IV REUNIÓN NACIONAL DE DIOXINAS, FURANOS Y COMPUESTOS ORGÁNICOS PERSISTENTES RELACIONADOS

Alicante, 26-28 Junio 2013
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Introduction

Landfill leachates are high polluted wastewaters generated by the combination of physical, chemical and microbial processes that transfer pollutants from solid wastes to the liquid phase. A relevant group of persistent organic pollutants (POPs) that have been disposed of in landfills over the years and detected in landfill leachates is the family of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). In fact, landfills and waste dumps are PCDD/Fs reservoirs in the environment. PCDD/Fs congeners with chlorine at 2,3,7,8 positions are of interest due to their toxicity and potential effects on human health, mainly due to their persistence and bio cumulative behaviour. These seventeen congeners will be the subject of this study and we will refer to them as PCDD/Fs from now on.

If leachates are not treated and disposed of safely, landfilled POPs can enter the environment via escaping leachates contaminating ground and surface waters. Thus, the treatment of hazardous leachates is of great importance to meet the disposal standards and to reduce the negative impact on human health and environment. One important criterion for the assessment of treatment technologies is the potential formation of toxic by-products that are themselves POPs. If POPs are treated with inappropriate technology high amounts of PCDD/Fs are likely to be formed and released. Scarce works deal with the change of PCDD/Fs during the advanced oxidation treatment of landfill leachate matrices. Thus, a more rigorous assessment in order to avoid the occurrence of highly toxic substances such as PCDD/Fs is needed.

Thus this work aims at:
- The assessment of PCDD/Fs concentration in leachates from a municipal solid waste landfill following the 1613 EPA method.
- The assessment of the change in PCDD/Fs concentration during the advanced oxidation treatment of landfill leachates.

Materials and Methods

Samples collection
Leachate waters from a municipal solid waste landfill located in Cantabria (Spain) were collected and kept under refrigeration.

Electrochemical oxidation experiments
Electrooxidation experiments of 1 L leachate samples were performed in batch mode in a laboratory DiaCell system (two circular electrodes: boron doped diamond (BDD) on silicon anode and stainless steel cathode, with surface area of 0.007 m$^2$) using an operational flowrate of 11 L/min and a current density of 900 A/m$^2$. PCDD/Fs were analyzed at 5, 30 and 180 minutes.

Fenton oxidation experiments
Fenton oxidation of 0.75 L leachate samples was carried out at room temperature in a magnetically stirred reactor. The initial pH was adjusted to 3 by adding H$_2$SO$_4$ and a mass ratio H$_2$O$_2$/Fe$^{2+} = 5.86$ was used. At the end of the experiment the excess of H$_2$O$_2$ was removed by adding NaHS$_2$O$_3$ and neutralization at pH 7.5 with sodium hydroxide was carried out before sample analysis. PCDD/Fs were analyzed at 180 minutes.

Samples preparation for PCDD/Fs analysis
Samples (0.5 L) were spiked with a mixture of $^{13}$C-labeled solution of PCDD/Fs (Wellington Laboratories) and after one hour PCDD/Fs were extracted three consecutive times with 60 ml of dichloromethane. Then, the extracts were concentrated in a Laborota 4000 rotatory evaporator, transferred to hexane and treated with H$_2$SO$_4$. Afterwards, the extracts were dried with sodium sulphate, concentrated, filtered through a 0.45 µm PTFE filter and cleaned-up by liquid-solid
adsorption in the Power-Prep™ system using silica, alumina and carbon columns. The purified final extracts were concentrated in the rotatory evaporator and then concentrated to dryness with a nitrogen stream.

**Instrumental Analysis**

The purified extracts were analyzed by the Chromatography Service (SERCROM) of the University of Cantabria using the DFS mass spectrometer (Thermo Fisher Scientific) in the multiple ion detection mode at a resolution of 10,000 (10% valley definition). Final results were expressed both in concentration and in I-TEQ values according to toxic equivalency factors (I-TEFs).

**Results and discussion**

**PCDD/Fs concentration in raw landfill leachate**

The total concentration of PCDD/Fs in three different leachate samples (S₁, S₂, S₃) ranged from 3710 pg/L for leachate S₃ to 4244 pg/L for leachate S₂. The profile was dominated by the presence of OCDD, accounting between 83% and 87% of the total PCDD/Fs. The second predominant congener was the 1,2,3,4,6,7,8-HpCDD contributing between 11% and 14% of the sum of PCDD/Fs. Expressing PCDD/Fs concentration as pg I-TEQ/l it ranged from 13.2 pg I-TEQ/L for sample S₂ to 17.22 pg I-TEQ/L for sample S₁.

![Figure 1](image1.png)

Figure 1. Comparison between PCDD/Fs concentration in raw, S₂, and electrochemical oxidized leachate samples (EOX).

Figure 1 shows a common pattern of decreasing PCDD/Fs concentration within the electrochemical treated leachate with respect to the untreated one. Regarding the major congeners (Figure 1b), a concentration reduction around 70% was reached after 180 min of electrochemical oxidation. In addition, at this time the I-TEQ of the raw leachate was reduced in 58%.

![Figure 2](image2.png)

Figure 2. Comparison between PCDD/Fs concentration in raw leachates S₁ and S₂ and their Fenton oxidized samples after 180 min

Figure 2 displays that the concentration of several PCDD/Fs congeners in Fenton treated leachates increased with respect to raw leachates. Regarding the two major PCDD/Fs congeners (Figure 2b), their concentration increased in the range of 37.5-150% after 180 min. In addition, at this time the I-TEQ of the leachate samples increased by 12.5% for S₁ and 128% for S₂.
for $S_3$. These results highlight the necessity of a more rigorous assessment of Fenton operating conditions in order to avoid the potential formation of these toxic byproducts.

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References