Characterization of landfill leachate by spectral-based surrogate measurements during a combination of different biological processes and activated carbon adsorption

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ABSTRACT

Surrogate measurements based on excitation-emission matrix fluorescence spectra (EEMs) and ultraviolet-visible absorption spectra (UV-vis) were used to monitor the evolution of dissolved organic matter (DOM) in landfill leachate during a combination of biological and physical-chemical treatment consisting of partial nitritation-anammox (PN-Anammox) or nitrification-denitrification (N-DN) combined with granular active carbon adsorption (GAC). PN-Anammox resulted in higher nitrogen removal (81%), whereas N-DN required addition of an external carbon source to increase nitrogen removal from 24% to 56%. Four DOM components (C1 to C4) were identified by excitation-emission matrix-parallel factor analysis (EEM-PARAFAC). N-DN showed a greater ability to remove humic-like components (C1 and C3), while the protein-like component (C4) was better removed by PN-Anammox. Both biological treatment processes showed limited removal of the medium molecular humic-like component (C2). In addition, the synergistic effect of biological treatments and adsorption was studied. The combination of PN-Anammox and GAC adsorption could remove C4 completely and also showed a good removal efficiency for C1 and C2. The Thomas model of adsorption revealed that GAC had the maximum adsorption capacity for PN-Anammox treated leachate. This study demonstrated better removal of nitrogen and fluorescence DOM by a combination of PN-Anammox and GAC adsorption, and provides practical and technical support for improved landfill leachate treatment.

Key words | denitrification-nitrification (N-DN), excitation-emission matrix-parallel factor analysis, GAC adsorption, landfill leachate, partial nitritation-anammox, UV-vis spectroscopy

HIGHLIGHTS

- PN-Anammox and N-DN were used to treat landfill leachate.
- The GAC adsorption was used as the polishing process to remove the bio-recalcitrant components.
- Biological processes affected the performance of GAC adsorption, PN-Anammox process was positive to prolong the column lifetime.
- Four fluorescence DOM components were identified and the dynamic changes of these components were investigated by EEM-PARAFAC.
- The combination of PN-Anammox and GAC removed nitrogen and fluorescence DOM better.

INTRODUCTION

Leachate, an inevitable consequence of landfilling, contains high concentrations of complex contaminants, such as dissolved organic matter (DOM), ammonium, heavy metals and xenobiotic contaminants (Oloibiri et al. 2011). When discharged, this leachate poses a serious risk to the environment. Young-age leachate contains high concentrations of biologically degradable organic matter, while mature leachate contains high loads of refractory dissolved organic matter (rDOM), such as humic and fulvic-like substances, which results in a low ratio of biological oxygen demand to chemical oxygen demand (BOD₅/COD < 0.3) (Li et al. 2011).

There is a wide range of technologies available to remove organic matter and other pollutants in leachate. Biological treatment is the most popular treatment used for removing biodegradable organic compounds and nitrogenous matter present in leachate. Conventional nitrification and denitrification (N-DN) systems can remove some refractory organic matter in leachate, but they are associated with high costs of aeration, substantial addition of organic carbon (for denitrification), and problems that include sludge production and toxic effects of high concentrations of ammonium, which significantly increase treatment costs (Li et al. 2018). The combination of partial nitritation (PN) and anoxic ammonium oxidation (Anammox) has been proven as an alternative and feasible technology to treat landfill leachate. PN-Anammox first converts half of the ammonium to nitrite and then combines the residual ammonium with the nitrite to dinitrogen gas and nitrate (Van Hulle et al. 2010). In comparison with N-DN, the PN-Anammox process consumes 63% less oxygen and no organic carbon, and the sludge production is reduced by about 90%. This saves 1–3 euro per kg N removed (Van Hulle et al. 2010).

Granular activated carbon (GAC) is an excellent adsorbent for removing various types of organic and inorganic compounds due to its characteristics of large surface area, thermostability and fast adsorption kinetics. Abbas et al. (2009) reported 50–70% COD removal by GAC adsorption during landfill leachate treatment. The high cost of operation and regeneration during leachate treatment is a limitation of GAC adsorption. In light of this, GAC adsorption is often used as a polishing step (after biological treatment) during landfill leachate treatment to improve the overall leachate treatment. For GAC adsorption, initial testing with a view to performance assessment is performed using batch experiments, in which kinetic and thermodynamic data (at equilibrium) is obtained. However, water treatment plants and industries usually operate on a continuous flow basis (Khraisheh et al. 2010). Therefore adsorption column testing is a more realistic representation of the GAC adsorption process, and column testing is appropriate for studying the performance of GAC (Khraisheh et al. 2010; Oloibiri et al. 2015).

