



Ozonation as polishing treatment of mature landfill leachate

Susana Cortez, Pilar Teixeira, Rosário Oliveira*, Manuel Mota

IBB – Institute for Biotechnology and Bioengineering, Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

ARTICLE INFO

Article history:

Received 9 March 2010

Received in revised form 18 June 2010

Accepted 21 June 2010

Available online 26 June 2010

Keywords:

Biodegradability
Hydrogen peroxide
Mature landfill leachate
Ozone
pH

ABSTRACT

Mature landfill leachate is typically resistant to biological processes. In order to enhance the biodegradability of a pre-treated mature landfill leachate, ozonation treatments in a lab-scale column were assayed under different ozone concentrations, contact time, initial pH, and hydrogen peroxide concentrations. Degradation of the landfill leachate by ozone was favoured at higher pH values and with the addition of H_2O_2 , both consistent with the enhanced production of the hydroxyl radical under such conditions. The highest organic reduction and biodegradability improvement was observed with the O_3/H_2O_2 process at $600\text{ mg } H_2O_2\text{ L}^{-1}$. This system was able to remove 63% of chemical oxygen demand (COD), 53% of total organic carbon (TOC), 42% of aromatic content (UV_{254}) and increased the leachate 5-day biochemical oxygen demand (BOD_5) to COD ratio from 0.01 to 0.17. Ozone combined with H_2O_2 contributed significantly to remove and change the recalcitrant organic matter and improved leachate biodegradability, which makes this process very attractive as pre-biological treatment.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Sanitary landfilling is still the most used and accepted method to eliminate municipal solid wastes worldwide due to its economic advantages [1]. Given the great chemical complexity and diversity of the leachate produced, sanitary landfills have searched for innovative leachate treatment technologies, in order to avoid discharges to the environment causing negative impacts to the biota or public health [2].

Leachate generated from mature landfills (with more than 10 years) is typically characterised by high ammonium (NH_4^+) content, a low 5-day biochemical oxygen demand (BOD_5) to chemical oxygen demand (COD) ratio (BOD_5/COD generally below 0.1), and high fraction of refractory and large organic molecules (humic substances) [2,3]. Humic substances consist of a structure of alkyl/aromatic units, mainly cross-linked by oxygen and nitrogen groups with the major functional groups being carboxylic acid, phenolic and alcoholic hydroxyls, as well as ketone and quinone groups [4].

Since biological treatments are not effective for the removal of refractory compounds and physico-chemical processes such as reverse osmosis and adsorption are non-destructive, innovative technologies have focused on advanced oxidation processes (AOPs) [1,5]. AOPs are attractive methods to eliminate the colour, to reduce

the organic load and to improve the biodegradability of recalcitrant contaminants of mature leachate [1,6,7]. These processes involve the production of powerful oxidising agents, mainly the hydroxyl radical ($\bullet OH$), from single oxidants, such as ozone [8], or from a combination of strong oxidants, e.g. O_3 and OH^- [9], H_2O_2 [10], irradiation, e.g. ultraviolet [11], ultrasound [12] or electron beam [13], and catalysts, e.g. transition metal ions or photocatalyst [14].

Molecular ozone is a strong oxidiser having high reactivity and selectivity towards organic pollutants such as humic substances [15]. The use of ozone at high pH (O_3/OH^-) or in combination with H_2O_2 (O_3/H_2O_2), both favouring the production of hydroxyl radicals that have an oxidation potential higher than that of ozone molecule, are attractive processes to oxidise the complex leachate mixtures [16]. It is expected that the use of such processes as pre-treatment, to reduce and convert the large refractory organic molecules, found in mature leachates, into smaller more biodegradable intermediates, followed by biological oxidation of these intermediates would result in economical savings and improvement of the treatment efficiency [11,17].

The treatment of mature landfill leachate using ozone, ozone at alkaline pH or ozone with hydrogen peroxide has been demonstrated in the literature. For instance, Tizaoui et al. [16] reported that ozone alone ensured a COD removal of about 27% after 60 min of ozonation, while the O_3 and H_2O_2 combination increased COD removal up to 48%. Hagman et al. [2] verified the same tendency obtaining an improvement in COD reduction from 22% for ozone alone to 50% when hydrogen peroxide was added. Goi et al. [18] studied the effect of pH on ozonation of a landfill leachate, achieving COD removal efficiencies of 24%, 29% and 41% at initial pH 4.5, 8.1 and 11, respectively. Many researchers [11,16,17,19,20]

* Corresponding author. Tel.: +351 253 604 409; fax: +351 253 678 986.

