

Comparative analysis of trace contaminants in leachates before and after a pre-oxidation using a solar photo-Fenton reaction

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Abstract Sanitary landfill leachates are a complex mixture of high-strength organic and inorganic persistent contaminants, which constitute a serious environmental problem. In this study, trace contaminants present in leachates were investigated by gas chromatography-mass spectrometry and gas chromatography-flame ionization detector before and after a pre-oxidation step using a solar photo-Fenton process. More than 40 organic compounds were detected and identified as benzene ($0.09 \pm 0.07 \text{ mgL}^{-1}$), trichlorophenol (TCP) ($0.18 \pm 0.12 \text{ mgL}^{-1}$), phthalate esters (Di-n-butyl phthalate (DBP), Butyl benzyl phthalate (BBP), Di(2-ethylhexyl) phthalate (DEHP)) (DBP: $0.47 \pm 0.01 \text{ mgL}^{-1}$; BBP: $0.36 \pm 0.02 \text{ mgL}^{-1}$; DEHP: $0.18 \pm 0.01 \text{ mgL}^{-1}$), among others. Toluene, pentachlorophenol, dimethyl phthalate, diethyl phthalate, and Di-n-octyl phthalate were never detected in any of the samples.

After the photo-Fenton treatment process, TCP decreased to levels below its detection limit, benzene concentration increased approximately three times, and DBP concentration decreased about 77 % comparatively to the raw leachate sample. The solar photo-Fenton process was considered to be very efficient for the treatment of sanitary landfill leachates, leading to the complete elimination of 24 of the detected micropollutants to levels below their respective detection limits and low to significant abatement of seven other organic compounds, thus resulting in an increase of the leachate biodegradability.

Keywords Sanitary landfill leachate · Organic micropollutants · Solar photo-Fenton · GC-FID · GC-MS

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Introduction

Landfill leachates are regarded as potentially hazardous wastewaters, which, unless returned to the environment in a carefully controlled manner, may cause harmful effects on both surface and groundwater surrounding the landfill site (Salem et al. 2008). Normally, new landfill leachates (<10 years) present high values of biochemical oxygen demand (BOD), (chemical oxygen demand (COD), nitrogen compounds, and biodegradability. However, mature leachates present a complex mixture of recalcitrant organic compounds, such as humic and fulvic acids, phenols, phthalates, xenobiotics, hormones, and pharmaceuticals, among other inorganic compounds (heavy metals) showing low biodegradability (Christensen et al. 2001; de Morais and Zamora 2005; Nagamori et al. 2005; Wiszniowski et al. 2006).

The European Union water policy is undergoing considerable changes at present. The Water Framework Directive

(European Commission 2000) provides a policy tool that enables this essential resource to be sustainably protected, including a list of 33 priority substances which represent a significant risk to or via the aquatic environment. In this context, the identification and quantification of trace-recalcitrant compounds in leachates is a recent concern in the scientific community due to their potential inherent toxicity. Complex samples as leachates typically require difficult sample preparation steps, such as dissolution of the sample, extraction of the diluted analytes to a standard level above their detection limit, chemical conversion of the analytes to a detectable form, and finally, removal of interfering species for detection of low concentrations of persistent target compounds (Ciola 1998; Harris 2005; Queiroz et al. 2001).

Conventional treatment technologies, including physical/chemical and biological processes are not able to yield a final treated leachate with enough quality to be discharged into natural water bodies. On the other hand, recently developed advanced oxidation processes (AOPs) have been considered as an effective technology to improve the biodegradability of mature landfill leachates (Vilar et al. 2011a, b, 2012a), through the generation of powerful reactive chemical species such as the hydroxyl radical, which are able to degrade even the most recalcitrant compounds into more biodegradable ones or complete mineralization into CO_2 , H_2O , and inorganic ions (de Morais and Zamora 2005; Gogate and Pandit 2004a, b). AOPs main disadvantage is the high costs associated with UV radiation generation and oxidants production (Koh et al. 2004; Zhang et al. 2006). However, they have been considered as one of the most promising options for leachates treatment and the high operation costs can be overcome with the use of solar renewable energy as UV/Vis photon source.

