Comparison of macro and micro-pollutants abatement from biotreated landfill leachate by single ozonation, O_3/H_2O_2, and catalytic ozonation processes

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Abstract

Micropollutants (MPs) in landfill leachate have attracted increasing attention because they pose a potential threat to the water environment and aquatic ecosystems once discharged into nearby aquifers without proper treatment. Although the ozone-based oxidative techniques perform well in MPs removal in low-strength water streams, their role in leachate containing high DOM concentration needs to be further explored. This study compared the single ozonation and two ozone-based AOPs (heterogeneous catalytic ozonation and O_3/H_2O_2 process) for polishing biotreated leachate. The removal efficiency and energy requirements of the macro and micro-pollutants were evaluated. Results revealed that the role of catalytic ozonation is mainly to enhance the direct ozone oxidation, while O_3/H_2O_2 process is to promote the indirect oxidation. The strengthening effect is most visible in the early stage (STOD < 2 $gO_3/gDOC$) for catalytic ozonation, whereas more pronounced in the later for O_3/H_2O_2 process. The removal of UV quenching substances correlates well to MPs elimination ($R^2 > 0.95$), which provide a surrogate-based predictive model for MPs removal in high-strength leachate. For energy, catalytic ozonation consumes the least amount of energy if the desired COD removal is ≤ 35%, otherwise, O_3/H_2O_2 process is the most energy-efficient. In any process, the MPs with O_3 or •OH reactivity could achieve more than 90% elimination when the COD removal exceeds 30%.

Key words: Landfill leachate, Ozone-based AOPs, Micropollutants, Surrogate-based prediction, •OH yield, Energy consumption

1. Introduction

The landfill leachate is a typical wastewater containing a high concentration and a wide range of organic and inorganic pollutants and is known as a refractory wastewater [1, 2]. The majority of the biodegradable organic matter is removed in the biological treatment process, but the refractory organic matter (such as humic acids) is hard to biodegrade and still remain in the biotreated leachate [3, 4] In addition, with the development of analytical techniques in recent years, various micropollutants (MPs) have been detected in the leachate [5 − 9]. Sui et al. [6] reported that fourteen MPs with a concentration distribution in a range of 0.4 μg/L to 350 μg/L were detected in the leachate collected from a landfill in Shanghai. The concentration of some MPs in the biotreated landfill leachate is still much higher than that in the urban sewage. As such, landfill leachate might be an underestimated source of MPs in the water environment [10]. Macro and micro- pollutants will discharge into the receiving environment if the leachate is improperly disposed, which may pose a threat to the surface and groundwater adjacent to the landfill, and inevitably cause damage to aquatic organisms [11, 12]. In this context, there is an urgent need for more efficient and reliable processes for advanced treatment of landfill leachate.

Ozonation has been proven to be a potential treatment for the removal of MPs in low-strength wastewater streams such as groundwater [13], surface water [14, 15], and secondary wastewater effluent [16 − 18]. Studies in recent years also showed that ozonation can play an important role in the advanced treatment of high-strength wastewater such as biotreated leachate [19, 20]. The ozone molecule (O_3) is a strong

oxidant with a redox potential (E^0) of 2.08 V, which can effectively degrade the molecular structure of humic substances and degrade organics via a series of chain reactions. During the ozonation process, dissolved organic matter (DOM) is oxidized by O_3 and/or hydroxyl radicals (•OH) formed from O_3 decomposition. The ozone-reactive compounds containing electron-rich groups react quickly with O_3, but the ozone-refractory substances can only be removed by •OH because of their extremely low reaction rate constants with O_3 [21]. In order to improve the conversion of O_3 to •OH, some technologies/chemicals (ultraviolet [22, 23], ultrasound [24], catalytic ozonation [25, 26], H_2O_2 [27, 28]) can be coupled to the ozonation process, resulting in ozone-based advanced oxidation processes (AOPs). Although various ozone-based AOPs can improve the treatment efficiency to a certain extent, the reaction mechanisms vary under different conditions. For example, there are three possible catalytic mechanisms in the process of heterogeneous catalytic ozonation: (i) ozone molecule is adsorbed on the surface of the catalysts and decomposed into •OH, (ii) organic compounds are adsorbed on the surface of the catalysts, and the adsorbed ozone molecule will react with these compounds, (iii) ozone molecule and organic compounds are both adsorbed on the surface of the catalysts, and as such their reaction is catalyzed [29]. For the O_3/H_2O_2 process, the transformation of O_3 to •OH is expressed by Eq. (1) – (4) [30].

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \quad (1)$$

$$HO_2^- + O_3 \longrightarrow HO_2^\bullet + O_3^{\bullet-} \quad (2)$$

$$O_3^{\bullet-} + H^+ \rightleftharpoons HO_3^\bullet \quad (3)$$

$$HO_3^{\bullet} \rightleftharpoons {}^{\bullet}OH + O_2 \quad (4)$$

In this system, O_3 actually reacts with the anions of hydrogen peroxide because the reaction rate constant of O_3 with H_2O_2 is very low (< 0.01 $M^{-1}s^{-1}$). This reaction is proved to be carried out via electron transfer [30]. The $O_3\bullet^-$ radical then becomes protonated and the ensuing $HO_3\bullet$ radical decomposed into •OH radical and oxygen molecules [31]. As such, the conversion reaction of O_3 towards •OH is accelerated by the addition of H_2O_2. Hence, increased understanding of the mechanism occurrence is essential for model-based optimization of the advanced treatment train. This profound knowledge is required to successfully implement AOPs in full scale. Based on this reason, sufficient information about the conversion of DOM surrogates is needed to provide insights into the reaction mechanism. Spectroscopic indicators as a surrogate for DOM in wastewater can reflect organics transformation. UV-visible (UV-vis) full spectra measurements have been used to study the DOM properties. Examples are the applications in the secondary effluents from WWTP [32 − 36] and biotreated landfill leachate [20]. Further data processing can provide in-depth information on the DOM of treated wastewater. Nanaboina [32], Audenaert [33] and Michael et al. [20] obtained differential absorbance spectra (DAS) from EfOM and leachate by computational UV-vis spectra data, respectively. These findings reveal differences between different wavelengths during DOM transformation as well as the specificity between high- and low-strength water streams. However, it is rare that the DAS concept is used to compare the reaction mechanisms of different ozone-based processes for treating leachate. As the ozone mass transfer and the formation of radicals is largely influenced by the types

of AOPs applied, some differences can be expected during the distinct processes. This could provide a new perspective for UV-vis full spectra application. In this study, various ozone-based oxidation processes were compared for this purpose.

MPs present in the leachate exhibit different apparent degradation rate constants, thereby affecting the ozone dosage and energy consumption during different AOPs. Moreover, the addition of assistant technologies/chemicals is bound to influence energy consumption. As such, it is necessary to establish an accurate calculation of ozone demand when the biotreated leachate is purified to a certain level, and to assess the energy consumption of different AOPs. It has often been reported that the ozone-based AOPs can considerably enhance the abatement of ozone-refractory MPs in surface water [14, 37] and effluents of municipal wastewater [38], but less reports on improvement of MPs elimination in biotreated landfill leachate. This study will investigate the enhancement mechanism of ozone-based AOPs for the MPs elimination in biotreated leachate, and evaluate their energy consumption.

The ozonation process generally involves two primary reaction stages, corresponding to the instantaneous phase that the applied ozone dose (AOD) < initial ozone demand (IOD) and the gradual phase that AOD > IOD, respectively [39 – 41]. Due to the different reaction mechanisms, the mass transfer and decomposition rates of ozone differ in two stages. As such, the ozone utilization efficiency and •OH yield in the different ozone-based AOPs may vary significantly during the course of the ozonation. Furthermore, the DOM concentration in leachate is much higher than that in municipal wastewater or surface water [42]. Such a high-strength water stream will inevitably

affect the generation (quenching) of •OH, the transformation of MPs, and the corresponding energy consumption. To our knowledge, a comparative study on ozone utilization efficiency, •OH yield and energy consumption evaluation of biotreated landfill leachate is relatively scarce. This kind of information can offer support for process selection, design, and modeling during pilot-scale and full-scale applications. In addition, few studies on the mathematical relationship for the removal between macro and micro-pollutants in leachate have been reported, and the relevant profound knowledge needs to be expanded. This supplemented knowledge is critical for predicting the MPs removal in the high-strength water matrix.