E-mail addresses: susana.cortez@deb.uminho.pt (S. Cortez),

pilar@deb.uminho.pt (P. Teixeira),

roliveira@deb.uminho.pt (R. Oliveira), mmota@deb.uminho.pt (M. Mota).

Table 1
Landfill leachate characteristics.

Parameter	Value
pH	3.5 ± 0.1
Conductivity (mS cm ⁻¹)	4.45 ± 0.03
COD (mg L ⁻¹)	743 ± 14
BOD ₅ (mg L ⁻¹)	10 ± 1
TOC (mg L ⁻¹)	284 ± 6
UV ₂₅₄	2.614 ± 0.023
N-NO ₃ ⁻ (mg L ⁻¹)	1824 ± 103
N-NO ₂ ⁻ (mg L ⁻¹)	<0.01
N-NH ₄ ⁺ (mg L ⁻¹)	714 ± 23
VSS (mg L ⁻¹)	79 ± 3

observed a significant enhancement in biodegradability, defined as the BOD₅/COD ratio, after ozonation. However, none of these reports evaluated the effect of different O₃ concentrations, O₃ at different pH values and O₃ with different H₂O₂ concentrations on leachate COD, BOD₅, pH, ultraviolet absorbance at 254 nm (UV₂₅₄) and nitrogenous compounds.

Therefore, the objective of this study was to investigate the ozonation of a mature landfill leachate, in order to transform refractory compounds and improve leachate biodegradability. Experiments were conducted at different ozone concentrations, contact time, initial pH and H₂O₂ concentrations in a lab-scale column. The leachate under study had already been treated in the treatment plant of the sanitary landfill, which comprises stabilisation, anaerobic ponds, an anoxic tank, aerated ponds and a biological decantation unit, together with an oxidation tank and two chemical precipitators. In spite of that, at the end of the process the leachate still did not meet the maximum allowable nitrogen and organic matter concentrations for direct or indirect discharge. In previous studies, we developed a biological process using an anoxic rotating biological contactor to remove nitrate. Despite its high efficiency in nitrate removal, it was not able to remove any of the refractory organic compounds still present, and an external carbon source had to be added, which represents an additional cost.

2. Materials and methods

2.1. Landfill leachate

The landfill leachate was collected from a municipal landfill in the North of Portugal before being discharged to the municipal sewer. This landfill has been in operation since 1998. The collected leachate was stored in closed containers at 4 °C until use. The characteristics of the leachate used in the investigated period are listed in Table 1. Taking into account the extremely low value of the BOD₅/COD ratio (0.01) and the high content of nitrogen-ammonium (N-NH₄⁺), this leachate can be considered mature and rich in refractory compounds. Another important feature of this leachate is the high nitrogen-nitrate (N-NO₃⁻) content.

2.2. Ozonation

The ozonation experiments were conducted in an acrylic column, semi-batch reactor, with a height of 69.5 cm and an internal diameter of 8.2 cm. Ozone was produced from pure and dry oxygen by corona discharge using an ozone generator (Anseros Periph-eral Com-AD-02), capable of producing up to 8 g O₃ h⁻¹. The ozone and oxygen mixture was continuously introduced into the column through a ceramic diffuser placed at the bottom and was allowed to react with each sample for 60 min. The inlet and outlet concentrations of ozone in the gas phase were measured at 254 nm using an ozone analyser (Anseros Ozomat GM-6000-OEM), throughout the experiments. The residual gas was vented through the catalytic ozone destruction unit. A needle valve and a gas flow meter were

placed before the column to control and measure the ozone and oxygen mixture flow rate in L h⁻¹. For every experiment the reactor was filled with one litre of leachate. Effluent samples were taken during reaction at the bottom of the column.

The effect of initial pH was studied adjusting the pH of the leachate with NaOH. In O₃/H₂O₂ experiments, the required amount of H₂O₂ was injected in a single-step to the column at time zero. The samples collected from these trials were treated with a saturated solution of NaOH to quench the reaction of residual H₂O₂.

All experiments were carried out at room temperature (20 ± 2 °C), performed in duplicate and the results were averaged.

