A comparative study of removal efficiency of organic contaminant in landfill leachate-contaminated groundwater under micro-nano-bubble and common bubble aeration

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Abstract
Landfill leachate-contaminated groundwater is widespread all over the world. In order to study the organic contaminant removal efficiency of landfill leachate-contaminated groundwater under oxygen micro-nano-bubble (MNB) aeration, a series of lab-scale experiments of oxygen MNB aeration as well as common bubble (CB) aeration were conducted. Firstly, the difference in mass transfer, microbial activity enhancement, and contaminant removal efficiency between MNB and CB aeration was estimated. Then, the composition variations of dissolved organic matter (DOM) in groundwater treated by MNB or CB aeration were characterized by ultraviolet–visible (UV–VIS) absorption spectrum and fluorescence excitation-emission matrix (EEM). The test results showed that the oxygen utilization efficiency and volumetric oxygen transfer coefficient of MNB aeration were 10 and 50 times that of oxygen CB aeration, respectively. On the 30th day after MNB aeration, the dehydrogenase activity (DHA) of groundwater increased by 101.25%. Compared with CB aeration, the chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD5), and ammonia nitrogen removal efficiency under MNB aeration increased by 29.72%, 13.43%, and 138.59%, respectively. With the biodegradation effect of MNB aeration, a large number of protein-like and soluble microbial by-product substances were degraded, and humic and fulvic acid-like substances were degraded to a certain level. Oxygen MNB aeration played a chemical oxidation effect while enhancing the biodegradation of groundwater, and it was an energy-efficient landfill leachate-contaminated groundwater treatment method.

Keywords Groundwater · Landfill leachate · Micro-nano-bubble aeration · Microbial activity · Dissolved organic matter

Introduction
Sanitary landfilling is the most widely applied solid waste management method (Kaza et al. 2018). In landfills, waste, liquid present in the waste, and percolated rain water interact and result in leachate. The leachate has high chemical oxygen demand (COD) content, high ammonium nitrogen content, and lasting toxicological characteristics (Alslaibi et al. 2011; Li et al. 2014; Regadio et al. 2012; Yang et al. 2013). When the liners of landfills failed, the leakage of leachate often leads to the contamination of groundwater and soil. Landfills are considered to be important sources of groundwater contamination. The major groundwater contaminants from landfill include ammonia and organic matter, such as COD and heavy metals (Tian et al. 2005; Alslaibi et al. 2011; Milosevic et al. 2012; Regadio et al. 2012; Smahi et al. 2013). These contaminants pose a great threat to human health.

Over the last few decades, a variety of different physical, chemical, and biological technologies have already been used to remove or degrade contaminants from landfill leachate-contaminated groundwater (Zhang and Zhou 2008; Grover et al. 2011). Permeable reactive barrier (PRB) is one of the most commonly used technologies for in-situ remediation of contaminated groundwater (U.S. EPA 2002).
Since the invention of PRB in the early 1990s, a variety of materials, such as zero-valent iron and activated carbons (Zhou et al. 2014), dewatered alum sludge and bio-char (Kankanige et al. 2019), and active chlorine (Mao et al. 2018), have been employed to remove contaminants including heavy metals, organic pollutants, and ammonia nitrogen. The stable reductions in BOD₅, COD, and ammonia nitrogen are usually achieved via processes such as adsorption, precipitation, denitrification, and biodegradation. Despite wide acknowledgment, there are still unresolved issues about long-term performance and high maintenance costs of PRB (Obiri-Nyarko et al. 2014; Shen et al. 2021). Another remediation of contaminated groundwater is advanced oxidation processes (AOP). Even though AOP is more effective than PRB, their potential application for in situ groundwater remediation poses challenges, such as safety and a relatively short radius of influence (Zhong et al. 2017). Therefore, it is urgent to find an effective, eco-friendly, and low-cost approach to remediate the landfill leachate-contaminated groundwater.

