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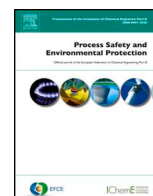
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Feasibility study on produced water oxidation as a pretreatment at offshore platform



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ABSTRACT

Produced water (PW) generated worldwide has lately become an issue of environmental concern. PW has a complex composition and a suitable treatment at offshore oil and gas platforms is required to achieve zero harmful discharge into the sea. The feasibility of electrochemical oxidation, heat-activated persulfate and ozonation was investigated as PW pretreatment. For comparison purposes, a common oxidant dosage level of 5% and 10% treatment equivalent chemical oxygen demand (COD) removal were established. Aiming to assess PW biodegradability, an assay for biological oxygen demand (BOD) for high salinity matrix was also developed as a tool to characterize treatment efficiency. Electrochemical oxidation was largely independent on the anode materials, and controlled by the applied charge passed through the system. Heat-activated persulfate reaction was time-consuming and dependent on activation temperature, as well as initial oxidant concentration. Both methods reduced COD and BOD without significantly improving PW biodegradability, probably due to by-products generation. Ozonation had the most promising results applying doses ranging from 3.5 to 151 mgO₃/L. The benzene in PW after ozonation reduced up to 71% alongside with > 70% toxicity reduction for tested doses. Ozonation also showed to marginally improve PW biodegradability, which underline the potential of ozone to facilitate a subsequent biological treatment.

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1. Introduction

Produced water (PW) is the water from underground formations that is brought to the surface during oil and gas extraction. It is the largest by-product associated with oil and gas production, and represents the largest volume waste stream into the marine environment worldwide (Neff et al., 2011). The volume and characteristics of PW generated vary considerably. It depends on the geographic location and age of the field, the geological formation, the extraction method, and the type of hydrocarbon product being produced (Alley et al., 2011; Jiménez et al., 2018). Overall, PW generated worldwide are steadily increasing. It is expected within the next few years that PW-to-oil ratios reach values well above ten (Scanlon et al., 2020).

In addition to the big volumes of PW generated and its variability, this water also has a very complex composition. It includes organic and inorganic substances, with the main components being salts, free and emulsified oils, phenols, organic acids, benzene, toluene,

ethylbenzene and xylene (BTEX), and polycyclic aromatic hydrocarbons (PAHs). PW may also contain other contaminants, including sulfides, ammonia and naturally occurring radioactive material (Alley et al., 2011; Neff et al., 2011; Røe Utvik, 1999; Veil et al., 2004). These compounds are associated with acute bio-toxicity and poor biodegradability, which might cause ecological damage without appropriate treatment prior to discharge (Chen et al., 2015). Research on distribution of associated PW chemical contaminants in the sea have indicated a prevalent level of contamination around the offshore platform itself (Niu et al., 2016). There is a growing recognition that the impacts of PW on the aquatic ecosystem, and eventually human health via food chains, can be cumulative and long-lasting (Dores et al., 2012; Neff et al., 2011). Studies concerning PW composition and toxicity assessment with aquatic organisms, including fish, crustaceans, bivalves and bacteria have shown that PW can elicit a range of acute and sublethal effects (Farmen et al., 2010; Hale et al., 2019; Hansen et al., 2019; Holth et al., 2008). However, even though the number of PW toxicity studies has been increasing over the time, limited studies have reported toxicity evaluation for real PW, and most of the studies are with synthetic PW (Sørensen et al., 2019).

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Due to the emerging environmental concern, many countries have implemented new directives and more strict regulatory standards with the addition of new target dissolved organic compounds. The regulations are site specific and depend on the location of the production asset (Lusini^{er} et al., 2020). At offshore platforms, PW is conventionally treated by means of gas–water–oil separation, sedimentation or cyclones, and coarse depth filtration (Coha et al., 2021). Chemicals present in PW are recalcitrant in nature and difficult to treat, and it often requires the combination of different processes owing to the matrix complexity. The conventional technologies currently used cannot reach the separation requirements at offshore platforms (Liu et al., 2021a,b). Therefore, an integrated solution to improve PW treatment at offshore platforms is required in order to meet strict regulation and reach a zero harmful discharge into the sea.

Unlike onshore processes, PW treatment at offshore reveals to be a challenge due to the absence of adequate space or weight capacity for the equipment used, which encourages the use of physically and chemically compact methods for operation in remote and harsh environments (Al-Ghouti et al., 2019). Recently, substantial research has been conducted on biological treatment coupled with Advanced Oxidation Processes (AOPs) as a promising alternative for PW treatment (Jiménez et al., 2017; Mohanakrishna et al., 2021). AOPs may represent valuable pretreatment options with high effectiveness on eliminating substances that may be toxic to microorganisms, which are sometimes exploited in subsequent biological treatment. Moreover, these technologies require a small surface area, which suits the in-situ operation at the offshore platforms. Studies on real PW samples by AOPs are limited, but the processes showed promising results for treating industrial effluents including from petrochemical industries (Dores et al., 2012; Gargouri et al., 2014; Miklos et al., 2018). Among AOPs, ozonation and anodic oxidation are the most widely researched techniques as an alternative for PW pretreatment (Coha et al., 2021; Jiménez et al., 2019). These methods were found to improve PW biodegradability (Mohanakrishna et al., 2021; Uma and Gandhimathi, 2020), and also decrease PW toxicity (Martin et al., 2010). In addition, the chemical oxidation process by persulfate has recently attracted much attention for the removal of pollutants due to high redox potential of the sulfate radical (2.5–3.1 V) (Guerra-Rodríguez et al., 2018). Fang et al. (2018) showed that UV–persulfate is a potential treatment for naphthenic acid degradation, and can be used in the further design of AOPs for oil sands process water reclamation. For the best of our knowledge, there are no studies with heat-activated persulfate as PW pretreatment. Overall, most of the research with chemical oxidation technologies has been with synthetic PW and targeting few individual compounds. Therefore, the interactive effects of PW composition and the oxidants, in terms of efficiency and toxicity are not well addressed, and more research is needed on demonstrating chemical oxidation potential in degrading refractory and toxic organics into readily biodegradable organic compounds.