2.3. Analytical methods

The leachate was characterised before and after ozonation, through analyses of pH, chemical oxygen demand (COD), total organic carbon (TOC), 5-day biochemical oxygen demand (BOD₅), nitrogen-nitrate (N-NO₃⁻), nitrogen-nitrite (N-NO₂⁻), nitrogen-ammonium (N-NH₄⁺), and UV absorbance at 254 nm. COD, BOD₅, N-NO₂⁻, and N-NH₄⁺ concentrations were determined according to standard methods [21]. Nitrate concentration was measured by high-performance liquid chromatography (HPLC), using a Varian Metacarb column (type 67H, 9 μm, 300 mm long, 6.5 mm internal diameter) and a mobile phase of 0.005 M sulphuric acid (H₂SO₄) at 0.7 mL min⁻¹. Column temperature was set at 60 °C and nitrate was detected by UV at 210 nm. Ultraviolet absorbance at 254 nm (UV₂₅₄) was monitored with a Jasco V-560 spectrophotometer. TOC measurements were performed using a Dohrmann DC-190 TOC Analyser.

3. Results and discussion

3.1. Effect of inlet ozone concentration and contact time

The effect of inlet ozone concentration was investigated at 63, 74 and 112 mg L⁻¹ NTP, corresponding to a gas flow rate of 2.5, 1.67 and 0.83 L min⁻¹, respectively. These experiments were carried out at the natural pH of the landfill leachate (pH 3.5). Table 2 presents the results of ozone consumption, COD, TOC, and UV₂₅₄ removal efficiencies, as well as N-NO₂⁻, N-NO₃⁻ and N-NH₄⁺ variations throughout time at different O₃ concentrations. Ozone consumption (OC) was calculated according to Eq. (1):

$$OC (\text{g O}_3 \text{ L}^{-1} \text{ liquid}) = \frac{Q_G}{V_L} \int_0^t ([O_{3G,i}] - [O_{3G,o}]) dt \quad (1)$$

where Q_G is the gas flow rate (L min⁻¹), V_L the liquid volume (L), and $[O_{3G,i}]$ and $[O_{3G,o}]$ are the ozone concentrations (g L⁻¹ NTP) in the gas stream at the inlet and outlet, respectively. The inlet ozone concentration remained constant over time for each experiment.

It was observed that COD and TOC removal efficiencies increased with contact time and ozone concentration. The highest ozone consumption was observed for the highest ozone concentration tested, suggesting a more effective use of the ozone supplied to the system. This fact is due to the higher ozone partial pressure that provides higher solubility of ozone, achieving maximum ozone mass transfer and consequent availability.

It is difficult to compare the removal efficiency values obtained herein with the ones presented in the literature because these depend on many factors (the type of reactor, pH, temperature etc.). Furthermore, the landfill leachate used in this study had the particularity of having been previously treated.

COD removal efficiency increased faster initially levelling off after 30 min (Table 2). The COD degradation was rapid during the initial period probably due to the availability of easily oxidisable compounds, such as phenols, quinones and aromatic acids. Further

Table 2
Effect of ozone concentration and contact time on OC, COD, TOC and UV₂₅₄ removal efficiencies; N-NO₂⁻, N-NO₃⁻ and N-NH₄⁺ concentrations.

O ₃ concentration (mg L ⁻¹ NTP)	Parameter	Contact time (min)					
		0	5	15	30	45	60
63	OC (g O ₃ L ⁻¹ effluent)		0.44	1.25	2.19	3.01	3.89
	COD removal (%)		4	6	7	10	10
	TOC removal (%)		2	4	5	6	7
	UV ₂₅₄ removal (%)		10	14	16	18	19
	N-NO ₂ ⁻ (mg L ⁻¹)	0.01	0.04	0.04	0.03	0.03	0.03
	N-NO ₃ ⁻ (mg L ⁻¹)	2045	2078	2088	2109	2106	2096
	N-NH ₄ ⁺ (mg L ⁻¹)	690	675	659	637	622	650
74	OC (g O ₃ L ⁻¹ effluent)		0.55	1.39	2.35	3.24	4.07
	COD removal (%)		6	10	14	16	17
	TOC removal (%)		3	8	9	11	11
	UV ₂₅₄ removal (%)		9	15	18	19	21
	N-NO ₂ ⁻ (mg L ⁻¹)	0.01	0.03	0.03	0.03	0.03	0.03
	N-NO ₃ ⁻ (mg L ⁻¹)	2089	2100	2129	2152	2157	2162
	N-NH ₄ ⁺ (mg L ⁻¹)	767	764	746	725	711	699
112	OC (g O ₃ L ⁻¹ effluent)		0.61	1.42	2.40	3.37	4.38
	COD removal (%)		10	13	17	20	23
	TOC removal (%)		5	8	10	13	14
	UV ₂₅₄ removal (%)		9	17	19	21	22
	N-NO ₂ ⁻ (mg L ⁻¹)	0.01	0.03	0.04	0.03	0.03	0.03
	N-NO ₃ ⁻ (mg L ⁻¹)	2059	2075	2123	2144	2154	2162
	N-NH ₄ ⁺ (mg L ⁻¹)	785	763	743	713	699	690

