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A B S T R A C T

Sanitary landfilling is one of the most common ways to eliminate solid municipal/urban wastes. Despite many advantages, this method leads to the generation of contaminated leachates that remains an unavoidable consequence of the waste disposal. Membrane technologies, such as reverse osmosis, are frequently used for leachate treatment as they generate good quality permeate with a high recovery rate. However, their primary drawbacks are fouling, eliminated by chemical wash, and the production of highly polluted concentrates. This paper aims to assess and optimize the use of wet air oxidation to treat reverse osmosis concentrates in terms of bio-refractory organic pollutants removal. Wet air oxidation was performed at elevated pressure and temperature using experimental design methodology with a 70% oxygen excess for 6 h in a stirred batch reactor. The effect of operating conditions was investigated with an experimental design where 3 factors (two quantitative ones: pressure and temperature and a qualitative one: seasonality of the effluent) have been considered. The chemical oxygen demand and the total organic carbon removals increased with the increase of temperature (from 200 °C to 300 °C) and no effect of the pressure was observed within the range 18 – 21 MPa. Wet air oxidation could achieve up to 99% removals for chemical oxygen demand and total organic carbon for the seasonality of October. Experiments also showed that increasing the initial pollutant concentration increased initial kinetic rates. Finally, models were established to calculate and predict pollution removal rate and its kinetic, in the domain of study.

1. Introduction

Nowadays, in most countries, the primary option to deal with municipal waste is sanitary landfilling. According to a report of the World Bank, in 2016 worldwide, almost 40% of the collected municipal solid waste was sent to landfill sites and for upper-middle-income countries, landfilling represented 54% of the waste management (Kaza et al., 2018). During landfill period, leachates are generated by excess rainwater percolating through solid waste layers. Landfill leachate is considered as a polluted stream since it contains large amounts of complex bio refractory compounds such as dissolved organic matter, humic and fulvic substances, anthropic pollution, heavy metals, and ammoniacal-nitrogen (Renou et al., 2008a; Youcai, 2018). Ammoniacal-nitrogen can be effectively removed from leachates by using a nitrification and denitrification process (Jokela et al., 2002). Nevertheless, characteristics vary from one site to another in terms of age, landfill design, volumetric flow, chemical composition, among others (Kurniawan et al., 2006; Oulego et al., 2016). Generally, leachates are classified by age: young, intermediate and old or stabilized for respectively less than 5 years, from 5 to 10 years and more than 10 years (Gautam et al., 2019; Kulikowska and Klimiuk, 2008; Renou et al., 2008b). After landfill site exploitation, biodegradability of the leachate reduces and bio-refractory leachates will still emanate from this process for more than a hundred years (Wang, 2013). With water scarcity and stricter environmental regulations, the collection and proper treatment of landfill leachates evolved as a major issue worldwide and its remediation remains a challenge. Renou et al. (2008a) reviewed landfill leachates managements and treatments, i.e., transfer to municipal sewage treatment plants, biological treatments and physical/chemical treatments.

The implementation of reverse osmosis (RO) appears as an efficient treatment separation process, especially for old leachates, as it produces a great amount of purified water (rejection rates for

chemical oxygen demand (COD) and heavy metals concentrations higher than 98% and 99% respectively) (Chianese et al., 1999; Renou et al., 2008a). However, RO still suffers from major drawbacks such as membrane fouling and generation of concentrates that cannot be discharged in the environment nor reused (Joo and Berrin, 2015). In some sites, concentrates are reinjected into the leachate reservoir as it can improve biodegradation rates in young landfills (Townsend et al., 1996). However, this practice is becoming illegal as it does not solve the treatment issue and does not meet with the current regulations. Therefore, further treatments need to be explored to treat efficiently landfill leachates concentrates to avoid soil and groundwater contamination along with maintaining ecological balance.

Wet air oxidation (WAO) processes with or without catalysts are widely studied for the treatment of effluents containing bio-refractory compounds (Bhargava et al., 2006). WAO is defined as an exothermic hydrothermal reaction carried out in an aqueous phase under elevated pressures and temperatures in presence of an oxidant. Several oxidants can be used (dioxygen from air, hydrogen peroxide or ozone) and temperature and pressure are usually set between 125 and 320 °C and 0.5 – 20 MPa, respectively (Mishra et al., 1995). Catalyst or oxidation promoters can be interesting to enhance the performance of the process, increasing the oxidation rates and lowering operating temperature. Although, issues involving leaching, additional treatment for recovery and potential toxicity of catalysts must be taken into consideration for process dimensioning. Moreover, it is unlikely to treat complex industrial wastewater with one type of catalyst (Baloyi et al., 2018; Levec and Pintar, 2007). Oxidation can also be carried out in supercritical water (above 374 °C and 22.1 MPa), which behaves as both liquid and gas whilst remaining a unique homogeneous phase. In this configuration, pressure and temperature are higher than in WAO, requiring specific reactors. Thence, residence times are quite low (from seconds to minutes) but operating conditions promote salt precipitation, plugging and corrosion. Owing to its high removal rates, supercritical water oxidation has been applied for the treatment of toxic and refractory effluents, such as pesticide production wastewater or landfill leachates (Scandelai et al., 2021, 2020; Xu et al., 2015).

Oxidation is a great destructive reaction that improves the biodegradability of recalcitrant organic pollutants by transforming them into stable products such as carbon dioxide, water and low molecular weight compounds as small acid compounds. WAO processes have been proved reliable and effective for waste treatment from different types of industries like chemical, pharmaceutical, natural wastewaters, oil refineries among others (Bhargava et al., 2006). Pinchai et al. (2019) focused their study on WAO for three concentrated synthetic bio-refractory effluents (pharmaceutical wastewater, bilge wastewater and gray wastewater) after membrane process and noted mineralization rates above 80% at 300 °C and 15 MPa. For continuous operation, autothermic WAO applies to effluents with a specific organic load represented by COD concentrations between 10 and 100 $gO_2.L^{-1}$. Below 10 $gO_2.L^{-1}$ exothermic heat from reaction is insufficient to maintain reaction temperature thus leading to very high energy need and above 100 $gO_2.L^{-1}$, effluent may undergo incineration for better process efficiency (Andreozzi et al., 1999; Lefèvre et al., 2011b).

