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Pilot-scale evaluation of ozone as a polishing step for the removal of nonylphenol from tank truck cleaning wastewater

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Abstract

The presence of nonylphenol (NP) in the wastewater of the tank truck cleaning industry is a major concern because of its endocrine disruptive properties. In this paper, the use of ozone for degrading NP from tank truck cleaning wastewater was investigated by operating a pilot-scale biological wastewater treatment in combination with an ozonation unit. The impact of the added ozonation step on the removal of NP, soluble chemical oxygen demand (sCOD) and total organic carbon (TOC) was monitored over one year. sCOD and TOC removal were not significantly enhanced, but the NP peak concentrations in the effluent were significantly lower than those obtained after biological treatment only: a relatively low NP concentration was observed, even when peak loads were present in the influent of the pilot-scale biological wastewater treatment plant (influent\textsubscript{bio}). Contrariwise, the effluent of the sole biological treatment follows the peak load trends of the influent\textsubscript{bio}. During the ozonation period, the average NP concentration in the combined biological-ozone unit was 0.29 µg/L, compared to 1.89 µg/L for the effluent obtained after a sole biological treatment, resulting in an improved average removal efficiency of 32%.

Keywords: ozone; nonylphenol; tank truck cleaning; nonylphenol ethoxylate, endocrine disruptor
1. Introduction

Endocrine-disrupting compounds are increasingly recognized as a severe threat to aquatic (micro-)organisms and public health (ECB, 2002). A considerable number of papers have been dedicated to the endocrine disruptive effects of alkylphenol ethoxylates (APEOs) and their degradation products, such as alkylphenols (AP) (Gabriel et al., 2008; Soares et al., 2008; Sharma et al., 2009; Mao et al., 2012; Acir et al., 2018). Nonyl- and octylphenol compete with 17β-estradiol for the binding site of the oestrogen receptor due to structural similarities, hereby disrupting the natural endocrine system, which could even, for example, increase the incidence of breast cancer after chronic exposure (Amaro et al., 2014; In et al., 2015; Yang et al., 2015; Noorimotlagh et al., 2020). Nonyl- and octylphenol ethoxylates are the most well-known APEOs used as non-ionic surfactants and are applied as cleaning, washing and surface-active agents in the textile industry (Olmez-Hanci et al., 2011; Araujo et al., 2018). NPEOs are produced from NP by reacting phenol with mixed nonenes in a batch process. Almost 40% of the produced NP is used for the production of resins and other plastics, and around 60% to produce NPEOs from NP and ethylene oxide. In the Europe Union (EU) alone, it is estimated that 10,000-50,000 tons of NP were produced in 2010 compared to 73,500 tons in 1997 (ECB, 2002; Bontje et al. 2004; AMEC, 2012). The European production of NPEOs in 2010 was approximately 32,000 tons (ECHA, 2014).

The European Union banned this type of surfactants for domestic usage back in 2003 (Renner, 1997; Council Directive 2003/53/EC, 2003), but non-ionic detergents are still allowed to be used for crucial industrial applications, such as manufacturing of plastics, textiles, paper and metal processing (Talmage, 1994; Cornelis et al., 2005). Therefore, non-ionic surfactants are still found in the produced wastewater. Nonylphenol (NP) is also present in the discharged wastewater from tank truck cleaning companies. NP ethoxylates (NPEOs) are released in the cleaning process of bulk tanks that contain residual NPEO loads. When this NPEO containing wastewater is treated in a biological wastewater treatment plant, NP is unintentionally produced (Ahel et al., 1994; Fujita et al., 2000). The presence of NP in tank truck cleaning effluent is a major concern because of its endocrine disruptive properties. High concentrations of NPEOs and their derivatives, such as NP, are frequently encountered in the influent of biological wastewater treatment plants (influencebio). As a consequence, effluents from the tank truck cleaning industry contain NP. Since the biological removal efficiency for these components is limited, the sole application of biological treatment is often insufficient to meet the EU limits for NP (i.e., 0.3 µg/L) discharge.
During biological wastewater treatment, ethoxylate (EO) chain shortening of NPEOs occurs, leading to the formation of short-chain NPEOs (e.g., NP1EO or NP2EO) (Ying et al., 2002). The EO-chain is further oxidized into nonyl phenoxy carboxylic acids and finally NP (ECB, 2002; Kovarova et al., 2013). Various publications have demonstrated that NP possesses more prominent endocrine disruptive characteristics than its precursor NPEO (Giger et al., 1984; Servos, 1999; Ying et al., 2002; Soares et al., 2008). The most accepted reason for the increased risks is the shortening of the NPEO’s ethoxylate chain (Soto et al., 1991; AMEC, 2012). The biodegradation of NP is low due to the branched alkyl chain and aromatic ring structure (Patoczka and Pulliam, 1990). Therefore, an additional wastewater treatment technique as a polishing step is required to guarantee the complete removal of NP.