increase in reaction time led to a slow change in organic removal rate, indicating the formation of by-products such as aliphatic acids and aldehydes, which were difficult to further degrade [15,16]. A similar tendency was observed with TOC removal efficiency. Wang et al. [10] and Chaturapruek et al. [15] also reported two kinetic periods in the COD and TOC removal efficiencies of a mature landfill leachate. Therefore, it is not always worthwhile to increase the ozone contact time.

The degree of carbon mineralisation (TOC removal) was lower than COD removal throughout the study. This phenomenon is probably related with the generation and accumulation of carboxylic acids and aldehydes as final products, rather than CO₂ [11,19].

The molecular ozone is very effective in the oxidation of aromatic compounds susceptible to electrophilic attack. Thus, ozonation can easily alter the molecular structure of the leachate organics from aromatic and unsaturated constituents to saturated intermediates [17,22]. The absorbance at 254 nm (UV₂₅₄) has been reported to be a qualitative indicator of aromatic and unsaturated compounds present in wastewater [17,23]. From Table 2 it can be observed that UV₂₅₄ removal efficiency increased with contact time and slightly improved with the increase of inlet ozone concentration. A rapid increase of the UV₂₅₄ removal efficiency was noted during the first 30 min, but the oxidation rate decreased as the reaction proceeded. UV₂₅₄ removal was, in general, higher than COD and TOC removal efficiencies. These results support the hypothesis that molecular ozone reacted promptly with aromatic and unsaturated compounds inducing the decrease of aromaticity, but generated compounds that react more slowly and are resistant to further oxidation such as carboxylic acids and aldehydes instead of CO₂, as mentioned above.

Mature landfill leachate typically presents high concentrations of nitrogenous pollutants. During these experiments only about 10% of nitrogen-ammonium was converted to nitrogen-nitrate due to the acidic conditions assayed (pH 3.5). In fact, previous studies [24,25] showed that this oxidation is negligible in acidic solutions because at pH lower than 7, ammonia (NH₃) exists in the aqueous solution essentially in its ionised form (NH₄⁺), which is not reactive toward ozone. Nevertheless, it should also be noted that species such as bromide are known to favour ammonia removal [24].

Once ammonium removal consumes ozone, it would be interesting to determine whether or not N-NH₄⁺ should be removed

before oxidation, by a biological nitrification process or by air stripping.

A slight decrease in pH from 3.5 to 3.0 was observed in these experiments (data not shown).

The biodegradability of an effluent can be described in terms of BOD₅/COD ratio. In order to assess the effect of different ozone concentrations on leachate biodegradability, BOD₅ measurements after 60 min of treatment were carried out and the results obtained are compiled in Fig. 1.

After ozonation, BOD₅ increased by about 80% at 63 mg O₃ L⁻¹ NTP, 160% at 74 mg O₃ L⁻¹ NTP, and 180% at 112 mg O₃ L⁻¹ NTP. Consequently, BOD₅/COD ratio increased with the increase of the ozone concentration from 0.03 at 63 mg O₃ L⁻¹ NTP to 0.06 at 112 mg O₃ L⁻¹ NTP.

According to the results, a gas flow rate of 0.83 L min⁻¹ and an inlet ozone concentration of about 112 mg L⁻¹ NTP were chosen for further experiments.