In this study, three distinct ozone-based oxidation processes for the leachate treatment are compared. The aims of this research are to: (i) investigate the transfer behavior of O_3 in different ozone-based AOPs, (ii) compare the removal efficiency and conversion characteristics of macro and micro-pollutants in different processes and explore the relationship between macro and micro-pollutants in terms of removal rate, (iii) assess the •OH yield per amount of ozone dose during different ozonation processes as a elucidation of the oxidation effect, (iv) to evaluate the energy requirements of target pollutants for a specific removal.

2. Materials and methods

2.1 Chemicals and catalysts

All chemicals were of analytical grade (purity of 98% or higher). Hydrogen peroxide (H_2O_2) used in the experiments had a concentration of 30 ωt%. H_2O_2 and micropollutants, including atrazine (ATZ), alachlor (ALA) and 17α-ethinylestradiol

(EE2) were purchased at Sigma-Aldrich (Belgium). GC-MS reagent grade dichloromethane (CH_2Cl_2), with a purity of over 99.8%, was purchased at Carl Roth Co., Germany. The catalyst used in this experiment was purchased from Shuimengyuan Technology Co., China. It is made of alumina pellets covered with cerium and manganese oxides. Such catalysts have been successfully applied to the tertiary treatment of coking wastewater with high concentrations of pollutants, and exhibit well performance in the presence of appropriate backwashing technology [43, 44].

2.2 Leachate sample

The biotreated leachate was collected from the IMOG landfill site in Moen, Belgium. The leachate of this landfill is first treated in a sequencing batch reactor (SBR). The biological stabilized leachate flows into the wetland to further remove nitrogen and phosphorus and suspended solids. Before the final discharge, activated carbon adsorption is used as the final polishing step to remove bio-refractory substances. The experiment sample was taken from SBR effluent and stored at 4℃ before use. The sample characteristics are: chemical oxygen demand (COD): 320 − 400 mg/L; total organic carbon (TOC): 110 − 140 mg/L; absorbance at the wavelength of 254 nm (α_{254}): 2.59 − 2.75 cm^{-1}; NO^-_2-N: 0.41 − 0.78 mg/L; pH: 7.8 − 8.4. Other details about the landfill site and pollutant composition have been described in previous studies [2, 45].

2.3 Procedure of the ozone-based oxidative techniques

The ozonation experiments were carried out in a semi-batch mode with a cylindrical reactor (2 L water volume) shown in Fig. 1. An ozone generator (COM-AD-02, Anseros GmbH, Germany) was applied to produce O_3 gas from pure O_2 gas. The ozone/oxygen

mixture gas entered the reactor at a constant flow rate (300 ± 10 mL/min), and the ozone concentration at the inlet was set to 48 ± 2 mg/L so that the total applied ozone dose throughout the experiment (90 min) was 8 gO_3/gDOC [2, 20]. An ozone concentration analyzer (GC-OEM, Anseros GmbH, Germany) was used to monitor the gaseous ozone concentration at the inlet and outlet. A Cole-Parmer DAQ module (model FN-18200-00) was to record the gas concentration once per second. At desired sampling times, 30 mL samples were collected for analysis. The experiment was carried out at room temperature. As target MPs with different reactivity with O_3 and •OH, atrazine (ATZ), alachlor (ALA), and 17α-ethinylestradiol (EE2) were spiked to the leachate at a concentration of 500 μg/L before the start of the ozonation.

The O_3/H_2O_2 experiment was carried out similar to the single ozonation experiment. H_2O_2 can promote the decomposition of O_3 on the one hand but on the other hand it can become a scavenger of •OH if the H_2O_2 is excessive. As such, the application method and dosage of H_2O_2 in the O_3/H_2O_2 process will affect its performance [46]. According to the previous research [2], H_2O_2 was fed into the reactor continuously using a peristaltic pump at a molar ratio of H_2O_2/O_3 of 0.5 in this experiment.

During the catalytic ozonation experiment, the reactor was filled with 25% − 35% volume of aluminum-based commercial catalysts before ozonation based on previous study [43, 44]. The rest of the experiment is carried out in a similar fashion as the single ozonation process.

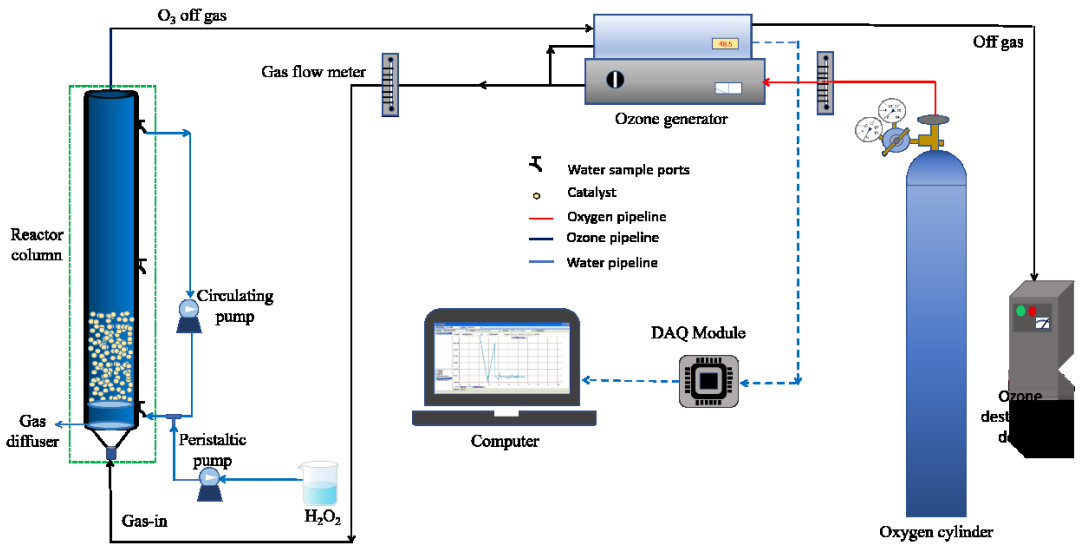

Fig. 1 Schematic representation of the experimental device used in this study.

2.4 Calculation of ozone mass balance and •OH exposure

Ozone balance was evaluated by recording continuously ozone concentration in the both gaseous at inlet and outlet. Two parameters for ozone consumption: i.e., applied ozone dose (AOD) and transferred ozone dose (TOD), can be calculated based on the ozone mass balance. AOD (mg/L) reflected the total amount of O_3 introduced to the water sample per unit of volume, as expressed in Eq (5). TOD (mg/L) represents the accumulated amount of O_3 that is transferred to the water sample per unit of volume, according to Eq (6). Ozone transfer yield can be calculated as the ratio of TOD to AOD (Eq. (7)). Another parameter related to the relationship between TOD and DOM was determined as the specific transferred ozone dose (STOD), which represents the ozone dose applied per unit of DOC. STOD (g O_3/g DOC) was used to compare the removal efficiency of organic matter with other studies [2].

$$AOD = \int_0^t \frac{[O_3]_{in} Q_{gas}}{V_{liq}} dt \quad (5)$$

$$TOD = \int_0^t \frac{Q_{gas}}{V_{liq}} ([O_3]_{in} - [O_3]_{out}) dt \quad (6)$$

$$\text{transfer yield}(\%) = \frac{TOD}{AOD} \times 100 \quad (7)$$

$$STOD = \frac{TOD}{[DOC]} \quad (8)$$

Where the $[O_3]_{in}$, and $[O_3]_{out}$ are the ozone concentrations (mg/L) in the gaseous phases at the reaction time. Q_{gas} (L/min) and V_{liq} (L) are the gas flow rate and the liquid volume, respectively.

The calculation of •OH exposure is usually based on a probe compound (e.g. para-chlorobenzoic acid) with low apparent second-order reaction rate constant with O_3 and high reaction rate constant with •OH [47]. It can be assumed that the removal of this compound is mainly due to the reaction with •OH and the contribution of its direct reaction with O_3 is negligible. ATZ is a kind of herbicide which barely reacts with O_3 (k_{O3} = 6.0 $M^{-1}s^{-1}$) but presents a high second-order reaction rate constant ($k_{\bullet OH}$ = 3.0× 10^9 $M^{-1}s^{-1}$) with •OH [48]. Due to these properties, this compound was selected in the present experiment as a probe to estimate the •OH exposure according to Eq. (9).

$$\bullet\,\text{OH exposure} = \int \bullet\,\text{OH}\, dt = \frac{ln\frac{MP_0}{MP_t}}{k_{\bullet\text{OH}}} \quad (9)$$

Where MP_t and MP_0 are the concentration of ATZ at the time of 0 and t.

