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Reducing the environmental impact of offshore H_2S scavenging wastewater via hydrothermal oxidation

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ABSTRACT

The discharge of H_2S scavenging wastewaters, containing spent and unspent scavengers (SUS), into the marine environment is a large contributor to the environmental impact of offshore oil and gas production. Hydrothermal oxidation (HTO) can be a viable method for on-site treatment of the SUS before discharge, but the effect of the process on the ecotoxicity of the effluent has not been investigated so far. The aim of this study was to investigate the potential of the HTO technology in reducing the environmental impact by linking the chemical process design with ecotoxicity reduction. For this, we combined HTO experiments on a SUS sample from an oil and gas platform in the North Sea with whole effluent ecotoxicity evaluation before and after the treatment. The HTO process was carried out under excess of oxygen, for temperatures and pressures in the range 199 to 350°C and 83 to 228 bar, respectively, and for reaction times of 5 to 360 min. Initially, the SUS sample exhibited very high ecotoxicity, which was drastically reduced by the HTO process. More specifically, the ecotoxicity towards bacteria was reduced more than 90% for all HTO conditions, while the reduction in algal toxicity was in the range 48% to 66%, 59% to 86% and 60% to 82% at reaction temperatures of 199°C, 279°C, and 350°C, respectively. Furthermore, this work shows how typical wastewater chemical analyses, such as COD and TOC, and ecotoxicity tests towards different organisms provide complementary information, which should be used in combination to optimize operating conditions of the HTO process.

1. Introduction

Produced water from offshore oil and gas production is one of the largest industrial direct discharges into the marine environment, estimated to 324 million m^3 annually in the North Sea (Karman and Smit, 2019; Neff et al., 2011; Scholten et al., 2000). While the discharge has been associated with detrimental effects on the environment it is a relative dilute stream and diverse in terms of chemical composition, hence difficult to treat. Alternatively, to reduce the overall environmental impact, smaller and more concentrated streams can be identified in offshore oil and gas production and treated prior to discharge. An example of such a stream is the wastewater from the H_2S scavenging of natural gas that results from the injection of aqueous H_2S scavengers aiming to convert the highly toxic and corrosive H_2S to less harmful compounds (Kelland, 2014). The H_2S scavenger is typically based on 1,3,5-hexahydrotriazines (henceforth "triazines"), that are widely used in the field, and particularly water-soluble variants such as 1,3,5-tri-(2--hydroxyethyl)-hexahydro-*S*-triazine (HET, also known as MEA-triazine) (Kelland, 2014; Taylor et al., 2019). Since HET is typically injected in stoichiometric excess, with respect to H_2S, it ends up partly unreacted (unspent scavenger), together with the reaction products (spent scavengers), in the wastewater stream that is separated from the natural gas (Kelland, 2014; Montesantos et al., 2022). In line with the reaction scheme generally accepted in the literature, the main scavenging reaction products that appear in the spent scavenger wastewater are monoethanolamine (MEA) and 5-(2-hydroxyethyl)hexahydro-1,3,5-dithiazine (DTZ) (Bakke et al., 2001; Romero et al., 2021; Taylor and Matherly, 2010). The injection formulation also contains trace amounts of formaldehyde, which is one of the reactants used for HET synthesis (Kelland, 2014). While the H_2S scavenging reaction reduces the operational and occupational challenges associated with H_2S, the environmental impact of the discharge is high, due to persistency and ecotoxicity of the associated compounds. In fact, it has been reported that the discharge associated to H_2S scavenging contribute up to 20% of the overall environmental impact factor (EIF) of North Sea offshore platforms (Reed and Rye, 2011; Stipanicev et al., 2018). In some

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installations of the North Sea, it was estimated that this discharge contributes for more than 10% of the total EIF, while being less than 0.1% in volume of the total produced water. Consequently, it is apparent that the treatment of this relatively small but highly concentrated stream can conveniently provide a significant decrease in the overall environmental impact of discharges associated with offshore oil and gas production.

Hydrothermal oxidation (HTO) of the spent/unspent scavenger (SUS) prior to discharge has recently been suggested as an efficient way to reduce the environmental impact of offshore discharge (Montesantos et al., 2022). Subcritical (i.e., 150-320°C) HTO using air as oxidant, referred industrially as wet air oxidation, is commonly used to remove organic pollutants in different industrial wastewater streams with moderate to high chemical oxygen demand (20-200 g/L COD) (Yousefifar et al., 2017). This process is commonly applied prior to biological treatment to reduce the wastewater toxicity (Kolaczkowski et al., 1999). HTO has minimal energy requirements since after start-up it can be autothermally sustained due to the exothermic oxidation reactions that produce enough heat when the COD exceeds 12–15 g/L (Debellefontaine and Foussard, 2000). In our laboratory activities in connection with offshore oil and gas operations, we have measured values of COD for the SUS in the range 120 to 320 g/L, i.e., well above the threshold for ensuring an autothermal process.

Montesantos et al. (2022) provided a proof-of-concept of the HTO process by testing the technology on a SUS sample at low (200°C) and high temperature (350°C). A substantial reduction of COD was observed with more than 50% reduction after 40 min at 200°C, while at 350°C 85% of COD was removed in 10 min. The possibility of attaining large COD reductions at low reaction times, and the relatively low flow rates of the SUS stream, suggested the feasibility of a small volume HTO unit to be installed offshore, where low footprint and low weight are important constraints. While the removal of COD was pronounced, an extensive analysis of the reaction products revealed C1-C4 carboxylic acids (up to 1.5 g/kg) and small amounts of pyridines and pyrazines (up to 330 mg/kg) in the HTO effluent.

Since the target of the on-site HTO treatment is to drastically reduce the environmental impact of the SUS wastewater discharge, it is deemed necessary to combine the chemical characterization (e.g., COD) to ecotoxicity tests to evaluate the effect of the discharge on the aquatic environment and to link it with the operating parameters of the HTO process. Thus, the aim of this work is to assess the efficiency of HTO in reducing the ecotoxicity of the SUS and to provide a combined basis (i.e., chemical and ecotoxicological) for process design. The HTO study was performed at three temperature levels (199°C, 279°C and 350°C) and for reaction times ranging from 5 to 360 min. The ecotoxicity was assessed using two different species in standardized test setups, covering acute toxicity using luminescence decrease of bacteria (*Aliivibrio fischeri*) after 15 and 30 min of exposure and acute/chronic toxicity using growth inhibition of marine algae (*Skeletonema pseudocostatum*) after 72 h of exposure.

