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Coupling membrane processes with wet air oxidation for the remediation of industrial effluents

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ABSTRACT

Membrane processes (ultrafiltration, membrane bioreactor, reverse osmosis) are relevant for the remediation of wastewater as they generate large volumes of high-quality permeate. However, the remaining concentrates are highly polluted and require further treatment. Membrane concentrates are sufficiently concentrated to undergo a highly efficient wet air oxidation treatment to degrade refractory molecules. Wet air oxidation was performed on five industrial membrane concentrates with varying organic pollutants: bilge wastewater, landfill leachates, a complex industrial effluent, pharmaceutical sludge and dairy wastewater. The results showed three categories: (i) a low effect of the anoxic heating period and significant effect of oxidation duration, (ii) a significant effect of both the anoxic heating period and duration and (iii) an outstanding effect of the anoxic heating period and low effect of oxidation duration. The best removals were achieved at 300 °C, with total organic carbon removals between 75 and 98% and chemical oxygen demand removals between 82 and 99%, along with complete removal of fluorescent footprints. The coupling of membrane processes and wet air oxidation was proven to be robust and flexible for a wide variety of membrane processes and pollutants. A mass balance on the treatment path, including membrane permeate and wet air oxidation outlet, was calculated to assess discharge feasibility. This research demonstrates the potential of the hybrid process for effectively treating membrane concentrates and generating a safer outlet.

1. Introduction

In recent years, the combination of industrial development and demographic growth has led to an increase in the generation of wastewater all over the world. Industries exert pressure on the water resource through water withdrawals and the discharge of effluents. Industrial water withdrawal represented 69% of the total water withdrawal in France in 2018, and the uptake differs between the types of industries [1]. The resulting wastewaters often contain a wide range of pollutants, including organic and inorganic compounds, which can be harmful to the ecosystem and human health, posing challenges for their effective treatment while ensuring compliance with regulation. Conventional processes based on biological or physicochemical processes often face limitations for the complete removal of organic pollutants, resulting in concerns about energy consumption, operational costs and the generation of by-products and sludge. In response to these challenges,

membrane processes have been considered for a wide range of applications as they offer interesting perspectives depending on the type and size of pollutants and allow high retention. Indeed, ultrafiltration (UF), reverse osmosis (RO) and membrane bioreactor (MBR) have been successfully applied in industries as treatment processes due to their high separation selectivity, continuous automatic operation, compactness, low energy consumption and production of permeate in compliance with discharge regulations. However, while generating large volumes of permeate with an outstanding quality, membrane processes (UF and RO) suffer from two major drawbacks: (i) membrane fouling, which can be minimized with wastewater pre-treatment and mitigated by physical or chemical cleanings, and (ii) the generation of polluted concentrates that require further treatments. Recent studies have also focused on mitigating membrane fouling through sludge granulation and dynamic scouring in MBR and led to improved filtration performance [2,3]. Depending on the quality of the concentrates, different disposal options

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are usually considered, such as a discharge to a wastewater treatment plant, evaporation or incineration.

In this context, the integration of membrane processes with the wet air oxidation (WAO) process presents a novel and promising treatment path for efficiently treating membrane concentrates of industrial effluents. WAO, with or without catalyst, seems an attractive technology that has been proven suitable for the treatment of medium–high concentrated refractory wastewater, as in the case of refinery spent caustic, animal by-products, residual sludge (i.e., Athos®) [4]. It is defined as an exothermic hydrothermal oxidation reaction in the aqueous phase under elevated pressure and temperature, where dissolved oxygen reacts with organic pollution. Temperature, pressure and chemical oxygen demand (COD) concentration ranges of this process are respectively from 125 to 300 °C, 0.5 to 20 MPa and 10 to 100 gO₂·L⁻¹ [5]. Its specific concentration range often aligns well with the characteristics of membrane concentrates, making autothermic WAO possible. Indeed, within this range, the heat needed for the process could be supplied by the exothermicity of the reaction. Beneath 10 gO₂·L⁻¹, advanced oxidation processes are more adapted since exothermic heat during WAO is insufficient to maintain the process temperature, leading to high energy consumption. Above 100 gO₂·L⁻¹, incineration is best suited as WAO's consumption of oxidant is high, leading to high compression costs [5,6]. WAO can achieve high removals and improve biodegradability of refractory compounds and enables water recovery at a lower energy cost and reduced air emissions (e.g., dioxins, furans). Decomposition products are mainly CO₂ in the gaseous phase and water and low molecular weight compounds (short chain fatty acids) in the liquid phase. Two main stages occur in WAO: a first physical stage where oxygen transfers from the gaseous phase to the liquid phase followed by a chemical stage oxidation reaction, initiated with free-radical intermediates from the dissolved oxygen and the dissolved organic matter. The choice of temperature, pressure and pH, among other factors affects removal rates and their effects have been reviewed [7–9].

The framework of this study is to evaluate the global performance of treatment path coupling membrane processes with WAO to treat efficiently polluted industrial effluents. This treatment path is poorly reported in literature though the concentration step could be beneficial to the WAO process. Indeed, by concentrating sufficiently the pollution using membrane processes, autothermic WAO is made possible, and polluted membrane concentrates are managed. Remaining effluents produced by the treatment path are easier to discharge as the pollution has been reduced by the WAO process. Pinchai et al. [10] focused their study on the treatment of three synthetic bio-refractory membrane concentrates by WAO (representing pharmaceutical wastewater, bilge wastewater and gray wastewater) after membrane process and reported removal rates above 80% at 300 °C and 15 MPa. Two other studies on dye waste and paper mills showed respective removals of 97% and 80% along with an increase of biodegradability [11,12]. The focus and the innovative part of the present study was set on strategic and real industrial effluents with various pollutants, flow rates and pollution concentrations such as bilge wastewater, landfill leachates, pharmaceutical and dairy effluents. These effluents are known to be produced in large flows and are also concentrated in pollutants, including recalcitrant ones [13–16]. Bilge wastewater is an oily wastewater generated aboard naval and commercial vessels and contains hydrocarbons, metals, detergents, fuels... [17]. During offshore crossing, bilge wastewater is collected and stored for further treatment onshore. UF membrane (300 kDa) could retain 97.7% of hydrocarbons and around 86.3% of oil present in bilge wastewater [17,18]. Landfill leachate is a liquid effluent generated by the percolation of rainwater (i.e., dependent of rainfall) through solid waste disposed in landfills, and waste degradation residues. Its chemical composition can be affected by many factors including the type of waste, weather, landfill age, and a wide range of hazardous compounds have already been identified, such as organic refractory pollutants (humic and fulvic acids), salts, heavy metals and inorganic pollutants [19]. The WAO treatment of landfill leachates RO concentrates has been studied in

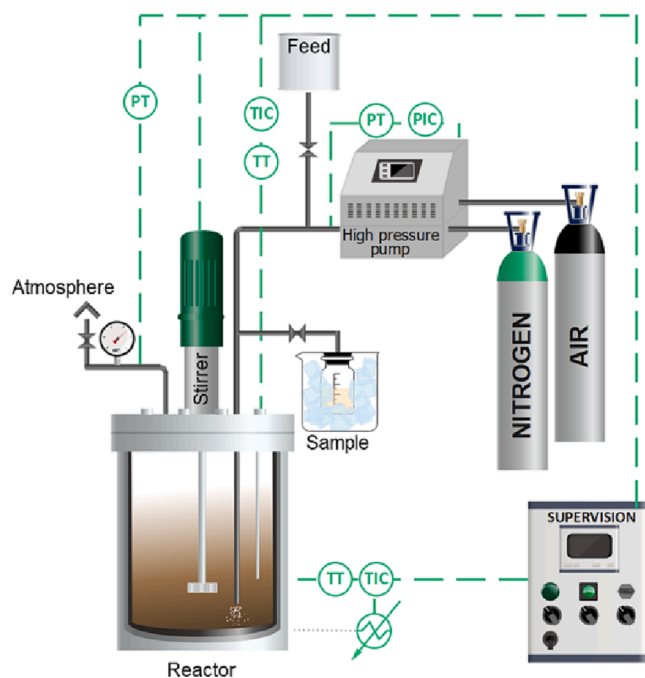


Fig. 1. Schematic diagram of batch WAO unit (TIC, PIC, temperature, pressure indicator and controller; TT, PT, temperature and pressure transmitter).

