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Monitoring Transitory Profiles of Leachate Humic Substances in Landfill Aeration Reactors in Mesophilic and Thermophilic Conditions

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Abstract

The presence of humic substances (HS) in landfill leachate is of great interest because of their structural stability and potential toxicity. This study examined the effects of temperature and waste age on the transformation of HS during in situ aeration of bioreactor landfills. By establishing aerobic conditions, dissolved organic carbon (DOC) rapidly accumulated in the bioreactor leachate. Fractional analysis showed that the elevated concentration of humic acids (HAs) was primarily responsible for the increment of leachate strength. Further structural characterization indicated that the molecular weight (MW) and aromaticity of HS were enhanced by aeration in conjunction with thermophilic temperature. Interestingly, elevation of HAs concentration was not observed in the aeration reactor with a prolonged waste age, as the mobility of HAs was lowered by the high MW derived from extended waste age. Based on these results, aeration may be more favorable in aged landfills, since dissolution of HAs could be minimized by the evolution to larger MW, in compared to young landfills. Moreover, increased operation temperature during aeration likely offers benefits for the rapid maturation of HS.

Keywords: Landfill aeration; Leachate strength; Humic substances; Temperature; Waste age

1. Introduction

Natural environment is suffering the negative consequences of municipal solid waste (MSW) landfilling, as many old dumping grounds did not incorporate the engineering design to better isolate the waste from the surrounding environment. Even in landfills designed with protection layers, uncontrolled leachate and gas may be released due to defects of the aged liner system. Unattended leachate discharge could pose threats to nearby water bodies and groundwater resources, leading to increased organic loading, concentrated inorganic ion and nutrients, as well as elevated levels of heavy metals and xenobiotic organic compounds [1]. Furthermore, the landfill gas, mainly comprised of CH₄, CO₂ and some nonmethane organic carbon (NMOC), could result in negative aspects associated with unpleasant odor, explosion, global warming and deleterious health effects [2]. On top of that, the long-term adverse environmental impact caused by MSW landfills may last for decades, or even centuries [3].

Many approaches have been developed to counteract the negative effects induced by landfill, such as capping, reactive barrier, and phytoremediation. However, the objections of these technologies for reasons of high cost or limited capacity have hindered their wide adoption. Unlike those passive measures, in situ aeration targets to reduce the pollution potential of the waste materials before contamination occurs [4]. By supplying a controlled amount of air to landfills, in situ aeration promotes aerobic biodegradation via interruption of existent anaerobic process [5]. In contrast to the slow rate presented by anaerobic pathway, in an aerobic environment biodegradable organic matter together with those semi-degradable and hardly

degradable organics such as cellulose and lignin could be oxidized into carbon dioxide in a significantly shorter timeframe [4]. This provides more immediate benefits, such as the rapid reduction of biological oxygen demand (BOD), ammonia, methane and odor compounds [4, 6-8]. In the long term, landfill stabilization is achieved more rapidly by a factor of 2 ~ 4, thereby lowering the cost for post closure care, and eventually earlier beneficial reuse of the land may be possible [6, 9, 10]. Over the last several decades, full scale aeration has been successfully demonstrated worldwide [4, 11, 12]. To optimize the aeration process, a series of operation parameters has been studied such as air pressure, aeration rate, air injection mode (active or passive, continuous or intermittent), aeration efficiency, moisture and temperature control, and off-gas treatment [6, 11-17].

Due to intensive aerobic conditions, exothermic reactions release energy bringing the temperature in the landfill body up to 60 °C [9, 17]. On one hand, microbiological activity and substrate degradation rate could be enhanced by the increased temperature [18]. On the other hand, bioprocess at higher temperature has been reported to be more susceptible to inhibition and environment change [19]. E.g. temperature above 40 °C may inhibit nitrification [5]. In landfill bioreactor at 45 °C, a delay of biodegradation process was observed, when operation condition was changed from anaerobic to aerobic at start-up phase [20]. Afterwards, the biodegradation rate at 45 °C was accelerated and eventually reached the same low emission potential as that at 35 °C and 40 °C [20]. However, in the literature, comparative evaluation on the aeration performance at respective mesophilic (30 - 40 °C) and thermophilic (50 -

60 °C) conditions is limited due to the shortage of reference data particularly from thermophilic studies.

