# O₃/H₂O₂ and UV-C light irradiation treatment of oil sands process water

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HIGHLIGHTS

- The effective treatment of OSPW with high mineralization up to 98% was achieved.
- Naphthenic acids present in OSPW were removed significantly.
- Acute toxicity of OSPW was removed significantly.
- O₃/H₂O₂ process was found as the best option from the economic point of view.

GRAPHICAL ABSTRACT
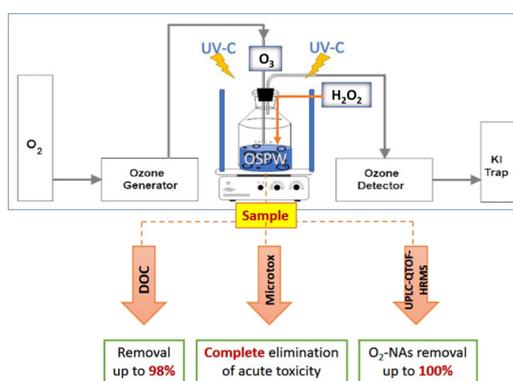
ABSTRACT

The oil sands industry generates large volumes of oil sands process water (OSPW). There is an urgent need for OSPW treatment to reduce process water inventories and to support current reclamation approaches. This study discusses how efficient ozone (O₃)-based combined advanced oxidation processes (AOPs), including hydrogen peroxide (H₂O₂) and UV-C, are at achieving mineralization while reducing the toxicity arising from such organic components as naphthenic acids (NAs) in OSPW. The results showed that the dissolved organic carbon (DOC) removals of 45%, 84%, 84% and 98%, obtained after 90-min treatments with O₃, O₃/H₂O₂, UVC/O₃ and UVC/O₃/H₂O₂, respectively, at a production rate of 6 g/L·h O₃ were considerably higher than at lower O₃ production rates. The acute toxicity on *Vibrio fischeri* was significantly reduced by all the treatments, which explains the high percentages of NA removal (up to 99% as confirmed by UPLC-QTOF-HRMS.) Mineralization (expressed as DOC removal) was highest with UVC/O₃/H₂O₂ at ca. 2 mg C/L in the treated effluent, which means that it could be used as cooling/boiling process water in bitumen upgrading units. However, considering the energy demand of the treatments tested, the treatment using O₃/H₂O₂ was found to be the most realistic for large-scale applications.

## 1. Introduction

Bitumen obtained from oil sands is an unconventional fossil fuel that became important in the market because of the increasing global demand for oil (Allen, 2008). However, processing bitumen generates such waste products as gases and produced water, which cause environmental problems (Boczkaj et al., 2018). Bitumen extraction from oil sands by caustic hot water generates nine cubic meters of raw tailings per cubic meter of oil

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produced (Brown and Ulrich, 2015). Oil sands process water (OSPW) consists of water, sand, clay, unrecovered bitumen and other organics such as naphthenic acids (NAs). It is stored in tailings ponds because of the zero-discharge approach. Typically, 80% of OSPW is reused in subsequent extraction processes, while the rest must be subject to further treatment (Brown and Ulrich, 2015; Mannina, 2017). As part of the industry's reclamation plan, the OSPW in tailings ponds needs to be treated and eventually discharged into land and/or water (Huang et al., 2018). The main concern in OSPW treatment is to reduce the amount of naphthenic acids (NAs) because they are present in higher concentrations (20–80 mg/L) than other organic compounds and their subchronic toxic effects on aquatic organisms are also greater (Fang et al., 2019).

Naphthenic acids are natural components of bitumen that solubilize during the extraction process. The term NAs mainly refers to alkyl-substituted cycloaliphatic carboxylic acids with lower amounts of acyclic aliphatic, aromatic olefinic, hydroxy, and dibasic acids (Headley and Mcmartin, 2004). NAs are expressed by the general formula $C_nH_{2n + z}O_x$, where n represents the number of carbon atoms, Z is a negative even integer associated with the ring structure and double bonds in the component, and x stands for the number of oxygen atoms (Leshuk et al., 2016; Meshref et al., 2017). Due to the complex nature of the NA mixture, the analytical methods developed to date can only detect the general profile of the mixture in terms of the carbon content and Z number not the individual components (Clemente and Fedorak, 2005).

The toxicity of OSPW in the environment could be economically reduced to some extent if treated biologically. However, biological treatments are very slow and not very efficient due to the bio-recalcitrant characteristics of most NAs (proportional to their structure) (Al Jibouri et al., 2018). Likewise, adsorption on organic-rich soil, biochar and activated carbon has been reported to be highly efficient at removing NAs. However, the regeneration or disposal of the adsorbent after use (Xu et al., 2017) requires an extra cost. Thus, advanced oxidation processes (AOPs) are essential if there is to be a balance between cost and efficiency, and further disposal processes after treatment are to be avoided.

Of all the AOPs, ozone ($O_3$) is particularly interesting because it has a wide range of applications in various kinds of effluents from different sectors and it is not limited to wastewater treatment. Because of its high reactivity it can also be used for disinfecting potable water, cleaning air, and processing and preserving food, as well as for health purposes (Karaca and Velioglu, 2007; Wei et al., 2017). Indeed, ozonation is currently used on a large-scale as a stage in municipal wastewater treatment because of its power to disinfect, decolor and deodorize, and degrade micropollutants and organic compounds. In terms of investment and operational costs, which has been reported to be 0.02–0.07 Eur/m$^3$ of treated wastewater, it is operationally feasible (Ried et al., 2009). However, the efficiency of the treatment depends on the complexity of the wastewater. Components that easily react with $O_3$ can be removed by direct reaction in anything from a few seconds to 2 min. Once they have been completely removed or their concentration has been decreased, the $O_3$ decomposition slows down. When this happens, and depending on the type of organic molecules and pH of the medium, indirect reactions start to play a more important role in removing recalcitrant components and improving treatment efficiencies (Beltran, 2004).

In the case of OSPW, several studies have focused on the potential decrease in NA concentration rather than mineralization to reduce the toxicity of the effluent and/or increase the biodegradability by either $O_3$ or $O_3$/$H_2O_2$ treatment (Afzal et al., 2015; Meshref et al., 2017; Scott et al., 2008; Wang et al., 2016). In some studies, $O_3$ has been applied in batch mode, i.e., it was fed into water to form a stock solution of $O_3$ to be transferred to the batch reactor all at once (Afzal et al., 2015). Other studies have been performed in semi-batch mode, $O_3$ being continuously bubbled into a batch reactor with a constant volume of OSPW. A very low dose of $O_3$ is eventually applied to transform the contaminants into other compounds and reduce the toxicity. In this case, no mineralization was observed after the treatment, but this was not the objective of these studies (Scott et al., 2008; Wang et al., 2016).