WAO process involves two main stages: a physical stage where the oxygen transfers from the gas phase to the liquid phase and a chemical stage where the oxidation reaction via a free-radical intermediate of the dissolved oxygen and the organic compound occurs. Many factors can influence degradation rate of the chemical stage such as oxidant partial pressure, temperature, pH, duration of reaction and oxidability of the compounds under consideration. The effect of reaction temperature has been detailed in several reviews: for non-catalytic WAO, simplified global Arrhenius dependent rates of pollutant removal are written as follows: $r_r = Ae^{(-E/RT)}(C_P)^m(C_{O_2,L})^n$ (Bhargava et al., 2006; Léonard et al., 2015), where r_r is the reaction rate ($mol.m^{-3}.s^{-1}$), A the pre-exponential factor ($mol^{1-m-n}.(m^{-3})^{m+n+1}.s^{-1}$), E the activation energy ($J.mol^{-1}$), R the gas constant ($J.mol^{-1}.K^{-1}$), T the reaction temperature (K), C_P the specific or global concentration of the pollution ($mol.m^{-3}$), $C_{O_2,L}$ the oxygen concentration in the liquid phase ($mol.m^{-3}$) and m and n the orders of the reaction. Also, an increase in temperature leads to an increase in the value of the diffusion coefficient (Wilke and Chang, 1955). Sufficient total pressure is required to maintain liquid phase and to provide sufficient oxygen in the liquid phase for pollution removal (Brunner, 2014). In most cases, oxygen from air is used in WAO and the oxygen is in excess to avoid transfer limitation and production of undesirable compounds. The pH of the effluent is also a parameter that can be considered since it can modify oxygen solubility and stability of radicals. Also, variations in pH leads to modifications in chemical structure of molecules.

The coupling between RO and WAO gathers pros and cons of each process yielding to a more efficient treatment. Indeed, RO applied to landfill leachates produces a very high-quality permeate (rejection rates higher than 99% for COD (Chianese et al., 1999)) but also a concentrate which requires further treatment and WAO remains an efficient process to degrade organic pollutants but needs a significant organic load to be autothermic in continuous operation. Thus, RO functions as a pretreatment, concentrating pollution in the range required for autothermic WAO. This treatment path is poorly reported in literature, was never applied for landfill leachates, and focused on the treatment of nanofiltration concentrates by WAO oxidation for disperse dye waste, showing retentions higher than 97% (Dhale and Mahajani, 2000). Verenich et al. (2000) also investigated the use of catalytic wet oxidation on concentrated paper mills (from evaporation and ultrafiltration) and reached COD and total organic carbon (TOC) removals between 50% and 80% and an increase in biodegradability.

The aim of this work was to investigate WAO treatment at lab-scale for real landfill leachate RO concentrates regarding composition variations for distinct periods of sampling and assess the roles of WAO operating conditions on conversion of bio-refractory compounds. Studies found in literature focusing on the use of WAO with promoters or catalysts and non-catalytic WAO helped provide guidelines for the choice of operating parameters ranges (Anglada et al., 2011; Galeano et al., 2011; Garg and Mishra, 2010; Oulego et al., 2015; Rivas et al., 2005). Because removal kinetics of complex effluents are difficult to understand in WAO, in-depth study through experimental design methodology has been done. Its objective is to reduce the number of experiments and find the best operating conditions for the considered effluent, using surface responses analysis while taking into consideration influence and interaction of operating parameters. Using this methodology, global oxidation kinetics for different seasonalities, temperatures and pressures over time will be studied.

2. Material and methods

2.1. Sample collection of landfill leachates

The leachates and RO concentrates used in this study were collected from the sanitary landfill site of Balançan (Cannet-des-Maures, France). It is a municipal landfill site that has operated since 1974, receiving approximately 1,70,000tons of waste per year during the last 10 years, and requires aftercare and maintenance (PIZZORNO Environnement, 2013). Samples were taken in January, May and October 2020 and were preserved in plastic containers to be transported to the laboratory and stored in a refrigerator at 4 °C. They were rapidly characterized after sampling, but characterization was also performed before each experiment, even though old leachates can be considered as stabilized leachates. The main characteristics of

Table 1
Characteristics of raw leachates and RO concentrates collected at different periods. The two most important parameters are written in bold.

Parameters	Method relative error (%)	Raw leachates			RO concentrated leachates		
		January	May	October	January	May	October
pH	± 0.1	8.0	8.2	8.2	7.8	7.7	7.6
Conductivity ($mS.cm^{-1}$)	± 0.5	12.5	20.4	29.7	14.7	22.5	40.2
Turbidity (NTU)	± 2	11.3	18.2	40.6	13.5	19.7	48.6
TC ($mgC.L^{-1}$)	± 5	1,207	2,145	3,229	1,339	2,670	4,662
IC ($mgC.L^{-1}$)	± 5	249	402	571	258	457	748
TOC ($mgC.L^{-1}$)	± 5	**958**	**1,743**	**2,658**	**1,081**	**2,213**	**3,914**
COD ($mgO_2.L^{-1}$)	± 4	**1,584**	**2,679**	**4,940**	**1,874**	**3,324**	**6,860**
$[Cl^-]$ ($g.L^{-1}$)	± 0.2	1.7	3.0	5.6	2.0	3.9	7.7
$[SO_4^{2-}]$ ($g.L^{-1}$)	± 0.2	1.4	2.5	4.9	1.8	3.5	8.1

TC: Total Carbon, IC: Inorganic Carbon, TOC: Total Organic Carbon, COD: Chemical Oxygen Demand.

these effluents are reported in Table 1. Leachate composition is prone to seasonal variations as the amount of rainfall throughout the year fluctuates. Leachates collected in January are more diluted than leachates from May; furthermore, the south of France suffers from heatwaves, making leachates more and more concentrated at the end of the year. This Table 1 gives the relationship between the seasonality and COD or TOC variations.

2.2. Wet air oxidation process

Wet air oxidation was carried out in a batch high pressure and high temperature reactor (autoclave) made of stainless steel (Fig. 1). An Inconel vessel with an effective and total volume of 650 mL was placed inside the reactor to avoid corrosion of reactor wall and loaded with 300 mL of the effluent. The characteristics of the reactor were a maximum pressure of 30 MPa and maximum temperature of 350 °C. The temperature inside the reactor was kept constant with a PID controller. A six-bladed stirrer (Maximator Dispersimax) was used for stirring, and set at a constant speed of 1,000 rpm during heating procedure and oxidation to ensure an adequate mass transfer of O_2 from the gas to the liquid phase throughout experiment (Lefèvre et al., 2011a). A motorized pump (Top Industrie PMHP 50–500) permitted the controlled injection of air and nitrogen inside the reactor. The autoclave was equipped for safety with a rupture disk to vent reactor in case of overpressure. A preliminary step of 10 min nitrogen sparging was carried out to remove dissolved oxygen, then reactor was pressurized with nitrogen for the heating procedure at variable pressures depending on the initial COD of RO leachates, for a sample volume of 300 mL and the excess of oxygen desired. Initial nitrogen pressure was calculated using Van der Waals equation of state to meet with total desired pressure of oxidation at the end of the heating phase (Lefèvre et al., 2011b). Once the operating temperature was reached, the oxidant, in our case, air, was sparged into the vessel until total pressure was obtained, considering this moment as the starting point of the experiment (t = 0). A liquid sample of 15 mL was withdrawn at this point to assess the extent of thermal degradation that occurred during the heating procedure. Liquid samples of 15 mL were then steadily collected from the reactor every 90 min, during 6 h, to follow evolution of different parameters. No pH adjustment was made for WAO treatment; temperature and pressure ranges were respectively 200 – 300 °C and 18 – 21 MPa. Previous experiments were carried out to confirm that sampling a total volume of 75 mL (5 samples of 15 mL) during experiments led to the same TOC and COD reductions than during experiments without sampling. After sampling, excess liquid contained in the tubes was pushed back into the reactor by injecting air, also permitting to adjust the pressure. Preliminary experiments were performed to investigate the effect of stirring speed and excess of oxygen on TOC and COD removal rates. Experiments were carried out with stirring speeds of 500, 800 and 1000 rpm and fixing other variables as constant (300 °C – 21 MPa – October – 70% oxygen excess – 60 min). These tests revealed higher TOC and COD removal rates at high-speed assessing a transfer limitation at lower speed (i.e., 1000 rpm was used). Experiments with oxygen excesses of 40%, 70% and 90% were carried out, with temperature, pressure, stirring speed and seasonality kept as constant (300 °C – 21 MPa – 1000 rpm – October – 60 min). These experiments revealed lower removal rates with an excess of 40%, and high TOC and COD removal rates with an oxygen excess of 70%; nevertheless, no significant increase was observed with higher oxygen excess. Therefore, the oxygen excess within further experiments was set at 70%.

