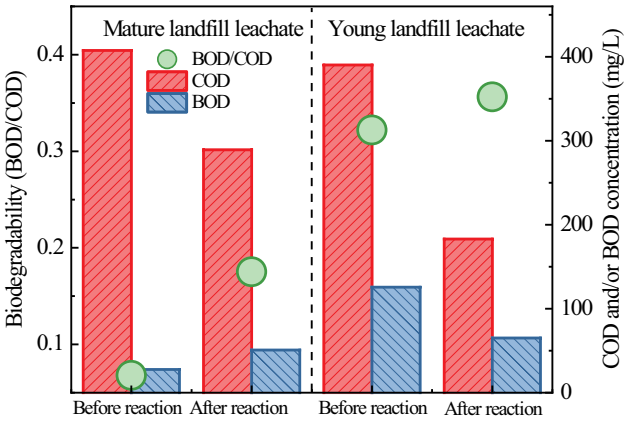

Fig. 6. Improvement of biodegradability of mature and young leachates by ozone process (oxygen flow rate = 9.80 mg/min and reaction time = 20 min).

favorable results were mainly attributed to the hydroxyl radical produced by ozone, which effectively degraded macro-molecular organics, thereby gradually increasing the biodegradability of the leachate. Specifically, the biodegradability of mature and young leachates increased from 0.068 and 0.322 to 0.175 and 0.356, respectively. Notably, the biodegradability improvement of young leachate was not as significant as that of mature leachate. This difference occurred because, prior to ozonation, the young leachate had higher biodegradability than mature leachate, and contained fewer recalcitrant unsaturated organics. Hydroxyl radicals produced by ozone could directly mineralize some organic substances to H_2O and CO_2. Therefore, the contribution of ozone in improving the biodegradability of young leachate was lower than when treating mature leachate.

3.6. Discussion on the characteristic DOM transformation in mature and young landfill leachates treated by ozonation

3D-EEM and UV-vis analyses both showed a significant difference in the organic constitution of mature and young landfill leachate. Specifically, mature leachate contained a comparatively higher concentration of benzene-ring substances, resulting in stronger aromatic degree, hydrophobicity, and higher molecular weight. The main reaction pathway by which ozone degrades aromatic substances involves first destroying benzene rings and then gradually mineralizing the resulting intermediate substances to H_2O and CO_2. If the concentration of aromatic substances is high (reflecting more benzene-ring substances), a large amount of aromatic structures will be attacked and destroyed, certainly increasing the concentration of intermediates. Previous studies reported that intermediate substances such as alcohol and small organic acids have a much slower reaction rate with ozone than humic acid. Hence, the mechanism of ozone treating humic substances in mature landfill leachate is the destruction of benzene-ring structure. However, the subsequent mineralization effect will inevitably be weakened because many intermediates are produced in the process. Consequently,

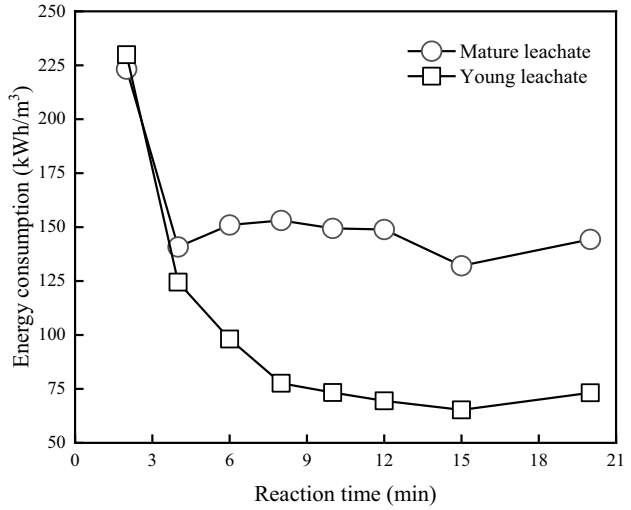

Fig. 7. Energy consumption of mature and young leachates treatment in ozone process over time (oxygen flow rate = 9.80 mg/min and reaction time = 20 min).

the biodegradability improvement that occurs following the ozonation of young leachate is not as significant as that for mature leachate. The humic substances structure is destroyed in the ozonation process; therefore, changes in the organic constitution of mature leachate are great and biodegradability also improves significantly, benefiting any subsequent biological treatment process.

