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# **TERTIARY TREATMENT OF BIOLOGICALLY PRE-TREATED LANDFILL LEACHATES BY NON-CATALYTIC WET OXIDATION**

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**Abstract**

Effluents from the biological treatment of landfill leachates continue to have great environmental impact, and there is still a need to develop feasible tertiary treatments for these aqueous wastes in order to comply with legislation. For this reason, the treatment of biologically pre-treated leachates by non-catalytic wet oxidation was here investigated and the effect of the main operating conditions, such as temperature (423- 483 K), pressure (2.0- 8.0 MPa) and pH (2.0 – 11.0), on the degree of mineralization, biodegradability, toxicity and colour were analysed. These results revealed the presence in the leachate of easily oxidizable compounds (10-25% of the initial COD), which were degraded at the beginning of the reaction, causing a fast reduction in COD and colour number and increasing the pH value. Once the most easily oxidized matter was degraded, COD decreased more slowly over time, showing asymptotic behaviour at high reaction times due to the presence of refractory compounds (35% of the initial COD in the best of the cases). Increases in pressure and/or temperature improved the degradation rate and the final degree of mineralization, although pressure had no significant effect on biodegradability, toxicity or colour reduction. Operating temperatures near 463 K and/or the addition of alkali to the leachate caused the appearance of coloured intermediates in the medium that significantly decreased the biodegradability of the effluent. With the exception mentioned above, the biodegradability of the leachate was greatly enhanced by wet oxidation. Thus, biodegradability indices ( $BOD_5/COD$ ) from 0.16 to 0.49 were obtained, the initial value being 0.012. Finally, the experimental results were successfully fitted to a pseudo-first order kinetic model.

**Keywords:** biodegradability, kinetic model, landfill leachates, toxicity, wet oxidation

**Nomenclature**

AOP = Advanced oxidation processes

AOS = Average oxidation state

$BOD_5$  = Biochemical oxygen demand (mg/L)

$BOD_5/COD$  = biodegradability index

CN = colour number

COD = chemical oxygen demand (mg/L)

$E_a$  = activation energy (kJ/mol)

$k_i$  = apparent reaction rate constant ( $s^{-1}$ )

LI = luminescence inhibition (%)

P = pressure (MPa)

$r_i$  = reaction rate of component i (mg/L s)

t = time (s)

T = temperature (K)

WWTP = wastewater treatment plant

$\alpha_i$  = oxygen reaction orders

## 1. Introduction

Leachates are defined as highly contaminated wastewaters generated by rainwater percolating through the waste layer in municipal landfill during the decomposition process of the solid wastes [1]. These wastewaters are often a mixture of high-strength organic and inorganic contaminants in dissolved or suspended form. Among all the pollutants present in the leachate, the refractory humic substances, mainly humic acids and fulvic acids, are the major components. Frequently, other compounds such as ammonium, heavy metals, chlorinated organic compounds, benzene, toluene and xylenes can also be found, although their concentrations depend on the age of the landfill, climate and the type of municipal waste [2-4]. Taking into account that landfilling is nowadays the main method for disposal of the huge amount of municipal solid wastes generated throughout the world, the development of affordable technologies for the treatment of such contaminated streams has become essential in the last few years [5,6].

Several types of treatments have been used in order to achieve a satisfactory degree of removal of refractory pollutants from landfill leachate. Due to their cost-effectiveness, biological processes are the methods most commonly adopted to remove the bulk of organic pollutants from landfill leachate.

Nevertheless, although biological processes are quite effective when they are applied to relatively young leachates, they are less efficient for the treatment of the older ones with higher content in refractory compounds and ammonium [7, 8]. The landfill leachate investigated in this study had already been treated biologically; however, it still had high chemical oxygen demand (COD), together with very low biodegradability and an intense dark colour. As a consequence, alternative or additional technologies are required in order to reduce its refractory pollutant load and/or improve its biodegradability. Advanced oxidation technology is considered as one of the most promising options for leachate treatment, due to its ability to enhance the biodegradability of the recalcitrant compounds [1]. These processes involve the generation of hydroxyl free radicals, which have very high oxidation potential, by means of the use of strong oxidants ( $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ), radiation (ultraviolet, ultrasound, electric beam) and/or catalysts (transition metal salts, photocatalysts) [8,9]. A detailed overview of the current advanced oxidation processes (AOPs) for leachate treatment can be found in Renou et al. [5] and Wiszniowski et al. [10]. One common drawback of AOPs is the high electrical energy demand of devices such as ozone generators, UV lamps and ultrasound systems, among others. The high chemical oxygen demand of the leachate results in rather high treatment costs. Wet oxidation competes in costs with other AOPs for the treatment of industrial wastewaters [11, 12] and therefore appears to be an attractive method for the treatment of landfill leachates. This technique is usually applied to contaminated waste streams which are too diluted to be incinerated ( $\text{COD} < 100 \text{ g/l}$ ) and/or with a level of biodegradability too low to be treated biologically ( $\text{BOD}_5/\text{COD} < 0.1$ ) [13]. As mentioned above, wet oxidation is an interesting technique for use with the non-biodegradable effluents of several industries, including the tertiary treatment of landfill leachates. However, research analysing the application of this treatment to leachates is scarce. Studies found in the literature are mainly focused on the use of promoters during the oxidation, such as 2,4,6-trichlorophenol and  $\text{NaNO}_2$  [14], potassium persulphate [15], peroxide [16] or Fenton reagent [17]. Other studies found in the bibliography used homogeneous [16] or heterogeneous catalysts [18-20].

Nevertheless, as far as we know, studies on the non-catalytic wet oxidation of leachates (pre-treated or not pre-treated) do not exist, despite the fact that the use of treatments in the absence of catalyst makes them simpler and cheaper. Besides, this information would be very useful as a step towards determining the best conditions for degradation. At the same time, it can also be used to establish the guidelines for the operation and design in systems with different catalysts and/or promoters.

In view of these considerations, the aim of this paper was to obtain an in-depth knowledge of the non-catalytic wet oxidation of biologically pre-treated landfill leachates, paying special attention to the effect of the main operational conditions on the degree of mineralization, biodegradability, toxicity and colour reduction. This work will permit progress in the implementation of this technique as a tertiary treatment after the in situ biological process.

## **2. Materials and methods**

### **2.1. Landfill leachate**

The leachate used in this study was taken from the La Zoreda landfill site (Asturias, Spain). This leachate was previously treated at the landfill by means of a pressurised nitrification–denitrification process, the leachate being characterized by a high volatile solids content (~14 g/L) and high oxygen solubility as a consequence of the pressure applied (2.5–3.0 bar). Biomass is subsequently separated using an ultrafiltration system. The plant treats up to 550 m<sup>3</sup>/day of leachate. Methanol is added as a source of easily biodegradable organic matter to carry out the denitrification process [21]. The leachate used in this work was collected from the final permeate. All the experiments were performed with the same leachate, i.e. proceeding from the same batch. This aqueous waste presents high COD values, very low biodegradability (non-biodegradable), intense colour and approximately neutral pH. A more detailed description of its characteristics and the variability found in the landfill site is shown in Table 1.

TABLE 1

## 2.2. Apparatus and procedure

Experiments were carried out in a 1 L capacity semi-batch reactor (Parr T316SS) equipped with two six-bladed magnetically driven turbine agitators. A more detailed description of the procedure can be found in Oulego et al. [22]. In a typical experiment, 0.7 L of landfill leachate was introduced into the reaction vessel, which was then heated and pressurized to the operating conditions under a continuous oxygen flow ( $2.33 \times 10^{-5} \text{ Nm}^3/\text{s}$ ). The oxygen was bubbled through the water reservoir in order for this gas to become saturated with water vapour before being sparged into the reaction vessel. A valve and a coil fitted to the top of the vessel allowed the withdrawal of samples during the reaction. Reaction temperature and pressure were maintained constant during the course of each experiment. Two bubblers filled with a concentrated sulphuric acid solution and two bubblers filled with a concentrated sodium hydroxide solution were installed at the end of the gas line with the purpose of absorbing ammonia and carbonates, should they be formed. All the experiments were done at least in duplicate as separate, independent experiments.

## 2.3. Analytical methods

COD concentration was determined by a colorimetric method according to Standard Methods [23] using a DR2500 spectrophotometer (Hach Company, USA). Biochemical oxygen demand ( $\text{BOD}_5$ ) was measured using a respirometric measurement system: Lovibond® OxiDirect unit. Manometric respirometers relate oxygen uptake to the change in pressure caused by oxygen consumption. A trap filled with KOH solution captured  $\text{CO}_2$  resulting from bacterial respiration. Total organic carbon (TOC) analysis was performed using a TOC analyser (Shimadzu TOC-V<sub>CSH</sub>). pH was measured by means of a pH- meter Jenway 3510.

Bacterial toxicity assessment was performed with *Vibrio fischeri*. For these bioassays, the commercial assay Biofix®Lumi-10 was employed using a freeze-dried selected strain of the marine bacterium (NRRL number B-11177). Toxicity was evaluated in samples diluted 1:5 and results are given as inhibition percentage (LI) in agreement with ISO 11348-3 [24]. The drop in light emission of the bacteria after a contact period of 15 min was measured and compared with a toxicant-free control (2% NaCl solution).

The pH of the samples was adjusted between 6.5 and 7.5. All analytical measurements were done at least in triplicate, and the standard deviation was found to be below 5% in all cases.

The colour number (CN), which is defined in equation 1, was used to monitor changes in the colour of the leachate during its oxidation. Spectral absorbance coefficients (SAC) are defined as the ratio of the values of the respective absorbance (Abs) over the cell thickness (x). This parameter was measured at 436, 525 and 620 nm using a UV/Vis spectrophotometer (Thermo Scientific, Helios  $\gamma$ ).

$$CN = \frac{SAC_{436}^2 + SAC_{525}^2 + SAC_{620}^2}{SAC_{436} + SAC_{525} + SAC_{620}} \quad (1)$$

$$SAC_i = \frac{Abs_i}{x} \quad (2)$$

Finally, average oxidation state (AOS) was calculated as follows [25]:

$$AOS = \frac{4(TOC - COD)}{TOC} \quad (3)$$

where COD and TOC values are expressed in mol O<sub>2</sub>/L and mol C/L, respectively.