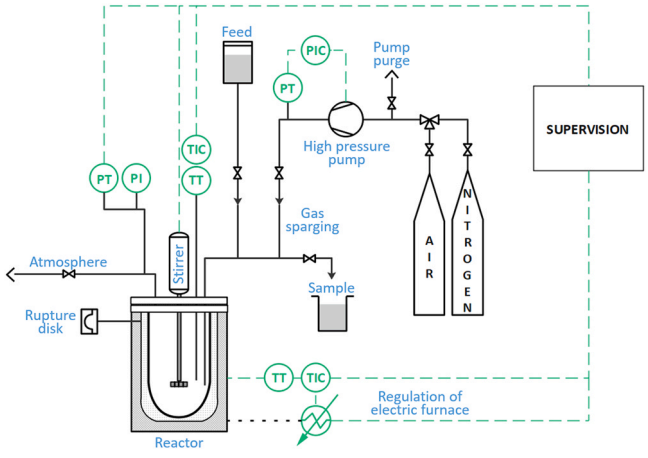

Fig. 1. Schematic diagram of batch WAO unit (TIC, PIC, temperature, pressure indicator and controller; PI, pressure indicator; TT, PT, temperature and pressure transmitter).

2.3. Design of experiments

Design of experiments are statistical methods that provide specific information for the selection and order of experiments (Box and Hunter, 1957; Droesbeke et al., 1997; Myers et al., 2016; Sarabia and Ortiz, 2009). They are used to identify the quantitative influence of chosen parameters by investigating the analytical responses of the experiment. It consists in performing a limited number of experiments where combinations are chosen to study the influence of operating parameters (factors). It is a useful approach to assess the adequate operating conditions, in this case study leading mainly to the highest TOC and COD removal rates. For this purpose, results for a set of experiments were used to establish prediction models for each investigated response. According to the literature and as discussed in the introduction, three factors have been chosen, two quantitative factors: pressure and temperature, and a qualitative factor, the seasonality of the leachate, where the seasonality represents the variations of global pollution criteria such as COD and TOC. As described in the previous section, the excess of oxygen ratio and the stirring speed for WAO were selected during preliminary

Table 2
Studied factors with their domains of variation.

Variable	Factors	Nature of the factor	Variation domains
X_1	Pressure	Quantitative	18 → 21 MPa
X_2	Temperature	Quantitative	200 → 300 °C
X_3	Seasonality	Qualitative	Jan – May – Oct

screening tests for these specific leachates to avoid any limitation in oxygen transfer (1000 rpm and 70% respectively for stirring speed and excess of oxygen). The factors are presented with their respective variation domains in Table 2.

To establish a relationship between the measured responses and the factors, polynomial models were used. A mixed model combining the model for the quantitative factors and the one for the qualitative factor was set. The two quantitative factors (pressure and temperature) were studied using a quadratic model as it allows to consider potential curvature and/or torsion of the surfaces in the domain. The second order model used is presented in Eq. (1).

$$\eta_{quanti} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad (1)$$

where η is the predicted response of the considered parameter, X_i are the coded values of variables (pressure and temperature), β_0 is the intercept term, β_i are linear coefficients for pressure and temperature and with β_{ii} and β_{ij} their squared effects and interaction effects.

The qualitative factor (seasonality) was studied using a "presence-absence" model to quantify the behavior of the three levels, its mathematical expression is presented in equation (2).

$$\eta_{quali} = \beta_0 + \beta_{3A} X_{3A} + \beta_{3B} X_{3B} \quad (2)$$

Finally, the mathematical model chosen for the design was a multiplicative model, its mathematical expression is presented in equation (3). Its purpose is to explore the effects of the quantitative and qualitative parameters while considering interactions between both types of parameters.

$$\eta = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{3A} X_{3A} + \beta_{3B} X_{3B} + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 + \beta_{13A} X_1 X_{3A} + \beta_{13B} X_1 X_{3B} + \beta_{23A} X_2 X_{3A} + \beta_{23B} X_2 X_{3B} \quad (3)$$

To evaluate the coefficients of this method, a set of 18 experiments is selected by using exchange algorithm based on D-optimality criteria (Table 3) since a "classical" design of experiment does not apply to the system used in this study (due to the mix of qualitative and quantitative variables) (Fedorov et al., 1972; Mitchell, 1974). Experiments 3, 14 and 17 were repeated twice to calculate the experimental variance and reinforce the reliability of the final model validations.

The quantitative responses studied for each experiment were COD and TOC removal rates with their absolute values. Other parameters such as IC, conductivity and pH were measured but not investigated for efficiency of WAO as there were no significant variations observed during WAO. The method used to quantify each response is detailed in the following paragraph. Moreover, temperature and pressure were recorded (with respective relative errors of 1% and 0.5%) throughout experiments to adjust the levels of the design with average values for further establishment of response models.

2.4. Chemical and physical analysis of leachates and treated effluents

Characterization was performed on raw leachates, concentrated leachates, and treated effluents. Several parameters were investigated to characterize the liquid fraction after WAO under different conditions to determine efficiency of the global process.

Table 3
Experimental design and operating conditions of the runs of the D-optimal design. The experiments written in italic are the duplicates.