2. Materials and methods

2.1. Materials

The SUS was retrieved from an offshore oil and gas production platform in the North Sea. The sample was collected downstream of two gas and water separators, delivered to our laboratory in June 2021 and stored at 4°C. The HTO effluent samples were also stored at 4°C between experiments and analyses, which took place within a few days after the HTO experiments. The experimental study was completed by April 2022. Oxygen ($O_2 > 99.9\%$) from Air Liquide was used as oxidant for the HTO experiments. The analytical standards dithiazine, (5-(2-hydroxyethyl)hexahydro-1,3,5-dithiazine, CAS number 88891–55-8, $\geq$ 98%) from Toronto Research Chemicals, triazine, (1,3,5-tri-(2-hydroxyethyl)-hexahydro-*S*-triazine, CAS number 4719–04-4, $\geq$ 95%) from Santa Cruz Biotechnology, and monoethanolamine, (CAS number 141-43-5, $\geq$ 99%) from Acros, were used for quantitative gas chromatography (GC), together with 1-propanol (CAS number 71-23-8, $\geq$ 99.5%) and methyl heptadecanoate (CAS number 1731-92-6, $\geq$ 99%) from VWR as internal standards. Diethyl ether (DEE, CAS number 60-29-7, > 99%) from Acros as an extraction solvent and 2-bromo-pyridine (CAS number 109-04-6, > 99%) from VWR as internal standard were used for semi-quantitative gas chromatography with mass spectrometry (GC-MS). Spectroquant Cell tests from Merck were used to quantify the COD (Product number: 114540, 114541, 114555, 101797).

2.2. Hydrothermal oxidation

The hydrothermal oxidation experiments were performed on a high pressure and temperature (HPHT) reactor following a procedure described in detail in a previous work (Montesantos et al., 2022). In short, approximately 20 g of deionized water was precharged into the reactor vessel and, after the vessel was sealed, it was purged and pressurized to 35 bar with O_2. The O_2 pressure was selected to ensure that for all experiments the available O_2 was equal or higher than the initial COD (i.e., COD_0) in the reactor (i.e., 106-145% of COD_0). Consequently, the reactor was heated to the selected reaction temperature and, when that temperature was reached, approximately 30 g of prediluted (approximately twofold dilution with demineralized water) SUS was injected to the reactor. The COD_0 in the reactor was calculated considering the predilution prior to the injection, as well as the further dilution in the reactor due to the precharged water. Henceforth the diluted SUS (i.e., approximately fivefold dilution) is considered the feed of the HTO reactions. In total, 21 HTO experiments were performed at 3 temperatures (199°C ± 1°C, 279°C ± 1°C, 350°C ± 2°C) and 4-5 reaction times (5–360 min). The reaction pressures were 88 bar ± 1 bar, 124 bar ± 7 bar and 215 bar ± 8 bar for the reactions at 199°C, 279°C and 350°C, respectively. To verify reproducibility, duplicate experiments were performed at 199°C and 40 min, 279°C and 10 min, 350°C and 10 min as well as 360 min, while the experiments at 350°C and 40 min were performed in triplicate. When the reaction time was elapsed, the reaction products were ejected through a tap water cooled condenser, into a cold dry trap (gas washing bottle immersed in ice and water), and the collected aqueous effluent was used for analytical characterization and ecotoxicity tests. The reaction conditions for all the experiments are reported in Table S1 in the Supplementary Information.

2.3. Analytical characterization

The analytical characterization of the SUS and the HTO effluent samples was performed utilizing the methodologies reported in a previous work (Montesantos et al., 2022). In short, the composition of the SUS was determined by gas chromatography. An external calibration method with an internal standard was used for HET and MEA utilizing a flame ionization detector, while DTZ was extracted in diethyl ether and quantified on a GC-MS using a similar quantitation methodology. For the COD measurements the Spectroquant cell tests were used in duplicate for all samples. The total carbon (TC) and total inorganic carbon (TIC) were determined on an AnalytikJena multi N/C 2100S analyzer and were used for the calculation of total organic carbon (TOC). Selected HTO effluent samples were qualitatively characterized using solid phase micro-extraction (SPME) GC-MS to identify organic species remaining after the HTO and evaluate their connection to ecotoxicity. The HTO products at 279°C were extracted with DEE and the extract was analyzed with GC-MS to quantify a number of pyridines and pyrazines with 2-bromo pyridine used as internal standard. In addition to the chemical characterization, the density and pH of the SUS and the samples after HTO were measured.

2.4. Ecotoxicity of hydrothermally oxidized H_2S scavenging wastewater

Test kits (ABOATOX, Finland) were used for quantification of

decrease in bacterial luminescence following the ISO 11348-3 standard with modifications (ISO, 2007). Freeze-dried bacteria, *Aliivibrio fischeri* (formerly *Vibrio fischeri*) were reconstituted in 12 mL saltwater solution (2 wt.%) and left for 20 min before the experiment was initiated. Five test concentrations were prepared from the stock solution of the SUS (diluted and undiluted) and from each of the HTO samples obtained at the different reaction temperatures (199, 279 and 350°C) and reaction times (5-360 min), by dilution with the 2% saltwater solution, resulting in a salinity between 2.0% and 3.5%. The salinity was measured using a conductivity meter (Cond 315i, WTW, Xylem Analytics, Germany). The exposure concentrations for the diluted SUS feed were 0.05%, 0.25%, 0.5%, 2.5% and 5% (v/v), while for the undiluted SUS they were 0.01%, 0.05%, 0.1%, 0.5% and 1% (v/v). The used concentrations for the samples treated with HTO were 0.25%, 0.5%, 1%, 2% and 4% (v/v). The stock solutions were prepared in 10 mL measuring vials at a concentration corresponding to twice the test concentration to allow for dilution with the reconstituted bacteria solution. The background luminescence of the 2% saltwater solution was corrected for by measuring 200 μL of the solution in 2 mL glass vials (Thermo Fisher Scientific™). Initial bacterial luminescence was measured by pipetting 100 μL of bacteria solution into 2 mL glass vials (Thermo Fisher Scientific™) and immediately measuring the luminescence using a luminometer (Luminoskan TL Plus, Thermo Labsystems) denoting the luminescence at time 0. Following the luminescence measurement, 100 μL of the double concentrated test solution was added to the bacteria solution yielding the final test concentrations, i.e., 0.05% - 5% (v/v) for the diluted SUS, 0.01% to 1% for the undiluted SUS, and 0.25% - 4% (v/v) for the HTO effluent samples. The experiment was carried out with duplicates for each tested concentration and the controls. Luminescence measurements were repeated after 15 min and 30 min. The tests were considered valid if the parallel determination of the controls did not deviate more than 3% and 30 min exposure to 3.4 mg/L of 3,5-dichlorophenol caused between 20% and 80% decrease in luminescence. A correction factor (f_{kt}) was calculated for control solutions according to ISO 11348-3 to determine the water-dependent decrease in luminescence (Eq. (1)) and for the test to be valid the correction factor should be between 0.6 and 1.8 (ISO, 2007):

