Combined ozone-activated sludge treatment of landfill leachate

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Abstract Biological treatment is widely preferred by many landfill owners to remove the bulk of the pollutants in leachate. Specific problems due to toxicity and nutrient deficiencies are however frequently reported. This study investigates the possibility of pre-treating leachate to decrease its toxicity and increase its biodegradability, using ozonation. Lab-scale and pilot testing has shown that nitrification toxicity was minimised by ozone pre-treatment. A decrease of the COD/BOD-ratio from 16 to 6 was achieved, making the pre-treated leachate co-treatable in municipal sewage treatment. The operational cost for the pre-treatment was estimated at 1.34 Euro/kg COD.

Keywords Advanced oxidation; biodegradability; landfill; leachate; nitrification; ozonation; ozone; sewage treatment; toxicity

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Introduction

Landfill leachate contains high concentrations of ammonia and poorly biodegradable organic compounds. In Flanders, Belgium, fifteen landfill sites are in operation today. Together, these sites produce an estimated 1 300 m^3 of leachate per day. The composition of the leachate of landfill sites varies in time and is especially dependent on the age of the landfill (Miller *et al.*, 1974; Lu *et al.*, 1984). Because of this variation in time, a wide variety of treatment technologies are used in day to day practice.

To remove the bulk of the leachate pollutants, biological treatment is widely preferred by many landfill owners. Anaerobic treatment and aerobic treatment by lagooning, reed beds, activated sludge and rotating biological contractors are well documented (Lugowsky *et al.*, 1989; Qasim *et al.*, 1994). More recently, membrane bioreactor technology is also successfully applied full-scale on leachate (Engelhardt *et al.*, 1998; Günder *et al.*, 1998). Good performances towards BOD, COD and heavy metal removal are obtained with biological technology when treating younger – biodegradable – leachate. Specific problems due to toxicity and nutrient deficiencies are however frequently reported (Boyle *et al.*, 1974; Qasim *et al.*, 1994).

When treating older – less biodegradable – leachate, permitted COD-levels for direct or indirect discharge often cannot be met by using biological treatment. Also, biological treatment becomes difficult when the regarded leachate is initiative or toxic. Additional effluent polishing using physico-chemical treatment (e.g. flocculation-precipitation, adsorption, etc.) is therefore often necessary. The physico-chemical processes, however, have a high operational cost and produce residuals which are sometimes difficult to dispose of.

Recent leachate research (Echegaray *et al.*, 1994; Steensen, 1997) has been focusing on the use of advanced oxidation processes, e.g. ozone or hydrogen peroxide/UV. With these "Advanced Oxidation Processes" (AOP): (1) partial pshysico-chemical degradation, (2) improvement of biodegradability and (3) reduced toxicity of the leachate may be achieved (Bowers *et al.*, 1991). After this AOP-pre-treatment the leachate can be degraded more effectively in biological treatment such as activated sludge process. As a consequence, expensive polishing and production of unwanted residuals can be avoided.

Our study investigates the possibility of using AOP for leachate treatment to achieve: (1)

low cost COD-removal and (2) improvement of biodegradability. Preliminary comparative lab-scale tests evaluating hydrogen peroxide/UV, photoassisted Fenton reaction, ozone, ozone/hydrogen peroxide and catalysed ozone oxidation were performed (Geenens *et al.*, 1999). Based on these preliminary results additional experiments concentrated on ozone treatment. The results of the ozone lab and pilot scale experiments are reported hereafter. With these experiments it was possible to determine the optimal set-up to decrease the COD/BOD-ratio of the leachate. Decreased COD/BOD-ratios of leachate imply increased biodegradability. The effluent produced in the ozone experiments (pre-treated leachate) was therefore subsequently tested for biodegradability and nitrification inhibition in activated sludge.

Advanced oxidation processes

"Advanced oxidation processes" (AOP) focus on generating OH radicals by chemical oxidation. Growing evidence in literature however pinpoints the likely involvement of other radicals (e.g., O-radicals) in chemical oxidation (Campen, 1993). Oxidising landfill leachate with this type of radicals results in – amongst others – addition of hydroxyl, ketone, aldehyde functions, etc. and in cleavage of aromatic rings, double bonds, mineralisation, etc. (Adriaens, 1997). The foregoing chemical oxidation results, in recalcitrant leachate, in a wanted (partial) degradation and detoxification.