The individual processes mentioned above have been studied extensively. However, only limited research has been done on the performance of a combination of biological and physical-chemical processes for landfill leachate treatment. In particular, the synergistic effect of combining different processes is still unclear, as is the effect of combining certain biological processes (N-DN or PN-Anammox) with the adsorption process.
Apart from nitrogen removal, a main parameter to assess for the performance of such (combined) leachate treatment is DOM removal. DOM is a heterogeneous mixture of organic matter, such as protein-like and humic-like substances and hydrophilic acids. DOM is ubiquitous in landfill leachate and plays a significant role in determining the performance of leachate treatment. The composition and structure of DOM varies dynamically during leachate treatment, which may increase the difficulty of investigating the removal of organic and inorganic pollutants during landfill leachate treatment (Yuan et al. 2018). It is therefore imperative to monitor the behavior of DOM in leachate treatment. COD is a conventional indicator of DOM. It quantifies the amount of oxidizable pollutants and can reflect an overall change of DOM. However, no detailed information of the compositional changes of DOM can be obtained from COD measurements.

Spectroscopic techniques such as fluorescence and ultraviolet-visible (UV-vis) absorbance are better suited for DOM characterization and can provide a fingerprint of the different components of DOM. These spectra have been widely applied to qualitatively and quantitatively characterize DOM properties due to their sensitivity, non-destructivity, and rapidity (Yuan et al. 2018). Studies focusing on adsorption processes have discussed the performance of UV-vis for monitoring organic compound changes (Sgroi et al. 2018). Due to the wide variety of chromophores in organic matter and possible presence of complex intramolecular interactions (Dryer et al. 2008), specific wavelengths (e.g., 254, 275 and 370 nm), have been frequently applied as simple surrogates to monitor DOM properties such as molecular size and aromaticity (Dryer et al. 2008; Sgroi et al. 2018).

Fluorescence spectroscopy is used to provide the amount and composition of fluorophores present in DOM using excitation-emission matrix spectroscopy (EEMs) by scanning a wide range of excitation and emission wavelengths. It provides a three-dimensional fluorescence intensity landscape in which the specific components of DOM (such as protein-like, fulvic-like, humic-like, and other aromatic xenobiotics) are present as distinctive peaks. The peak intensity is directly proportional to the concentration of the responsible fluorophore at low concentrations at which the inner filtering effects are negligible (Henderson et al. 2009). However, fluorophores with dissimilar chemical structures have the potential to overlap in EEM spectra. In order to make a quantitative identification of different fluorophores, multivariate statistical methods such as parallel factor analysis (PARAFAC) are applied. PARAFAC is a mathematical separation tool that can successfully decompose EEMs into a combination of several independent fluorescent groups (Murphy et al. 2013). The intensities and the relative distributions of PARAFAC components are related to the presence of fluorescent components. EEM-PARAFAC techniques are currently being developed as surrogates for conventional water quality parameters to explore the dynamic changes of DOM in wastewater (Murphy et al. 2013).

In this study, PN-Anammox and N-DN processes were used as biological techniques to treat landfill leachates, while GAC was used as a polishing process to remove the bio-recalcitrant components. Spectral-based surrogate measurements were applied to assess the performance of the combined processes to treat landfill leachate and to obtain an insight into DOM component changes, which helps to better understand the synergistic effect of different biological processes and adsorption. This will support the further optimization of combined landfill leachate treatment processes. The goal of this work was (i) to compare the performance of N-DN and PN-Anammox to treat leachate, (ii) to use UV-vis and fluorescence EEM measurements for identification of DOM components during the combined treatment and (iii) to assess the feasibility of spectral-based surrogate measurements for monitoring the changes of DOM components during the entire leachate treatment.

METHODS

Leachate sampling

The raw landfill leachate was collected during the summer from the IMOG landfill site in Moen (Belgium). The on-site treatment facility and sampling procedures are described in Oloibiri et al. (2015). The collected leachate was stored in the dark at 4 °C without any pH correction until treatment. Typical physical and chemical characteristics of the raw leachate are given in Table 1. Leachate was treated separately with either PN-Anammox or N-DN. The biologically treated effluent was then collected and stored at 4 °C before the GAC column test (performed at room temperature).