3.2. Effect of initial pH

The effect of initial pH on ozone consumption and degradation of the landfill leachate pollutants by ozonation is given in Table 3. OC, COD and TOC removal efficiencies increased as the pH raised because under basic pH higher number of ozone molecules are decomposed to generate OH⁻ and •OH radicals and a less selective

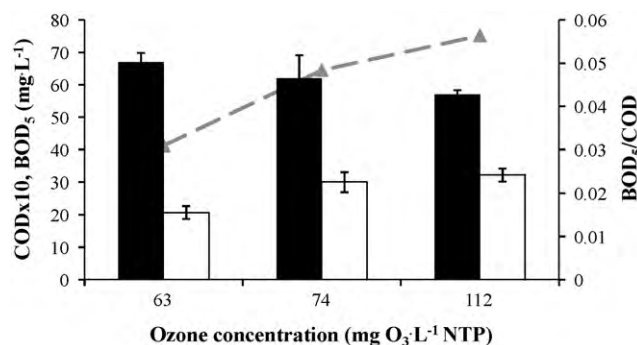


Fig. 1. Effect of ozone concentration on COD (■), BOD₅ (□), and BOD₅/COD ratio (▲) after 60 min of treatment.

Table 3

Effect of initial pH on OC, COD, TOC and UV₂₅₄ removal efficiencies; N-NO₂⁻, N-NO₃⁻, and N-NH₄⁺ concentrations after 60 min of ozonation with an ozone concentration of 112 mg O₃ L⁻¹ NTP.

Parameter	pH 3.5 ^a	pH 7	pH 9	pH 11
OC (g O ₃ L ⁻¹ effluent)	4.38	4.89	5.05	5.14
COD removal (%)	23	30	36	40
TOC removal (%)	14	21	28	32
UV ₂₅₄ removal (%)	22	22	22	22
N-NO ₂ ⁻ (mg L ⁻¹)	0.03	0.06	0.13	0.08
N-NO ₃ ⁻ (mg L ⁻¹)	2162	2188	2228	2263
N-NH ₄ ⁺ (mg L ⁻¹)	690	619	565	548

^a pH 3.5 was the natural pH of the landfill leachate.

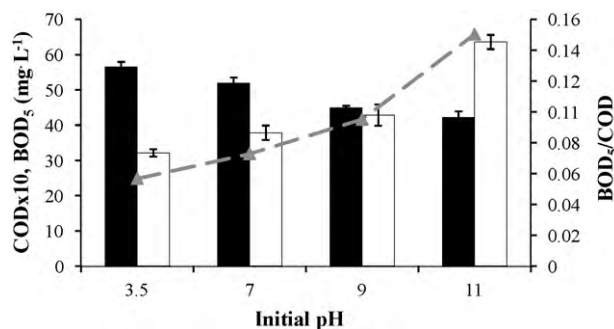


Fig. 2. Effect of initial pH on COD (■), BOD₅ (□), and BOD₅/COD ratio (▲) after 60 min of ozonation with an ozone concentration of 112 mg O₃ L⁻¹ NTP.

and more powerful hydroxyl oxidation dominates [26,22]. UV₂₅₄ removal efficiency was not affected by pH.

The results show that ozonation at high pH values favoured the conversion of ammonium (in the un-ionised form) to nitrate (Table 3), as also observed by Singer and Zilli [27].

In these experiments, after 60 min of reaction only a slight decrease in pH values was noticed (data not shown). The maximum drop (2.2 units) was observed at initial pH 7. Probably carbonates accumulated in the treated leachate as a result of mineralisation at basic pH, while carboxylic acids and aldehydes [10] were produced by direct ozonation reactions at pH 7.

Fig. 2 depicts the results of COD, BOD₅, and BOD₅/COD as a function of initial pH, after ozonation. BOD₅ increased about 180% at pH 3.5, 230% at pH 7, 275% at pH 9 and 455% at pH 11. The raise in BOD₅ can be due to the transformation of the refractory large compounds into smaller and more biodegradable products [10].

3.3. Effect of hydrogen peroxide concentration

The AOP experiments associating ozone and hydrogen peroxide (O₃/H₂O₂) were performed with H₂O₂ at 200, 400 and 600 mg L⁻¹. According to Staehelin and Hoigné [28], the lower limit for the effectiveness of the H₂O₂/O₃ process is in a pH range of 5–7, therefore, the O₃/H₂O₂ process was applied to leachate, after correction to pH 7.