Experiment	Pressure (MPa)	Temperature (°C)	Seasonality
1	18	200	October
2	21	200	October
3	18	200	May
3′	18	200	*May*
4	19.5	250	May
5	21	300	October
6	21	200	May
7	21	200	January
8	18	250	October
9	18	300	January
10	21	300	January
11	19.5	250	January
12	19.5	200	October
13	21	250	October
14	18	200	January
14′	18	*200*	*January*
15	18	300	May
16	19.5	300	October
17	18	300	October
17′	18	300	*October*
18	21	300	May

Oxidation evolution was monitored by analyzing the samples with following measurements. pH was measured at 20 °C using a CONSORT p800 pH-meter with a HI 1131 probe calibrated with pH 4 and 7 buffer solutions with a relative error of ± 0.1% Conductivity was measured at 25 °C using a WTW Cond 3110 with a TetraCon 325 cell, with prior calibration with three standard solutions of conductivities of 147 µS.cm^{-1}; 1413 µS.cm^{-1} and 12.88 mS.cm^{-1}, with a relative error of ± 0.5%. Turbidity was measured using WTW Turb 550 IR in Nephelometric Turbidity Unit (NTU) after standard calibration using 3 solutions at 1,000, 10 and 0.02 NTU. The relative error of this method is ± 2%. Mineralization rate of leachate RO concentrates during WAO was determined by TOC analysis. TOC and IC were measured using Shimadzu TOCL-$L_{CSH/CSN}$ Total Organic Carbon Analyzer. TOC was determined after Total Carbon (TC) and IC measurements. TC carbon is obtained after catalytic combustion at 680 °C; IC is obtained by acidification of the sample before catalytic combustion at 680 °C and stripping (TOC = TC - IC), as programmed in TC and IC methods A non-dispersive IR source detector is used to detect CO_2 produced after combustion. Two calibrations curves were plotted with two standard solutions, one for TC and one for IC. TC standard was prepared with potassium hydrogen phthalate (0.2125 g in 1 L of ultrapure water) and IC standard was prepared with sodium carbonate and sodium bicarbonate (respectively 0.4412 g and 0.3497 g in 1 L of ultrapure water). Samples were characterized after dilution with ultrapure water and filtered through a 0.45 µm nylon filter. Mean values were obtained after measurements in triplicates. For highly mineralized samples with high IC concentration, classical TOC estimation was impossible and Non-Purgeable Organic Carbon (NPOC) method was used. COD reductions were measured on unfiltered samples using commercial tube tests WTW C4/25 (25 – 1500 $mgO_2.L^{-1}$) containing mercury sulfate to reduce chlorine interferences. Dilutions were made to provide samples in the range of tube test, dilutions and blank were done with ultrapure water. Tubes containing 3 mL of the sample and commercial reagents were heated in COD reactor from HACH at 150 °C for 2 h then left to cool at room temperature for 1 h. The COD readings were obtained using PhotoLab S6 WTW photometer with programmed method for range 25 – 1,500 $mgO_2.L^{-1}$. The relative error of this method is ± 4%. Anion concentrations of chloride, nitrate and sulfate were quantified using ion chromatography (883 Basic IC plus Metrohm) with prior calibration using a 150 ppm NaCl solution, $NaNO_3$ and $(NH_4)_2SO_4^{2-}$ solutions at 100 ppm at maximum concentrations, then diluted with ultrapure water. Samples were

diluted with ultrapure water to fit in calibration curve and filtered through a 0.45 µm nylon filter. Relative error for this method is ± 5%. An analysis of the gas fraction was performed on a gas sample withdrawn at the end of oxidation, at room temperature. The gas composition in the reactor was used to evaluate oxidation efficiency and check the mass balance. For that purpose, a sample bag was placed at the vent of the autoclave to collect gases. Detection was done using the Geotech GA5000 portable analyzer capable of identifying CO_2, CH_4, O_2 and H_2S.

3. Results and discussion

3.1. Validation of the models

The analysis of data obtained for the 18 (+ 3 replicates) experiments was performed by AZURAD® software, using a statistical approach at first for a global evaluation of data. Then, from the experimental results, the estimation of the model coefficients (3) has been calculated using multi-linear regression. To validate the postulated model, ANOVA test was used, and regression models' adequacy and significance were checked for each selected response. The significance and accuracy of the model were then validated by analyzing the statistical and experimental variances (p-value and R^2). The value of the variance was calculated from the 3 replicates (experiments 3, 3′, 14, 14′ and 17, 17′) and showed a very good repeatability of responses which verifies the robustness of the model. This indicated that variations in responses were function of the variations of the levels of the factors, and not function of the experiment itself. For each model, theoretic values were calculated in the entire domain of interest and compared to experimental responses. To consolidate model validity, duplicate experiments were included in ANOVA tests. Models were proven to be accurate if the theoretic responses corroborated with experimental responses.

3.1.1. Models for COD and TOC removals

Results were examined for each sample withdrawn from the reactor during WAO. After 6 h of oxidation, removal rates for all experiments including duplicates indicated COD removals varying from 56% to 94%, with an average removal of (74 ± 14)% and TOC removals varying from 50% to 99% with an average of (74 ± 20)%. For the study of COD and TOC responses for all the times of sampling, models were proven accurate as experimental data, shown in the next sections, were consistent with calculated responses. For example, a maximum difference of 6.9% suggested model is satisfactory for determining COD responses in the domain of interest. The regression was proven reliable with a coefficient of determination value of 0.946 and p-values for regression and validation value of 0.02% and 28.41% respectively. Stated model is valid to predict COD removal after 6 h of oxidation in the domain of interest. For TOC removal rate model, regression was also proven as reliable with a coefficient of determination value of 0.989. The maximum difference observed between experimental and model TOC response was of 4.8% attesting the stated model is valid. Predictive models were also obtained for all the times of sampling. Coefficient of determination had values between 0.845 and 0.989 for TOC removals (%) and between 0.779 and 0.987 for COD removals (%). The values of the coefficients of the models after 6 h are presented in Table 4. They reveal a strong influence of reaction temperature represented by the coefficient β_2, meaning there is an important positive effect of temperature on COD and TOC removal rates. Coefficient β_1 representing pressure, β_{3A} and β_{3B} representing the presence or absence of seasonalities have lower values and are considered as less significant in comparison with temperature (i.e. whatever the seasonality the removal rates (%) are not significantly impacted).

Table 4
Coefficient values to calculate COD and TOC removal rates after 6 h of oxidation.

Coefficients	η_{COD}	η_{TOC}
β_0	73.58	74.68
β_1	0.50	-1.72
β_2	14.09	21.43
β_{1-1}	1.62	-0.87
β_{2-2}	0.31	1.07
β_{1-2}	1.60	0.65
β_{3A}	-2.97	-1.22
β_{3A1}	0.73	3.77
β_{3A2}	3.71	-1.71
β_{3B}	-1.15	-2.51
β_{3B1}	-0.55	2.64
β_{3B2}	2.61	2.57

Table 5
Coefficients values to calculate initial COD oxidation rates.