Landfill stabilization is often a matter of time. Landfill waste carries varied characters and reacts differently to the external stimuli at its different periods of time [16, 21]. In this regard, the inception time of aeration is of great significance for success in landfill treatment [10]. However, little research to date has provided the sound evidences about the effects of waste age on aeration, and thus the right time to start aeration.

In the past decades, HS have received increasing attention, as they sustain plant growth [22], lead to the formation of disinfection by-products [23], and affect the fate of persistent organic pollutants and heavy metals [24, 25] etc. Regarding their structure, HS are supermolecular associations by relatively small and heterogeneous molecules of various origins, which self-assemble by hydrophobic interactions and hydrogen bonds [26, 27]. The dissolved HS are generally subdivided into two fractions based on their alkali and acid solubility. Humic acids (HAs) are insoluble at acidic conditions ($\text{pH} < 1$), while fulvic acids (FAs) are soluble at the full pH range. Percolated water in landfill washes out HS in the appearance of yellowish or brownish color. Generally, HS are abundant in the leachate representing up to 90% of DOC, while the HAs account for 0.4% - 44% and FAs comprise 23% - 56 % [28-30]. As landfill ages and humidification process proceeds, HS percentage in leachate increases [28, 31]. However, Nanny et al. observed an opposite change over time [29]. The properties of HS are affected by the landfill age and landfill operation mode [22,

32, 33]. Therefore, variations in HS structure could reflect the chemical and biological mechanisms involved [33]. In most cases, leachate HS data are collected from traditional anaerobic landfills. In contrast, only very few studies have been conducted on HS formation, transfiguration and humification in aerobic landfill conditions [22, 33].

In this study, HS were extracted from leachate samples derived from four lab-scale aerobic and anaerobic bioreactors, which differed in operation temperature and waste age. Detailed characterization such as elemental analysis, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS) and solid-state ^{13}C nuclear magnetic resonance (^{13}C -NMR) were conducted to determine how the structure of HS changed in each bioreactor. In particular, the properties of HS from different bioreactors were compared to understand the influences of aeration, temperature and waste age on the chemical and biological mechanisms involved in different operation modes.

2. Materials and methods

2.1 Aged waste preparation

Synthetically aged waste was prepared in the lab simulating the waste composition of closed landfill or dumping ground. By this way, the variance of aged waste composition among the bioreactors was minimized, therefore allowing for more comparable results. Fresh MSW was prepared by mixing food waste, yard waste, paper, plastics and textile at a ratio of 60/15/10/10/5 (w/w). The composition of waste

materials was determined according to other studies [34, 35]. The initial water content of the fresh waste mixture was 52%. The element composition was 63% C, 0.6% N, 10% H and 25% O (by weight). The synthetic MSW mixture (55 kg) was mingled with 5.5 kg of compost (Corona Florist & Nursery Pte. Ltd., Singapore) and loaded into an acrylic bioreactor, with dimensions 1100 mm $\times$ 500 mm (L $\times$ D). The compost, which was less reactive, served as a dilution agent, and at the same time buffered the pH to prevent undesirable acidification [36, 37]. Pre-aeration for 2 weeks, inoculation with anaerobic digested sludge, and leachate recirculation were also conducted to shorten the acid phase and rapidly initiate methane production. (Details of the bioreactor operation are included in the supplementary material). The aged waste was ready after 150 days, when a constant-low biogas production rate was achieved (Fig. S2).