The Fenton process has gained great interest in recent years due to its high efficiency to generate hydroxyl radicals through the decomposition of H_2O_2 by Fe^{2+} in acidic conditions (Fenton 1894). The combination of hydrogen peroxide and Fe (II) with UV-visible radiation, i.e., the photo-Fenton process, has an even higher hydroxyl radical production yield than the conventional Fenton process. The oxidation power is increased due to the photoreduction of Fe^{3+} to Fe^{2+} and the generation of a catalytic cycle that involves the formation of two hydroxyl mol per mol of H_2O_2 initially decomposed (Gallard and De Laat 2001; Kim and Vogelpohl 1998; Nogueira et al. 2007). Hermosilla et al. (2009) showed that the amount of iron needed for the photo-Fenton treatment of leachates was 32 times lower than for the conventional Fenton process, in order to achieve the same COD and dissolved organic carbon (DOC) removal efficiency, besides reducing the iron sludge volume from 25 to 1 % of the final volume of treated leachate.

Using leachates from two old sanitary landfills situated in the north and center part of Portugal, Vilar et al. (2011a,

2012a) showed that the treatment in a 15,000/5,000 m^3 capacity aerated lagoon promoted the biological oxidation of the leachates, leading to 88/84 %, 57/49 %, and 63/39 % elimination of the BOD_5 , DOC, and COD respectively. At this point, the pretreated leachates presented a low BOD_5/COD ratio and additional biological (anoxic and aerobic stages)/sedimentation processes showed negligible DOC removal efficiencies indicating that the remaining organic carbon was refractory. Afterwards, a solar photo-Fenton process was successfully applied for the further treatment of the leachate samples preliminary treated in the aerated lagoon system, showing an important enhancement of biodegradability. Calculations were made to estimate the photo-treatment time and the hydrogen peroxide consumption necessary to reach the biodegradability threshold (Vilar et al. 2011a, b, 2012a, b).

The first objective of the present study was the identification and quantification of trace compounds present in a raw landfill leachate, which might be responsible for its recalcitrant character, using gas chromatography-flame ionization detector (GC-FID) and gas chromatography-mass spectrometry (GC-MS) techniques. Furthermore, the leachate sample was also analyzed after a solar photo-Fenton oxidation process, with the purpose of establishing a possible correlation with the enhancement of the leachate biodegradability during the oxidation treatment.

Experimental methodology

Leachate samples

Leachate samples were collected from a sanitary landfill located in the north of Portugal, covering an area of 20.5 hectares and receiving 1,223 tons of municipal solid wastes per day since 1999 (Vilar et al. 2012a). The existing leachate treatment system includes a reception/equalization lagoon with pure oxygen injection, an activated sludge reactor with anoxic and aerobic tanks, a secondary clarifier, a coagulation/flocculation system, and a nonaerated retention lagoon. The treated effluent is then transported to a municipal wastewater treatment plant (WWTP). Table 1 presents the main chemical/physical characteristics of the leachate after the second clarifier pretreatment, which was used for this study and addressed as raw leachate.

Leachate pre-oxidation using a solar photo-Fenton reaction

Solar CPC pilot plant

The solar photo-Fenton experiment was carried out under sunlight in a pilot plant with a photocatalytic system, constituted by compound parabolic collectors (CPCs) (4.16 m^2),

Table 1 Landfill leachate characterization (Vilar et al. 2011b)

| Parameters | Raw leachate | LLOPT |
|--|--------------|-------|
| pH | 7.6 | 2.9 |
| T (°C) | 21.5 | – |
| Conductivity (mS cm ⁻¹) | 20.7 | – |
| Volatile suspended solids (mg L ⁻¹) | 235 | – |
| Total suspended solids (mg L ⁻¹) | 337 | – |
| COD (mg O ₂ L ⁻¹) | 4,505 | 1,174 |
| BOD ₅ (mg O ₂ L ⁻¹) | 300 | 260 |
| BOD ₅ /COD | 0.07 | 0.22 |
| D _t (%) ^a | 13 | 61 |
| DOC (mg C L ⁻¹) | 1,098 | 470 |
| Dissolved iron (mg (Fe ²⁺ +Fe ³⁺) L ⁻¹) | 8.5 | 39.3 |
| Absorbance at 254 nm (diluted 1:25) | 1.07 | – |
| Nitrite (gN-NO ₂ ⁻ L ⁻¹) | 0.5 | <0.01 |
| Nitrate (gN-NO ₃ ⁻ L ⁻¹) | 0.09 | 1.2 |
| Ammonium (gN-NH ₄ ⁺ L ⁻¹) | 0.2 | 0.2 |
| Total nitrogen (gNL ⁻¹) | 1.8 | 1.7 |
| Phosphates (mg PO ₄ ³⁻ L ⁻¹) | 3.2 | 2.9 |
| Total phosphorous (mg P L ⁻¹) | 10.8 | 11.4 |
| Sulfate (g SO ₄ ²⁻ L ⁻¹) | 0.4 | 2.6 |
| Chloride (g Cl ⁻ L ⁻¹) | 3.8 | 3.2 |