Advanced Oxidation Processes (AOPs) are a class of wastewater treatment techniques that have gradually gained recognition during the last decade. The application potential of AOPs lies mainly in the treatment of wastewater containing recalcitrant organic compounds. The removal of these compounds by conventional techniques, which are mainly based on aerobic or anaerobic biological degradation of organic matter, is generally not achievable due to their low biodegradability (Oller et al., 2011; Dewil et al., 2017; Van Aken et al., 2015, 2017). AOPs are mostly used in combination with biological wastewater treatment. They are all based on the oxidation of the organic compounds by OH-radicals (OH\(^\bullet\)), which are compounds containing an unpaired electron. Most radicals are highly unstable and immediately react with another molecule to obtain the missing electron. Various types of AOPs have been developed, including ozone and hydrogen peroxide-based AOPs, which differ in the production pathway of the OH\(^\bullet\) (Glaze et al., 1987; Gottschalk et al., 2009).

The degradation of NP and its degradation products by AOPs is treated in a few publications. Ning et al. (2007a, 2007b) studied the kinetic reaction mechanism of the direct and indirect oxidation by ozonation of nonyl- and octylphenol. In their work, direct and indirect oxidation by ozone was investigated by adjusting the pH of the aqueous solution. The kinetic rate constants of NP were reported to be 3.90 \(10^4\) M\(^{-1}\)s\(^{-1}\) and 1.1 \(10^{10}\) M\(^{-1}\)s\(^{-1}\) for direct and indirect oxidation, respectively. Kim et al. (2005) performed electrochemical degradation experiments on NP, which resulted in the formation of benzoquinone intermediates. In these publications, the effect of the composition of real industrial wastewater on the removal efficiency of AOPs was not investigated.

The focus of this paper is to investigate the removal efficiency of NP in real industrial wastewater using combined biological-ozone degradation. For that purpose, a pilot-scale biological wastewater treatment plant was coupled with an ozone installation and operated on-
site at a tank truck cleaning company to effectively optimize and analyze the decrease of the NP concentration, soluble chemical oxygen demand (sCOD) and total organic carbon (TOC) of the treated wastewater. In addition, the paper explores the impact of ozonation on the ecotoxicity of the wastewater.

2. Materials and methods

2.1 Pilot-scale biological wastewater treatment

Two sequencing batch reactors (SBRs) with a maximum volume of 1 m$^3$ were used in parallel for the long-term pilot-scale experiments. The first SBR (SBR 1) provided the biological treatment only, whereas the effluent of the second SBR (SBR 2) was additionally subjected to ozonation as a polishing step. The full installation was constructed in a 20 ft shipping container and was placed on-site at the premises of a tank truck cleaning company (Antwerp, Belgium). This company mainly cleans tanks containing chemical loadings, including NPEO.

A schematic overview of the pilot-scale installation used in the tests is provided in Fig. 1. The pilot-scale installation was fed with wastewater originating from the full-scale physicochemical treatment unit of the company, which is the same as being fed to the full-scale biological wastewater treatment. The wastewater was introduced in a buffer tank with a volume of 400 L, connected to SBR 1 and SBR 2. At the start of the experiments, activated sludge (AS) originating from the biological wastewater treatment of the tank truck cleaning company was introduced in the SBRs. Both SBRs were operated at a mixed liquor suspended solids concentration (MLSS) between 2.5 and 3 g/L to ensure good settling of the sludge. The diluted sludge volume index (DSVI) was 206 mL/g, indicating a poor settleability of the sludge flocs. Operational parameters of both SBR 1 and SBR 2 were chosen in such way that the same substrate (S) to biomass (X) ratio (S/X) was achieved as on full-scale, i.e., 0.19.