Table 4

Effect of hydrogen peroxide concentration on OC, COD, TOC and UV₂₅₄ removal efficiencies; N-NO₂⁻, N-NO₃⁻, and N-NH₄⁺ concentrations after 60 min of ozonation with an ozone concentration of 112 mg O₃ L⁻¹ NTP at pH 7.

Parameter	0 mg H ₂ O ₂ L ⁻¹	200 mg H ₂ O ₂ L ⁻¹	400 mg H ₂ O ₂ L ⁻¹	600 mg H ₂ O ₂ L ⁻¹
OC (g O ₃ L ⁻¹ effluent)	4.89	5.19	5.30	5.40
COD removal (%)	30	47	57	63
TOC removal (%)	21	38	50	53
UV ₂₅₄ removal (%)	22	30	36	42
N-NO ₂ ⁻ (mg L ⁻¹)	0.06	0.08	0.14	0.12
N-NO ₃ ⁻ (mg L ⁻¹)	2188	2191	2171	2166
N-NH ₄ ⁺ (mg L ⁻¹)	619	621	632	632

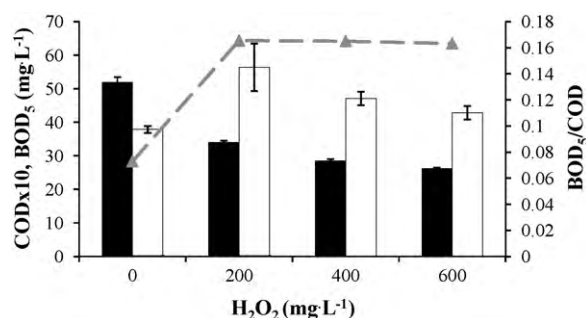


Fig. 3. Effect of hydrogen peroxide concentration on COD (■), BOD₅ (□), and BOD₅/COD ratio (▲) after 60 min of ozonation with an ozone concentration of 112 mg O₃ L⁻¹ NTP at pH 7.

Table 4 presents the results of ozone consumption, COD, TOC, and UV₂₅₄ removal efficiencies, as well as nitrogenous compounds concentrations after ozonation at different H₂O₂ concentrations. Additionally, and as a control, landfill leachate was treated with hydrogen peroxide only at the same concentrations for 60 min and during the experiments no changes of parameters were detected since the hydrogen peroxide alone is not a strong oxygen transfer agent (data not shown).

The O₃/H₂O₂ process enhanced the degradation of the landfill leachate compared to O₃ only. In the O₃/H₂O₂ system the production of hydroxyl radicals is significantly high, thus these results confirmed that the oxidation of this effluent was mainly due to these chemical species. In addition, they also promoted an increase in UV₂₅₄ removal.

Some authors [16,22,29] report that an increase in hydrogen peroxide concentration will not always increase organic compounds degradation. In effect, supplying hydrogen peroxide in excess will change its role from being the initiator for the production of •OH radicals to inhibitor of ozone decomposition through free radical reactions. As a consequence, degradation of the organic matter in the leachate diminishes. In this work, since for the tested amounts of H₂O₂ the oxidation rate increased as the hydrogen peroxide concentration increased, that trend was not observed and perhaps the optimum hydrogen peroxide dose was not found.

Considering nitrogenous pollutants, as is shown in Table 4, nitrogen-ammonium was converted to nitrogen-nitrate and it was not verified a significant difference between the treatments with O₃ only and O₃/H₂O₂, for the different amounts of H₂O₂ assayed.

Results of the effect of O₃ only and O₃/H₂O₂ on biodegradability are presented in Fig. 3. Biodegradability improved in both systems; however, the O₃/H₂O₂ process presented noticeable higher BOD₅/COD values. A BOD₅/COD ratio of about 0.17 was achieved for the different concentrations of peroxide.

A simplistic economical analysis of the operating costs associated to each AOP studied, such as expenses of reagents and energy, was performed. The calculated costs, based on 60 min of operating time and considering 0.09 € kW h⁻¹; 0.35 € kg⁻¹ NaOH, 0.33 € L⁻¹ H₂O₂ (35%) and 0.08 € m⁻³ O₂, are summarised in Table 5.

Table 5
Operating costs for the AOPs studied.

