

Treatment of Landfill Leachate by H₂O₂ Promoted Wet Air Oxidation: COD-AOX Reduction, Biodegradability Enhancement and Comparison with a Fenton-type Oxidation

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Treatment experiments of a landfill leachate were performed by wet air oxidation (WAO) with the addition of H₂O₂ (as free radical promoter), and a Fenton-type (at pH \cong 7) process, in order to compare COD (chemical oxygen demand) and AOX (adsorbable organic halogen) reduction as well as biodegradability enhancement measured by OUR respirometric parameter. The WAO reactions were performed in a batch reactor at various temperatures in the range of $T = 430\text{--}500$ K employing a concentration of $c = 0.88$ mol L⁻¹ of H₂O₂. The same H₂O₂ concentration was used in the Fenton-type-pH \cong 7 experimental session considering H₂O₂/Fe(II) mole ratios of 5, 10 and 15. Similar results were obtained in COD abatement but appreciably different performance in AOX removal and biodegradability enhancement was observed. A comparison between the treatment trials brought to the evidence that Fenton-Type-pH \cong 7 process has poor performance in biodegradability enhancement, diversely the H₂O₂ promoted WAO get to better performances even at mild temperature. This process could be considered as advantageous solution in landfill leachate pre-treatment when the main objectives are COD and AOX degradation together with the biodegradability enhancement for final treatment in common biological aerobic wastewater treatment plants.

Key words:

Wet air oxidation, landfill leachate, COD-AOX, H₂O₂, respirometry, biodegradability

Introduction

Leachate coming from solid waste landfills constitutes one of the biggest threats to ground water pollution, because this liquid waste contains a lot of harmful and scarcely degradable priority pollutants. When a controlled landfill is dug, a collection system on the bottom is designed to capture the liquid leaching the waste mass into a contained zone. This mixture of water and pollutants is usually pumped out and treated prior to disposal. Some leachate disposal methods can be pre-treatment before discharge in public sewers, solar evaporation in shallow basins, land application and complete treatment followed by discharging in receiving waters. All these techniques are applicable depending on landfill leachate quality that is usually a high-strength liquid waste characterized by high organic as well as nitrogen compounds, and the presence of toxic elements.¹

Generally, the leachate quality is variable from landfill to landfill, and, over time, as a particular landfill ages, the complexity of this liquid waste

may reduce the possibility of identifying the presence of a large number of compounds in micro-amounts or determining the majority of the relevant compounds. Failure to identify a component does not mean the pollutant has no environmental or health concern, so it is important to consider some useful analytical descriptors like parametric measures and the evaluation of biodegradability or toxicity.

There is no doubt that some non-specific organic sum parameters such as COD (chemical oxygen demand) and AOX (adsorbable organic halogen), together with the biodegradability assay by respirometry can be useful in the characterization of leachate when it is necessary to decide how to treat this liquid waste prior to disposal, yet some parameters such as AOX and biodegradability by respirometry are not commonly applied. BOD₅/COD ratio is more frequently used to assay biodegradability but this method could be not so useful in prompt evaluation of aerobic biological treatment potential.

Even if there are many alternatives for leachate pre-treatment, treatment and disposal, biological

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processes ensure a necessary stability, sustainability and environmental tolerance; they are therefore usually preferred by many liquid waste management operators, moreover in some experiences combined chemical and biological systems have shown good performance.²

Nevertheless, traditional biological processes, such as activated sludge, often reveal scarce efficiencies in treatment of this kind of liquid waste because toxicity of biomasses occurs and extensive biological activity is required for effective degradation of the typical large amounts of not readily oxidized organic matter.^{3,4} Many references about leachate treatment can be found in recent studies, some of which investigate ammonia removal in leachate,^{5,6} others report studies conducted to assay enhancing biological treatability in traditional wastewater treatment plants, as well as treatment possibilities by anaerobic processes.^{7,8} Many experiences demonstrate how kinetic parameters of activated sludge are useful in describing the biodegradability potential,⁹ but only a few experiments have been carried out on the biodegradability of substrates by respirometric assays even if respirometry is recognized to be a practical technique in obtaining information about the performance of aerobic and anaerobic biomass.^{10,11}