3.7. Energy consumption

Energy consumption is an important consideration in wastewater treatment, and in ozonation process the electrical consumption is the most significant considering that ozone is produced via high-pressure discharge in an ozone generator. As shown in Fig. 7, the highest energy consumption occurred at a reaction time of 2 min. The optimum efficacy of ozonation in treating mature and young landfill leachates occurred at a reaction time 15 min, which also corresponded to the lowest energy consumption, that is, 132.1 and 65.3 kWh/m^3 for mature and young leachate, respectively. In other words, the energy consumption during ozonation of mature leachate was twice that of treating young leachate.

4. Conclusions

The efficacy of ozonation in treating mature and young landfill leachates differed significantly. The molecular structure of organic matter in young landfill leachate was relatively simple, while mature leachate mainly contained macro-molecular organics that had complex structure and high humification degree. In landfill leachate, small molecular organic matter can be effectively removed by ozone. The reaction mechanism of ozone reacting with humic substances mainly involved destroying aromatic substances and chromophores. Moreover, ozonation was especially effective in removing organic pollutants from mature landfill leachate.

References

[1] C. Qi, J. Huang, B. Wang, S. Deng, Y. Wang, G. Yu, Contaminants of emerging concern in landfill leachate in China: a review, Emerging Contaminants, 4 (2018) 1–10.
[2] M.D. Meena, R.K. Yadav, B. Narjary, G. Yadav, H.S. Jat, P. Sheoran, M.K. Meena, R.S. Antil, B.L. Meena, H.V. Singh, V. Singh Meena, P.K. Rai, A. Ghosh, P.C. Moharana, Municipal solid waste (MSW): strategies to improve salt affected soil sustainability: a review, Waste Manage., 84 (2019) 38–53.
[3] B. Gu, S. Jiang, H. Wang, Z. Wang, R. Jia, J. Yang, S. He, R. Cheng, Characterization, quantification and management of China's municipal solid waste in spatiotemporal distributions: a review, Waste Manage., 61 (2017) 67–77.
[4] R. Campuzano, S. González-Martínez, Characteristics of the organic fraction of municipal solid waste and methane production: a review, Waste Manage., 54 (2016) 3–12.
[5] F. Shen, J. Liu, Y. Dong, C. Gu, Insights into the effect of chlorine on arsenic release during MSW incineration: an on-line analysis and kinetic study, Waste Manage., 75 (2018) 327–332.
[6] Y. Wang, X. Zhang, W. Liao, J. Wu, X. Yang, W. Shui, S. Deng, Y. Zhang, L. Lin, Y. Xiao, X. Yu, H. Peng, Investigating impact of waste reuse on the sustainability of municipal solid waste (MSW) incineration industry using emergy approach: a case study from Sichuan province, China, Waste Manage., 77 (2018) 252–267.
[7] Y. Zhang, Q. Li, J. Jia, A. Meng, Thermodynamic analysis on heavy metals partitioning impacted by moisture during the MSW incineration, Waste Manage., 32 (2012) 2278–2286.
[8] F.A.M. Lino, K.A.R. Ismail, Incineration and recycling for MSW treatment: case study of Campinas, Brazil, Sustainable Cities Soc., 35 (2017) 752–757.
[9] C. Cimpan, A. Maul, M. Jansen, T. Pretz, H. Wenzel, Central sorting and recovery of MSW recyclable materials: a review of technological state-of-the-art, cases, practice and implications for materials recycling, J. Environ. Manage., 156 (2015) 181–199.
[10] C. Montejo, C. Costa, M.C. Márquez, Influence of input material and operational performance on the physical and chemical properties of MSW compost, J. Environ. Manage., 162 (2015) 240–249.
[11] Z. Cheng, Z. Sun, S. Zhu, Z. Lou, N. Zhu, L. Feng, The identification and health risk assessment of odor emissions from waste landfilling and composting, Sci. Total Environ., 649 (2019) 1038–1044.
[12] H. Zhang, F. Schuchardt, G. Li, J. Yang, Q. Yang, Emission of volatile sulfur compounds during composting of municipal solid waste (MSW), Waste Manage., 33 (2013) 957–963.
[13] M.K. Iqbal, T. Shafiq, A. Hussain, K. Ahmed, Effect of enrichment on chemical properties of MSW compost, Bioresour. Technol., 101 (2010) 5969–5977.
[14] L. Behrooznia, M. Sharifi, R. Alimardani, S.H. Mousavi-Avval, Sustainability analysis of landfilling and composting-landfilling for municipal solid waste management in the north of Iran, J. Cleaner Prod., 203 (2018) 1028–1038.
[15] Z. Wang, J. Li, W. Tan, X. Wu, H. Lin, H. Zhang, Removal of COD from landfill leachate by advanced Fenton process combined with electrolysis, Sep. Purif. Technol., 208 (2019) 3–11.
[16] W. Chen, A. Zhang, G. Jiang, Q. Li, Transformation and degradation mechanism of landfill leachates in a combined process of SAARB and ozonation, Waste Manage., 85 (2019) 283–294.
[17] A. Zhang, Z. Gu, W. Chen, Q. Li, G. Jiang, Removal of refractory organic pollutants in reverse-osmosis concentrated leachate by microwave–Fenton process, Environ. Sci. Pollut. Res., 25 (2018) 28907–28916.
[18] Y. Wang, W. Tang, J. Qiao, L. Song, Occurrence and prevalence of antibiotic resistance in landfill leachate, Environ. Sci. Pollut. Res., 22 (2015) 12525–12533.
[19] A. Paskuliakova, S. Tonry, N. Touzet, Phycoremediation of landfill leachate with chlorophytes: phosphate a limiting factor on ammonia nitrogen removal, Water Res., 99 (2016) 180–187.
[20] X. Liu, Z. Shu, D. Sun, Y. Dang, D.E. Holmes, Heterotrophic nitrifiers dominate reactors treating incineration leachate with