2.5 Analytical methods

Standard methods were used to determine the quality analysis of biotreated leachate [49]. COD and nitrite were determined using commercial Hach test kits and a spectrophotometer (DR6000, Hach, USA) according to standard methods. The total organic carbon (TOC) in the samples were tested by a TOC analyzer (TNM-L ROHS, Shimadzu, Japan). The UV-vis absorption spectra between 210 and 450 nm was measured using a Shimadzu UV-1601 spectrophotometer (Japan) with 1 cm quartz

cuvette. The absorbance at 254 nm (α_{254}) and 436 nm (α_{436}) were derived from UV-vis spectra data at specific wavelengths. The samples were diluted 5 times when measured UV-vis absorbance because of the high concentration of DOM. Differential absorbance spectra (DAS) were obtained by calculating the difference between the initial absorbance spectra before treatment and the spectra after specific time intervals, according to the literature [32]. Dissolved ozone concentrations were determined by the indigo method [50]. MPs concentrations were measured by GC-MS analysis after extraction with dichloromethane, according to Liu et al [51]. The more detailed introduction for the MPs analysis procedure presented in Text S1 in the Supplementary Information (SI).

3. Results and discussion

3.1 Comparison of ozone mass transfer in different ozonation processes

Ozone mass transfer can intuitively reflect the utilization of O_3 during the ozonation process. Fig. 2 depicts the characteristics of ozone mass transfer in three different ozonation processes.

3.1.1 Gas phase ozone concentration

Experimental plots of ozone concentration at outlet as a function of reaction time during the ozonation of biotreated leachate are displayed in Fig. 2a. It can be seen the ozone concentration at outlet of the three ozonation systems have a common feature: the curve is divided into two stages, i.e., a rapid increase stage (the first 15 min) and a slow increase stage (after 15 min). At the end of the reaction (90 min), the outlet gas concentrations of single ozonation, O_3/H_2O_2, and catalytic ozonation reached 33, 20,

246 and 27 mg/L, respectively. It should be noted that, in the first stage, the outlet gas
247 concentration of the catalytic ozonation increases the slowest compared to the other two
248 systems, which could be attributed to the adsorption of O_3 by the catalyst [52]. In the
249 second stage, the ozone concentration at outlet of the single ozonation and catalytic
250 ozonation continues to rise, while it remains constant in the O_3/H_2O_2 process. This
251 demonstrates that the ozone utilization efficiency gradually decreases in the first two
252 systems but remained stable in the O_3/H_2O_2 process. This result could be since different
253 systems exhibit different reaction mechanisms. The ozone consumption in single
254 ozonation and catalytic ozonation systems ascribes primarily to the reaction between
255 ozone-reactive substances and O_3. As the ozonation progressed, the content of ozone-
256 reactive substances gradually decreased, resulting in a reduction in ozone consumption.
257 Contrastingly, additional H_2O_2 in the O_3/H_2O_2 system can promote ozone
258 decomposition [53], which leads to a significant difference in ozone concentration
259 between the liquid and gas phases, thereby increasing the ozone transfer from the gas
260 phase to the liquid phase.

261 **3.1.2 Profile of ozone transfer**

262 The ozone transfer efficiency is a crucial parameter to evaluate ozone utilization in
263 ozone-based AOPs. Generally, high mass transfer efficiency means high ozone
264 utilization level. Fig. 2b presents the evolution of the transferred ozone dose (TOD) and
265 the ozone transfer yield as a function of the applied ozone dose (AOD). Obviously, two
266 distinct stages can be observed in the ozone transfer yield curve in all three systems. A
267 strong decrease in ozone transferred yield is observed during the first 300 mg/L of AOD,

ranging from 100% to approximately 65%, 71%, 74%, respectively, for the single ozonation, O_3/H_2O_2, and catalytic ozonation processes. Above 300 mg/L of AOD, the transfer yield slowly decreases to reach a value of 49%, 64%, and 59% for the single ozonation, O_3/H_2O_2, and catalytic ozonation processes, respectively. The lowest ozone transfer yield occurs in the single ozonation process, which implies that additional chemicals and/or technology can effectively improve the ozone utilization.

In the ozone-based AOPs, UV, H_2O_2, and ultrasound, could promote the decomposition of dissolved ozone during ozonation. In this research, the dissolved ozone concentration in the single ozonation and the catalytic ozonation increases consistently over time (Fig. 2c). In the first 350 mg/L of TOD, the dissolved ozone concentration rises rapidly, reaching 10 mg/L and 9 mg/L, respectively. After that, the dissolved O_3 concentration reached a plateau. In comparison, during the O_3/H_2O_2 process, the dissolved ozone concentration reached a peak value of 4 mg/L after a TOD of 200 mg/L and then a downward trend is observed (to almost 0 mg/L). This phenomenon seems to indicate that the catalyst has a negligible effect in promoting ozone decomposition compared with hydrogen peroxide. It should be noted that no dissolved O_3 was detected during the TOD of 60 mg/L in any of the three ozonation systems, suggesting that the water matrix consumed all of the transferred ozone. Usually, the ozone consumption in the initial stage can be expressed by instantaneous (initial) ozone demand (IOD, mg/L) [54, 55]. The curve in Fig. 2c showed that the IOD of all the three systems was roughly the same at about 60 mg/L. This is owing to the fact that the IOD depends on the nature of the leachate rather than the applied treatment technology. Previous studies have

reported the IOD was 130 mg/L during the ozonation for the leachate treatment [2]. The differences in these IOD values may be attributed to the nature of the water matrix.

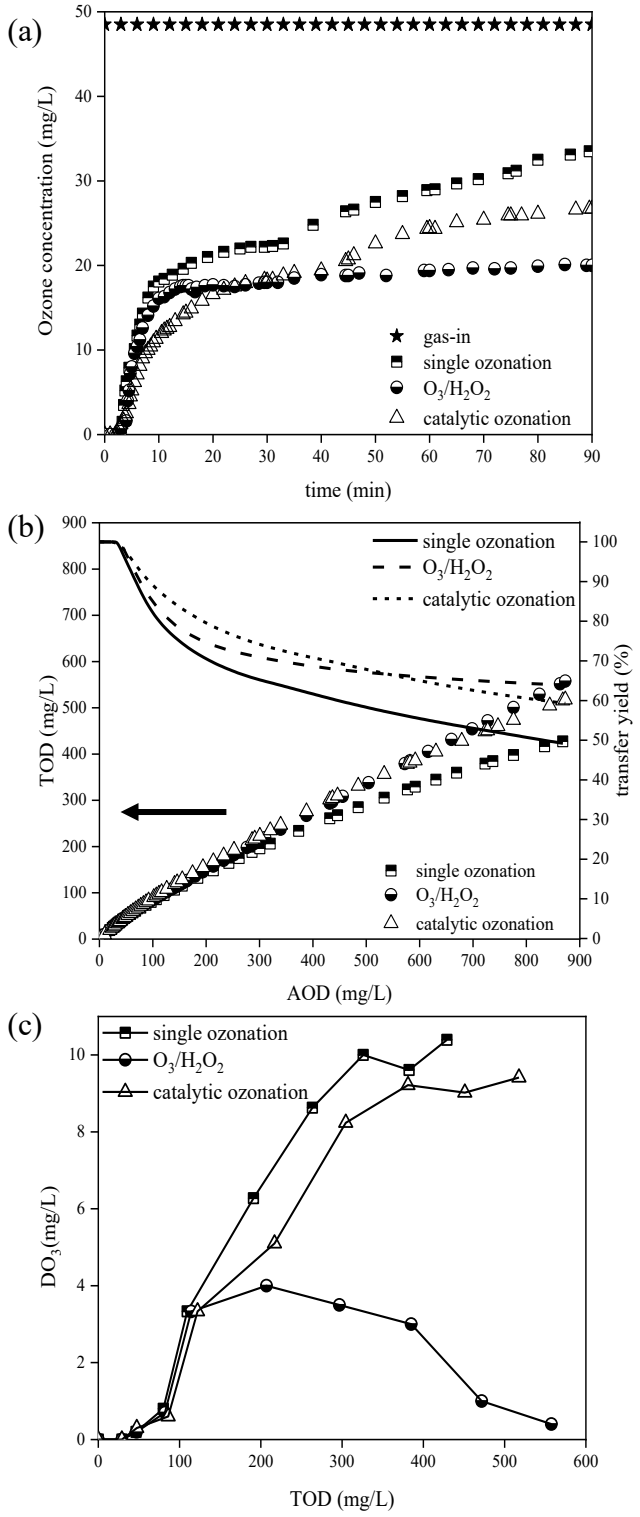

Fig. 2 Comparison of different types of ozonation behavior for the biotreated leachate. (a) Gaseous ozone concentrations at inlet and outlet as a function of ozonation time. (b) Related parameters for the ozone mass transfer. (c) Dissolved ozone curve as function of transferred ozone dose.