Optimized amounts of oxidants are crucial for increasing treatment efficiency, mineralizing by-products and, consequently, reducing toxicity. The optimization of these parameters and the overall process depends on the configuration of individual units (El-Naas et al., 2017). Furthermore, whether the feeding methods operate in batch, semi-batch or continuous modes, and the reactor design are also critical for successful treatment. For those treatments that bubble $O_3$ into the effluent, it has been reported that the size of the $O_3$ bubbles has an effect (Chu et al., 2007; Xia and Hu, 2019). The study by Chu et al. confirmed the enhancement in mass transfer, and the corresponding improvement in the amount of total organic carbon (TOC) removed per gram of $O_3$ consumed by accelerated formation of hydroxyl radicals (OH•) when a microbubble generator was used instead of a conventional bubble contactor (Chu et al., 2007).

This study explores the treatment of OSPW that aims to mineralize rather than transform contaminants by semi-batch $O_3$-based AOPs. $O_3$ was fed into the reactor by a microporous diffuser and combined with $H_2O_2$ and/or ultraviolet C irradiation (UV-C) in an attempt to increase the concentration of radicals and boost the effectiveness of the degradation of recalcitrant contaminants. The semi-batch system was chosen over the batch reactor so that the supply of $O_3$ was continuous and the target of high mineralization could be reached. This would not have been possible with a batch reactor because of the instability and low solubility of $O_3$ in water. To the best of our knowledge, this paper is the first to study the use of combined $O_3$-based treatments in the presence of UV-C irradiation to treat OSPW. The optimum amounts of reactant, reaction time and the effect of applying UV-C were systematically studied, and the feasibility of the applied processes, including economic issues, is discussed. High levels of mineralization will make it possible to reuse the treated OSPW and/or discharge it into the environment rather than storing it in tailing ponds which currently cover more than 130 km$^2$ of the landscape.

## 2. Experimental

### 2.1. Materials

Raw OSPW was collected from an oil sands tailings pond in northern Alberta, Canada, and stored at 4 °C until used. Initial DOC (in the form of dissolved carbon – dissolved inorganic carbon) and the conductivity of raw OSPW were measured periodically to confirm its stability. Only insignificant differences between the measurements were observed. Before the treatments, OSPW was filtered using a 0.45 μm nylon membrane to remove any suspended solids that might increase the consumption of reagents and decrease light transmittance (an important parameter in light-based treatments). The DOC of raw OSPW was 96 ± 5 mg C/L. Table 1 presents the initial characteristics of the OSPW used in this study after filtration. Hydrogen peroxide ($H_2O_2$, 35 wt%) was acquired from Acros Organic. Sodium bisulfite (NaHSO$_3$, 40%, Panreac) was used to quench the residual $H_2O_2$ in the samples and stop the reaction, while potassium iodide (KI, Sigma-Aldrich) was used as an $O_3$ trap to remove residual gaseous $O_3$ after treatment. Sulfuric acid and sodium hydroxide solutions (1 M) were used for pH adjustment in samples collected for biological-based analyses when needed.

### 2.2. Experimental methods

$O_3$ based experiments were performed in a laboratory scale semi-batch system consisting of an $O_3$ generator (Anseros COM-AD-02), a quartz

**Table 1**
Initial physico-chemical characteristics of raw OSPW.

| DOC (mg C/L) | COD (mg O$_2$/L) | pH | Conduct. (mS/cm) | [NAs] (mg/L) | Toxicity[a] (EC$_{50}$) |
|---|---|---|---|---|---|
| 96 ± 5 | 270 | 8.5 | 4.6 | 21 | 19% ± 3% Very toxic |

[a] Toxicity on *V. fischeri*.

reactor, a residual $O_3$ measurer (Anseros GM-6000-RTI) and a KI $O_3$ trap. $O_3$ was produced from pure oxygen by an $O_3$ generator and fed into the quartz reactor containing 300 mL of effluent through an inert porous diffuser. The outlet gas stream of the reactor was connected to an $O_3$ analyzer to measure residual $O_3$ during the treatment. The production rates of the $O_3$ for the treatment of 300 mL OSPW were 0.9 g/h, 1.8 g/h and 2.7 g/h, which were equivalent to 3 g/L·h, 6 g/L·h and 9 g/L·h, respectively. In the treatments involving $H_2O_2$, the desired amounts of $H_2O_2$ were added to the effluent at once just before the $O_3$ feed was started. The doses of $H_2O_2$ were calculated based on the weight/weight ratio of $H_2O_2$ to the initial chemical oxygen demand (COD) and ranged between 0.1 and 5. In UV-C combined treatments, the reactor was surrounded by four UV-C low-pressure lamps (Philips, 15 W each) that emitted mostly at 254 nm. Blank experiments were also conducted to establish the effectiveness of the individual processes. All the treatments took 90 min in natural pH conditions. Samples were collected every 30 min for detailed analysis. The dissolved $O_3$ concentrations of the collected samples were measured by the indigo colorimetric method described in *Standards Methods* (APHA, 1992).

### 2.3. Analytical methods

Dissolved Organic Carbon (DOC) was measured by a Shimadzu TOC-L (CSN 638–91,109-48) analyzer. Microtox® acute toxicity of the raw/ treated OSPW on *V. fischeri* bacteria was investigated using the standard 81.9% screening test with a Microtox®500 Analyzer. The extent to which the samples inhibited *V. fischeri* was measured after 15 min cultivation on the basis of the change in the intensity of the luminescence. The results were expressed as the $EC_{50}$ concentration, defined as the effective nominal concentration of raw/treated OSPW by volume percent that reduced the intensity of light emission by 50%. Classical NA concentrations of raw/ treated OSPW were determined by ultrahigh-performance liquid chromatography coupled with a quadrupole time-of-flight high resolution mass spectrometer (UPLC-QTOF-HRMS, Agilent 1260 Infinity combined with HRMS Sciex 5600 + ,) using a Phenomenex Luna, Omega Polar C18 column. NAs in samples were extracted by SPE cartridges and reconstituted in a 50/50 mixture of ACN/MeOH (acetonitrile/methanol) before the analyses. The detailed analysis protocol is given in the Supplementary Information.