$$f_{kt} = \frac{I_{kt}}{I_0} \tag{1}$$

where f_{kt} is the correction factor at time t (15 min or 30 min), I_{kt} is the luminescence at time t (15 min or 30 min) and I_0 is the luminescence at time 0. The relative decrease in luminescence for each sample was calculated according to Eq. (2).

$$Rel_t = 1 - \frac{I_{kt}}{f_{kt} \cdot I_0} \tag{2}$$

where Rel_t is the relative decrease in luminescence at time t (15 min or 30 min), I_{kt} is the luminescence at time t (15 min or 30 min) and I_0 is the luminescence at time 0. The relative decrease in luminescence at 15 min and 30 min was plotted in the statistical software R loaded with the drc-package and used to estimate concentration-response curves, EC-values and their corresponding 95% confidence intervals using a log-normal function (Ritz and Streibig, 2005).

The algal growth inhibition test was conducted with marine algae *Skeletonema pseudocostatum* (formerly *S. costatum*) obtained from the Norwegian Institute for Water Research, Oslo, Norway (NIVA-BAC 1). It was grown continuously in 100 mL bluecap bottles containing filtered (pore size 0.45 μm, Whatman®, Merck Life Science) natural seawater (obtained from DTU Aqua, Technical University of Denmark) enriched with nutrients following ISO 10253 (ISO, 2016). The medium was continuously bubbled with atmospheric air to avoid sedimentation of the algae and to allow for CO_2 transfer to the aqueous phase. The bottles were illuminated from the side with fluorescent tubes (30W/33; Philips Amsterdam, The Netherlands) with an intensity of 63 μmol m^{-2} s^{-1} ± 2 μmol m^{-2} s^{-1} measured by LI-189 Quantum/Radiometer/Photometer (LI-COR, Nebraska, USA) at a temperature of 20°C ± 2°C.

The 72 h tests were conducted with modifications of the ISO 10253 standard for marine algal growth inhibition test with *Skeletonema* sp. and *Phaeodactylum tricornutum* (ISO, 2016). A range of test concentrations was prepared from stock solutions from the three reaction temperatures (199°C, 279°C and 350°C) and the reaction times (5–360 min) diluted in ISO 10253 algal media based on synthetic seawater. These were then inoculated with the appropriate amount of exponentially growing algal culture to obtain an initial final density of $2{\cdot}10^4$ cells/mL. The cell density was measured by a coulter counter (Beckman Multisizer™ 3, Indianapolis, USA). In practice, 250 μL of an exponentially growing algal culture of $2{\cdot}10^6$ cells/mL was added to 25 mL of each exposure concentration and 4 mL was transferred to 20 mL scintillation vials ($n = 3$), and placed on an orbital shaker (IKA® Schüttler MTS 4) mounted with a rack and continuously illuminated from below with fluorescent tubes (30 W/33; Philips, Amsterdam, The Netherlands) with an intensity of 81 μmol m^{-2} s^{-1} ± 7 μmol m^{-2} s^{-1} measured by LI-189 Quantum/Radiometer/Photometer (LI-COR, Nebraska, USA). Due to the turbidity of some HTO samples (i.e., 5–10 min at 279°C and 5–40 min, at 350°C) a preliminary test for shading of light interfering with ecotoxicity was carried out. However, as the average light path in the media was kept low by testing in 20 mL vials with only 4 mL algal suspension illuminated from below and the relatively high dilution factor used in the setup, no interference with ecotoxicity was observed due to shading.

The concentrations tested for the diluted SUS were 0.0125%, 0.025%, 0.075%, 0.125% and 0.25% (v/v), while for the undiluted SUS they were 0.001%, 0.005%, 0.01%, 0.05% and 0.1% (v/v). The used concentrations for the samples treated with HTO were 0.05%, 0.1%, 0.3%, 0.5% and 1% (v/v). For each concentration three replicates were made, and six replicates were used for the control group. All samples were incubated as described above, and validity criteria stated in ISO 10253 were met for all tests, i.e., control growth rate of minimum 0.9 day^{-1} and a maximum change in pH of 1 unit during the 72 h of incubation. Samples of 0.4 mL were taken at times 0 h and 72 h and extracted with 1.6 mL acetone. The algal growth rates were calculated based on the *in vitro* fluorescence of algal pigments as a surrogate for biomass as described by Mayer et al. (1997). The fluorescence was 430 nm and 670 nm for excitation and emission wavelengths. Background fluorescence was corrected by measuring a blank sample containing the medium and acetone. To avoid interference with precipitates the supernatant of each sample was gently transferred to a new vial before fluorescence measurement. The algal growth rates were calculated assuming exponential growth following Eq. (3).

$$\mu = \frac{\ln N_n - \ln N_0}{t_d} \tag{3}$$

where μ is the growth rate (d^{-1}), N_0 is the initial biomass, N_n is the final biomass and t_d is the length of the test period (d). Additionally, the inhibition was calculated as the growth rate of the control related to the growth rate in each individual exposure following Eq. (4).

$$I_i = \left(1 - \frac{\mu_i}{\mu_c}\right) * 100 \tag{4}$$

where I_i is the percentage inhibition of growth for concentration i, and μ_i is the mean growth rate for concentration i and μ_c is the mean growth rate for the control. Growth inhibition based on growth rates was plotted in the statistical software R loaded with the drc-package and used to estimate concentration-response curves, EC-values and their corresponding 95% confidence intervals using a log-normal function (Ritz and Streibig, 2005).