In recent years, micro-nano-bubbles (MNB) technology has received continuous attention in the field of wastewater treatment (Zhang and Guiraud 2017; Ye et al. 2019). As a kind of fine bubble, micro-nano-bubble (MNB) has a small diameter (with a diameter of 200 nm–50 μm), large specific surface area, high mass transfer efficiency (Xiao and Xu 2020; Bai et al. 2021a, b), strong migration ability (Kristen et al. 1993; Li et al. 2014), and low rising velocity in liquid. It persists for long periods and significantly improves gas solubility (Hu and Xia 2018; Feng et al. 2020). In addition, the collapse of MNB can lead to the formation of hydroxyl radicals (·OH) (Li et al. 2009; Takahashi et al. 2007). The great standard redox potential (2.80 V) of ·OH is conducive for decomposing organic contaminants. Some studies about contaminant removal efficiency under MNB aeration have shown satisfactory performance. As a pretreatment technique, MNB has been shown to be highly beneficial for downsizing the water/wastewater treatment plants and improving the quality of product water (Kazuyuki et al. 2009, 2010). In an aerobic biofilm system, air nano-bubble aeration accelerated the growth of the biofilm and achieved better removal efficiency of COD and ammonia nitrogen. The dehydrogenase activity was as maximum as six times higher than that of traditional aeration (Xiao and Xu 2020). In membrane bioreactor, oxygen MNB markedly enhanced the removal efficiency of contaminants compared with conventional air aeration, and the pure oxygen provided a high dissolved oxygen condition which would influence the biomass activity by affecting the enzymatic activities (Zhuang et al. 2016). However, the application of MNB in the remediation of landfill leachate-contaminated groundwater is scarce. Since the main contaminants of landfill leachate-contaminated groundwater are different from that of industrial-contaminated groundwater, and they are degradable and transformable. And their concentrations fluctuate greatly in time and space. So, it is still unknown whether MNB can be successfully used to remediate landfill leachate-contaminated groundwater.

The objective of the present work was to evaluate the effect of oxygen MNB aeration on the organic contaminant removal and composition variation of landfill leachate-contaminated groundwater. Furthermore, the difference between oxygen MNB and common bubble (CB) aeration was investigated. Specifically, the groundwater samples were treated by oxygen MNB or CB aeration at first. The mass transfer efficiency of MNB and CB aeration was estimated. Then, the contaminant removal and microbial activity enhancement efficiency of MNB aeration on landfill leachate-contaminated groundwater were evaluated. After that, the composition variation of dissolved organic matter (DOM) in groundwater before and after MNB or CB aeration was characterized. At last, the energy consumption of MNB and CB aeration was analyzed.

**Materials and methods**

**Materials**

Landfill leachate was collected from Woqishan Landfill (Wenzhou, Zhejiang province, China). The collected leachate was stored in a brown glass reagent bottle in the refrigerator at 4 °C. The landfill leachate was diluted 20 times with distilled water, and it was taken as the synthetic landfill leachate-contaminated groundwater sample. Raw groundwater in this study is referred to as the synthetic landfill leachate-contaminated groundwater. The average composition of the synthetic landfill leachate-contaminated groundwater was given as follows: pH, 8.8; total dissolved solids (TDS), 1.23 × 10⁻³ µg/L; COD, 320 mg/L; BOD₅, 91 mg/L; ammonia nitrogen, 123.15 mg/L; total nitrogen (TN), 249 mg/L. Reagents for testing COD (20–1500 mg/L range) and ammonia nitrogen (0.4–50 mg/L range) were obtained from HACH (Loveland, CO, USA). Trihydroxymethyl aminomethane (chemical pure, CAS: 1185–53-1), triphenyl tetrazolium chloride (chemical pure, CAS: 298–96-4), Na₂SO₃ (analytical reagent, CAS: 7775–83-7), Na₂SO₄ (analytical reagent, CAS: 7757–82-6), formaldehyde (analytical reagent, CAS: 50–00–0), and acetone (analytical reagent, CAS: 67–64-1) were obtained from Macklin (Shanghai Macklin Biochemical Co., Ltd, China).