AOP for treatment of landfill leachate focuses on the use of ozone and/or hydrogen peroxide as an oxidising agent (Hirvonen *et al.*, 1995; Steensen, 1997), potentially catalysed by the use of UV (Hirvonen *et al.*, 1996; Schröder, 1996), Fenton (Kim *et al.*, 1997) or activated carbon (Campen *et al.*, 1993; Steensen, 1997). Oxidising agents like air, chlorine, chlorodioxide, hypochloric acid and permanganate (Bowers *et al.*, 1991) are also used in AOP but have no applications in leachate treatment.

Materials and methods

Ozonation of a recalcitrant leachate – generated at a 1.5 km^2 large landfill containing both household and hazardous industrial waste – was tested on a laboratory and pilot scale. The typical characteristics of this leachate illustrate its recalcitrant nature and the inadequacy of the biological treatment (Table 1).

Additional 24-hour-biodegradability tests (Germirli *et al.*, 1991) with adapted activated sludge and nitrification inhibition tests (ISO 9509, 1989) were performed for both diluted and non-diluted leachate.

Ozone lab-scale test

The tested leachate was filtered (0.2 µm) before ozone treatment in order to minimise suspended solids and iron. As a consequence the COD and iron concentration of the tested

Table 1 Main characteristics of the investigated leachate (1997; *N* = 12)

Parameter	Average	STD
BOD (mg/l)	43	14
COD (mg/l)	895	91
SS (mg/l)	51	19
NH_4^+-N (mg/l)	626	55
KjN (mg/l)	695	96
Total P (mg/l)	9.2	1.1
$CaCo_3$ (mg/l)	703	148
pH (Sörensen)	8.2	0.2
Conductivity (µS/cm)	5 823	5 921

sample was reduced to respectively 385 and 1 mg/l. A bubble column with a height of 37 cm and a diameter of 2 cm was applied in continuous operation. Sampling of the effluent for each test was done after achieving equilibrium (Figure 1).

Ozone concentrations (in ozone/oxygen mixture) and dosages (in leachate) of respectively 5-35 g/Nm^3 and 90-900 mg/l were evaluated. COD-removal and possible BOD-production was measured. In addition both ozone consumption (mg/l) and specific ozone consumption (g/g COD) were determined for different ozone dosages.

Ozone pilot test

Two months of on site pilot testing were performed, evaluating the feasibility of combined ozone-activated sludge treatment of the leachate involved. A flow of 100-400 l/h was treated.

The leachate was sand filtered before ozone treatment. A bubble column with a height of 2.37 m and a diameter of 0.4 m was applied in a continuous operation. Due to the limited height of the reactor, a relatively high ozone concentration was found in the residual gas. Consequently an efficient thermal ozone destruction was installed on the residual gas.

Sampling of the sand filtered influent and ozonated effluent for each test was done after achieving equilibrium (>five times hydraulic retention time). BOD, COD, SS, NH_4^+-N, NO_x-N, pH and Fe were analysed on daily basis. Gas flow, liquid flow, ozone concentration in influent, effluent and residual gas was monitored. Gas pressure was registered to back calculate gas flow and concentrations to standard pressure (1.013 bar). Correction towards temperature was not done (operational temperature (5-10°C). Ozone concentrations and dosages of respectively 140-160 g/Nm^3 and 0.7-2.8 g/l were evaluated. In addition both ozone consumption (mg/l) and specific ozone consumption (g/g COD) were determined for different ozone dosages.

Results

Ozone lab-scale test

Results of the ozone lab-scale test are listed in Table 2. Up to 30% of COD-removal was achieved with a specific ozone consumption of 1.5 g/g COD. The COD/BOD-ratio of the leachate (21 on average) could be reduced to as low as 9 (test run number 5) with a residence time of 36 minutes and an ozone dosing of 865 mg/l.

