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Ozonation of biologically treated landfill leachate: efficiency and insights in organic conversions

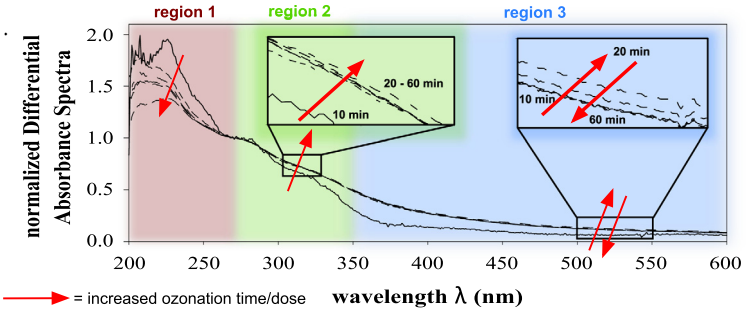
Michael Chys [a,b,*], Violet A. Oloibiri [a,c,d], Wim T.M. Audenaert [a,b], Kristof Demeestere [c], Stijn W.H. Van Hulle [a,b]

[a] LIWET, Department of Industrial Biological Sciences, Ghent University, Graaf Karel de Goedelaan 5, B-8500 Kortrijk, Belgium
[b] BIOMATH, Department of Mathematical Modelling, Statistics and Bioinformatics, Ghent University, Coupure Links 653, B-9000 Gent, Belgium
[c] EnVOC, Department of Sustainable Organic Chemistry and Technology, Ghent University, Coupure Links 653, B-9000 Gent, Belgium
[d] Kenya Industrial Research and Development Institute, P.O. Box 30650-00100, Nairobi, Kenya

HIGHLIGHTS

- Ozonation efficiency of biological landfill leachate was assessed.
- pH significantly impacted the COD removal efficiency.
- Organic matter conversions were assessed using UV–visible measurement calculations.
- Spectral changes are uniform after an initial reaction phase.
- Differences in working mechanism are seen compared to municipal effluent ozonation.

GRAPHICAL ABSTRACT



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ABSTRACT

Biologically stabilized landfill leachate contains a significant amount of recalcitrant organic matter, often expressed as Chemical Oxygen Demand (COD). To meet regulatory requirements, (a combination of) advanced treatment techniques such as ozonation and granular activated carbon adsorption must be applied. However, the mechanisms occurring during ozonation of the complex matrix are not well understood. Therefore, transformations were studied (in a lab-scale semi-batch reactor) into detail based on COD measurements and UV–visible spectral calculations. First of all, a declining initial COD (COD_0 from 1846 to 112 mg O_2 L^{-1}) resulted in a decreasing trend of UVA_{254} removal efficiency (respectively from 1.5 to 0.42 m^{-1} absorption decrease mg^{-1} O_3) which was not seen for COD removal efficiency (no clear trend noticeable; average of 0.34 mg COD removed mg^{-1} O_3). For low COD_0, the amount of most reactive moieties is less, resulting to further reactions with the formed intermediates. An increased pH probably resulted in a higher production of hydroxyl radicals (HO·). Using similar ozone doses, more COD was removed at higher pH values. Secondly, spectral calculations (such as differential absorbance) gave more insights into the reaction mechanism. It is hypothesized that after an initial period during which ozone selectively oxidized some species, ozonation of landfill leachate led to a significant HO· production, dominating the ozone reaction mechanism.

* Corresponding author at: LIWET, Department of Industrial Biological Sciences, Ghent University, Graaf Karel de Goedelaan 5, B-8500 Kortrijk, Belgium. Tel.: +32 (0)56 241211; fax: +32 (0)56 241224.
E-mail address: Michael.Chys@UGent.be (M. Chys).

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1. Introduction

Due to both low investment and exploitation costs, landfilling of waste is historically widely employed [1]. Nowadays, landfilling is mostly replaced by alternatives but currently existing landfills still pose a serious environmental burden because of the generation of leachates. These leachates have a distinctive character and contain a high concentration of (recalcitrant) organic compounds (e.g. amines, alcohols, aliphatic compounds, carboxylic acids), often expressed as Chemical Oxygen Demand (COD) [2]. Biological processes such as conventional activated sludge (CAS) processes are commonly employed for leachate treatment but are seriously hampered by their inability to degrade the large content of bio-recalcitrant organic matter (e.g. humic and fulvic acids) [3]. Furthermore, nutrient imbalances such as high ammonium nitrogen, low phosphorus and biologically degradable carbon content frequently occur in landfill leachate and make it difficult to maintain proper biological treatment and decent effluent quality. Therefore, post-treatment of biological effluents is still necessary to further remove organic matter [4,5]. The aforementioned limitations of biological techniques in addition to restrictive environmental legislations and the need for cost-effective treatments have led to an increased interest in the use of (advanced) oxidation processes ((A)OPs) such as Fenton, photocatalysis, UV/H_2O_2 and ozonation as a valuable addition to conventional treatment techniques [6–13].