In the present work, the feasibility of three chemical oxidation technologies were investigated as PW pretreatment. The main goal was to remove organic species and improve PW biodegradability, alongside with toxicity reduction to bacteria for a subsequent biological process, as well as to the marine environments. This research provides background knowledge on electrochemical oxidation, heat-activated persulfate and ozonation that may suggest a way forward to assist the development of chemical oxidation pretreatment at offshore platforms improving the treatment efficiency of PW.

2. Materials and methods

2.1. Chemicals

The chemicals used in the experiments, sodium persulfate (SPS) ($\text{Na}_2\text{S}_2\text{O}_8$, $\geq 98\%$), potassium iodide (KI, $\geq 99\%$), sodium bicarbonate

(NaHCO_3 , $\geq 99\%$), sodium sulfite (99.0%), sodium hydroxide (NaOH, 99.0%) were analytical reagent grade and purchased from Sigma-Aldrich. Water used for dilutions and stock solutions was purified by Millipore reverse osmosis purification system (PURELAB[®] flex, Milli-Q[®]).

2.2. Experimental procedure

A real PW sample from an offshore platform in the North Sea was used in the experiments. In this study, PW refers to the effluent sampled after hydrocyclone separation of dispersed oil droplets and before discharged into the sea. Once received at the laboratories, PW was stored in the dark under refrigeration at 4 °C until experiments were performed. PW was treated by electrochemical oxidation, heat-activated persulfate and ozone. In order to compare the treatment efficiency of the three methods, a common dose level of 5% and 10% equivalent of chemical oxygen demand (COD) reduction was established. For SPS and ozonation, the dose was calculated based on equivalent transfer of electrons, more detailed explanation concerning electrochemical oxidation and the equivalent oxidant dose for each method is in Table SM1 of Supplementary Material.

2.2.1. Electrochemical oxidation

The electrochemical system functioned as a batch recirculation system, consisting of a filter press electrochemical cell and a reservoir. PW was added to the reservoir, pumped through the reactor and recirculated to the reservoir, through a cooling jacket to offset the heat from the electrodes and maintain ambient treatment temperature. A volume of 0.7 L of PW was used for each run, pumped through the system with a flowrate of 0.7 L/min. Two different anode materials, boron doped diamond (BDD) and dimensional stable anode/ Cl_2 (DSA/ Cl_2), were tested with a fixed graphite cathode, each with a 10 cm² active surface area. The cell was primarily used in 1-chamber configuration with a 3 mm inter electrode gap and turbulence promoters. A 2-chamber configuration was also tested, with a Nafion 212 cation exchange membrane separating the anolyte from the catholyte. The mass transfer coefficient of the 1-chamber reactor was determined to $2.52 \cdot 10^{-5}$ m/s using the ferro-ferri cyanide redox pair at a flowrate of 0.7 L/min. All experiments were completed in duplicates.

2.2.2. Heat-activated persulfate

The experiments were carried out in 250 mL-Erlenmeyer placed on a heated stirring plate set at 150 rpm. The oxidant was added from the stock solution (2 M, 476 g/L of $\text{Na}_2\text{S}_2\text{O}_8$; SPS) when the temperature of the PW was stable. Three different temperatures were tested: 40 °C, 65 °C and 80 °C along with different SPS doses. SPS was introduced in doses that achieve stoichiometrically complete degradation based on defined target COD removal. In total, five different doses were tested ranging from 0.09 to 6.2 g SPS/L, which is equivalent to 0.5% and 30% COD reduction, respectively. SPS depletion was analyzed over the time by taking 0.1 mL of sample and mixed with 4.9 mL of KI/ NaHCO_3 solution freshly prepared and let it to react for 20 min. The concentration of SPS was measured by a spectrophotometric method using KI. The method used was suggested by (Lee et al., 2015) and is a modified method from Liang et al., 2008a,b. More details can be found in Supplementary material. pH and conductivity changes were recorded before and after the experiment. Samples for bromine (mg Cl_2 /L) analysis and BOD test were taken at the end of each experiment.

2.2.3. Ozonation

The ozonation experiments were conducted in a column made of plexiglass with 1 L capacity and conducted in semi-batch experiments. Ozone was produced from an ozone generator, which was supplied by compressed oxygen with the delivered dosage

controlled through a gas-flow regulator. Ozone concentration before entering in reaction column was monitored with a BMT 965 ST analyzer. After passing through the analyzer, the generated O_3 was dispersed into the reaction column from a ceramic diffuser placed on the bottom of the column. An ozone trap washing bottle containing KI (2%; 20 g KI in 1 L) solution was connected to the reactor outlet to absorb residual ozone concentration in the gas phase. The ozone dosage ranged from 3.5 to 151 mg O_3/L . High ozone doses (84 mg O_3/L and 151 mg O_3/L) were defined for comparison purposes, in order to match the 5% and 10% COD equivalent removal to the doses used in electrochemical oxidation and heat-activated SPS experiments. The effectiveness of the treatment was evaluated by COD, BOD_5 , and more specific parameters such as BTEX and VFA were also analyzed for the two lowest doses that aimed to reduce PW toxicity. The experiments were carried out at room temperature (ca. $20\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$).

2.3. Ecotoxicological evaluation of samples after ozonation

Ecotoxicological evaluation of untreated and ozonated PW samples was assessed using photobacterium *Vibrio fischeri* (*V. fischeri*) from the commercial the standardized test (Biotox Reference: ISO Standard 11348-3, 2007) BioTox™ assay kit. Each test consisted of five concentrations with two replicates and two control replicates without adding any test chemical. pH of PW samples were 7.0 ± 0.2 , thus no adjustments were needed. The PW sample was diluted two-fold with ultrapure water following a series of five-fold dilutions using 2% NaCl solution. After that 100 μL of test solutions was mixed with 100 μL luminescent bacterial suspensions, and light emission was measured after 15 and 30 min contact. GraphPad Prism version 8.2.0 supporting computer software with a standard log-linear model was used to calculate the effect concentrations (EC_{50}) for the inhibition of *V. fischeri* with 95% confidence intervals. A concentration-response curves were fitted by non-linear regression assuming a logarithmic-normal distribution of data.