3.2 Comparing the performance of different ozonation processes from the perspective of macro-pollutants removal

3.2.1 DOM spectral variation characteristics

After the leachate was subjected to ozonation, the absorbance at 254 (α_{254}) and 436 nm (α_{436}) decreased (Fig. 3). It is seen that the decay of α_{436} is much more pronounced than that of α_{254}, independent of the ozonation programs. The molar ratio of O_3 to DOC is equal when their mass ratio is 0.4 [56]. Under such conditions, the α_{436} exhibits high removal rates which is > 60%, as highly conjugated molecules that strongly absorb at this wavelength could react preferentially with O_3. In comparison, the α_{254} is only reduced by less than 35% because the products of the hydroxylation reaction between aromatic compounds and O_3 still absorb at the wavelength of 254 nm [21, 56]. Moreover, the reaction between these substances and O_3 is one of the main pathways for generating •OH during ozonation, which is an important oxidant for mineralizing ozone-refractory substances [56].

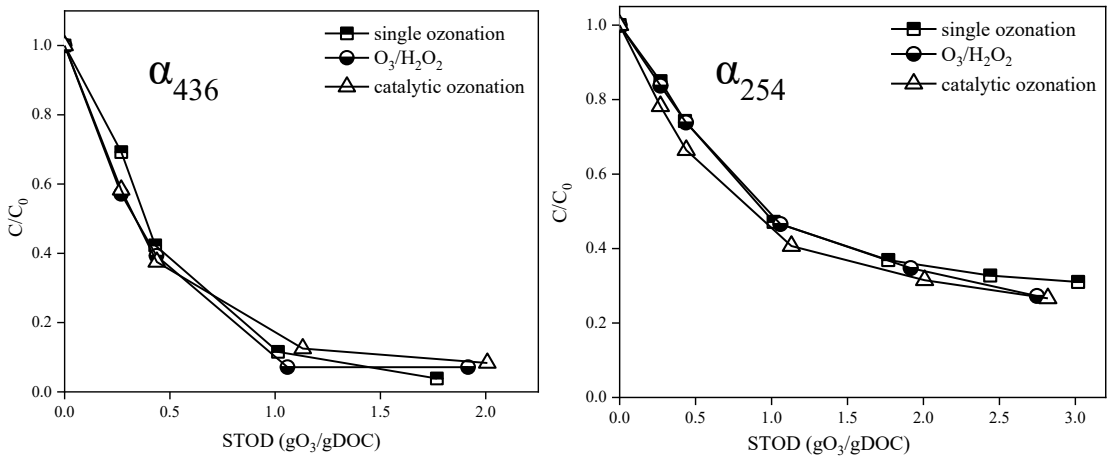

Fig. 3 Relative residual in absorbance at 436 and 254 nm as a function of STOD.

With the exception of the absorbance at some selected wavelengths, full spectra UV-vis analysis was also used to profoundly compare DOM changes during different ozonation

processes. The changes of the UV-vis spectra as function of the treatment time among three ozonation processes are shown in Fig. 4 and Fig. S1. A general decrease in absorbance due to partial oxidation of the chromophore moieties of the DOM is observed in all processes. These observations are consistent with earlier findings in both leachate and less polluted secondary effluent [20, 32, 33]. DAS quantifies the difference between the initial absorption spectra and that at any treatment duration (Fig. S2). It shows that the differential absorbance magnitude of DOM increases monotonically with treatment time at $\lambda > 240$nm. Moreover, a shoulder peak can be distinguished at a band with λ_{max} = 280nm, which indicates that O_3 has a preferential affinity for substances with absorbance in this wavelength [57]. The DAS data are further processed (by the differential absorbance at 280nm as a local maximum occurred) to obtain the normalized DAS (NDAS) spectra (Fig. 5a − c). To facilitate the discussion, the NDAS spectra are divided into three main regions: region 1 (210 − 240 nm), region 2 (240 − 280 nm) and region 3 (280 − 450 nm). The same features at $\lambda > 240$ nm are observed in the NDAS spectra of leachate treated by different ozonation processes. It can be found that the vertical arrangement of the curves in region 2 is opposite to that in region 3, especially during the first 45 min of treatment. This may indicate that transformation products of DOM that initially absorbed at higher wavelengths contributed to the formation of products absorbed at lower wavelengths. After 45 min of treatment, the NDAS curves almost completely overlap since the compounds preferential attacked by O_3 are almost depleted.

The changes in NDAS at specific treatment time are presented in Fig. 5d − i. It can be

seen that the NDAS curves obtained from different ozonation processes are also highly coincident in region 2 and 3. This phenomenon implies that the difference of treatment processes has little effect on the conversion of UV quenching substances (UVQS). This is strong evidence that the degradation of UVQS is dominated by direct ozone oxidation even under the condition of •OH exposure, which was also confirmed in •OH quenching experiments [2, 40]. Nonetheless, various oxidation systems have effect on the degradation rate of UVQS, as reflected in Fig. S3. In the first 30 minutes, the catalytic ozonation has the fastest degradation of UVQS, after that, the O_3/H_2O_2 system is the fastest. This result is in step with the ozone mass transfer efficiency and indicates that catalytic ozonation can accelerate the direct ozone oxidation.

The evident divergences in region 1 (Fig. 5) among three ozonation systems are noteworthy. Fig. 5 shows that the NDAS value of the O_3/H_2O_2 system is much higher than that of the other two systems after 15min of treatment, and the NDAS value of the ozonation and catalytic ozonation systems drops monotonically due to the increase of the absorbance with treatment time. Compounds with functional groups such as carboxyls, carboxylates, aldehydes and esters strongly absorb UV light in 200-220 nm wavelength range [58]. Absorbance at 215 nm wavelength is used to identify most organic acids due to absorbance by the carbonyl group [59]. Hence, the phenomena occurring in region 1 can be explained by (i) The ozonation process leads to the accumulation of degradation products containing carbonyl [60 − 62], (ii) the accumulation of these compounds is inhibited under high •OH exposure [63], and (iii) the catalyst has little substantial effect on the improvement of •OH yield, while the

addition of H_2O_2 can significantly improve the •OH yield in the ozonation process (Quantification of •OH would be discussed in the followed section 3.4).

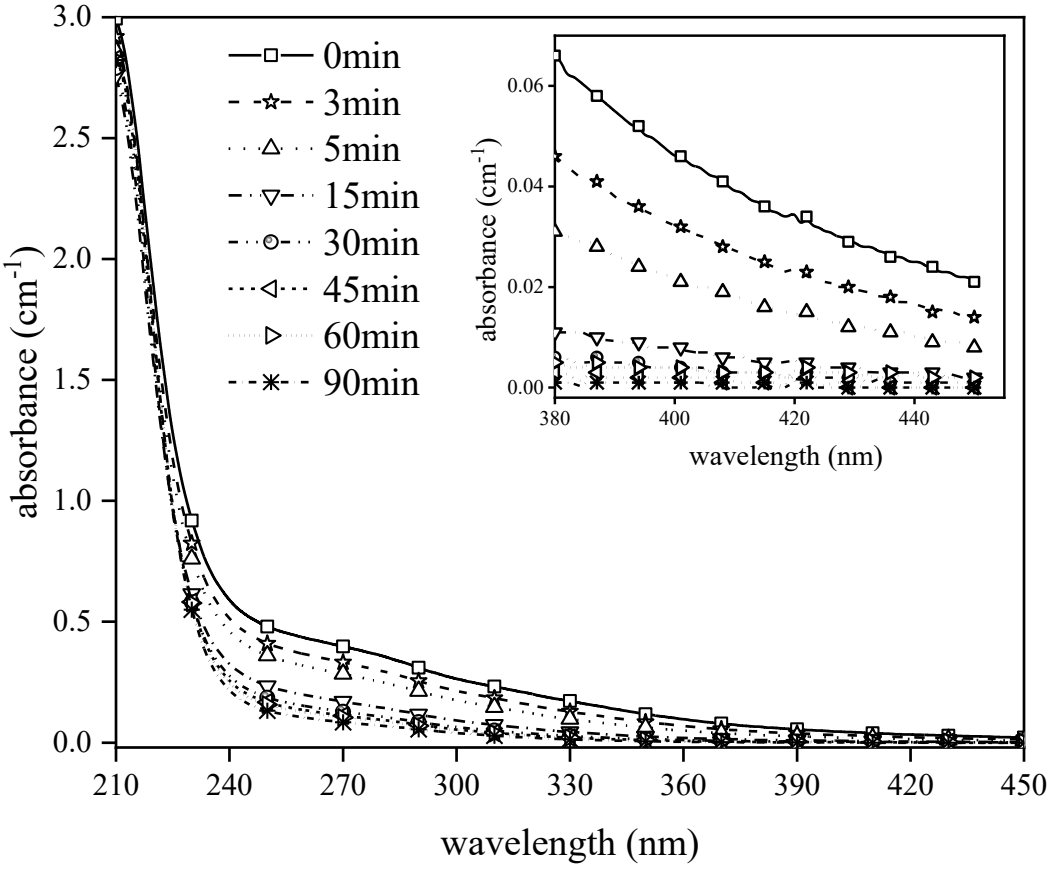

Fig.4 Evolution of the absorbance spectra of biotreated leachate (diluted 5×) during single ozonation. The inset shows a more detailed view on the changes in specific wavelength regions.