2.2 Column experiments

The aged waste (66% in water content (w/w)) was transferred into four bioreactors (L $\times$ D: 500mm $\times$ 190mm) containing each approximately 6.5 kg of waste (Fig. S3). Air was supplied through an acrylic pipe erected in the middle of the reactor.

Upon loading, the bioreactors were purged with N₂ and operated under anaerobic condition for another two weeks for stabilization at room temperature (35 °C). Then, two reactors (AR35 and AR55) converted into aerobic conditions using air flow rate approximately 0.016 L/min $\cdot$ kg dry material (DM). That was considered as time zero

for all subsequent experiments. The flow rate was controlled by a ball valve and monitored by a digital flow meter (TSI 4000 series, USA). For AR55, the reactor was heated up with a heating belt, with a ramp of 2 °C/day until 55 °C. The temperature was recorded by a thermoprobe inserted in the middle of the waste layer. Another reactor called NR35 was kept under anaerobic conditions throughout the whole experiment as a control. The fourth reactor LR35 was maintained in anaerobic conditions similar to NR35 until day 155, and afterwards it was converted to aerobic conditions as AR35.

On day 1, 3 and 5 per experimental week, 200 mL of deionized (DI) water was trickled from the top of each reactor. The produced leachate was temporarily withheld at the bottom marble layer before fully discharged every other water addition. This means that discharge took place after two water additions (400 mL water addition). Comparing to 400 mL DI water added, an average of 370 mL leachate was collected in the anaerobic reactor during each discharge process, whereas an average of 320 mL leachate was obtained in the aerobic reactor. The lower volume of leachate in aerobic reactors was due to the accelerated water evaporation by aeration and high temperature. Leachate sample was passed through 0.45 µm syringe filter (Cronus, UK) and stored at 4 °C before DOC analysis (Analytik Jena AG Multi N/C 2100 system, Germany). The duration of the experiments lasted for 396 days. The results were normalized to 400 mL water addition (the volume of incoming DI water) and plotted in Fig. 1. In particular, leachate samples were collected at two different periods for DOC fractionation to investigate the temporal variation of carbon distribution of

different organic components. The sample in period I was represented an average property from the 4 consecutive days of leachate collection, i.e. days 73, 77, 82 and 87, when 200mL leachate from each day were combined together to reach a total volume of 800mL. Period II was at days 215, 220, 224 and 229. Each 800 mL leachate sample was analyzed in duplicates.

2.3 DOC fractionation and HS extraction

Leachate organic matter was separated into HAs, FAs, and HyI fractions using the method described by Christensen et al. [38]. Briefly, the HAs were precipitated by adjusting leachate pH lower than 1 and then separated by centrifugation and filtration. Purification and protonation of HAs was conducted by dialyzing HAs solution (HAs redissolved in 0.05 M NaOH) against DI water, 0.1 M HCl and DI water sequentially. Amberlite XAD-8 resin was employed to retain FAs by adsorption. The residual dissolved organic matter not absorbed onto the XAD-8 resin was considered as hydrophilic fraction (HyI). The concentration of HyI fraction was represented by measuring the DOC content of the sample passing through the XAD-8 resin. The amount of HAs was calculated as the difference between the initial DOC content in the sample and the DOC content in the sample after acidification and filtration. The theoretical content of FAs was determined as the difference between the DOC content in the sample after acidification and filtration and the DOC content in the sample passing the XAD-8 resin column. FAs retained by XAD-8 resin was eluted out by a 0.1 M NaOH solution, which later was allowed to flow through a H-saturated cation

exchange resin (AM-PG-50) for purification. The recovery rates of the FAs from the XAD-8 resin adsorbents were around 90% and the recovery rates of the FAs after AG-MP-50 resin were about 80%. The purified HAs and FAs solutions were freeze dried. The obtained powder from the duplicate was ground together and subjected to structural analysis as one effective sample.