high free ammonia concentrations, ACS Sustainable Chem. Eng., 6 (2018) 15040–15049.
[21] T.C. Santini, Y.G. Peng, Microbial fermentation of organic carbon substrates drives rapid pH neutralization and element removal in bauxite residue leachate, Environ. Sci. Technol., 51 (2017) 12592–12601.
[22] B.K. Tripathy, M. Kumar, Sequential coagulation/flocculation and microwave-persulfate processes for landfill leachate treatment: assessment of bio-toxicity, effect of pretreatment and cost-analysis, Waste Manage., 85 (2019) 18–29.
[23] A.R. Ishak, F.S. Hamid, S. Mohamad, K.S. Tay, Stabilized landfill leachate treatment by coagulation-flocculation coupled with UV-based sulfate radical oxidation process, Waste Manage., 76 (2018) 575–581.
[24] M.S. Yusoff, H.A. Aziz, M.F.M.A. Zamri, F. Suja, A.Z. Abdullah, N.E.A. Basri, Floc behavior and removal mechanisms of cross-linked *Durio zibethinus* seed starch as a natural flocculant for landfill leachate coagulation-flocculation treatment, Waste Manage., 74 (2018) 362–372.
[25] H. Bakraouy, S. Souabi, K. Digua, O. Dkhissi, M. Sabar, M. Fadil, Optimization of the treatment of an anaerobic pretreated landfill leachate by a coagulation–flocculation process using experimental design methodology, Process Saf. Environ. Prot., 109 (2017) 621–630.
[26] V. Oloibiri, S. De Coninck, M. Chys, K. Demeestere, S.W.H. Van Hulle, Characterisation of landfill leachate by EEM-PARAFAC-SOM during physical-chemical treatment by coagulation-flocculation, activated carbon adsorption and ion exchange, Chemosphere, 186 (2017) 873–883.
[27] S. Zhang, Y. Long, Y. Fang, Y. Du, W. Liu, D. Shen, Effects of aeration and leachate recirculation on methyl mercaptan emissions from landfill, Waste Manage., 68 (2017) 337–343.
[28] I.A. Talalaj, P. Biedka, Impact of concentrated leachate recirculation on effectiveness of leachate treatment by reverse osmosis, Ecol. Eng., 85 (2015) 185–192.
[29] Y. Su, J. Wang, H. Xia, B. Xie, Comparative network analysis revealing the mechanisms of antibiotic resistance genes removal by leachate recirculation under different hydraulic loadings, Sci. Total Environ., 649 (2019) 318–326.
[30] W. Huang, Z. Wang, Q. Guo, H. Wang, Y. Zhou, W.J. Ng, Pilot-scale landfill with leachate recirculation for enhanced stabilization, Biochem. Eng. J., 105 (2016) 437–445.
[31] Z. Ye, H. Zhang, X. Zhang, D. Zhou, Treatment of landfill leachate using electrochemically assisted UV/chlorine process: effect of operating conditions, molecular weight distribution and fluorescence EEM-PARAFAC analysis, Chem. Eng. J., 286 (2016) 508–516.
[32] Z. Gu, W. Chen, Q. Li, Y. Wang, C. Wu, A. Zhang, Degradation of recalcitrant organics in landfill concentrated leachate by a microwave-activated peroxydisulfate process, RSC Adv., 8 (2018) 32461–32469.
[33] A. Zhang, Z. Gu, W. Chen, Q. Li, Degradation of leachate from a semi-anaerobic aged refuse biofilter by the ZVI/H_2O_2 process coupled with microwave irradiation: optimization, organics transformation, and reaction mechanisms, Environ. Sci. Water Res. Technol., 4 (2018) 1695–1709.
[34] W. Chen, A. Zhang, Z. Gu, Q. Li, Enhanced degradation of refractory organics in concentrated landfill leachate by Fe^0/H_2O_2 coupled with microwave irradiation, Chem. Eng. J., 354 (2018) 680–691.
[35] Y. Deng, C.M. Ezyske, Sulfate radical-advanced oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate, Water Res., 45 (2011) 6189–6194.
[36] Y. Wang, X. Li, L. Zhen, H. Zhang, Y. Zhang, C. Wang, Electro-Fenton treatment of concentrates generated in nanofiltration of biologically pretreated landfill leachate, J. Hazard. Mater., 229–230 (2012) 115–121.
[37] P. Frangos, H. Wang, W. Shen, G. Yu, S. Deng, J. Huang, B. Wang, Y. Wang, A novel photoelectro-peroxone process for the degradation and mineralization of substituted benzenes in water, Chem. Eng. J., 286 (2016) 239–248.