## 3. Results and discussion

### 3.1. Dissolved organic carbon (DOC) removal

DOC analysis is a fast and easy technique for evaluating treatment efficiencies, which is particularly important in the treatment of real effluents with complex organic compositions such as OSPW. For this reason, the effect of combining $H_2O_2$ and UV-C in a single $O_3$ treatment was assessed initially by DOC removal.

The initial tests on OSPW were conducted with single ozonation in semi-batch mode, and $O_3$ production rates of 0.9 g/h, 1.8 g/h and 2.7 g/ h, which removed 33%, 45% and 53% of DOC, respectively, after 90 min treatment. Scott et al. previously reported a DOC removal of approximately 25% after OSPW had been subject to treatment for 130 min, in which $O_3$ was fed into the system continuously to reach 35 mg/L of dissolved $O_3$ in the reactor (Scott et al., 2008). Although our DOC removal results were better, single ozonation seems not to be sufficient to completely mineralize the recalcitrant components in OSPW. Introducing promoters of $O_3$ decomposition to increase the concentration of OH• radicals, and consequently the number of indirect reactions, can favour the mineralization of recalcitrant components.

Introducing $H_2O_2$ into the system significantly increased the efficiency of DOC removal (Fig. 1), as expected. The literature shows that, in the presence of $H_2O_2$, the conversion rate of $O_3$ to HO• and the amount of dissolved $O_3$ increase. Besides, HO• and $HO_2$• radicals can be generated by either activating $H_2O_2$ with $O_3$ or decomposing $O_3$ with $H_2O_2$ (Boczkaj et al., 2017). Thus, the addition of $H_2O_2$ to OSPW just before the ozonation started
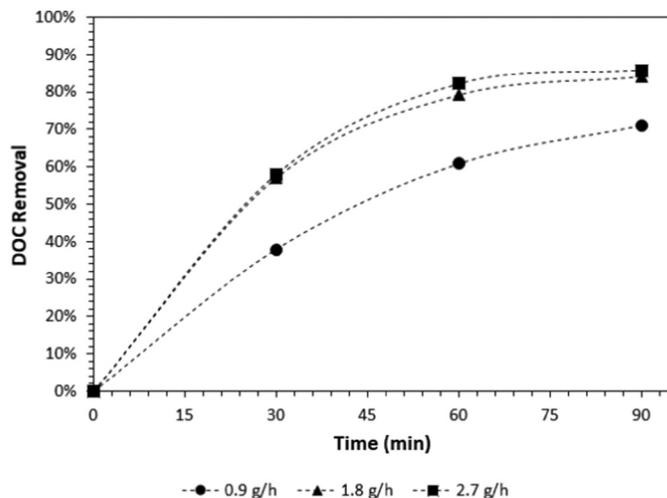


**Fig. 1.** DOC removal efficiency by $O_3$/$H_2O_2$ treatment with varied production rates of $O_3$ and a constant $H_2O_2$/COD ratio of 2.

doubled the DOC removal. Specifically, DOC removals were 71% and 84% after 90 min of $O_3$/$H_2O_2$ treatment with an $O_3$ production rate of 0.9 and 1.8 g/h, respectively, and $H_2O_2$/COD = 2. Increasing the $O_3$ production rate to 2.7 g/h (and maintaining the $H_2O_2$/COD ratio of 2) led to a DOC removal of 86%. This indicates that, in the presence of $H_2O_2$, $O_3$ production rates higher than 1.8 g/h do not lead to significant changes in DOC removal, as will be further discussed below. As DOC removal is a function of the $O_3$ dose in single ozonation, the insignificant improvement in DOC removal at a higher $O_3$ dose in $O_3$/$H_2O_2$ points to an optimum $O_3$/$H_2O_2$ ratio. So, the higher $O_3$ consumption probably accounts for the reaction between HO• and $O_3$. For this reason, combining ozonation with UV-C was proposed with $O_3$ production rates of 0.9 g/h and 1.8 g/h.

Integrating UV-C into the $O_3$-based treatments (Fig. 2A) considerably enhanced the efficiency of the treatment, allowing shorter treatment times. This is probably due to the synergetic effect of the $O_3$ treatment combined with UV-C and/or $H_2O_2$, which may form hydroxyl, peroxyl and superoxide radicals that, according to the literature, increase the reaction efficiency (Liu et al., 2004; Lucas et al., 2010). Moreover, during UV-C and $O_3$ treatment $H_2O_2$ can be produced (in-situ) as well as radicals, as reported in previous studies, which favours DOC removal (Kim et al., 2019; Summerfelt, 2003). After 90 min, DOC removal by single ozonation with 0.9 g/h and 1.8 g/h increased from 33% and 45% to 67% and 84%, respectively, solely due to its combination with UV-C. When $H_2O_2$ was added to the UV-C/$O_3$ system, DOC removals after 90 min reached 87% and 98% for 0.9 g/h and 1.8 g/h $O_3$ production rates, respectively. Remarkably, this triple combination (i.e., UV-C/$O_3$/$H_2O_2$) conducted with 1.8 g/h of $O_3$ and an $H_2O_2$/COD ratio of 2, led to DOC removals of 65% and 92% in 30 min and 60 min, respectively.

The DOC removal trends after treatment with UV-C/$O_3$/$H_2O_2$ (Fig. 2B) and either $H_2O_2$/COD = 1.05 or $H_2O_2$/COD = 2 were very similar, reaching 83% and 87%, respectively, after 90 min. Any increase or decrease in the $H_2O_2$ dose noticeably decreased the removal efficiency, which may be due to either a lower production of radicals (in the case of the lowest dose) or to the scavenging effect of $H_2O_2$ itself (in the case of the highest dose) (Demir-Duz et al., 2020).