In leachate pre-treatment, advanced oxidation processes (AOP) are frequently used and many bench-scale experiments are reported about Fenton processes and ozonation,^{12,13} however, not many experimental data are available on wet oxidation of leachate.¹⁴

In this work, an experimental assay is carried out to test leachate treatment by H₂O₂ promoted wet air oxidation and a Fenton-type treatment at neutral pH (uncommon Fenton-type processes),¹⁵ in particular abatement of COD and AOX parameters together with effects on biodegradability are presented and evaluated.

The final goal of the experiments was to test the potential of the H₂O₂ promoted wet air oxidation and the Fenton-type oxidation in managing pre-treatment of the leachate for final depuration by a biological wastewater treatment plant. COD and AOX were chosen to depict general parametric organic characterization of the leachate and the SOUR (specific oxygen uptake rate) respirometric biodegradability parameter was introduced because it was considered a good parameter for aerobic short-term biological oxygen demand assessment in aerobic wastewater treatment management. The H₂O₂ radical promoter was used as a catalyst as suggested by other researchers who have performed some interesting experiments in wet air oxidation of pure organics.¹⁶

Materials and methods

Leachate used in experimental sessions was drawn from the collection tank of an old municipal landfill, in this tank the liquid is decanted for about three months in dry seasons and about two weeks in rainy periods. The leachate was roughly filtered before testing; its basic characterization is shown in Table 1.

Table 1 – Some proprieties of the landfill leachate

Parameter	Value
pH	6.7 ± 0.1
COD (γ/mg L ⁻¹)	2200 ± 10
AOX (γ/mg L ⁻¹)	4.38 ± 0.05
alcalinity (γ/mg L ⁻¹)	650 ± 10
NH ₄ ⁺ (γ/mg L ⁻¹)	370 ± 10
NO ₃ ⁻ (γ/mg L ⁻¹)	15 ± 1
PO ₄ ³⁻ (γ/mg L ⁻¹)	11 ± 1
Ca ²⁺ (γ/mg L ⁻¹)	540 ± 10
Mg ²⁺ (γ/mg L ⁻¹)	320 ± 10
K ⁺ (γ/mg L ⁻¹)	300 ± 10
Na ⁺ (γ/mg L ⁻¹)	360 ± 10
Cl ⁻ (γ/mg L ⁻¹)	630 ± 10
SO ₄ ²⁻ (γ/mg L ⁻¹)	220 ± 10
Fe tot (γ/mg L ⁻¹)	150 ± 10

Wet air oxidation (WAO) experimental tests were carried out in a 400 mL stainless steel pressure vessel (Parr Instruments Inc., model 4562) with Teflon[®] liners, working in batch mode with inlet-outlet valves, mixer, cooling device, and automatic control of temperature and pressure. Fenton process was performed in a 200 mL reactor equipped with a magnetic stirrer and charged by a spike-pump device to add H₂O₂ reagent all at once, temperature reaction was maintained at $T = 290$ K. Respirometric tests were carried out in a batch one-litre closed respirometer with a thermostatic mantel for temperature maintenance and an oxymeter able to store data. Chemical oxygen demand (COD) was determined by the colorimetric method of Standard Methods for the Examination of Water and Wastewater¹⁷ and AOX parameter was evaluated following ISO 9562 standard by means of an ECS1000 Euroglas AOX analyzer. All the analytical measures were repeated three times and the average value was considered, AOX measure was determined as the arithmetic mean of five determinations following ISO standard.

In WAO, hydrogen peroxide (H₂O₂) was added as radical promoter at a 0.88 mol L⁻¹, the radical promoter was obtained from an Aldrich *w* = 30 % hydrogen peroxide solution in water A.C.S. reagent. In Fenton-type process, the Fe(II) reagent was obtained from an Aldrich FeSO₄ salt A.C.S. reagent.

