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Comparative study of the destruction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans during Fenton and electrochemical oxidation of landfill leachates

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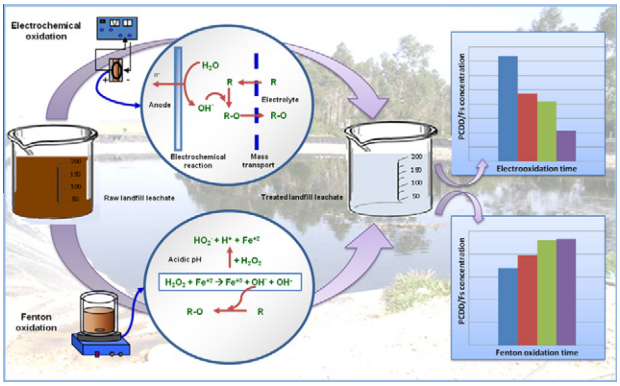
HIGHLIGHTS

- ▶ Landfill leachates were treated using electrochemical and Fenton oxidation.
- ▶ Raw and oxidized samples were characterized for COD and PCDD/Fs concentration.
- ▶ Around 90% removal of COD was achieved with both AOPs after 180 min.
- ▶ Electrooxiation reduced the concentration of most PCDD/Fs and the sample toxicity.
- ▶ Fenton caused the formation of PCDD/Fs increasing the sample toxicity.

GRAPHICAL ABSTRACT



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ABSTRACT

Two advanced oxidation processes (AOPs) that provide a broad-spectrum contaminant destruction option were applied to the treatment of the leachates, namely electrochemical and Fenton oxidation. Despite the similar efficiency in the oxidation of major organic contaminants, approximately 90% reduction of chemical oxygen demand after 180 min, our results showed a different behaviour of both AOPs in the oxidation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). A concentration reduction of 73% for 1,2,3,4,6,7,8-HpCDD and of 71% for OCDD was reached after 180 min of electrochemical oxidation and the total toxic equivalent of the sample was reduced in 58%. However, Fenton oxidation followed a different trend and for similar operation times, it was detected an increase in the concentration of several PCDD/Fs congeners, specially stressed for the major congeners 1,2,3,4,6,7,8-HpCDD, OCDD and OCDF, and in the total toxicity of the sample between 12.5% and 128%. Comparison of the results and the rationale behind their difference are finally discussed.

1. Introduction

Landfills serve as the ultimate solid waste disposal in countries worldwide. The percolation of rainwater through the landfill layers and wastes decomposition produces highly polluted wastewater termed as landfill leachate and characterized by its high concentration of organic and inorganic contaminants including humic acids (HAs), ammonia nitrogen, heavy metals, xenobiotics and inorganic salts (Urtiaga et al., 2009). Furthermore, the presence of some hazardous compounds such as aromatic compounds, halogenated compounds, phenols and pesticides, some of which are persistent organic compounds (POPs), has been detected in landfill leachates (Öman and Junestedt, 2008). The Stockholm Convention on POPs states that POPs waste should be destroyed or disposed of in a way that the POPs content is destroyed or irreversibly transformed. In this context it is critical that the destruction methods used do not create by-products that are themselves POPs (Stockholm Convention, 2001).

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A large part of POPs has been deposited in landfills along the history and many of them, especially those contained within consumer goods, are still widely deposited in industrial countries. Some relevant POPs present in landfills are polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) (Weber et al., 2008). PCDD/Fs family comprises 210 congeners, among them those 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 bioccumulative behaviour (Martínez et al., 2006). Moreover, the low POPs levels of PCDD/Fs is high compared with most contaminated wastes and consequently most PCDD/Fs-contaminated wastes are excluded from the obligations and therefore continue to be disposed in landfill sites (Weber et al., 2011).

PCDD/Fs can enter the environment via escaping leachate, in fact, although there are not many studies the presence of PCDD/Fs has been reported in several landfill leachates samples (Casanovas et al., 1994; Pujadas et al., 2001; Choi and Lee, 2006). If not treated and disposed safely, landfill leachate could be a major source of water contamination because it could percolate through soil and subsoil, causing high pollution to receiving waters (Aziz et al., 2010; Rocha et al., 2011). Therefore, 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. The choice of the treatment method is essentially based on the composition and properties of the landfill leachate, which are influenced by the type of wastes and the age of the landfill (Urtiaga et al., 2009). One important criterion for assessment of treatment technologies is the potential formation of POPs and other toxic by-products, in particular whether the highly toxic PCDD/Fs are formed and under which operation conditions their formation is relevant (Weber, 2007).