2.4. Analytical methods

The pH and conductivity was measured by Thermo Scientific Orion Star™ A215 pH/conductivity Benchtop Meter. Total COD was measured using Hach Lange™ kit LCK1814. The principal is based on the oxidizable substances that react with sulfuric acid and potassium dichromate solution in the presence of silver sulfate as a catalyst. Chloride is masked by mercury sulfate. The reduction in the yellow coloration of Cr^{6+} is evaluated. Samples were diluted whenever needed to fit in the range of salinity (1.0–20 g/L chloride) and COD (7 mg O_2/L – 70 mg O_2/L) of the kit. This test complies with the standard: ISO 6060–1989 and DIN 38409-H41-H44.

Bromine measured as chlorine was determined photometrically using Hach Lange™ kit LCK310. Bromide present in untreated PW was analyzed by Thermo Scientific Dionex™ IC S-5000 conductivity detector and using an anion-exchange column equipped with a guard column (IonPac AS22, 4 × 250 mm, Ionpac AS22 Guard column, 4 × 50 mm, Thermo Scientific). Benzene, toluene, ethylbenzene and xylene, as well as volatile fatty acids were analysed by gas chromatography (more information in [Supplementary material](#)). Nutrients i.e. $PO_4\text{-P}$, $NO_3\text{-N}$, $NO_2\text{-N}$, $NH_4\text{-N}$ were analyzed by SKALAR San++ continuous flow analyzer (by Skalar Analytical B.V. analysis, software San series FlowAccess™ V3). Prior analysis all samples were filtered by nylon 0.2 μm filters.

2.4.1. Biological oxygen demand – adapted procedure

Biological oxygen demand (BOD) was measured by the manometric respirometric test. The pressure changes was measured by a manometer and converted to oxygen consumption by the respirometric OxiTop® measuring system. The procedure was as follow. PW samples were diluted 1.5-fold in order to have a conductivity range

from 53 mS/cm to 57 mS/cm. Samples (164 mL) were collected in 250 mL amber bottles. In total, four high salinity adapted carriers (K1, AnoxKaldnes™ carriers) were added into the BOD bottle as inoculum together with a magnetic stirring rod. To prevent nitrification bacteria, three drops of N-Allylthiourea ($C_4H_8N_2S$) ATU were also added to the sample bottle. Before screwing the pressure measuring heads onto the bottles, each sample bottle had a rubber sleeve in the bottleneck that have been filled beforehand with sodium hydroxide tablets to absorb carbon dioxide. The bottles were placed on a switched-on stirrer platform to ensure maximum mixing of the samples, and inside of the incubator to prevent exposure to light at $20\text{ }^\circ\text{C}$ for a period of 5 days. If hypobromous acid (HBO_r) was present ($>0.1\text{ mg Cl}_2/L$) in the oxidized samples, 550 mg/L sodium sulfite (Na_2SO_3) was added into each sample and stirred for 1 h in order to avoid any interference with BOD test.

3. Results

3.1. PW characteristics

The main characteristics of the PW samples are presented in [Table 1](#). The PW in this study exhibited a neutral pH, which according to literature it can range from 4.3 to 10 ([Jiménez et al., 2018](#)). It also showed a high ammonium concentration, and low COD ([Jiménez et al., 2018](#) and references therein). The high BOD_5/COD ratio of 0.41 indicates the biodegradable nature of the PW.

3.2. Electrochemical experiments

3.2.1. Anode material and influence of current density

Comparison between the trend of COD removal, as a function of time, for both electrodes at 80 mA/cm², 160 mA/cm² and 360 mA/cm² is presented in [Fig. 1\(a\)](#). The results showed that COD removal was largely independent on anode material, since there was no differences comparing both electrodes materials i.e. BDD and DSA/Cl₂ when applying the same current density. The results presented in [Fig. 1\(b\)](#) shows that COD removal was mainly governed by the amount of charge passed through the system (Q). For the two lowest current densities tested (80 mA/cm² and 160 mA/cm²) less than 20% COD removal was achieved in 30 min. When current density was doubled (320 mA/cm²) a 40% of COD was reached within the same period of time. In fact, increasing the current density resulted in an enhancement of the oxidation rate, which in this case showed to be indirect oxidation by electrochemically generated chemical oxidants, and not electrochemical oxygen transfer reactions mediated by

Table 1
Initial characteristics of offshore PW samples in this study.

Parameters	Range or value
pH	7–7.4
Conductivity (mS/cm)	87–88
Salinity (g Cl/L)	69
Total COD (mg O_2/L)	490–528
BOD_5/COD	0.41
TOC (mg/L)	149–168
NH_4^+ (mg N/L)	38–50
Bromide (mg/L)	78–85
Benzene ($\mu\text{g/L}$)	614
Toluene ($\mu\text{g/L}$)	185
Ethylbenzene ($\mu\text{g/L}$)	64
<i>m-p</i> -Xylene ($\mu\text{g/L}$)	154
<i>o</i> -Xylene ($\mu\text{g/L}$)	73
Acetic acid (mg/L)	192
Propionic acid (mg/L)	39
Iso-butyric acid (mg/L)	10
Butyric acid (mg/L)	11
MicroTox®- <i>V.fischeri</i> (TU_a) ^a	0.15

^a Toxic Unit (TU_a) = $100/EC_{50}$.