### 3. Results and discussion

#### 3.1. Preliminary tests.

An oxidation experiment at 6 MPa and 453 K of pressure and temperature, respectively, was performed in order to assess the oxidizability of the landfill leachate. These experimental conditions were selected taking into account the typical values for wet oxidation processes and the good results obtained when they were used for the treatment of real coke wastewaters [22]. The initial pH of the landfill was 6.8. Figure 1 shows the evolution of the key parameters (COD, TOC, AOS, biodegradability index (BOD<sub>5</sub>/COD), luminescence inhibition (LI), colour number (CN) and pH) during the experiment.

FIGURE 1

As can be seen in Figure 1a, the COD value showed a fast decrease during the first 30 min and then remained practically constant until 90 min, decreasing again after that time. This suggests the presence of some more easily oxidized compounds, which are degraded at the beginning of the reaction when the desired operating conditions have not yet been achieved.



The graphs of the operating conditions (temperature and pressure) changing with time are shown in Figures S1 to S3 of the Supplementary Material. The TOC value evolved in a similar way, reaching a removal percentage of 18% at the end of the heating period (90 min). The experimental COD and TOC data were successfully fitted to a pseudo-first order kinetic model with asymptotic values, i.e., remaining COD ( $COD_{\infty}$ ) and TOC ( $TOC_{\infty}$ ), respectively. The values of the kinetic constants,  $COD_{\infty}$  and  $TOC_{\infty}$  are shown in Table 2. A reduction in leachate COD during the heating up period of the bioreactor was also observed by Anglada et al. [16]. Chen et al. pointed out the same behaviour for the wet oxidation of printing wastewaters [26]. According to these authors, this behaviour was partly due to the loss of volatile organics with continuous stirring, as well as to the thermolytic decomposition of some unstable constituents of the effluent. The same phenomena are likely to have occurred in this work, being responsible for the initial mineralization observed. Once volatile organics had been stripped and the most easily oxidized COD had been degraded to more refractory compounds, the COD and TOC remained constant until the desired operating conditions were achieved and the oxidation process was reactivated. This occurred after 90 min when the COD and TOC began to decrease again. It is likely that the formation of radicals responsible for the subsequent oxidation began during this period. During the last phase of oxidation, the average oxidation state (AOS) increased from -3.6 to -1.9, indicating that COD removal was higher than TOC reduction. The increase in the AOS was greater between 90 min and 150 min (see Figure 1b), which suggests that the formation of reaction intermediates was faster during this period. From this point onwards, the increase in the AOS was less marked, revealing the partial oxidation of these intermediates to carbon dioxide.

Both COD and TOC parameters showed asymptotic behaviour at the end of the experiment and remained constant after almost 5 hours. Anglada et al. [16] also reported that COD removal in municipal landfill leachates became negligible for treatment times greater than 2 h (at 453 K, 2.5 MPa and pH 8.4) due to the formation of recalcitrant organic compounds such as low molecular weight carboxylic acids. Final COD and TOC reductions were 49% and 35%, respectively.

According to Wang et al. [14] the wet air oxidation of fulvic acid (unmixed with other compounds) (200 mg/L), carried out at 423 K and 0.5 MPa of O<sub>2</sub> for 4 h, yielded 12.2% TOC removal. Anglada et al. [16] reported a 28% COD reduction after 4 h during the non-catalytic wet oxidation of a leachate at 453 K, 2.5 MPa and pH 8.4. We obtained higher COD removals than Anglada et al. [16] since the operating pressure used was higher and the pH of the medium was lower. High pH values hinder oxidation, as will be explained later (see section 3.2.3). Besides, it should be noted that the leachate used in the study of Anglada et al. was not previously treated biologically and it presented higher COD and BOD<sub>5</sub> values. Comparing our results with those obtained using other AOPs, COD removals achieved after the non-catalytic wet oxidation are similar to those reported in the bibliography for ozonation (50-70%) or Fenton treatment (45-75%), but lower than the reductions achieved combining oxidants or adding an irradiation system [18, 27-29]. For instance, COD removal rates as high as 90% were reported using O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> as oxidants, whereas photo-Fenton processes showed COD reductions in the range of 70% to 78% [5].

The wet oxidation process also improved the biodegradability of the leachate and the BOD<sub>5</sub>/COD ratio evolved from an initial value of 0.012 to 0.29 after 8 h (see Figure 1c). This final value is slightly lower than those reported in the bibliography using other AOPs [28, 29]. Nevertheless, it should be noted that in those studies the leachates were not biologically pre-treated and the initial biodegradability index ranged from 0.10 to 0.20. In our case, the initial value was extremely low since the leachate had been pre-treated biologically, so the relative increase in the biodegradability using wet oxidation was higher than the results reported using other AOPs. Colour removal was positively influenced by the non-catalytic wet oxidation treatment, which led to a significant reduction in intensity (see Figure 1e). Thus, the colour of the leachate changed from dark brown to pale yellow. Unlike COD and TOC evolution, the colour number progressively decreased from the beginning. This suggests that the coloured compounds, mainly humic acids, are the first to be degraded during the attack of the hydroxyl radicals. As can be seen in Figure 1f, the removal of these acids coincides with a fast increase in the pH of the medium. It can also be noted that the colour number achieved a constant value after 100 min of reaction (see Figure 1e), which indicates that refractory COD was mainly due to non-coloured compounds.

Finally, the toxicity increased slightly during the first minutes, when the easily oxidized COD was degraded, and then remained approximately constant (see Figure 1d).

The pH of the medium varied from an initial value of 6.8 to a final value of 11.10 (see Figure 1f).

According to Garg and Mishra [27], the pH of a leachate without biological pre-treatment did not show any significant change during the non-catalytic experiment at 0.7 MPa and temperatures between 383 K and 423 K. This difference could be due to the loss of alkalinity during the biological treatment because of our leachates had a low alkalinity (see Table 1). Thus, the buffering capacity of the leachate was lower in the pre-treated leachate.

### 3.2. Effect of the operating variables

The influence of operating variables such as pressure, temperature and initial pH was studied in order to explain their effect on the oxidation process.

#### 3.2.1. Effect of pressure

In order to evaluate the effect of the dissolved oxygen concentration, the non-catalytic wet oxidation of the biologically pre-treated landfill leachate was performed at 453 K, initial pH 6.8 and oxygen pressures in the range of 2.0 - 8.0 MPa. Figure 2 summarises the results obtained for each pressure.

FIGURE 2

Results showed that both COD and TOC removals increased with the increase in the oxygen pressure. The evolution of TOC data with pressure is shown in Figure S4 of the Supplementary Material. As expected in free-radical processes, a high concentration of dissolved oxygen in the liquid phase was beneficial to the oxidation of pollutants. The main role of oxygen in the oxidation pathway is to participate in the radical initiation process. A higher concentration of dissolved oxygen implies an increase in the number of radicals generated and thus an enhancement in the degradation rate when the oxidation takes place through a radical pathway. In the range of pressures considered, the behaviour of the system was correctly fitted to a pseudo-first order mechanism with respect to the oxidizable pollutant:

$$-r_{COD} = k_{COD} (COD - COD_{\infty}) \quad (4)$$

$$-r_{TOC} = k_{TOC} (TOC - TOC_{\infty}) \quad (5)$$

The asymptotic values included in equations 4 and 5 and the kinetic constant values are reported in Table 2. These results showed that an increase in the oxygen pressure accelerated the degradation rate. Additionally, the kinetic constant obtained at 8.0 MPa was four-fold higher than the constant at 2.0 MPa,  $(5.15 \pm 0.02) \times 10^{-5} \text{ s}^{-1}$ . Besides, the increase in pressure also reduced the remaining COD (or TOC) at the end of the experiment. Thus, the final COD reductions achieved at 2.0, 4.0, 6.0 or 8.0 MPa were 36%, 42%, 49% and 58%, respectively. Using the data summarized in Table 2, the oxygen reaction order ( $\alpha$ ) was calculated by correlating the oxygen concentration and the reaction rate constant at different working pressures ( $k = k' C_{O_2}^\alpha$ ). The equilibrium concentration of oxygen was calculated employing Henry's law and empirical correlations [30]. The oxygen reaction orders obtained for COD and TOC were  $0.70 \pm 0.04$  ( $r^2 = 0.991$ ) and  $0.66 \pm 0.05$  ( $r^2 = 0.990$ ), respectively. These values are in accordance with Bhargava et al. [31] and Mishra et al. [32], who reported that the orders with respect to dissolved oxygen obtained during the wet oxidation of different industrial wastewaters are usually in the range of 0.3 to 1.0.

The evolution of the average oxidation state (Figure 2b) revealed that this parameter converged gradually to a value of -2.0 approximately, regardless of the selected pressure, indicating that changes in oxygen concentration had no effect on the ratio between oxidation and decarboxylation.

As shown in Figure 2f, an increase in pressure led to lower pH values. Thus, the final pH values obtained after 8 h at 2.0 and 8.0 MPa were 11.8 and 10.7, respectively. A possible explanation is that higher concentrations of dissolved oxygen favour the formation of carboxylic acids of low molecular weight as final products, which compensates in part for the loss of acidity caused by the oxidation of fatty, humic and fulvic acids.

Concerning the biodegradability index and the colour number, the effect of pressure on both parameters was negligible (Figure 2c and e). Regardless of the selected pressure, a final biodegradability of around 0.25 and a colour number of approximately 0.06 were achieved at the end of the reaction. Finally, toxicity bioassays revealed that increases in pressure had a somewhat negative effect on the toxicity of the final products (see Figure 2d). Thus, the initial inhibition percentage of the pre-treated leachate was 42%, obtaining final values of luminescence inhibition of 52%, 56% and 62%, after the wet oxidation treatment at 2.0, 6.0 or 8.0 MPa, respectively.

These results are similar to those reported by Cassano et al [33], in which inhibition values between 60 and 80% were obtained during the biological degradation when followed by solar photo-Fenton of medium-age landfill leachate. However, Gotvajn et al. [34] reported lower values ranging from 5 to 42% when tannery landfill leachates were treated by coagulation-flocculation combined with  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ .

### 3.2.2. Effect of temperature

Figure 3 shows the effect of temperature on the non-catalytic wet oxidation of the leachate. These experiments were conducted at temperatures ranging from 423 to 483 K.

