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Ozonation and perozonation on the biodegradability improvement of a landfill leachate

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ABSTRACT

Landfill leachate effluent as the permeate stream from a reverse osmosis treatment is usually resilient to biological processes due to its very low biodegradability. In order to treat and enhance the biodegradable character of these streams, ozonation was evaluated at a lab-scale and different ozone inlet concentrations, initial pH's, and hydrogen peroxide dosages were tested aiming to promote efficiency.

The depuration of the landfill leachate by ozone was favored when high pH values were applied or when hydrogen peroxide was used as co-oxidant; both situations were consistent with the major production of hydroxyl radicals. Indeed, the highest organic load removal and biodegradability improvement was observed with the O_3/H_2O_2 process using $4\,g\,H_2O_2\,L^{-1}$. This system was able to eliminate 45% of the chemical oxygen demand (COD), 89% of color and also increase the leachate BOD_5/COD ratio from 0.05 to 0.29 permitting the treated wastewater discharge for the local sewage collector. Moreover, single ozonation also promoted an expressive removal of the recalcitrant organic matter (43% of COD) and increased leachate biodegradability (BOD_5/COD up to 0.22), which makes this process a viable option as a pre-biological treatment.

1. Introduction

The population growth joined with the urban development leads to extremely high domestic solid wastes production entailing suitable management technologies to protect both environment and human health. The landfilling method is one of the most common procedures for the ultimate disposal of these pollutants [1], minimizing the ecological impact by allowing the waste decomposition under controlled conditions, besides presenting economic advantages [2]. The main issue regarding such techniques is related with the formation of large amounts of an aqueous effluent (known as leachate) due to the water content of the wastes, the rainwater that percolates through the waste bed and the aqueous remains produced during the pollutants biological oxidation [3].

The landfill leachates present complex composition, encompassing high organic loads as well as inorganic substances and heavy metals [4], depending, among other factors, of the landfill age [5]. This wastewater constitutes, thus, a potential threat for the quality of groundwater and its management requires special attention. It is well known that the leachate characteristics change over time, and the treatment of these streams in conventional depuration plants is hardly accomplished due to the awkward features as the high content of pollutants and low biodegradability [3]. Nevertheless, the leachate handling must meet the quality level established for the final discharge into surroundings.

For this reason, aiming to fulfill current environmental legislation, a suitable treatment system must be developed, which has also to be robust enough to accomplish sharp variations on the inlet effluent composition [1]. Conventionally, landfill leachate is treated by biological processes; however, the implementation of bio-systems may be inadequate due to the effluents' toxic characteristic and low BOD/COD ratio generally resulting in low efficacies [5,6]. Since these traditional technologies are not

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effective for the removal of refractory compounds and the physico-chemical processes are non-destructive, advanced oxidation processes (AOPs) arise as alternative methodologies [7].

Chemical oxidation by advanced processes has as purpose to reach complete mineralization (into water and carbon dioxide) [8], or, when economically more advantageous, enhance the biodegradability of biorecalcitrant organic pollutants up to a value that will allow a posterior biological treatment [9,10].

AOP's encompass ozonation which is a treatment based on the high oxidant power of ozone, that can be used to decompose large organic molecules into smaller and less complex ones occurring at normal pressure and temperature being, hence, industrially interesting [10,11]. This process can be enhanced by promoting the formation of highly reactive agents, such hydroxyl radical (•OH), from ozone decomposition. The use of ozone at alkaline conditions (O_3/OH^-) or in combination with strong oxidants such as H_2O_2 (O_3/H_2O_2) favors the production of these species [12,13] that have an oxidation potential higher than the one attributed to molecular ozone. These processes can be, thus, attractive to treat complex streams such as leachate [3]. The chain radical reactions are non-selective. Contrarily, ozone molecule only undertakes specific reactions with compounds encompassing high electronic density sites leading to low molecular weight by-products generally no further reactive. Therefore, ozonation is usually more efficient when the conditions support •OH production [14,15]. Nevertheless, if reactions are incomplete, the AOPs can also promote the formation of refractory and more toxic by-products than the original pollutants. The economic factor is another restriction due to the high operational costs when high strength wastewaters are involved. A significant economic drawback derives from reactants consumption (e.g. H_2O_2) and the electrical power required to produce ozone in situ. The major factor that can affect ozonation efficiency in the oxidation of refractory contaminants is the presence of carbonate and hydrogencarbonate ions in wastewaters composition which can compete with the substrate for HO• radicals. Besides, the excess of H_2O_2 on the Perozonation experiments, may also present a scavenging effect on the generated radical hydroxyls, reducing thus the process efficiency [13].

