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Evaluation of Fenton and ozone-based advanced oxidation processes as mature landfill leachate pre-treatments

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ABSTRACT

Fenton treatment (Fe^{2+}/H_2O_2) and different ozone-based Advanced Oxidation Processes (AOPs) (O_3, O_3/OH^- and O_3/H_2O_2) were evaluated as pre-treatment of a mature landfill leachate, in order to improve the biodegradability of its recalcitrant organic matter for subsequent biological treatment. With a two-fold diluted leachate, at optimised experimental conditions (initial pH 3, H_2O_2 to Fe^{2+} molar ratio of 3, Fe^{2+} dosage of 4 mmol L^{-1}, and reaction time of 40 min) Fenton treatment removed about 46% of chemical oxygen demand (COD) and increased the five-day biochemical oxygen demand (BOD_5) to COD ratio (BOD_5/COD) from 0.01 to 0.15. The highest removal efficiency and biodegradability was achieved by ozone at higher pH values, solely or combined with H_2O_2. These results confirm the enhanced production of hydroxyl radical under such conditions. After the application for 60 min of ozone at 5.6 g O_3 h^{-1}, initial pH 7, and 400 mg L^{-1} of hydrogen peroxide, COD removal efficiency was 72% and BOD_5/COD increased from 0.01 to 0.24. An estimation of the operating costs of the AOPs processes investigated revealed that Fe^{2+}/H_2O_2 was the most economical system (8.2 € m^{-3} g^{-1} of COD removed) to treat the landfill leachate. This economic study, however, should be treated with caution since it does not consider the initial investment, prices at plant scale, maintenance and labour costs.

1. Introduction

The generation of leachate remains an inevitable consequence of the practice of waste disposal in sanitary landfills (Wang et al., 2010). Leachate from mature landfills is typically characterised by high ammonium (NH_4^+) content, low biodegradability (low BOD_5/COD ratio) and high fraction of refractory and large organic molecules such as humic and fulvic acids (de Morais and Zamora, 2005; Deng and Englehardt, 2006). In many cases, after treatment by a series of oxidation processes, mature landfill leachate still presents high concentrations of recalcitrant and nitrogenous compounds. Biological processes are not effective for this type of leachate.

In the last two decades, AOPs have been considered an attractive means to eliminate colour, reduce the organic load and improve the biodegradability of recalcitrant contaminants of mature leachates (Deng and Englehardt, 2006; Kochany and Lipczynska-Kochany, 2009; Renou et al., 2008). These processes involve the production of free radical species, mainly the hydroxyl radical ($^{\bullet}OH$). The hydroxyl radical is produced from single oxidants such as ozone (O_3), or from a combination of strong oxidants such as O_3 and hydroxide (OH^-), O_3 and hydrogen peroxide (H_2O_2), or ferrous ions (Fe^{2+}) with H_2O_2 (Renou et al., 2008; Rosenfeldt et al., 2006). The combination of Fe^{2+} and H_2O_2 is called Fenton oxidation.

Fenton oxidation has been extensively studied for the treatment of mature landfill leachates. In this advanced oxidation technology, under optimum pH, ferrous ions react with hydrogen peroxide to generate the hydroxyl radical in a very simple and cost-effective manner (Deng and Englehardt, 2006).

Ozone (not decomposed, pH < 6) is a strong oxidiser having high reactivity and selectivity towards organic pollutants such as aromatic compounds (Lucas et al., 2010; Lin et al., 2009). Furthermore, as the standard oxidation potential of the hydroxyl radical ($E_0 = 2.80$ V) is much higher than that of ozone ($E_0 = 2.07$ V), the use of ozone at high pH (O_3/OH^-) or in a combination with H_2O_2 (O_3/H_2O_2) favours the production of hydroxyl radicals and accelerates the removal of recalcitrant organic matter from complex wastewater matrices (Lucas et al., 2010; Tizaoui et al., 2007). Ozonation under alkaline conditions and the combination of ozone with hydrogen peroxide have proved to be effective advanced oxidation processes for landfill leachate (Haapea et al., 2002; Tizaoui et al., 2007).

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Although AOPs are very effective for the treatment of refractory organic pollutants, if they are applied as the only treatment process, they will be expensive. A promising economical alternative to complete the oxidation of refractory compounds is the use of an advanced oxidation technology as pre-treatment to convert initially biorecalcitrant compounds into more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biomass and water (Lin and Kiang, 2003).

This research was conducted to investigate the efficacy and feasibility of Fenton treatment and different ozone-based advanced oxidation processes (O_3, O_3/OH^- and O_3/H_2O_2) as pre-treatment steps of a mature landfill leachate, in order to improve its biodegradability for subsequent biological treatment. The effects of initial pH, oxidants concentration and reaction time on the performance of each AOP tested were evaluated in terms of COD, total organic carbon (TOC), BOD_5, nitrogenous compounds and aromaticity. A rough estimate of the operating costs involved in each type of pre-treatment was also performed to compare their economical feasibility.