Experimental procedures

The single-stage PN-Anammox reactor is given in the Supplementary Information (Figure S1). The set-up and start-up of this reactor were similar to Gao et al. (2015a) and its detail description can also be found in Gao et al. (2015a).
The reactor was operated under a hydraulic retention time (HRT) of 1.68 days during the experiments.

The N-DN set-up was operated as a pre-denitrification process and its detail information is also given in Figure S1. The influent flow rate was set at 60 mL/h (HRT = 4.17 days), and the influent to sludge recycle ratio was set at 1:3 (Jingqian et al. 2010). After 90 days of operation, glucose (4,000 mg COD per day) was added to the denitrification reactor as an additional carbon source to support the growth of denitrifying bacteria.

A glass column with an internal diameter of 1.1 cm and a length of 50 cm was filled with 20 cm (9 g) of GAC as an adsorbent (Organosorb 10³, Desotec, Belgium) (Gao et al. 2015b; Oloibiri et al. 2017), as shown in Figure S1. The biotreated leachate samples were pumped through the column from top to bottom at flow rates of 60 mL/h and 360 mL/h, resulting in a filtration rate of 3 and 18 BV per hour, respectively. The experiment was ended at 150 and 500 bed volume (BVs), respectively, due to pore blockage of the column.

**Analytical methods**

Samples of raw and biotreated leachate were collected and analyzed for ammonium (NH₄⁺-N), nitrite (NO₂⁻-N), nitrate (NO₃⁻-N), COD and conductivity to evaluate the performance of the treatment systems. Ammonium was detected using Hach Lange test kits LCK 303 and LCK 302, and nitrite was measured using Hach NitriVer® Nitrite Reagent Powder. Those analysis were performed on a designated spectrophotometer (Hach Lange DR 2800 spectrophotometer) according to Standard Methods (Eaton et al. 2005). Nitrate content was measured using a Shimadzu UV-1280 spectrophotometer. The COD of the leachate samples was determined with the potassium dichromate method according to Standard Methods (Eaton et al. 2005).

Fluorescence analysis of all (treated) leachate samples was carried out using an RF-5301 PC Shimadzu spectrophotometer equipped with a 1 cm quartz cuvette. Samples were diluted (50–200 times) to reduce the fluorescence intensity and minimize inner-filtering effects. The scanning field was set at excitation wavelengths of 220–450 nm in 5 nm increments, and emission wavelengths of 290–600 nm in 1 nm increments. Distilled deionized water (DDW) recorded as blank EEM was subtracted from the EEMs of the samples. The fluorescence intensity of the diluted sample was normalized by the Raman peak of DDW at an excitation wavelength of 350 nm. The specific UV-vis absorbance at 254 nm (for all samples), 275 and 370 nm (for GAC adsorbed samples) was obtained with a Shimadzu UV-1280 spectrophotometer.

**PARAFAC modeling**

PARAFAC analysis of combined EEM datasets was performed based on the PARAFAC tutorial in the DOMFluor toolbox on MATLAB software. The modeling procedure included the removal of Raman and Raleigh scattering, split-half validation, and residual analysis as described in literature (Murphy et al. 2013). The fluorescence dataset of raw leachate and biotreated leachate included 208 EEMs, the dataset of GAC adsorption treated leachate included 41 EEMs. The maximum fluorescence intensity (Fmax) for each component was used to represent relative concentrations of the fluorescence DOM (FDOM) quantity. A four component PARAFAC model (C1, C2, C3, and C4) was chosen as the optimum number of components in this study, based on split-half validation and core consistency test. The percentage abundance of each Fmax value to the total sum (in other words, the percentage of C1, C2, C3 or C4) was considered as a measure for chemical composition.