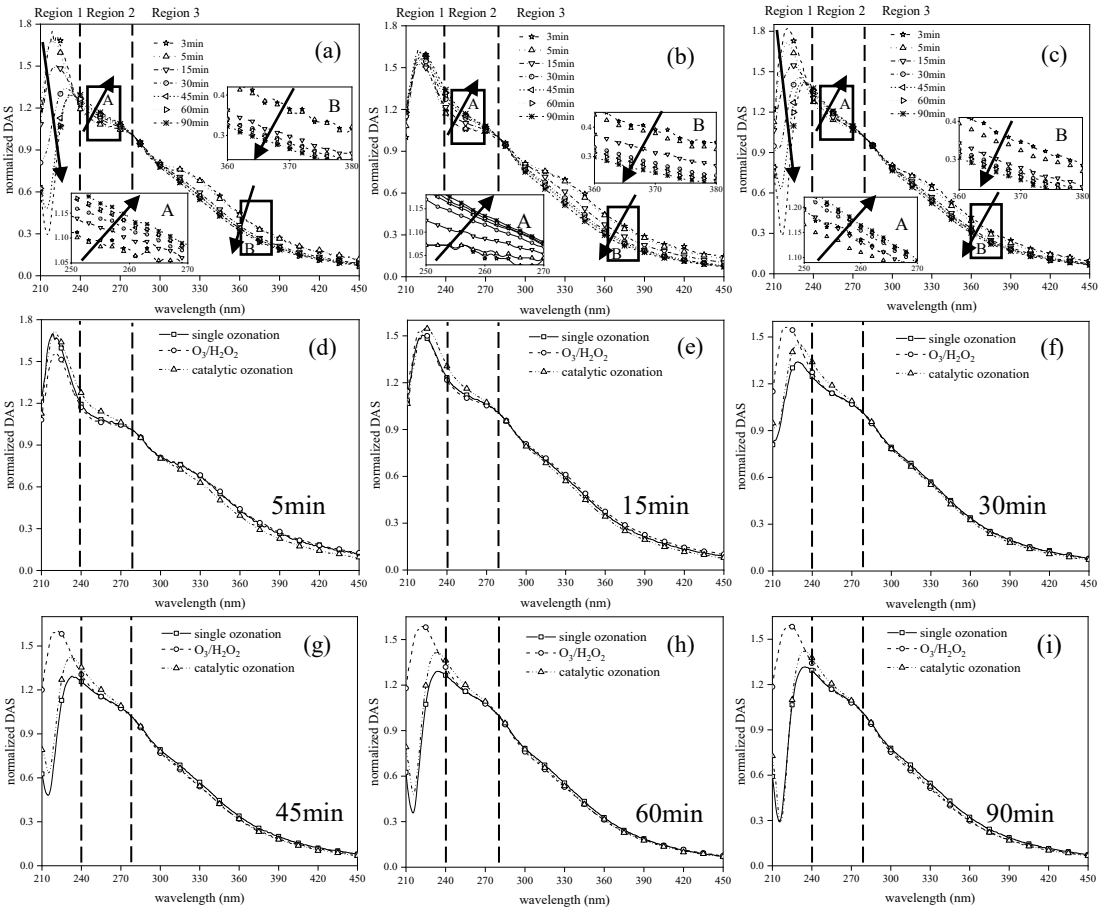

Fig. 5 Comparison of normalized DAS during various processes and at different reaction time intervals. (a) single ozonation, (b) O_3/H_2O_2 process, (c) catalytic ozonation, and (d) – (f) NDAS at specific time. The insets show a more detailed view on the changes in specific wavelength regions. The arrows indicate changes in the order of the curves during treatment.

3.2.2 COD removal efficiency

Fig. 6a depicts the evolution of COD with respect to the specific transferred ozone dose (STOD) during the three processes. When it comes to COD removal, it is clear that ozone-based AOPs (catalytic ozonation and O_3/H_2O_2) outperforms single ozonation. Further comparison of these two AOPs shows that the COD removal in the catalytic ozonation is larger than that of the O_3/H_2O_2 process when the STOD < 2 $gO_3/gDOC$, while the situation is reversed when the STOD > 3 $gO_3/gDOC$. The kinetic curves shown in Fig. S4 can reflect the rate of DOM degradation. Two stages can be identified

376 in the single ozonation and catalytic ozonation processes, whereas the curve of the
377 O_3/H_2O_2 process is not divided. Such two-stage COD degradation indicates that the
378 DOM of the leachate is composed of compounds with varying reactivity towards O_3,
379 and the addition of H_2O_2 significantly improves the ozone-refractory substances
380 removal in the later stage. Similar phenomena have been observed in previous studies
381 on ozonation of leachate and municipal wastewater effluents, illustrating the
382 complexity of these water matrices [16, 64, 65]. The kinetic constants are determined
383 for these processes by using a pseudo-first-order kinetic model and summarized in
384 Table 1. For the first kinetic regime, the COD degradation rate constant obtained from
385 the catalytic ozonation is 2.9 times that of single ozonation, while the constant of the
386 O_3/H_2O_2 process is equivalent to that of single ozonation. In the second stage, the COD
387 degradation rate constant of O_3/H_2O_2 is 2.7 times that of single ozonation and 1.9 times
388 that of catalytic ozonation. Fig. 6b further explores the contribution of different stages
389 among various processes to COD removal. It can be seen the COD removal caused by
390 single ozonation and catalytic ozonation mainly occurred in the first 45 min of the
391 reaction (>70% contribution) and the contribution after that was less than 30%.
392 Contrastingly, the contribution at the latter stage during the O_3/H_2O_2 system is more
393 than 40%, indicating a relatively high •OH yield in the later stage as mentioned in the
394 section 3.2.1.
395 The different COD removal trends can be ascribed to the different reaction mechanisms.
396 Generally, the ozone-based AOPs include the direct oxidation introduced by O_3 and the
397 indirect oxidation caused by •OH [66]. Moreover, the amount of ozone involved in

direct or indirect oxidation reactions is related to the characteristics of the water matrix and the stage of the reaction. The ozone demand is high in the early stage of ozonation due to the existence of a large amount of electron-rich DOM. Under this situation, O_3 is extremely unstable, and its decomposition is governed by radical chain reactions of O_3 and electron-rich DOM [21]. As a result, in the initial stage with high ozone demand, the catalytic ozonation performs the best COD removal because of the highest ozone mass transfer. However, as the reaction progresses, the fraction of ozone-reactive DOM decreases. Consequently, in the later stage of the O_3/H_2O_2 process, ozone molecules are more likely to react with the deprotonated form of hydrogen peroxide (HO_2^-, Eq. (2)) rather than with ozone-refractory DOM due to the fact that the second-order reaction rate constant of O_3 with HO_2^- (150-1500 $M^{-1}s^{-1}$) are higher than that of O_3 with ozone-refractory substances (such as 0.01-100 $M^{-1}s^{-1}$ for carboxylic acids) at the pH range 7-8 of the typical leachate [21]. Therefore, the •OH yield of the O_3/H_2O_2 process is higher than that of the catalytic ozonation process in the later stage of the reaction. That is why the catalytic ozonation process performed better in the early stage, while the O_3/H_2O_2 process showed stronger capabilities in the later stage for the COD removal.

To conclude, for the implication of the practice, catalytic ozonation is appropriate for treating wastewater with high ozone reactivity, while the O_3/H_2O_2 process for low ozone reactivity. In other words, catalytic ozonation should be used in the early stage for the biotreated leachate, and the O_3/H_2O_2 process is adopted after the COD removal is >30%.