FIGURE 3

The evolution of COD and TOC were also successfully fitted to a pseudo-first order kinetic model (see Figure 3 for COD and Figure S5 for TOC). The most relevant results of the fitting are depicted in Table 2. These results showed that an increase in the operating temperature resulted in an increase in the degradation rate and a decrease in the refractory COD or TOC. Thus, the kinetic constant for COD removal at 483 K,  $(3.55 \pm 0.10) \times 10^{-4} \text{s}^{-1}$ , has a value approximately three times higher than that obtained when the temperature was set at 423 K. At the same time, 69% and 35% of the initial COD was considered as refractory in the runs carried out at 423 K and 483 K, respectively.

It must be taken into account that the concentration of oxygen was constant for a given run but varied from run to run as temperature changed. Therefore, kinetic constants shown in Table 2 are also dependent on oxygen concentration, the kinetic orders being  $0.70 \pm 0.04$  (COD) and  $0.66 \pm 0.05$  (TOC), as previously commented. Assuming an Arrhenius type temperature dependence, the next expression can be deduced:

$$k = k_0 C_{\text{O}_2}^\alpha \exp\left(-\frac{Ea}{RT}\right) \quad (6)$$

By correlating  $\ln\left(\frac{k}{C_{\text{O}_2}^\alpha}\right)$  versus  $1/T$ , the activation energies ( $Ea$ ) were determined for the non-

catalytic wet oxidation of leachates:  $29.8 \pm 0.9$  kJ/mol (for COD,  $r^2=0.998$ ) and  $18.7 \pm 0.8$  kJ/mol (for TOC,  $r^2=0.995$ ).

The plots with fittings of the  $E_a$  for COD and TOC are shown in Figure S6. Garg and Mishra [27] obtained a slightly lower value for the activation energy, around 24 kJ/mol for COD, when the wet oxidation of leachate was carried out at temperatures between 383 K and 423 K, at 0.7 MPa and in presence of  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_3$  acting as catalyst and promoter, respectively. However, the values here calculated are lower than those reported in the literature for the non-catalytic wet oxidation of wastewaters from different industries, which usually range between 40 and 100 kJ/mol [22, 31, 32]. It is worth noting that in this work the refractory COD (or TOC) was considered in the kinetic model.  $E_a$  values were also calculated without considering the refractory COD (or TOC) and, in that case, the values obtained were higher ( $55 \pm 4$  and  $31 \pm 4$  kJ/mol for COD and TOC, respectively), and more similar to those found for other wastewaters.

On viewing the results in Figure 3b, the final average oxidation state of the end products was higher when higher temperatures were used. This indicates that the final degree of oxidation of the refractory products at elevated temperatures is higher than at low temperature, probably due to the presence of a higher proportion of carboxylic acids, which have an average oxidation state ranging between 0 and +4 [35].

Higher temperatures also favoured the alkalinisation of the medium (see Figure 3f). Final pH values of around 11.3 were achieved at 483 K, whereas it was 9.7 for 423 K. The increase in pH was more marked for initial reaction times, that is, during the degradation of the most oxidizable compounds. These findings suggest that high temperatures improved the degradation of fatty, humic and fulvic acids.

Findings on biodegradability are not so easy to interpret (Figure 3c); at first glance, it seems that an increase in temperature improves the biodegradability of the effluent. Hence, the biodegradability indices after 4 h of treatment at 423 K and at 483 K were 0.05 and 0.48, respectively. However, the biodegradability dropped sharply when temperature was 468 K, the value being 0.02 after 4 h. In addition to this, the colour number decreased throughout the reaction at all assayed temperatures, except for 468 K (see Figure 3e).

In this case, colour initially decreased during the first 90 minutes and then began to increase. These facts suggest the formation of quinone-like compounds at this temperature. These aromatic compounds, which are highly coloured and toxic even at low concentrations, have been reported as intermediates during the wet oxidation of phenolic compounds by several authors [31, 36]. It seems reasonable to consider that the formation rate of quinone-like compounds increased with temperature [36, 37]. These species are characterised by a low biodegradability index and intense colouration, two characteristics observed in Figures 3c and e. For temperatures lower than 468 K, the presence of these quinone-like compounds in the medium is negligible (no colour and high biodegradability index). On the other hand, when the temperature was 468 K, the formation rate is high enough to allow their accumulation (as indicated by an intense yellow colour and low biodegradability index). This is also in accordance with the toxicity evolution shown in Figure 3d. As can be seen in the graph, the toxicity of the samples at 468 K progressively increased once the desired temperature and pressure conditions were reached, following the same trend as the colour number. At a temperature of 483 K, it was observed that these quinone-like compounds did not accumulate, as indicated by the fact that the biodegradability index was higher and the colour number was lower. It seems reasonable to assume that at this temperature the degradation rate of the quinone-like compounds exceeded their formation rate, avoiding the presence of a significant concentration of these species.

### 3.2.3. Effect of initial pH.

Figure 4 shows the effect of modifying the initial pH of the landfill leachate on its degradation.

#### FIGURE 4

COD and TOC experimental data were also successfully fitted to a pseudo-first kinetic model, considering the terms due to the refractory COD or TOC (see Figure 4 for COD, Figure S7 for TOC and Table 2). By comparison of the various kinetic constants, it can be concluded that the initial acidification of the leachate had practically no effect on the COD removal rate, as is illustrated by the fact that the kinetic constants for COD removal obtained at 453 K and 8.0 MPa without pH adjustment (pH= 6.8) and at pH 2.0 were  $(2.05 \pm 0.06) \times 10^{-4} \text{ s}^{-1}$  and  $(2.18 \pm 0.08) \times 10^{-4} \text{ s}^{-1}$ , respectively.

Rivas et al. [20] also studied the influence of pH on wet air oxidation of landfill leachate, reporting that the acidification of landfill leachate to pH values below or equal to 4 led to a 25% COD elimination by precipitation of humic acids. In our study, COD analysis was performed without sample filtering, so the positive effect due to precipitate formation at low pH was not observed.

On the contrary, when the initial leachate was basic, COD and TOC removals significantly decreased. Thus, the kinetic constants for COD removal at initial pH values of 6.8, 10.0 and 11.0 were  $(2.05 \pm 0.06) \times 10^{-4} \text{ s}^{-1}$ ,  $(1.44 \pm 0.05) \times 10^{-4} \text{ s}^{-1}$ ,  $(1.24 \pm 0.04) \times 10^{-4} \text{ s}^{-1}$ , respectively. Similar behaviour was reported by Wang et al. [14] during the wet oxidation of fulvic acids in presence of trichlorophenol. As shown in Figure 4b, basic media favoured the formation of compounds with higher average oxidation states. This behaviour suggests that higher initial pH values favoured the oxidation reactions (incorporation of an oxygen atom by forming a carbon–oxygen bond) rather than the decarboxylation reactions (splitting of  $\text{CO}_2$ ).

With regard to pH evolution (Figure 4f), a progressive alkalisation was observed during the reaction time for the runs carried out with acid leachates. Nevertheless, the wet oxidation of basic leachate led to an initial acidification of the medium. Depending on the initial acid or basic character of the leachate, the behaviour of the biodegradability also changed. Therefore, for the runs without initial pH adjustment or at pH 2.0, the biodegradability index progressively increased during the whole of the reaction, whereas at pH 10 and 11, this parameter reached a maximum and then started to decrease. In any case, the most biodegradable effluent was obtained for the run without initial pH adjustment. Comparing Figures 4c and e, it can also be concluded that an increase in the colour number was correlated with a reduction in the biodegradability index. As was previously explained, this suggests the formation of toxic coloured compounds at basic pH. Toxicity data (Figure 4d) also proved that an initial high pH value during the wet oxidation process had a negative effect on the subsequent biological treatment, as can be seen by the value of the inhibition percentage. After 8 h of wet oxidation at pH 10 and 11, values of 75% and 80% were obtained, respectively. These values of LI are approximately two times higher than that obtained at pH 2.0.



It is noteworthy that an improvement in the percentage of luminescence inhibition was obtained when initial acid pH was used. Thus, the final value of LI was around 12% lower than the initial one.

TABLE 2

### 3.3. Kinetic model

Taking into account the aforementioned experimental data, the kinetic models for the non-catalytic wet oxidation of biologically pre-treated landfill leachates, without initial pH adjustment, can be expressed by the following equations (time is expressed in seconds, temperature in Kelvin, concentrations in mg/L). The way to determine the model parameters is shown in section 8 of the Supplementary Material:

$$-r_{COD} = 1.79 \cdot e^{\frac{-3586}{T}} C_{O_2}^{0.70} (C_{COD} - C_{COD_\infty}) \quad (7)$$

$$-r_{TOC} = 1.85 \cdot e^{\frac{-2244}{T}} C_{O_2}^{0.66} (C_{TOC} - C_{TOC_\infty}) \quad (8)$$

These kinetic models are suitable when the operating conditions fall in the following ranges: 423 - 483 K, 2.0 - 8.0 MPa and initial pH 6.8. All the experiments presented in this study were simulated using equation 7 or 8 with a good degree of concordance ( $r^2 > 0.985$ ) (see Figure S8 and S9 of the Supplementary Material).

### 3.4. Quality of the final effluent

Wet oxidation as a sole treatment for landfill leachates produced an effluent containing values of COD too high to be discharged directly into the environment. Nevertheless, by selecting the appropriate conditions of temperature, pressure and pH, an effluent with similar characteristics to those obtained in municipal wastewaters can be obtained. Thus, this effluent could be treated together with municipal wastewaters in a municipal wastewater treatment plant (WWTP). As can be observed in Figure 5, working at temperatures between 423 K and 483 K, pressures in the range of 2.0 MPa to 8.0 MPa and initial pH between 2.0 and 11.0, the treated effluent presents COD and BOD<sub>5</sub> values lower than 1000 and 400 ppm, respectively, which were reported as maximum values in the municipal wastewaters [38].

With regard to the question of the final colour, basic initial pH values are not recommended because the effluent obtained had a strong yellow colouration, whereas municipal wastewaters may only exhibit colour variations from beige to grey. Another alternative for the management of this effluent would be its recirculation to the previous biological treatment, thus being treated together with the raw leachate.