**Experiment methods**

The schematic of the experimental apparatus is shown in Fig. 1. MNB and CB column were consisted of a plexiglass
cylinder with an inner diameter of 260 mm and a height of 650 mm. There was 20-L landfill leachate-contaminated groundwater in MNB and CB column, respectively. Oxygen with a concentration of 99.9% was used as the gas phase of aeration. A pressurized dissolution-type MNB generator (XZCP-K-1.1, Yunnan Xiazhichun Environmental Protection Technology Co., Ltd, China) was used for MNB aeration. The method of MNB aeration was described in previous literature (Bai et al. 2021a, b). CB was generated by the tube with a diameter of 3 mm. During the MNB and CB aeration, oxygen was injected at a rate of 1.8 L/min and the DO concentration in MNB and CB column was recorded by DO meter (YSI ProSolo). According to previous studies, the bubble size of MNB was mainly in the range of 1–7 μm and 20–200 nm (Bai et al. 2021b). And the CB ranged from 0.6 to 10 mm. CB and MNB aeration started at the same time and lasted for 5 min. Once the aeration was finished, the groundwater samples containing oxygen MNB or CB were sealed in six brown glass reagent bottles, respectively. And these bottles were stored for 3 d, 5 d, 10 d, 15 d, 20 d, and 30 d, respectively, at 20 °C in an incubator (Boxun, XPS-250B-Z). At the end of each storage, the groundwater samples were analyzed.

Analysis

The variation of dissolved oxygen (DO) value during aeration was used to estimate the mass transfer efficiency of MNB and CB aeration.

The concentration variations of COD, 5-day biochemical oxygen demand (BOD₅), and ammonia nitrogen in groundwater samples before and after MNB or CB aeration were used to evaluate the contaminant removal efficiency of MNB aeration on landfill leachate-contaminated groundwater. COD and ammonia nitrogen were measured colorimetrically. BOD₅ was determined by the dilution and seeding method (SEPA 2002).

All analytical measurements were done at least in triplicate, and the standard deviation was found to be below 5% in all cases.

The ultraviolet–visible (UV–VIS) absorption spectrum and fluorescence excitation-emission matrix (EEM) were used to characterize the composition variation of dissolved organic matter (DOM) in groundwater before and after MNB or CB aeration. The molecular electronic absorption spectra were obtained using the UV–VIS Spectrophotometer (Shimadzu, UV3600) in quartz cuvettes (3 mL and 1 cm optical path). UV–VIS absorbance spectra were conducted under a wavelength range of 200–600 nm at 1-nm intervals. Fluorescence excitation-emission matrix (EEM) analysis was made with a fluorescence spectrometer (Edinburgh Instruments, FS5) under the excitation (Ex) wavelength of 230–550 nm at 5 nm increments across an emission (Em) wavelength of 250–650 nm at 1-nm intervals. UV–VIS absorbance and EEM analysis were made with groundwater samples diluted at 1:20.

Dehydrogenase activity (DHA) is a group of enzymes involved in the redox reaction in cellular respiration using organic matter as the substrate and plays a crucial role in cell energy metabolism. Analysis of DHA is a common test for the quantification of microbial activity. In this study, the triphenyl tetrazolium chloride (TTC)-DHA test was used to compare differences in the microbial activity of the groundwater before and after MNB or CB aeration, respectively. The test of DHA was done according to the research work of Wang et al. (2017).