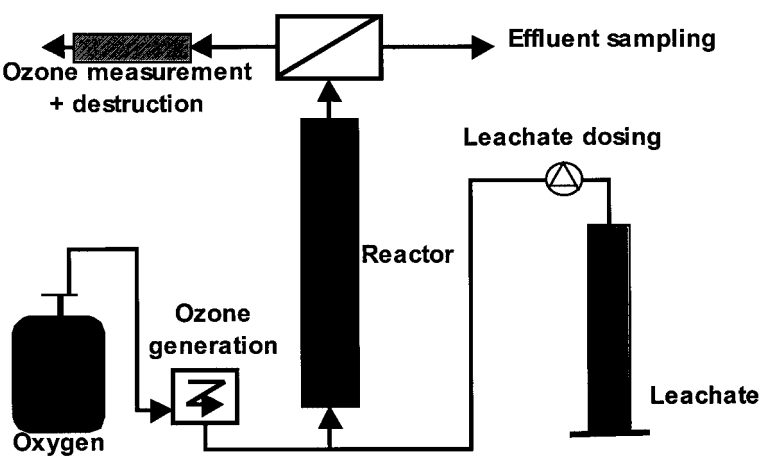

Figure 1 Scheme of the lab-scale continuous ozone reactor

Table 2 Results of the performed ozone lab-scale tests on leachate

Test run number	1	2	3	4	5	6
Ozone flow (Nml/min)	80	80	80	80	80	80
Residence time (min)	17	17	31	31	36	64
Ozone dosing (mg/l)	93	281	97	269	865	273
COD-removal (%)	8.5	11	13	12	30	22
Ozone consumption (mg/l) (g/g COD)	93	187	94	206	404	203
COD/BOD-ratio	23	15	121	38	9	123

Ozone pilot test

The investigated ozone dosages and the effect on COD/BOD-ratio are given in Figure 2. Best results towards decreasing this ratio (16.1 decreased to 5.8) were obtained at a residence time of 2.2 hours in the reactor, an ozone influent concentration of 140 g/Nm^3, an ozone dosing of 2.8 g/l, resulting in a specific ozone dosing of 3.7 g/g $COD_{removed}$.

A correlation was found between the COD-removed (%) and the BOD-produced (mg/l) during ozonation of the investigated leachate (Figure 3). Ozone dosages between 0.7 and 2.8 g/l resulted in an increasing BOD-production with increasing COD-removal.

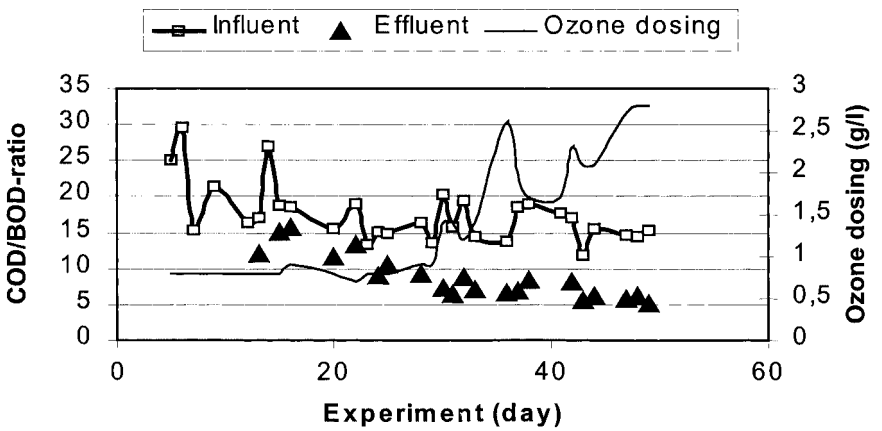

Figure 2 Pilot testing results illustrating the obtained decreased COD/BOD-ratios after ozonation