FIGURE 5

#### 4. Conclusions

Non-catalytic wet oxidation as the sole technique for the treatment of biologically pre-treated leachates provides moderate COD and TOC removals, obtaining final conversions ranging from 20 to 65 % for these parameters. Additionally, the biodegradability of the landfill leachate was improved, and after 4 h of treatment, it is possible to obtain a biodegradable effluent ( $BOD_5/COD > 0.2$ ) that is also uncoloured ( $CN < 0.05$ ).

Experimental results also revealed that COD and TOC removal can be improved by increasing temperature and/or pressure. The values of the activation energies were found to be  $29.8 \pm 0.9$  kJ/mol (COD) and  $18.7 \pm 0.8$  kJ/mol (TOC) and oxygen reaction orders were  $0.70 \pm 0.04$  (COD) and  $0.66 \pm 0.05$  (TOC). An increase in temperature also had a positive effect on the biodegradability index, improving it greatly, whereas an increase in pressure exerted practically no effect on it. Significant decreases were observed in the values of the colour number in almost all the cases, changing from dark brown to pale yellow. The toxicity values were almost unaffected by pressure and temperature. An exception was observed when the temperature was 468 K, since the biodegradability index decreased significantly and both the colour number and toxicity increased markedly, due to the presence of quinone-like compounds. The adjustment of the initial pH to basic values led to the attainment of a final effluent with low biodegradability and higher toxicity than the raw landfill leachate. On the other hand, when the initial pH was acid, the biodegradability index showed a satisfactory increase and the treated effluent was much less toxic than the leachate itself.

Consequently, this technology is an attractive option to complete the treatment at the landfill site and convert the leachate into an effluent that is more suitable for treatment in a municipal wastewater treatment plant (WWTP). Further work, including the investigation of the economic aspects should be undertaken in order to show the convenience of this tertiary treatment.

### Acknowledgements

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**Declaration of interests**