### 3.2. $O_3$ consumption analysis

Beltrán reported that when ozone dissolves in water it decomposes to free radicals, and indirect reactions start alongside the direct reactions. This decomposition mechanism is heavily dependent on such features of the effluent as its pH and the compounds present in it (Beltran, 2004). In a recent study, the treatment of a petroleum refinery wastewater effluent with the same ozonation system showed a reverse balance between $O_3$
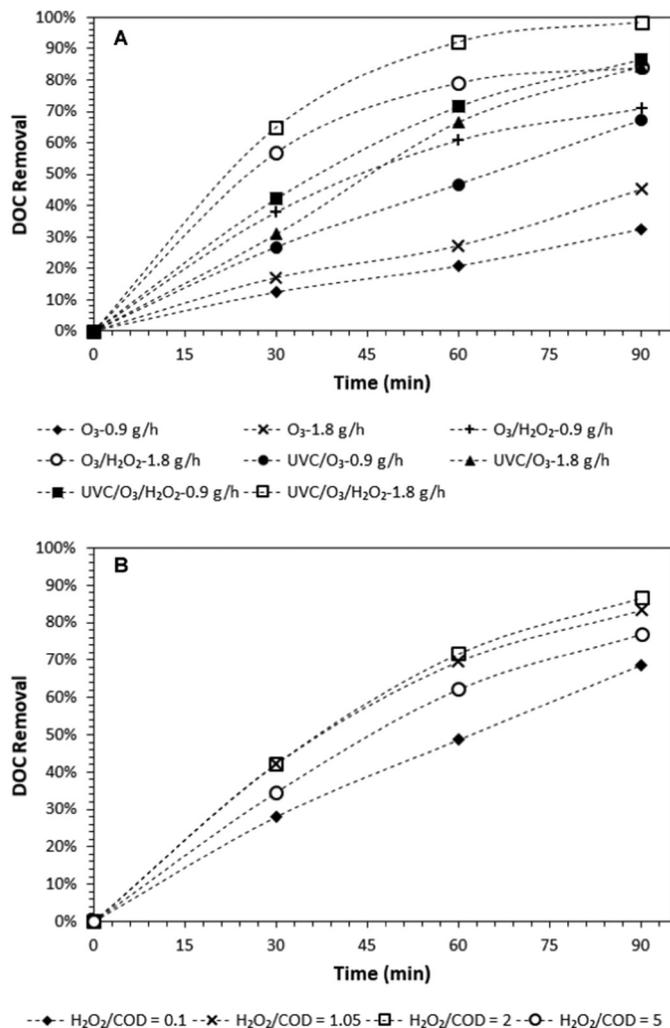
Fig. 2. DOC removal efficiency by UV-C based treatments with varied production rates of $O_3$ with/without a constant $H_2O_2$/COD ratio of 2 (A), varied ratios of $H_2O_2$/COD and a constant $O_3$ production rate of 0.9 g/h (B).



Fig. 3. $O_3$ consumption during a 90-min treatment by $O_3$ and $O_3$/$H_2O_2$ with $H_2O_2$/ COD = 2 and varied $O_3$ production rates (A) and different AOPs with an $O_3$ production rate of 1.8 g/h (B).

and the $H_2O_2$ concentrations, suggesting that TOC removals would be highest by ensuring an optimum ratio between $O_3$ and $H_2O_2$ (Demir-Duz et al., 2020). Thus, this analysis attempted to clarify the tendency to consume the oxidants used to treat OSPW.

The mass balance of $O_3$ within the system was determined by Eq. (1). Here, the residual concentrations of dissolved $O_3$ were not taken into account because they were very low (3–8 mg/L) compared to the inlet and outlet concentrations. However, it is interesting to mention that the concentrations of dissolved $O_3$ in samples collected after 90 min of treatment were in the following order: UV-C/$O_3$/$H_2O_2$ < UV-C/$O_3$ < $O_3$ < $O_3$/$H_2O_2$. Residual $O_3$ was lower in experiments performed in the presence of UV-C light (approx. 3.8 mg/L for UV-C/$O_3$/$H_2O_2$ and UV-C/$O_3$). This is in agreement with the amount of $O_3$ consumed by those treatments, as shown in Fig. 3B. So, the $O_3$ consumptions of those systems with UV-C light (and an $O_3$ feed ratio of 1.8 g/h) increased to ca. 2 g after 90 min compared to 0.5 g in the processes that do not have UV-C irradiation. The higher $O_3$ consumption shown by these UV-C based processes accounts for the photodecomposition of $O_3$, which yields $H_2O_2$ and subsequently hydroxyl radicals, among others (Lucas et al., 2010). Similarly, the $O_3$ consumption in the $O_3$/$H_2O_2$ system (Fig. 3A) was higher than that of single ozonation. This result was expected since $H_2O_2$ accelerates the $O_3$ decomposition ratio, which eventually leads to the formation of hydroxyl radicals especially at alkaline pH (Beltran, 2004).

$$O_3 \text{ consumption (reacted + dissolved) (g)} = O_3 \text{ (inlet) (g)} - O_3 \text{ (outlet) (g)} \quad (1)$$

The relationship between $O_3$ consumption and DOC removal (Fig. 4) revealed that those treatments that used $H_2O_2$, either with or without UV-C, promoted the efficient consumption of $O_3$ in terms of DOC removal. In the presence of $H_2O_2$, the DOC removals of the treatments almost doubled, although the amounts of $O_3$ consumed were almost the same for the treatments conducted without $H_2O_2$. In other words, when single ozonation is applied, $O_3$ is mainly consumed due to the transformation of the OSPW components rather than mineralization, probably because of insufficient degradation by the HO• pathway. Also, the molar ratios of $O_3$(consumed)/DOC(removed) for the treatments conducted with 1.8 g/h $O_3$ production rates were calculated as 4, 6, 21 and 18 for treatments with $O_3$, $O_3$/ $H_2O_2$, UV-C/$O_3$ and UV-C/$O_3$/$H_2O_2$, respectively. It should be pointed out here that although the lowest ratio of $O_3$(consumed)/DOC(removed) might be economically favorable, the $O_3$ was used more effectively in the $O_3$/ $H_2O_2$ treatment ($O_3$(consumed)/DOC(removed) = 6) since DOC removal was 45% and 84% for the $O_3$ and $O_3$/$H_2O_2$ treatments, respectively. Similarly, according to our previous study of the treatment of another kind of petroleum refinery wastewater by $O_3$-based processes, the molar ratio of $O_3$(consumed)/DOC(removed) for the optimized $O_3$/$H_2O_2$ treatment was around 6 (Demir-Duz et al., 2020).