Coefficients	
β_0	-8.32
β_1	1.17
β_2	-1.85
β_{1-1}	1.73
β_{2-2}	-4.63
β_{1-2}	-2.58
β_{3A}	7.66
β_{3A1}	-1.05
β_{3A2}	-1.31
β_{3B}	3.60
β_{3B1}	-1.31
β_{3B2}	1.61

3.1.2. Model for initial kinetic rates

The initial kinetic rates (COD oxidation rate over the first 180 min) were also used as a response for the design of experiments. The coefficients of the model are presented in Table 5. Model's accuracy was validated through the use linear regression and statistical and experimental variances, with a coefficient of determination of 0.763 and p-values for regression and validation of respectively 7.89% and 10.05%. With a value of − 1.85, the coefficient of temperature β_2 suggests that an increase in temperature decreases the value of the COD oxidation rate in concordance with previous results. This process requires a high temperature to sufficiently initiate WAO.

3.2. Process performances

The different operating conditions established by the design lead to a set of responses for two major parameters to evaluate oxidation efficiency. Pollution removal quantification was investigated through TOC and COD concentrations as mineralization by-products are complex to identify in leachate. Pollution removal and absolute values were considered for qualification of degree of oxidation. Removal rates were calculated as presented in Eq. (4), by considering the total volume withdrawn from the reactor for each time of sampling during the experiments:

$$\eta_{i,exp}(\%) = \frac{(V \times [i]_0 - (V - V_{sample}) \times [i]_t)}{(V \times [i]_0)} \quad (4)$$

where V stands for the initial volume of effluent in the reactor, V_{sample}, the total volume withdrawn from the reactor cumulated throughout the time (L), $[i]_0$ and $[i]_t$ the concentrations (TOC and COD) before WAO and throughout the experiment respectively ($mg.L^{-1}$).

In the following paragraph and as example, experimental responses are presented for the duplicate of the seventieth experiment (18 MPa – 300 °C – October), for both aqueous and gaseous phases.

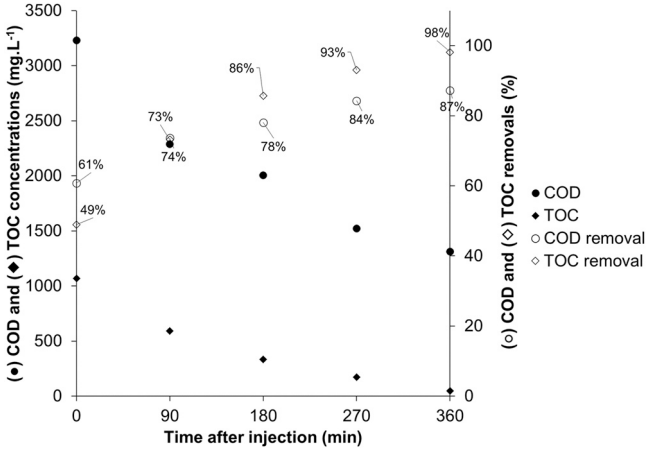

Fig. 2. Evolution of (•) COD and (◆) TOC concentrations with their corresponding removal (○, ◇) rates during WAO (300 °C – 18 MPa – October; initial COD: 8250 $mgO_2.L^{-1}$and initial TOC: 2094 $mgC.L^{-1}$).

The initial characteristics for this experiment are concentrations of 2094 $mgC.L^{-1}$ and 8250 $mgO_2.L^{-1}$ of TOC and COD respectively.

3.2.1. Validation of global behavior and mass balance

The experiments were carried out at original pH of concentrated leachates (7.7 ± 0.1) to reduce the use of chemicals to correct pH value. Results indicated a maximum pH variation of 0.5 after the 6 h of oxidation indicating a very low pH variation during WAO. In addition, conductivity of the treated effluent indicated no significant variation throughout experiment. Therefore, these parameters were uninvestigated for the study of WAO. The two principal parameters used for characterization were TOC and COD. IC concentration decreased after the heating procedure in absence of oxygen as thermic degradation had occurred and stayed constant during oxidation, while changing dissolved CO_2 concentration in the liquid phase and. Initial IC concentration was recuperated after the cooling of the treated effluent; thus, IC was not considered for the efficiency study of WAO. Thermal degradation of concentrated leachates was evaluated when the required temperature of experiment was reached. COD concentration decreased from 8250 to 1312 $mgO_2.L^{-1}$ in correspondence with a TOC decreasing from 2094 to 0.05 $mgC.L^{-1}$ indicating that after 6 h of oxidation, operating conditions allowed COD and TOC removals of 87% and 98% respectively, assessing efficiency of WAO on the removal of leachates' bio-refractory compounds. The remaining COD and TOC were attributed to the presence of low-molecular-weight compounds refractory to WAO as explained by García et al. (2020) who studied the WAO of humic acids and revealed a formation and accumulation of refractory compounds during oxidation. Experimental oxidations kinetics are shown in Fig. 2.

A carbon mass balance was established from liquid and gas phase TC compositions to validate global process efficiency. The inlet was characterized as TC concentration in raw concentrated leachates. The outlet was characterized as the sum of TC concentration in treated effluent after 6 h of oxidation and the mass of carbon from CO_2 and CH_4 production in gas phase. Masses were obtained with ideal gas law and molar fraction measured experimentally. An acceptable deviation of – 16% was calculated, attributed to a slight understated measurement of dissolved carbon in feed.

3.2.2. Effect of temperature, pressure and seasonality

COD and TOC removals as well as concentrations removed were plotted after 6 h of oxidation for the three tested pressures and seasonalities (Fig. 3). Temperature seems to be the factor which controls the degradation of organic matter whereas pressure and seasonality appear to have lower impact on degradation in the domain of study. García et al. (2020) reported similar effects on the increase of removals as a function of temperature and no improvement of removals as a function of pressure, as Demesa et al. (2015). However, the initial pollution concentration varies depending on the month of sampling, meaning that the impact in terms of removal rate (%) is low but the total amount of pollution removed is significantly higher for the month with the highest initial pollution concentration (i.e., for the seasonality of October). High temperature almost achieved complete COD and TOC removals (> 87% and > 96% respectively) for the same duration of experiment. On average, maximum differences of 10% and 4% were noted for COD and TOC removals respectively for experiments under same temperature and seasonality with different levels of pressure after 6 h of oxidation. COD removals reported by García et al. (2020) on humic acids are in the same range and noted that an increase in temperature leads to high removal rates (%) in shorter time (84% of humic acids were degraded at 220 °C after 100 min). Temperature dependance was also found by Zerva et al. (2003) on oily wastewaters and by Mucha and Zarzycki (2008) on sewage sludge. Lin and Ho (1997) noticed that removals were not impacted by the pressure and recommended working at the lowest pressure for capital cost. The major role of pressure in this process is to maintain oxidation reaction in the liquid phase and enhance dissolved oxygen concentration in the effluent. Hence, the total pressure of 18 MPa appears to be sufficient for this case study.