| Table 1 | Physical-chemical characteristics of raw, PN-Anammox treated and N-DN treated leachate |
| Leachate source | COD (mg/L) | COD removal (%) | UV₂₅₄ (WL/nm) | UV₂₅₄ removal (%) | Cond (mS/cm) | NH₄⁺-N (mg/L) | NO₂⁻-N (mg/L) | NO₃⁻-N (mg/L) | TN (mg/L) |
| Raw leachate | 814 ± 87 | 3.85 ± 0.07 | 13.0 ± 1.1 | 287 ± 81 | 19 ± 9 | 11 ± 5 | 347 ± 69 |
| PN-Anammox | 655 ± 84 | 12–56 | 3.75 ± 0.11 | 0.2–8.7 | 13.4 ± 0.7 | 72 ± 34 | 45 ± 24 | 45 ± 32 | 149 ± 46 |
| N-DN (without glucose addition) | 708 ± 81 | 10–42 | 3.69 ± 0.09 | 0.3–6.2 | 13.6 ± 1.4 | 144 ± 40 | 84 ± 47 | 133 ± 42 | 291 ± 101 |
| N-DN (with glucose addition) | 615 ± 29 | 8–45 | 3.79 ± 0.03 | 0.6–2.7 | 14.2 ± 0.4 | 98 ± 35 | 22 ± 9 | 112 ± 19 | 204 ± 55 |

COD, chemical oxygen demand; Cond, conductivity; TN, total nitrogen; WL, wavelength. Values were calculated as average ± standard deviation (total number of samples = 133).
GAC adsorption column modeling

GAC breakthrough curves were described using the Thomas model. This model is derived from a mass balance of the system and is able to evaluate the GAC column performance and predict the adsorption capacity and rate constant (Oloibiri et al. 2005). The Thomas model is used for nearly complete breakthrough, thus the final removal during the experiments will be low. It is applicable for removal efficiencies between 5 and 95% (Han et al. 2007). In addition, this model, which assumes the adsorption follows Langmuir kinetics with no axial dispersion, is also derived with the assumption that the rate driving force obeys second-order reversible kinetics, which can be best described by Equation (1) (Khraisheh et al. 2010):

\[ \ln \left( \frac{C_0}{C_t} - 1 \right) = (k_T q_0 m/Q) - (k_T Q_0 V) \]  

where \( C_0 \) is the influent COD concentration (mg/L), \( C_t \) is the effluent COD concentration (mg/L) at time \( t \) (min), \( k_T \) is the Thomas rate constant (mL/min/mg), \( q_0 \) is the maximum column adsorption capacity (mg/g), \( m \) is the mass of GAC (g), \( V \) is the cumulative liquid throughput volume (L), and \( Q \) is the volumetric flow rate (mL/min).

Hence, in this study, \( k_T \) and \( q_0 \) were obtained, respectively, from the slope of \((-k_T C_0/Q)\) and the intercept of \((k_T q_0 m/Q)\) of the plot of \( \ln (C_0/C_t - 1) \) versus \( V \).

The uptake of the fluorescence DOM components by GAC was calculated from the column experimental data, as follows (Jamil et al. 2019):

\[ q = Q/m_{GAC} \sum_{i=1}^{n} \Delta t_i \cdot \left[ F_0 - 0.5(F_{out, i-1} + F_{out, i}) \right] \]  

where \( q \) is the amount adsorbed between two consecutive time points ((R.U.)/g GAC), \( m_{GAC} \) is the mass of GAC in column (g), \( Q \) is flow rate (L/h), \( \Delta t_i \) is time interval between two sampling times (h), \( F_0 \) is the influent fluorescence intensity (R.U.), \( F_{out, i} \) is the effluent fluorescence intensity at time \( i \) (R.U.), \( F_{out, i-1} \) is the effluent fluorescence intensity at time \( i-1 \) (R.U.).

The partitioning coefficient \( K_p \) (L/g GAC) is the ratio of the amount adsorbed per g GAC and per unit solution concentration of each component, which can reflect the affinity of adsorption for each fluorescence component during the GAC adsorption process. This value was calculated as follows:

\[ K_p = q/F_{out, i} \]  

RESULTS AND DISCUSSION

Performance of biological processes for landfill leachate treatment

Common parameters of raw and biotreated leachates

COD was used as the conventional indicator to follow the overall changes of the bulk DOM during the entire leachate treatment train. As shown in Table 1, the COD of raw landfill leachate varied between 750 and 1,120 mg/L. The seasonal effects were considered to be the influencing factor of leachate quality. The COD of PN-Anammox and N-DN (without glucose addition) treated leachate varied respectively from 440 to 781 mg/L and from 470 to 1,005 mg/L. The decrease of COD was higher when glucose was added to the denitrifying area; however, this increases sludge production and treatment costs (as was also noticed in this research).