### 3.3. Removal of NAs

Detailed analyses of NAs in raw and treated effluents play an important role in evaluating the success of the treatment. NAs are considered to be the
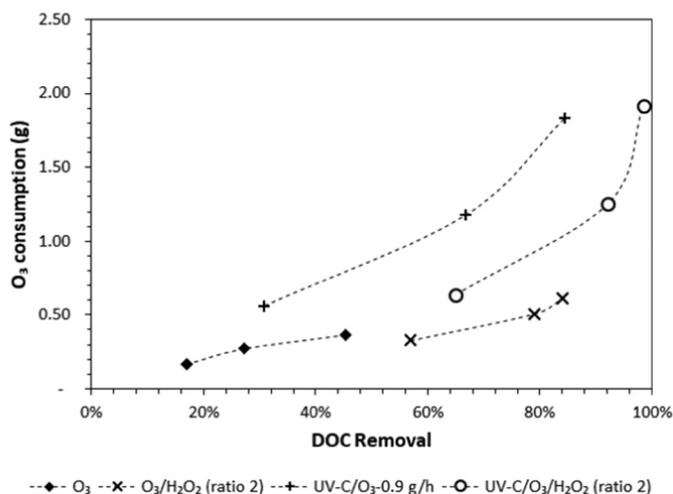
**Fig. 4.** The relationship between $O_3$ consumption and DOC removal% for different AOPs with an $O_3$ production rate of 1.8 g/h. For each line, 1st point = 30 min, 2nd point = 60 min and 3rd point = 90 min sample.

components of OSPW that most contribute to the acute and chronic toxicity of various aquatic organisms (Benally et al., 2018). Therefore, monitoring the evolution of NAs during treatments could clarify the changes in toxicity as well as the treatment efficiency.

The classical formula $C_nH_{2n+z}O_2$ represents the NAs that are initially in high concentrations, while the formula $C_nH_{2n+z}O_x$ with x > 2 represents the NAs formed after oxidation (Meshref et al., 2017). Due to the wide range of NAs present in OSPW, they can be detected by a general profiling based on n and z instead of individual identification (Clemente and Fedorak, 2005). The removal efficiency results are presented based on the carbon number of the compounds and the double bond equivalence (DBE) number, which refers to the hydrogen deficiency (DBE = $-z/2$) (Fang et al., 2019). The initial classical NA concentration of raw OSPW used in this study was 21 mg/L according to UPLC-QTOF-HRMS quantification, which is in the same range of concentration reported previously (Xue et al., 2017).

Fig. 5A presents the general NA profile of the raw OSPW. Predominantly, NAs with a carbon number higher than 12 and a DBE number higher than 4 were detected in raw OSPW, while generally low concentrations of NAs were detected in treated samples (data provided in the supplementary document). In contrast, even after single ozonation with the lowest $O_3$ production rate, 97% of NAs were removed while DOC removal was quite low (Figs. 5B and S1). This behaviour has already been observed by Scott et al. (2008). By taking into consideration the difference due to the increased $O_3$ production rate, Figs. S1–S3 clearly show that some NA fractions decreased as the $O_3$ production rate increased. In general terms, the DBE factor of the NAs decreased after all of the treatments. At first glance, C18 NAs were more resistant to removal by single ozonation with 0.9 g/h $O_3$ (Fig. S1), and they were almost completely removed in the sample treated with 1.8 g/h $O_3$ (Fig. S2). C14–16 components increased slightly, which was expected due to the formation of lower carbon molecules by breaking bonds. These reformed C14–C16 molecules, as well as other high carbon molecules, were further removed when the $O_3$ production rate was increased to 2.7 g/h (Fig. S3). Additionally, the removal ratios of C7–13 components increased, and DOC analyses showed that the $O_3$ production rate was also higher which, in turn, increased mineralization. However, considering the DOC removal of the different treatments, the NAs might have been transformed by single ozonation rather than mineralization (Table 2). This transformation is due to the oxidation of classical NAs after $O_3$ treatment which produces a shift in the distribution to more oxygen-rich species, as reported previously (Lyons et al., 2018). On the other hand, combining $O_3$, $H_2O_2$ and/or UV-C technologies led to 97–99% removal of classical NAs (Figs. S4–S9) and improved mineralization with up to 98% of DOC removal.

Fig. 6A/B reveals that classical NAs with carbon numbers between 11 and 21 and DBE numbers between 2 and 10 were almost completely removed by all treatments supported by the results mentioned above. The main differences in the removal efficiencies for different treatments were more observable at carbon numbers lower than 11. The lowest removal rate for carbon numbers 7–10 was observed for the sample treated with 0.9 g/h $O_3$. In fact, it was observed that new C7–8 components were produced with a DBE number of 0 rather than being removed, which confirms the lower mineralization for this treatment. With the addition of more oxidants that either increased the amount of applied $O_3$ or added $H_2O$ and/or UV-C, the removal of C8–10 reached a maximum while the amount of C7 components produced decreased due to mineralization.

### 3.4. Toxicity evaluation

The toxicity of OSPW has frequently been studied as an indicator of the treatment's effectiveness. Raw OSPW presents acute toxicity due to the presence of NAs and other organic components such as polycyclic aromatic hydrocarbons (PAHs), BTEX (benzene, toluene, ethyl benzene, and xylenes) and phenols (Li et al., 2017). Therefore, due to the complex nature of OSPW, toxicity is assessed for the entire OSPW composition or for its main constituents, such as NA or other organic fractions instead of individual components (Garcia-Garcia et al., 2011a, 2011b; Li et al., 2017). Unless treated effluent is reused in the plant, it needs to be safely discharged and this requires an effective treatment that can reduce its toxicity.

Microtox® is a rapid and relatively economic method commonly used to monitor the acute toxicity of effluents like OSPW (Scott et al., 2008). In the literature, values of $EC_{50} < 25\%$ are defined as very toxic, while $25\% < EC_{50} < 75\%$ are toxic and $EC_{50} > 75\%$ are considered non-toxic (Jiménez et al., 2019). An inhibition test is recommended for effluents with low levels of toxicity, for which $EC_{50}$ values cannot be calculated (SDI, 2006).

Toxicity tests performed with *V. fischeri* on treated OSPW samples (*T*) revealed that 90 min of single $O_3$ treatment at the lowest $O_3$ production rate (i.e., 0.9 g $O_3$/h) reduced the toxicity of OSPW from an $EC_{50}$ value of 19% in raw OSPW to 42% in the ozonated sample. This would still be considered toxic. Higher $O_3$ production rates decreased the toxicity to suitable ranges. The maximum inhibition effects found in these samples after 90 min of single ozonation with $O_3$ production rates of 1.8 g/h and 2.7 g/h were 33% and 37%, respectively. That is, the reduction in luminescence intensity did not reach 50%, which demonstrates the non-toxic features of the treated OSPW. In the case of combined treatments, the acute toxicity also decreased significantly in accordance with the mineralization levels obtained, as shown by the DOC analysis (Table 2). A 90-min treatment with $O_3/H_2O_2$ ($H_2O_2/COD$ = 2) also resulted in a maximum inhibition effect of 43% and 26% for a 0.9 g/h and 1.8 g/h $O_3$ production rate, respectively, which reduced toxicity more than single ozonation. After 90 min of combined treatment of UV-C/$O_3$/$H_2O_2$ the toxicity showed a maximum inhibition of 33% and 22% for the 0.9 g/h and 1.8 g/h $O_3$ production rate (with $H_2O_2$/COD = 2), respectively, which would mean the lowest toxicity.