LLOPT Landfill leachate at the optimum photo-treatment time

^a Biodegradability according to the Zahn-Wellens test (EPA 1998)

mounted on a fixed platform tilted 41 ° (local latitude) (Vilar et al. 2011b). The solar collectors are made up of four CPC units (1.04 m²) with five borosilicate tubes each (Schott-Duran type 3.3, Germany, 280 nm at cut-off, 46.4 mm internal diameter, 1,500 mm length, and 1.8 mm thickness) connected by polypropylene junctions. The intensity of solar UV radiation is measured by a global UV radiometer (ACADUS 85-PLS) mounted on the pilot plant at the same angle, which provides data in terms of incident W_{UV} m⁻². Eq. (1) allows to obtain the amount of accumulated UV energy ($Q_{UV,n}$ kJ L⁻¹) received on any surface in the same position with regard to the sun, per unit of volume of water inside the reactor, in the time interval Δt :

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV} G_n \frac{A_r}{1000 \times V_t}; \quad \Delta t_n = t_n - t_{n-1} \quad (1)$$

where t_n is the time corresponding to n water sample (s), V_t total reactor volume (L), A_r illuminated collector surface area (m²), and $\overline{UV} G_n$ average solar ultraviolet radiation (W m⁻²) measured during the period Δt_n (s).

Experimental procedure

A volume of 50 L of sanitary landfill leachate was added to the recirculation tank of the CPC units (2.08 m²) and

homogenized by turbulent recirculation during 15 min in darkness (a first control sample was taken to characterize the wastewater). pH was adjusted with H₂SO₄ (Panreac, 98 % purity) to 2.6–2.9 and another sample was taken after 15 min to confirm the pH. Afterwards, iron salt (60 mg Fe²⁺ L⁻¹) was also added (FeSO₄·7H₂O, Panreac) and well homogenized for 15 min and a third sample was taken for iron concentration control. Finally, the first dose of hydrogen peroxide (30 % w/v, Panreac) was added, the CPCs were uncovered and samples were taken at predefined times to evaluate the degradation process. The hydrogen peroxide concentration was maintained in excess, between 200 and 500 mg L⁻¹, by supplementing small amounts of H₂O₂ as consumed.

Analytical determinations

Evaluation of H₂O₂ concentration during experiments was performed by the metavanadate method, based on the reaction of H₂O₂ with ammonium metavanadate in acidic medium, which results in the formation of a red-orange color peroxovanadium cation, with maximum absorbance at 450 nm (Nogueira et al. 2005). Iron concentration was determined by colorimetry with 1,10-phenantroline according to ISO 6332. Sulfate, chloride, nitrate, and nitrite were measured by ion chromatography (Dionex DX-120), using a Dionex Ionpac AS9-HC 4 mm×250 mm column. The program for anions determination comprises a 20 min run using 9 mM Na₂CO₃ as eluent, at a flow rate of 1.0 mL min⁻¹. Ammonium, phosphates, total phosphorous, total nitrogen, and COD were determined by Merck® Spectroquant kits.

The quantification of total suspended solids and volatile suspended solids was carried out according to the standard methods (Clesceri et al. 1998). DOC was measured in a TC-TOC-TN analyzer (Shimadzu, model TOC-VCSN) provided with a NDIR detector. UV-vis spectrum between 200–700 nm, absorbance at 450 nm (vanadate method), 510 nm (phenanthroline method), and 254 nm (aromatic content) were obtained using a Unicam Helios α spectrophotometer. All samples were pre-filtrated through 0.2 μm Nylon VWR membrane filters before analysis. pH, temperature and conductivity were measured using a pH meter Hanna HI 4522.