Furthermore, removal rates did not vary significantly for experiments with different seasonality and same temperature and pressure, though the amount of oxidized matter per volume of treated effluent is not the same for the three seasonalities. The maximum oxidized amount was observed for the month of October at 300 °C – 21 MPa with COD and TOC removals respectively of 93%

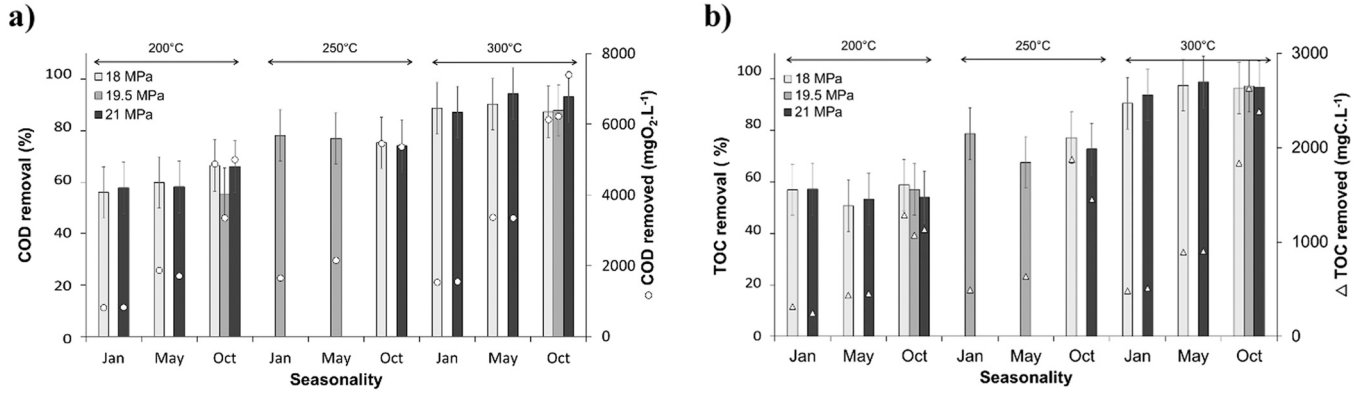

Fig. 3. Effect of pressure and temperature on a) (○)COD and b) (△)TOC removal rates with their respective removed amount per volume of treated effluent.

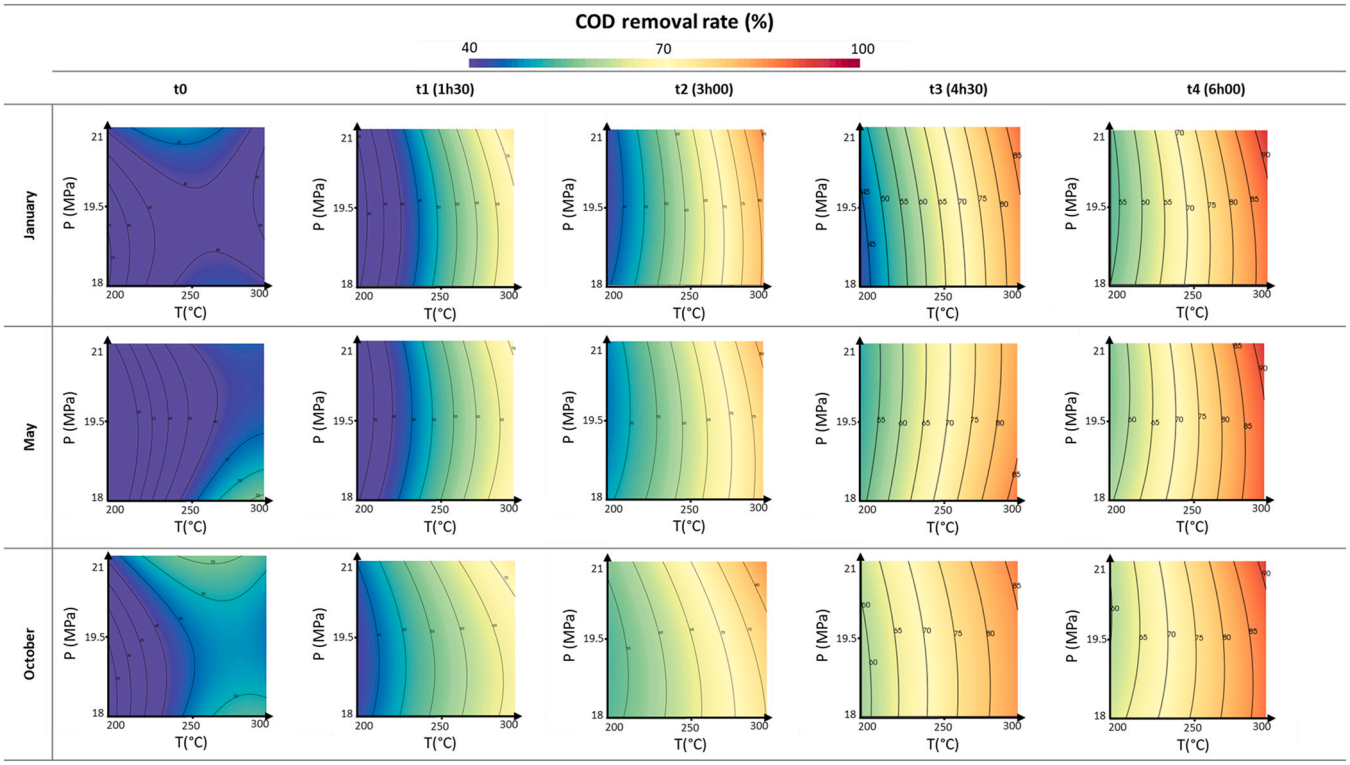

Fig. 4. Response surface plots of COD removal rates as a function of pressure and temperature, for all three seasonalities and during the 6 h of oxidation.

and 97%, corresponding to degraded amounts per volume of treated effluent of 7,394 $mgO_2.L^{-1}$ and 2,382 $mgC.L^{-1}$.

The use of the design allows the display of the responses in 3D with response surfaces and contour plots of the predicted responses by the models, as a function of pressure and temperature.

The results of the design are reported graphically in Fig. 4, where COD removal rates are presented as a function of time for the three seasonalities for each time of sampling. Regarding COD removal iso-response curves, there is a clear dependance of temperature on oxidation reaction. The thermal pollution removal measured for the first sample ranged from 12% to 61%, under the operating conditions of 200 °C – 21 MPa – May and 300 °C – 18 MPa – October respectively, in correspondence with TOC reductions of 9% and 50%. The initial pollution was considered for the determination of COD and TOC removals, as thermal degradation is a phenomenon that occurs during the heating procedure, even for industrial bubble columns. Once the oxidation reaction has started, the second sampling (after 90 min), reveals iso-response curves with the same shape, suggesting pressure's effect is marginal on COD removal as determined previously, in the domain of study. Additionally, the results do not indicate a dependance of the seasonality, initial COD concentration does not affect the final COD removal rates though as stated previously, greater absolute amounts are removed for high initial concentration. The maximum removal obtained after 6 h of oxidation is over 90%. However, given the residual COD concentration in the final effluent, October is the month where the highest quantity of pollution is removed. For initial COD and TOC average concentrations of 7,938 $mgO_2.L^{-1}$ and 2,406 $mgC.L^{-1}$, quantities removed per volume of treated effluent were between 3,734 and 7,252 $mgO_2.L^{-1}$ for COD and between 882 and 2,360 $mgC.L^{-1}$ for TOC.