3. Results and discussion

3.1. Characterization of the spent and unspent scavengers

The physicochemical properties of the as received SUS (i.e., undiluted) are reported in Table 1.

The COD and TOC values are around 25–30% higher than the values of the spent and unspent H_2S scavengers collected in a previous sampling campaign from the same offshore installation (Montesantos et al., 2022). This reflects the variability in the concentration of the organic species in the SUS wastewaters at offshore oil and gas production platforms, which can be induced by variations of natural gas flowrate and composition over time, variations in the mass fraction of HET in different batches of the commercial scavenging product, as well as by non-automatic regulation of the scavenger injection system. The concentration of unreacted HET is quite high in this sample, which indicates a large excess of injected triazine relative to the H_2S content in the natural gas in the period preceding the wastewater sampling. The SUS sample has a slightly higher density and pH compared to the values of the previous SUS sample (i.e., 1049 kg/m^3 vs. 1042 kg/m^3 and pH 9.4 vs. 8.9), which is in line with a higher mass fraction of unreacted HET. The ecotoxicity of the SUS is significant as very low concentrations of SUS resulted in 50% inhibition (EC_{50}) for the tested bacteria and algae. In fact, the two EC_{50} values shown in Table 1 indicate that when the SUS sample was diluted 4167 or 23256 times it still inhibited 50% of the bacterial luminescence and algal growth, respectively. This is markedly higher than the average dilution required for produced water streams originating from 25 platforms in the North Sea to reach 50% inhibition (i.e., 14 times dilution for algae and 9.1 times dilution for bacteria) (de Vries and Jak, 2018).

3.2. Removal of COD and TOC

In Fig. 1a and Fig. 1b, the COD and TOC reduction is reported, respectively, as a function of the reaction time.

The COD_0 was calculated to 61 g/kg ± 2 g/kg and the TOC_0 to 17 g/kg ± 1 g/kg using the measured COD of the undiluted SUS in Table 1 and the approximately fivefold dilution in the HTO experiments described in Section 2.2. Overall, a significant reduction of both COD and TOC is observed for all reaction temperatures. As can be seen from Fig. 1, for both the COD and TOC removal a marked difference in the rate of removal of COD and TOC can be observed between the reactions at 199°C and the reactions at the higher temperature levels. This is in line with previous observations regarding the reaction rate constant at 350°C being 70 times higher than at 200°C (Montesantos et al., 2022). On the other hand, the difference between the reactions at 279°C and 350°C is not apparent.

An additional observation is that most of the TOC and COD at the higher temperatures (i.e., 279°C and 350°C) was removed during the first 5–10 min of the treatments. Finally, the experiments at 350°C and 360 min (not shown in Fig. 1 for visual convenience) show that in this set of experiments a residual COD (6 g/kg) and TOC (3 g/kg) remains even after long reaction times. While this could be interpreted as a presence of recalcitrant organic compounds, it is most likely caused by the chemical reactions slowing down substantially due to the depletion of oxygen in the reactor. To confirm this hypothesis, an experiment was performed at 350°C with a reaction time of 40 min and with an amount of oxygen being 280% of COD_0. This resulted in residual concentrations of 0.5 g/kg COD and 0.4 g/kg TOC, which were 13 and 10 times lower than the corresponding values for the experiments shown in Fig. 1, which were obtained with an amount of oxygen being 136% of COD_0. These improved reductions are in line with previously published data and clearly show that the process at high temperature, when given enough time and oxygen, can proceed to almost complete COD and TOC removal (Montesantos et al., 2022). However, it is observed that the extent of excess of oxygen influences the reaction kinetics as the rate of oxidation changes if 36% or 180% O_2 excess is used.

To assess the state of oxidation, the literature suggests combining the TOC and COD in ways that can provide information about the removal of COD due to partial or complete oxidation (Jochimsen and Jekel, 1997; Mantzavinos et al., 2000). The fraction of the total COD removal caused by partial oxidation reactions can be visualized by using Eq. (5).

$$\varepsilon = \frac{COD_0\left(\frac{TOC}{TOC_0}\right) - COD}{COD_0 - COD} \quad (5)$$

where COD_0 and COD are the chemical oxygen demands at the initial time and at the generic time, respectively, while TOC_0 and TOC are the analogous quantities for the total organic carbon. The calculated ε values for the three reaction temperatures and the reaction time range 5-40 min are reported in Fig. 2.

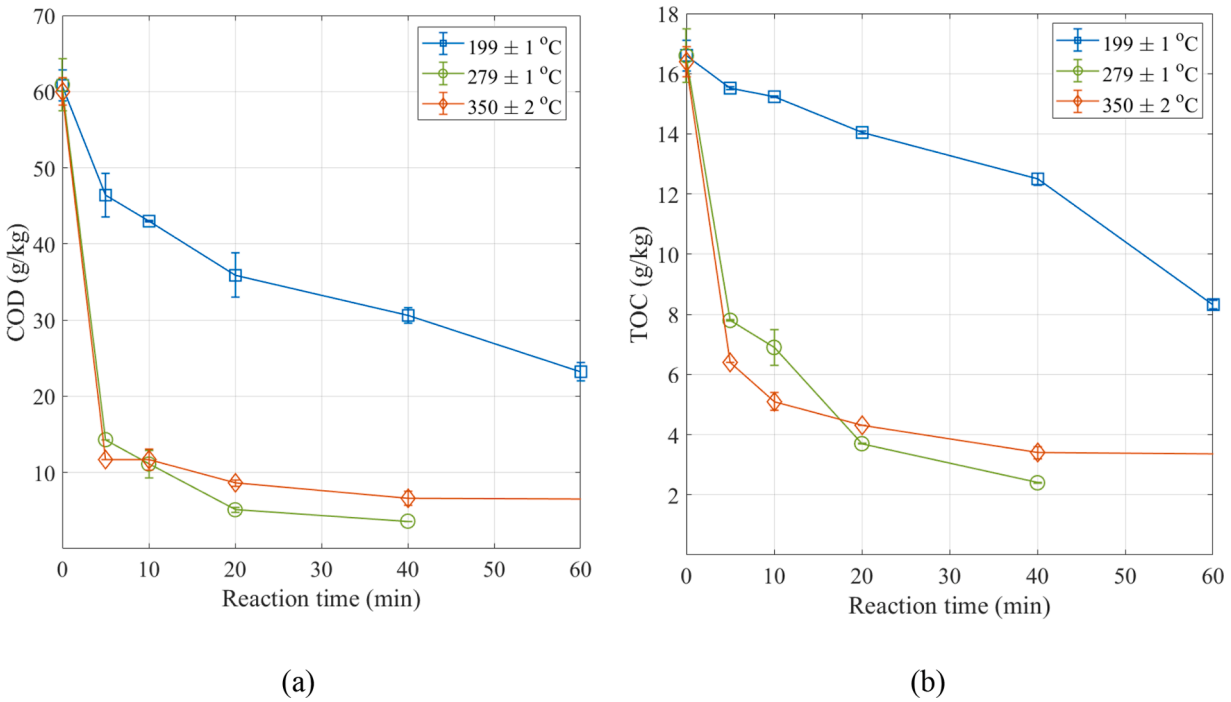
As can be seen from Figs. 1 and 2, for the lower temperature (199°C) the COD removal is limited and mainly due to partial oxidation reactions of the feed compounds to intermediates and products, while the TOC is not significantly reduced. At the two higher temperatures the COD is mainly removed by complete mineralization of the SUS constituents (ε values between 0.1 and 0.3), which implies the formation of CO_2, H_2O, N_2 and inorganic salts (i.e., SO_4^{2-} and NH_4^+) (Montesantos et al., 2022).