previous work [20]. Regarding landfill leachate treatment, RO was effective for retentions higher than 98% of heavy metals, COD and salts [15]. In the case of pharmaceutical industries, wastewater is generated during manufacturing processes, and can contain spent solvents, refractory organic pollutants, pharmaceutical residues and salts [21]. For the treatment of pharmaceutical wastewater, the use of RO led to removals of COD higher than 98% [22]. In some cases, MBR achieved removals between 98 and 100% of the biochemical oxygen demand along with an average removal of 95% of the COD [23]. Lastly, for dairy wastewater, RO is a common process to reduce the volume of pollution where water recovery of RO can be above 95% [24]. However, concentrates are highly concentrated in protein, lactose, fat, ashes and chemicals from membrane cleaning steps [16]. When dairy concentrates are chemical free, they may be valorized as animal feed [25]. To follow up the performance of WAO on such industrial membrane concentrates, global parameters such as COD or total organic carbon (TOC) are commonly used and are consistent. In addition, complementary analysis such as fluorescence spectroscopy can be reliable and interesting and has been used extensively to characterize natural dissolved organic matter in soil, seawater and estuarine water [26,27]. It could be used to give additional information on organic matter degradation during WAO. In terms of process monitoring, fluorescence spectroscopy has been used to measure the quality in wastewater treatment plants, or to characterize industrial effluents (pulp mill, textile) [28–30]. A simple and common method to measure the fluorescence of molecules is to record 3D excitation-emission matrices (EEMs) and reveal family-like complex compounds such as fulvic and humic acid-like compounds through peak-picking method [26]. Such matrices have been investigated in literature and seem to be pertinent for the monitoring of the WAO process [31,32]. To extend knowledge on the feasibility of this treatment path coupling membrane filtration (UF, MBR or RO) with WAO, a study focusing on the global performance of pollution removal by WAO for the treatment of different pollution types was set. Five strategic industrial effluents concentrated with membranes (leachates, pharmaceutical wastewater, bilge wastewater, dairy wastewater and complex industrial effluent) were tested for opportunities of reuse or discharge to the environment. The effect of the heating period of the reactor as a part of the efficiency of the WAO has been studied and classified the feasibility of treatment of

the five effluents, according to total pressure, temperature, heating and oxidation duration. In this context, TOC and COD removals were analyzed over the time of heating and oxidation in the liquid phase. 3D EEMs were also established for fingerprinting pollution characteristics throughout WAO.

2. Material and methods

2.1. WAO process and experimental procedure

Non-catalytic WAO was considered for this study as issues involving depletion of metal resource, leaching, additional cost for treatment and recovery and potential toxicity of catalysts can conflict with environmental policies. WAO tests were carried out with industrial membrane concentrates in a batch stainless steel autoclave (Fig. 1) designed to withstand operating pressures and temperatures up to 30 MPa and 350 °C, respectively. An Inconel vessel (350 mL) was used to prevent corrosion of the reactor walls. The system was heated with an electric furnace (3,100 W) and the operating temperature was kept constant with a proportional-integral-derivative (PID) regulation. The reactor was equipped with a Rushton type six-bladed stirrer (Maximator Dispersimax) mixing at a velocity of 1,000 rpm to limit mass transfer resistance and promote oxygen transfer from the gas phase to the liquid phase [33]. Moreover, oxygen was injected with a 70% excess according to the COD concentration of the inlet [5]. Stirring velocity and excess of oxygen were chosen based on a prior study and state of the art [33,34]. Transfer limitations were not observed at high mixing velocities (> 1,000 rpm). A high-pressure pump (Top Industrie PMHP 50–500) allowed the introduction of nitrogen and air into the reactor. For safety reasons, the reactor was equipped with a rupture disk for pressure relief. Depending on the COD concentration of the inlet, WAO runs were performed with effluent volumes ranging from 200 to 300 mL. Before pressurization, nitrogen was sparged into the effluent for 10 min to remove oxygen. Air was then flushed, and the reactor was pressurized with nitrogen. Experiments were divided into five steps: (i) effluent injection and nitrogen sparging (10 min) into the autoclave followed by nitrogen pressurization, (ii) heating period in absence of air, (iii) air injection at a fixed operating pressure, (iv) oxidation and regular withdrawals of samples for analysis, and (v) cooling and final withdrawal. The nitrogen injected for the heating procedure had variable pressure depending on the initial pollution concentration (e.g., COD) of the effluent, the volume of effluent injected in the autoclave and the excess of oxygen. The pressure was calculated according to the Van der Waals equation of state and measured experimentally, so that the air injected at the end of the heating period up to the preset working pressure corresponded to the fixed excess of oxygen [5]. The heating period was carried out in the absence of dissolved oxygen, as nitrogen was previously sparged into the effluent. The first contact between the effluent and the oxidant (oxygen from air) was considered the starting point of the WAO reaction ($t = 0$ min). At this point, a sample of 15 mL was withdrawn to assess the thermal degradation using a tube connected to a micrometric valve. Liquid samples with volumes between 5 and 15 mL were steadily collected every 90 min during a 6-hour period, cooled during the withdrawal, and then analyzed. A supplementary study was conducted without sampling to confirm that COD and TOC removals were unchanged compared to the removals achieved with the sample ($5 \times 15 \text{ mL} = 75 \text{ mL}$). Moreover, after each sample was withdrawn, air was reinjected into the autoclave to push back the effluent inside the reactor, while readjusting the pressure loss during the withdrawal (5% pressure decrease). Experiments were carried out at the original pH of the effluent. In the pH range (5–10) of the studied effluents, preliminary experiments have shown no significant effect of pH on the WAO performances [34]. The temperatures tested in this study were 200, 250 and 300 °C, as 350 °C is the maximum operating temperature of the autoclave. Experiments were conducted with a constant total pressure of 18 MPa, as it is sufficient to maintain the system in liquid phase and provide

the excess of oxygen (i.e., 70%). In the case of dairy wastewater, a 0% excess of oxygen was chosen to work with the lowest possible volume of effluent and the highest COD. In other words, the reaction was theoretically performed according to stoichiometric WAO reaction. Additional experiments were carried out at 300 °C with a total pressure of 21 MPa (70% excess of oxygen) to study the effect of operating pressure on pollution removal. This set of operating conditions was used to rapidly screen the performance of the process on each effluent. These conditions have been previously determined from a complete study on landfill leachates, using design of experiments in the same operating condition ranges and based on the state of the art [7,20,35,36].

2.2. Characterization

Characterization was performed on raw effluent, permeate, concentrate and WAO outlet. The membrane concentrates were used as an inlet for the WAO process. Parameters were also investigated during WAO to analyze the performance of the process. Classical parameters such as pH (CONSORT p800 pH-meter, HI 1131 probe, calibrated with buffers at pH 4 and 7 with a relative error of $\pm 0.1\%$) and conductivity corrected at 25 °C (WTW Cond 3110, TetraCon 325 cell, calibrated with standard solutions with conductivities of $147 \mu\text{S}\cdot\text{cm}^{-1}$, $1,413 \mu\text{S}\cdot\text{cm}^{-1}$ and $12.88 \text{ mS}\cdot\text{cm}^{-1}$, with a $\pm 0.5\%$ relative error) were measured. The WAO removal rates were quantified using COD and TOC analyses. COD was measured on unfiltered samples diluted with ultrapure water, with commercial tube tests (WTW C4/25 with a test range of 25–1,500 $\text{mgO}_2\cdot\text{L}^{-1}$). 3 mL of a homogenous sample were injected into COD reagent vial and heated at 148 °C for 2 h, then cooled for absorbance reading (PhotoLab S6 WTW photometer, with a relative error of $\pm 4\%$). For sludgy effluents (pharmaceutical wastewaters), solid TOC was measured using the SSM–5000A Solid sample Combustion Unit (Shimadzu) on raw effluent. TOC measurements with the liquid and solid methods were compared for the other effluents of the study but no significant difference was noted, so the liquid method was used. TOC concentration (liquid method) was estimated by quantifying total carbon (TC) and inorganic carbon (IC), or non-purgeable organic carbon (NPOC) through catalytic combustion of TC at 680 °C and acidification of the sample for IC quantification (Shimadzu TOCL-L_{CSH/CSN} Total Organic Carbon Analyzer). Anion concentrations of chloride, nitrate and sulfate were quantified with a relative error of $\pm 5\%$ using ion chromatography (883 Basic IC plus Metrohm) with prior calibration using a 150 ppm NaCl solution; NaNO₃ and (NH₄)₂SO₄ solutions with a maximum of 100 ppm concentrations, then diluted with ultrapure water. Samples were diluted with ultrapure water to fit in calibration curves and filtered through a 0.45 μm nylon filter. Results presented in this study will consider the overall uncertainty on COD and TOC (concentrations and removals (%)) with the corresponding method of analysis and dilution preparation. Pollution removal quantification was investigated through TOC and COD concentrations, as mineralization by-products are complex to identify in industrial effluents. Pollution removals and absolute values were considered to qualify the degree of thermal degradation and oxidation. Removal rates were calculated by considering the total volume withdrawn from the reactor for each time of sampling during the experiments.