Results and discussion

Contaminant removal efficiency

Figure 2 showed that the concentration of COD, BOD₅, and ammonia nitrogen in groundwater all decreased after MNB
and CB aeration. The COD concentration in groundwater treated by MNB aeration was higher than that in groundwater treated by CB aeration within 10 days after aeration. Compared with MNB aeration, more oxygen escaped from groundwater in CB aeration. The dominance of COD removal efficiency was attributed to the aerated gas stripping under mechanical mixing rather than O$_2$-induced oxidation (Yu et al. 2015). While the COD concentration in groundwater treated by MNB aeration decreased continuously, and it was less than that treated by CB aeration eventually. Specifically, on the 30th day after aeration, the COD removal efficiency was 50.94% under MNB aeration and it was 39.27% under CB aeration. There were two reasons for the higher COD removal efficiency in MNB aeration. First, MNB aeration could lead to the generation of ·OH (Li et al. 2009; Takahashi et al. 2007). The non-biodegradable compounds were decomposed into biodegradable compounds. Then, it was decomposed by the microorganisms. Second, MNB played a role in oxygen storage with their in situ sustaining dissolution in groundwater, which provided sufficient electron donors during contaminants decomposition (Xiao and Xu 2020). The BOD$_5$ concentration in groundwater treated by both MNB and CB aeration was almost the same within 10 days. This was because the non-biodegradable substances were decomposed into biodegradable substances by oxidation of ·OH while the biodegradable substances were degraded. However, the value of BOD$_5$ concentration in groundwater treated by MNB aeration gradually became less than that in groundwater treated by CB aeration with time. On the 30th day after aeration, the BOD$_5$ removal efficiency was 94.91% by MNB aeration, while it was 83.67% in groundwater treated by CB aeration. An important reason was probably owing to the improved biomass activity by the higher oxygen transfer efficiency for the greater saturation DO level of MNB (Lee and Kim 2013). The ammonia nitrogen concentration decreased during the initial 5 days after MNB and CB aeration and increased continuously thereafter. On the 3rd day after aeration, 16.77% and 22.05% of ammonia nitrogen were removed by MNB and CB aeration, respectively. However, on the 30th day, the ammonia nitrogen removal efficiency decreased to 12.55% under MNB aeration, and it decreased to 5.26% under CB aeration. The main reason for the decrease in ammonia nitrogen removal efficiency was that organic nitrogen was transformed into ammonia nitrogen in ammoniation. Another reason was that the nitrification reaction stopped when the concentration of BOD$_5$ was less than 20 mg/L on the 15th day after MNB or CB aeration. In addition, it could be concluded that the MNB aeration had better ammonia nitrogen removal efficiency than the CB aeration. As a whole, MNB aeration showed relatively better performance. Compared with CB aeration, the COD, BOD$_5$, and ammonia nitrogen removal efficiency under MNB aeration increased by 29.72%, 13.43%, and 138.59% on the 30th day after aeration, respectively.

Previously, some researchers tried to treat landfill leachate-contaminated groundwater by conventional aeration. Yao (2018) found that the COD removal efficiency in landfill leachate-contaminated groundwater was around 30% after aeration treatment for 20 days. Yu (2020) found that the removal efficiency of ammonia nitrogen was 63.15% after continuous in situ conventional aeration for 32 days on 0.5 h per day. It can be concluded that compared with conventional aeration, MNB aeration has prominent COD removal efficiency. Besides, the PRB technique was used to remediate landfill leachate-contaminated groundwater. In general, BOD$_5$ and COD removal efficiency of 80% and 50% are usually achieved via PRB (Zhou et al. 2014; Kankanige et al. 2019; Mao et al. 2018). Although the MNB aeration and PRB have almost the same contamination removal efficiency, MNB aeration has a lower cost than PRB. That is, MNB aeration is an economical and effective method for remediation of landfill leachate-contaminated groundwater, and it has a broad application prospect in groundwater and wastewater treatment (Rojviroon and Rojviroon 2022; Wu et al. 2021; Agarwal et al. 2011).

It is notable that MNB aeration could significantly improve COD, BOD$_5$, and ammonia nitrogen removal efficiency. An important reason for this was the improved biomass activity by the higher oxygen transfer efficiency of MNB aeration (Xiao and Xu 2020) and the generation of ·OH during the oxygen MNB generation (Takahashi et al. 2007). Figure 3a shows the DO variations in groundwater during MNB and CB aeration. The DO value, with the initial value of 4.7 mg/L, increased gradually with time. During MNB aeration, the DO increased to the maximum value of 39.27 mg/L rapidly within 100 s, and afterward, it kept the
same value. However, it increased continuously during the whole process of CB aeration and reached 8.36 mg/L at the end. This was owing to the high mass transfer efficiency in MNB aeration (Bai et al. 2021a, b).