The absorbance at 254 nm (UV254) is a qualitative indicator of aromatic compounds and other unsaturated carbon bonds (Gao et al. 2008b). From Table 1, it can be seen that biological treatment removes COD better than UV254, as the latter is not significantly reduced by the PN-Anammox and N-DN processes. This result suggests the decrease of COD during biological treatments is not because of aromatic compounds and other unsaturated compounds being bio-recalcitrant, but is mainly related to UV254-insensitive compounds such as tryptophan-like substances. In general, it shows that it is quite difficult to remove all organic matter by biological treatment.

Concentrations of nitrate, nitrite, ammonium, total nitrogen (TN) and conductivity are also given in Table 1. During the experimental period, the TN concentration ranged between 81 and 210 mg/L in the effluent of the PN-Anammox process, with a maximum TN removal of 81%. This was clearly less in the N-DN process, especially when no glucose was added as the denitrifying bacteria lacked a carbon source for denitrification. The nitrogen removal increased to 56% with glucose addition. However, this raised the cost, which shows the limitation of conventional N-DN processes to treat landfill leachate.

EEM-PARAFAC analysis of raw and biotreated leachate

The contour plots of the four EEM components identified by the PARAFAC model are shown in Figure S2. The corresponding excitation-emission loadings of each component are given in Figure S3. Based on the EEM regions defined
by Chen et al. (2003) and the supporting literature shown in Table 2, component 1 (C1, Ex. 235 and 300 nm; Em. 415 nm) and component 3 (C3, Ex. 245, 300, and 380 nm; Em. 460 nm) are both categorized as humic- and fulvic-like components. Component 2 (C2, Ex. 270 and 350 nm; Em. 435 nm) is affiliated with humic-like components; and component 4 (C4, Ex. 230 and 280 nm; Em. 343 nm) can be associated with protein- and tryptophan-like components. Fluorescence peaks at shorter wavelengths are associated with smaller molecular compounds. As such, C1, which was less hydrophobic with a smaller molecular size, probably originates from microorganisms that are commonly present in surface water and wastewater (Sgroi et al. 2017). C2 is associated with a longer emission wavelength, reflecting a more hydrophobic character and a larger molecular size. C3, composed of even larger compounds compared to C1 and C2, might originate from terrestrial sources impacted environments, as is also the case for C2 (Sgroi et al. 2017, 2018). C4, finally, represents rather small molecular compounds comprised of biodegradable fractions (in other words, protein-like substances) (Lu et al. 2009; Yang et al. 2019), and soluble microbial byproduct-like fractions (in other words, tryptophan-like substances) (Chen et al. 2003). More information on the position of defined fluorescence components is given in Table 2.

The Fmax of each component was determined to track changes in FDOM during leachate treatment. As shown in Table 3, FDOM associated with humic-like and fulvic-like components composed 80–86% of the total fluorescence intensity in both raw and biotreated leachate, whereas protein-like FDOM contributed to less than 20%, showing that fulvic-like and humic-like substances were the dominant components of DOM during the entire treatment train. Furthermore, the low value for the Fmax of C4 indicated that the landfill leachate from IMOG is biologically stabilized (as the landfill under study produces mature leachate).

Table 3 shows that PN-Anammox reduced the fluorescence intensity of C1, C2 and C4 by 9, 6 and 37%, respectively, whereas no significant decrease of C3 was observed, most probably because of the large molecular size and complex structure. Humic-like components, commonly associated with slowly degrading or recalcitrant DOM, is thus clearly more persistent compared with protein-like components. Microbial degradation has been regarded as a source rather than a sink of humic-like FDOM. Stedmon & Markager (2005) identified five humic-like fluorescence fractions that were produced during microbial incubations. Megali Amado et al. (2007) found that bacterial degradation of DOM in tropical freshwaters increased humic-like fluorescence. So the high humic-like

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**Table 2** Peak wavelengths and chemical groups associated with the defined EEM components from the PARAFAC analysis, as retrieved from other studies