Before biological tests and other analyses involving chemical oxidation, the excess of hydrogen peroxide present in some samples was removed using a small volume of 0.1 g L⁻¹ solution of catalase (2,500 U mg⁻¹ bovine liver) after adjusting the sample pH to 6.5–7.5. BOD₅ was determined according to Organization for Economic Cooperation and Development (OECD)-301 F test using an OxiTop® system (manometric respirometry) (Clesceri et al. 1998). A 28-day biodegradability Zahn-Wellens test was performed according to the OECD and EPA guidelines (EMPA 1992; EPA 1998). 250 mL of the pretreated samples, collected at different photo-Fenton reaction times without hydrogen peroxide, were added to an open-glass

vessel, magnetically stirred and kept in the dark at 25 °C. Activated sludge from Freixo WWTP, Porto, Portugal, previously centrifuged, and mineral nutrients (KH₂PO₄, K₂HPO₄, Na₂HPO₄, NH₄Cl, CaCl₂, MgSO₄, and FeCl₃) were added to the samples. The control and blank experiments were prepared using glucose as carbon source, which is highly biodegradable, and distilled water respectively. Then, the mineral nutrients and the activated sludge were also added. The percentage of biodegradation (D_t) was determined by the following equation (Eq. (2)):

$$D_t = \left[1 - \frac{C_t - C_B}{C_A - C_{BA}} \right] \times 100 \quad (2)$$

where C_A and C_{BA} are the DOC (mgL⁻¹) in the sample and in the blank, respectively, measured 3 h after starting the experiment, and C_t and C_B are the DOC (mgL⁻¹) in the sample and in the blank, respectively, measured at the sampling time t . The photo-Fenton pretreated samples are considered biodegradable when D_t is higher than 70 % (EMPA 1992).

Pretreatment, extraction, and preconcentration of the samples

The pretreatment, extraction, and preconcentration of the samples were carried out in the Sanitation Laboratory of the Federal University of Ceará, Brazil. Firstly, the leachate samples were acidified with HCl (PA degree—Synth) until pH3.0. Then, the samples were vacuum filtered through 0.45 μm glass fiber filters (Whatman). The solid-phase extraction was performed using C-18 cartridges (Supelco) (500 mg, 6 mL) and a vacuum manifold system. Following the extraction, the cartridges were vacuum dried and eluted with 2 mL of acetone (PA degree—Dinâmica) and 2 mL methanol (PA degree—Dinâmica). The extracts were used for GC-FID and GC-MS analyses. Before GC-MS analyses, the solution was passed through 2 g of sodium sulfate anhydrous to remove any residual trace of water, further eluted with 1 mL of acetone and 1 mL methanol, and then reduced until dryness in the incubator at 60 °C. Then, a derivatization reaction was performed by silylation with the reagent N,O-Bis(trimethylsilyl) trifluoroacetamide, in a water bath at 60 °C for 30 min. A 100 μL aliquot of the reagent was used in the derivatization of the raw leachate and 50 μL in the case of the photo-treated leachate.

Qualitative analysis (GC-MS)

The identification of trace compounds in raw and photo-treated leachate samples was performed using a QP-2010 PLUS GC-MS (Shimadzu) system with a nonpolar capillary column Rtx-5MS (30 m×0.25 mm×0.25 μm), from

Supelco. 1 μL of sample was manually injected, using a 10 μL Hamilton microsyringe. The chromatographic conditions of the method herein employed were based on methods previously developed by Thomas (2001), Bila et al. (2007), and Guedes Maniero et al. (2008), and later optimized by Rocha et al. (2009) and Rocha (2010), namely concerning the gas flow and the temperature ramp program. The oven temperature program was: initial temperature of 80 °C (hold 1 min), 30 °Cmin⁻¹ until 120 °C, 10 °Cmin⁻¹ until 280 °C (hold 4 min), and 10 °Cmin⁻¹ until 300 °C (hold 1 min), with a total run time of 23.25 min. The injection method included a split of 1:50. The helium carrier gas flow was maintained at 1.93 mLmin⁻¹ and pressure at 130 kPa min⁻¹. The MS method was operated in full-scan mode (m/z ranging from 40 to 460), with an injector temperature of 280 °C, ion source temperature of 200 °C, and detector temperature of 290 °C. Peak identification was based on the comparison with the NIST05.LIB GC/MS library (National Institute of Standards and Technology, U.S. Commerce Department), considering only the compounds which showed a reliable similarity percentage (>90 %).