As shown in Fig. 3b, the DO peak value of groundwater during MNB aeration was greater than that during CB aeration, although the same amount of oxygen was injected. If the dissolved phase of oxygen is regarded as the effective use of oxygen, the oxygen utilization efficiency can be calculated by the following equation:

\[
R = \frac{(m - P_{DO} \times V)}{m} \times 100\% \tag{1}
\]

where \( R \) is oxygen utilization efficiency, %; \( m \) is oxygen input mass, mg; \( P_{DO} \) is the peak value of DO, mg/L; and the \( V \) is the volume of groundwater sample, L. As shown in Fig. 3b, the oxygen utilization efficiency of MNB aeration was 10 times that of CB aeration. The fast increase rate of DO, the great DO peak value, and the higher oxygen utilization efficiency in groundwater during MNB aeration resulted from the high mass transfer efficiency of MNB (Bai et al. 2021a, b). In order to investigate the mass transfer efficiency of MNB and CB aeration, the volumetric oxygen transfer coefficient \( (k_La) \) of MNB and CB was calculated by the following equation (Bai et al. 2021a, b):

\[
d\frac{dC^*}{dt} = k_La \left( C^* - C_s \right) \tag{2}
\]

where \( k_La \) is the volumetric mass transfer coefficient, 1/s; \( C^* \) is DO concentration at time \( t \), g/m\(^3\); and \( C_s \) is DO concentration at saturation, g/m\(^3\). The \( k_La \) values of MNB and CB are shown in Fig. 3b. The \( k_La \) of MNB was 50 times that of CB. The reason for this phenomenon was that the small bubble size of MNB led to the increase of gas–liquid interfacial area per unit of gas volume (Hu and Xia 2018; Xiao and Xu 2020; Bai et al. 2021a, b) and the overpressure on the interface of MNB according to the Epstein-Plesset equation (Duncan and Needham 2004). The great \( k_La \) of MNB was speculated to be the main reason for the improved contaminant removal performance (Zhuang et al. 2016).

DHA is the representation of the oxidative dehydrogenation process responding to oxygen supplementation, so it is commonly used for evaluating the activities of aerobic microorganisms in activated sludge (He et al. 2007; Zou et al. 2009). In this research, the DHA of groundwater before and after aeration was investigated to reveal the influence of MNB and CB aeration on the microbial activity of groundwater. Figure 4 shows the variations of DHA of groundwater before and after MNB or CB aeration. The DHA of all the groundwater samples increased gradually with time. From the 20th to the 30th day after aeration, it increased sharply with the accumulation of activated microorganisms. And it in groundwater treated by MNB aeration was 101.25% higher than raw groundwater. In addition, the DHA in groundwater treated by MNB aeration was always higher than that in groundwater treated by CB aeration. The reason was that the DO concentration of groundwater treated by MNB aeration was considerably high (39.27 mg/L), which provided sufficient electron donors during the metabolic process and significantly accelerated the enzymatic activity (Zhuang et al. 2016). The high microbial activity in groundwater treated by MNB aeration was the reason for high COD, BOD\(_5\), and ammonia nitrogen removal efficiency under MNB aeration.