<table>
<thead>
<tr>
<th>Component</th>
<th>Associated chemical components</th>
<th>Hydrophilicity</th>
<th>Location Ex/Em (nm)</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Humic- and fulvic-like components</td>
<td>Less hydrophobic acids (Chen et al. 2003)</td>
<td>235, 300/415</td>
<td>250, 320/425 (Oloibiri et al. 2017)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>230, 320/420 (Lu et al. 2009)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Large molecular size (Lu et al. 2009)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>Humic- and fulvic-like components</td>
<td>Hydrophobic acids (Chen et al. 2003)</td>
<td>245, 300, 380/460</td>
<td>250, 310, 370/460 (Oloibiri et al. 2017)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Larger molecular size (Lu et al. 2009)</td>
<td></td>
<td>250, 310, 360/460 (Lu et al. 2009)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrophilic acid fractions (Chen et al. 2005)</td>
<td></td>
<td>220, 280/340 (Lu et al. 2009)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrophilic neutral fractions (Chen et al. 2005)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Small molecular size (Lu et al. 2009)</td>
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<td></td>
</tr>
</tbody>
</table>
FDOM fractions observed in our study could also be explained by microbial degradation during the PN-Anammox process. The N-DN process (without glucose addition) removed the fluorescence intensity of C1, C2, C3 and C4 by 13, 10, 15 and 41% respectively. When glucose was added, their removal changed to 22, 9, 22 and 20% respectively. In both N-DN processes, higher removal of C1 and C3 was achieved compared to the PN-Anammox process, which could be attributed to the high biodegradation capacity of heterotrophic anoxic bacteria for fulvic-like substances (Yang et al. 2019). In all biological treatments, the removal of C2 remained below 10%. For C4, more divergent results were observed, i.e. PN-Anammox and N-DN (without glucose addition) removed about 40% of C4, whereas this was only half with the N-DN process with glucose addition. On the one hand, bacterial degradation could produce microbial byproduct-like material that possibly increased the fluorescence signal of tryptophan-like residues (Lakowicz 2006), whereas on the other hand, bacteria preferentially consumed glucose rather than protein- and tryptophan-like FDOM (indicated by C4). It is important to consider that C4 residues in effluents of biotreated leachate may reduce the availability of activated carbon pores for other components due to their smaller sizes, which are more conducive to being able to enter the pores.

**Performance of GAC adsorption post-treatment**

**COD removal of GAC treated leachate**

GAC column experiments were performed with PN-Anammox and N-DN treated leachate. Based on the COD breakthrough curves (Figure 1) and the Thomas model, parameters describing the adsorption process were calculated and are summarized in Table S1. Graphical plots are given in Figure S4.

At a flow rate of 3 BV/h, a slower breakthrough is shown in Figure 1(b) for adsorption of N-DN (with glucose addition) treated leachate. This is again most likely due to the concentrations of large molecular components; for example, the high concentration of C3 in PN-Anammox treated leachate can pose a problem for GAC adsorption. The steep increase in COD breakthrough for N-DN treated

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**Table 3** The maximum fluorescence intensity values ($F_{max}$) of the EEM-PARAFAC components (average ± standard deviation, total number of samples = 208) and the percentage removal in PN-Anammox and N-DN treated leachate

<table>
<thead>
<tr>
<th></th>
<th>$F_{max}$ (R.U.)</th>
<th>$F_{max}$ removal (%)</th>
<th>$F_{max}$ (R.U.)</th>
<th>$F_{max}$ removal (%)</th>
<th>$F_{max}$ (R.U.)</th>
<th>$F_{max}$ removal (%)</th>
<th>$F_{max}$ (R.U.)</th>
<th>$F_{max}$ removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw leachate</td>
<td>128 ± 17</td>
<td>52 ± 8</td>
<td>90 ± 10</td>
<td>68 ± 29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PN-Anammox</td>
<td>116 ± 19</td>
<td>9.0</td>
<td>49 ± 9</td>
<td>5.9</td>
<td>93 ± 9</td>
<td>No removal</td>
<td>43 ± 18</td>
<td>36.9</td>
</tr>
<tr>
<td>N-DN (without glucose addition)</td>
<td>111 ± 12</td>
<td>13.3</td>
<td>47 ± 8</td>
<td>9.9</td>
<td>77 ± 17</td>
<td>14.6</td>
<td>40 ± 19</td>
<td>40.8</td>
</tr>
<tr>
<td>N-DN (with glucose addition)</td>
<td>100 ± 6</td>
<td>22.1</td>
<td>48 ± 3</td>
<td>9.0</td>
<td>70 ± 11</td>
<td>21.9</td>
<td>55 ± 12</td>
<td>19.7</td>
</tr>
</tbody>
</table>

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**Figure 1** COD breakthrough curves of adsorption of PN-Anammox, N-DN (without glucose addition) and N-DN (with glucose addition) treated leachates, at a flow rate of (a) 18 BV/h and (b) 3 BV/h.
leachate without glucose addition might be caused by the high nitrite concentration which was not corrected during the COD measurement (as such this is considered to be an artefact).