2.4 Characterization of HS sample

Elemental analysis was performed on freeze-dried samples of HS (5 mg) by using Vario EL cube (Elementar Analysensysteme GmbH, Germany). The solid-state ^{13}C -NMR was performed on a Bruker AVANCE III 400WB spectrometer. MALDI had the advantage of forming singly charged ions. Combined with TOFMS, it could detect the absolute MW of HS rather than the apparent MW detected in high performance size exclusion chromatography [39]. In details, the HS samples were dissolved in 50% acetonitrile (ACN) and 0.1% trifluoroacetic acid (TFA), then mixed with same amount of matrix solution containing 10 mg/mL of α -cyano-4-hydroxycinnamic acid (CHCA) in 0.1%TFA-50%ACN, and spotted onto a 384-well stainless-steel MALDI target plate (Applied Biosystems, USA). An ABI 4800 MALDI TOF/TOF mass spectrometer (Applied Biosystems, USA) was used to analyze the samples on the MALDI target plates. For MS analyses, typically 1600 shots were accumulated for each sample. The MALDI spectra of HS in current study were consistently found to contain a number of common peaks. It was difficult to assign the origins to peaks in the low m/z range, as they could be attributed to

matrices, contaminants or HS fragments during ionization. Thus only the largest m/z peak with signal-to-noise ratio over 3 in each spectrum, which was more likely associated with the ionized HS molecule, was reported in this work.

3. Results and discussion

3.1 DOC

The variation of the organic load in the leachate characterized by DOC is shown in Fig. 1. After the two-week stabilization stage, the DOC value in all reactors was around 811 ± 67 mg/L, suggesting no significant statistical difference among bioreactors. The DOC in NR35 gradually decreased to less than 30 mg/L at the end of the experiment, triggered by the compounded effects of leaching and anaerobic degradation. The divergences between NR35 and LR35 before day 155 (when both reactors under anaerobic conditions) were negligible, indicating a comparable setup of the column experiments.

The DOC value in the aerobic reactors showed a dramatic increment immediately after aeration. DOC in AR35 reached its maximum value (1440 mg/L) on day 9, while AR55 reached the maximum value (1980 mg/L) on day 18. Compared to NR35, those values were 1.8 and 4.1 times higher, respectively. The higher DOC in AR55 compared to AR35 before day 37 demonstrated the accelerated leaching of organic matter at higher temperature. More interestingly, the higher temperature could also expedite the attenuation of leachate strength, as seen by the rapid drop of DOC in

AR55 than AR35. The final DOC concentration in AR35 and AR55 was 110 mg/L and 70 mg/L, respectively.

The organic carbon discharge in each drainage process could be calculated as $\text{DOC} \times \text{leachate volume}$. The total organic carbon load in terms of accumulated DOC discharge was determined at 14.4 g and 12.7 g in AR35 and AR55, respectively. The lower leachate loading in AR55 may be attributed to enhanced biological respiration, by which C was removed in CO_2 emission.

The DOC in LR35 reactor also presented an increase of 30% when converted into aerobic conditions, confirming that aeration enhanced organics dissolution in the present study. Similar results were reported by Oncu et al. [17] observing increased organic loads in the leachate during aeration. Over 32-month aeration in Dorfweiher landfill, concentrations of COD and BOD_5 were increased from 2000 mg/l up to 8100 mg/l and 70 mg/l up to 570 mg/l, respectively [17]. Moreover, both concentrations showed a fluctuating regime during aeration and no reduction trend was observed [17]. The constant enhancement in leachate strength during the whole aeration period was different with the temporary increment found by Prantl et. al. [40] and Raga and Cossu [20], where COD in aeration reactor rose up in first few days or months, while followed by a rapid reduction. The initial increase period was explained by the mobilization effects of the mechanical disturbance by air injection [40]. However, the persisting increased leachate strength in current and Oncu et al.'s [17] studies suggested other mechanisms behind. In addition, the darker color of leachate after

aeration in current study indicated the presence of high concentration of HS, and led to the following exploration.