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proofs



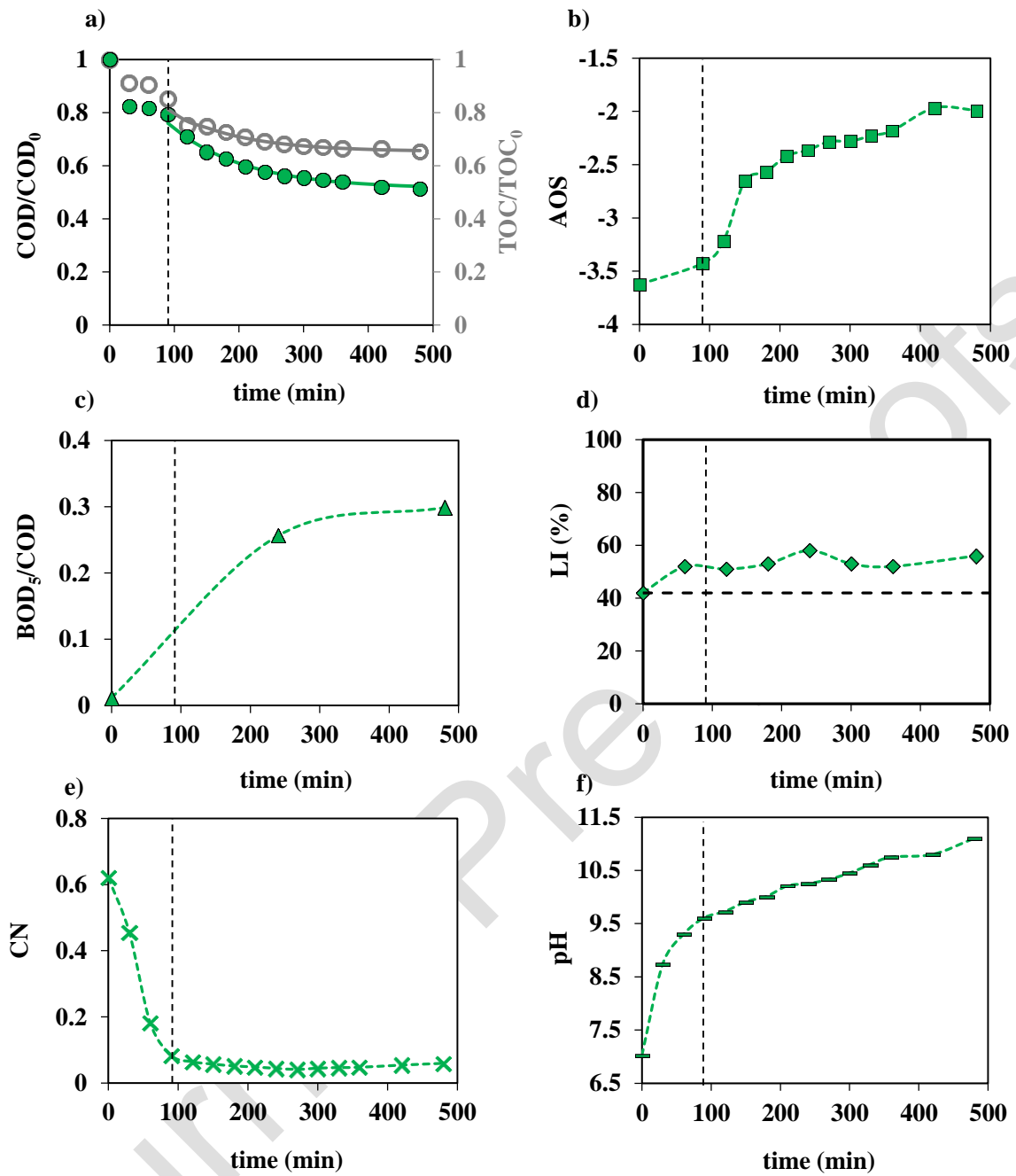
**Figure 1**

Figure 2

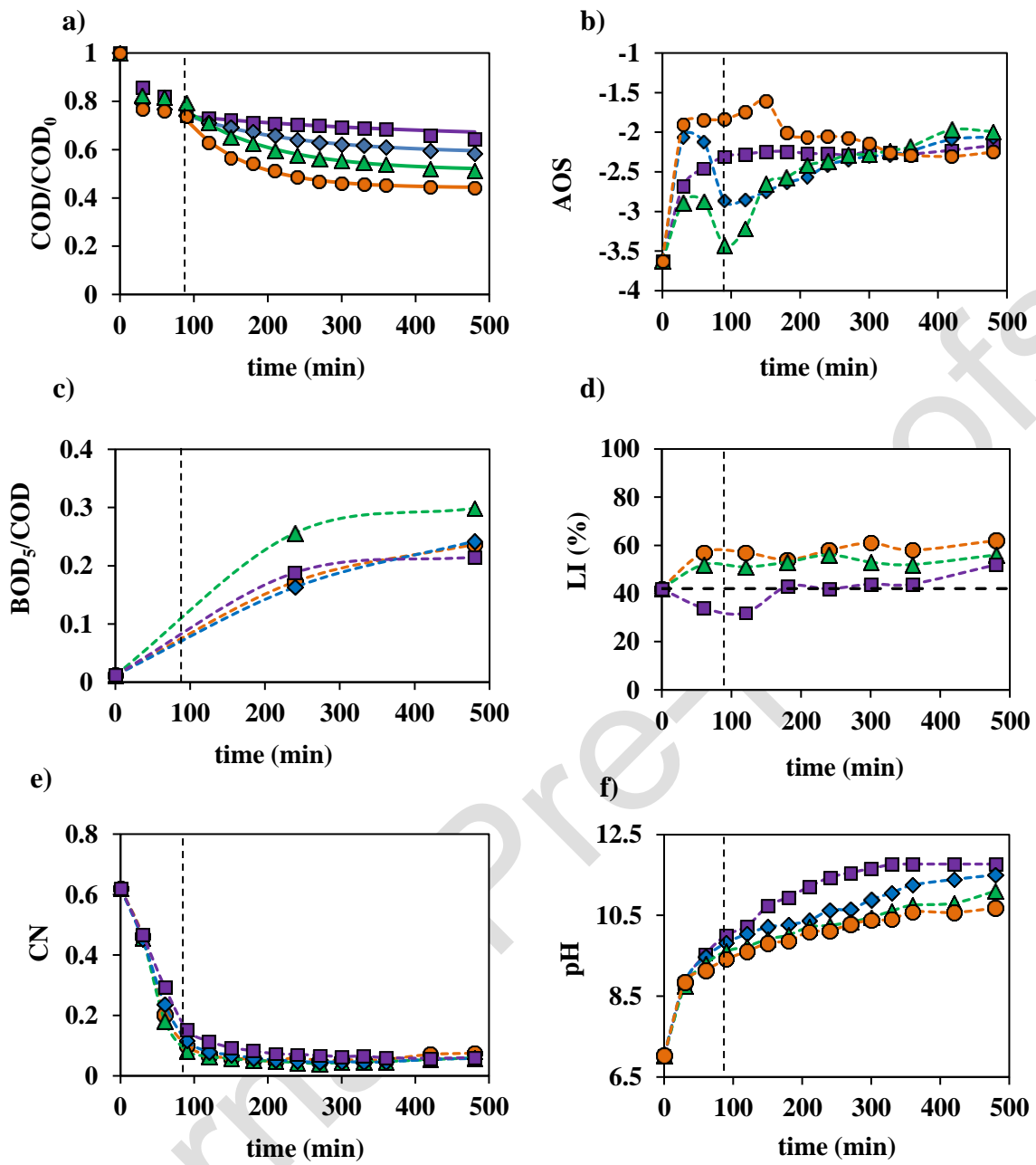


Figure 3

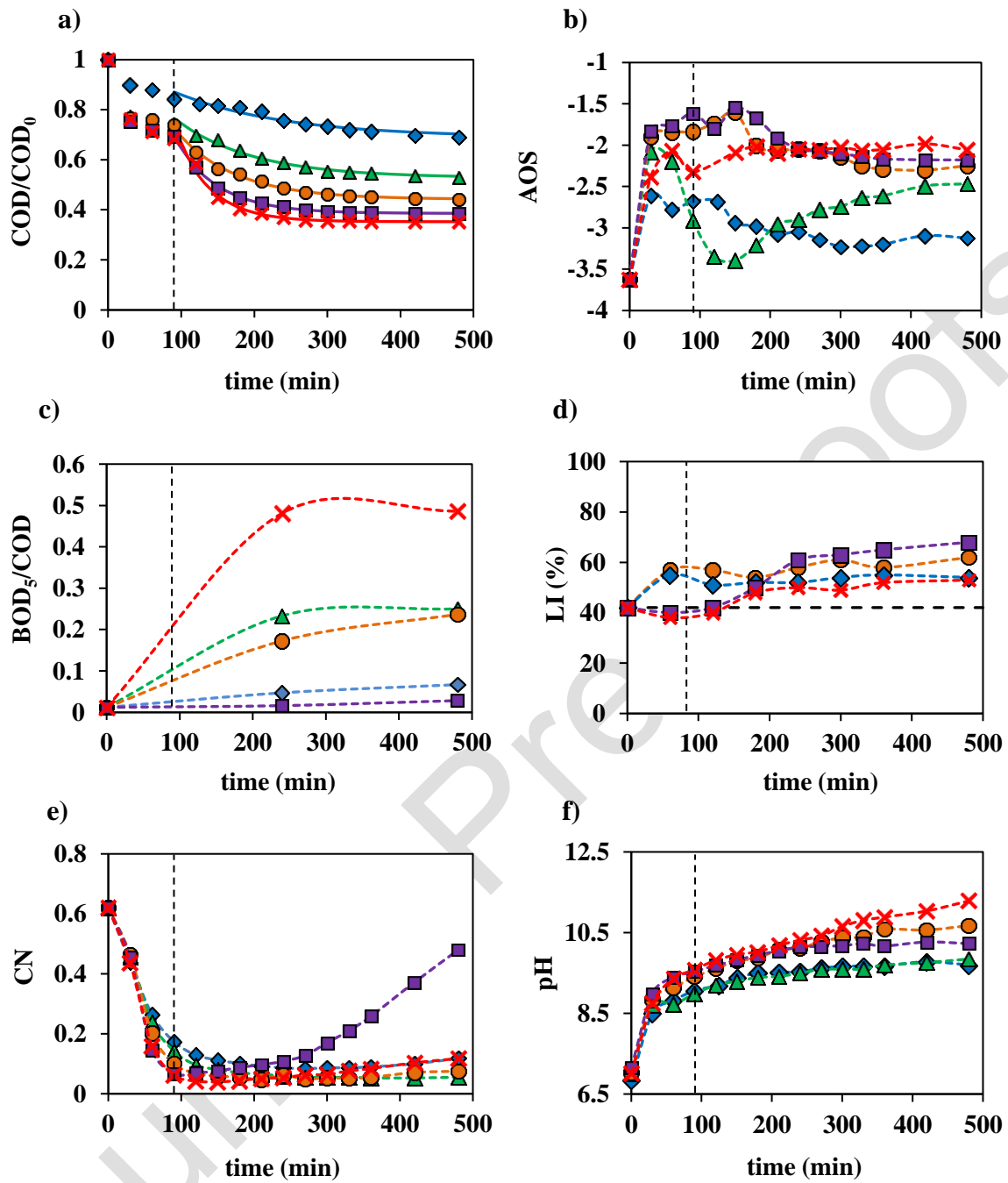


Figure 4

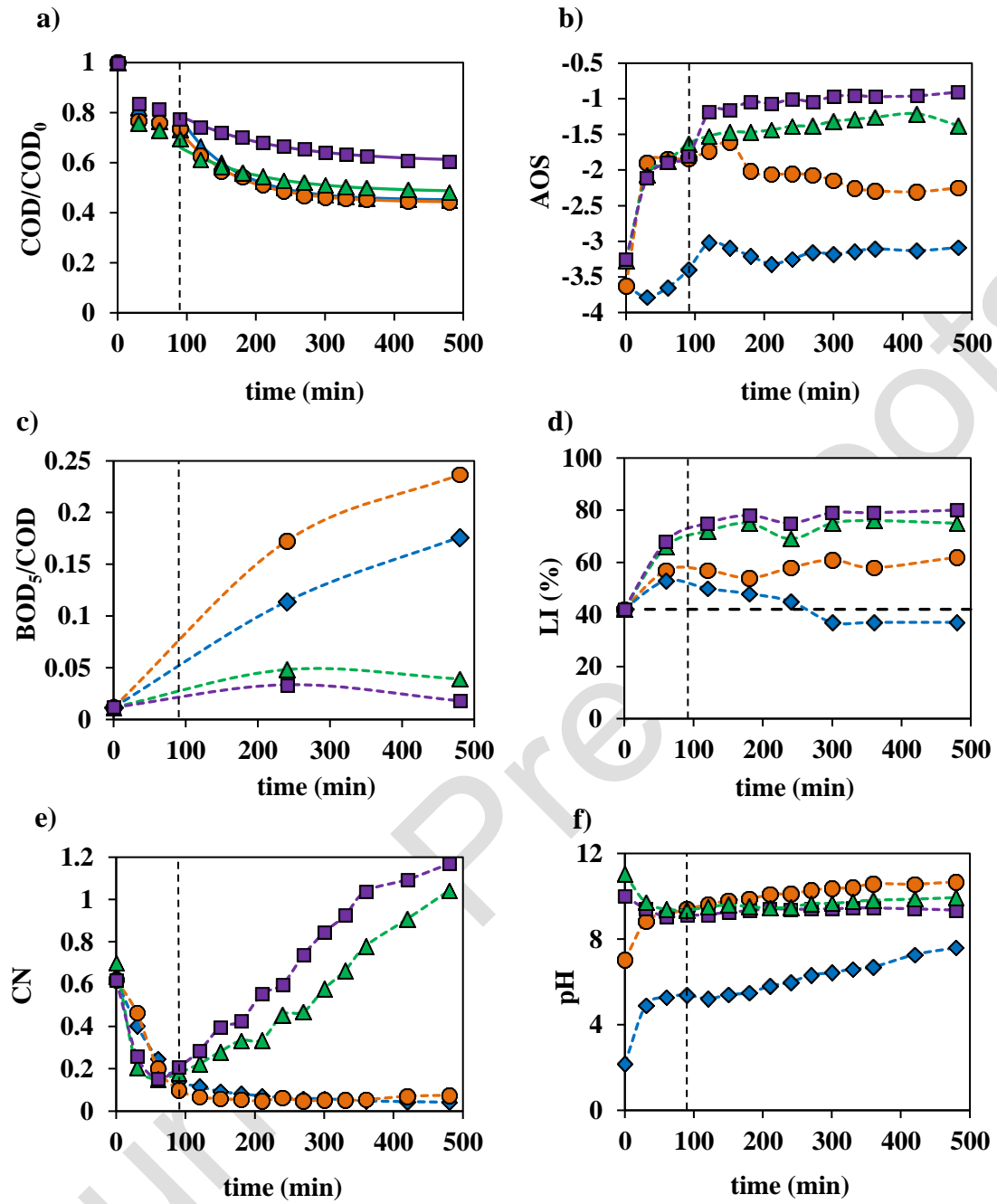
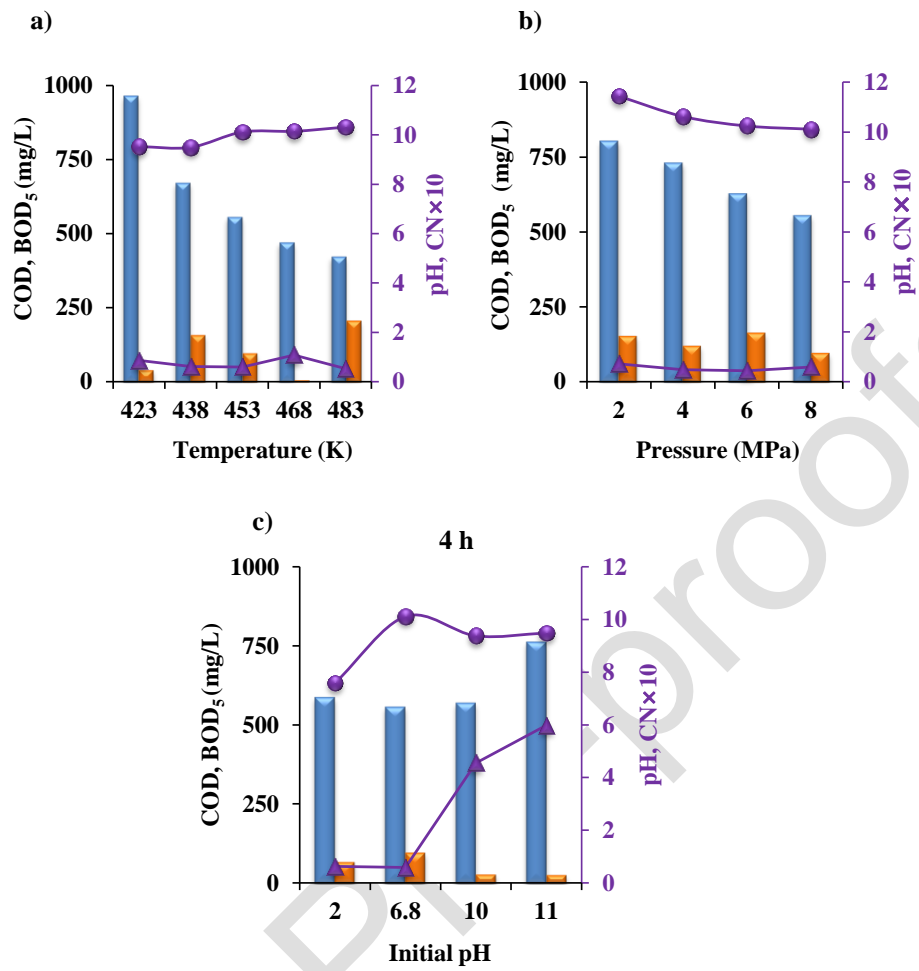


Figure 5



**Figure captions**

**Figure 1.** Evolution of different parameters during the non-catalytic wet oxidation of biologically pretreated landfill leachates with an initial COD = 1143 mg/L at 6 MPa, 453 K and pH 6.8: a) COD (●) and TOC (○), b) AOS, c) BOD<sub>5</sub>/COD, d) luminescence inhibition (LI), e) colour number (CN) and f) pH. Solid lines denote model curve according to Table 2. Vertical broken lines indicate the approximate time needed to achieve the required temperature and pressure conditions. Horizontal broken line in d) indicates the initial luminescence inhibition.