Fluorescence EEMs (Perkin Elmer FL 6500) were used to qualitatively measure the presence of specific organic compounds [26,37,38]. Chen et al. [39] divided the spectral fluorescence window into five regions (regions I to V), that are characteristic of family-like fluorescent molecules (maximal intensities in the EEM), and this cartography was confirmed by several authors [40,41]. The first two regions are associated with small protein-like compounds, such as tyrosine and tryptophan-like compounds, that emit at short wavelengths (under 380 nm). Region IV is associated with soluble microbial by-product-like compounds with protein-like structures, which also emit under 380 nm. Regions III and V are associated with fulvic acid-like and humic acid-like compounds, respectively, which usually emit at longer

Table 1

Characteristics of membrane concentrates of bilge wastewater, landfill leachates, complex industrial effluent, pharmaceutical MBR sludge and dairy wastewater. (N.A: not available due to high concentration in Cl^- interfering with measurement; *: After dialysis)

Parameters	Bilge wastewater	Landfill leachates	Complex industrial effluent	Pharmaceutical MBR sludge	Dairy wastewater
pH	8.7	7.6	8.2	7.6	5.7
Conductivity ($mS \cdot cm^{-1}$)	19.2	40.2	199.0	9.3	12.9
IC ($mgC \cdot L^{-1}$)	76	748	86	142	5
TOC ($mgC \cdot L^{-1}$)	354	3,914	7,300 4,324* 15,920*	12,258	85,400
COD ($mgO_2 \cdot L^{-1}$)	610	6,860	N.A	18,430	364,000
$[Cl^-]$ ($g \cdot L^{-1}$)	3.6	7.7	106.0	–	–
$[SO_4^{2-}]$ ($g \cdot L^{-1}$)	3.5	8.1	–	–	–
Specific pollution	Oils, hydrocarbons, heavy metals	Humic and fulvic acid-like compounds, heavy metals	Complex and confidential	Active ingredients and organic compounds	Organic compound (proteins, fats) and cleaning agents

wavelengths (over 380 nm, up to 550 nm). EEM measurements were obtained using a Perkin Elmer FL 6500 spectrometer (xenon source 40 kW, 100 Hz) in the liquid phase. Excitation wavelengths varied from 220 to 415 nm and emission spectra were automatically repeated and recorded between 200 and 560 nm with 5 nm excitation wavelength increments. The scanning monochromator speed was set at $1,200 \text{ nm} \cdot \text{min}^{-1}$, and both the excitation and emission slits widths were set at 5 nm. To avoid interference from inner filter effects and/or quenching, samples were diluted to adjust TOC to a value of $5 \text{ mgC} \cdot \text{L}^{-1}$. EEMs were recorded using a 1 cm path length quartz cell. The measured EEMs were then corrected (by subtracting ultrapure water EEM and scattering) and recalculated considering the dilution factors [37,42]. For the five different fluorophore regions of the cartography of Chen et al. [39], following integration method was used: $Fluorescence \ Volume = \sum_{ex} \cdot \sum_{em} \cdot I(\lambda_{ex} \cdot \lambda_{em}) \cdot \Delta \lambda_{ex} \cdot \Delta \lambda_{em}$ where $\Delta \lambda_{ex}$ is the excitation wavelength interval (5 nm), $\Delta \lambda_{em}$ is the emission wavelength interval (0.5 nm) and $I(\lambda_{ex} \cdot \lambda_{em})$ is the fluorescence intensity at each excitation-emission pair [39].

2.3. Wastewater origins and characteristics

Bilge wastewater, landfill leachates, a complex industrial effluent, pharmaceutical MBR sludge and dairy wastewater were chosen. For four

cases, industrial scale membrane processes (UF, RO, MBR) have been proven reliable for the concentration of the pollution (bilge wastewater, landfill leachates, pharmaceutical wastewater and dairy wastewater). Average characteristics of the feed for the four WAO experiments performed on each effluent are reported (Table 1).

Bilge wastewaters (feed wastewater after decantation, concentrate and permeate) were collected from an UF unit (300 kDa) placed in a ferry capable of producing about $1.5 \text{ m}^3 \cdot \text{h}^{-1}$ of permeate (with a volumetric concentration factor ranging from 25 to 40) [17]. Leachates, RO concentrate and permeate were collected from a municipal sanitary landfill site of southern France, which has been operating since 1974. The RO system has been implanted on-site since 1999, producing the average annual production of $80,000 \text{ m}^3$ of permeate. The composition and concentration of pollutants fluctuates throughout the year due to weather conditions. The landfill leachates studied here were collected in October 2020, which represents the most concentrated leachate of the year (RO recovery rate of 40%). The complex industrial effluent was collected from an industry specialized in hazardous wastewater treatment, after a physical-chemical process. Due to its high salinity, membrane dialysis was conducted at lab scale using dialysis tubing (6–8 kDa Spectra/Por®1, Spectrum™) to retain organic pollution and limit the presence of chloride (which poses a corrosion problem for WAO step). The COD and TOC concentrations of the dialysis retentate were of

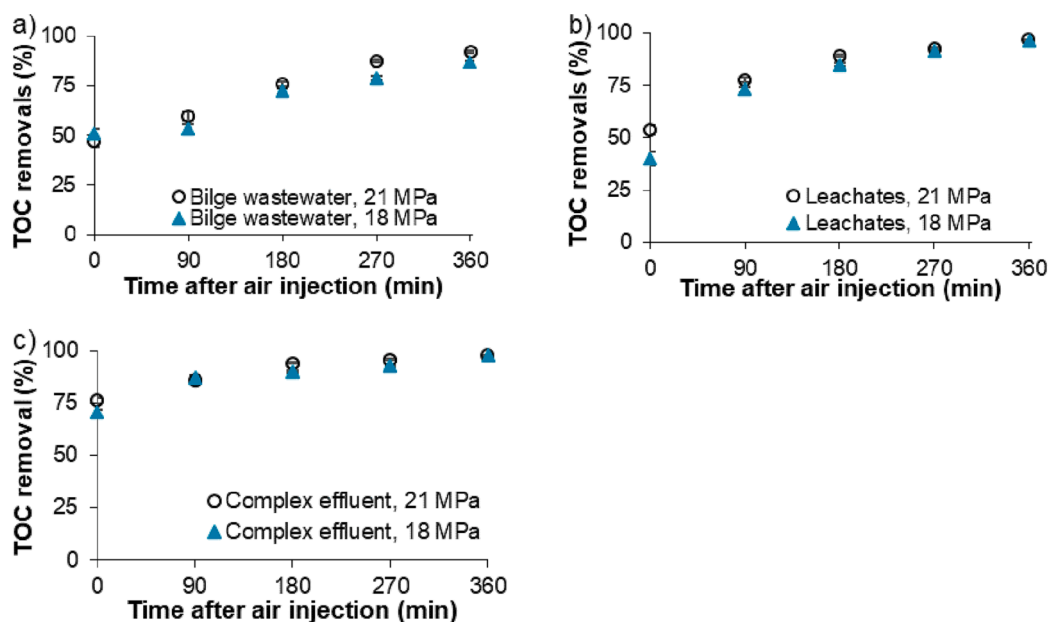


Fig. 2. Evolution of TOC removals for a) bilge wastewater (COD_{ini} : $610 \text{ mgO}_2 \cdot \text{L}^{-1}$), b) leachate RO concentrates of October (COD_{ini} : $6,860 \text{ mgO}_2 \cdot \text{L}^{-1}$), and c) the complex industrial effluent (COD_{ini} : $15,920 \text{ mgO}_2 \cdot \text{L}^{-1}$) at \circ 21 MPa and \blacktriangle 18 MPa and at a constant temperature of $300 \text{ }^\circ\text{C}$.