The effect of the seasonality was also investigated by comparing the decrease of COD over time for the three seasonalities at 300 °C and 21 MPa, as presented in Fig. 5. The effluent with the highest initial concentration (i.e., October) was subject to the most important removal during the first 180 min 60% COD removal was

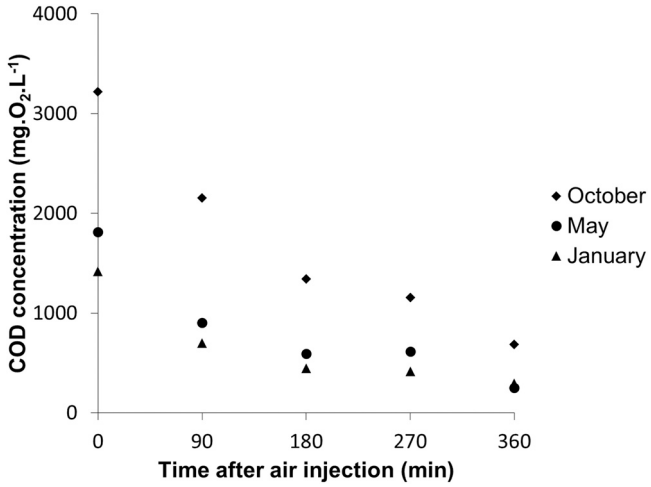

Fig. 5. Evolution of COD concentration during WAO for the seasonalities of (◆) October (•) May and (▲) January at 300 °C and 21 MPa.

obtained during the heating procedure leading to a COD concentration of 3,220 $mgO_2.L^{-1}$ at time of air injection, then followed by a removal of 1,880 $mgO_2.L^{-1}$ over the first 180 min. For the seasonalities of May and January, respectively, 50% and 23% of removal was obtained during the heating procedure and the amount removed during the first 180 min was 1,221 $mgO_2.L^{-1}$ for the seasonality of May and 974 $mgO_2.L^{-1}$ for the seasonality of January.

Also, the values presented in Table 6 show a strong dependance to temperature, as commented with previous data. For each seasonality, the model suggests that temperatures between 280 and 300 °C allow the optimal rate for initiation of WAO. This figure also confirmed that the initial pollution concentration was a contributing

Table 6
COD oxidation rates ($mgO_2.L^{-1}.min^{-1}$) over the first 180 min.

Temperature (°C)	Seasonality	Pressure (MPa)		
		18	19.5	21
200	January	-0.40		-3.64
200	May	-5.04		-6.01
200	October	-17.60	-7.36	-8.15
250	January		-1.92	
250	May		-4.54	
250	October	-3.29		-8.07
300	January	-4.83		-8.01
300	May	-6.19		-10.10
300	October	-9.42	-20.88	-11.86

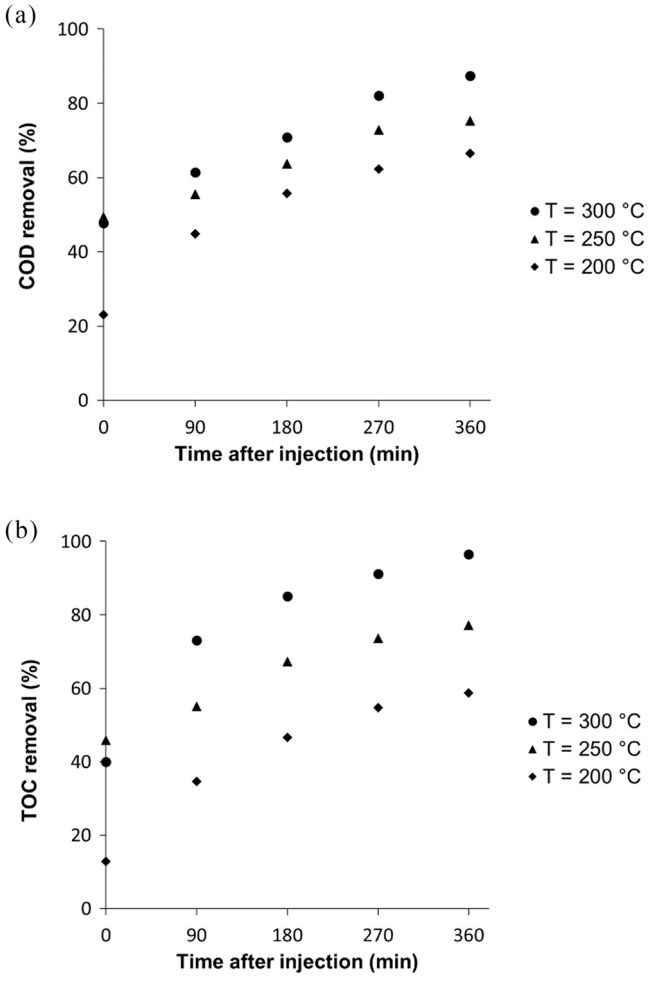

Fig. 6. Effect of temperature (•) 300 °C, (▲) 250 °C and (◆) 200 °C on (a) COD and (b) TOC removals for a constant pressure of 18 MPa and the seasonality of October.

factor in removal rates, e.g., for the seasonality of October, initial kinetic removal rates are more important (from - 7.50 to – 15.07 $mgO_2.L^{-1}.min^{-1}$).

According to the results, a high temperature of 300 °C, a sufficiently concentrated leachate and an appropriate total pressure to maintain the system in a liquid phase are the best operating parameters to carry out WAO.

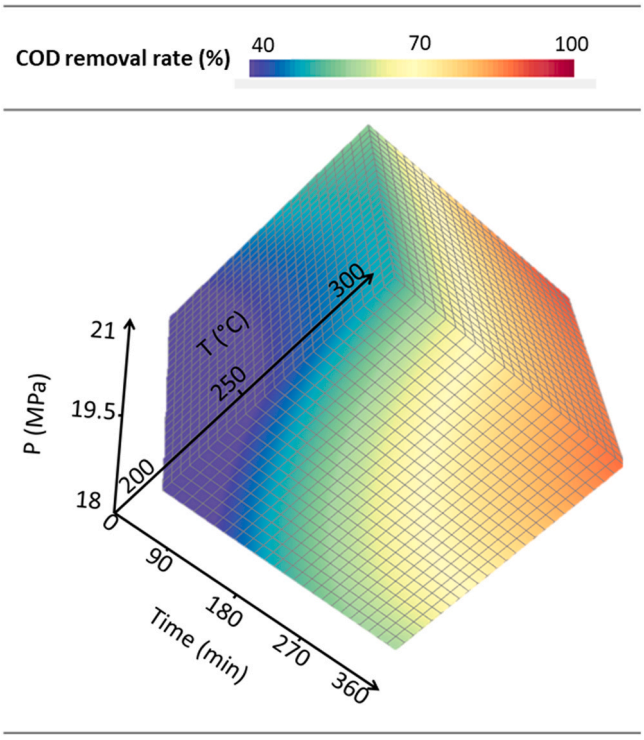

Fig. 7. Cube of response for COD removal rate for the month of October as a function of pressure, temperature and time.