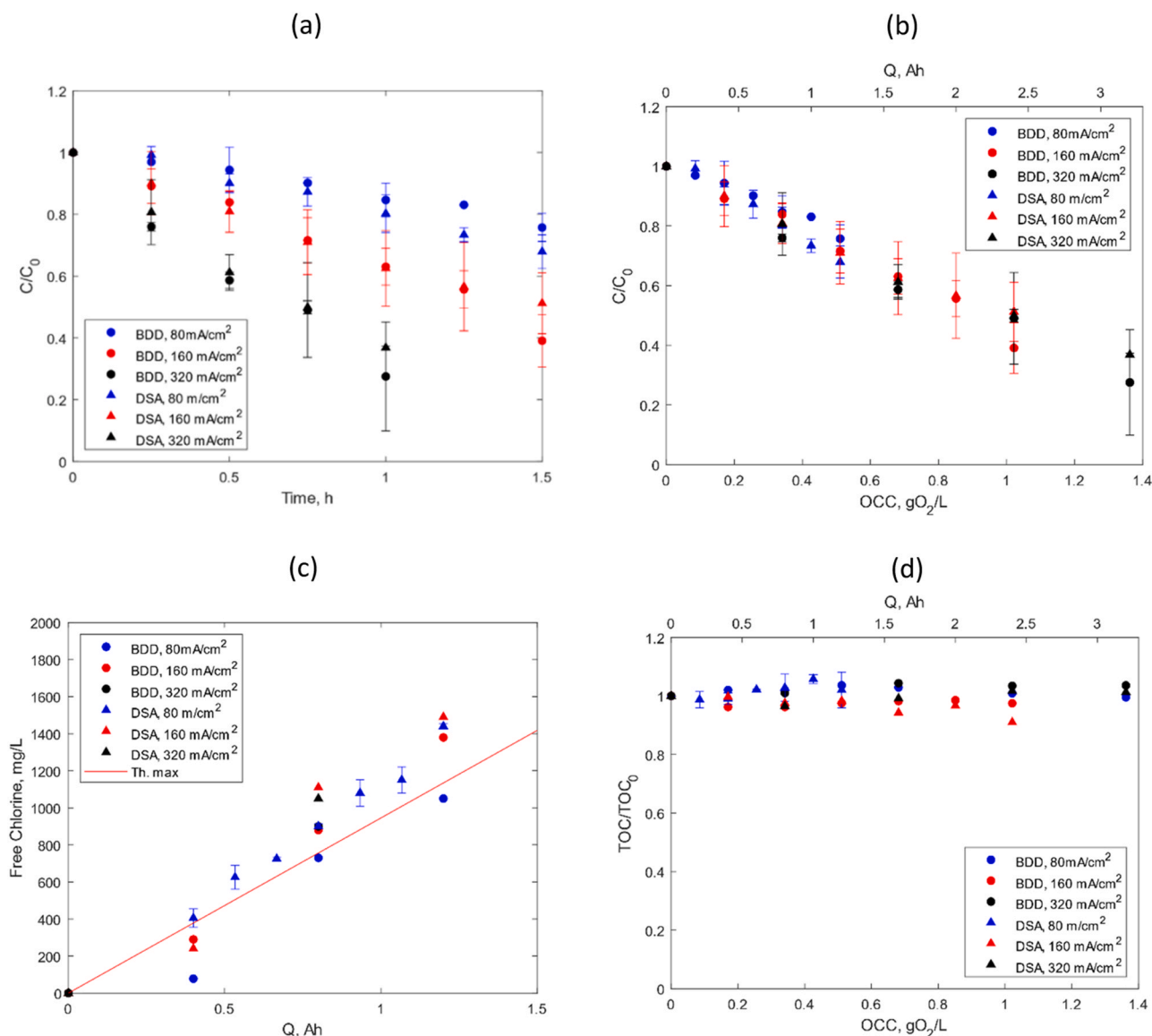


Fig. 1. (a) Relative COD removal vs. time; (b) Residual active chlorine formation during electrochemical oxidation; (c) Relative TOC removal vs. specific charge passed through the solution (upper x-axis) and OCC (bottom x-axis); (d) Relative COD removal vs. specific charge passed through the solution (upper x-axis) and OCC (bottom x-axis). Error bars represent the standard deviations.

physorbed hydroxyl radicals (in the case of non-active anode, BDD) or chemisorbed active oxygen (in the case of active anode, DSA). This is seen as the COD removal is seemingly not limited by mass transfer, as the degradation rate increases even when using 20 times the limiting current. Nevertheless, other authors reported that treatment time could be substantially reduced using BDD comparing with other anodes due to the higher amount of oxidant species generated (e.g. Gargouri et al., 2014). Unlike BDD, the DSA anode is very active for active chlorine species (e.g., Cl₂, HClO and ClO⁻), when Cl⁻ is present in the solution, and these species are the main responsible for indirect oxidation of organic compounds.

In the present study, high chloride concentration (69 g Cl/L) of PW seemed to have played an important role on anodes performance due to the occurrence of secondary reactions. The work carried out by (Da Silva et al., 2013), compared the COD removal efficiencies of three classes of PW (namely, fresh, brine, and saline) at two different anode materials i.e. Ti/IrO₂-Ta₂O₅ and BDD. In fresh and brine PW ([Cl⁻] < 1.6 g/L), differences between electrodes were registered with better COD removal efficiencies for BDD. However, when testing with saline PW (characterized by higher chloride and

COD concentrations) both anodes had similar COD removal. The similar COD removal efficiencies obtained at both anodes at higher concentrations of Cl⁻ in solution was related to the electrogeneration of strong oxidant species, such as hypochlorite, favoring a faster COD abatement (Da Silva et al., 2013). In fact, BDD is expected to produce higher amount of inefficient perchlorate by oxidation of chloride (Brillas and Martínez-Huitle, 2015). Considering the PW characteristics in this study and the fact that DSA-electrodes are known for being good electrocatalysts for active chlorine production, it can be assumed that the production of species like hypochlorite, favored a fast oxidation of dissolved organic compounds, thus resulting in a similar performance with BDD.

The generation of hypochlorite was analyzed and results are shown in Fig. 1(c). The low COD concentration gave rise to the electrochemical oxidation of chloride, and the COD instead undergoes chemical oxidation by hypochlorite. The generation of hypochlorite confirms the dependence on chlorine evolution. In general, the generation of hypochlorite followed the theoretical max that assumes only electron transfer with chloride. This is an advantage as far as scaling go, as it is possible to accelerate the degradation at the