**Characteristics of DOM before and after aeration**

**UV–VIS absorbance spectra of groundwater**

The UV–VIS absorbance spectra (200–600 nm) of groundwater before and after MNB or CB aeration are presented in...
The DOM in landfill leachate-contaminated groundwater was complex, so there was no obvious absorption peak in the UV–VIS absorbance spectra of groundwater. According to Yan et al. (2013), (2016), and Qadaf et al. (2021), the changes in the composition and reactivity of DOM in water treatment can be quantified based on UV–VIS absorbance spectra and Gaussian distribution band components. The constituting bands are referred to as A0 (210 nm), A1 (236 nm), A2 (270 nm), A3 (313 nm), A4 (374 nm), and A5 (523 nm). Specifically, the hydrophobic basic (HPOB) fraction has the highest intensity of A1. The hydrophobic acidic (HPOA) fraction has significantly higher contributions of A1 and A2. Transphilic base (TPHB) is of negative value for all the bands except A1, and the contribution of A3 is very significant. Transphilic neutral (TPHN) has high contributions of A1 and A2, and relatively lower contributions of A3 and A4 (Yan et al. 2016). Based on the results shown in Fig. 5, it could be concluded that MNB aeration removed the fractions of HPOA, HPOB, HAPON, and TPHA, while the CB aeration mainly removed TPHA fractions. In addition, it also can be seen in Fig. 5 that the absorption of raw groundwater in the ultraviolet region (wavelength < 290 nm) was strong, and then it decreased sharply after MNB and CB aeration. According to the research work of Chen et al. (2019), the absorption in the wavelength below 250 nm indicates the presence of conjugated unsaturated bonds, and it in the range of 250–290 nm suggests the existence of heterocyclic aromatic hydrocarbon. Thus, it can be concluded that the aromatic organic matters in groundwater were degraded or decomposed into small molecular substances by MNB or CB aeration, and the UV-quenching polar functional groups were destructed during these treatments.

The UV–VIS absorbance spectra of groundwater before and after aeration are further analyzed, and the results are shown in Fig. 6. The ratio of $E_{250}/E_{365}$ correlates strongly with the averaged molecular weight of organic matter, and the ratio of $E_{300}/E_{400}$ represents the humification, aromaticity, and molecular weight of organic matter (Peuravuori and Pihlaja 1997; Artingera et al. 2000). In this research, the values of $E_{250}/E_{365}$ and $E_{300}/E_{400}$ decreased from 9.2 to 2.8 and from 4.5 to 2.2 on the 30th day after MNB or CB aeration, respectively. The phenomenon revealed that the molecular structure degree and condensation degree of organic matter in groundwater decreased after MNB and CB aeration. In addition, the specific absorbance of $E_{254}$, $E_{280}$, and $S_{239-400}$ can be used to explain the degradation pathway of DOM in groundwater (Kavurmaci and Bekbolet 2014; Gregory et al. 1997; Guo et al. 2011). $E_{254}$ is a distinctive feature of electronic spectra of aromatic compounds. $E_{280}$ represents the relative hydrophobic size of organic matter. Likewise, $S_{239-400}$ characterizes the change in benzene compounds. As seen in Fig. 6b, the values of $E_{254}$, $E_{280}$, and $S_{239-400}$ decreased with time after MNB and CB aeration, suggesting that the aromatic C=C structure was broken. Therefore, MNB and CB aeration reduced the aromaticity and hydrophobicity of organic matter and reduced the concentration of organic matter in groundwater. As seen from Fig. 6a, on the 30th day after aeration, the values of $E_{250}/E_{365}$, $E_{300}/E_{400}$, $E_{254}$, $E_{280}$, and $S_{239-400}$ of groundwater treated by MNB aeration were lower than that of groundwater treated by CB aeration, which indicated that more organic matter with complex structure was transformed into biodegradable organic matter and further degraded in groundwater by MNB aeration.
EEM of groundwater

As shown in Fig. 7, the fluorescent components in groundwater before and after oxygen MNB or CB aeration were analyzed by EEM. The fluorescence EEM spectra can be divided into five unique Ex/Em regions that represent different DOM types, based on the quantification analysis of Chen et al. (2003): region I at Ex/Em of 220–250 nm/250–330 nm and region II at Ex/Em of 220–250 nm/330–380 nm. Regions I and II are associated with protein-like substances. Hudson et al. (2008) found that the substances in regions I and II are related to microbial activity and can be formed by microbial activity. In addition, compared with humic acid-like substances, the protein-like substances have a simple structure and are more likely to be used by microorganisms as an energy source or as a material for synthesizing other substances. Region III at Ex/Em of 220–250 nm/380–650 nm, and it is identified as fulvic acid-like substances. According to Jouraiphy et al. (2008), fulvic acid-like substances can only be degraded to a certain level. Region IV at Ex/Em of 250–550 nm/250–380 nm, and it is referred to as soluble microbial by-product substances which are accessible and easily biodegradable compounds, such as fatty acids (Sun et al. 2016). Region V at Ex/Em of 250–550 nm/380–650 nm, and it is ascribed as humic acid-like substances which are hard biodegradable (Heo et al. 2015; Sun et al. 2016). The humic acid-like substances are derived from the biodegradation of organic matter.