An SBR cycle time of 8 h was applied, and each cycle consisted of 4 stages. During the first stage (duration 300 min) aerobic treatment conditions were applied, keeping the dissolved oxygen (DO) concentration of the AS between 1 and 3 mg O$_2$/L by intermittent aeration. 50 L of fresh influent bio was introduced in the bioreactor during this stage. Throughout stage 1, the reaction mixture was continuously stirred using propeller mixers (ProMinent, Belgium). The second stage consisted of the continuous aeration of the bioreactor. This short phase of 10 minutes was included to enhance the settling properties of the AS. During the settling phase (stage 3, 120 min), the mixer and aeration were switched off to enable the AS to settle. The cycle was completed by a discharge stage (50 min), during which 50 L of treated wastewater
was discharged using a floating valve. The total duration of each cycle was 8 h, resulting in 3
cycles performed per day.

The operating volume of the AS system of both SBRs was 700L ($V_{AS}$). Since 50 L of fresh
influent$_{bio}$ was added to the AS system in each cycle, 150 L was treated daily. The hydraulic
retention time (HRT) of the SBR was then 4.7 days, as shown in equation (1).

$$HRT_{pilot\ reactor} = \frac{V_{AS}}{V_{influent_{bio} \ d}} \approx 4.67 \ d$$ (1)

The S/X ratio of the biological wastewater treatment on pilot-scale is determined by equation
(2):

$$\left( \frac{S}{X} \right)_{pilot\ reactor} = \frac{kg \ COD}{kg \ VSS \ d} = \frac{COD_{influent_{bio}} \times V_{influent_{bio}}}{MLSS_{pilot\ reactor} \times V_{AS}} = 0.21$$ (2)

With:

$COD_{influent_{bio}} = 3000.10^{-6} \frac{kg \ COD}{L}$

$V_{influent_{bio} \ d} = 150 \ L/day$

$MLSS_{pilot\ reactor} = 3.10^{-3} \frac{kg \ VSS}{L}$

$V_{AS} = 700 \ L$

The calculated S/X ratio was 0.21, which approximately corresponds to the S/X ratio of the
company's biological wastewater treatment (0.19).
Fig. 1. Schematic representation of the pilot-scale biological wastewater treatment & ozone purification unit.
2.2 Pilot-scale ozone treatment

A series of lab-scale ozone experiments was performed on the effluent of the company applying
an ozone flow rate of 0.68 g O₃/h on 1 L samples (results not shown). The NP concentration
was seen to decrease from 0.56 ± 0.03 to 0.20 ± 0.02 µg NP/L after 5 min ozone treatment time,
resulting in an NP removal of 65%. Based on these results, an ozone treatment duration of 3 h
per cycle was selected for the pilot-scale ozonation unit.

During the pilot scale tests, the effluent of the biological treatment of SBR 2 was subjected to
ozonation. As shown in Figure 1, the ozonation was directly applied on the effluent via a
recirculation system installed over the effluent tank. The ozone system consisted of an oxygen
concentrator (SEP-300, Anseros) to generate a 90% oxygen containing gas stream from ambient
air, which was subsequently fed to an ozone generator (COM-AD-01-IP, Anseros) to produce
ozone via high voltage gas discharge (corona discharge). The maximum ozone production of
the generator was 2.75 g O₃/h at a gas flow rate of 100 L/h at 20 °C. This flow rate was kept
constant throughout the pilot plant operation. The ozone stream was injected in the recirculation
loop using a venturi-system. An in-line static mixer was installed to increase the gas-liquid
transfer. The ozone installation was switched on during the filling/aeration phase of the
biological treatment for 1 h followed by a 1 h resting period resulting in a total duration of the
ozonation of 3 h per cycle. After 1 h of ozonation, the wastewater was saturated with ozone.
The subsequent resting period allowed consuming the dissolved ozone. This way of ozone
injection is more energy-efficient than the continuous injection of ozone gas (Gottschalk et al.,
2009). The water was pumped through the ozonation unit at a fixed flow rate of 1 m³/h using a
centrifugal pump.