The positive influence of $O_3$-based treatments on the toxicity of OSPW has also been reported in other studies (Al Jibouri et al., 2018; Meshref et al., 2017). However, unlike what has been found in this study, the DOC reduction reported is quite small. Therefore, to determine the most appropriate treatment for OSPW, parameters such as mineralization and economy, not just toxicity, need to be assessed.

### 3.5. Operational comparison of treatments

The balance between operational costs and treatment efficiencies is important if treatment processes are to be feasible. Although high degrees of mineralization can be provided by different combinations of UV-C, $O_3$ and $H_2O_2$, operational costs must also be considered when deciding on how best to treat OSPW. The end use of the effluent should also be borne in mind. Comparing the energy consumption of the various treatments may help to resolve this issue.
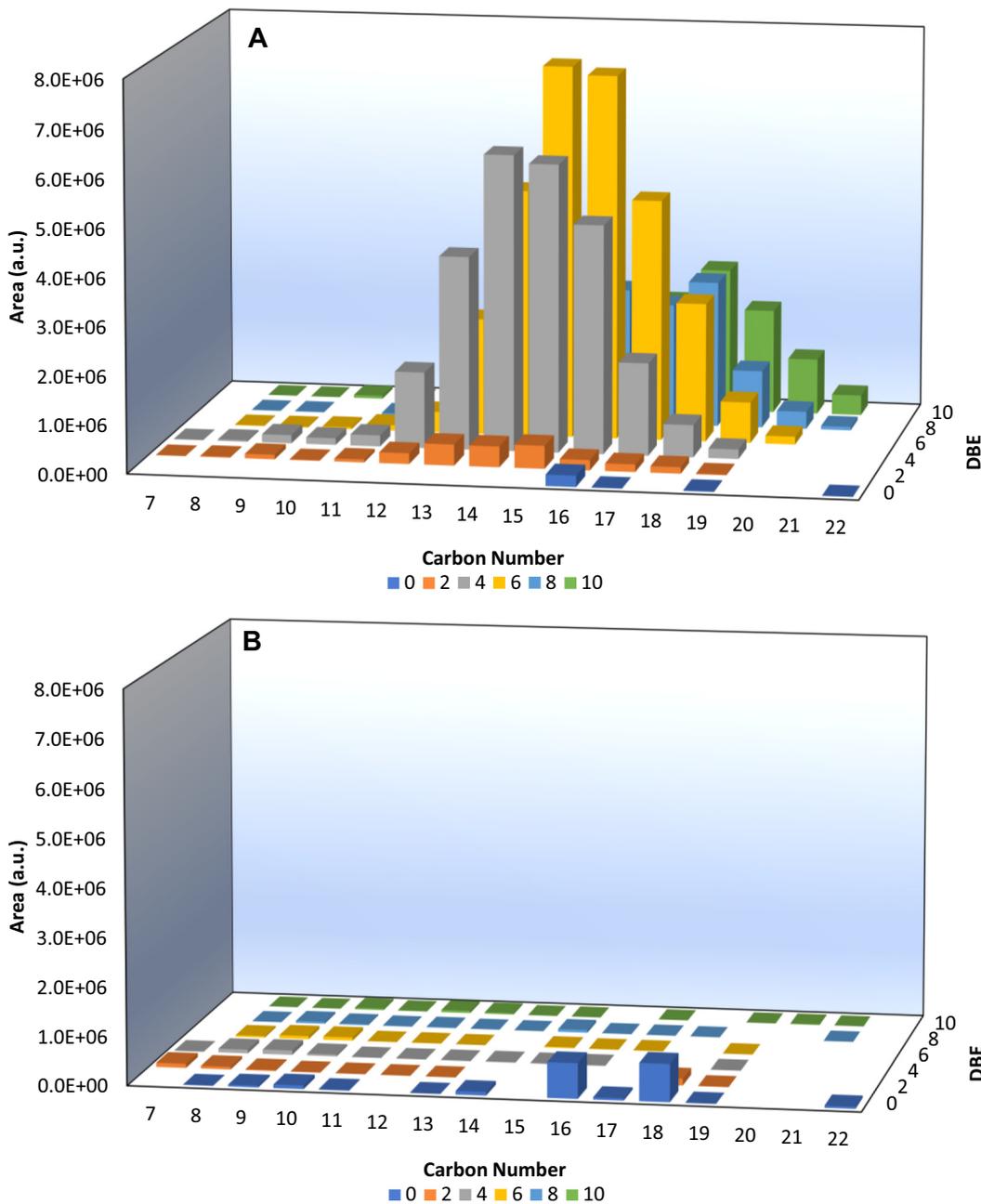
**Fig. 5.** NA profile of raw OSPW (A) and OSPW after 90 min single ozonation with an O₃ production ratio of 0.9 g/h (B). For the sake of comparison, y-axis scale of both figures is the same.