Experimental

The WAO reactions were started after 90 mL of the leachate and 10 mL of the radical promoter (0.88 mol L⁻¹) were introduced into the reactor and the air pressure was charged following the fixed temperatures (ranging between 430–500 K) to maintain wet conditions (2 MPa for 430 K; 2.5 MPa for 460 K; 3.5 MPa for 500 K) together with the excess oxygen load.

The abatements of COD (starting from an initial concentration of $\gamma_0 = 2000 \pm 10$ mg L⁻¹) and AOX (starting from initial concentration $\gamma_0 = 4.38 \pm 0.05$ mg L⁻¹) were measured at various times ($t = 15, 30, 60, 120$ min) compared to the reactions without the H₂O₂ radical promoter (blank) and those with the addition of H₂O₂ (H₂O₂ added). COD and AOX analyses were performed on the cooled samples when each fixed time-temperature reaction was finished. A sample matching to the 30 min – 500 K reaction was drawn to assay the biodegradability variation.

In Fenton-type experiments, an aliquot of 90 mL of the leachate was charged in the 200 mL reactor together with the calculated amount of Fe(II) salt, then, while the stirring device was running, 10 mL of the H₂O₂ was added with a spike injection. The process temperature was maintained at 290 K and the reaction time was set at 60 min for each test (average time chosen reasonably to compare the tests). When the reaction time was finished, a sample was drawn for analytical measurements. In each trial, hydrogen peroxide was added at 0.88 mol L⁻¹ (the same concentration of the WAO reactions) and the Fe(II) reagent was dissolved in the mixture in order to assure three selected H₂O₂/Fe(II) mole ratios: 5, 10, and 15.

In these Fenton-type tests, no correction of the pH was intentionally proposed in the experiments in order to test performance at neutral pH, these trials were focused on the maximum reduction of costs of additives in a potential scale-up. Ordinary Fenton process efficiency is recognized to be lower at neutral pH due to the tendency of ferric oxyhydroxide precipitation that occurs at pH > 4–5; however, the use of large amounts of acids to achieve the optimum pre-treatment, followed by base to neutralize mixture, gives the water a salinity

that could sometimes be unsuitable for successive biological treatment¹⁵ (the Fenton-type experiment described in this note was carried out also to evaluate alternatives to these problem).

Schematics of the oxidation system devices are given in Fig. 1.

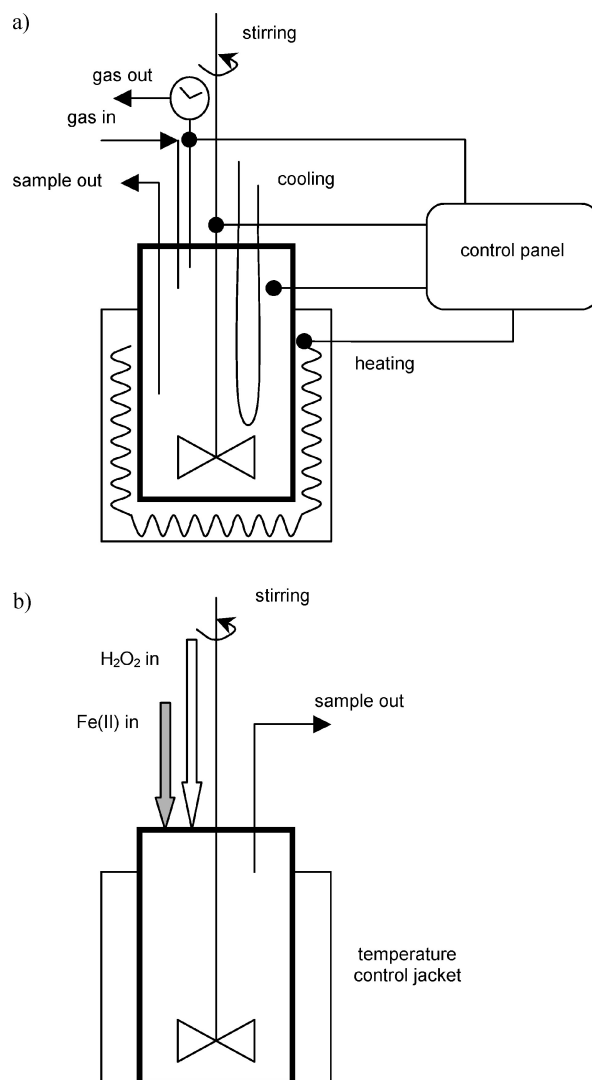


Fig. 1 – Simplified drawing of Wet Air Oxidation (A) and Fenton-type (B) reactors