The injection of ozone gas increased the oxidation-reduction potential (ORP) of the treated
wastewater. During the settling phase of the AS, the ozone generator was switched off, resulting
in a decrease of the ORP to approximately 215 mV. During the filling/aeration phase, a
maximum ORP of 250 mV for the ozonated wastewater was recorded, which is relatively low
compared to the literature. If the water pH is neutral, an ORP value of 650-700 mV is expected
for ozone disinfection units (Suslow, 2004). A possible explanation for the low ORP values is
the positioning of the ORP sensor in the effluent tank instead of the ozone bubble column. The
effluent tank of SBR 2 contains 220 L water, whereas the bubble column has a reactor volume
of 10 L. Consequently, the dissolved ozone gas was diluted while entering the effluent tank.
Despite the sufficient water flowrate of 1 m³/h, the ozone injection time of 1 h followed by a 1
h resting was too short to reach the maximum ORP value in the effluent tank.
2.3 Sampling
During the first couple of days of pilot plant operation, a sample was taken on a daily basis, after which the sampling interval was changed to weekly. A portable automatic water sampler (Bühler 2000, HACH) was used to collect the ozonated effluent and all samples were cooled at 7°C before analysis. In addition to automatic water sampling of the ozonated effluent, samples were also taken manually from the effluent of the reference reactor and influentbio. Each wastewater sample was transferred to the lab using amber glass bottles and filtered through glass fibre filters (Macherey-Nagel GF – 3; 0.6 µm) to remove insoluble particles that could interfere with the analysis or damage the analytical equipment.

2.4 Analytical methods
The concentration of NP was determined using an HPLC Infinity 1200 LC system (Agilent Technologies, Waldbronn, Germany) coupled to a triple quadrupole mass spectrometer (API 3000, Applied Biosystems, Carlsbad, CA, USA), equipped with an electrospray probe working in negative mode. The measurements were performed on a Poroshell EC-C18 (150 x 2.1 mm, 2.7 µm) column (Agilent Technologies). The column was operated under isocratic conditions, using a mobile phase consisting of MeOH + 0.05% ammonia:H₂O 90/10 (v/v) (Fisher) at a flow rate of 0.2 mL/min. The sample injection volume was 5 µL, and the column temperature was kept constant at 40°C using a thermostatted column compartment. MS/MS analyses were carried in Multiple Reaction Monitoring (MRM) mode for better sensitivity and specificity. More details on the MS parameters are described in Mignot et al. (2019). Isotopically labelled NP was used as an internal standard for the quantification of NP. Due to the low NP concentrations present in the wastewater samples, a sample pre-treatment was necessary. Liquid-liquid extraction was performed to extract NP from 30 mL of wastewater to 100 µL octanol, as described by Mignot et al. (2019).

The sCOD was measured following ISO 6060:1989 (LCK 514 test tubes, Hach). A sample volume of 2 mL was added to a test tube followed by incubation for 15 min at 170 °C. The sCOD was determined by a photometric analysis of the test tube using a DR 3900 spectrophotometer (Hach). The Total Organic Carbon (TOC) concentration was measured using a TOC-L analyzer (Shimadzu). A sample volume of at least 15 mL was required for TOC determination. Some of the water samples were also analyzed for ecotoxicity, using commercially available acute ecotoxicity test kits. The 48 h Daphnia Magna water flea immobilization test (OECD, 2004) was used to determine the ecotoxicity based on Daphnia...
immobilization. In addition, the algae growth inhibition was determined by the 72 h *Pseudokirchneriella subcapitata* algal growth inhibition test (OECD, 2011).

