Elimination of typical polycyclic musks in a full-scale membrane bioreactor combined with anaerobic–anoxic–oxic process in municipal wastewater treatment plant
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ABSTRACT
The objective of this study was to investigate the removal of 11 synthetic polycyclic musks in a municipal wastewater treatment plant located in Jilin, China, by using a membrane bioreactor combined with anaerobic–anoxic–oxic process. The analysis of synthetic polycyclic musks was conducted with gas chromatography/mass spectrometry after solid-phase extraction. The removal efficiency of 11 synthetic polycyclic musks ranged from 65.9% (3-methylcyclopentadecanone) to 84.6% (Galoxolide) in the influent. Along the treatment process, it was observed that the anaerobic tank could remove the synthetic polycyclic musks effectively whereas the role of the membrane was to adsorb the musks, which could be ascribed to the relatively strong hydrophobic property of the musks. The sludge–water distribution coefficients (Kd values) as indicator of adsorption propensity for the sludge from anaerobic, anoxic, oxic and membrane tanks were measured. The high value of Kd, above 5.0 litres per gram of suspended solids, showed most of the musks could be removed by sludge through the adsorption process; thus the removal rate from the water phase caused by adsorption in the wastewater treatment plant can be predicted.

INTRODUCTION
Water resource shortage could be resolved by reclamation and reuse of treated wastewater from sewage treatment plants (STPs) and it is considered an economical and effective measure to overcome this worldwide problem. However, some micropollutants in the sewage may cause potential risk to the environment if the domestic wastewater is not treated properly. The musks as micropollutants are discharged into domestic wastewater and enter the STPs. As reported by some researchers, in Europe, 77% of fragrance ingredients used in products were estimated to discharge to the sewer system (Reiner et al. 2007; Homem et al. 2015; Godayol et al. 2015). As a result, some portion of musks may be released into surface waters if these micropolllutants are incompletely removed in STPs. Some main compounds of polycyclic musks such as 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(g)-2-benzopyran (Galaxolide, HHCB, C18H26O) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (Tonalide, AHTN, C18H26O) have been measured in biota living in contaminated aquatic environments (Lv et al. 2010; Pedrouzo et al. 2011; Morales et al. 2012; Figueiredo et al. 2016; Li et al. 2016). These compounds could be bioaccumulated in organisms due to their lipophilic characteristics (logKow) and slow biodegradation rates (the half-life of HHCB in soils is approximately 128 days) (Fromme et al. 2001; Lee et al. 2010; Pedrouzo et al. 2011; Homem et al. 2015; Godayol et al. 2015; Figueiredo et al. 2016). The exposure experiments of synthetic polycyclic musks to human showed that these chemicals can enter the human body by diffusion through the skin (Fromme et al. 2001; Gatermann et al. 2002; Lee et al. 2010; Lv et al. 2010; Figueiredo et al. 2016; Li et al. 2016) and can be accumulated in human adipose tissues. Although musks are not considered to pose significant risk to human health, the long-term effects of polycyclic musks on humans and the environment are hard to predict.

The merit of employing the membrane bioreactor (MBR) for treating domestic wastewater containing polycyclic musks is it could retain all biomass and has a long
sludge retention time (SRT). The long SRT and low ratio of food to microorganisms (F/M) have positive effects on the elimination of micropollutants. There are several studies on the removal of micropollutants by MBR systems (Mitra et al. 2016; Zhang et al. 2016) in laboratory scale. The information on the removal and behavior of synthetic musks in a large scale MBR plant for municipal wastewater treatment and reclamation is very limited. Furthermore, the fate of synthetic polycyclic musks in a wastewater treatment plant is not clear.

The objective of this study is to: (1) investigate removal characteristics and mechanism of 11 synthetic polycyclic musks in a full-scale MBR plant combined with the anaerobic–anoxic–oxic process (A2/O-MBR) with a planned treatment capacity of 60,000 m3/d for municipal wastewater treatment and reclamation; the plant serves a population of about 400,000, and the daily flow rate is about 60,000 m3; (2) analyze contribution of adsorption by sludge to elimination of musks by measuring sludge–water distribution coefficients (Kd values).