Given that specific oxygen uptake rate (SOUR) is intended as the rate of substrate-equivalent dissolved oxygen consumption divided by the concentration of biomass in the respirometer, the deviation of SOUR from endogenous rate after leachate injection into the reactor has been chosen as a biodegradability testing because it could be considered a most directly appreciable expression of biological oxidation of exogenous substrates.¹⁸

In the endogenous respirometric test, the maximum specific oxygen uptake rate (SOUR_{max}) was defined in relation to exogenous phase that begins

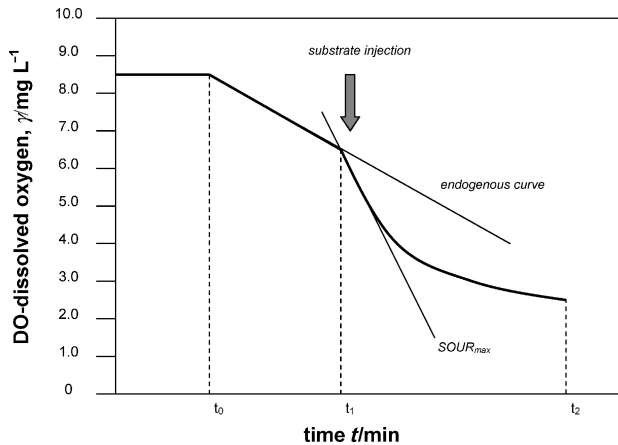


Fig. 2 – Typical respirometric dissolved oxygen concentration versus time trend (endogenous test)

after the substrate injection; it can be obtained from the endogenous plot of substrate-equivalent dissolved oxygen (γ_{S_0}) vs. time in the respirometric test (Fig. 2) by means of the following equation:

$$SOUR_{\max} = \max \left(\left(\frac{d\gamma_{S_0}}{dt} \right) \right)_{t \in (t_1, t_2)} \quad (1)$$

The improvement of the biodegradability of the treated leachate was evaluated by comparison of $SOUR_{\max}$ of the treated samples with the $SOUR_{\max}$ of the raw leachate.

The activated sludge used in respirometric tests was arranged in a concentration of about 2000 mg L⁻¹ VSS added of $\gamma = 10\text{--}15$ mg L⁻¹ of allylthiourea for nitrification inhibition, the injection volume was set to 10 mL, and temperature was maintained constantly at 290 K during the tests. Other details about respirometer are described elsewhere.¹⁹

Results and discussion

As previously observed, WAO and Fenton type tests were performed to assay pre-treatment potential of the leachate in order to manage its depuration in a conventional aerobic wastewater treatment plant.

Figs. 3 and 4, show the WAO treatment of COD and AOX during reaction time. An appreciable enhancement was noticed of abatement with temperature, and this behaviour was observed in many other experiments.^{20,21} The addition of H₂O₂ homogeneous oxidant promoted extensive oxidation and also improved abatement of the organic and halorganic content. Generally, reduction percent of COD was higher than AOX, and this fact could be expected because of the scarce dehalogenation that occurred during this specific