As shown in Fig. 7, for raw groundwater, fluorescence mainly appeared in regions II, III, IV, and V, and region V had the highest fluorescence intensities. This meant there were protein-like, fulvic acid-like, soluble microbial by-products, and humic acid-like substances in landfill leachate-contaminated groundwater. After MNB or CB aeration, the fluorescence intensities of groundwater samples in five regions all increased and then decreased with time. And on the 30th day after MNB or CB aeration, the fluorescence intensities of groundwater samples were all far less than that of raw groundwater. The result was consistent with the decrease in COD and BOD₅ concentration. Therefore, the content of DOM in groundwater was decreased by MNB and CB aeration.

To obtain more details on the transformation of DOM components of groundwater after MNB or CB aeration, EEM spectra were analyzed using the fluorescence regional integration (Chen et al. 2003), and the results are shown in Fig. 8a. The area sum of the five regions decreased. This trend confirmed that MNB or CB aeration could reduce DOM content in groundwater again. Specifically, on the 30th day after aeration, the area of regions I and II both decreased, and they in groundwater treated by MNB aeration were less than them in groundwater treated by CB aeration. The results revealed that a large number of protein-like substances were degraded after MNB or CB aeration, and MNB aeration degraded protein-like substances more effectively than CB aeration. There were two possible reasons for this phenomenon. On the one hand, the groundwater treated by MNB aeration had a stronger microbial degradation effect (Xiao and Xu 2020). On the other hand, the MNB aeration had an oxidizing effect while enhancing the biodegradation of groundwater (Takahashi et al. 2007). A part of aromatic protein-like substances with good structural stability was eliminated by the oxidizing effect of MNB aeration. As seen in Fig. 8a, the decrease of soluble microbial by-product substances (region IV) was observed in both groundwaters treated by MNB and CB aeration, while MNB aeration achieved higher removal efficiency of such components. The difference was attributed to the fact that
the groundwater treated by MNB aeration has higher microbial activity (Fig. 4). In addition, it can be noticed from Fig. 8a that there were still soluble microbial by-product substances in groundwater on the 30th day after MNB aeration. That is, the groundwater after MNB aeration can be further treated by biodegradation, such as further oxygen MNB aeration. Although regions III and V were related to fulvic acid-like substances and humic acid-like substances, which were reported to be non-biodegradable compounds, they were found to be degraded to a certain extent in groundwater treated by MNB and CB aeration. This phenomenon was consistent with the research result of Derrien et al. (2019) that humic and fulvic acid-like substances could only be degraded to a certain level by biodegradation. Because the reason might be that there were some specific types of microbial enrichment in groundwater treated by MNB and CB aeration. MNB aeration also showed higher removal efficiency of such components. The above results clearly showed that MNB aeration promoted the degradation of DOM in landfill leachate-contaminated groundwater.