MATERIALS AND METHODS

Municipal wastewater treatment plant

Figure 1 shows the schematic diagram of the A2/O-MBR process for the municipal wastewater treatment plant (MWTP) which consisted of an anaerobic reactor (A1), anoxic reactor (A2), oxic reactor (O) and membrane tank (MBR). The hollow-fiber polyvinylidene fluoride membrane modules (Siemens Co.) with 0.04 μm nominal pore size and 182.9 m2 total membrane area are submerged in the MBR tank. The treatment plant is mainly designed for removal of nitrogen and phosphorus in the municipal wastewater. The phosphorus in raw wastewater could be removed through phosphorus release in the anaerobic tank and the balance then would be further removed in the oxic tank by phosphorus-accumulating organisms (PAOs). The removal of excess sludge which is full of PAOs in the oxic tank would be conducted if necessary. The removal of NO3 occurred in the anoxic tank through the denitrification process. Part of the organic matter in wastewater was consumed by PAOs and denitrifying microorganisms, and the balance of organic matter would be further degraded by aerobic microorganisms in the oxic tank. The sludge recirculation from MBR tank to aerobic tank was at a ratio of 400%. In addition, the recirculation ratio from the oxic tank to anoxic tank, and anoxic tank to anaerobic tank, was 500% and 120%, respectively. A large portion of MBR effluent was used for landscape irrigation and the balance was further treated by a reverse osmosis (RO) membrane in order to obtain high quality of treated water which was supplied to a city park. Table 1 shows the operation conditions of the A2/O-MBR plant.

Water sampling from bar screen chamber effluent, anaerobic tank, anoxic tank, oxic tank, MBR membrane tank and effluent was conducted during the period of July to December 2015. The analysis of chemical oxygen demand (COD), ammonium nitrogen (NH4+-N), total nitrogen (T-N), total phosphorus (T-P), and total suspended solids (TSS) for collected samples followed the standard methods (APHA 2005).

Materials and reagents

The reference standards of 11 synthetic polycyclic musks (see Table 2) and the internal standard of deuterated (d3) AHTN were purchased from Dr. Ehrenstorfer, Augsburg, Germany. The organic solvents such as methanol, acetone and dichloromethane were HPLC grade and supplied by Fisher, USA.

Sample preparation

Water samples of 500 mL were collected from each sampling point, as stated in the ‘Municipal wastewater
treatment plant section, and stored at 4°C immediately. Pretreatment of the collected water samples was completed within 48 h. The water samples were filtered with 1 μm glass fiber filter (Whatman, USA) for removing the sludge or suspended solid. The biosolid fraction from the filtration was frozen at –20°C whereas the filtrate was further treated through solid phase extraction (SPE) using 60 cc/200 mg Oasis HLB cartridges (Waters, USA). The cartridge was eluted with 10 mL ethyl acetate and the extracted sample was cleaned by a silica gel cartridge. Then, the sample was evaporated under a gentle nitrogen stream at 40°C following the addition of 100 ng AHTN-d3. Subsequently, the extracted sample was dissolved again in 100 μL n-hexane for gas chromatography-mass spectrometry (GC/MS) analysis. On the other hand, the sludge sample was initially treated with ultrasonic solvent extraction (USE) according to the method by Ternes with some modification (Ternes et al. 2005), then followed the same treatment as for the water sample.

Chromatography and mass spectrometry

Analysis and quantification of water samples after treatment through SPE were performed using an Agilent 7890N gas chromatograph with a 5975C mass selective detector equipped with an Agilent 7683B automatic liquid sampler and an HP-5MS GC column (30 m, 0.25 mm i.d., 0.25 μm film thickness). Helium gas was used as carrier and the column temperature was set from 50°C to 300°C. The injector temperature and ion source temperature were kept at 250°C, meanwhile MS transfer line temperature was at 260°C. Data acquisition was performed in the SIM (single ion monitoring) mode for quantification of targeted compounds. A calibration curve for each synthetic polycyclic musk was developed with the concentration range 0.05–10 μg/mL using 100 ng internal standard.

RESULTS AND DISCUSSION

General performance of the A²/O-MBR process

Table 3 shows the general performance of the A²/O-MBR process for treating municipal wastewater. It was observed that stable effluent concentrations of TSS, COD, NH₄⁺-N, T-N and T-P were obtained after the treatment although most of these parameters were fluctuating in the influent concentration. The average removal efficiencies of TSS,
COD, NH₄-N and T-P achieved above 95%, and removal efficiency of T-N reached 77%. Especially, the removal efficiency of TSS is over 98%. The result showed that treatment performance of the A²/O-MBR process was quite stable, and the treatment of conventional pollutants is good during the period of study.