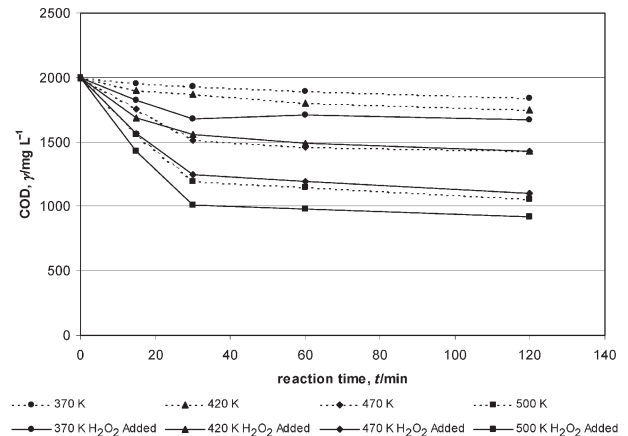


Fig. 3 – COD removal versus reaction time in WAO with and without H₂O₂ addition

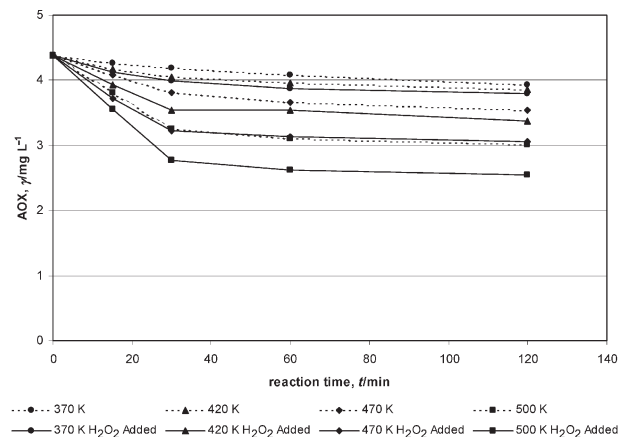


Fig. 4 – AOX removal versus reaction time in WAO with and without H₂O₂ addition

WAO process but further specific investigations are required.

A 60-min test was chosen to compare the COD and AOX parameters because this reaction time was reasonably considered the medium reaction time for potential scale-up of WAO and Fenton-type process design. The blank-60 min WAO reaction has brought to an abatement of COD from 5 % (for 370 K) to 45 % (for 500 K), indeed the use of the H₂O₂ promoter improved the effectiveness of the COD abatement in the range from 10 % (for 370 K) to 55 % (for 500 K). The blank-60 min WAO reaction reduced AOX in a range from 6 % (for 370 K) to 30 % (for 500 K), and the H₂O₂ added reaction gave an abatement range from 10 % (for 370 K) to 40 % (for 500 K).

In WAO experiments H₂O₂ addition increased performances in COD and AOX abatement, this should be connected to the enhance of the oxidant power in the mixture by H₂O₂ radical promoter.

During the tests, pH values were measured without marked variations in the range 5–7. A mild

acid value was expected because the end byproducts of oxidation mainly consisted of short-chain organic acids with typical difficulties in further thermal oxidation.²²

Fenton-type treatment of the leachate gave the results presented in Fig. 5. Applying 60 minutes reaction time, three H₂O₂/Fe(II) mole ratios (5, 10, 15) were investigated and a rather high abatement of the COD was observed (ranging from 50 and 70 %). For a H₂O₂/Fe(II) mole ratio equal to 10, the COD reduction was similar to that obtained in a H₂O₂ added WAO-60 minutes reaction time at 500 K. This high performance is difficult to explain because of the chemical complexity of the leachate and the unconventional design of the Fenton system (one of the purposes of our experiments was to evaluate performance without pH corrections), but we could not exclude that some Fe-complexing species compounds of the leachate had a role in the process.

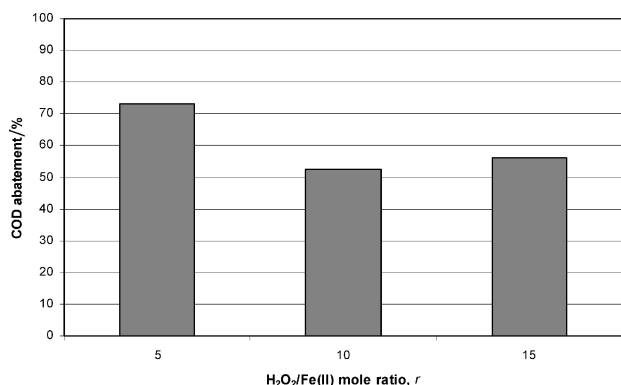


Fig. 5 – Percent COD reduction versus H₂O₂/Fe(II) molar ratio in Fenton-type treatment

The H₂O₂/Fe(II) ratio could be useful to assay the radical promoter power added to the process and it represents an evaluation of the degree of the radical promoted oxidation, in our experiments this value was set to a high value to maintain extreme chemical oxidation versus coagulation,²³ nevertheless, a resulting high concentration of iron leads to high production of iron sludge at the end of treatment;²⁴ further considerations could not be obtained from these trials.