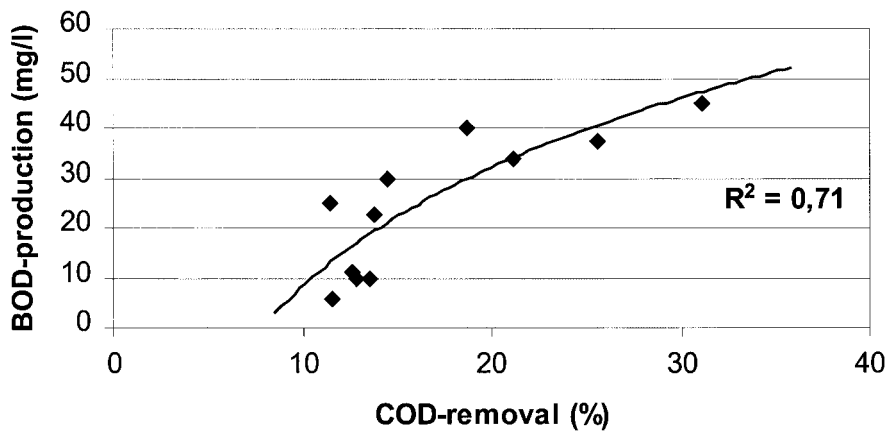

Figure 3 BOD-production versus COD-removal for the tested leachate (influent COD/BOD-ratio: 17-20) during pilot testing

Another correlation was found between the applied ozone dosage and the resulting COD/BOD-ratio of the effluent (Figure 4). At a relatively constant COD/BOD-ratio for the influent, the effluent COD/BOD-ratio decreases with increasing ozone dosage. An effluent COD/BOD-ratio of 6 was achieved at an ozone dosage of 2.5 g/l.

Inhibition and biodegradation

Both leachate and ozone pre-treated leachate were tested for inhibition of activated sludge nitrification and for biodegradability. High biological COD-removal performance (81%) and decreased nitrification inhibition (21%) was achieved when the pre-treated leachate (10 volume %) was co-treated with household wastewater (Table 3).

Discussion

The performed lab-scale tests show the capacity of using ozone pre-treatment to decrease the COD/BOD-ratio of leachate. The necessity of high ozone dosages to achieve this decrease of COD/BOD-ratio is confirmed by on-site pilot testing. Ozone dosages as high as 2.8 g/l were necessary to decrease the COD/BOD-ratio of the leachate from 16 to 6. Similar and higher ozone dosages (2.3-3.8 g/l) have been reported in literature (Echegaray *et al.*, 1994; Smitt *et al.*, 1993) for decreasing COD/BOD-ratios of specific biologically resistant contaminants (e.g. benzene, toluene, etc.). The observed transformation of recalcitrant COD to biodegradable COD during ozonation is related to chemical modification of the leachate constituents (e.g. humic acid and aromatic compounds). A strong oxidant – such as ozone – can be responsible for a range of chemical reactions in leachate, such as hydroxylation, dechlorination, N-oxidation, mineralisation to carbon dioxide, . . . Many of these reactions result in reduced toxicity and improved biodegradability. Mineralisation on the other hand, results in COD-removal.

The maximal achieved COD-reduction (45%) was obtained at an ozone dosage of 2.5 g ozone/l. Compared to literature results this performance is bad. To achieve similar

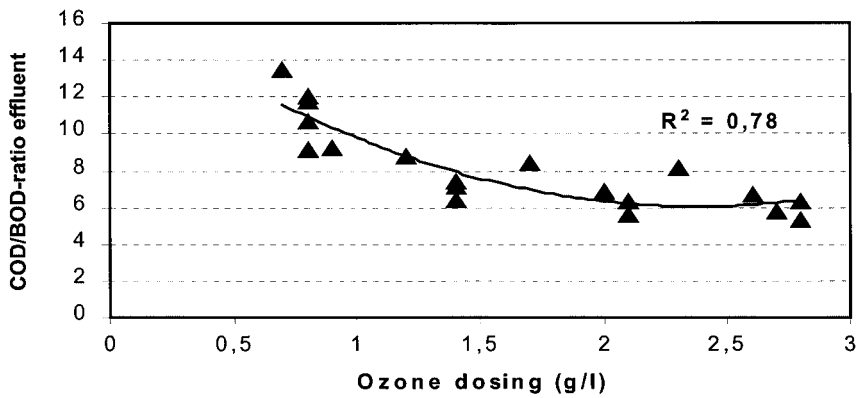

Figure 4 The COD/BOD-ratio versus ozone dosage for the tested leachate (influent COD/BOD-ratio: 17-20) during pilot testing