3.2 Analysis by MALDI-TOF-MS

Table 1 and 2 summarize the largest m/z peak observed in MALDI spectra for HAs and FAs leachate samples. The highest mass detectable for HAs in NR35-I, AR35-I and AR55-I were at m/z 1914, 2480 and 2480, respectively, whereas peaks as high as m/z 2212, 2483 and 2870 were observed for HAs from NR35-II, AR35-II and AR55-II, respectively. Compared to period I, the HAs in period II contained a higher MW, indicating humification progress along with time. This observation is consistent with that of Kang [32], who also reported that the MW of HS tended to be higher as landfill aged. Moreover, the HAs in aerobic reactors displayed higher MW than anaerobic ones from the same sampling period, implying more intensive polymerization process in aerobic conditions. According to Piccolo [41], the MW of HS could be increased by incorporation of new components through -C-O- or -C-C- bonds. These new covalent bonds could be achieved via an oxidative-coupling reaction catalyzed by oxidative enzymes such as peroxidases and phenoloxidases [27, 42]. Since these enzymes are more abundant and more active under aerobic condition [43, 44], the HS elongation is expected to be more efficient in aeration reactors.

It was further noted that HAs from LR35-II exhibited the largest MW (3548), 43% higher than that of HAs from AR35-I. Both reactors had been subjected to the same duration of aeration (2 months), but starting at different points. The commencement of

aeration in younger waste age produced HAs with a smaller size (such as AR35-I). The early aeration may interrupt the size evolution of HAs, as it leached out a substantial amount of organic matters. It resulted in deficiency of precursor substances from forming larger HA molecules via intermolecular association [26]. The bigger size of HAs in LR35-II was likely ascribed to the already attained higher MW due to waste aging under previous prolonged anaerobic condition.

The differences of MW among FAs were minor. Therefore, the compositional and structural variations in different FAs samples (Table 2 and 4) can only be explained by the alteration of side-chains in lignin-like constituent [45]. Due to the preservation of the main aromatic carbon network, changes of the MW were minor.

3.3 Elemental Analysis

According to elemental analysis, the element content for HS was in the typical range as reported in the literature (Table 1 and 2). The low H/C and high N/C values were associated with high degree of humification, due to mineralization of alkyl carbon branch and preservation of nitrogen [46]. Thus, the decreasing H/C ratio and slight increasing N/C ratio along with time suggested that the degree of aromaticity and maturity of FAs increased with operation time in NR35, AR35 and AR55, respectively. However, it is difficult to presume a clear trend of the compositional change for HAs along with time, attributed to the complexity in the formation of HAs. On one hand, alkyl carbon was frequently incorporated in the HAs molecule, such as lipid, peptide and polysaccharide. On the other hand, the existent alkyl carbon was

lost as CO₂ during humification, as aliphatic structures also presented a carbon source for microorganism [47]. The ambiguity in the temporal variation of H/C and N/C ratios in HAs was also observed in other relative studies [31, 32].

The H/C ratio of HS in the same sampling period had the following order: AR55 < AR35 < NR35. This suggests that aeration could enhance the humification degree of HS. This conclusion is consistent with the findings of previous research, which claimed that aeration could help to achieve rapid maturation of the humic acids in waste materials [22]. Moreover, it was noticed that the maturation of the HS was further accelerated by high temperature.

3.4 Solid-state ¹³C-NMR

Based on previous NMR studies [51-53], the spectra could be split into eight main spectral regions as shown in Tables 3 and 4. The signals in 43-60 ppm and 141-162 ppm are typical in spectral of lignin structural units, which could be attributed to methoxyl group (O-CH₃) and oxygen-substituent aromatic carbon (aromatic C-O) [52]. Compared with HAs from NR35, these two lignin fingerprints were more abundant in HAs from aerobic reactors, with the highest aromatic C-O percentage present in AR55. Moreover, HAs from AR55 displayed more intensive resonances in the region of aromatic carbon (110-140 ppm) and weaker signals in 0-43 ppm region for alkyl carbon than that from AR35. Overall, aromaticity of HAs was increased under aeration and further reinforced by thermophilic temperature. It was also noticed that the drop in COOH content in HAs along with time in NR35,

AR35 and AR55 was distinct, which could be considered as C loss in the form of CO₂ during biological mineralization [47].