**Table 2**
Toxicity tests on *V. fischeri* performed with the samples collected after 90 min of different treatments.

| Process | Treatment conditions | | | Degradation assessment | | Toxicity assessment | |
|---|---|---|---|---|---|---|---|
| | O₃ (g/h) | H₂O₂/COD | UV-C | DOC removal (%) | O₂-NAs removal (%) | EC₅₀ (%) | Inhibition effect (%) |
| Raw OSPW | – | – | – | | | 19 | 99 |
| O₃ | 0.9 | – | – | 33 | 97 | 42 | 62 |
| | 1.8 | – | – | 45 | 98 | | 33 |
| | 2.7 | – | – | 53 | 99 | | 37 |
| O₃/H₂O₂ | 0.9 | 2 | – | 71 | 98 | | 43 |
| | 1.8 | 2 | – | 84 | 97 | | 26 |
| UV-C/O₃ | 0.9 | – | Applied | 67 | 97 | | 24 |
| | 1.8 | – | Applied | 84 | 100 | | 41 |
| UV-C/O₃/H₂O₂ | 0.9 | 2 | Applied | 87 | 98 | | 33 |
| | 1.8 | 2 | Applied | 98 | 96 | | 22 |
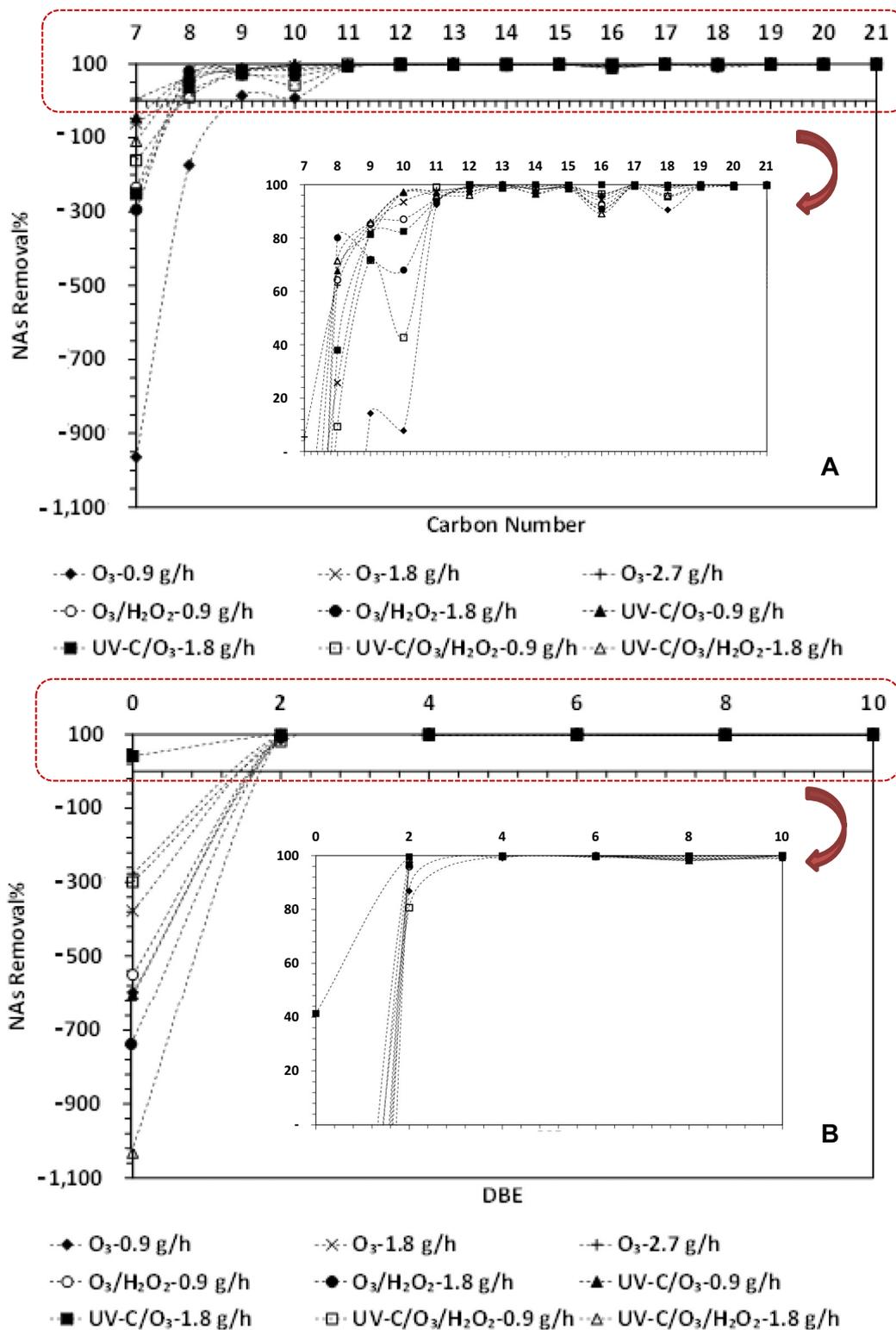
**Fig. 6.** Classical NA removal after 90 min treatment by different AOPs with respect to carbon number (A) and DBE number (B). The insets in the figure zoom are the positive part of the y axis (0–100% range).

The energy consumption of the treatments can be assessed by Eq. (2), reported by Bolton et al., based on the electrical energy per order (EEO) in a batch system (Bolton et al., 1996).

$$EEO \left( \frac{kWh}{m^3} \right) = \frac{P(kW) * t(h) * 1000}{V(L) * \log \left( \frac{C_i}{C_f} \right)} \qquad (2)$$

where P(kW), t(h), $C_i$ and $C_f$ and V(L) represent rated power, reaction time, initial and final concentration, and treated volume of OSPW, respectively.

In previous studies, this equation was slightly modified using initial and final TOC instead of a target compound concentration because of the complex nature of real effluents (Demir-Duz et al., 2020; Jiménez et al., 2019). In this study, the calculations used DOC removal expressed

by Eq. (3), since the objective was to increase DOC removal by mineralization.

$$EEO\left(\frac{kWh}{m^3}\right) = \frac{P(kW) * t(h) * 1000}{V(L) * \log\left(\frac{DOC_i}{DOC_f}\right)} \tag{3}$$

The EEO of the processes applied for 90 min was calculated using the energy consumption of the current laboratory-scale system. The P (kW) of the magnetic stirrer and UV-C lights was 0.002 and 0.06, respectively, while the P of the $O_3$ generator was calculated from either the amount of $O_3$ produced or the amount consumed. The rated power of $O_3$ generation was 10 kW/kg $O_3$ according to the supplier. As shown in Table S1, when the energy consumption was calculated from the amount of $O_3$ produced, the EEO for 90 min of single ozonation was higher than that of some of the combined AOPs because the DOC removals were very low. The UV-C/$O_3$ treatment also resulted in a high energy demand. However, in the presence of UV-C, a higher $O_3$ production rate resulted in a lower EEO as the removal efficiency was higher. EEO values decreased from 322 kWh/m$^3$ and 383 kWh/m$^3$ for single ozonation to 102 kWh/m$^3$ and 122 kWh/m$^3$ for the $O_3$/$H_2O_2$ combination with $O_3$ production rates of 0.9 g/h and 1.8 g/h, respectively, and a $H_2O_2$/COD ratio of 2. This indicates that the $O_3$/$H_2O_2$ treatment had a marked benefit on both energy cost and mineralization and that by applying 1.8 g/h of $O_3$ in combination with $H_2O_2$ ($H_2O_2$/COD ratio of 2) DOC removal was as high as 84%. Applying an $O_3$ feed above 1.8 g/h increased the EEO significantly since DOC removal did not improve under this condition. The amount of electrical energy required by the treatments with the UV-C/$O_3$/$H_2O_2$ system, an $O_3$ production rate of 1.8 g/h and a $H_2O_2$/COD ratio of 2 was greater than the amount required by the $O_3$/$H_2O_2$ treatment (221 kWh/m$^3$ and 122 kWh/m$^3$, respectively). However, the %DOC removal obtained by combined UV-C/$O_3$/$H_2O_2$ was remarkably high (98%), which would allow the treated effluent to be reused in the plant. In contrast, decreasing the dose of $O_3$ to 0.9 g/h considerably increased the EEO, up to 406 kWh/m$^3$ for the same $H_2O_2$/COD ratio = 2. Thus, it could be concluded that $O_3$/$H_2O_2$ provides an effective treatment at less electrical cost, while UV-C/$O_3$/$H_2O_2$ provides a better quality effluent that can be reused rather than discharged.