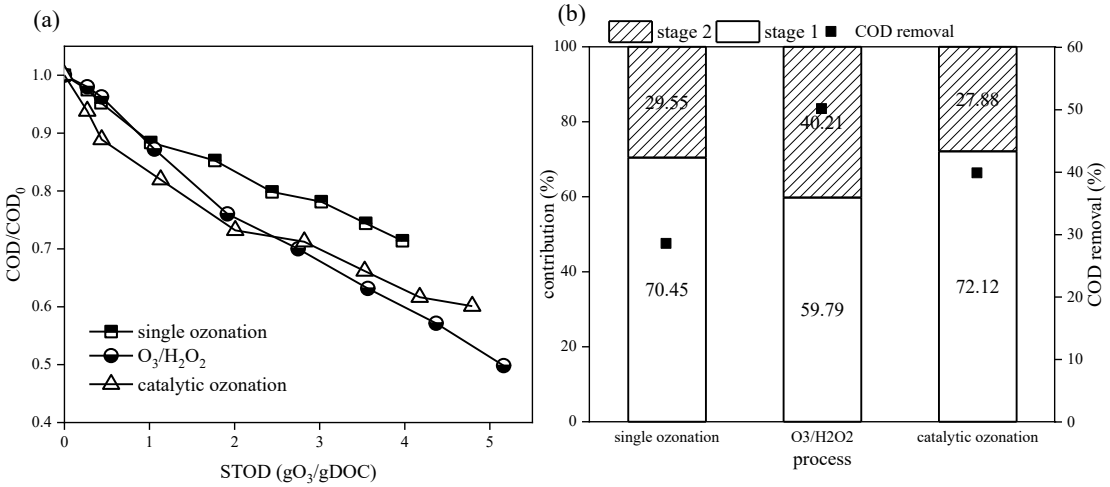

Fig. 6 (a) The evolution of COD with respect to the specific transferred ozone dose and (b) the contribution to the COD removal for the two stages during various ozonation processes.

Table 1

The COD degradation rate constants in different reaction stages.

	First stage		Second stage	
	K_1 (min^{-1})	R^2	K_2 (min^{-1})	R^2
Single ozonation	0.0082	0.99	0.0028	0.98
O_3/H_2O_2	0.0076	0.99	0.0076	0.99
Catalytic ozonation	0.0234	0.99	0.0041	0.97

3.3 Degradation of micropollutants and the relationship of removal between macro and micro-pollutants.

The micropollutants in the leachate pose potential risks to the surface water and groundwater around the landfill [10], therefore the concentration of micropollutants in the discharged leachate has to be strictly controlled. Fig. 7 describes the transformation of selected MPs with different ozone reactivity (The characteristics of compounds are shown in Table S1) during ozonation. It can be seen that EE2 is completely degraded within 0.45 $gO_3/gDOC$ by all three processes and the fastest removal of EE2 occurs in catalytic ozonation. This indicates that the degradation of ozone-reactive compounds is controlled by direct reaction with O_3, and the catalysts can accelerate the reaction due to its capacity to absorb O_3. These results are in agreement with the previous findings

435 from studies on the abatement of MPs by the ozone-based AOPs [66]. In comparison,
436 ATZ and ALA are only removed less than 28% and 52% at the same ozone dose. The
437 complete elimination of ozone-refractory compounds by indirect oxidation (•OH) is
438 less possible at the initial stage. On the one hand, O_3 is rapidly consumed during the
439 IOD stage [2], on the other hand, the •OH scavengers in the water matrix inhibit the
440 •OH formation at low ozone doses [67]. Fig. 7b shows that the existence of catalyst has
441 little effect on improving the ATZ removal compared with the single ozonation, whereas
442 continuous addition of hydrogen peroxide can increase the degradation rate of ATZ,
443 especially during the later stage of the ozonation. Specifically, to remove more than 90%
444 of ATZ, the ozone required by the single ozonation is 3 $gO_3/gDOC$, while the O_3/H_2O_2
445 process only needs 2 $gO_3/gDOC$, which reduces ozone consumption by a third. In
446 addition, it can be found that regardless of the ozonation types, the degradation
447 efficiency of ALA in the leachate is always higher than that of ATZ, whereas the
448 situation is the opposite in the synthesized aqueous [68]. This phenomenon is ascribed
449 to the different second-order reaction rate constants of these two compounds with O_3
450 and •OH. The reaction in synthetic aqueous is dominated by direct ozone oxidation,
451 resulting in faster degradation of ATZ due to higher reaction rate constants towards O_3
452 (Table S1). Conversely, O_3 could react with the DOM in the actual leachate to initiate
453 the chain reaction of •OH formation [56, 69], resulting in •OH leading the reaction
454 process. Therefore, ALA with higher •OH reactivity is removed faster in the actual
455 leachate.

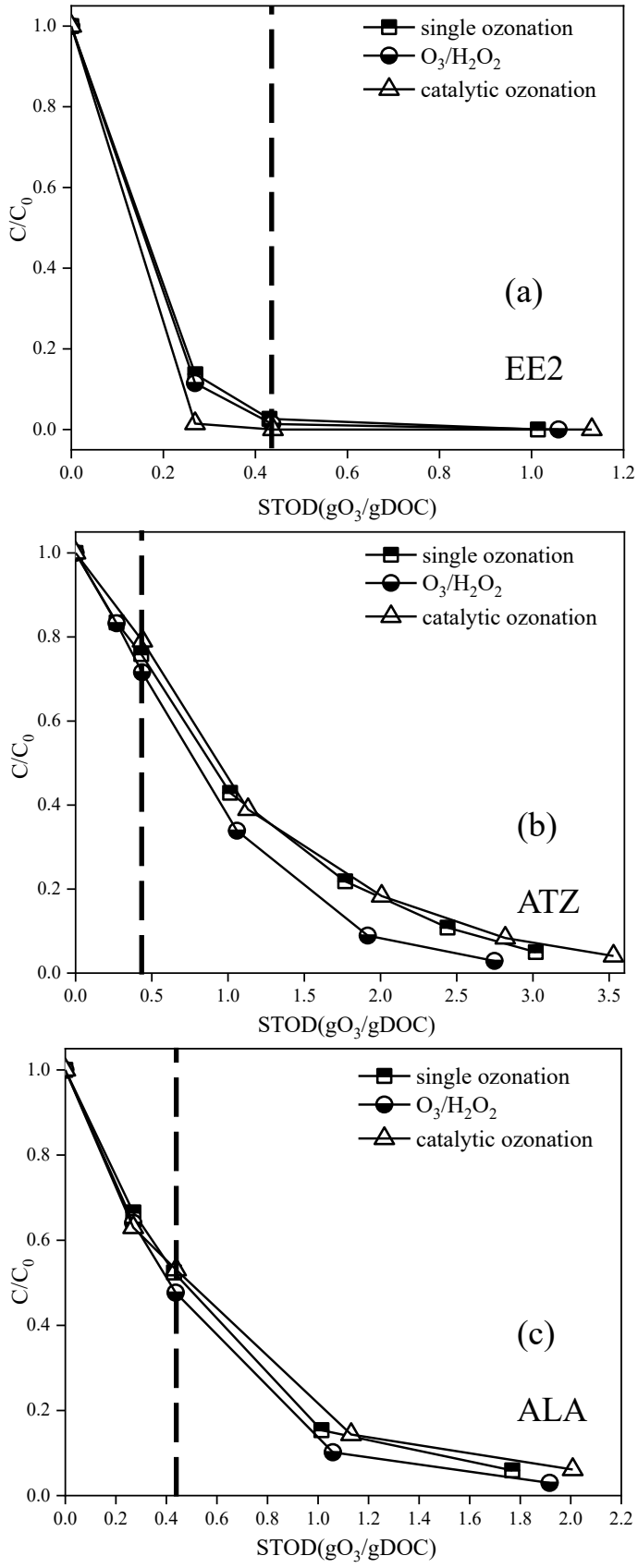

Fig. 7 Transformation of various MPs with different ozone reactivity as a function of the STOD for the three processes. The dashed lines represent the ratio of IOD to DOC.

Comparing the removal efficiency of macro (assessed as α_{254} and COD) and micro-pollutants (Fig. 8 and Fig. S5), it can be found that when the COD removal exceeds 5%, the EE2 removal in all the three processes can exceed 90%. Likewise, once the COD removal reaches more than 20% and 30%, the majority of ALA and ATZ in the leachate can be eliminated. This phenomenon suggests that when the COD reduction of biotreated leachate exceeds 30%, those MPs with O_3- and/or •OH -reactive can achieve satisfactory removal efficiency treated by ozone (AOPs). From another perspective, even if the ozone-refractory MPs were wholly eliminated, more than 60% of the COD remaining in the leachate matrix could not be removed. This on the one hand reflects the diversity of DOM in the leachate [64], and on the other hand, indicates that the ozone-based processes may cause the accumulation of small molecular carboxylic acids, which is consistent with previous literature [70].