Study of spectra for HAs from LR35-II indicated the abatement in percentage of aromatic carbon and an increase for alkyl carbon. Considering the increase in MW, the reduction in aromaticity could be interpreted by the coupling interactions of HAs with more aliphatic component during polymerization, such as lipid and peptides. The augment of N content (7.04%) in its element composition emphasized the importance of peptides during the increment of HAs molecule. Incorporation of peptides could also be revealed by the increase of the relative intensity in 43-60 ppm and 162-290 ppm, as resonances in these two regions may also derive from α carbon and carbonyl carbon of polypeptides, respectively.

Similar to HAs, the degree of aromaticity in FAs was increased by aeration and thermophilic temperature (Table 4). Moreover, compared with NR35, FAs from aeration reactors revealed 20% - 50% higher content in carboxylic carbon. The increase in carboxyl carbon was accompanied by the decrease in alkyl carbon and O-alkyl carbon, indicating that the main structural variation in FAs originated from the oxidation of alcohol side chain of lignin structure to yield by carboxylation a COOH group [54].

3.5 DOC fractionation

The measured distribution of leachate DOC into HAs, FAs and HyI fractions is shown in Fig. 2. It was observed that the percentage of HAs was increased by aeration.

In NR35-I, HAs contributed 46% of DOC, while it was for 76% and 64% in AR35-I and AR55-I respectively. Two potential mechanisms may play significant roles for the enhancement of HAs dissolution from waste matrix. First, aeration could increase the pH value of leachate from 7 to 8-9 (Fig. 3). At higher pH, more acidic groups of HAs were deprotonated, giving the humic particles more negative charges. The resulted higher electrostatic repulsion dispersed large aggregates into smaller humic associates and consequently increased the dissolution of HAs [55]. Second, aerobic condition enriched carboxylic group in the structure of HAs. For instance, the COOH abundance was 26% higher in HAs from AR35-I (12.7%) than HAs from NR35-I (10.1%). The larger hydrophilicity (due to higher content of carboxylic group) of HAs could prevent strong molecular association by hydrophobic forces, resulting in HAs molecular aggregate with smaller size [26] and higher leachability.

In period II, the HAs percentage in all fractions decreased considerably, which represented 41%, 59% and 53% in NR35-II, AR35-II and AR55-II, respectively. Most likely, the key factor for the decrease of HAs levels was the reduced HAs pool in the waste matrix, as lots of HAs had already been leached out in the previous 215 days. Furthermore, the decrease of COOH content in HAs structure in period II was also considered to reduce the mobility of the HAs (Table 3), as the decrement in hydrophilicity (due to lose of COOH group) tightened the hydrophobic forces between humic assemblings. When humic molecules remained being confined in strong hydrophobic association of apparently large molecular size [56], it could hardly be liberated to dissolve in water. Moreover, the increase in size of the single HAs

molecule was another possible reason for the reduction of HAs abundance. However, as the pH kept higher in aeration reactors, the HAs abundance in AR35-II and AR55-II were still larger than in NR35-II.

Different from AR35 and AR55, there was no increase of HAs concentration in LR35 when aeration was commenced later. It might be explained that larger MW (3548) in HAs from LR35-II had a lower mobility, resulting in limited dissolution. Although after aeration pH was increased and carboxylic groups were accumulated in molecular structure, the larger MW of HAs from LR35-II could cushion the dissolution effects of the abovementioned alterations and prevent itself from being washed out. As MW of HAs was positively correlated with the landfill age, it was assumed that aeration could lead to less leaching of larger molecular-weight HAs in old landfills. Subsequently it could reduce the risks of elevated leachate loading.