It must be noted that EEO values were calculated for the laboratory-scale system used in this study and only show how EEO can be changed by single or combined treatment methods. They do not reflect the realistic energy demand for a full-scale application. For this reason, Table S1 presents the EEO values calculated from the amount of consumed $O_3$ in view of the fact that the gas feeding technique (by porous diffuser) means that the system has low $O_3$ transfer capacity. On the other hand, transferred $O_3$ can increase by more than 90% for up-scaled $O_3$ reactors. The normalized EEO values (calculated relative to the amount of consumed $O_3$) decreased 3-to-8 fold in both single ozonation and $O_3$/$H_2O_2$ systems depending on the $O_3$ doses applied, while they decreased much less for the processes that applied UV-C light and had the highest EEO values of all the processes studied. It should also be taken into account that UV-C irradiation was kept constant in this study (60 W, supplied by 4 lamps). This needs to be studied further so that the reactor can be optimized. As such, the irradiance applied, and the length and position of the lamps must be explored since they may be able to reduce the energy demand associated with the applied UV-C irradiation. Sarkar et al. used a 13 W low-pressure Hg lamp to treat a secondary effluent. It was placed in the center of the reactor in a quartz protective sleeve and the EEO of the UV/$H_2O_2$ treatment was calculated to be 8.53 kWh/m$^3$ for their system while the EEOs of $O_3$, $O_3$/$H_2O_2$ and UV/$O_3$/$H_2O_2$ were 202, 212 and 166 kWh/m$^3$, respectively (Sarkar et al., 2014). Pisarenko et al. evaluated an $O_3$ and $O_3$/$H_2O_2$ oxidation process on a pilot scale for trace contaminants in drinking water and for water reuse applications, where the $O_3$ transfer efficiency was 95%. An EEO value between 0.004 and 2.6 kWh/m$^3$ was reported for various contaminant removals and system configurations (Pisarenko et al., 2012).

Thus, the EEO of large-scale optimized treatment systems, equipped with the best lamp type and $O_3$ production/injection systems and with a good reactor design, may be much lower than the values that are presented in our study. Miklos et al. recently reviewed EEO values for numerous AOPs from the literature and compared the median values of several processes. According to their report, $O_3$, $O_3$/$H_2O_2$, $O_3$/UV, UV/$H_2O_2$, which had median EEO values < 1 kWh/m$^3$, were found to be more realistic for full-scale applications (Miklos et al., 2018). It is worth mentioning that EEO is also highly dependent on the characteristics of the water: e.g. concentration of contaminants, turbidity, presence of recalcitrant components and radical scavengers (Miklos et al., 2018). Nonetheless, as a first step in the evaluation, both the EEOs and the experimental results obtained throughout the present study point to the $O_3$/$H_2O_2$ system as being a feasible candidate for a scale-up study for OSPW treatment. On the other hand, UV-C/$O_3$/$H_2O_2$ gives better effluent quality at a higher EEO cost.

## 4. Conclusions

This study explored an efficient and environmentally friendly treatment that can add value to the industry's reclamation plan for OSPW, which is currently stored in tailings ponds until it can be treated properly. To this end, $O_3$-based AOPs including different combinations of $O_3$, $H_2O_2$ and UV-C were investigated as possible treatments for OSPW. The aim was to mineralize the recalcitrant components rather than transform them, to reclaim the treated effluent for reuse for bitumen extraction or upgrading units, or safely discharge it into the environment without lowering the quality of the products or causing corrosion in the process units.

An optimized $O_3$/$H_2O_2$ system can be regarded as a feasible method for treating OSPW in terms of the degree of mineralization it can achieve and the elimination of acute toxicity. Here, this system was found to have a final DOC of up to ca. 15 mg C/L and to completely eliminate acute toxicity. This guarantees that effluents can be safely discharged or reused in the extraction process. Reusing higher quality treated effluents in the extraction process can be a solution to the current problems caused by decreasing extraction efficiencies over time and increasing pollution by storing OSPW in tailings ponds.

When UV-C light was irradiated during $O_3$/$H_2O_2$ treatment, the final DOC was reduced to 2 mg C/L with the consequent decrease in toxicity. This method allows the treated effluent to be reused as cooling/boiling water in the units used for bitumen upgrading. However, in this case, a post treatment after AOP would be needed to reduce the conductivity and prevent corrosion in the cooling/boiling water units. The operation costs are also expected to increase slightly in the case of a large-scale application. On the basis of our observations at the lab-scale, these costs were calculated to be approximately 30 kWh/m$^3$ and 300 kWh/m$^3$ for $O_3$/$H_2O_2$ and UV-C/$O_3$/$H_2O_2$, respectively. Therefore, an overall assessment should be made of the costs of water processing or purchasing for these systems.

The real effluent used in this study provides important information about the efficiency of various AOPs if they are extrapolated to a larger scale. The efficiency shown by $O_3$/$H_2O_2$ and UV-C/$O_3$/$H_2O_2$ treatments may have the following benefits: i) less water will be used because the bitumen and heavy oil extraction plants will require less external water in the search for more resource-efficient and environmentally friendly processes; and ii) land will be able to be recovered and reclaimed, thus decreasing the negative impact on the local fauna and possible seepage to surface water.

## CRediT authorship contribution statement

**Hande Demir Duz:** Investigation; Data curation; Resources; Writing – original draft; Writing – review & editing. **Sandra Contreras:** Conceptualization; Funding acquisition; Resources; Supervision; Writing – review & editing. **Mayra G. Álvarez:** Methodology; Supervision; Writing – review & editing. **Leonidas A. Perez-Estrada:** Methodology; Data curation; Formal analysis; Investigation; Writing – review & editing. **Mohamed Gamal El-Din:** Conceptualization; Funding acquisition; Resources; Supervision; Writing – review & editing.

## Declaration of competing interest

## Acknowledgements

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.154804.

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