Stronger mathematical relationship occurs between α_{254} and micropollutants (Fig. S5). When assembled these data related to the removal of α_{254} and MPs, one can found that the percent removal of MPs correlated well with the percent reduction in α_{254} in all three ozone-based processes. Table 2 summarize the linear regression fitting of the data. If a compound was removed to below the detection limit, the relevant data points were not included in the regression line. Overall, the R^2 value is > 0.95 for all the tested compounds, which provides a support for the surrogate-based prediction. Thereupon, a predictive model can be constructed to roughly estimate the MPs removal efficiency using the monitored α_{254} values. The slopes of the regression lines indicate that the MPs degradation is actually faster than the α_{254} reduction. This ensures that the entire range

of MPs degradation (0 − 100%) is covered. Previous studies also have shown that α_{254} reductions can be correlated to MPs removal [56, 71, 72]. This level of accuracy is acceptable for users that are unable to measure MPs but do have the ability to monitor α_{254}, which saves a lot of time and money and requires much less experience. Similar proposals have also been mentioned in previous reports [72]. This strategy is potentially able to the online assessment of process performance and treatment effects.

Note that the ALA and ATZ regression lines present intercept values with opposite signs. Typically, the intercepts for ozone-resistant compounds yet reactive with •OH should be negative [72]. However, it was noticed that the intercept for ALA was positive, indicating that •OH was produced substantially in the initial stage of leachate ozonation, but such yield of •OH is insufficient for causing the ATZ degradation in the presence of competition from the more reactive DOM. Therefore, a certain reduction in α_{254} occurred before substantial ATZ destruction was experienced. This is why the intercept of the regression line for ATZ is negative.

Table 2

The relationship between percent removal of MPs by ozonation and percent removal of α_{254}.

MPs	Slope	Intercept	R^2	N
Atrazine (ATZ)	1.44	-12.27	0.957	16
Alachlor (ALA)	1.24	14.45	0.957	11
17α-thinylestradiol (EE2)	1.84	58.57	1	3

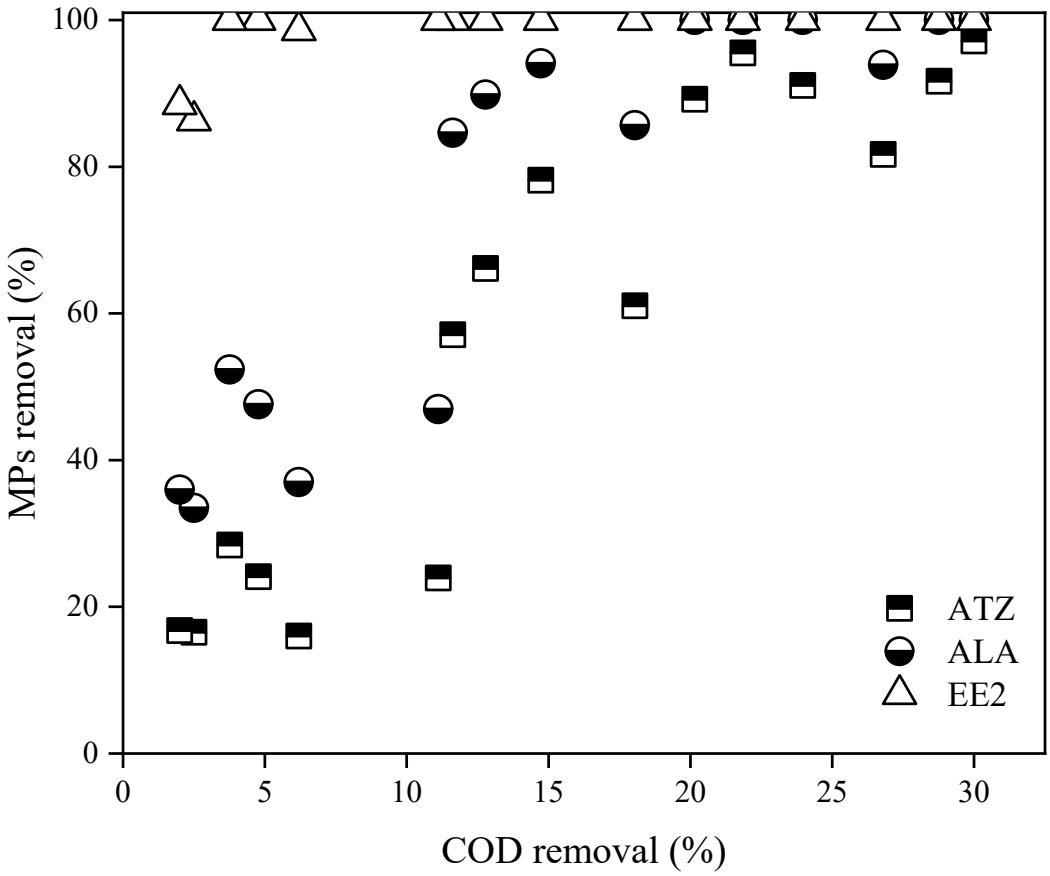

Fig. 8 Correlation between relative removal of COD and degradation of MPs.

3.4 Oxidation efficiency

In terms of oxidation efficiency, the •OH formation yield from ozone decomposition for each process can be well reflected with the $R_{\cdot OH\ O_3}$ concept [73], which is a modified version of the R_{ct} concept introduced by Hoigné and Bader [74]. This parameter is calculated as the •OH exposure per consumed O_3, represented in Eq. (10), which is more meaningful for measuring ozone efficiency.

$$R_{\cdot OH\ O_3} = \frac{\text{•OH exposure}}{\Delta O_3} \quad (10)$$

Fig. 9 exhibits the relationship between ozone consumption and •OH exposure which calculated by Eq. (9) based on ATZ removal. The data fit a two-stage linear model well during all the three processes. The first stage occurs before the IOD, and the second

511 stage occurs after the IOD. This phenomenon is consistent with the observation of
512 Alberto Cruz-Alcalde [46]. The $R_{.OH\ O_3}$ values of two stages are summarized in Table
513 3. It can be seen the $R_{.OH\ O_3}$ value in the second stage is always higher than that of the
514 first stage no matter what kind of process. This is because the water matrix presents a
515 strong ozone demand in the first stage, and the high concentration of ozone-reactive
516 DOM trigger more intense direct oxidation, leading to O_3 partial depletion without
517 conversion to •OH [2]. In the second stage, the ozone consumption caused by direct
518 oxidation is gradually reduced until stable conditions are reached [39], resulting in more
519 amount of O_3 participating in the indirect oxidation initiated by •OH.
520 Furthermore, it can be noticed that the $R_{.OH\ O_3}$ of the three processes are roughly equal
521 in the first stage. This result indicates that in water matrix with high DOM concentration,
522 •OH is mainly generated from the chain reaction of O_3 and reactive DOM, irrespective
523 of additional auxiliary techniques [75 − 77]. When more O_3 than the IOD is applied, the
524 $R_{.OH\ O_3}$ value of the O_3/H_2O_2 process is significantly increased, which is 1.4 times that
525 of the single ozonation process. Note, however, that the $R_{.OH\ O_3}$ value for the catalytic
526 ozonation and the single ozonation process are close. This result suggests the addition
527 of H_2O_2 increases the generation of •OH, while the catalyst has little effect for the
528 conversion of O_3 towards •OH. This phenomenon further demonstrate that the addition
529 of catalyst mainly promotes the direct oxidation reaction between O_3 and organic
530 matters, rather than the indirect oxidation.