Quantitative analysis (GC-FID)

The quantification of the selected organic micropollutants in both raw and photo-treated leachate samples was performed with a 17A GC/FID (Shimadzu) system, equipped with a reverse phase DB-5 capillary column (30 m×0.25 mm×0.25 μm), from J&W Scientific. Each of the selected trace compounds were quantified using the external standardization method (Rocha 2010; Rocha et al. 2009).

Volatile organic compounds (VOCs) and chlorophenols

Individual and multielemental stock solutions of benzene, toluene, trichlorophenol, and pentachlorophenol were prepared in methanol, with a theoretical concentration of 5,000 mgL⁻¹. Standard solutions between 10 and 1,000 mgL⁻¹ were prepared by dilution of the stock solutions and injected in the GC/FID to obtain the calibration curve for each compound. The adopted method included a splitless injection of 1 μL of extract, an injector temperature of 250 °C, and interface temperature of 250 °C. The oven temperature program was: initial temperature of 40 °C, 7 °Cmin⁻¹ until 100 °C, 60 °Cmin⁻¹ until 180 °C, and 10 °Cmin⁻¹ until 230 °C (hold 1 min), with a total run time of 17 min. The hydrogen carrier gas flow was maintained at 1 mLmin⁻¹.

Phthalate esters

Standard solutions composed by six phthalate esters: (di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), di(2-ethylhexyl) phthalate (DEHP), dimethyl phthalate (DMP),

diethyl phthalate (DEP), and di-n-octyl phthalate (DnOP), supplied by Supelco, were prepared in methanol in a concentration ranging between 20 and 200 mgL⁻¹ and finally injected in the GC-FID to obtain the calibration curve for each compound. The adopted method included a splitless injection of 1 µL of extract, an injector temperature of 280 °C, and detector temperature of 280 °C. The oven temperature program was: initial temperature of 90 °C, 35 °Cmin⁻¹ until 175 °C, and 12 °Cmin⁻¹ until 290 °C (hold 1 min), with a total run time of 16 min. It was also used a pressure ramp program with an initial pressure set at 78 kPa and an increase of 5 kPa min⁻¹ until 155 kPa. The hydrogen carrier gas flow was maintained at 1.68 mLmin⁻¹.

Results and discussion

Chemical/physical characteristics of the leachate samples

Table 1 presents the main chemical/physical characteristics of the raw leachate and the photo-treated leachate at the optimum photo-treatment time (Vilar et al. 2011b). The raw leachate presents a strong dark-brown color, associated with a strong content of organic matter and nitrogen, and low biodegradability, according to the BOD₅/COD ratio and Zahn-Wellens test. This leachate also presented a high aromatic content measured in terms of absorbance at 254 nm (the wavelength at which the aromatic compounds present a maximum absorption) (Mrkva 1983). Other relevant points were the high conductivity, which could be attributed to the high concentrations of chloride, sulfate, and ammonium, and the high concentration of suspended, dissolved, and volatile solids.

Figure 1a presents the photo treatment of the leachate, using a solar photo-Fenton reaction (pH=2.8; [Fe²⁺]=60 mgL⁻¹), achieving 86 % mineralization (DOC_{final}=134 mgL⁻¹) and 94 % aromatic content reduction after 110 kJ_{UV} L⁻¹ and consuming 306 mM of H₂O₂ (Rocha et al. 2011). Figure 1b shows a very important increase of BOD₅/COD ratio (from 0.07 to 0.44), indicating that photo-oxidation treatment leads to more biodegradable organic carbon, which can be assimilated by the activated sludge. According to the Zahn-Wellens test (Fig. 1b), which involves longer periods of contact (28 days) of the sample with microorganisms to allow some adaptation of the biomass, the biodegradability of the leachate was enhanced during the photo-Fenton treatment achieving a value higher than 70 % biodegradation after 28 days. Although sample 10 or 11 seems to be the best point to stop the pre-oxidation process, samples 7, 8, and 9 also present high biodegradability levels of 61, 66, and 68 %, respectively, which corresponds to savings in the UV energy requirements of 50, 41, and 24 % and H₂O₂ consumption of 54, 47, and 22 %, relatively to sample 10. In order to establish a correlation