[38] Z. Li, S. Yuan, C. Qiu, Y. Wang, X. Pan, J. Wang, C. Wang, J. Zuo, Effective degradation of refractory organic pollutants in landfill leachate by electro-peroxone treatment, Electrochim. Acta, 102 (2013) 174–182.
[39] Y. Zhao, Chapter 5 - Leachate Treatment Engineering Processes, Z. Youcai, Ed., Pollution Control Technology for Leachate from Municipal Solid Waste, Elsevier, 2018, pp. 361–522, https://doi.org/10.1016/B978-0-12-815813-5.00005-X.
[40] M. Bourgin, B. Beck, M. Boehler, E. Borowska, J. Fleiner, E. Salhi, R. Teichler, U. von Gunten, H. Siegrist, C.S. McArdell, Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: abatement of micropollutants, formation of transformation products and oxidation by-products, Water Res., 129 (2018) 486–498.
[41] Y. Deng, J.D. Englehardt, Treatment of landfill leachate by the Fenton process, Water Res., 40 (2006) 3683–3694.
[42] J. Sun, X. Li, J. Feng, X. Tian, Oxone/Co^{2+} oxidation as an advanced oxidation process: comparison with traditional Fenton oxidation for treatment of landfill leachate, Water Res., 43 (2009) 4363–4369.
[43] C. Jung, Y. Deng, R. Zhao, K. Torrens, Chemical oxidation for mitigation of UV-quenching substances (UVQS) from municipal landfill leachate: Fenton process versus ozonation, Water Res., 108 (2017) 260–270.
[44] A. Gupta, R. Zhao, J.T. Novak, C. Douglas Goldsmith, Application of Fenton's reagent as a polishing step for removal of UV quenching organic constituents in biologically treated landfill leachates, Chemosphere, 105 (2014) 82–86.
[45] S.M. Iskander, R. Zhao, A. Pathak, A. Gupta, A. Pruden, J.T. Novak, Z. He, A review of landfill leachate induced ultraviolet quenching substances: sources, characteristics, and treatment, Water Res., 145 (2018) 297–311.
[46] P. Oulego, S. Collado, A. Laca, M. Díaz, Tertiary treatment of biologically pre-treated landfill leachates by non-catalytic wet oxidation, Chem. Eng. J., 273 (2015) 647–655.
[47] P. Wang, G. Zeng, Y. Peng, F. Liu, C. Zhang, B. Huang, Y. Zhong, Y. He, M. Lai, 2,4,6-Trichlorophenol-promoted catalytic wet oxidation of humic substances and stabilized landfill leachate, Chem. Eng. J., 247 (2014) 216–222.
[48] N.M. Ghazi, A.A. Lastra, M.J. Watts, Hydroxyl radical (OH) scavenging in young and mature landfill leachates, Water Res., 56 (2014) 148–155.
[49] X. Chai, Y. Hao, G. Liu, Z. Li, Y. Zhao, The effect of aerobic conditions on the complexation ability between mercury and humic acid from landfill leachate and its implication for the environment, Chemosphere, 92 (2013) 458–463.
[50] J. Niu, T. Zhang, Y. He, H. Zhou, A. Zhao, Y. Zhao, Pretreatment of landfill leachate using deep shaft aeration bioreactor (DSAB) in cold winter season, J. Hazard. Mater., 252–253 (2013) 250–257.
[51] Water Quality-Determination of the Chemical Oxygen Demand-Dichromate Method, Ministry of Ecology and Environmental of the People's republic of China, 2017.
[52] C. Tizaoui, L. Bouselmi, L. Mansouri, A. Ghrabi, Landfill leachate treatment with ozone and ozone/hydrogen peroxide systems, J. Hazard. Mater., 140 (2007) 316–324.
[53] W. Peng, A. Pivato, F. Garbo, T. Wang, Stabilization of solid digestate and nitrogen removal from mature leachate in landfill simulation bioreactors packed with aged refuse, J. Environ. Manage., 232 (2019) 957–963.
[54] W. Cheng, X. Quan, X. Huang, C. Cheng, L. Yang, Z. Cheng, Enhancement of micro-filtration performance for biologically-treated leachate from municipal solid waste by ozonation in a micro bubble reactor, Sep. Purif. Technol., 207 (2018) 535–542.
[55] F. Wang, D.W. Smith, M. Gamal El-Din, Aged raw landfill leachate: membrane fractionation, O_3 only and O_3/H_2O_2 oxidation, and molecular size distribution analysis, Water Res., 40 (2006) 463–474.
[56] P.G. Coble, Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, Mar. Chem., 51 (1996) 325–346.