3.3. Chemical composition of the hydrothermal oxidation effluent

Due to the observation of residual COD and TOC in the HTO samples even at high temperatures and long reaction times (i.e., 350°C and 360 min), the chemical composition of the HTO effluent was investigated. Qualitative SPME GC-MS showed several organic water-soluble compounds produced during the reaction, including pyrazine, pyridine, quinoline, and some of their alkyl derivatives. An example chromatogram of the oxidation products at 350°C and 360 min is reported in Fig. 3a, with some of the chemical structures corresponding to the major peaks. These appear to be intermediate oxidation products of HET and DTZ, as they all contain 1-2 nitrogen atoms while no HET, DTZ or MEA were detected in any of the HTO effluent samples. Although the chemical classes identified are in line with the data published by Montesantos et al. (2022), the number of organic species observed in this work was

Table 1
Physical, chemical, and ecotoxicological characterization of spent/unspent scavenger wastewater (undiluted SUS). Errors are the standard deviation of duplicate or triplicate measurements and the ranges for ecotoxicity are the 95% confidence intervals. Ecotoxicity values are given as percent by volume of sample required to inhibit 50% of luminescence or growth for bacteria and algae, respectively. HET: MEA-triazine; MEA: monoethanolamine; DTZ: dithiazine, COD: chemical oxygen demand; TOC: Total organic carbon; TC: Total carbon: TIC: Total inorganic carbon.

Physical and chemical parameters		Specific chemicals and ecotoxicity	
COD (g/kg)	305 ± 1	HET (g/kg)	131 ± 21
TC (g/kg)	87 ± 1	MEA (g/kg)	60 ± 16
TIC (g/kg)	4 ± 1	DTZ (g/kg)	25 ± 1
TOC (g/kg)	83 ± 1	EC_{50} *A. fischeri* (%)	0.024 [0.015-0.032]
pH at 21°C	9.4	EC_{50} *S. pseudocostatum* (%)	0.0043 [0.004-0.0046]
Density at 20°C (kg/m^3)	1049 ± 1		



(a) (b)

Fig. 1. Reduction in COD (a) and TOC (b) with reaction time for three different reaction temperatures. The error bars show the standard deviation of duplicate COD and triplicate TOC measurements for single or duplicate oxidation experiments.

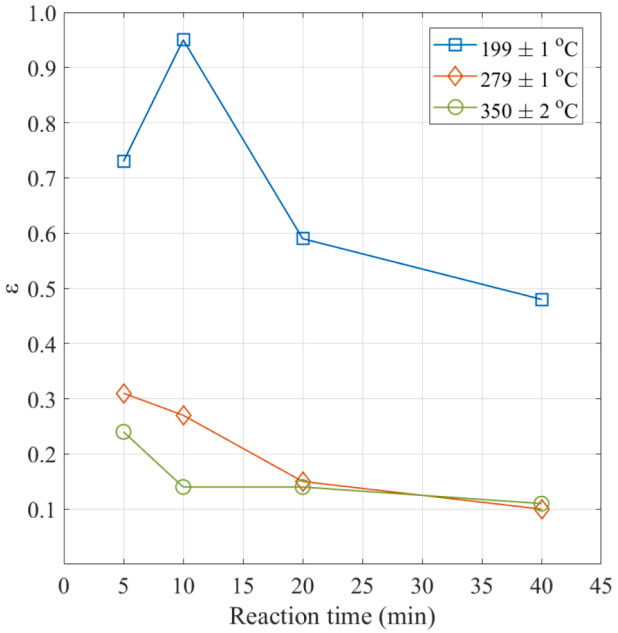


Fig. 2. Fraction of COD removed by partial oxidation of SUS at the different reaction temperatures.

larger. For example, Fig. 3b shows the chromatograms (normalized to the peak with the largest height) of two HTO experiments at 350°C after 40 min with two different O_2 levels (low: 136% of COD_0 and high: 280% of COD_0). In line with the observation regarding COD and TOC (Section 3.2), a lower excess of oxidant leads to a lower extent of the oxidation reactions, as reflected by the chromatogram referred to high oxygen excess, which is devoid of most peaks.

The fact that the peak of pyridine is the only significant one remaining even at long times and with high excess of oxygen is an indication that it is a relatively slow reacting N-compound in the SUS oxidation products. However, it should be noted that this comparison is qualitative, and it was shown in a previous work that at 350°C and high oxygen excess, the pyridine can be oxidized down to only a few mg/kg (Montesantos et al., 2022). This is reflected by the COD reduction achieved in the two experiments of Fig. 3b, that was 90% and 98% for the low and high O_2 excess, respectively. The latter value is in line with the published data on a different SUS, indicating that the HTO process is not very sensitive towards the initial mass fraction of HET, MEA and DTZ (Montesantos et al., 2022). In general, hydrothermal oxidation is robust towards moderate concentration changes of the feed, even though the monitoring of the COD changes is essential for continuous operation, to efficiently control the process and avoid issues like runaway reaction temperatures or unsatisfactory extent of oxidation (Bhargava et al., 2006).