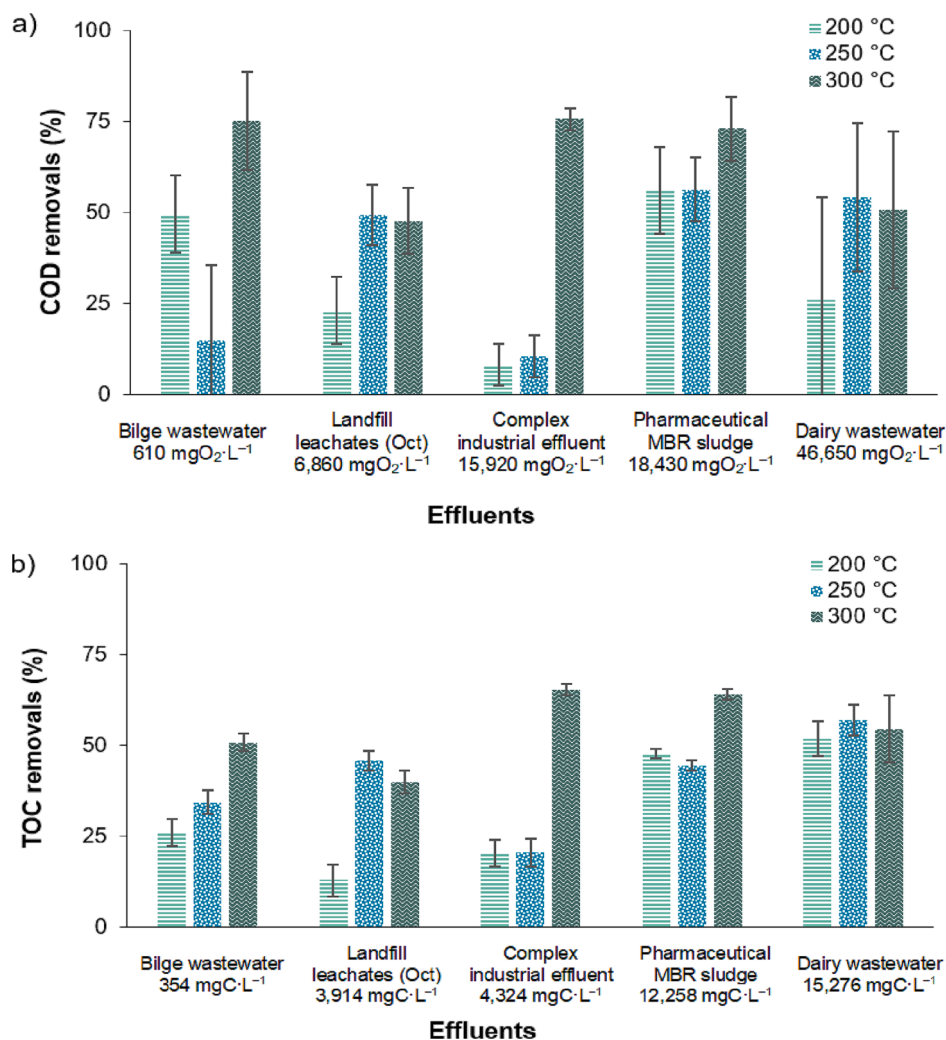


Fig. 3. Anoxic thermal degradation in terms of a) COD removals and b) TOC removals at three different temperatures.

15,920 mgO₂·L⁻¹ and 4,324 mgC·L⁻¹, respectively. Pharmaceutical wastewaters (feed water, concentrate and permeate) were collected in February 2021 from a MBR (membrane pore size of 0.02 μm) in a wastewater treatment plant located in a pharmaceutical industry in southern France. This unit enables the production of 18–20 m³·h⁻¹ of permeate. The last effluent was dairy wastewater (RO concentrate), collected from a French dairy cooperative capable of concentrating dairy wastewater mix up to a volumetric concentration factor of 6, resulting in a mineral matter concentration of 30 g·L⁻¹ and a COD concentration of approximately 360 gO₂·L⁻¹. A 7.8 dilution was used to reach a 46,650 mgO₂·L⁻¹ COD with ultrapure water to meet the potential autothermic WAO COD range. Depending on their stability, samples were stored in plastic containers in a 4 °C refrigerator or frozen.

3. Results and discussion

The treatment path performance was examined through COD and TOC analyses in the liquid or solid phase. The study focused on two pressures and three temperatures. Effect of the anoxic heating period was also investigated at the three temperatures of the study. In the case of leachates, the pharmaceutical MBR sludge and the dairy wastewater, effect of inlet pollutant concentration was studied.

3.1. Influence of total pressure on COD and TOC removals by WAO

The effect of pressure on global performances was assessed by

modifying total pressure (from 18 to 21 MPa) and maintaining initial excess of oxygen constant between both studies and at a constant temperature of 300 °C (Fig. 2). This test could not be performed with the pharmaceutical wastewater and the dairy wastewater due to high inlet concentration, available effluent volumes and/or autoclave configuration. At the maximum, a difference of 9% was measured for the bilge wastewater during WAO. TOC removal rates were not greatly impacted by changing the total pressure from 18 to 21 MPa. Moreover, similar effects of pressure were noted for the COD removal rates, with relative differences of 10%, 7% and 8% for the bilge wastewater, the landfill leachates and the complex industrial effluent, respectively.

It has been proven by previous authors that an increase in the partial pressure of O₂ has a positive impact on the mineralization and conversion of the organic fraction of pollution [4,43,44]. The effect might be due to oxygen availability in the gas phase. Oxygen transfers to the liquid phase according to Henry's law, as the concentration of dissolved O₂ is proportional to the partial pressure of O₂ in the gaseous phase. In the present study, total pressure was increased but excess of oxygen remained constant at the two studied pressures. Availability of dissolved oxygen should be the same at both pressures and no limitation of transfer should be observed. These results are coherent with literature and suggest it is preferable to work with the lowest pressure in the range of this study to reduce compression costs, as working at higher pressure has no positive impact on removal. Yet, this total pressure must be sufficient to maintain system in the liquid phase.

3.2. Influence of anoxic heating periods on COD and TOC removals

The effluents tested in this study underwent a heating period in absence of oxygen. The durations of the heating periods were of 40, 60 and 90 min for experiments conducted at 200, 250 and 300 °C respectively. Thermal degradation was assessed at the end of the heating period by collecting a sample (t_0). Comparisons of COD and TOC removals (%) are presented at 200, 250 and 300 °C for the five effluents (Fig. 3). The effluents were either weakly affected by the heating period (bilge wastewater, landfill leachates and the complex industrial effluent), or strongly affected (pharmaceutical MBR sludge and dairy wastewater, with TOC removal > 50%). In the first case, TOC removals were lower than 25% at 200 °C while COD removal seemed more affected by the heating period for bilge wastewater only (Fig. 3a). In the latter case, TOC removals were not impacted by the temperature increase ($54 \pm 6\%$), while a low effect on COD removal was observed at 200 °C and a significant effect at 250 and 300 °C. Moreover, an increase in the temperature (300 °C) and the duration of the heating (90 min) promoted the degradation of TOC and COD for most effluents. Lei et al. [45] showed a 34% TOC removal for a textile industry wastewater after the heating period of a WAO experiment at 200 °C and 6 MPa, although studies are scarce [46,47]. Overall, it appears that the heating period is given less attention in the literature even though it may significantly contribute to the removal of TOC and COD. Some studies have presented high removals during the first minutes of WAO, which could have occurred during the heating period. Carrier et al. [46] showed COD, TOC or dissolved organic carbon removal after the heating period ranging from 8 to 70%, whilst other studies showed that 100% of the pollution was still present at t_0 , with removals of organic pollution after 5 to 20 min [44,45,48]. As shown here, the degradation of the pollution during the heating period should be considered in real industrial application as it may have a positive impact on performance.

Differences in COD and TOC removals at the same temperature could be explained by the breakage of molecules in the aqueous phase resulting in lower COD values. Under elevated temperature and pressure, hydrogen bonded structures of aggregates may have broken down, generating smaller molecules (isomerization, hydrolysis reactions) [49]. A majority of degradation products remained in the aqueous phase as they can be highly soluble in water [50]. In the case of bilge wastewater, TOC removal reached 26%, whereas COD removal reached 50%. This suggests molecules might have been broken down into smaller molecules in aqueous phase, leading to a small change in TOC concentration, as it characterizes the liquid phase. On the other hand, COD has been more significantly reduced: molecules can be smaller but are still concentrated and have lower needs in terms of oxygen to be degraded. The latter has already been observed in WAO of textile industry wastewater, where COD and TOC removals were achieved during the heating period (24% and 8% respectively) and the COD removal was more impacted. The authors suggested hydrogen production during the heating, which did not affect TOC concentration [51]. Lei et al. [45] also noticed thermal degradation before the addition of oxidant in the treatment of dyeing wastewater membrane concentrates (34% TOC removal), among other studies [46,47]. Additionally, it appears necessary to monitor COD and TOC during WAO as they may vary differently throughout the process, corroborating Lei et al. [51] on the effect of oxygen in the WAO of textile industry wastewater. Also, due to the complexity of the effluent, other families of oxidants may be present, promoting significant oxidation of the organic fraction of the pollution or thermosensibility. Although, no noticeable increase in reactor pressure, which could be attributed to gas production, was observed during the heating period (data in Appendix A. Supplementary material).

As COD and TOC removals were high for the complex industrial effluent and the pharmaceutical MBR sludge, it was important to verify whether these removals occurred during the sample withdrawal from the reactor (due to vapor loss, disruption of the gaseous phase, presence of volatile molecules in the gas phase, etc.). The heating of the complex

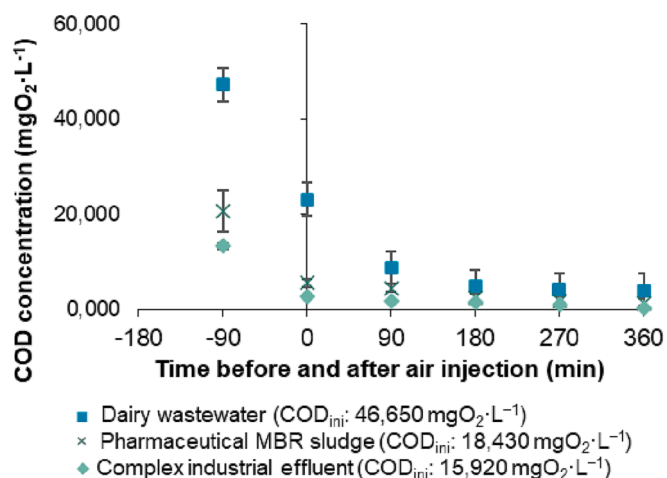


Fig. 4. Effect of the duration on the COD removal for three effluents at 300 °C.

industrial effluent was performed in the reactor in presence of nitrogen up to a temperature of 300 °C, then a sample was collected after cooling the reactor to assess the COD and TOC removals. At this point, 69% and 72% of COD and TOC were removed, respectively, corroborating previous results (removals of 66% and 70%, respectively, corresponding to a relative difference of only less than 4% and 3%).