Removal of synthetic musks in the A²/O-MBR process

The concentration of 11 synthetic polycyclic musks along the treatment process is shown in Figure 2. It was observed that the concentration of musks was in decreasing trend along the treatment process. Among 11 synthetic polycyclic musks, AHTN and HHCB with influent concentrations of 206.6 ng/L and 124.7 ng/L, respectively, were sharply decreased to 77.8 ng/L and 51.8 ng/L, respectively, in the anaerobic stage. Results showed that all of the 11 synthetic polycyclic musks could be removed effectively just in the anaerobic tank, which could be ascribed to the relatively strong hydrophobic property of the polycyclic musks (logKow: 5.1–6.3). However, the removal efficiencies of musks were 23.6% and 45.4% in the MBR, which showed that the membrane plays a rejection role for 11 musks. In general, the removal efficiencies of 11 musks were from 65.9% to 84.6% in the A²/O-MBR process. The removal of musks by sorption was higher in the A²/O-MBR process than in the up-flow anaerobic sludge bed, as it depends on adsorption onto sludge and the sorption capacity of the biomass (which was higher for the aerobic flocs due to their lower particle size) and on the biomass concentration inside the reactor (Alvarino et al. 2016). By comparing these results with the results previously reported (Ternes et al. 2003; Yang & Metcalfe 2006; Zhou et al. 2009), it was found that the removal efficiency of 11 synthetic polycyclic musks in the A²/O-MBR process was better than in the conventional treatment process employed by these other researchers. The removal efficiency of musks was in the range of 43.4–56.9% in the Yang & Metcalfe (2006) study, and it is higher than the efficiency of ultraviolet treatment and vertical flow reed bed treatment (Kupper et al. 2006; Reif et al. 2011). Significant positive correlation was observed between concentrations of musks ($R^2 = 0.9868$) indicating that musks have similar tendencies to partition between sludge and aqueous as shown by their similar Kow values.

Adsorption of synthetic polycyclic musks onto sludge and distribution in sludge–water

The concentrations of musks were measured in the sludge collected from the anaerobic tank, anoxic tank, oxic tank and membrane tank to investigate the removal of musks through adsorption by sludge. As shown in Figure 3, the concentration of musks adsorbed by sludge was in the range of 80.6–513.9 ng/g. This result showed that polycyclic musks were easily adsorbed on
the sludge, which is also supported by their high log\(K_{ow}\) values. The high adsorption capacities of sludge for musks indicated that a significant portion of musks were removed through the adsorption process in the \(\text{A}^2/\text{O}-\text{MBR}\) process. Although there is possibility of microorganisms degrading the musks, biodegradation is not focused on in this study.

The solid–water distribution coefficient \(K_d\) can be employed to predict the adsorption in wastewater treatment plant processes \((\text{Ternes} \text{ et al.} \text{, 2004})\). The \(K_d\) of musks could be computed by using Equation (1) in order to analyze their adsorption quantities onto sludge in the \(\text{A}^2/\text{O}-\text{MBR}\) process.

\[
K_d = \frac{C_s}{C_w}
\]

where \(K_d\) is the sorption coefficient \((\text{L/g-SS})\), \(C_s\) is the adsorbed concentration per amount of suspended solids \((\text{ng/g-SS})\), \(C_w\) is the measured concentration in aqueous phase \((\text{ng/L})\). Table 4 shows the \(K_d\) values of musks in anaerobic, anoxic, oxic and membrane tanks. It was found that the adsorption coefficients of the 11 synthetic polycyclic musks onto sludge were all above 5.0 L/g-SS in each unit of the \(\text{A}^2/\text{O}-\text{MBR}\) process. This result indicated that the 11 synthetic polycyclic musks have a high tendency to partition onto the sludge and subsequently contributed to the high removal efficiencies of the musks in the \(\text{A}^2/\text{O}-\text{MBR}\) process, which could explain the obtained high removal efficiencies as described above, and this can be compared with previous studies \((\text{Nöthe} \text{ et al.}, \text{2007}; \text{Zhou} \text{ et al.}, \text{2009}; \text{Li} \text{ et al.}, \text{2016})\). These \(K_d\) values indicate that a significant portion of these substances are sorbed onto sludge, which should be mainly due to hydrophobic interactions, and these values are higher than those determined \((\text{between 3.7 and 4.3})\) for primary and secondary sludge by several authors \((\text{Simonich} \text{ et al.}, \text{2002}; \text{Joss} \text{ et al.}, \text{2005})\). However, in batch experiments, \text{Artola-Garicano} \text{ et al.} \text{(2003)}\) and \text{Ternes} \text{ et al.} \text{(2004)}\) measured lower log\(K_d\) values \((\text{down to 3.2})\), which might indicate that other sludge properties rather than organic carbon content are crucial for sorption of musk fragrances or that equilibrium conditions in batch experiments are different from those in full-scale treatment plants. This is in agreement with previous studies which reported that musks can be easily adsorbed onto the activated sludge as the sewage is well mixed with the sludge \((\text{Ternes} \text{ et al.}, \text{2004}; \text{Thomas} \text{ et al.}, \text{2009}; \text{He} \text{ et al.}, \text{2013})\). Thus, the adsorption of musks onto sludge in the biological wastewater treatment process could play a very important role for removing the 11 synthetic polycyclic musks in municipal wastewater. In addition, removal rate of the musks from water phase caused by a MWTP could be predicted based on the \(K_d\) values. Although most of the adsorption coefficients did not change regularly along the technological process, they were higher in A1 and MBR tanks. \(K_d\) values of HHCB and AHTN decrease gradually along the treatment process; \(K_d\) values of MA and MT increase gradually along the treatment process.