2. Materials and methods

2.1. Landfill leachate

Landfill leachate was collected from a municipal landfill in the North of Portugal, in operation since 1998. The current treatment plant in the sanitary landfill comprises stabilisation, anaerobic ponds, an anoxic tank, aerated ponds and a biological decantation unit, together with an oxidation tank and two chemical precipitators. However, even after the post-treatment at the end of the process, the leachate still does not meet the maximum allowable nitrogen and organic matter concentrations for direct discharge, according to DL 236/1998, of August 1 (Portuguese Ministry of Environment, 1998). The characteristics of the undiluted leachate are listed in Table 1.

The low value of the BOD_5/COD ratio (0.01) and the high content of nitrogen-ammonium (N-NH_4^+), indicate that this leachate is mature and must be rich in refractory compounds. Another important feature of this leachate is the high nitrogen-nitrate (N-NO_3^-) content. An economical approach to treat this leachate can be achieved by combining an advanced oxidation process with the degradation of the refractory compounds into biodegradable organic matter, and using these products as a carbon source for removal of nitrogenous compounds in biological processes.

All experiments were carried out with two-fold diluted leachate due to the high nitrate load of the undiluted leachate, since the Fenton treatment or a different ozone-based advanced oxidation process (O_3, O_3/OH^- and O_3/H_2O_2) would be applied as pre-treatment step, in order to improve the leachate biodegradability for subsequent biological treatment.

Table 1
Landfill leachate characteristics.

Parameter	Value	Emission limit value (DL 236/1998)
pH	3.5 ± 0.1	6.0–9.0
Conductivity (mS cm^{-1})	4.45 ± 0.03	–
COD (mg L^{-1})	743 ± 14	150
BOD_5 (mg L^{-1})	10 ± 1	40
TOC (mg L^{-1})	284 ± 6	–
N-NO_3^- (mg L^{-1})	1824 ± 103	11
N-NO_2^- (mg L^{-1})	0.010 ± 0.002	–
N-NH_4^+ (mg L^{-1})	714 ± 23	8
P-PO_4^{3-} (mg L^{-1})	0.479 ± 0.054	10 (mg total P L^{-1})
VSS (mg L^{-1})	79 ± 3	60 (mg TSS L^{-1})
UV_{254}	2.614 ± 0.023	–

2.2. Fenton treatment procedure

Fenton oxidation experiments were carried out at room temperature (22 ± 1 °C) and atmospheric pressure in magnetically stirred batch reactors with two-fold diluted leachate. The pH of the leachate was adjusted using H_2SO_4 95–97% (w/w). The predetermined Fe^{2+} dosage was achieved by adding the necessary amount of solid $FeSO_4 \cdot 7H_2O$. A calculated volume of 35% (w/w) H_2O_2 solution was added in a single step. After the fixed oxidation time (120 min), sodium hydroxide was added to increase the pH above 7 and mixed for 10 min. Stirring was turned off and the sludge was allowed to settle for one hour. Finally the supernatant was centrifuged for 10 min at 10,000 rpm and the samples were analysed. Experiments were conducted in duplicate and the results were averaged.

2.3. Ozonation procedure

Ozonation experiments were performed in an acrylic column, 69.5 cm high and 8.2 cm internal diameter. Ozone was produced from pure oxygen using an ozone generator (Anseros Peripheral Com-AD-02). The ozone and oxygen mixture was continuously introduced into the column through a ceramic diffuser placed at the bottom and 1 L of two-fold diluted leachate was treated for 60 min. The inlet and outlet concentrations of ozone in the gas phase were measured at $\lambda = 254$ nm using an ozone analyser (Anseros Ozomat GM-6000-OEM) throughout the experiments. The gas flow rate was 50 L h^{-1} and the input ozone concentration was about 0.112 g O_3 L^{-1}. The residual gas was vented through the catalytic ozone destruction unit. Effluent samples were withdrawn regularly and analysed.

Ozonation experiments were carried out at adjusted pH values of 7, 9, and 11. These pH values were achieved using sodium hydroxide (NaOH). Advanced oxidation with hydrogen peroxide and ozone was also studied. In these tests the pH of the leachate was adjusted to 7 (Staehelin and Hoigné, 1982) and, before ozone was supplied, H_2O_2 at concentrations of 100, 200 or 400 mg L^{-1} was injected in a single step to the column. The samples collected from these experiments were treated with NaOH to quench the reaction of residual H_2O_2.

All experiments were carried out at room temperature in duplicate and the results were averaged.

2.4. Analytical methods

The leachate was characterised before and after oxidation experiments. COD, BOD_5, nitrogen-nitrite (N-NO_2^-), and nitrogen-ammonium (N-NH_4^+) concentrations were determined according to Standard Methods (APHA et al., 1989). It is important to note that during this work, since acidic and basic pH can affect microbial activity, BOD_5 measurements were done after neutralizing the pH of the sample, as recommended in Standard Methods (APHA et al., 1989).

Nitrate (NO_3^-) 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 (H_2SO_4) 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 (UV_{254}) was obtained with a Jasco V-560 spectrophotometer using a 1 cm quartz cell. TOC analyses were performed using a Dohrmann DC-190 TOC Analyser.

3. Results and discussion

The mature landfill leachate was treated in order to decompose its recalcitrant compounds and increase its biodegradability using