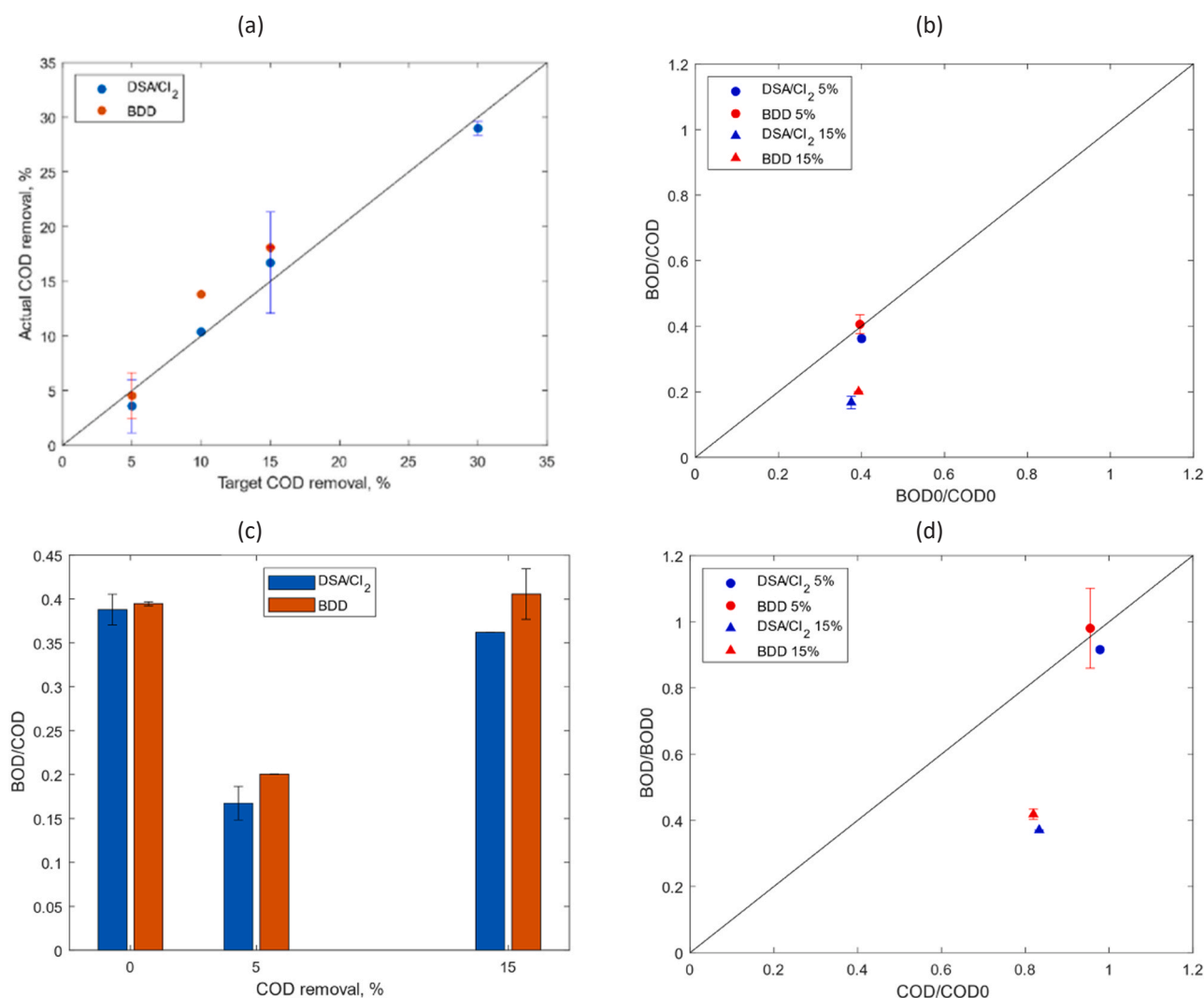


Fig. 2. (a) COD removal (%) of the effluents vs. the target value; (b) BOD/COD ratio at the different EO doses (eq. COD removal %); (c) Relative BOD removal vs. the relative COD removal; (d) The BOD/COD ratio of the treated PW vs. the initial BOD/COD ratio. Error bars represent the standard deviations.

cost of power efficiency, but it also brings challenges. The hypochlorite driven degradation brings an increased risk of formation of difficult to degrade halogenated by-products, undermining the purpose of pretreatment to provide an easier biologically degradable water matrix. The effect of the electrochemical treatment on the water matrix is in line with the assumption that the COD removal mainly happens through chemical oxidation. TOC remained more or less constant during the treatment (Fig. 1(d)) indicating that the effluents had some recalcitrant compounds (or degradation by-products) that were not oxidized under these experimental conditions. Hypochlorite is not a strong enough oxidizing agent to completely mineralize the organic compounds, but forming recalcitrant compounds giving a false COD abatement (Da Silva et al., 2013).

3.2.2. COD and BOD removal

The theoretical and the experimental COD removal is shown in Fig. 2(a). The EO treatment had a target COD removal of 5%, 10%, 15% and 30% using the DSA/Cl₂ anode, and 5%, 10% and 15% using the BDD anode. The target removal was generally met, except for DSA/Cl₂ at 5% equivalent COD removal, which around 2.5% of COD was removed. This result is rationalized partly with the electrochemical formation of additional oxidants such as active chlorine, as previously discussed. The BOD to COD ratio before and after treatment at the target COD removal of 5% and 15% is illustrated in Fig. 2(b)–(d).

At the more conservative 5% COD removal, the BOD and COD seem to be the same, having similar BOD and COD removals and similar BOD to COD ratio before and after treatment. The BOD decreased comparatively more during the electrochemical treatment, compared to COD. This was more pronounced for the larger COD removal, and at approximately 15% COD removal around 60% of BOD was removed. The BOD results suggested that biofilm attached on the carriers used for BOD test were unable to (or could barely) adapt to the treated PW. Recalcitrant intermediates such as organochlorinated species could have been produced, as already confirmed by other authors with BDD (Sales Solano et al., 2013) and DSA-type anodes and might induce high toxicity (Feng et al., 2016).