**CONCLUSIONS**

The removal of synthetic polycyclic musks in each treatment tank of a full-scale \(\text{A}^2/\text{O}-\text{MBR}\) process was systematically evaluated. The removal efficiencies of musks were about 65.9–84.6% in the \(\text{A}^2/\text{O}-\text{MBR}\) process with average influent concentration in the range of 70.3–206.6 ng/L. Along the treatment process of the \(\text{A}^2/\text{O}-\text{MBR}\), it was observed that musks could be removed effectively in the anaerobic tank, which could be attributed to the relatively strong hydrophobic property of the polycyclic musks. In the solid–water distribution coefficient analysis, adsorption coefficients of musks were above 5.0 L/g-SS in each bioreactor of the \(\text{A}^2/\text{O}-\text{MBR}\) process and this indicated the polycyclic musks had a high tendency to partition onto the sludge. As a result, partial removal of these musks observed during wastewater treatment was mainly due to adsorption onto sludge. Removal rate of the musks from the water phase caused by the adsorption process onto sludge in a MWTP could be reasonably predicted based on the \(K_d\) values.

**Table 4** | \(K_d\) values for musks in anaerobic, anoxic, oxic and membrane tanks

<table>
<thead>
<tr>
<th>Musks</th>
<th>Anaerobic</th>
<th>Anoxic</th>
<th>Oxic</th>
<th>MBR</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFHB</td>
<td>8.1</td>
<td>6.7</td>
<td>5.5</td>
<td>5.3</td>
</tr>
<tr>
<td>AHTN</td>
<td>17.2</td>
<td>16.9</td>
<td>10.9</td>
<td>6.3</td>
</tr>
<tr>
<td>ATII</td>
<td>11.1</td>
<td>10.9</td>
<td>13.2</td>
<td>10.8</td>
</tr>
<tr>
<td>DPMI</td>
<td>8.9</td>
<td>7.6</td>
<td>10.3</td>
<td>9.8</td>
</tr>
<tr>
<td>ADBI</td>
<td>12.3</td>
<td>11.2</td>
<td>10.5</td>
<td>15.1</td>
</tr>
<tr>
<td>AHMI</td>
<td>9.8</td>
<td>10.6</td>
<td>12.4</td>
<td>11.3</td>
</tr>
<tr>
<td>MX</td>
<td>10.8</td>
<td>11.2</td>
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<td>10.4</td>
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<tr>
<td>MK</td>
<td>13.5</td>
<td>12.9</td>
<td>15.1</td>
<td>16.0</td>
</tr>
<tr>
<td>MM</td>
<td>12.5</td>
<td>11.6</td>
<td>13.2</td>
<td>10.9</td>
</tr>
<tr>
<td>MA</td>
<td>10.2</td>
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<td>13.7</td>
</tr>
<tr>
<td>MT</td>
<td>6.8</td>
<td>7.6</td>
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</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

This study was supported by China Postdoctoral Science Foundation (No. 20080440374), Jilin Province Education Department (No. 2016136) and Natural Science Foundation of Jilin City (No. 20163301).

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First received 21 March 2018; accepted in revised form 14 September 2018. Available online 28 September 2018