3.4. Ecotoxicity of spent and unspent H_2S scavengers before and after hydrothermal oxidation

Reference tests with 3,5-dichlorophenol were carried out for *S. pseudocostatum* yielding EC_{50} of 1.6 mg/L (95% confidence interval [0.87-2.3]). For *A. fischeri* an exposure to 3.4 mg/L 3,5-dichlorophenol for 30 min resulted in a decrease in luminescence by 28%. Both values were within the expected range for the substance and test organisms according to the international testing guidelines (ISO, 2016, 2007). Table 2 shows the ecotoxicity of whole samples of HTO effluents when tested in standardized bacterial and algal tests. The 50% effect concentration (EC_{50}) for the diluted SUS (i.e., the reactor feed) prior to HTO was 0.12% [0.075-0.16] and 0.022% [0.02-0.023] for bacteria and algae, respectively.

Fig. 4 shows the decrease in ecotoxicity, expressed as $\frac{1}{EC50}$, relatively to the value of the ecotoxicity at the initial time of the reaction $\left(\frac{1}{EC50_0}\right)$, while the EC_{50} data are reported in Table 2. As can be seen, for the bacteria a reaction time dependent decrease in ecotoxicity is observed for both the low (199°C) and medium (279°C) reaction temperatures, resulting in a complete removal of ecotoxicity within the tested concentration range (EC_{50} > 20%) after 60 min and 40 min of reaction time,

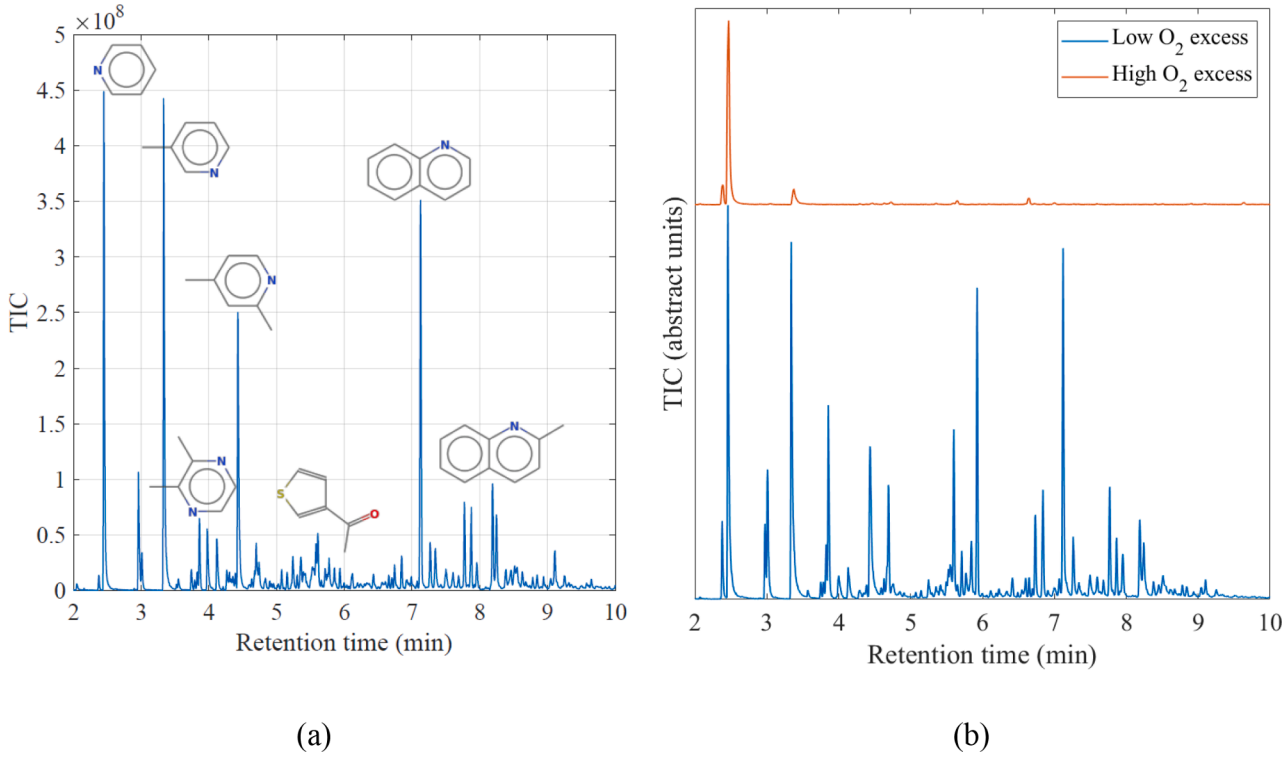


Fig. 3. Solid phase micro extraction GC-MS chromatogram of HTO products at (a) 350°C, 360 min and oxygen 136% of COD_0, and (b) comparison between the HTO product at 350°C and 40 min with low (blue, 136% of COD_0) and high (red, 280% of COD_0) O_2 excess.

Table 2
50% effect concentrations (EC50) shown as percent by volume for bacteria and algae after 30 min and 72 h exposure, respectively, for HTO effluents at different reaction temperatures (°C) and reaction times (min). The numbers in square brackets are the 95% confidence interval of the effect concentration fitted with a log-normal function. The EC_{50} values for the diluted SUS (i.e., the reactor feed) was 0.12% [0.075-0.16] and 0.022% [0.02-0.023] for bacteria and algae, respectively. N/A: Not tested. *Highest tested concentration.