AOX decrease during Fenton-type reactions was not much evident; in fact, a less than 10 % reduction was measured in the experimental sessions compared to the H₂O₂ added WAO process, where it reached about 40 %, the designed Fenton-type test showed limited efficiencies.

From these tests, thermal contribution to the oxidation process appears essential to give efficiency in removal of organic halogen compounds but other considerations cannot be exposed without a single characterization of the halorganics of the leachate.

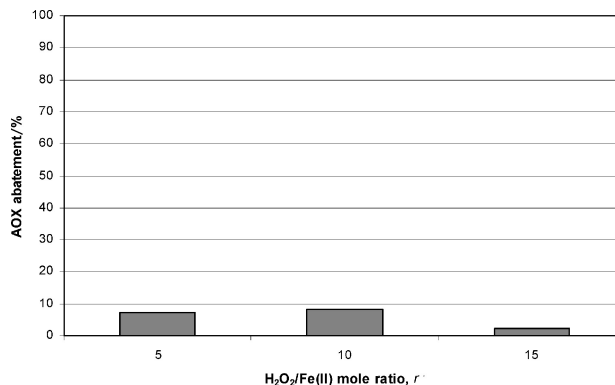


Fig. 6 – Percent AOX reduction versus H₂O₂/Fe(II) mole ratio in Fenton-type treatment

Furthermore, during these oxidation experiments on the leachate, significant differences were demonstrated in examining the biodegradability assays by respirometric parameter $SOUR_{max}$. When the WAO treatment was employed, an appreciable growth in $SOUR_{max}$ was noted and H₂O₂ promoted conditions improved these $SOUR_{max}$ values further.

It is well known that when WAO is applied efficiently to liquid waste treatment, the organic compounds are mainly degraded to low molecular mass, oxygenated compounds such as carboxylic acids, thus improving biodegradability,²² and these effects are significant when high temperature is used.

In our tests, the data on H₂O₂ added-WAO showed an observable $SOUR_{max}$ enhancement even at lower temperatures (Fig. 7), since the $SOUR_{max}$ parameter represents an estimate of the easy biological oxidation of the substrates of the leachate, $SOUR_{max}$ could be used to monitor the potential to abate refractory compounds in the leachate.

As a hypothesis, this performance could be explained by the thermal and radical assisted WAO decomposition of the complex-refractory compounds, which leads to a liquid mixture more amenable for aerobic biodegradation and, as a result, for conventional aerobic wastewater treatment.

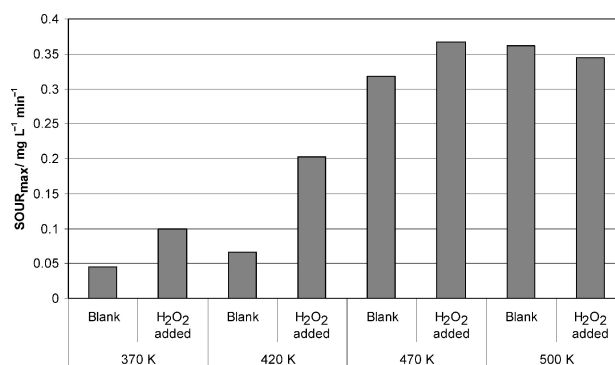


Fig. 7 – Values of the $SOUR_{max}$ parameter in blank and H₂O₂ promoted WAO reactions