3.2.3. Kinetics and effect of reaction time

The data obtained from the design were utilized to perform kinetic studies. A typical kinetic feature was obtained with a two-step reaction (Fig. 6). In average, after 180 min of oxidation, pollution removal leveled off, indicating probable formation of short-chained organic compounds resistant to WAO. One way to limit this phenomenon could be the use of catalysts or higher temperature, as suggested by Lin et al. (1996).

Experimental COD oxidation removal rates were evaluated for the initiation of the reaction on the first step (from 0 to 180 min). It is noted that the greatest removal rates were found for the seasonality of October with COD oxidation rates varying between - 9.42 and - 20.88 $mgO_2.L^{-1}min^{-1}$ at 300 °C (Table 6).

The feature of the removal rates versus temperature revealed the importance of the duration of the reaction. Thence, in hindsight, duration was included in the design of experiment to study its influence.

This study was conducted following the parameters of the design. The duration of oxidation was not set as a parameter of interest as the objective of the study was to assess the feasibility of WAO for the treatment of concentrated leachates, where the refractory compounds can be a limiting parameter in oxidation, in agreement with previous results on similar effluents (Goi et al., 2006). Nevertheless, a post-treatment of the duration of oxidation was performed to maintain a continuity in the surface responses for the duration parameter. The design contained the three initial factors (pressure, temperature and seasonality) and time, where time was a qualitative variable with five levels (0 – 90 – 180 – 270 and 360 min). Results were, in this case, a cube of responses, for example the cube obtained for the seasonality of October is presented in Fig. 7. At a constant pressure of 18 MPa, the surface responses were plotted, as

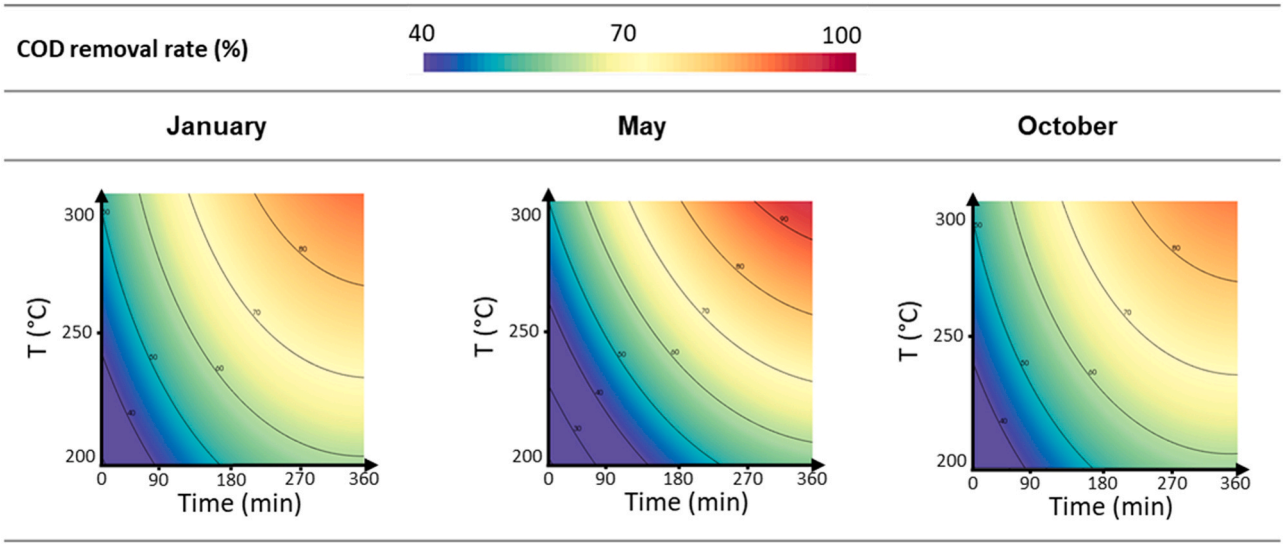

Fig. 8. Response surfaces for COD removal for the three seasonalities as a function of temperature and time.

presented in Fig. 8. For COD removals higher than 80%, oxidation must at least last for 4 h, as for TOC removals.

4. Conclusion

This study investigated the treatment of concentrated leachates by non-catalytic WAO using experimental design methodology. WAO was efficient for the remediation of old leachates concentrated by RO and sampled at three different seasons. The significant factor governing COD and TOC removals is the temperature, in accordance with the models' values. The highest yields were achieved after 6 h of oxidation at 300 °C – 21 MPa for the month of October with 93% COD removed and 97% TOC removed. Also, a duration of at least 4 h is needed to reach 80% COD and TOC removals. Kinetic study confirmed that elevated temperature and inlet COD concentration were important factors for the initiation of the reaction and oxidation rates decreased throughout time due to the formation of compounds refractory to WAO. On the other hand, no dependance of pressure was demonstrated in the studied domain. At maximum, differences of 10% and 4% were noted for COD and TOC removal rates respectively. Models based on experimental data were established to calculate COD and TOC concentrations and removal rates at different times throughout experiment and a model for the estimation of the kinetic rate, tested through ANOVA and R^2.

To conclude, RO provided a concentrated effluent that could reduce the cost of WAO while permitting greater removals for high initial pollution concentrations. Criteria for the discharge to the environment of landfill leachates are presented in the decree of non-hazardous landfills (Ministère de l'écologie, du développement durable et de l'énergie, 2016). The mix between RO's permeate and WAO outlet, regarding conversion rate of RO, reached TOC criteria for a discharge in the environment (< 70 $mgC.L^{-1}$) in all the experiments conducted at 300 °C with TOC of the mix in the range of 10 – 57 $mgC.L^{-1}$. COD discharge criteria (< 125 $mgO_2.L^{-1}$) was not fully reached , at minimum the residual COD concentration of the mix was of 179 $mgO_2.L^{-1}$.

The treatment pathway shows high potential for the remediation of old and stabilized leachates, with great removal efficiencies and without the addition of catalysts, chemicals and oxidation promoters, at lower cost than incineration. Further work is required to scale up from the batch reactor to the industrial bubble column under wet air oxidation conditions (de Souza et al., 2022). Indeed, bubble size and interfacial area can be impacted by pressure, temperature and gas and liquid velocities. Also, deeper investigation of discharge criteria and cost analysis are necessary for industrial feasibility and environmental. In the future, the environmental significance of this study is to strongly reduce, with the use of a hybrid process (membrane + WAO), the pollution in terms of COD and TOC concentrations with the WAO of membrane concentrates, while generating a global outlet including membrane permeate to discharge the entire treated effluent, whatever the nature of the effluent.

Declaration of Competing Interest

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

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