To achieve high COD removal at low cost with GAC adsorption, a flow rate of 3 BV/h (in other word, empty bed contact time of 19 min) was chosen for subsequent experiments. As mentioned before, with PN-Anammox, N-DN (without glucose addition) or N-DN (with glucose addition) as a single treatment only limited COD removal was obtained. Combining these biological processes with GAC adsorption resulted in additional COD removal of 23, 16 and 35%, respectively, after 500 BVs (as shown in Figure 1). This rather low additional COD removal indicated the need for other polishing steps, although previous studies have demonstrated the feasibility of GAC alone to remove organics from biological effluent (Gao et al. 2013b; Oloibiri et al. 2015). Nevertheless, this study focused on the insights into the specifics of organic matter removal. This can be of interest in relation to the combination with a biological pre-treatment process and/or a subsequent polishing step.

**UV-vis analysis of GAC treated leachate**

Particular wavelengths (e.g., UV\textsubscript{254}, UV\textsubscript{275} and UV\textsubscript{370}) were measured as surrogates for DOM properties to indicate the dynamic changes of the chemical groups in DOM. As shown in the literature (Dryer et al. 2008), UV\textsubscript{275} and UV\textsubscript{370} are indicators for carboxylic chromophores and phenolic groups, respectively. Aromaticity, as an important indicator of DOM reactivity, is located at a wavelength of 254 nm (UV\textsubscript{254}). As shown in Figure 2, the adsorption of COD and UV-absorbance showed similar trends, which demonstrated that UV-absorbance can serve as a good surrogate to indicate the changes of chemical groups during GAC adsorption. For example, the \( C_t / C_0 \) value of UV\textsubscript{370} increased...
as well as that of COD after 225 BVs in the adsorption of N-DN (without glucose addition) treated leachate, indicating that this adsorption behavior may be related to the removal of phenolic chromophores. However, as there were no significant differences between UV-vis spectra and COD, it was necessary to apply other spectral measurements to capture the detailed information of DOM component changes during the entire treatment train.

EEM-PARAFAC analysis of GAC treated leachate

Based on EEM-PARAFAC analysis, breakthrough curves for COD and fluorescence fractions are shown in Figure 2. For PN-Anammox treated leachate, the adsorption efficiency of GAC can be ranked as C4 > C1 > C2 > C3, with a removal of about 100, 58, 50 and 19% after 500 BVs. So, GAC adsorption is able to remove both hydrophilic and hydrophobic components, but is more effective for the latter because of the hydrophobic interactions between the GAC surface and the organic components. Apart from GAC affinity, the plots shown in Figure 2 might also be influenced by the initial concentration of the components. For example, C4 was removed entirely due to its low concentration in PN-Anammox treated leachate. Comparing C2 and C3, a similar adsorption can be seen before 150 BVs because sufficient GAC pores were available. After that point, the relative concentration of C3 increased rapidly because of the reduced number of available GAC pores for larger and more condensed molecular matter.

Comparing the PN-Anammox and N-DN treatment processes, there was no significant difference in the overall removal of C1 and C2 during GAC adsorption, as shown in Figure 2 and Table 4. For N-DN (without glucose addition) treated leachate, the order of fluorescence intensity reduction at 500 BVs was C4 > C1 > C3 > C2. Initially, the four FDOM components were adsorbed by GAC at a similar rate. However, from 75 to 354 BVs, the effluent concentrations of C2 and C3 strongly increased to achieve a pseudo-steady state at higher BVs. For C4, only 78% (compared to complete removal with PN-Anammox treated leachate) was removed at 500 BVs, most probably because of the relatively high concentrations in the effluent of the N-DN reactor, which showed the limitation of GAC adsorption for the removal of hydrophilic components. The GAC removal of C3 in N-DN (without glucose addition) treated leachate was higher (56% at 500 BVs) than in PN-Anammox treated leachate, whereas this removal efficiency decreased to <3% when glucose was added to the N-DN process.