Reaction	Bacteria (*Aliivibrio fischeri*)			Algae (*Skeletonema pseudocostatum*)		
Temp. (°C)	199 ± 1	279 ± 1	350 ± 2	199 ± 1	279 ± 1	350 ± 2
Pressure (bar) / t (min)	88 ± 1	124 ± 7	215 ± 8	88 ± 1	124 ± 7	215 ± 8
5	2.8 [2.2-3.4]	2.2 [2.1-2.4]	1.2 [1.1-1.3]	0.041 [0.037-0.045]	0.093 [0.071-0.11]	0.085 [0.079-0.091]
10	3.1 [2.6-3.7]	3.0 [2.8-3.2]	1.4 [1.2-1.6]	0.059 [0.049-0.069]	0.15 [0.12-0.17]	0.054 [0.050-0.058]
20	3.9 [3.3-4.5]	11 [3.5-19]	>20*	0.064 [0.054-0.074]	0.055 [0.037-0.073]	0.093 [0.079-0.11]
40	3.7 [3.3-4.0]	>20*	4.4 [3.6-5.3]	0.059 [0.042-0.076]	0.052 [0.044-0.06]	0.12 [0.07-0.16]
60	>20*	N/A	N/A	0.057 [0.037-0.076]	N/A	N/A
360	N/A	N/A	2.2 [1.9-2.6]	N/A	N/A	0.062 [0.051-0.073]

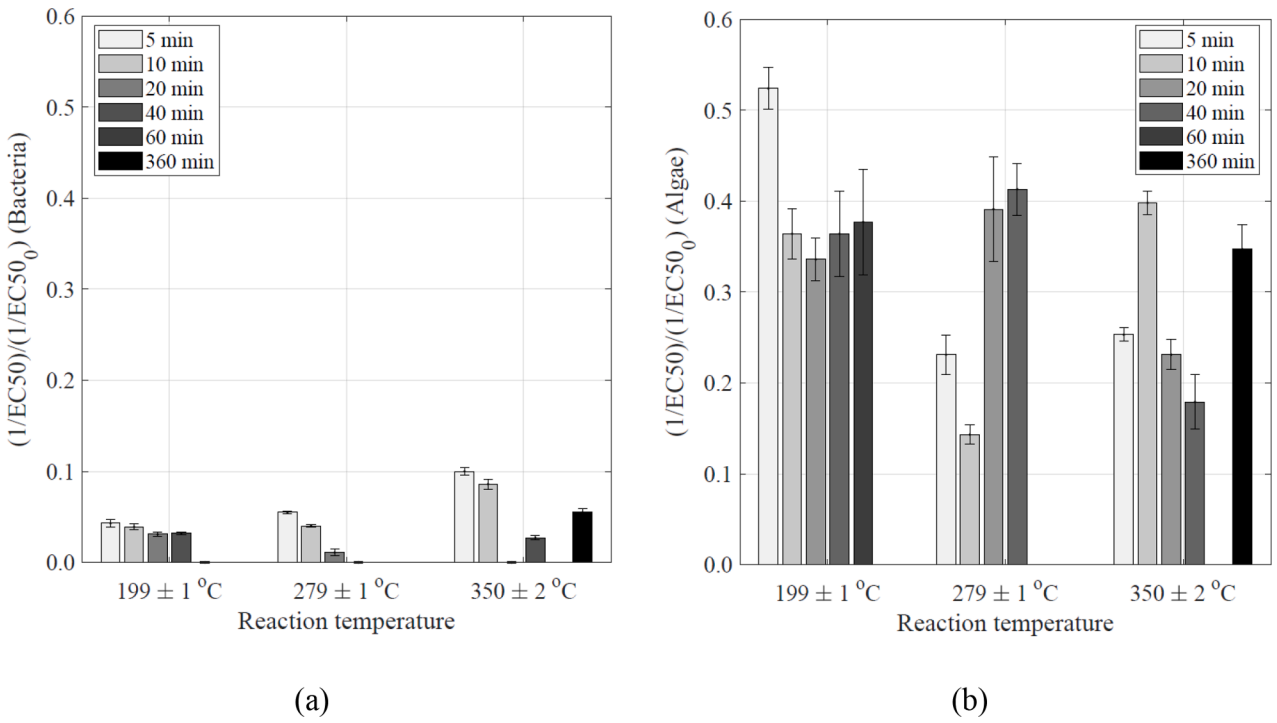


Fig. 4. Relative ecotoxicity reduction of the HTO effluent with respect to the diluted SUS (i.e., HTO reactor feed) at different reaction temperatures. Data for reaction times 5 to 360 min are shown for tests with (a) bacteria (*Aliivibrio fischeri*) and (b) algae (*Skeletonema pseudocostatum*).

respectively (Fig. 4a). At the highest temperature (350°C) a complete removal of ecotoxicity is observed after 20 min of reaction time. However, increases in ecotoxicity are observed for longer reaction times of 40 min and 360 min, resulting in EC_{50} values of 4.4% [3.6-5.3] and 2.2% [1.9-2.6], respectively. Consequently, the results suggest that optimizing the HTO reaction times around 20 min, 40 min and 60 min for high, medium, and low temperatures, respectively, would give the highest decrease in ecotoxicity for the bacteria (*A. fischeri*). The increasing ecotoxicity at longer treatment times does not have a clear explanation but it is probably related to the low unreacted oxygen in the reactor, as mentioned previously. This is observed by the comparison of the HTO experiments performed at 40 min and 350°C, with high O_2 excess (i.e., 280% of COD_0) that resulted in EC_{50} values of 0.11% and 9.4% for algae and bacteria respectively, compared to EC_{50} values of 0.059% and 3.7% (Table 2) for the oxidation at the same temperature and reaction time with low oxygen excess (i.e., 136% of COD_0).

Considering literature EC_{50} data for pyridine and applying the dilution factor required to reach 50% inhibition at the largest mass fraction of pyridine observed at 279°C and 20 min (Table S2), the measured pyridine only accounts for approximately 4% of the observed effect expressed as toxic units (here defined as 100/EC50) (Liu et al., 1998). Even when including the toxic units of all chemical parameters (NH_4^+, NO_3^-, SO_4^{2-}, formic acid, acetic acid, succinic acid, pyrazines and pyridines) in the present and the previous work on HTO of SUS (Montesantos et al., 2022), the sum of toxic units still accounts for $< 10\%$ of the observed ecotoxic response. The relatively low accountable contribution is common for complex effluents unless the response can be associated with few highly toxic compounds driving the response (Baun et al., 2004).