Previous research comparing different AOPs showed that especially ozonation could be an (economically) favorable technique [11,14]. However, oxidation techniques are not suitable as a replacement for a biological treatment or too expensive as a final polishing step [15]. Ozonation after CAS processes as a preceding step to granular activated carbon treatment might therefore be a more cost-effective alternative. Chys et al. [11] obtained a decrease in total operation expenses from 1.32 to 1.20 € m^{-3} of treated leachate by adding an ozonation step before activated carbon filtration [11]. Additionally, ozonation has also shown to convert recalcitrant compounds into smaller and more biodegradable components improving the overall leachate biodegradability, often expressed as Biochemical Oxygen Demand (BOD_5) [13,15,16]. Mainly an increase of hydroxyl and carboxylic groups were found as main by-product formation during leachate ozonation [17]. Contrastingly, as leachate is highly toxic from nature, it has mostly been noticed that ozonation did not lead to an increase (and even a decrease) of toxic compounds [18].

The characteristic fluctuation of the load and type of organic matter present in landfill leachate directly impacts the ozonation process and all downstream processes. Although much information is already available for low strength wastewater streams (e.g. secondary effluent of municipal wastewater treatment plants (WWTPs) [19]), studies about the oxidative treatment of high strength wastewater streams such as biologically treated landfill leachate to understand the occurring reactions are rather scarce. A more profound knowledge is needed for successful implementation of advanced processes in full-scale treatment trains.

Organic matter significantly impacts the process performance as it directly reacts with produced hydroxyl radicals (HO·) and ozone itself. Next to the organic matter, ozone reaction pathways (and formation/consumption of HO·) are directly influenced by pH. Ozone has the ability to efficiently oxidize organic matter at slightly alkaline pH, which is the typical pH of most (biologically treated) landfill leachates. Operating ozonation at alkaline pH favors the production of HO· which can accelerate the removal of recalcitrant organic matter. For instance, Cortez et al. [13] reported up to 36% COD removal at pH 9 compared to 23% COD removal at pH 3.5 [13]. Li et al. [20] observed 87–100% color removal when oxidizing landfill leachate at slightly alkaline pH [20].

Ozonation processes applied for landfill leachate treatment are mostly evaluated by basic surrogates such as COD or Total Organic Carbon (TOC), representing the complex organic matrix. With the exception of the absorption coefficient at some selected wavelengths, e.g. 254 nm or 436 nm, changes of the organic matter during landfill leachate ozonation have rarely been evaluated based on full spectrum UV–visible (UV–vis) analyses. However, some authors already used UV–vis to acquire more in-depth information on ozonation of low strength wastewater streams. For example, Nanaboina and Korshin [21] and Audenaert et al. [19] obtained differential absorbance spectra (DAS; difference between the initial spectrum and spectra after a certain treatment time) from UV–vis measurements [19,21]. Based on DAS, besides a decreasing overall absorbance, also differences between different wavelengths can be seen. It was shown that some wavelengths (especially those within the 260–280 nm range) are more impacted by ozone oxidation than others [19,21]. Based on normalized DAS (changes in DAS are plotted relatively to a single wavelength), Audenaert et al. [19] hypothesized that compounds absorbing at higher wavelengths were transformed to products absorbing at lower wavelengths during O_3 treatment [19]. The use of the absorbance slope index (ASI), calculated as the ratio of the slope of the absorbance spectrum between 254 and 272 nm and the slope between 220 and 230 nm, was firstly introduced by Korshin et al. [22] in natural water studies [22]. Audenaert et al. [19] used the ASI to evaluate ozonation and UV/H_2O_2 processes as tertiary treatments of WWTP effluent [19]. Using both DAS and ASI, it could be illustrated that some clear differences in working mechanism exist between the two processes [19]. To the best of our knowledge, DAS and ASI have not been used yet to evaluate changes in UV–vis spectra during ozonation of landfill leachate. As the ozonation process and consequently the formation of radicals is largely influenced by the amount of organic matter present, some differences can be expected compared to low strength wastewater studies.

The present study aims to increase the knowledge on the ozonation step of high strength wastewater as part of a complete treatment train. Therefore, the effect of such a treatment on other downstream processes (e.g. activated carbon filtration) is of high significance. As the occurring reaction pathways are not well known for ozonation of high strength wastewater, especially the evaluation of the working mechanism based on spectral changes in the complete spectrum and comparison with previous low strength wastewater studies is seen as a major purpose through-out this study. Therefore, the objectives of the research are to evaluate alterations of ozone dose, initial pH and especially organic matter content while assessing the specific ozonation efficiency. Secondly, DAS and ASI are used to assess spectral changes during ozonation. This enables a more in-depth investigation of the occurring changes, which is highly important to gain insights in the dominating reaction pathways. These are needed for future implementation, development and control of such an ozonation step in the complete treatment train.

2. Materials and methods

2.1. Sample collection and experimental set-up

Landfill leachate was collected after biological treatment at the IMOG landfill site in Moen, Belgium (www.imog.be) and exhibited general stabilized leachate characteristics (pH: 8.2–8.5; NO_2^-–N: 0.33–0.66 mg L^{-1}; NO_3^-–N: 3.9–19.5 mg L^{-1}; NH_4^+–N: 2.42–9.22 mg L^{-1}). The configuration of the treatment plant contains a primary filtration followed by an oil–water-separator and two parallel sequencing batch reactors (SBRs). More details about the plant