### 3. Results and discussion

The pilot plant was operated in different phases. First, a stabilization phase (Phase I) was executed to acclimatize the AS. During Phase II, the ozone step was discontinued for SBR2 as well, and both reactors continued the acclimation. In Phase III, ozonation was resumed until the end of the pilot plant experiment. The NP concentration, sCOD and TOC of the ozonated effluent during the different phases are shown in Fig. 2 and Fig. 3, respectively. The vertical dotted lines indicate each different phase. The horizontal line in Fig. 2 defines the legal limit for NP concentration in effluent water (0.3 µg/L) while the sCOD discharge limit (10 days average) is 300 mg O₂/L as shown in Fig. 3.

![Fig. 2. Nonylphenol concentration of the effluent treated with ozone (○) for the complete duration of the pilot plant experiment.](image)

### 3.1 Stabilization phase

Phase I, which lasted 76 days, is a stabilization phase. During this phase, the AS of both biological SBR systems was acclimatized to the conditions present in the SBR reactors. The NP concentration of the ozonated effluent was on average 0.38 µg/L, which is just above the discharge limit of NP of 0.3 µg/L. As shown in Fig. 3, the average sCOD value of the ozonated effluent during the stabilization period was 152 mg O₂/L. Fig. 3 also shows the TOC of the ozonated effluent.
During the second phase (total duration of 100 days), the ozone generator was switched off to study the absence of ozonation on the effluent. The NP concentration in the effluent increased from 0.27 µg/L (day 81) to 0.66 µg/L (day 88). A similar trend was observed for the sCOD (maximum 307 mg O\textsubscript{2}/L) and TOC (maximum 81 mg C/L). The NP concentration on day 118 was 0.34 µg/L and increased to 0.50 µg/L, reaching a new peak. Even though no ozone was injected, the NP concentration decreased, and the discharge limit of NP was still achieved on days 138 and 159, while an increase in sCOD and TOC from day 118 to 138 is shown in Fig. 3. A peak value in sCOD and TOC of 262 mg O\textsubscript{2}/L and 73 mg C/L, respectively, occurred on day 138. The average NP concentration, sCOD and TOC during Phase II were 0.41 µg/L, 183 mg O\textsubscript{2}/L and 51 mg C/L, respectively. Compared to the stabilization phase, the average NP and sCOD showed an increase of 7% and 20%, respectively. In general, it can be concluded that the absence of ozonation resulted in a lower NP and sCOD removal. Moreover, peaks in NP and sCOD were observed during Phase II, indicating that the effluent is more prone to fluctuations. These fluctuations in NP, sCOD and TOC in the effluent are partly due to the different tank cleaning activities, meaning that the wastewater composition depends on the content of the tanks that have been cleaned at that time.

### 3.3 Phase with ozone

At the start of Phase III, the ozone generator was put into operation for SBR 2. During this phase, water samples of the effluent of the reference reactor and the influent\textsubscript{bio} were analyzed to determine the NP concentration to understand its effect on the obtained effluent. As a result,
a mass balance of NP could be developed. An example is given in Table 1 for day 285 during phase III.

**Table 1.** Nonylphenol, sCOD and TOC of influentbio, SBR 1 and SBR 2 on day 285 (Phase III).

<table>
<thead>
<tr>
<th></th>
<th>NP (µg/L)</th>
<th>sCOD (mg O₂/L)</th>
<th>TOC (mg C/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influentbio</td>
<td>2.21</td>
<td>1,950</td>
<td>640</td>
</tr>
<tr>
<td>SBR 1</td>
<td>1.27</td>
<td>236</td>
<td>74</td>
</tr>
<tr>
<td>SBR 2 + O₃</td>
<td>0.11</td>
<td>61</td>
<td>22</td>
</tr>
</tbody>
</table>

In Table 1, the effect of ozonation on the NP, sCOD and TOC removal, compared to influentbio, is presented. The NP removal of SBR 1 is 43% while the ozonated effluent achieved an NP removal of 95% complying with the discharge limit of 0.3 µg/L. This indicates that ozonation is efficient to ensure the removal of NP from the wastewater to meet the imposed legislation. For day 285, SBR 1 obtained an sCOD and TOC removal of 88% and 89%, respectively. Whereas, SBR 2 achieved a higher sCOD and TOC removal of 97% for each, indicating the positive effect of ozonation.