**Figure 2.** Evolution of different parameters during the non-catalytic wet oxidation of leachates at different pressures: (■) 2.0 MPa, (◆) 4.0 MPa, (▲) 6.0 MPa and (●) 8.0 MPa: a) COD, b) AOS, c) BOD<sub>5</sub>/COD, d) luminescence inhibition (LI), e) colour number (CN) and f) pH. In all cases: initial COD = 1143 mg/L, T = 453 K and pH = 6.8. Solid lines denote model curve according to Table 2. Vertical broken lines indicate the approximate time needed to achieve the required temperature and pressure conditions. Horizontal broken line in d) indicates the initial luminescence inhibition.

**Figure 3.** Evolution of different parameters during the non-catalytic wet oxidation of leachates at different temperatures: (◆) 423 K, (▲) 438 K, (●) 453 K, (■) 468 K and (✕) 483 K: a) COD, b) AOS, c) BOD<sub>5</sub>/COD, d) luminescence inhibition (LI), e) colour number (CN), and f) pH. In all cases: initial COD = 1143 mg/L, P = 8.0 MPa and pH = 6.8. Solid lines denote model curves according to Table 2. Vertical broken lines indicate the approximate time needed to achieve the required temperature and pressure conditions. Horizontal broken line in d) indicates the initial luminescence inhibition.

**Figure 4.** Evolution of different parameters during the non-catalytic wet oxidation of leachates at pH: (◆) 2.0, (●) 6.8, (▲) 10 and (■) 11: a) COD, b) AOS, c) BOD<sub>5</sub>/COD, d) luminescence inhibition (LI), e) colour number (CN) and f) pH. In all cases: initial COD = 1143 mg/L, T = 453 K P = 8.0 MPa. Solid lines denote model curves according to Table 2. Vertical broken lines indicate the approximate time needed to achieve the required temperature and pressure conditions. Horizontal broken line in d) indicates the initial luminescence inhibition.

**Figure 5.** Summary of the most relevant results obtained: (■) COD, (■) BOD<sub>5</sub>, (▲) CN and (●) pH, after 4 h of wet oxidation as a function of the operating conditions employed: a) temperature, b) pressure and c) initial pH.

**Tables****Table 1.** Physicochemical characteristics of the stabilized landfill leachate used in this study and variability found at the landfill site.

<b>Parameter</b>	<b>Leachate used in this study</b>	<b>Variability found at the landfill site</b>
pH	6.8	6.8-7.5
COD (mg O <sub>2</sub> /L)	1143	1000-1600
TOC (mg/L)	225	200-320
BOD <sub>5</sub> (mg O <sub>2</sub> /L)	8.5	<65
Colour Number	0.622	0.6-0.7
Alkalinity (mg CaCO <sub>3</sub> /L)	17.3	15-20
Conductivity (μS/cm)	11430	11000-14000
NH <sub>4</sub> <sup>+</sup> (mg/L)	5	<50
NO <sub>3</sub> <sup>-</sup> (mg/L)	403	400-700
NO <sub>2</sub> <sup>-</sup> (mg/L)	1	<2
PO <sub>4</sub> <sup>3-</sup> (mg/L)	5.4	5-15

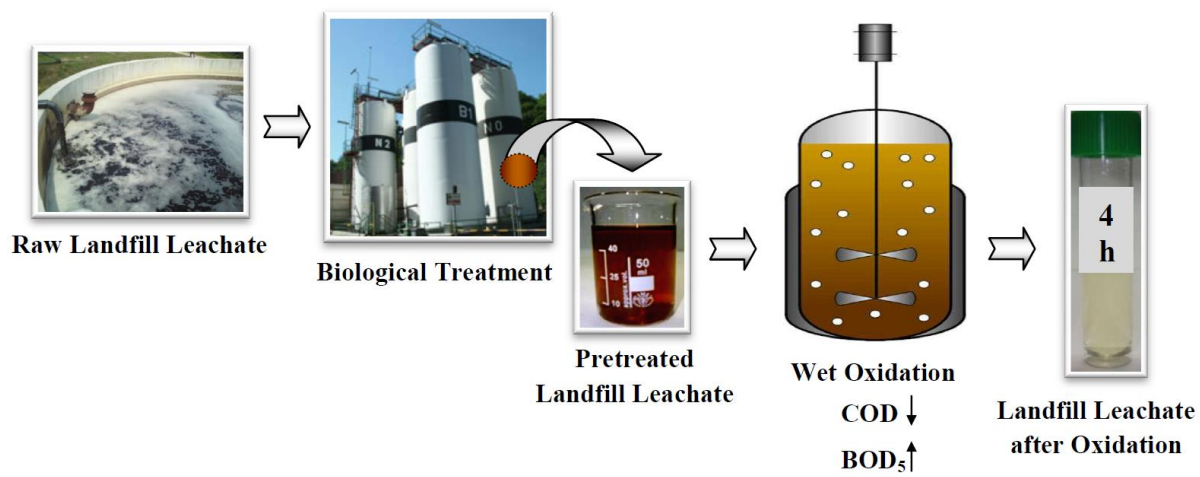
**Table 2.** Relevant kinetic data for the non-catalytic wet oxidation of biologically pretreated landfill leachate.

<i>Effect of pressure</i>					
T (K)	453				
P (MPa)	2.0	4.0	6.0	8.0	
$C_{O_2}$ (M)	$1.0 \times 10^{-2}$	$2.9 \times 10^{-2}$	$4.8 \times 10^{-2}$	$6.7 \times 10^{-2}$	
$k_{COD}$ ( $s^{-1}$ )	$(5.15 \pm 0.02) \times 10^{-5}$	$(1.12 \pm 0.03) \times 10^{-4}$	$(1.43 \pm 0.05) \times 10^{-4}$	$(2.05 \pm 0.06) \times 10^{-4}$	
$COD_{\infty}$ (mg/L)	$737 \pm 2$	$668 \pm 1$	$587 \pm 3$	$484 \pm 4$	
$r^{2a}$	0.991	0.996	0.993	0.993	
$k_{TOC}$ ( $s^{-1}$ )	$(6.12 \pm 0.02) \times 10^{-5}$	$(1.22 \pm 0.04) \times 10^{-4}$	$(1.59 \pm 0.04) \times 10^{-4}$	$(2.27 \pm 0.07) \times 10^{-4}$	
$TOC_{\infty}$ (mg/L)	$179.17 \pm 0.02$	$165.44 \pm 0.03$	$146.92 \pm 0.05$	$116.15 \pm 0.03$	
$r^{2b}$	0.992	0.992	0.994	0.991	
<i>Effect of temperature</i>					
P (MPa)	8.0				
T (K)	423	438	453	468	483
$C_{O_2}$ (M)	$6.0 \times 10^{-2}$	$6.4 \times 10^{-2}$	$6.7 \times 10^{-2}$	$6.9 \times 10^{-2}$	$7.2 \times 10^{-2}$
$k_{COD}$ ( $s^{-1}$ )	$(1.10 \pm 0.03) \times 10^{-4}$	$(1.57 \pm 0.04) \times 10^{-4}$	$(2.05 \pm 0.06) \times 10^{-4}$	$(2.83 \pm 0.09) \times 10^{-4}$	$(3.55 \pm 0.10) \times 10^{-4}$
$COD_{\infty}$ (mg/L)	$788 \pm 2$	$604 \pm 3$	$484 \pm 4$	$441 \pm 3$	$403 \pm 2$
$r^{2a}$	0.992	0.993	0.993	0.992	0.993
$k_{TOC}$ ( $s^{-1}$ )	$(1.52 \pm 0.05) \times 10^{-4}$	$(1.95 \pm 0.07) \times 10^{-4}$	$(2.27 \pm 0.07) \times 10^{-4}$	$(2.82 \pm 0.06) \times 10^{-4}$	$(3.33 \pm 0.07) \times 10^{-4}$
$TOC_{\infty}$ (mg/L)	$165.89 \pm 0.04$	$140.00 \pm 0.02$	$116.15 \pm 0.03$	$107.07 \pm 0.05$	$99.68 \pm 0.02$
$r^{2b}$	0.990	0.990	0.991	0.996	0.996
<i>Effect of initial pH</i>					
T (K)	453				
P (MPa)	8.0				
pH	2.0	6.8	10.0	11.0	
$C_{O_2}$ (M)	$6.7 \times 10^{-2}$	$6.7 \times 10^{-2}$	$6.7 \times 10^{-2}$	$6.7 \times 10^{-2}$	
$k_{COD}$ ( $s^{-1}$ )	$(2.18 \pm 0.08) \times 10^{-4}$	$(2.05 \pm 0.06) \times 10^{-4}$	$(1.44 \pm 0.05) \times 10^{-4}$	$(1.24 \pm 0.04) \times 10^{-4}$	
$COD_{\infty}$ (mg/L)	$514 \pm 2$	$484 \pm 4$	$557 \pm 2$	$690 \pm 3$	
$r^{2a}$	0.990	0.993	0.991	0.991	
$k_{TOC}$ ( $s^{-1}$ )	$(2.32 \pm 0.07) \times 10^{-4}$	$(2.27 \pm 0.07) \times 10^{-4}$	$(1.35 \pm 0.04) \times 10^{-4}$	$(8.58 \pm 0.02) \times 10^{-5}$	
$TOC_{\infty}$ (mg/L)	$108.77 \pm 0.02$	$116.15 \pm 0.03$	$170.26 \pm 0.01$	$192.40 \pm 0.03$	
$r^{2b}$	0.993	0.991	0.992	0.995	

<sup>a,b</sup>referred to the goodness of  $k_{COD}$  and  $k_{TOC}$  fitting, respectively



**Graphical abstract**



Journal Pre-proof

**Highlights**

- Non-catalytic wet oxidation is a feasible solution for biotreated leachates.
- COD and TOC removals up to 65% and colour reductions of 90% were obtained.
- Biodegradability of biotreated leachate was greatly enhanced after wet oxidation.
- 25% of initial COD was oxidized fast, whereas 35% remained at the end in the medium.
- Treatability of this effluent in a municipal WWTP was highly improved.