3.3. Influence of oxidation duration on COD and TOC removals by WAO

WAO was conducted for a total duration of 6 h after the anoxic heating period to gain knowledge on global behavior of pollution removal. Indeed, depending on the type of effluent, effects varied. As seen before, effluents could undergo a significant degradation during the anoxic heating period, but in some cases, the effect of injecting oxygen (from air) inside the reactor was different (Fig. 4). Pharmaceutical MBR sludge and the complex industrial effluent were less affected by the duration of WAO as most of the removal appeared during the heating period (> 73%) and during the first 90 min. Furthermore, the duration of oxidation had an impact on dairy wastewater, as COD removals were observed during the heating period (50% removal) and continued to increase after the first 180 min of WAO, eventually stabilizing.

3.4. Influence of temperature on COD and TOC removals by WAO

The effect of temperature within the 200–300 °C range was investigated in terms of COD and TOC removals (Fig. 5). Even though the highest performance was attained at elevated temperature (300 °C), the overall performance of the process could be affected by the temperature. Three groups could be highlighted: (i) COD and TOC removals behaved similarly throughout WAO regarding the temperature variation, (ii) COD and TOC removals behaved differently throughout WAO regarding the temperature variation, and lastly (iii) TOC removals were only weakly affected by the temperature variation.

In the case of bilge wastewater (study's least concentrated effluent), temperature was an important parameter in pollution removal. However, whilst COD and TOC were gradually removed, the three curves decreased over time during the experiment (Fig. 5a–b). Portela et al. [52] studied WAO on oily waste and attributed the limitation in pollution removal to the presence of by-products such as low-molecular-weight compounds (carboxylic acids), which could explain the observed results.

For leachates, the results indicated an increase in the removal rate (Fig. 5c–d). For instance, by increasing the temperature from 200 °C to 300 °C, the average COD and TOC removals (%) throughout WAO were 19% and 36% higher, respectively, and this difference stayed constant throughout the experiment. Also, higher temperatures resulted in higher

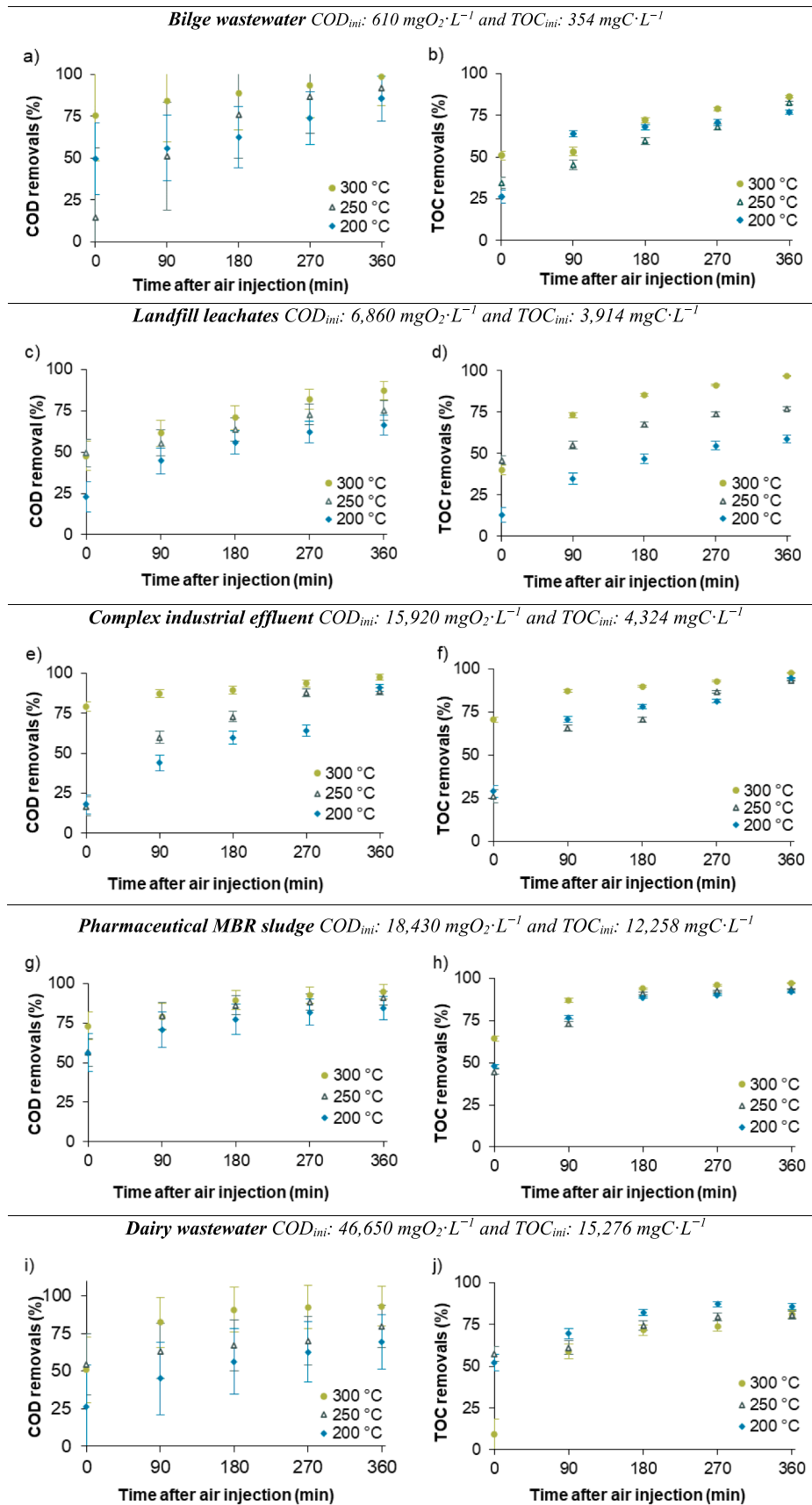


Fig. 5. Evolution of COD (left) and TOC (right) removals rates for different effluents.

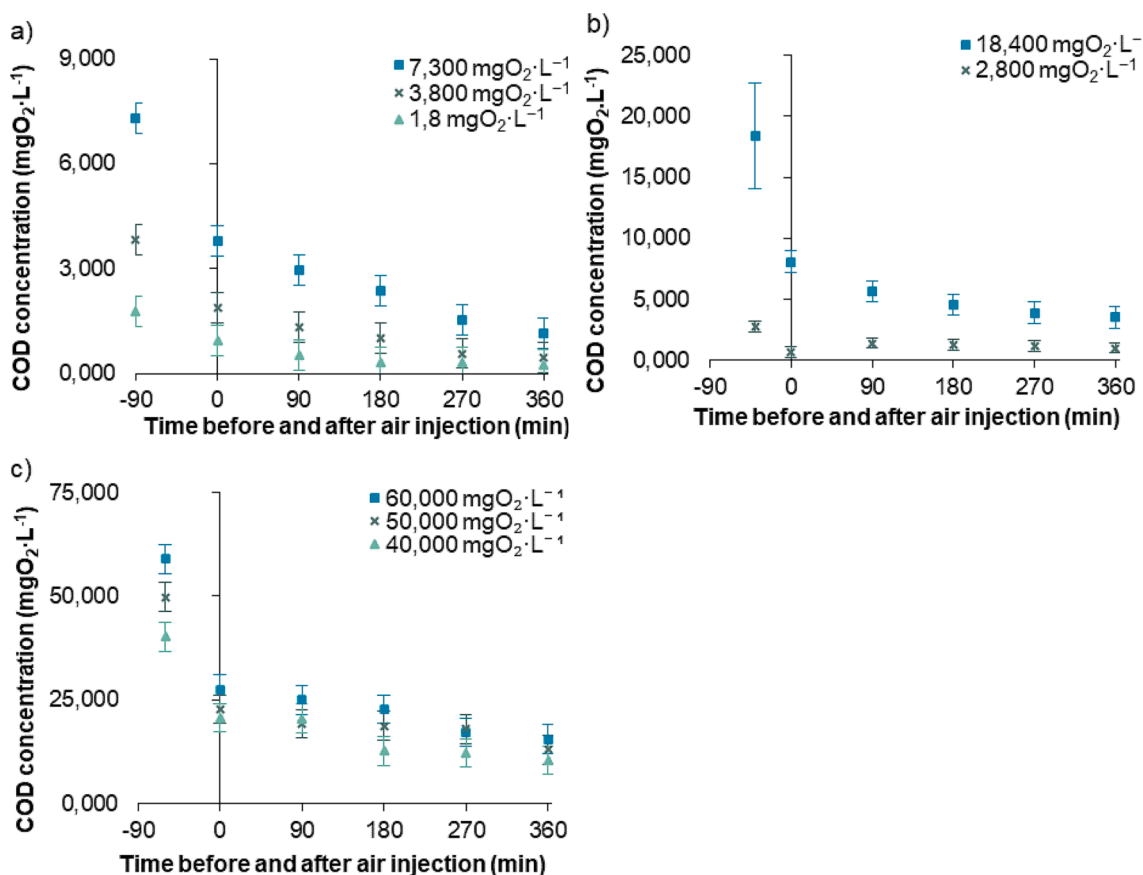


Fig. 6. Evolution of COD concentration for 3 RO concentrates of a) landfill leachates [300 °C – 18 MPa], b) pharmaceutical MBR sludge [200 °C – 18 MPa] and c) dairy wastewater [250 °C – 21 MPa].