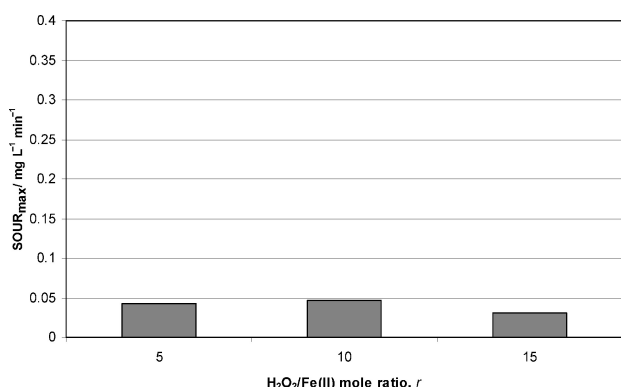


Fig. 8 – Values of the $SOUR_{max}$ parameter in Fenton-type reactions

In the case of Fenton-type reactions, we revealed scarce effect on biodegradability improvement; in fact $SOUR_{max}$ values were low and constant with the molar ratio changes (Fig. 8). Even if organic compounds were somewhat degraded since good COD abatement was revealed, the presence of refractory compounds remained significant after this treatment because, in respirometric assays, the biological oxidation of the substrates did not appear easily.

Conclusion

This work considers homogeneous H₂O₂ promoted wet air oxidation and Fenton-type treatment of COD and AOX parameters of a leachate. The results obtained were compared in order to extrapolate pre-treatment design data for managing this liquid waste in a conventional municipal biological wastewater treatment plant. A good reduction in COD was achieved in both the treatments and the abatement percentages were similar, AOX abatement was generally more difficult. This fact confirms the difficulties to treat halorganics of landfill leachate and for this specific situation, an evident AOX decrease was observed only in H₂O₂ added WAO reaction.

When compared to the Fenton-type at neutral pH process, the use of H₂O₂ added WAO resulted in a better abatement of COD and AOX. This characteristic is more appreciable at higher temperature (500 K) which could be considered a high temperature in a wet air oxidation process using H₂O₂ as homogeneous oxidation promoter (this WAO process for liquid wastes can be considered similar to a homogeneous catalytic one and thus the maximum process temperatures should be below 520 K).

The Fenton-type treatment led to the highest abatement in COD (nearly 70 %) at a H₂O₂/Fe(II) mole ratio of 5 and 60 min reaction time. In this sit-

uation, a high H₂O₂/Fe(II) ratio was applied with a consequently high consumption of H₂O₂ in the reaction and an expected residual sludge.

As previously observed, these Fenton-type tests were achieved without pH optimization, so it can be noted that the performance of the Fenton process can increase in an acidic environment.

The AOX in the leachate was barely oxidized by Fenton-type process and further investigation in this case is required.

To sum up, the Fenton-type process experiment can be essentially applied for COD abatement in the management of landfill leachate considered for the tests, but this pre-treatment seems inadequate in AOX removal and in enhancement of leachate biodegradability.

The evidence of an advanced biodegradability performance for the H₂O₂ promoted WAO treatment confirms the potential of this system in leachate pre-treatment when the final goal is to improve effectiveness of finishing biological treatment. The purpose to discharge the treated leachate to a biological municipal wastewater treatment plant as well as the reduction of additives and sludge handling in pre-treatment must be carefully planned. From an economic and management point of view it is necessary to weigh up the higher costs of WAO thermal supply together with its ecological and technical advantages.

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Symbols and abbreviations

COD	– chemical oxygen demand
BOD ₅	– biochemical oxygen demand
AOX	– adsorbable organic halogen
DO	– dissolved oxygen concentration
SOUR	– specific oxygen uptake rate, mg mg ⁻¹ min ⁻¹
SOUR _{max}	– maximum specific oxygen uptake rate, mg mg ⁻¹ min ⁻¹
γ _{so}	– substrate-equivalent dissolved oxygen, mg L ⁻¹ O ₂
γ _X	– biomass concentration, mg L ⁻¹ VSS
<i>c</i>	– concentration, mol L ⁻¹
<i>m</i>	– mass, mg
<i>r</i>	– mole ratio
<i>T</i>	– temperature, K
<i>t</i>	– time, min
<i>w</i>	– mass fraction, %

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