Table 3 Main characteristics of the investigated leachate (1997; *N* = 12)

	% COD-removal		% Nitrification inhibition	
Sample	**Average**	**STD**	**Average**	**STD**
Leachate	54	40	80	22
COD/BOD >8	*N* = 7		*N* = 8	
Ozone pre-treated leachate	81	33	21	34
COD/BOD <8	*N* = 8		*N* = 16	

COD-removal, a dose of only 1.2 g/l was needed in the research performed by Steensen *et al.* (1997). These large differences can be explained by the different composition of the leachate investigated. Particularly the relative abundance of scavenging components in the leachate (e.g. Fe^{3+} and HCO_3^-) may be responsible for the higher ozone consumption.

Although a correlation was found between COD-removal and BOD-production during ozonation, one should realise that the BOD-production is possibly limited to a maximum. Equilibrium between breakdown of recalcitrant COD and BOD-production on the one hand, and further mineralisation of this produced BOD to carbon dioxide on the other, can result in such a maximum. In the presented results however, the achievement of such a maximum was not straightforward.

The biological treatment of the investigated leachate proved to be especially difficult towards nitrification. Even at the tested dilution (10 vol.% leachate and 90 vol.% sewage), nitrification could not be achieved. In contrast, any ozone pre-treated leachate with a COD/BOD-ratio < 8 could successfully be nitrified with activated sludge. Although the specific nature of the inhibitive constituents of the leachate could not be pinpointed, it is clear that ozonation plays a detoxifying role. In addition to an enhanced nitrification, also improved biological COD-removal was obtained after ozonation.

In view of the presented results there is high potential for pre-treatment of leachate with ozone followed by further co-treatment in a sewage treatment plant (STP).

Dilution of the pre-treated leachate (10 vol.%) in STP-influent results in an increased biodegradation and a minimised nitrification inhibition. An operational cost of 1.34 Euro/kg COD for the ozone pre-treatment of 1 081 kg leachate COD per day was calculated for the investigated application. An estimated investment cost of 860 000 Euro (all-in) was associated with the required ozonation infrastructure (buffer tank, instruments, reactors, generators, safety equipment, etc. included; capacity: 32 kg ozone/h).

Conclusions

Ozonation can be successfully applied for COD-removal from leachate. Full-scale treatment of leachate with ozone can however be expensive.

Pre-treatment of leachate with ozone before activated sludge treatment can be, instead, very cost-effective. By pre-treating leachate with ozone, partial degradation, increased biodegradability and minimized toxicity can be achieved. Treating this pre-treated leachate together with sewerage in a sewage treatment plant (Figure 5) may have large potential. On the basis of the presented pilot research and a cost-benefit analyses, a proposal for full-scale application has been put forward.

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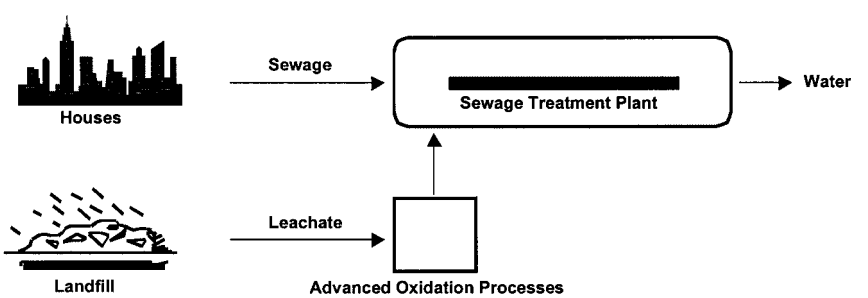

Figure 5 Effective co-treatment of AOP-pre-treated leachate in a sewage treatment plant

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