pollution removals (66–87% of COD and 59–96% of TOC removed between 200 and 300 °C, respectively). These removal rates are within the range reported in other studies on humic acids and fulvic acid which have similar structures to the pollutants found in leachates [53]. Whilst high removals were reached, some oxidation by-products remained. In the case of WAO of several types of sewage sludge, researchers observed this tendency and concluded on the presence of refractory by-products formed during the first oxidation step, less sensitive to oxidation. For instance, the oxidation of aromatic alcohols was very successful. However the presence of carboxylic acids/salts (like acetic acid) lowered the TOC conversion rate as these compounds are refractory to WAO (presence of a plateau in the removal rate), though acetic acid is a biodegradable compound [54–56]. This could be the case after 6 h of oxidation. The complex industrial effluent (Fig. 5e–f) also revealed similar TOC and COD removal behaviors, except during the last 90 min. A 2-step feature could be noticed and less perceptible at high temperature. The highest removal rate for COD was noted during the first 180 min while for TOC, it was during the first 90 min.

For pharmaceutical MBR sludge (Fig. 5g–h), the inlet COD concentration was high, within the range to undergo autothermic WAO. After 6 h of oxidation, the differences in removal between low and high temperatures were of 10% and 5% for COD and solid TOC removals, respectively. These results align with the findings of Zhan et al. [57], who studied catalytic WAO for pharmaceutical wastewaters with high COD concentrations (8,000–12,000 mgO₂·L⁻¹) and observed an increase in COD removals with higher temperature. A 2-step feature could be noted for both parameters with the highest removal rate observed during the first 180 min, followed by a plateau (indicative of potential refractory pollutants to WAO). Regarding dairy wastewater (Fig. 5i–j), which also has a high organic load, COD removals reached 96%, but no obvious effect was observed between 250 and 300 °C (Fig. 5i). Also, a 2-

step feature could be noticed with a high removal increase during the first 90 min for both parameters, but this tendency became less noticeable as temperature increased. The effect of temperature was noticed by Piotrowska et al. [55] on dairy sewage, where a temperature of at least 250 °C was necessary to convert the pollutants into water and carbon dioxide.

3.5. Influence of inlet concentration on COD and TOC removals by WAO

As the composition of industrial effluents is prone to variations over time, the effect of inlet concentration was studied whenever possible. Fig. 6a shows the decrease in COD concentrations during WAO for three leachates (collected at three different periods of the year) at 300 °C – 18 MPa. The leachate with the highest initial COD concentration exhibited the highest amount removed in the shortest reaction time. In this case, 48% of the COD was removed during the heating period, and the final removal reached 87% resulting in a final COD concentration of 1,155 mgO₂·L⁻¹. A similar trend was observed for the pharmaceutical MBR sludge (Fig. 6b), where the high-concentration sludge achieved 85% COD removal, with a final COD concentration of 3,649 mgO₂·L⁻¹. In contrast, the less concentrated sludge achieved a 70% COD removal, leading to a final COD concentration of 1,039 mgO₂·L⁻¹. It is recalled that even higher removal rates could be achieved at 250 °C (91%). However, the initial COD concentration of the dairy wastewater (Fig. 6c) did not significantly impact the COD removal during WAO. Removals were mostly attributed to anoxic thermal degradation, suggesting that this type of effluent may not be the most adapted for industrial WAO applications.

The initial COD concentration had a positive impact on the removal efficiency of two different industrial effluents, which is an advantageous factor in terms of operational costs. This finding is in agreement with

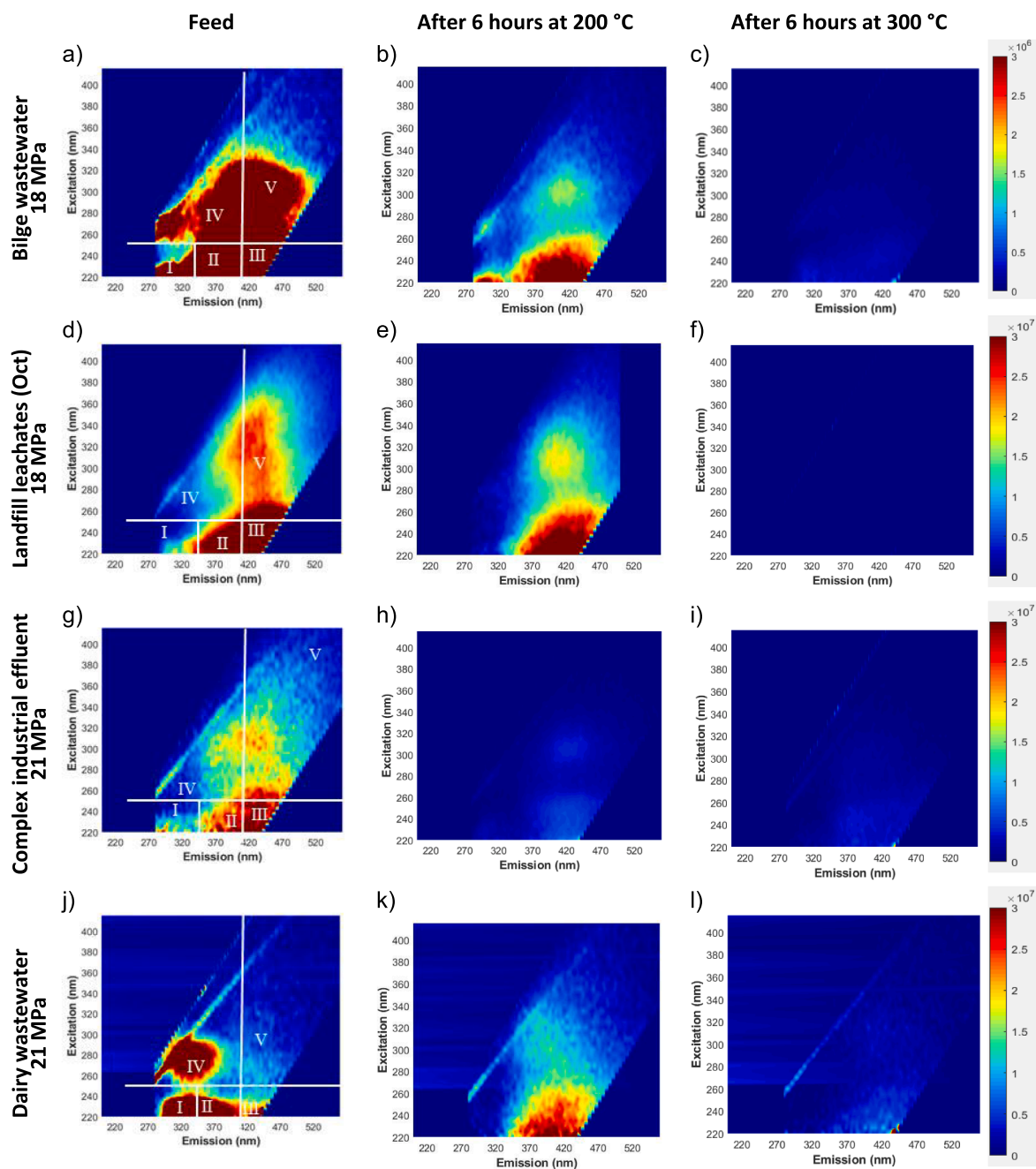


Fig. 7. EEMs of bilge wastewater UF concentrates a) before WAO and after 6 h of WAO at b) 200 °C and c) 300 °C, landfill leachates RO concentrates (October) d) before WAO and after 6 h of WAO at e) 200 °C and f) 300 °C, the complex industrial effluent dialyzed g) before WAO and after 6 h of WAO at h) 200 °C and i) 300 °C and the dairy wastewater RO concentrates j) before WAO and after 6 h of WAO at k) 200 °C and l) 300 °C.

observations in the literature [44,58]. It is possible that at higher concentrations, there is a greater likelihood of molecular collisions with radicals generated from dissolved oxygen, enabling a self-sustaining WAO process, dependent on the heat produced by these reactions [58]. Other studies have reported a negative effect of higher initial pollution concentration regarding single or pure compounds [59]. It was also noticed that the inlet concentration variation had little effect on the removal efficiency (%) over time for the three effluents tested. For example, after 6 h of WAO, final COD removals reached 81, 80, and 78% for dairy wastewater with initial concentrations of 40, 50 and 60 gO₂L⁻¹, respectively. Although similar removals (%) were achieved, the quantities of COD degraded were higher for higher inlet concentration, as observed in landfill leachates and pharmaceutical MBR

sludge. This phenomenon was also demonstrated in the oxidation of landfill leachates, where similar removal efficiencies (%) but different quantities removed were depicted through the design of experiments and response surface plots [20].