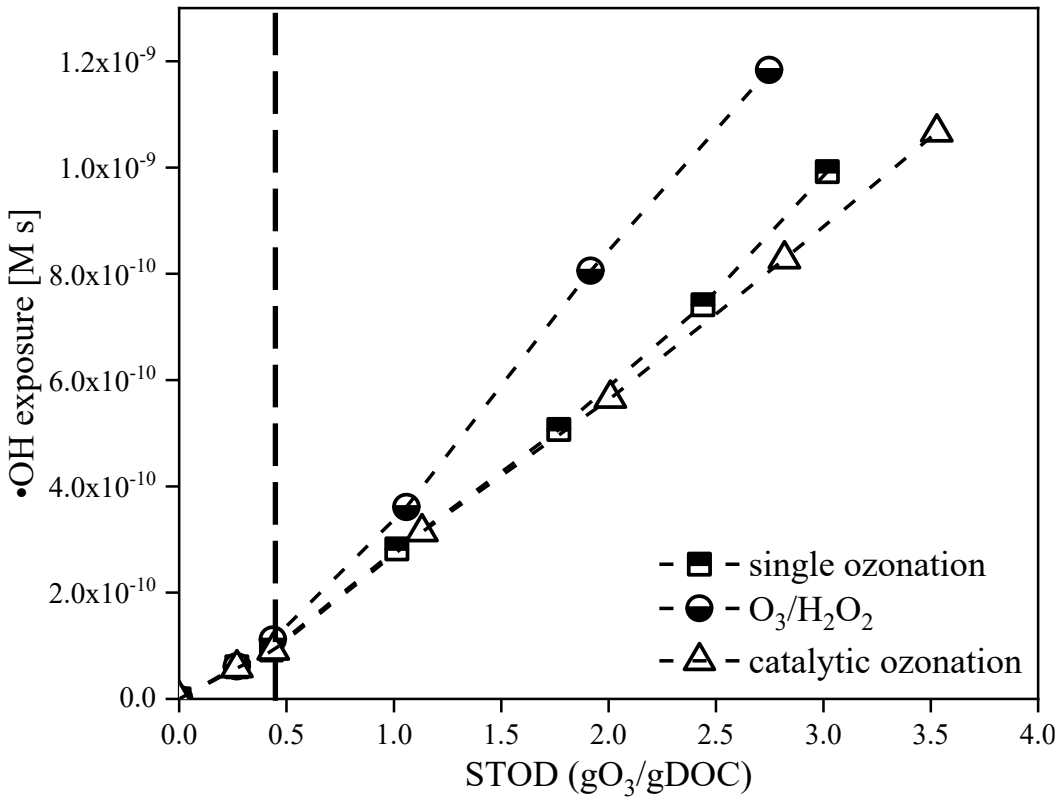

Fig. 9 The relationship of •OH exposure vs TOD during three ozonation processes. Dashed line indicates the IOD value.

Table 3
The $R_{\cdot OH\ O_3}$ values of two stages in vary processes ($\times 10^{-8}$ M·s·gDOC/gO_3).

	First stage	Second stage
Single ozonation	9.93	13.5
O_3/H_2O_2	10.1	19.1
Catalytic ozonation	9.61	13.0

3.5 Energy consumption

The energy consumption of the ozone-based AOP is mainly attributed to the applied ozone dose (AOD). In this work, the addition of H_2O_2 in the O_3/H_2O_2 process should be included in the energy consumption (molar ratio of H_2O_2/O_3 of 0.5). In order to calculate the energy requirements, according to the previous literature [37], it is assumed that an average energy requirement of 15 kWh/kg for O_3 and of 10 kWh/kg for H_2O_2 production. The calculation of energy consumption is based on the ozone dose [37]. Fig. S6 depicts the logarithmic decrease of various compounds and COD based

on the applied ozone dose (AOD), from which the ozone dose-based rate constant obtained, and the rate constants for the transformation of the compounds and COD degradation are summarized in Table S2. Note that the rate constants of COD degradation are different for the two stages during the single and catalytic ozonation.

Table 4
Energy requirements in kWh/m^3 for elimination of the selected compounds and COD at a desired removal level

process	EE2	ATZ	ALA	COD removal level			
	90%	90%	90%	20%	30%	35%	40%
Single ozonation	0.46	6.64	2.70	7.35	14.25	-	-
O_3/H_2O_2	0.49	5.14	2.70	4.69	7.87	9.63	11.53
Catalytic ozonation	0.40	6.06	2.58	3.06	7.83	10.48	13.34

The energy requirements for COD achieving different removal levels are listed in Table 4. Since the degree of COD removal treated by the single ozonation did not exceed 30% during the entire experiment, the case of COD removal exceeding 30% is not considered when calculating energy. Apparently, the energy requirements of these two ozone-based AOPs for COD degradation is much lower than that the single ozonation. Both the catalytic ozonation and the O_3/H_2O_2 process can reduce around 45% of the energy consumption for the 30% COD removal. Further comparing these two AOPs, the O_3/H_2O_2 process requires less energy when the desired COD removal is more than 35%.

The energy requirements for micropollutants achieving 90% elimination vary in the range from 0.40 kWh/m^3 to 6.64 kWh/m^3 (Table 4), depending on the type of micropollutants and the pattern of treatment processes. For EE2, the catalytic ozonation performs the best treatment efficiency, saving 15% of energy compared to the single ozonation. The most energy-saving pattern for ATZ transformation is the O_3/H_2O_2 process, which reduces energy consumption by 23% compared to the single ozonation.

566 However, as far as ALA elimination is concerned, the energy consumption for the three
567 processes has little difference. This fact is due to the different reactivity of this
568 compound towards O_3 and •OH, and the different reaction mechanisms of each process.
569 In addition, the energy required to achieve 30% COD degradation is sufficient to
570 simultaneously eliminate more than 90% of the MPs, which is consistent with the
571 relationship between the removal efficiency of macro and micro-pollutants according
572 to Fig. 8. Compared with the transformation of MPs in surface water, wastewater
573 effluent and synthetic wastewater in the previous studies [37, 78], the energy
574 consumption in this work is remarkably higher because the biotreated landfill leachate
575 contains a higher concentration of DOM, which can compete with MPs for oxidants.

576 ## 4. Conclusion

577 A comparison study was carried out on the performance of various ozonation processes
578 (single ozonation, catalytic ozonation, and O_3/H_2O_2 process) polishing bio-stabilized
579 landfill leachate. The ozone utilization efficiency and the energy requirements for
580 removing different pollutants were evaluated. The following conclusions were obtained
581 from this research:
582 Compared with single ozonation, both the catalytic ozonation and O_3/H_2O_2 processes
583 could improve ozone utilization efficiency to differing extent. The role of catalytic
584 ozonation is mainly to enhance the direct ozone oxidation, while O_3/H_2O_2 process is to
585 promote the indirect oxidation. The effective stages in which catalytic ozonation and
586 O_3/H_2O_2 processes play a strengthening role are different. The strengthening effect is
587 most visible in the early stage (STOD < 2 $gO_3/gDOC$) for catalytic ozonation, whereas
588 more pronounced in the later stage for O_3/H_2O_2 process.

589 Although all the three ozonation processes perform well for UV quenching substances,
590 apparent differences in COD degradation occurred among these processes. The highest
591 COD degradation of biotreated leachate was observed in O_3/H_2O_2 process (50%),
592 followed by catalytic ozonation (40%) and single ozonation (29%) at the same AOD.
593 Furthermore, catalytic ozonation and O_3/H_2O_2 processes accelerate the kinetics of COD
594 degradation in the first and second stages, respectively.
595 The additional auxiliary techniques have little enhancement on removing ozone-
596 reactive DOM since they can be completely removed in the IOD stage regardless of the
597 process type. Nevertheless, the ozone-refractory MPs can be reduced faster in the
598 O_3/H_2O_2 process compared with single ozonation. The O_3/H_2O_2 process has a 40%
599 higher •OH yield than the single ozonation, and catalytic ozonation contributes
600 negligibly to the enhancement of O_3 towards •OH conversion.
601 According to the mathematical relationship of percent removal between macro and
602 micro-pollutants, the α_{254} can be used as an online monitoring surrogate to predict the
603 MPs removal in biotreated leachate ($R^2 > 0.95$).
604 The energy consumption required to remove ozone-refractory MPs (e.g., ATZ and ALA
605 in the present research) is roughly 6 − 15 times higher than that of ozone-reactive MPs
606 (such as EE2). For COD elimination, catalytic ozonation consumes the least amount of
607 energy if COD removal is ≤ 35%, otherwise, O_3/H_2O_2 process is the most energy-
608 efficient. In any process, the MPs with O_3 or •OH reactivity could achieve more than
609 90% elimination when the COD removal exceeds 30% in the biotreated leachate. This
610 indicates that MPs can be removed simultaneously with the degradation of macro-

pollutants in the deep purification of the biotreated leachate without additional energy.

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Supplementary Materials

Supplementary material associated with this article can be found, in the online version.

CRediT authorship contribution statement

Hao Wang: Conceptualization, Investigation, Methodology, Formal analysis, Software, Writing-original draft, Writing-review & editing, Visualization. **Siyu Zhang**: Investigation, Conceptualization, Methodology, Writing-review & editing. **Xuwen He**: Conceptualization, Supervision. **Yongyuan Yang** and **Xuetong Yang**: Methodology. **Stijn W.H. Van Hulle**: Funding acquisition, Supervision, Writing-review & editing.

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