In this context, the use of ozone has been studied for the oxidation of various effluents, with promising results in the degradation of landfill leachates [3,5,7,11,16] involving considerable depletions of chemical oxygen demand and color, with also the advantage of biodegradability increase.

Within this context, the main goal of this work was to obtain a suitable technology to depurate a landfill leachate aiming to enhance its biodegradability meeting the legal limits for the discharge of this liquid effluent to the sewage to be further treated in a municipal wastewater treatment plant generally based on activated sludge, providing reliable results that can increase the industrial application of AOPs through the integration with a biological oxidative system. The data gathered here led to the design and building of an industrial installation based on AOPs to deal with this specific effluent with the intention of an immediate industrial application. Aiming to give answer to a real environmental problem, experiments were conducted to compare the efficacy using ozone-based advanced oxidation processes involving O_3 and O_3/H_2O_2.

2. Materials and methods

2.1. Landfill leachate characteristics

The leachate samples were collected from a municipal landfill in the center region of Spain. The raw stream is pre-treated in situ by reverse osmosis, resulting in two types of effluents, the concentrate and the permeate. The concentrated course must be subsequently treated [2], while the last one still does not accomplish the characteristics permitting their discharge to the sewage due to the high organic content represented as chemical oxygen demand, COD, so that this will be the effluent under study. The physicochemical characteristics of the permeate leachate are analysed and listed in Table 1. It should be noticed that as previously referred the low biodegradability detected inhibits the direct application of biological methodologies.

Table 1
Chemical composition of the permeate effluent and the errors associated to each parameter.

pH	7.1	
COD ($mg\,O_2\,L^{-1}$)	1880	±8%
BOD_5 ($mg\,O_2\,L^{-1}$)	90	±20%
BOD_5/COD	0.05	
Toxicity[a] (%)	0	±8%
Biodegradability[a] (%)	2	±8%

[a] Assessed by respirometric methods.

2.2. Experimental set-up

All the experiments were evaluated bearing in mind operational cost restrictions ensuring that all procedures can be performed without high investments. Probably higher oxidant (O_3 or H_2O_2) doses would lead to more significant depletions. Nevertheless, that would increase the operating costs of the global treatment making it not possible to commercialize.

The ozonation experiments were held in a stirred reactor operating in a semi-continuous mode. The liquid was charged at the beginning of the experiment and ozone was continuously introduced trough two porous diffusers placed in the liquid bulk. Ozone was generated from a pure oxygen stream (500 mL min^{-1}) in an ozone generator BMT 804N (BMT, Berlin, Germany) and the gas ozone concentration was measured using a BMT963 vent ozone analyzer (BMT, Berlin, Germany) [17].

The oxidation experiments proceeded as follows: 500 mL of the effluent was added to the reactor, brought to the desired temperature and the experiment started when the ozonated oxygen begun to run. The stirring speed was maintained at 750 rpm to ensure negligible external mass transfer resistances during the experiments guarantying chemical regime [18].

2.3. Analytical methods

During the experimental period, samples were withdrawn in certain intervals of time to analyze chemical oxygen demand (COD), biochemical oxygen demand (BOD_5) and color and also to access their toxicity and biodegradability by respirometry and luminescence techniques. The characterization analyses of the initial and treated leachate including BOD_5 and COD were performed according to Standard Methods [19], in a WTW CR 3000 thermoreactor and a WTW MPM 3000 photometer for COD while a WTW inoLab 740 was used to measure the dissolved oxygen for BOD_5. Color was determined by spectroscopy using a T60 (PG instruments) spectrophotometer. pH was attained by a Crison micropH 2000. Color data are reported as the absorbance of the samples in the wavelength of the visible region with the maximum absorption (λ = 380–750 nm) which is considered as a quantitative estimation of the color of the solution. Color depletion was followed by UV–vis spectrophotometry with a T60 UV/vis spectrophotometer.

Respirometric techniques were used to infer about the effluent biodegradability and toxicity over activated sludge. Respirometry allows measuring the biological oxygen consumption rate under