**Supplementary Material to**

**‘Tertiary treatment of biologically pretreated landfill  
leachates by non-catalytic wet oxidation’**

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(12 Pages, 9 Figures)

**Table of contents**

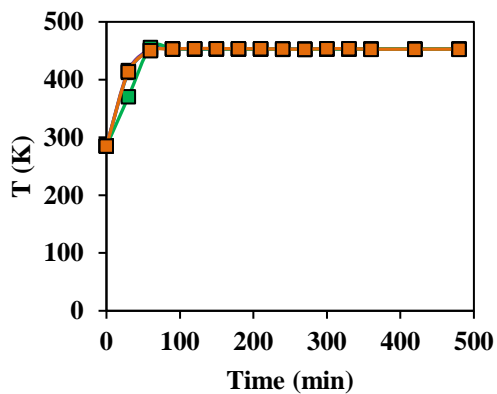
- 1. Graph of the operating conditions changing with time for the experiments at different pressures (Figure S1).**
- 2. Graph of the operating conditions changing with time for the experiments at different temperatures (Figure S2).**
- 3. Graph of the operating conditions changing with time for the experiments at different pH (Figure S3).**
- 4. Evolution of TOC data with the actual fit of the first order kinetics for the experiments at different pressures (Figure S4).**
- 5. Evolution of TOC data with the actual fit of the first order kinetics for the experiments at different temperatures (Figure S5).**
- 6. Plots with the fittings of the Ea for COD and TOC (Figure S6).**
- 7. Evolution of TOC data with the actual fit of the first order kinetics for the experiments at different pH (Figure S7).**
- 8. Determination of the model parameters.**
- 9. Comparison between the experimental data and the theoretical values for COD obtained through the kinetic model (Figure S8).**

**10. Comparison between the experimental data and the theoretical values for TOC obtained through the kinetic model (Figure S9).**

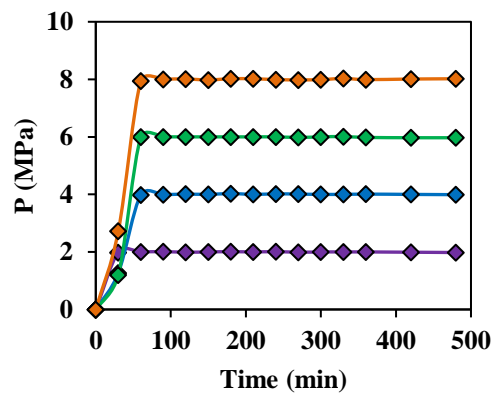
Corresponding author's e-mail: [mariodiaz@uniovi.es](mailto:mariodiaz@uniovi.es)  
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1. Graph of the operating conditions changing with time for the experiments at different pressures (Figure S1).

a)

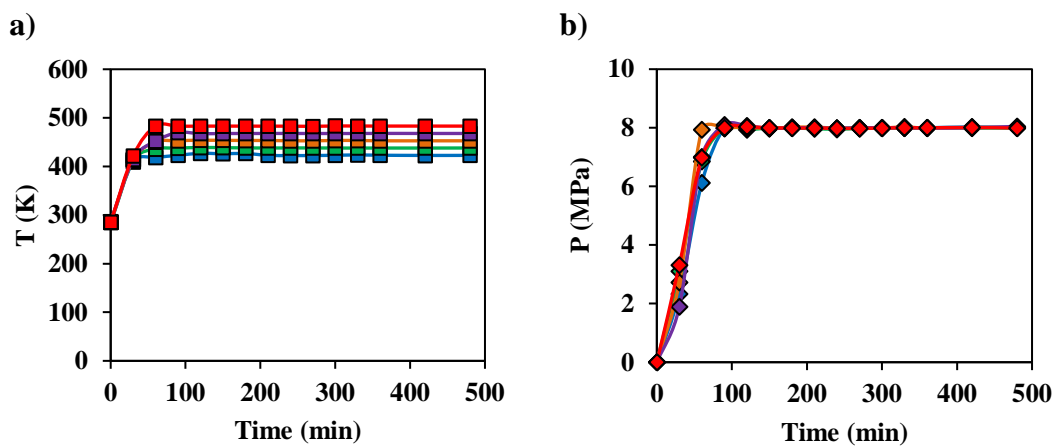


b)



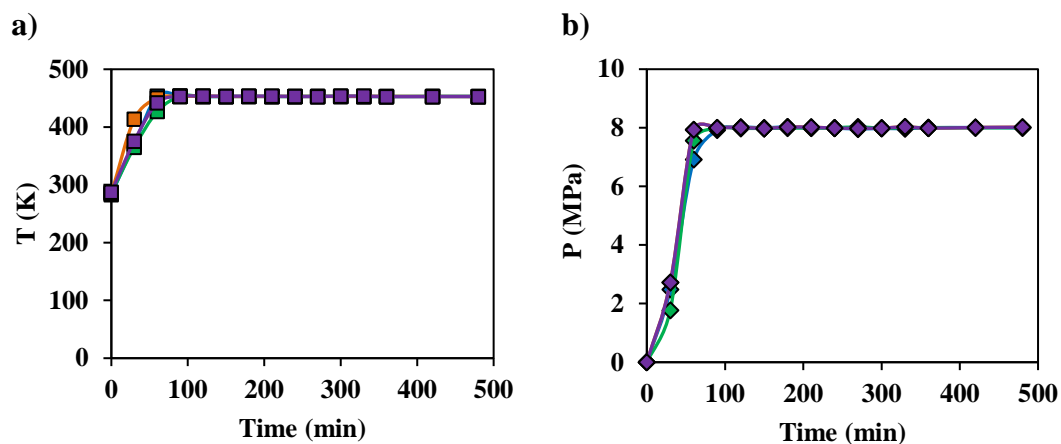
**Figure S1.** Change of temperature a) and pressure b) with time during the non-catalytic wet oxidation of leachates at different pressures: 2.0 MPa (purple symbols), 4.0 MPa (blue symbols), 6.0 MPa (green symbols) and 8.0 MPa (orange symbols).

2. Graph of the operating conditions changing with time for the experiments at different temperatures (Figure S2).



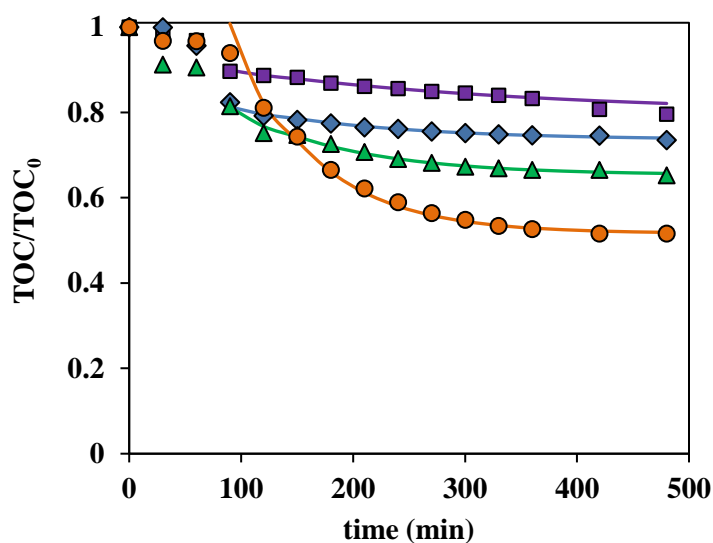
**Figure S2.** Change of temperature a) and pressure b) with time during the non-catalytic wet oxidation of leachates at different temperatures: 423 K (blue symbols), 438 K (green symbols), 453 K (orange symbols), 468 K (purple symbols) and 483 K (red symbols).

3. Graph of the operating conditions changing with time for the experiments at different pH (Figure S3).



**Figure S3.** Change of temperature a) and pressure b) with time during the non-catalytic wet oxidation of leachates at different pH: 2.0 (blue symbols), 6.8 (orange symbols), 10.0 (green symbols) and 11.0 (purple symbols).

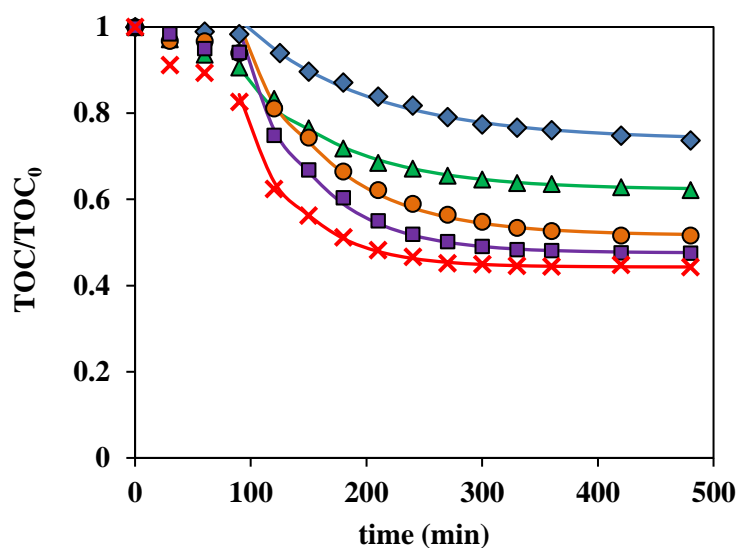
4. Evolution of TOC data with the actual fit of the first order kinetics for the experiments at different pressures (Figure S4).



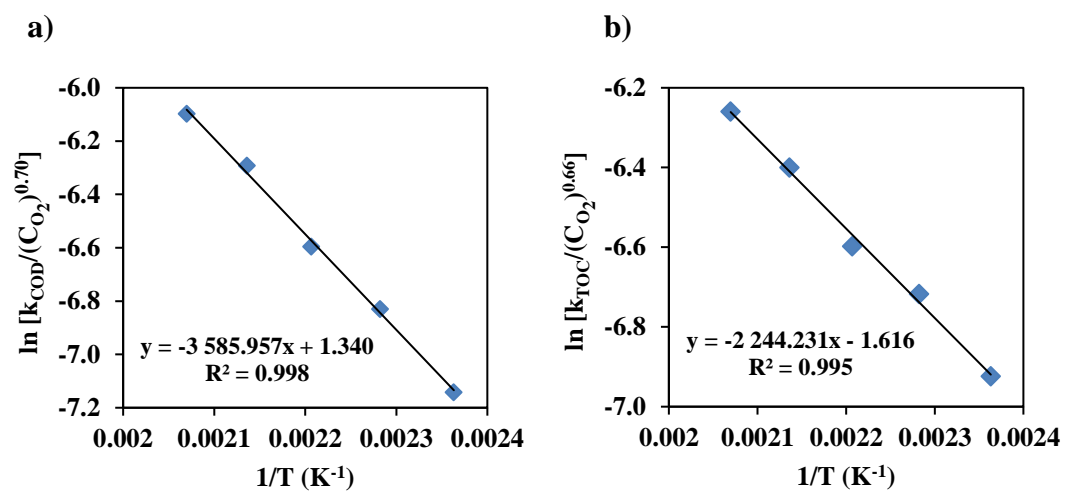
**Figure S4.** Evolution of TOC data during the non-catalytic wet oxidation of leachates at different pressures: (■) 2.0 MPa, (◆) 4.0 MPa, (▲) 6.0 MPa and (●) 8.0 MPa. In all cases: initial TOC = 225 mg/L, T = 453 K and pH = 6.8. Solid lines denote the actual fits of the first order kinetics according to equation 8 and Table 2.