The lack of causality is also highlighted by the decrease in COD (Fig. 1) not directly reflecting the decrease in ecotoxicity (Fig. 4a) for the bacteria. For example, the oxidation at 199°C yields a decrease in COD of 61% after 60 min reaction time, while the corresponding decrease in ecotoxicity of the bacteria is complete within the tested concentration range. While full chemical characterization of samples is practically unfeasible, these results highlight the complementary use of biological and chemical assessment to better understand the response and optimization parameters when working with complex reactive processes and matrices in order not to overlook possible dependencies.

The algal growth inhibition test showed a reaction time dependent decrease in ecotoxicity for 5 min and 10 min at 199°C resulting in 48% and 64% removal of ecotoxicity (here defined as 1/EC50 and reported in Fig. 4), respectively. At reaction times >10 min there was no further statistically significant decrease in ecotoxicity resulting in an average EC_{50} value for the remaining time points of 0.06% ± 0.003% (Table 2). A similar trend was observed for the HTO at 279°C, with a respective ecotoxicity mitigation of 77% and 86% compared to the diluted SUS (Fig. 4b). After 20 min HTO, the ecotoxicity increased to levels similar to ≥10 min reaction at 199°C. The increase in ecotoxicity after 20 min could be due to formation of relatively toxic compounds such as formaldehyde, caused by triazine degradation, and pyridines, produced in the partial oxidation process, at concentrations which can contribute to growth inhibition of algae.

At the reaction temperature of 350°C a decrease in ecotoxicity of 75% after 5 min of treatment was observed. An apparent increase in ecotoxicity was observed after 10 min, following a decrease again after 20 min (Table 2 and Fig. 4b). A previous work (Montesantos et al., 2022) showed that the mass fraction of pyridines exhibits a local maximum for a reaction time of 10 min at 350°C, and this could contribute to the observed local maximum in ecotoxicity. Beyond 10 min there is a time-dependent decrease in ecotoxicity resulting in 82% removal of ecotoxicity after 40 min of treatment. After 360 min of treatment, there is a 94% increase in ecotoxicity compared to the 40 min treatment, which has no clear explanation, and may be connected to undesirable non-oxidation hydrothermal reactions occurring due to the low residual amount of oxygen in the reactor. The abovementioned effect of the excess of oxygen was tested for the experiments at 350°C and 40 min for both bacteria and algae, leading to a 61% and 46% reduction of ecotoxicity, respectively, for the high O_2 excess (280% of COD_0) experiment compared to the low O_2 excess (136% of COD_0). It has to be remarked that, though there is a clear reduction of ecotoxicity compared to the feed in all cases, the local variations after 10 min of reaction times are

not always statistically significant when considering 95% confidence intervals. The trends of the ecotoxicity during the first five minutes of reaction, however, qualitatively aligns with the variations of the chemical parameters (COD, TOC), exhibiting marked decreases in both cases.

Independently of reaction time and temperature, the algal test showed higher sensitivity than the bacterial test. In general, the chronic endpoint of the algae is more susceptible to be impacted by compositional changes in the media than the acute response of the bacteria. Consequently, the matrix itself has a lower threshold for a response to occur, which could result in small variations in, e.g., pyridine to be expressed as a response. This type of effects is rather difficult to quantify with a relatively high complex interaction between the chemical composition and biological response. Therefore, it is important to stress that the approaches (chemical and biological) should be used in a complementary way for better optimization of the process parameters, such as the reaction time, the reaction temperature, and the O_2 supply. However, it is key to highlight that chemical parameters such as COD and TOC are inherently contributing to the environmental impact thus a reduction of those is in itself beneficial. The two species used in this study should only be used as indicators for relative decreases in ecotoxicity and results of these tests do not necessarily reflect effects in the marine environment. Thus, for further assessment of the environmental impact in terms of marine ecotoxicity a broader range of tests and organisms is required, preferably covering mutagenicity and chronic endpoints. Inferring ecotoxicity from standard chemical parameters (e.g., COD, TOC) should be done with caution. As shown in this study, while large COD/TOC reductions generally correspond to ecotoxicity reductions, when observing the data in further detail it can be seen that the ecotoxicity trends may present remarkable differences from the trends in COD and TOC, which can lead to different choices for the optimal design parameters for the reactor. Additionally, unless highly toxic components are present in the samples, chemical analysis will be insufficient to fully describe the ecotoxic effect of a relatively complex mixture such as the SUS and its HTO products. In such cases, the complementary use of specific chemical analyses and ecotoxicity testing of whole samples is recommended.

4. Conclusions

This study shows that hydrothermal oxidation significantly reduces the environmental impact of spent/unspent H_2S scavengers (SUS), based on large COD and TOC reductions together with reduction of ecotoxicity on two test species. Specifically, the ecotoxicity towards bacteria (*Aliivibrio fischeri*) was reduced for all reaction conditions by more than 90% compared to the reactor feed (i.e., diluted SUS) and reached full mitigation, within the tested concentration range, for reaction times in the range 20 to 60 min, with optimal reactions times decreasing with the reaction temperature. In addition, the ecotoxicity reduction using algae (*Skeletonema pseudocostatum*) as test organisms was found to range between 48–66%, 59–86% and 60–82% for the oxidation reaction temperatures of 199°C, 279°C, and 350°C, respectively.

Furthermore, this work shows that the identification of optimal process parameters (e.g., temperature, oxygen supply, reaction time) for the design of the hydrothermal oxidation process should be based on a combination of chemical (e.g., COD) and ecotoxicity analysis on multiple organisms, rather than based on COD only.

These results provide offshore oil and gas operators with a solid foundation for designing the hydrothermal oxidation process as an on-site treatment method for the SUS wastewater before discharge and for optimizing operational parameters to reduce ecotoxicity. In addition, this work opens further research towards better understanding of the compositional effects of SUS wastewaters as well as introducing the complementary use of specific chemical analyses and whole sample ecotoxicity testing.

CRediT authorship contribution statement

Nikolaos Montesantos: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Validation, Writing – original draft, Writing – review & editing. **Lars M. Skjolding:** Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Validation, Writing – original draft, Writing – review & editing. **Anders Baun:** Writing – review & editing, Supervision. **Jens Muff:** Conceptualization, Writing – review & editing, Funding acquisition, Supervision. **Marco Maschietti:** Conceptualization, Methodology, Writing – review & editing, Funding acquisition, Project administration, Supervision.

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.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.119507.

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