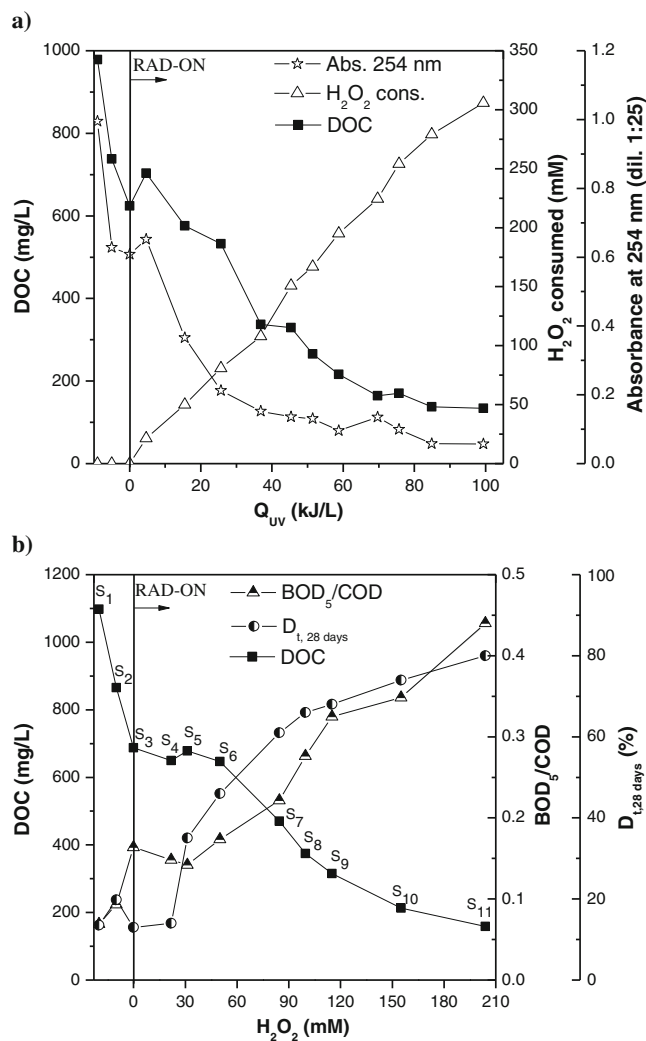



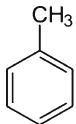
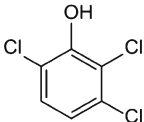
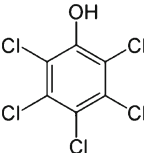
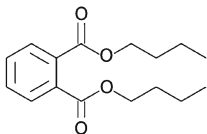
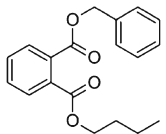
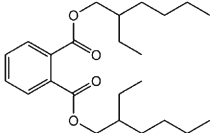
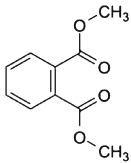
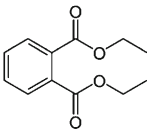
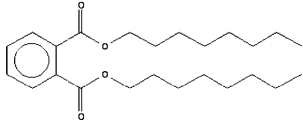
Fig. 1 (a) DOC degradation of landfill leachate, H₂O₂ consumed, and aromatic content at 254 nm during the photo-Fenton reaction as a function of the amount of accumulated UV energy per liter of effluent; (b) DOC degradation of landfill leachate, BOD₅/COD ratio, and percentage of biodegradation after 28 days (Zahn-Wellens test) during the photo-Fenton reaction as a function of the H₂O₂ consumed

between the leachate biodegradability increase after the oxidation process and the type of organic micropollutants present in solution, a detailed analysis of specific organic compounds will be discussed in the following sections using the photo-treated sample number 7, corresponding to a photo-treatment energy of 29.2 kJ_{UV} L⁻¹ and a consumption of 90 mM of H₂O₂ (57 % mineralization and 86 % reduction of aromatic content in terms of absorbance 254 nm).