AOP	Operating costs (€ m ⁻³ g ⁻¹ of COD removed)
O ₃ /pH 3.5 ^a	64.0
O ₃ /pH 7	49.4
O ₃ /pH 9	41.7
O ₃ /pH 11	38.2
O ₃ /200 mg H ₂ O ₂ L ⁻¹	31.9
O ₃ /400 mg H ₂ O ₂ L ⁻¹	26.6
O ₃ /600 mg H ₂ O ₂ L ⁻¹	24.7

^a pH 3.5 was the natural pH of the landfill leachate.

The lowest operating cost was 24.7 € m⁻³ g⁻¹ of COD removed for the experiment carried out with the O₃/H₂O₂ system at 600 mg H₂O₂ L⁻¹. Considering the operating costs of O₃ alone, significant reductions in the treatment costs were obtained under basic pH and with hydrogen peroxide. It is important to note that a fine tuning of the operating conditions could considerably change the operating costs obtained for each treatment process.

Though there was a significant improvement in biodegradability, a BOD₅/COD ratio higher than 0.4, which is the minimum value considered appropriate for the efficient application of a biological treatment [30] was never achieved, for all processes tested, emphasising the highly recalcitrant properties of the landfill leachate studied.

Probably coupling one of O₃/H₂O₂ conditions tested with other physico-chemical treatment process would ensure a BOD₅/COD ratio higher than 0.4 before the biological treatment, without increasing significantly the operation costs. For instance, in the treatment of a landfill leachate, Monje-Ramirez and Velásquez [19] and Bila et al. [20] also applied ozonation preceded by the coagulation/flocculation of colloids and found significant biodegradability improvement.

4. Conclusions

In the polishing treatment of a mature landfill leachate, the combined effect of ozone with hydrogen peroxide induced higher COD and TOC removal efficiencies as well as higher leachate biodegradability, comparatively to ozone alone at natural pH. These results are related with the enhanced production of hydroxyl radicals in the presence of H₂O₂. For comparison purposes only, estimates of operating costs were calculated. It was found that O₃/H₂O₂ at 600 mg H₂O₂ L⁻¹ was the most economical process (24.7 € m⁻³ g⁻¹ of COD removed) to treat the leachate tested.

Since before being discharged the leachate must be denitrified, which demands the presence of a carbon source, future studies are planned to optimise the O₃/H₂O₂ system in order to obtain even more biodegradable compounds, which could be used in the biological process.

Acknowledgements

Susana Cortez and Pilar Teixeira fully acknowledge the financial support provided from Fundação para a Ciência e Tecnologia (FCT) through the grants SFRH/BD/24715/2005 and SFRH/BPD/26803/2006, respectively.

References

[1] S. Renou, J. Givaudan, S. Poulain, F. Dirassouyan, P. Moulin, Landfill leachate treatment: review and opportunity, *J. Hazard. Mater.* 150 (2008) 468–493.