3.6 Future perspectives

The abovementioned assumptions are supported by the literature. Increased organic loads in the leachate have been observed by the current study and Oncu et al [17]. COD decrease after aeration was reported by Ritzkowski et al. [5], Prantl et al. [14] and Raga and Cossu [20]. Many factors including waste age, waste types as well as aeration procedures, might play different roles in these studies leading to different results. Nevertheless, it is noticeable that waste age in the current study and Oncu's pilot project (4-11 years) is much younger compared with the waste materials used by

Ritzkowski et al. (13-35 years) [5], Prantl et al. (8-17 years) [14] and Raga and Cossu (5-15 years) [20].

In real case studies, the situation would be considerably complicated by the high heterogeneity in the waste materials and large variation in the boundary conditions. The current study was based on laboratory scale experiments, and it had not yet attained a certainty to match with a scaled-up setup and the real scenario. Therefore, in the next step, more HS data from field aeration projects should be collected to further verify the hypothesis obtained in current work. Nevertheless, the findings from the current work could be used as a precaution, when aeration is proposed for a young landfill. For example, preliminary investigation of HAs profile should be added into the monitoring plan. Remediation technologies should consider the possibility of the increment in leachate HAs concentration, as dissolved HAs may affect the mobility of heavy metals or organic pollutants especially in the case of unattended leaking. Furthermore, if leachate treatment process is employed along with aeration, more emphases should be put on physical-chemical processes, such as coagulation, membrane filtration and high advanced oxidation, because the HAs are not readily biodegradable and they can pass through the biological treatment processes compromising the quality of the effluent.

4. Conclusions

Structural analysis of the extracted leachate HS showed that the polymerization and condensation of HS was increased with aeration and high temperature, in

correspondence to the smaller H/C ratio and higher aromaticity index in aerobic HS. Further studies on leachate HAs, FAs and HyI fractionation revealed that aeration dramatically raised the percentage of HAs, which were contributable to the DOC elevation. Enrichment of the COOH group in HAs structure under aerobic condition was potentially responsible for the enhanced dissolution of HAs. The observed higher pH after aeration could also facilitate the HAs release. However, aeration did not enhance HAs detachment from waste materials with prolonged anaerobic aging, most likely due to the limitation in mobilizing the aged HAs, which had higher MW.

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Fig. 1 Variations of leachate DOC in each reactor. “↔” indicates the sampling periods for humic matter analysis: period I (day 73, 77, 82 and 87) and period II (day 215, 220, 224 and 229). “↑” indicates the start of aeration in LR35.

Fig. 2 Distribution of DOC into HyI, FAs, and HAs in the leachate from period I and period II

Fig. 3 pH variation in leachate from each reactor

Table 1. Elemental composition^a, atomic ratio and MW for HAs samples in present study and for landfill leachate HA in the literatures

HA	NR35-I	AR35-I	AR55-I	NR35-II	AR35-II	AR55-II	LR35-II	Literature ^b
N%	4.23±0.01	5.93±0.01	4.68±0.02	3.85±0.03	4.06±0.01	3.61±0.01	7.04±0.01	1.79-8.30
C%	51.71±0.22	51.02±0.21	51.67±0.06	52.56±0.71	53.46±0.04	53.51±0.21	49.86±0.02	40.06-64.94
H%	5.68±0.04	5.47±0.01	5.53±0.01	6.09±0.07	6.02±0.01	5.72±0.03	6.08±0.01	5.54-8.80
H/C	1.31	1.28	1.28	1.38	1.34	1.27	1.45	1.25-1.88
N/C	0.07	0.10	0.08	0.06	0.07	0.06	0.12	0.02-0.11
MW ^c	1914	2480	2480	2212	2483	2870	3548	1490-3940 ^d

^aMean value (n=2)

^bRef.[24, 29, 32, 33]

^cThe largest m/z peak detected by MALDI-TOF-MS.