3.6. Evolution of fluorescent footprints

EEMs are an interesting tool to detect the presence of several fluorescent footprints that can be found in polluted effluents. Measurements were possible on four of the five wastewaters tested: bilge wastewater, landfill leachates, the complex industrial effluent and the dairy wastewater. These footprints revealed the presence of aromatic molecules, often refractory to biological degradation, such as polycyclic aromatic

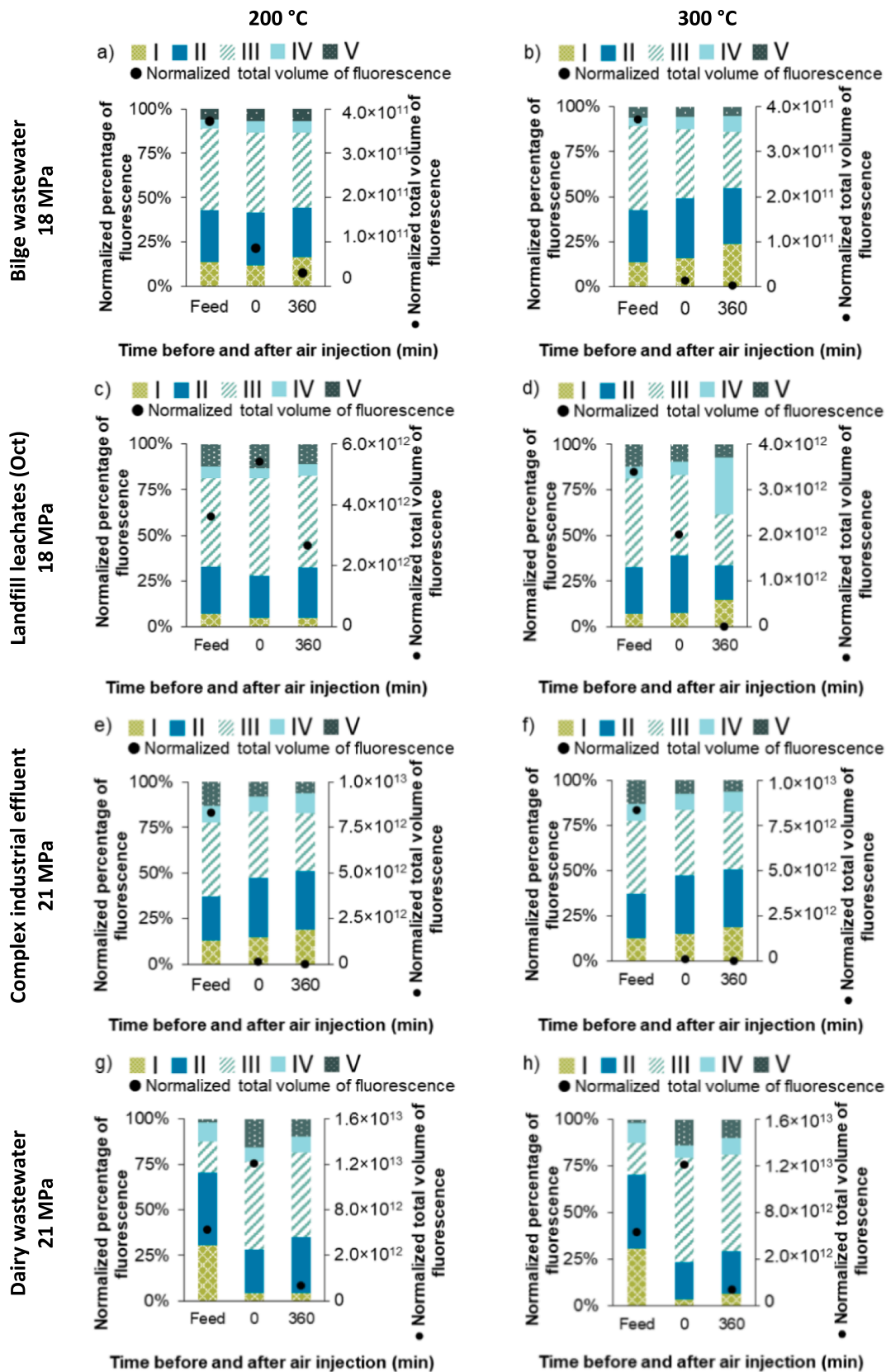


Fig. 8. Evolution of the five regions of the EEMs during WAO for bilge wastewater UF concentrates a) at 200 °C and b) 300 °C, landfill leachates RO concentrates (October) c) at 200 °C and d) 300 °C, the dialyzed complex industrial effluent e) at 200 °C and f) 300 °C and the dairy wastewater RO concentrates g) at 200 °C and h) 300 °C.

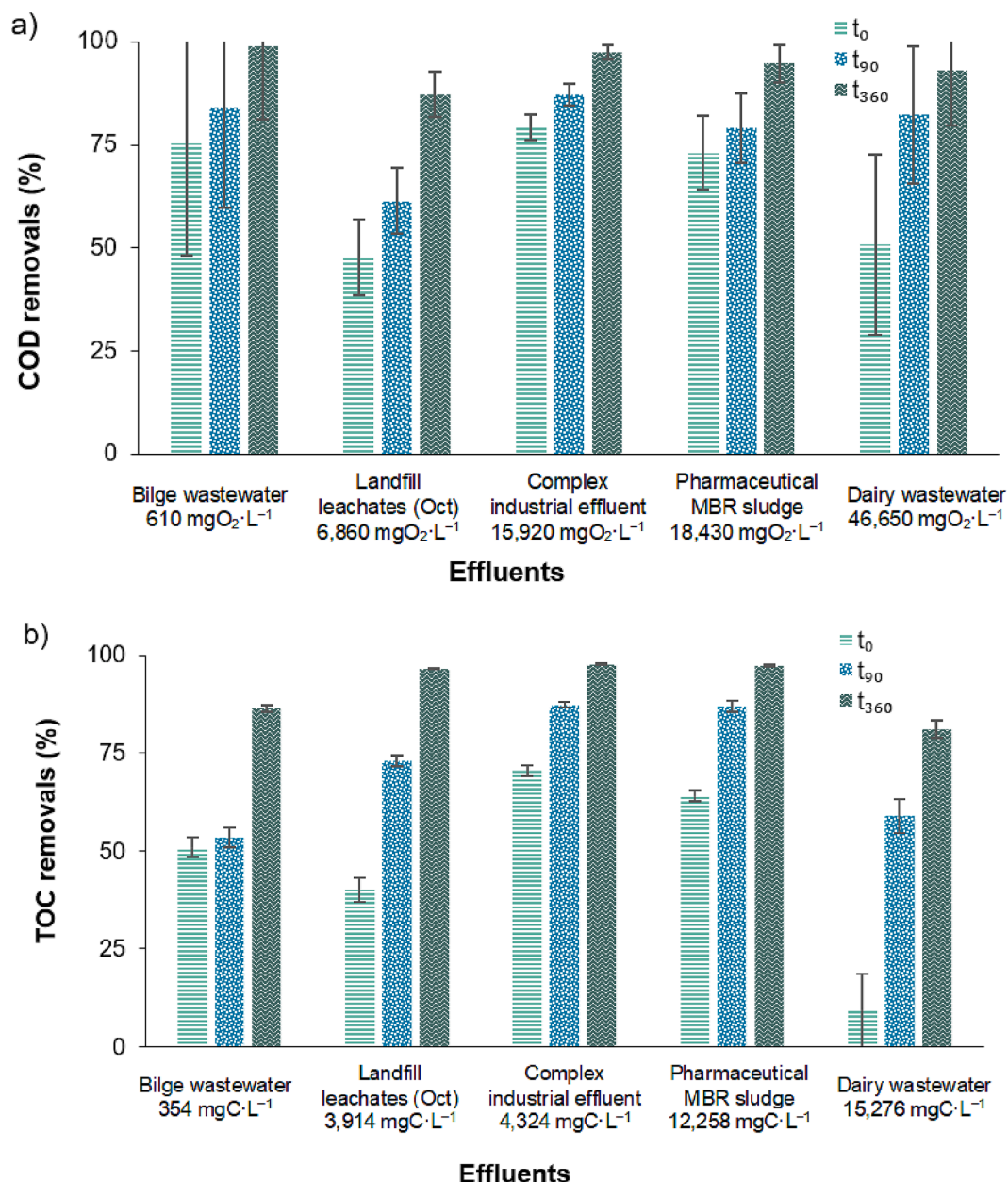


Fig. 9. Comparison of WAO performances for a) COD removals and b) TOC removals at the end of the anoxic heating period (t_0), after 90 min (t_{90}) and after 360 min (t_{360}), at 300 °C.