- [2] M. Hagman, E. Heander, J.L.C. Jansen, Advanced oxidation of refractory organics in leachate—potential methods and evaluation of biodegradability of the remaining substrate, *Environ. Technol.* 29 (2008) 941–946.
- [3] T.A. Kurniawan, W.H. Lo, G.Y. Chan, Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate, *J. Hazard. Mater.* 129 (2006) 80–100.
- [4] H.R. Schulten, B. Plage, M. Schnitzer, A chemical-structure for humic substances, *Naturwissenschaften* 78 (1991) 311–312.
- [5] D. Geenens, B. Bixio, C. Theoye, Combined ozone-activated sludge treatment of landfill leachate, *Water Sci. Technol.* 44 (2001) 359–365.
- [6] J.L. de Moraes, P.P. Zamora, Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, *J. Hazard. Mater.* 123 (2005) 181–186.
- [7] J. Kochany, E. Lipczynska-Kochany, Utilization of landfill leachate parameters for pre-treatment by Fenton reaction and struvite precipitation—a comparative study, *J. Hazard. Mater.* 166 (2009) 248–254.
- [8] C. Di Iacomi, R. Ramadori, A. Lopez, Combined biological and chemical degradation for treating a mature municipal landfill leachate, *Biochem. Eng. J.* 31 (2006) 118–124.
- [9] P. Haapea, S. Korhonen, T. Tuhkanen, Treatment of industrial landfill leachates by chemical and biological methods: ozonation, ozonation hydrogen peroxide, hydrogen peroxide and biological post-treatment for ozonated water, *Ozone Sci. Eng.* 24 (2002) 369–378.
- [10] F. Wang, M.G. El-Din, D.W. Smith, Oxidation of aged raw landfill leachate with O₃ only and O₃/H₂O₂: treatment efficiency and molecular size distribution analysis, *Ozone Sci. Eng.* 26 (2004) 287–298.
- [11] J.J. Wu, C.C. Wu, H.W. Ma, C.C. Chang, Treatment of landfill leachate by ozone-based advanced oxidation processes, *Chemosphere* 54 (2004) 997–1003.
- [12] S. Wang, X. Wu, Y. Wang, Q. Li, M. Tao, Removal of organic matter and ammonia nitrogen from landfill leachate by ultrasound, *Ultrason. Sonochem.* 15 (2008) 933–937.
- [13] B. Bae, E. Jung, Y. Kim, H. Shin, Treatment of landfill leachate using activated sludge process and electron-beam radiation, *Water Res.* 33 (1999) 2669–2673.
- [14] S.P. Cho, S.C. Hong, S. Hong, Study of the end point of photocatalytic degradation of landfill leachate containing refractory matter, *Chem. Eng. J.* 98 (2004) 245–253.
- [15] A. Chaturapruek, C. Visvanathan, K.H. Ahn, Ozonation of membrane bioreactor effluent for landfill leachate treatment, *Environ. Technol.* 26 (2005) 65–73.
- [16] C. Tizaoui, L. Bouselmi, L. Mansouri, A. Ghrabi, Landfill leachate treatment with ozone and ozone/hydrogen peroxide systems, *J. Hazard. Mater.* 140 (2007) 316–324.
- [17] A. Imai, K. Onuma, Y. Inamori, R. Sudo, Effects of pre-ozonation in refractory leachate treatment by the biological activated carbon fluidized bed process, *Environ. Technol.* 19 (1998) 213–221.
- [18] A. Goi, Y. Veressina, M. Trapido, Combination of ozonation and the Fenton processes for landfill leachate treatment: evaluation of treatment efficiency, *Ozone Sci. Eng.* 31 (2009) 28–36.
- [19] I. Monje-Ramirez, M.T.O.D. Velásquez, Removal and transformation of recalcitrant organic matter from stabilized saline landfill leachates by coagulation–ozonation coupling processes, *Water Res.* 38 (2004) 2359–2367.
- [20] D.M. Bila, A. Filipe Montalvão, A.C. Silva, M. Dezotti, Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement, *J. Hazard. Mater.* 117 (2005) 235–242.
- [21] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, seventeenth ed., American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC, 1989.
- [22] A.Y. Lin, C. Lin, J. Chiou, P.A. Hong, O₃ and O₃/H₂O₂ treatment of sulfonamide and macrolide antibiotics in wastewater, *J. Hazard. Mater.* 171 (2009) 452–458.
- [23] M.F. Sevimli, Post-treatment of pulp and paper industry wastewater by advanced oxidation processes, *Ozone Sci. Eng.* 27 (2005) 37–43.
- [24] J. Tanaka, M. Matsumura, Application of ozone treatment for ammonia removal in spent brine, *Adv. Environ. Res.* 7 (2003) 835–845.
- [25] S.H. Lin, C.L. Wu, Removal of nitrogenous compounds from aqueous solution by ozonation and ion exchange, *Water Res.* 30 (1996) 1851–1857.
- [26] C.A. Somensi, E.L. Simionatto, S.L. Bertoli, A. Wisniewski Jr., C.M. Radetski, Use of ozone in a pilot-scale plant for textile wastewater pre-treatment: physico-chemical efficiency, degradation by-products identification and environmental toxicity of treated wastewater, *J. Hazard. Mater.* 175 (2010) 235–240.
- [27] P.C. Singer, W.B. Zilli, Ozonation of ammonia in wastewater, *Water Res.* 9 (1975) 127–134.
- [28] J. Staehelin, J. Hoigné, Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide, *Environ. Sci. Technol.* 16 (1982) 676–681.
- [29] I. Akmehtmet Balcloglu, M. Ötker, Treatment of pharmaceutical wastewater containing antibiotics by O₃ and O₃/H₂O₂ processes, *Chemosphere* 50 (2003) 85–95.
- [30] G. Tchobanoglous, F. Burton, Wastewater Engineering: Treatment, Disposal and Reuse, third ed., Metcalf and Eddy, Inc., McGraw-Hill Inc., New York, 1991.