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Tertiary treatment of biologically pre-treated landfill leachates by non-catalytic wet oxidation

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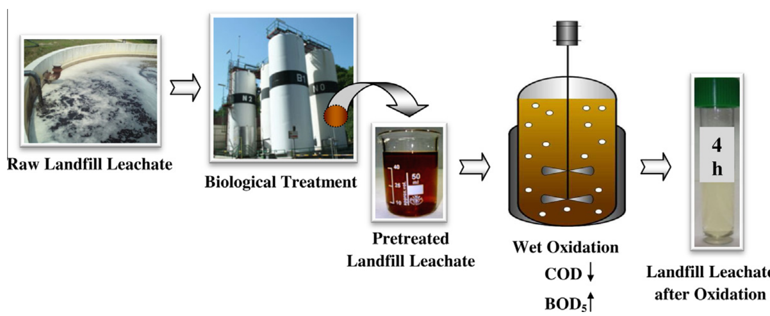
HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



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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 analyzed. 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.

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Nomenclature

AOP	advanced oxidation processes	LI	luminescence inhibition (%)
AOS	average oxidation state	P	pressure (MPa)
BOD_5	biochemical oxygen demand (mg/L)	r_i	reaction rate of component i (mg/L s)
BOD_5/COD	biodegradability index	t	time (s)
CN	colour number	T	temperature (K)
COD	chemical oxygen demand (mg/L)	WWTP	wastewater treatment plant
E_a	activation energy (kJ/mol)	α_i	oxygen reaction orders
k_i	apparent reaction rate constant (s^{-1})		

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 (H_2O_2, 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 (COD < 100 g/l) and/or with a level of biodegradability too low to be treated biologically (BOD_5/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 $NaNO_2$ [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 pressurized 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^3/day of leachate. Methanol is added as a source

Table 1
Physicochemical characteristics of the biologically pre-treated landfill leachate used in this study and variability found in the landfill site.

Parameter	Leachate used in this study	Variability found in the landfill site
pH	6.8	6.8–7.5
COD (mg O_2/L)	1143	1000–1600
TOC (mg C/L)	225	200–320
BOD_5 (mg O_2/L)	13.5	<65
Colour number	0.622	0.6–0.7
Alkalinity (mg $CaCO_3$/L)	17.3	15–20
Conductivity (μS/cm)	11,430	11,000–14,000
NH_4^+ (mg/L)	5	<50
NO_3^- (mg/L)	403	400–700
NO_2^- (mg/L)	1	<2
PO_4^{3-} (mg/L)	5.4	5–15