[57] Z. Gu, W. Chen, Q. Li, A. Zhang, Treatment of semi-aerobic aged-refuse biofilter effluent from treating landfill leachate with the Fenton method, Process Saf. Environ. Prot., 133 (2020) 32–40.
[58] Y. Shutova, A. Baker, J. Bridgeman, R.K. Henderson, Spectroscopic characterisation of dissolved organic matter changes in drinking water treatment: from PARAFAC analysis to online monitoring wavelengths, Water Res., 54 (2014) 159–169.
[59] F.J. Rodríguez-Vidal, M. García-Valverde, B. Ortega-Azabache, Á. González-Martínez, A. Bellido-Fernández, Characterization of urban and industrial wastewaters using excitation-emission matrix (EEM) fluorescence: searching for specific fingerprints, J. Environ. Manage., 263 (2020) 110396, doi: 10.1016/j.jenvman.2020.110396.
[60] H. Yu, F. Qu, X. Zhang, S. Shao, H. Rong, H. Liang, L. Bai, J. Ma, Development of correlation spectroscopy (COS) method for analyzing fluorescence excitation emission matrix (EEM): a case study of effluent organic matter (EfOM) ozonation, Chemosphere, 228 (2019) 35–43.
[61] W. Chen, Z. Gu, P. Wen, Q. Li, Degradation of refractory organic contaminants in membrane concentrates from landfill leachate by a combined coagulation-ozonation process, Chemosphere, 217 (2019) 411–422.
[62] S. Huo, B. Xi, H. Yu, L. He, S. Fan, H. Liu, Characteristics of dissolved organic matter (DOM) in leachate with different landfill ages, J. Environ. Sci., 20 (2008) 492–498.