^dRef.[38, 39, 48]

Table 2. Elemental composition^a, atomic ratio and MW for FAs samples in the present study and for landfill leachate FA in the literatures

FA	NR35-I	AR35-I	AR55-I	NR35-II	AR35-II	AR55-II	LR35-II	Literature ^b
N%	2.36±0.02	3.27±0.01	3.53±0.01	2.18±0.03	3.59±0.01	3.73±0.02	2.07±0.01	1.68-12
C%	48.31±0.30	47.33±0.16	47.47±0.02	52.06±0.83	49.19±0.04	46.82±0.19	51.42±0.27	36.8-55.66
H%	5.30±0.08	4.82±0.02	4.75±0.05	5.65±0.03	4.92±0.01	4.66±0.01	5.33±0.02	4.3-9.6
H/C	1.31	1.21	1.19	1.29	1.19	1.19	1.23	1.34-2.53
N/C	0.04	0.06	0.06	0.04	0.06	0.07	0.03	0.03-0.23
MW ^c	2072	2071	2071	2072	2071	2072	2097	1000-2310 ^d

^aMean Value (n=2)

^bRef.[29, 32, 49]

^cThe largest m/z peak detected by MALDI-TOF-MS.

^dRef.[38, 39, 50]

Table 3. ^{13}C -NMR Chemical shift regions and their relative contributions of the leachate HAs

HAs	Assignment	NR35-I	AR35-I	AR55-I	NR35-II	AR35-II	AR55-II	LR35-II
0-43ppm	alkyl	20.74	22.53	18.81	20.38	16.58	14.19	29.40
43-60ppm	O-CH ₃ /NCH	12.57	12.96	13.95	13.36	15.54	15.04	16.30
60-92ppm	O-alkyl	17.64	15.73	16.83	20.91	20.29	19.67	18.27
92-110ppm	O-C-O anomeric	5.00	4.52	4.98	4.87	5.10	4.62	3.65
110-141ppm	aromatic C-H & C-C	20.89	19.24	21.92	21.52	22.75	25.37	13.21
141-162ppm	aromatic C-O	9.92	8.94	10.56	9.15	9.74	11.09	4.02
162-190ppm	COO/N-C=O	10.06	12.70	10.07	8.05	7.73	7.58	12.84
190-220ppm	C=O	3.17	3.39	2.88	1.77	2.28	2.45	2.31
aromaticity		0.36	0.34	0.37	0.34	0.36	0.41	0.20

Table 4 ^{13}C -NMR chemical shift regions and their relative contributions of the leachate FAs

FAs	Assignment	NR35 -I	AR35 -I	AR55 -I	NR35 -II	AR35 -II	AR55 -II	LR35- II
0-43ppm	alkyl	43.30	36.23	34.58	43.22	36.99	33.41	41.07
43-60ppm	O-CH ₃ /NCH	8.22	8.93	8.24	7.48	8.91	8.47	8.93
60-92ppm	O-alkyl	13.68	12.70	11.72	13.88	12.10	10.87	13.09
92-110ppm	O-C-O anomeric	1.27	2.10	2.10	2.10	2.29	2.02	2.23
110-141ppm	aromatic C-H & C-C	12.83	14.11	14.68	13.96	13.64	16.14	11.96
141-162ppm	aromatic C-O	4.69	5.82	6.51	5.18	6.02	7.64	4.78
162-190ppm	COO/N-C=O	13.48	16.03	18.09	11.72	16.56	17.68	14.67
190-220ppm	C=O	2.53	4.07	4.09	2.48	3.50	3.78	3.27
aromaticity		0.21	0.25	0.27	0.22	0.25	0.30	0.20