**Fig. 4.** Evolution of nonylphenol concentration of the effluent without ozone (△), with ozone (○) and the influent (□).

An overall increase in NP concentration in the influentbio was observed in the course of the pilot plant experiment, reaching a maximum NP concentration of 23.13 µg/L on day 341 before initiating a decrease as seen in Fig. 4. The NP concentration of the effluents of SBR 1 and 2 also increased during the same period, reaching a maximum of 4.56 and 1 µg/L, respectively. In contrast, the sCOD (Fig. 5) and TOC (Fig. 6) of influentbio remained reasonably constant during Phase III with an average sCOD and TOC of 2027 mg O₂/L and 691 mg C/L, respectively.
At the beginning of Phase III, the NP concentration of the ozonated effluent immediately decreased fairly below the imposed discharge limit and in some cases even below the limit of quantitation (LOQ) of the LC-MS analysis (0.17 µg/L), as seen in Fig. 4. Likewise, the sCOD and TOC values decreased in the same way during that phase. However, in Fig. 2, it is apparent that the NP concentration was already decreasing at the end of phase II. It is difficult to explain this decrease, but it might be related to a decreasing NP concentration in the influent_{bio}. The NP data of influent_{bio} at the start of phase III was at a low level (3.00 µg/L), which appears to support the assumption that the NP loading in the influent_{bio} was rather low at the end of phase II. Until day 313, some fluctuations in the NP concentration of the ozonated effluent are observed (Fig. 4) without exceeding the discharge limit of NP. From day 313, an increase in NP concentration was observed, resulting in a maximum of 0.99 µg/L on day 341. The settleability of the AS was poor during this phase, which resulted in a high suspended solids concentration in the effluent. It is known that NP strongly adsorbs to sludge flocs, which could explain the NP peak (Soares et al., 2008). Also, influent_{bio} reached its highest NP concentration in this period. After 4 weeks, the discharge limit of NP was again achieved and maintained until the end of the pilot plant experiment. During phase III, the average NP concentration of the ozonated effluent was 0.29 µg/L. Furthermore, the imposed discharge limit of NP was, apart from day 320 until 368, always respected. Based on the obtained NP concentrations, it can be concluded that ozone has a positive effect on degrading NP.
A relationship between the effluent of SBR 1 and the influent bio is depicted in Fig. 4. An increase in NP concentration of the influent bio led to a higher NP concentration in the effluent of SBR 1. Moreover, the effluent of SBR 1 was subjected to the fluctuating NP concentrations from influent bio. In contrast, the NP concentration in the ozonated effluent was relatively constant throughout the experimental campaign. The sCOD and TOC of the effluent of each SBR were in line with the influent bio. Sometimes this resulted in sCOD values above 500 mg O₂/L for the effluent of SBR 1. The ozonated effluent complied with and maintained the discharge limit of sCOD even during sCOD peak loads from the influent bio.

Based on the results shown in Fig. 4, the removal efficiency of NP during Phase III was calculated. Table 2 summarises the NP, sCOD and TOC removal efficiency of SBR 1 and SBR 2.

**Table 2.** Summary nonylphenol, sCOD and TOC removal efficiency of SBR 1 and SBR 2 during Phase III.

<table>
<thead>
<tr>
<th></th>
<th>Average concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NP (µg/L)</td>
</tr>
<tr>
<td>Influent bio</td>
<td>4.95</td>
</tr>
<tr>
<td>SBR 1</td>
<td>1.89</td>
</tr>
<tr>
<td>SBR 2 + O₃</td>
<td>0.29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Average removal efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR 1/Influent</td>
<td>0.62</td>
</tr>
<tr>
<td>SBR 2 + O₃/Influent</td>
<td>0.94</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Enhanced removal</th>
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<tbody>
<tr>
<td></td>
<td>0.32</td>
</tr>
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</table>