hydrocarbons (PAHs) and commonly found in bilge wastewater [60]. The aim of using EEMs was to monitor the evolution of fluorescent footprints (representing only a portion of the organic matter) during WAO and compare them with the initial feed quality. This approach could be an original parameter for linking the complexity of the pollution with classical parameters as COD and TOC. To ensure the EEMs were not altered by the oxidative or reductive state of the sample, a reducing agent (sodium thiosulfate) was added in some cases. All spectra were standardized for each effluent, corrected with each dilution factor and are presented in Fig. 7. For bilge wastewater UF concentrates, four footprints were observed: a small volume for tyrosine-like molecules and greater volumes for tryptophan-like molecules, fulvic acid-like compounds and humic acid-like compounds. After 6 h of oxidation at 200 °C, all footprints were still present though degradation was significant (80% of overall fluorescence removed), nonetheless aggregates were still present as fluorescence provides complexity characteristics of pollution (Fig. 8a). In contrast, after 6 h of oxidation at 300 °C (Fig. 8b), no

footprints were observed, and an overall removal of 98% of fluorescence was quantified. For leachates, two main peaks were identified: humic and fulvic acid-like compounds in the RO concentrates and a small volume of tryptophan-like molecules. At 200 °C (Fig. 8c), fulvic acid-like substances appeared more resistant to oxidation as a residue was still present even after 6 h of WAO. The overall fluorescence removal was 41% in this case. However, after 6 h of oxidation at 300 °C (Fig. 8d), both substances were removed (99% decrease in overall fluorescence). It is noted that by following fluorescence every 90 min, humic acid-like compounds were removed more rapidly than fulvic acid-like compounds. Perhaps, the degradation of humic acid-like substances led to the formation of less complex aggregates such as fulvic acid-like compounds which contributed to the region III throughout WAO until complete destruction of the footprint. The presence of refractory fulvic compounds could explain the plateau observed in Fig. 5 at 200 °C. At 300 °C, all fluorescence was removed after 90 min, indicating the pollution in the WAO outlet was less complex. Dairy wastewaters

Table 2

Performance summary and assessment of discharge possibility after 6 h of WAO at 300 °C.

Effluents	Treated concentrate flowrate m ³ ·h ⁻¹	Permeate quality COD / TOC (mg·L ⁻¹)	After WAO COD / TOC (mg·L ⁻¹)	Possibility to discharge (treated concentrate + permeate) in the environment?
Bilge wastewater (UF)	0.04–0.06	23 / 14	9 / 25	✓ [61]
Landfill leachates (RO)	0.13	25 / 22	1,155 / 85	✓ [62]
Complex industrial wastewater (dialysis)	0.26–0.35	–	405 / 142	✓
Pharmaceutical MBR sludge (UF)	7	236 / 37	12,258 / 1,330	✓ to the wastewater treatment plant
Dairy wastewater (RO)	–	0 / 0	1,576 / 4,000	✓ to the industrial wastewater treatment plant

typically contain aromatic proteins, detectable through fluorescence spectroscopy, including peaks for tyrosine, tryptophan and soluble microbial by-product-like compounds, as well as a fulvic acid-like peak. After 6 h of WAO at 200 °C, the peaks for tyrosine and tryptophan disappeared, but fulvic acid-like compounds remained significantly present (4% reduction). The overall fluorescence decreased of 40% (Fig. 8g). On the other hand, when WAO was conducted at 300 °C, overall fluorescence decreased of 99% and no major peak was found (Fig. 8h). The last fluorescent effluent was the complex industrial effluent, which is characterized by the presence of humic and fulvic acid-like compounds. The WAO at 200 °C led to a removal of 87% of the overall fluorescence volume (Fig. 8e) while WAO at 300 °C led to a removal of 91% of the overall fluorescence volume (Fig. 8f). However, in the case of this effluent both temperatures led to high removal of fluorescence (i.e., complexity in molecules) and no major peak was found after WAO.

3.7. Global performance and assessment of liquid discharge of the complete treatment line

As mentioned before, less attention is given to the anoxic heating period in literature even though great removals can be achieved during this period and similar to ones in a preheated effluent for a WAO at industrial scale in a bubble column. Also, typical durations of WAO (after air injection) are between 15 and 120 min. To give an overview and compare performances of the five types of pollutions, COD (Fig. 9a) and TOC (Fig. 9b) removals are presented after the anoxic heating period, after 90 min and after 360 min, at the temperature leading to the best removals: 300 °C. As seen in Fig. 9, anoxic heating period can be responsible for a significant degradation of pollution, due to the large variety of compounds found in the industrial effluents and that can be oxidants. Nevertheless, this removal was not systematically high. Three types of behavior were noticed: (i) the effluent underwent a low COD removal (less than 50%) during the heating period (i.e., landfill leachates) and the injection of oxygen was responsible for a COD and TOC removal increase up to 62% and 73%, respectively, after 90 min of WAO, along with respective total removals of 87% and 97% after 360 min of WAO. (ii) The effluent underwent a high removal during the anoxic heating period (> 50%), a slow degradation during the first 90 min and high removals after long WAO (i.e., bilge wastewater and the pharmaceutical MBR sludge). (iii) The effluent underwent a high removal during the anoxic heating period (> 50%), a rapid degradation during the first 90 min and no necessity to pursue long WAO (i.e., the dairy wastewater and the complex industrial effluent).

Finally, the feasibility study of WAO of industrial membrane concentrates was assessed and most of the organic fraction of pollution was degraded. Regardless of the type of effluent, COD and TOC removals were higher than 66% and 59%, respectively. Removals of both parameters were presented in terms of concentrations in Table 2. Evaluation and validation of the final global outlet were made to state the possibility of discharge in the environment for bilge wastewater and landfill leachates in compliance to their respective regulation (in France), in terms of COD and TOC final concentrations [61,62]. In particular, the treated bilge wastewater UF concentrates could be directly discharged at sea, along with the UF permeate which is already discharged at sea [61]. In the case of landfill leachates, discharge may be possible for the global outlet including permeate according to the French regulation for classified installation for environment protection [62]. In the case of the complex industrial effluent, discharge of the dialysate (TOC and COD free) was possible, as well as the WAO outlet (TOC current concentration regulation below 500 mgC·L⁻¹ for an environmental discharge). For the last two effluents (pharmaceutical MBR sludge and dairy wastewater), the recycling on the industrial site could be possible, or considering the membrane process efficiency variation and production of permeate, the global effluent could comply with regulation. However, an exhaustive characterization of the global outlet considering all parameters of the regulations would be necessary for a validation of discharge of all effluents.

4. Conclusion

This study investigated the performance of coupling membrane processes with WAO for treating industrial effluents. Five membrane concentrates were studied: bilge wastewater, landfill leachates, a complex industrial effluent, pharmaceutical MBR sludge and dairy wastewater. Results showed successful treatment of membrane concentrates by WAO at high temperatures (300 °C) without significant effect of total pressure variation. Higher effluent concentrations resulted in higher quantities removed, whilst removals (%) remained relatively similar.

Three behaviors were observed during WAO regarding COD and TOC removals. Firstly, the anoxic heating period showed varying effects depending on temperature, duration and pollution. The latter should be systematically considered as it can lead to significant removals (TOC removals over 50% for pharmaceutical MBR sludge and dairy wastewater), despite being occasionally described in the literature. Secondly, WAO achieved high removals within short durations, as observed for bilge wastewater and landfill leachates. Lastly, sustained WAO for several hours resulted in high removals, however, scaling up to the industrial scale may pose challenges. The best removals were achieved at 300 °C, with TOC removals of 75–98% and COD removals of 82–99% after 6 h of oxidation. Studying both COD and TOC is important because of different behaviors, varying industry regulations and effluent characteristics. Fluorimetry effectively monitored the WAO process, although further research is needed. WAO mitigated persistent pollutants (humic acid-like compounds), with high TOC and COD removals confirmed by fluorimetry at high temperature (99% decrease in fluorescence intensity). While great TOC and COD removals were achieved for most effluents, the complex industrial effluent and pharmaceutical MBR sludge primarily showed removals during the anoxic heating period, suggesting limited suitability for industrial scale WAO. Coupling membrane processes with WAO showed potential for COD and TOC removals in the liquid phase, making discharge to the environment or a wastewater treatment plant feasible based on TOC and COD removals alone. Further studies are required to assess the life cycle analysis and cost-effectiveness of the treatment path, considering environmental and economic aspects. Tests in a continuous bubble column are foreseen to validate performance at the industrial scale and autothermicity, along with thorough characterizations.

CRedit authorship contribution statement

Emilie Gout: Investigation, Visualization, Writing – original draft. **Fatimatou Toure Lo:** Investigation, Visualization. **Mathias Monnot:** Conceptualization, Supervision, Writing – review & editing. **Olivier Boutin:** Writing – review & editing. **Pierre Vanloot:** Writing – review & editing. **Magalie Claeys-Bruno:** Methodology, Software, Writing – review & editing. **Philippe Moulin:** Conceptualization, Supervision, Writing – review & editing.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2023.144937>.

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