As discussed above, the content of DOM in groundwater decreased after MNB or CB aeration processes. And the content changes were different for different kinds of DOM. Figure 8b shows the relative excitation-emission area volume of I–V regions in groundwater on the 30th day after MNB or CB aeration. As a whole, after MNB or CB aeration, the relative content of the biodegradable substances (regions I, II, and IV) decreased, while it increased for non-biodegradable
substances (regions III and V). It indicated that compared with fulvic and humic acid-like substances, more biodegradable substances were degraded. There were more humic acid-like substances and less protein-like substances in groundwater treated by MNB aeration than in groundwater treated by CB aeration. The result showed that MNB played a more effective role in biodegradation. As discussed in “Contaminant removal efficiency,” groundwater treated by MNB aeration had higher microbial activity than groundwater treated by CB aeration. And it was reported that the soluble microbial by-product substances resulted from microbes during substrate metabolism (Li et al. 2013). So, the relative content of soluble microbial by-product substances in groundwater treated by MNB aeration was more than that in groundwater treated by CB aeration, and its value was relatively high (Fig. 8b). Furthermore, soluble microbial by-product substances were biodegradable compounds. Thus, the groundwater treated by MNB aeration could be further treated by biodegradation.

Energy consumption

Based on the experimental condition, the preliminary energy consumption in MNB and CB aeration was estimated based on the same DO value of 8.37 mg/L. In this study, the CB aeration was achieved by directly injecting oxygen into groundwater from the oxygen bottle, so there was no electricity consumption during the procedure. As shown in Fig. 3a, in order to obtain the DO value of 8.37 mg/L, oxygen MNB and CB aeration lasted for 8 s and 5 min, respectively. The electricity and oxygen consumptions of MNB aeration were 8.8 kW and 0.24 L, while they were 0 kW and 9 L in CB aeration. Although the electricity consumption of MNB aeration was more than that of CB aeration, the oxygen consumption of MNB aeration was much less than that of CB aeration. So, it can be concluded that MNB aeration was a more energy-efficient landfill leachate-contaminated groundwater treatment method.

Conclusions

Organic contaminant removal of oxygen MNB aeration from landfill leachate-contaminated groundwater was studied by comparing it with oxygen CB aeration. At first, the mass transfer efficiency of MNB and CB aeration was estimated. Secondly, the contaminant removal and microbial activity enhancement effect of the two kinds of aeration on landfill leachate-contaminated groundwater were evaluated. At last, the composition variations of DOM in groundwater before and after aeration were characterized. Based on the test results, the following conclusions can be drawn.

The maximum DO value, oxygen utilization efficiency, and $k_{La}$ in groundwater treated by oxygen MNB aeration were 39.27 mg/L, 5.32%, and 0.264 1/s; they were 4.8, 10, and 50 times that in groundwater treated by oxygen CB aeration, respectively. In addition, the DHA of groundwater increased by 101.25% by oxygen MNB aeration. Oxygen MNB aeration could effectively remove organic contaminants in landfill leachate-contaminated groundwater. On the 30th day after MNB aeration, the COD, BOD$_5$, and ammonia nitrogen removal efficiency were 50.94%, 94.91%, and 12.55%, and they were increased by 29.72%, 13.43%, and 138.59% compared with CB aeration, respectively.

MNB aeration destructed the UV-quenching polar functional groups and made the aromatic organic matters in groundwater degraded or decomposed into small molecular

![Excitation-emission area volumes of I–V regions in different groundwater samples: (a) normalized excitation-emission area volume and (b) relative excitation-emission area volume](image)
substances. With the treatment of MNB aeration, more refractory organic matters were transformed into biodegradable organic matter, and the hydrophobic fractions as well as transphilic acids were removed. The content of DOM in groundwater decreased sharply after oxygen MNB aeration. With the biodegradation effect of MNB aeration, a large number of protein-like and soluble microbial by-product substances were degraded, and humic as well as fulvic acid-like substances were degraded to a certain level. The groundwater treated by MNB aeration can be further treated by biodegradation. Oxygen MNB aeration had an oxidizing effect while enhancing the biodegradation of groundwater contaminants. It is proven to be an energy-efficient landfill leachate-contaminated groundwater treatment method.

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Author contribution Mei Bai: conceptualization, data curation, writing – original draft. Zhibin Liu: conceptualization, writing – review and editing, supervision, funding acquisition. Liangtong Zhan: funding acquisition, project administration. Zhu Liu: data curation. Zhanhuang Fan: funding acquisition, project administration.

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Data availability The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

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