3.3. Heat-activated persulfate experiments

3.3.1. Effect of temperature and sodium persulfate initial dose

A series of experiments were performed as preliminary test to access the oxidant consumption over the time a mild and medium temperatures i.e. 40 °C and 65 °C, respectively. The effect of temperature at two different SPS doses is presented in Fig. 3(a). The results showed that SPS consumption was highly dependent on the temperature of the solution. At 40 °C, the concentration of SPS was somehow constant for 72 h. On the other hand, at 65 °C SPS concentration in solution reduced to 65% in 20 h, and continuously

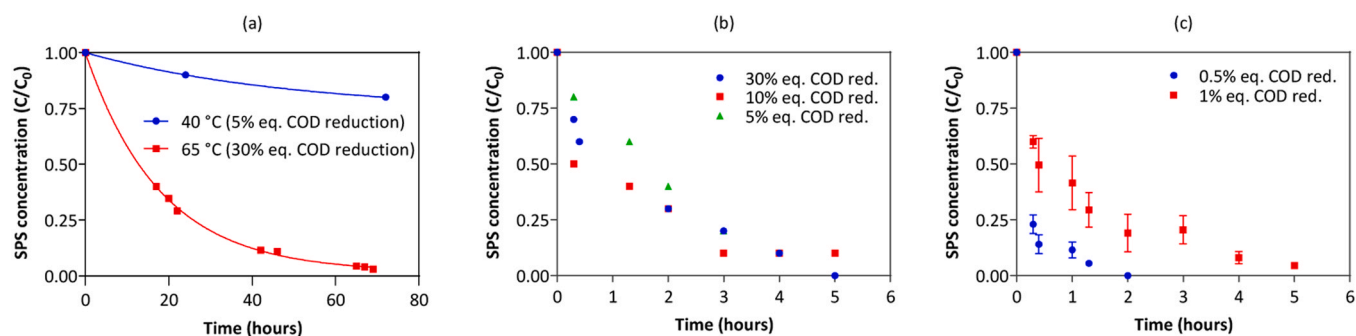


Fig. 3. (a) Relative SPS concentration vs. time at two different temperatures and oxidant doses; (b) Relative SPS concentration vs. time at 80 °C testing high (c) Relative SPS concentration vs. time at 80 °C testing low oxidant doses. Error bars represent the standard deviation.

decreased until 72 h. According to literature, the increase of the oxidant consumption with the increase of temperature can be attributed to several factors such as (i) faster oxidation of organics in solution by sulfate radicals or (ii) an increase in the unproductive decomposition of the oxidant, generating sulfate anions, protons, and oxygen (Dominguez et al., 2021). There was no changes of PW pH at 40 °C, but at 65 °C the COD reduced up to 56% and pH decreased dramatically to 1.2 due to proton release. Even though a faster SPS decomposition at 65 °C was observed comparing with 40 °C, a long period (more than 3 days) was still required for oxidant consumption. The increase of temperature from 65 °C to 80 °C reduced 15-fold the reaction time for SPS consumption (Fig. 3(b)). Besides temperature, the initial concentration of SPS also influence the process. Among high SPS doses (5%, 10% and 30% eq. COD reduction), there was no significant differences in terms of oxidant consumption rate. The reaction showed to be faster for the low SPS doses, mainly at 0.5% eq. COD reduction (Fig. 3(c)). At 89 mg SPS/L (0.5% eq. COD reduction), the concentration rapidly decreased (77%) within 30 min, and continuously declined steadily until it reached 0.6 mg SPS/L after 2 h (97.6% reduction). As clearly shown, longer oxidation time (5 h) is required for the complete consumption of SPS at higher initial concentrations. Besides the long treatment time, other authors have reported that addition of higher concentrations of oxidant does not always result in an improvement in the process effectiveness because persulfate may act as a scavenger of sulfate radicals (Gao et al., 2012; Moreno-Andrés et al., 2019).

3.3.2. COD and BOD removal

The measured COD of treated PW never met the theoretical values (values can be found in Fig. SM 1 of Supplementary Material). Only the thermolysis (i.e., PW without SPS under 80 °C for 5 h) resulted in 13% COD removal. Evaporation of organic volatile compounds such as volatile fatty acids due to high temperature (80 °C) must have contributed to these results. When adding the oxidant, the experimental COD removal was up to 4 times higher than the theoretical values. This means that experimental COD removal ranged from 19% to 33% instead of the theoretical values from 0.5% to 10%. Previous studies have shown the impact of matrix characteristics on the activated-persulfate reactions. For example, Nihemaiti et al. (2018) detected higher values of degradation rates of some organic chemicals in the presence of chloride radicals in activated persulfate system. The presence of high concentrations of chloride enhance bleaching caused by direct attack of produced reactive chlorine species generated by oxidation with sulfate radicals (Benndesen et al., 2012; Tan et al., 2014). It is also possible that the produced reactive chlorine species catalyze the propagation reactions resulting in more sulfate radicals. The reactivity of these radicals with organic contaminants or participation in chain propagation reactions is not well understood, and it is traditionally assumed that they have an overall negative impact on the activated

persulfate performance (Liang et al., 2006). However, the present results suggest that chloride might play an important role in heat activated persulfate applications, and it should not strictly be considered as scavenger, as produced chlorine radicals can participate in propagation reactions with persulfate and increase the overall production of sulfate radicals (Benndesen et al., 2012).

The COD/COD₀ ratio of untreated and treated PW at 80 °C and the target SPS doses equivalent to 0.5%, 1%, 5% and 10% COD reduction is illustrated in Fig. 4. The addition of SPS enhanced COD removal, which was favored at higher oxidant concentration. High SPS doses did not result in an effective process for the PW treatment due to the formation of potentially toxic transformation products, which triggers a new concern. This result was expressed on BOD results for SPS doses equivalent to 5% and 10% COD reduction (890 mg SPS/L and 1827 mg SPS/L, respectively). The BOD results demonstrated that the level of toxicity increased and was high enough to destroy microbial activity resulted from the oxidation of bromide by sulfate radicals. Similar results were also obtained for EO at the same dose of 5% and 10% eq. COD reduction (Section 3.2.2). In this case, it seemed that large quantities of SPS generated high amounts of sulfate ions that are classified as pollutants at high concentrations. Moreover, the presence of bromide in saline waters can have significant reactivity with sulfate radicals (Wang et al., 2020). A significant fraction of sulfate radicals in solution can be scavenged by bromide and converted to bromine radical species (Yang et al., 2014). This could result in the generation of by-products such as hypobromous and bromamines, which are relatively stable and more difficult to break. The generation of oxidation by-products was not further investigated in this study.