**Fig. 6.** Evolution of TOC of the effluent without ozone (△), with ozone (○) and the influent (□).
The average NP concentration of influent\textsubscript{bio} (4.95 µg/L) is in line with previous reported literature. However, the NP data of the influent\textsubscript{bio} must be interpreted with caution because it is difficult to compare with the literature due to the different wastewater environments. Numerous studies have determined the NP concentration in the raw influent of municipal wastewater treatment plants, which was seen to vary from 0.1 up to 96.4 µg/L (Nakada et al., 2006; Soares et al., 2008; Klečka et al., 2010; Camacho-Muñoz et al., 2014). However, these publications analysed the NP concentration of the raw influent of the wastewater treatment plant instead of the influent\textsubscript{bio}. Additionally, these wastewater samples were taken from municipal instead of industrial wastewater treatment plants and could therefore contain a lower NP loading.

The effluent of SBR 1 contained an average NP concentration of 1.89 µg/L which is, compared to the literature, a relatively high concentration for a final effluent after a biological treatment. Johnson et al. (2005) summarized the available literature on NP present in the final effluent of municipal wastewater treatment plants. Interestingly, some effluents have a higher NP concentration than the influent. It is known that NP can be produced during the biological treatment due to the biodegradation of NPEO and NP is therefore often found in higher concentrations in the effluent than in the influent (Soares et al., 2008). Camacho et al., for example, obtained NP concentrations between 5.85 and 25.1 µg/L in the final effluent while the influent contained a range of 1.64 - 1.95 µg/L. In other words, the low NP concentrations in the effluent of SBR 1 could be the result of low a NPEO loading in the influent\textsubscript{bio}.

Remarkably, the NP concentration of the ozonated effluent always remained low. As a result, the discharge limit of 0.3 µg/L for NP was almost always achieved as previously reported. The average NP removal efficiency of the ozonated effluent compared to the influent\textsubscript{bio} was 94% while SBR 1 achieved 62%. Consequently, ozonation significantly improved the average NP removal by 32%.

In other words, the ozone treatment guarantees an effluent in which the NP concentration remains relatively low, even if peak loads are observed in the influent of the biological treatment, while the effluent obtained after treatment without ozone follows the trend of the
peak loads of the influent. It can even be concluded that ozone treatment is necessary to achieve the NP discharge limit of 0.3 µg/L.

A difference in sCOD and TOC values between the two different effluents is also clearly visible in Fig. 5 and Fig. 6. The average sCOD and TOC values of the effluent of SBR 1 were 319 mg O_2/L and 115 mg C/L, respectively. If these results are compared to the sCOD and TOC values of the influent_{bio}, an average removal efficiency for both parameters can be determined. The biological wastewater treatment without an ozone polishing treatment reached an average sCOD and TOC removal efficiency of 84% and 83%, respectively. Furthermore, lower sCOD and TOC values for the ozonated effluent were observed: 155 mg O_2/L and 68 mg C/L, resulting in an even higher (however minor) average sCOD and TOC removal efficiency of 92% and 90%, which is positive. Worth noting, during Phase III, the enhanced sCOD removal efficiency was necessary to meet the discharge limit of sCOD. The maximum sCOD load may not be higher than 500 mg O_2/L and the maximum moving 10-day sCOD average is 300 mg O_2/L. The average sCOD of SBR 1 was 319 mg O_2/L compared to 155 mg O_2/L for the ozonated effluent. In other words, ozonation could guarantee an average sCOD lower than 300 mg O_2/L.

It is true that ozonation of phenolic compounds such as NP can lead to the formation of toxic by-products. Most literature sources refer to possible degradation products of phenol while addressing the degradation of NP. The decomposition of NP by ozonation can lead to a cleavage of the aromatic ring or the decomposition of the alkyl side chain (ElShafei et al., 2017). Firstly, the ring cleavage results in the formation of different aldehydes and carboxylic acids, e.g. maleic acid (Olmez-Hanci et al., 2013). These compounds are less harmful compared to the phenolic precursor. Secondly, the decomposition of de alkyl side chain can result in the formation of dihydroxy phenols due to the addition of hydroxyl radicals to the ortho or para position. Such phenolic intermediate by-products could be more toxic than NP as stated by reviewer’s comment. However, Ning et al. (2007) indicated that the site of the ozone attack was not on the alkyl chain but at the aromatic ring structure.