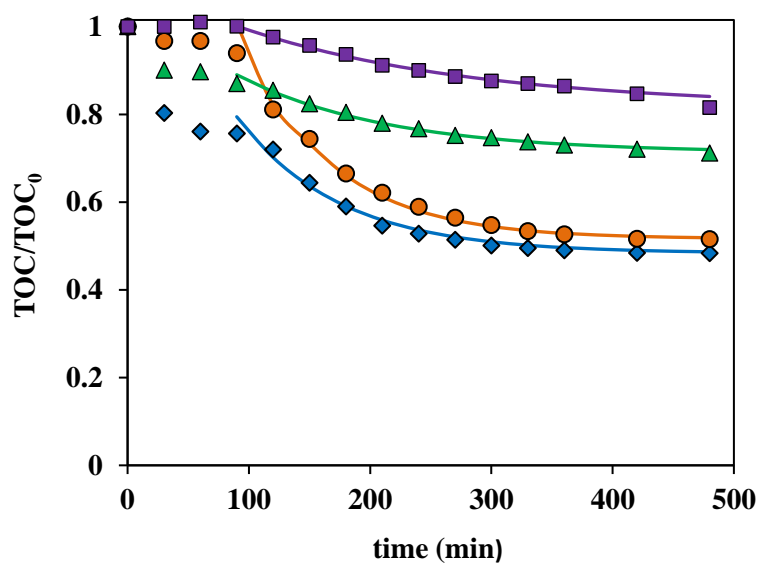
5. Evolution of TOC data with the actual fit of the first order kinetics for the experiments at different temperatures (Figure S5).



**Figure S5.** Evolution of TOC data during the non-catalytic wet oxidation of leachates at different temperatures: (◆) 423 K, (▲) 438 K, (●) 453 K, (■) 468 K and (×) 483 K. In all cases: initial TOC = 225 mg/L, P = 8.0 MPa and pH = 6.8. Solid lines denote the actual fits of the first order kinetics according to equation 8 and Table 2.

**6. Plots with the fittings of the Ea for COD and TOC (Figure S6).****Figure S6.** Plot with the fittings of the Ea: a) COD and b) TOC.

7. Evolution of TOC data with the actual fit of the first order kinetics for the experiments at different pH (Figure S7).



**Figure S7.** Evolution of TOC data during the non-catalytic wet oxidation of leachates at different pH: (◆) 2.0, (●) 6.8, (▲) 10.0 and (■) 11.0. In all cases: initial TOC = 225 mg/L, T = 453 K and P = 8.0 MPa. Solid lines denote the actual fits of the first order kinetics according to equation 8 and Table 2.

## 8. Determination of the model parameters.

The exponential kinetic models here proposed for COD and TOC were shown as follows:

$$-r_{COD} = k_{0,COD} \cdot e^{\frac{-E_{aCOD}}{T}} C_{O_2}^{\alpha_{COD}} (C_{COD} - C_{COD_{\infty}})$$

$$-r_{TOC} = k_{0,TOC} \cdot e^{\frac{-E_{aTOC}}{T}} C_{O_2}^{\alpha_{TOC}} (C_{TOC} - C_{TOC_{\infty}})$$

COD<sub>∞</sub> and TOC<sub>∞</sub> values were calculated as the COD and TOC values at infinite time.

The oxygen reaction orders, α<sub>COD</sub> and α<sub>TOC</sub>, were determined by correlating the oxygen concentration and the reaction rate constant of COD and TOC, respectively, at different working pressures:  $k_i = k'_i C_{O_2}^{\alpha_i}$ .

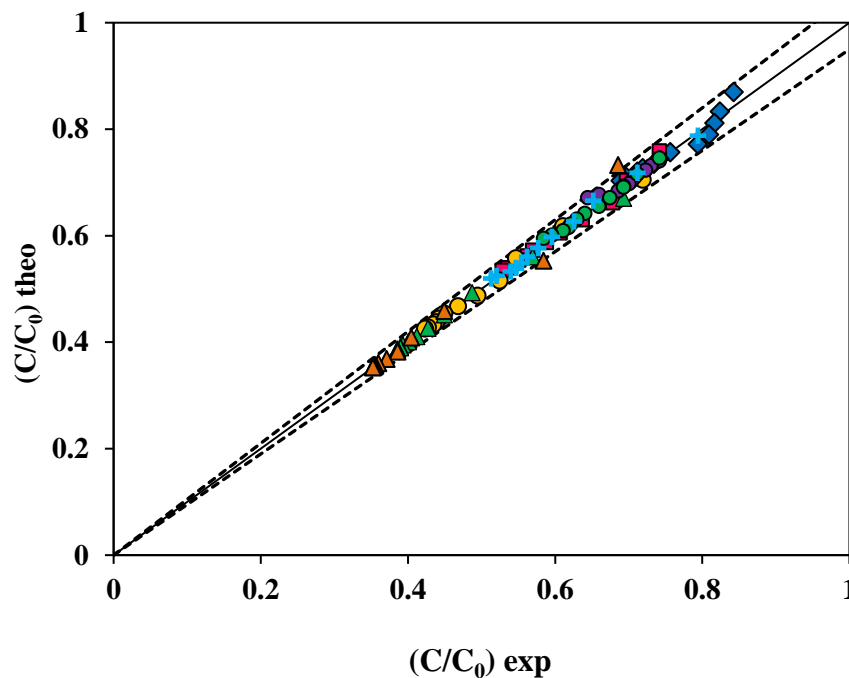
The values of the activation energies, E<sub>aCOD</sub> and E<sub>aTOC</sub>, were calculated considering that the kinetic constants depended on the oxygen concentration and assuming an Arrhenius type temperature dependence. Thus, the following expression can be deduced:

$$k_i = k_{0_i} C_{O_2}^{\alpha_i} \exp\left(-\frac{E_{a_i}}{RT}\right)$$

By correlating  $\ln\left(\frac{k_i}{C_{O_2}^{\alpha_i}}\right)$  versus 1/T, the activation energies (E<sub>a</sub>) were determined for COD and TOC.

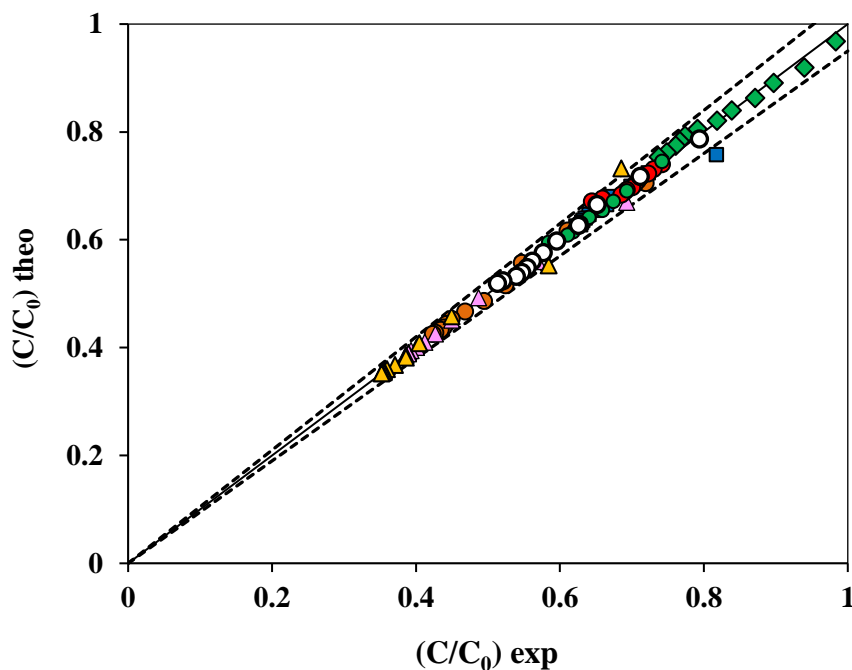
The pre-exponential factors were determined using Solver, which is a what-if analysis tool.

9. Comparison between the experimental data and the theoretical values for COD obtained through the kinetic model (Figure S8).



**Figure S8.** Comparison of the experimental data with the theoretical values for COD obtained by means of equation 7: at different pressures (initial COD concentration = 1143 mg/L,  $T = 453$  K and  $pH = 6.8$ ): (●) 2.0 MPa, (●) 4.0 MPa, (+) 6.0 MPa and (●) 8.0 MPa; at different temperatures (initial COD concentration = 1143 mg/L,  $P = 8.0$  MPa and  $pH = 6.8$ ): (◆) 423 K, (■) 438K, (●) 453 K, (▲) 468 K and (▲) 483 K. Broken lines indicate a 5% error range.

10. Comparison between the experimental data and the theoretical values for TOC obtained through the kinetic model (Figure S9).



**Figure S9.** Comparison of the experimental data with the theoretical values for TOC obtained by means of equation 8: at different pressures (initial TOC concentration = 225 mg/L,  $T = 453$  K and  $\text{pH} = 6.8$ ): (●) 2.0 MPa, (●) 4.0 MPa, (○) 6.0 MPa and (●) 8.0 MPa; at different temperatures (initial TOC concentration = 225 mg/L,  $P = 8.0$  MPa and  $\text{pH} = 6.8$ ): (◆) 423 K, (■) 438 K, (●) 453 K, (▲) 468 K and (▲) 483 K. Broken lines indicate a 5% error range.