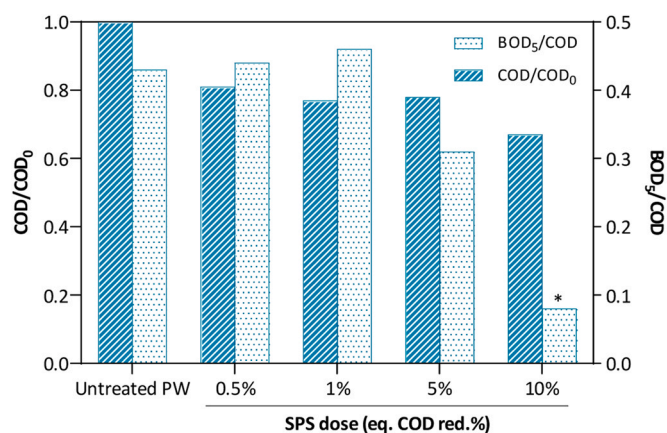


Fig. 4. Normalized concentration of COD and BOD₅/COD ratio for untreated PW and the four different SPS doses tested at 80 °C.

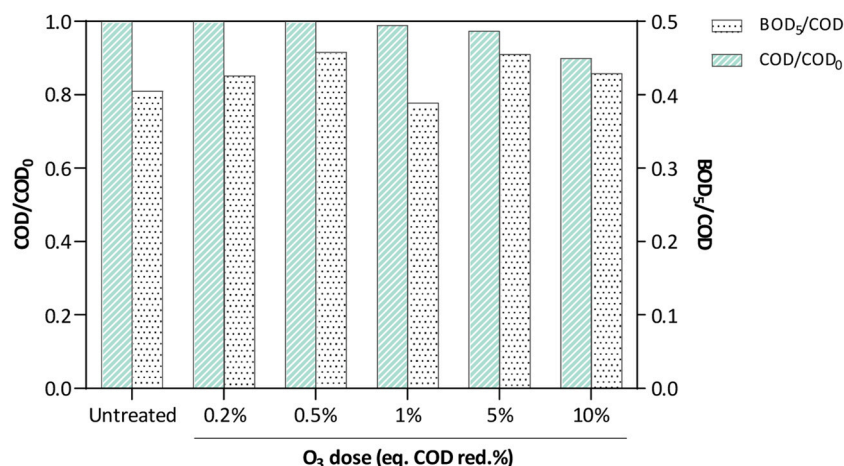


Fig. 5. Normalized concentration of COD and BOD₅/COD ratio observed for untreated PW and the five different ozone doses tested.

3.4. Ozonation experiments

3.4.1. COD and BOD removal

The effect of ozone dose on PW treatment was studied with five ozone doses ranging from 3.5 mg O₃/L to 151 mg O₃/L, corresponding to the theoretical COD removals presented in Fig. 5. The theoretical doses of 5% and 10% tCOD were very close or matched the experimental tCOD removals obtained in the ozonated samples. In specific, 2.7% and 10% COD removal was achieved, respectively. Low doses aimed to remove toxicity, thus COD removal was not observed for 0.2%, 0.5% and 1% equivalent COD reduction.

The impact of ozone dose on promoting PW biodegradability was assessed and results are also presented in Figure. Overall, ozonation slightly enhanced PW biodegradability when comparing with the untreated PW. The results showed that the optimum dose was 7.8 mg O₃/L, which slightly improved BOD₅/COD ratio from 0.41 to 0.46. This means that long-chain compounds were partially oxidized, promoting a faster degradation for a potential subsequent biological treatment. PW biodegradability was not improved increasing the ozone dose. This can be justified either by complete mineralization of biodegradable substances, or incomplete oxidation. Moreover, if by-products are generated during PW ozonation, some might be toxic to microorganisms and/or not biodegradable, thus affect BOD results. It is important to point out that initial PW biodegradability was already high (BOD₅/COD = 0.41), indicating that most of the organic compounds were biodegradable. PW from different fields and low BOD/COD could lead to a more clear improvement in PW biodegradability by ozonation. For example, pretreatment of ship-board oily wastewater by ozone (contact time = 75 min, 2 g O₃/L) improved biodegradability index from 0.36 to 0.52 (Uma and Gandhimathi, 2020). Accordingly to the literature, chemical oxidation effect on PW biodegradability is more pronounced in the case of BOD/COD ratio less than 0.1, indicating the non-biodegradability of the matrix. Chen et al. (2015) have reported a 3.3 fold increase of BOD/COD ratio when initial biodegradability ratio of the petroleum refinery wastewater was 0.098 (contact time = 40 min, 2.19 g O₃/h).

3.4.2. Acute toxicity tests

Toxicity values for ozonated PW samples expressed as TU_a (100/EC₅₀) are presented in Fig. 6(a). The results showed a clear PW toxicity reduction, which had an initial TU_a of 0.15 and decreased up to 0.01. At an assay time of 30 min of exposure, the inhibition percentage of *V. fischeri* in untreated PW was 44%. Ozonation was able to reduce up to 40% of PW toxicity. This result indicates that toxic compounds usually present in PW, such as dissolved and

dispersed oil were at some extent removed without generation of more toxic compounds. Nevertheless, toxic oxidation and halogenation intermediates were dominant for the medium doses, which might have been generated but further oxidized for the highest ozone dose (151 mg O₃/L) resulting in toxicity reduction at the similar level with low doses (3.5 and 7.8 mg O₃/L). Dispersed and dissolved oil and organic compounds have been reported to induce PW toxicity, but assessing the contribution of each class to the total toxicity is complex (De Brito et al., 2019). Based on the results presented in Table 2, it is possible to attribute at some extent the toxicity reduction to the removal of easily oxidized organic compounds. Ozonation removed 71% benzene followed by 65% toluene, 19% and 30% for ethylbenzene and xylene, respectively. Moreover, complete removal of butyric acid (11 mg/L in untreated PW) and 46–51% of propionic acid were also achieved. The concentration of acetic acid remained unaltered. Previously, studies have already reported that acetic acid is difficult to remove from PW, and considered recalcitrant due to low reactivity with radicals (Jiménez et al., 2019). However, acetic acid is biodegradable and could be easily removed in a subsequent potential biological treatment, as relatively simpler molecules are more feasible for biological degradation.