Advanced oxidation processes (AOPs) have been widely applied to enhance the biotreatability and for the mineralization of recalcitrant organics in landfill leachate obtaining satisfactory results. Despite the high efficiency of AOPs in the oxidation of major contaminants, scarce references deal with the oxidation of PCDD/Fs in landfill leachate matrices. This fact has been highlighted by Weber (2007) who established in a general way that a detailed assessment of non-combustion technologies with respect to PCDD/Fs formation was still lacking.

On the one hand, some authors reported that PCDD/Fs degradation occurred during the treatment of synthetic and real aqueous solutions with AOPs such as Photo-Fenton, Fenton-like and UV/O_3 (Vollmuth and Niessner, 1997; Wenzel et al., 1999; Katsumata et al., 2006). On the other hand, a concentration increase and/or formation of PCDD/Fs congeners have been reported after treatments like UV, ozone and photolysis to synthetic and real waters containing, among other compounds, chlorinated organic compounds (Vollmuth et al., 1994; Vollmuth and Niessner, 1995; Fukushima et al., 2000). Considering the previous reports on the contradictory role of AOPs in the formation of persistent organic pollutants, improving our understanding of the degradation/formation potential of PCDD/Fs is a timely endeavour.

Our research aims at providing better understanding of the byproducts formation in the advanced oxidation of landfill leachates with especial attention on PCDD/Fs. Two different AOPs have been studied, Fenton and electrochemical oxidation making a comparison of the obtained results.

2. Materials and methods

2.1. Reagents and materials

EPA 1613 standard solutions in nonane (CS-1–CS-5, PAR, LCS and ISS, Wellington Labs., Ontario, Canada) were used for instrument calibration, recovery, quantification and quality control. Toluene, dichloromethane, hexane and acetone (for organic trace analysis) and sulphuric acid, sodium sulphate and sodium hydroxide were purchased from Merck (Darmstadt, Germany). Ferrous sulphate hepta hydrate, sodium thiosulphate and ammonium hydroxide were purchased by Panreac. Hydrogen peroxide was provided by Solvay Interox (Spain). Silica, alumina and carbon columns were purchased from Technospec (Barcelona, Spain). 2.7 μm glass microfiber filter, 0.45 μm Millex syringe filters and Oasis HLB cartridge were purchased from Whatman, Millipore and Waters, respectively.

Leachate waters from a municipal solid waste landfill located in the Cantabria region, Spain, were collected from June 2010 to March 2011, and they were kept under refrigeration until their analysis. Physico-chemical characteristics of leachate samples, DOC, COD, $N-NH_4^+$, Cl^- were determined according to standard methods previously described (Primo et al., 2008).

2.2. Electrochemical oxidation experiments

Electrooxidation experiments of 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 each and an electrode gap of 5 mm) using a 1 L feed tank magnetically stirred and a recirculation pump that provides an operational flowrate of 11 L min^{-1} (Cabeza et al., 2007; Anglada et al., 2011). Three experiments at 5, 30 and 180 min respectively were carried out working with a current density of 900 A m^{-2}.

2.3. Fenton oxidation experiments

Fenton oxidation was carried out at room temperature and atmospheric pressure in a magnetically stirred reactor according to the experimental procedure described elsewhere (Primo et al., 2008). Working with a feed volume of 0.75 L, the initial pH was adjusted to 3 by adding H_2SO_4 and the optimized mass ratio H_2O_2/Fe^{2+} equal to 5.86 $((H_2O_2/COD = 1.7)/(Fe^{2+}/COD = 0.29))$ was employed. Results were analyzed at different treatment times of 5, 30 and 180 min respectively. When the oxidation time was reached the excess of H_2O_2 was removed by $NaHS_2O_3$ and neutralization at pH 7.5 with sodium hydroxide was carried out before sample analysis.

2.4. PCDD/Fs analysis

Standard Method US-EPA 1613 (1994) for PCDD/Fs was applied in this study. Samples (0.5 L) were spiked with 10 μL of a 15 ^{13}C-labelled PCDD/Fs solution (EPA 1613 LCS) dissolved in acetone and Kept to 1 h. PCDD/Fs were extracted with three portions of 60 mL aliquots of dichloromethane. The organic extract was then concentrated in a rotatory evaporator (Laborota 4000), transferred to hexane and treated with sulphuric acid. Afterwards, the extract was dried with sodium sulphate, concentrated using the rotary evaporator to approximately 1–2 mL and filtered through a 0.45 μm PTFE filter. Then, the clean-up of the filtered extract was performed using an automated system (Power-Prep™, Fluid Management Systems Inc., Waltham, MA, USA) through a multilayer silica column, then a basic alumina and finally a PX-21 active carbon column. The purified extract was concentrated by means of the rotatory evaporator and transferred into a vial to be concentrated to dryness under a nitrogen stream.

Purified samples were analyzed by the Chromatography Service (SERCROM) of the University of Cantabria. Before the chromatographic analysis, internal syringe standards (EPA 1613 ISS) were added to the sample. The analysis was carried out by High