An almost linear breakthrough curve of C3 was observed to reach saturation at 500 BVs, because of its high concentration (as shown in Table 4) and the limited remaining available pores of GAC. In the N-DN process with glucose addition (Figure 2 (C2)), the C4/C3 of COD and C4 increased quickly before 30 BVs, indicating that in the early treatment stage C4 contributed the most to the COD among the adsorbed components. It can be seen that only 56% of C4 was adsorbed at 500 BVs. The reason for that lower adsorption of C4 in the N-DN process with glucose addition is that glucose rather than the tryptophan-like components was preferentially consumed by bacteria, which may lead to an accumulation of C4 as mentioned before.

The removal of COD and FDOM components by GAC adsorption improved when leachate was pretreated by PN-Anammox or N-DN and different biological processes affected the lifetime of GAC in different ways. As shown in Figure 2, N-DN treated leachate demonstrated a faster breakthrough in terms of COD or C3 after 500 BVs. In contrast, for PN-Anammox treated leachate, the adsorption column had a good capacity to remove fluorescence components after 500 BVs, especially for C4. Overall, these results agreed well with the previous modeling result (as shown in Table S1) that PN-Anammox was beneficial to the adsorption capacity of GAC and able to prolong the life of adsorption column.

Table 4: COD and Fmax values of EEM-PARAFAC components in the influent (0 BVs) and effluent (500 BVs) of the GAC column at a 3 BV/h flow rate

<table>
<thead>
<tr>
<th>Influent concentration of GAC (0 BVs)</th>
<th>Effluent concentration of GAC (500 BVs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>C1</td>
</tr>
<tr>
<td>PN-Anammox + GAC</td>
<td>520</td>
</tr>
<tr>
<td>N-DN (without glucose addition) + GAC</td>
<td>615</td>
</tr>
<tr>
<td>N-DN (with glucose addition) + GAC</td>
<td>600</td>
</tr>
</tbody>
</table>
FDOM uptake and partitioning coefficients

For each of the three treatment processes, C1 showed the highest amount adsorbed in the GAC column (Table 5), which was related to the relatively high concentrations of C1 in the biotreated leachate. Also the smaller molecular size of C4, and thus easy access to the pores of the GAC column, favored its adsorption, particularly in the N-DN processes. In the N-DN process without glucose addition, more C2 was adsorbed than C3, whereas the opposite was found for the other processes. This might be attributed to the concentration gradient from the accumulation of larger molecules.

Calculated $K_p$ values, included in Table 5, show a different trend among the EEM-PARAFAC compounds, showing for example the lowest and highest partitioning coefficient for C5 and C4, respectively, for the PN-Anammox process, indicating an inverse relationship with the molecular size of the adsorbates. Moreover, the component concentrations also play a significant role in adsorption (as was also noticed in this research). For example, C3 with lower concentration had a higher partitioning coefficient compared to C2 for the N-DN (without glucose addition) process. The lower $K_p$ value was obtained when glucose was added to the N-DN process, which can be attributed to the reduction in the available pores caused by the high concentration of C4, as mentioned previously, and the size exclusion effect caused by the high concentration of C3, which may hamper the larger molecular components from entering GAC micropores and mesopores (Jamil et al. 2019).

### CONCLUSIONS

A combined treatment of biologically stabilized landfill leachate with PN-Anammox and GAC adsorption was shown to be effective for both nitrogen and DOM removal, without the need for external carbon addition.

Four FDOM components were defined by fluorescence EEM and PARAFAC analysis: C4 could mainly be reduced by a biological treatment, whereas the removal of C1, C2 and C3 was limited ($\leq 22\%$), particularly in the absence of glucose as a carbon source, which had a negative effect on the C4 removal. Combining GAC adsorption with PN-Anammox prolonged the adsorption column lifetime as the C4 component was completely removed from the PN-Anammox treated leachate and a good capacity to remove COD and other components was retained. Lower C4 removal and better C3 adsorption were noticed for N-DN treated leachate. Addition of glucose in the latter process did speed up the breakthrough of all four EEM-PARAFAC compounds in the GAC column, which is also unfavorable from an economical point of view. Partition coefficient analysis indicated an inverse relationship with the molecular size of the adsorbates for the PN-Anammox process. The influence of FDOM concentrations on other processes was noted and helped to further understand the adsorption behavior.

It was demonstrated that applying spectral measurements in combination with EEM-PARAFAC provides useful insights into the behavior of DOM throughout the complete leachate treatment process. As such, valuable information is available for plant operators for monitoring, optimization and control during landfill leachate treatment.

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### DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.
REFERENCES


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