The main drawback identified in the use of O₃ for PW pretreatment is related to the presence of bromide in the initial matrix. In PW, ozone rapidly reacts with bromide and produces the oxidant bromine (Jung et al., 2017). The presence of HBrO (mg Cl₂/L), the predominant form of bromine under the tested conditions, was measured in treated PW by the different ozone doses and results are presented in Fig. 6(b). There was a linear increase of HBrO with the ozone dose, with a more distinct concentration for the highest dose (151 mg O₃/L). This result is in line with literature results, which concluded that initial ozone dose in artificial saltwater affects the residual ozone concentration and bromine formation (Jung et al., 2017). In the present study, PW has approx. 50 mg N/L of ammonium thus hypobromite is masked by the formation of monobromamine, which can be slowly oxidized by ozone to nitrate and bromide. In literature, it is still not clear whether bromide might influence matrix toxicity or not. Recently, Liu et al. (2021a,b) reported the contributions of four toxicants to the acute toxicity of offshore PW were quantified and ranked as PAHs > bromoform > phenols > dibromopentane, which means that aromatics contributed to higher acute toxicity than brominated by-products. Bearing in mind that optimization was not the goal of this work, oxidation by-products were not further investigated in the present research, but should be consider in future research.

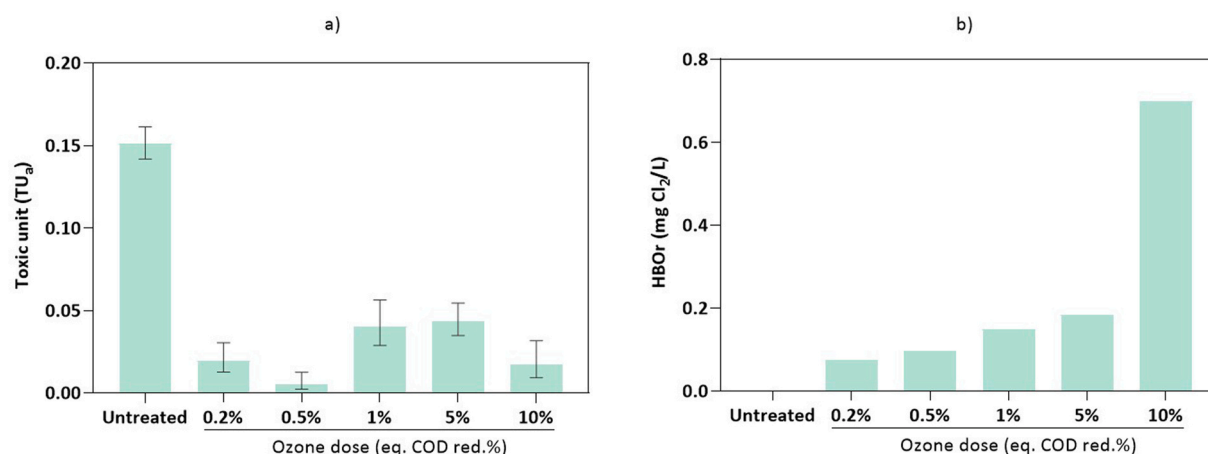


Fig. 6. (a) Microtox® acute toxicity values represented as TU₄ (100/EC₅₀) for untreated PW and the five different ozone doses tested. Error bars represent the standard deviation of each experiment performed in duplicate; (b) Hypobromous acid (HOBr) concentration in PW for untreated and after ozonation.

Table 2

BTEX (μg/L) and VFA (mg/L) concentration for untreated and ozonated PW samples.

Compounds	O ₃ dose (mg O ₃ /L)		
	0	3.5	7.8
BTEX (μg/L)			
Benzene	614	213	177
Toluene	185	74	65
Ethylbenzene	64	53	52
<i>m-p</i> -xylene	154	112	108
<i>o</i> -xylene	73	58	57
VFA (mg/L)			
Acetic acid	192	166	175
Propionic acid	38	19	21
Butyric acid	11	<LOQ	<LOQ

<LOQ: below the limit of quantification.

3.4.3. Energy consumption

Comparing with others AOPs in literature, ozonation has the lowest energy consumption, which often represents a major fraction of the operating costs (Milkos, 2018). Ozonation treatment cost-effectiveness was measured through energy consumption considering the ozone generator consumption of 0.015 kW h/g. The costs of ozonation ranged from 0.05 kW h/m³ to 2.3 kW h/m³, corresponding to lowest and highest tested O₃ dose, respectively. According to results previously discussed, the best option for PW ozonation treatment would be applying a dose of 7.8 mg O₃/L as low energy consumption (0.12 kW h/m³) was achieved, alongside with PW toxicity reduction and biodegradability index improvement. Integration of chemical oxidation as PW pretreatment prior subsequent biological process would thus, enhance the efficiency and reduce the treatment time, which will also be reflected in treatment costs. Moreover, ozonation as PW pretreatment will require low oxidant dose compared to complete treatment (complete mineralization) and thus, more feasible to implement offshore. Previous studies have shown that ozonation coupled with biological treatment in an aerobic sequential batch reactor was considered an effective and economic method due to improvement of organic removal efficiency and biodegradability index in oily bilge water (Momani et al., 2011; Uma and Gandhimathi, 2020).

4. Conclusions and future perspectives

Three chemical oxidation methods were compared for PW pretreatment, and different performances were observed. The

electrochemical oxidation of PW was efficient for COD reduction in terms of partial conversion, independent of electrode material and mainly governed by the amount of charge passed through the system. This reveals to be an advantage since EO can be designed using simple cost-effective electrodes for large-scale industrial applications. PW treatment by heat activated persulfate was time consuming and highly dependent on temperature and also initial oxidant dose. Moreover, for both methods BOD analysis based on the developed adapted procedure indicated that high doses might contribute to the generation of oxidation by-products. Among the three chemical oxidation methods tested, ozonation showed to be the most feasible process with low oxidation by-products generation, high oxidation of organics i.e. BTEX. Low ozone doses 3.5 mg O₃/L and 7.8 mg O₃/L decreased more than 70% benzene, alongside with PW toxicity reduction (>70%) and slightly enhanced PW biodegradability. The results underline that ozonation is a promising method to facilitate a subsequent PW biological treatment and improve PW treatment at offshore platforms. It has the potential to bring PW to a quality that meet the requirements in the new future regulation, and prevent long-term exposure risks of toxic chemicals discharge into the sea. Future research should focus on better understand the by-products formation during PW chemical oxidation. Moreover, the physical and chemical properties of PW vary widely, thus PW from different fields could give more insights on ozonation potential as PW treatment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.psep.2022.02.008](https://doi.org/10.1016/j.psep.2022.02.008).

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