Supplementary information

Table S1
Removal efficiency of fluorescent substances in mature and young leachates

Time (min)	Young leachate				Mature leachate							
	Y-P1		Y-P2		M-P1		M-P2		M-P3		M-P4	
0	200/310	239.50	275/305	277.70	225/350	240.90	250/450	385.90	280/355	349.70	310/405	312.40
2	225/330	102.50	270/300	113.40	225/350	219.50	250/455	332.30	280/355	279.40	315/405	266.20
4	225/295	46.50	270/300	29.08	225/360	205.90	250/450	287.30	275/360	235.00	315/405	233.20
6	/	/	/	/	230/350	175.70	255/430	206.00	280/360	182.90	315/410	200.20
8	/	/	/	/	225/340	144.00	235/420	149.50	280/375	125.20	320/415	155.60
10	/	/	/	/	225/340	140.60	250/435	135.50	280/280	98.35	315/415	121.50
12	/	/	/	/	225/340	113.70	240/425	108.40	280/360	76.11	320/405	97.62
15	/	/	/	/	225/355	57.34	240/415	83.05	285/360	56.19	320/405	77.23
20	/	/	/	/	220/350	42.60	240/405	64.46	285/365	36.27	315/410	59.18

Table S2
Specific absorbance of mature and young leachates

Sample	Index	0 min	2 min	4 min	6 min	8 min	10 min	12 min	15 min	20 min
Mature	E_{280}	0.8510	0.8297	0.7288	0.6593	0.6617	0.6230	0.5699	0.5252	0.3050
Young		0.3391	0.2803	0.1842	0.1765	0.1614	0.0300	0.0328	0.0318	0.0290
Mature	E_{240}/E_{280}	1.5257	1.3866	1.4774	1.592	1.5759	1.5920	1.6031	1.6116	1.7738
Young		1.3680	1.4024	1.3882	1.3501	1.3761	2.5333	2.2348	2.1289	2.1793
Mature	$A_{226–400}$	114.8723	110.9512	97.4257	89.3902	89.7648	84.8912	77.7369	72.1071	41.6642
Young		47.7388	39.4804	25.9616	22.6212	24.9445	4.8421	5.1465	4.7862	4.4971
Mature	E_{250}/E_{365}	3.8244	3.2605	3.7560	3.9552	3.9864	4.0308	3.9501	5.3546	3.9552
Young		2.5948	2.7163	2.6839	2.7500	8.9667	6.7037	7.3913	6.9275	2.7500
Mature	E_{240}/E_{420}	7.2093	5.7872	7.2213	7.5950	7.5023	7.5692	7.3600	11.7865	7.5950
Young		2.5948	2.7163	2.6839	2.7500	8.9667	6.7037	7.3913	6.9275	2.7500
Mature	E_{300}/E_{400}	2.9967	2.7464	3.0823	3.0388	2.9871	2.9816	2.8806	3.8265	3.0388
Young		2.0061	2.1106	2.1369	2.1536	6.5625	5.9756	5.8462	5.8611	2.1536

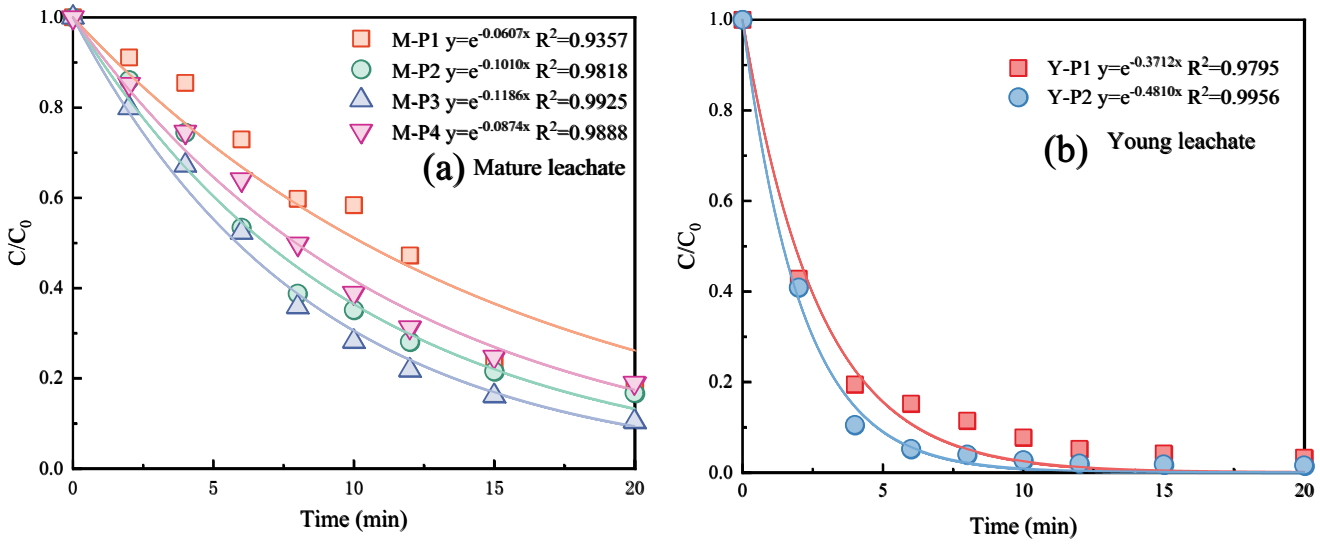

Fig. S1. Kinetic fitting of fluorescent substances removal in (a) mature and (b) young leachates in ozone process.