Therefore, some water samples obtained during Phase III were also collected for an ecotoxicity analysis. The results of the ecotoxicity analyses of the reference effluent (SBR 1), ozonated effluent (SBR 2) and the influent_{bio} are shown in Table 3.
Table 3. Ecotoxicity in the ozonated effluent compared to effluent from the reference reactor and the influent\textsubscript{bio}.

<table>
<thead>
<tr>
<th>Day</th>
<th>Reactor</th>
<th>Growth inhibition (%)</th>
<th>Immobilization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>194</td>
<td>SBR 2 + O\textsubscript{3}</td>
<td>60 ± 14</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Influent</td>
<td>100 ± 0</td>
<td>100</td>
</tr>
<tr>
<td>199</td>
<td>SBR 1</td>
<td>94 ± 10</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>SBR 2 + O\textsubscript{3}</td>
<td>83 ± 15</td>
<td>55</td>
</tr>
<tr>
<td>208</td>
<td>SBR 2 + O\textsubscript{3}</td>
<td>100 ± 0</td>
<td>80</td>
</tr>
</tbody>
</table>

The results, shown in Table 3, indicate that the influent\textsubscript{bio} showed complete inhibition and immobilization. The influent\textsubscript{bio} is wastewater that only underwent a physicochemical treatment, meaning that it still has a high pollution degree. In terms of algae inhibition, no significant difference was observed between the ozonated and reference effluents (same order of magnitude). Interestingly, the reference effluent showed the lowest Daphnia immobilization, up to 20%, while this was about 70% for the ozonated effluent. A direct explanation could not be identified. Petala et al. (2006) and Von Gunten (2018) reported that the formation of degradation products by the ozone polishing step could cause higher ecotoxicity. Furthermore, Poelmans et al. (2020) investigated the effect of ozonation as polishing step on the removal of ecotoxicity from tank truck cleaning wastewater. Despite its positive effect on the effluent quality with a COD-decrease up to 70%, the ecotoxicity is highly dependent on the formation of ecotoxic by-products which may even lead to an increase in ecotoxicity. In addition, Poelmans et al. (2020) stated that ozonation as a pre-treatment step for wastewater from tank truck cleaning did not create a higher ecological effluent quality. This paper therefore confirms the importance of the effect of ozonation on ecotoxicity.

4. Conclusions

The effect of ozone as a polishing treatment was studied by using a pilot-scale biological SBR system combined with an ozonation unit. During the ozonation phase, the obtained effluent from the SBR underwent an ozonation treatment as a polishing step. The average nonylphenol concentration, sCOD and TOC values during phase III were 0.29 µg/L, 155 mg O\textsubscript{2}/L and 68 mg C/L, respectively. The combination of biological wastewater treatment with ozonation as a polishing step was able to remove on average 94% of the nonylphenol from the influent\textsubscript{bio}, while SBR 1 could only remove 62%. In other words, ozonation significantly improved the average nonylphenol removal efficiency by approximately 32%.
Moreover, the ozonated effluent was less influenced by the nonylphenol peak concentration observed in the influent$_{bio}$ compared to the effluent of the reference SBR. These findings suggest that the ozone treatment guarantees an effluent in which the nonylphenol concentration remains relatively low, even if peak loads are observed in the influent of biological treatment. At the same time, the effluent without ozone follows the trend of the peak loads in the influent$_{bio}$. Worth noting, the sCOD and TOC removal were also slightly enhanced by introducing ozone as a post-treatment after the biology.

In general, it can be concluded that ozone treatment is efficient and necessary to achieve the discharge limit of 0.3 µg/L for nonylphenol in the effluent. The optimization of the ozonation process was proved efficient but could be further explored in future research. It might be interesting to explore different process parameters of the ozonation polishing step, such as the residence time ozone reactor or the ozone concentration as well as to study different industrial wastewater matrices.

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References