Quantitative analysis (GC-FID)

Table 2 presents the average concentrations of VOCs (benzene), chlorophenols (trichlorophenol (TCP)), and phthalate esters (DBP, BBP, and DEHP) that were identified in both raw and photo-treated leachate. Toluene, pentachlorophenol (PCP),

Table 2 Average concentrations of VOCs, chlorophenols, and phthalate esters in the raw leachate and after photo-Fenton oxidation

| Compound | Chemical structure | Raw leachate | Leachate at the optimum phototreatment time |
|---|---|--------------|---|
| <i>Volatile Organic Compounds(VOCs) and Chlorophenols (mg L⁻¹)</i> | | | |
| Benzene |  | 0.09 ± 0.07 | 0.30 ± 0.02 |
| Toluene |  | nd | nd |
| TCP |  | 0.18 ± 0.12 | < 0.07 |
| PCP |  | nd | nd |
| <i>Phthalate Esters (mg L⁻¹)</i> | | | |
| DBP |  | 0.47 ± 0.01 | 0.11 ± 0.02 |
| BBP |  | 0.36 ± 0.02 | 0.30±0.07 |
| DEHP |  | 0.18 ± 0.01 | 0.18 ± 0.07 |
| DMP |  | nd | nd |
| DEP |  | nd | nd |
| DnOP |  | nd | nd |

Nd not detected, TCP trichlorophenol, PCP, pentachlorophenol

and DMP, DEP, and DnOP esters were not detected in either of the leachate samples. These specific compounds were selected due to their reported presence in different leachates from sanitary landfills, in high concentrations (Baun et al. 2004; Jonsson et al. 2003; Marttinen et al. 2003; Nascimento Filho et al. 2003; Öman and Junestedt 2008). For example, Jonsson et al. (2003) studied the presence of phthalates and their degradation products (monoesters and phthalic acid) in leachates from 17 different landfills in Europe. The authors reported the presence of phthalate esters in 11 landfills and identified DEP ($1\text{--}33\ \mu\text{gL}^{-1}$), DBP ($1\text{--}23\ \mu\text{gL}^{-1}$), BBP ($2\text{--}7\ \mu\text{gL}^{-1}$), and DEHP ($3\text{--}460\ \mu\text{gL}^{-1}$). Among the phthalates, DEHP, BBP, and DBP, are the primary phthalate esters recognized as endocrine disruptors (Loureiro 2002).

Benzene concentration in the photo-treated leachate was three times higher compared to the raw leachate, probably as a result of the degradation of other more complex aromatic compounds, such as BBP and DBP, whose degradation efficiencies were 15 and 77 %, respectively. However, the photo-oxidation was not able to decrease DEHP concentration, considering the photo-treatment energy used. According to Chen et al. (2009), a photo-Fenton pretreatment of a DEHP solution with 60 min of irradiation using a 254 nm, 360 W mercury lamp, increased the BOD₅/COD ratio from 0.19 to 0.45, correlated with an increase of the leachate biodegradability. The complex mixture of high-strength organic and inorganic persistent contaminants present in the leachate, and the low amount of energy used in our system can explain the low efficiency in DEHP degradation when compared to the work of Chen et al. (2009), which used a pure solution of DEHP.

Qualitative analysis (GC-MS)

The GC-MS qualitative evaluation of the two samples was made using the NIST05.LIB database. The efficiency of photo-treatment was calculated on the basis of peak areas ratios. Figure 2 shows the chromatogram of the raw leachate, where 164 peaks were detected. The 40 most intense peaks were identified and are presented in Table 3, for both raw and photo-treated leachate, together with the respective fitting probabilities and peak areas. Of the identified compounds, 26 in the raw leachate were eliminated below the respective detection limit, 5 compounds were removed by percentages ranging between 37 and 56 %, and 9 other compounds increased their concentration (e.g., peaks 28 and 39, corresponding to phthalic acid and mono-2-ethylhexyl phthalate (MEHP) (Fig. 2), respectively), which can result from the degradation of DBP, BBP, and DEHP (Loureiro 2002).

Chen et al. (2009) showed that the application of the photo-Fenton process to DEHP degradation resulted in different intermediate products, as phthalic acid, MEHP, methyl 4-hydrobenzoate, and octyl 4-hydroxybenzoate. Using Fenton and TiO₂ photocatalytic systems, Bajt et al. (2001) and Kaneco et al. (2006), also showed that the main photoproduct of DBP is phthalic acid, which is in agreement with the increase of its peak area after the photo treatment. Xu et al. (2009) reported the study on BBP degradation using a TiO₂/UV system (350 nm black blue fluorescent UV lamps, 30 Wm⁻²), and identified mono-butyl phthalate, mono-benzyl phthalate, and phthalic acid as the major intermediates of BBP degradation. The shorter the carbon chain length of phthalate

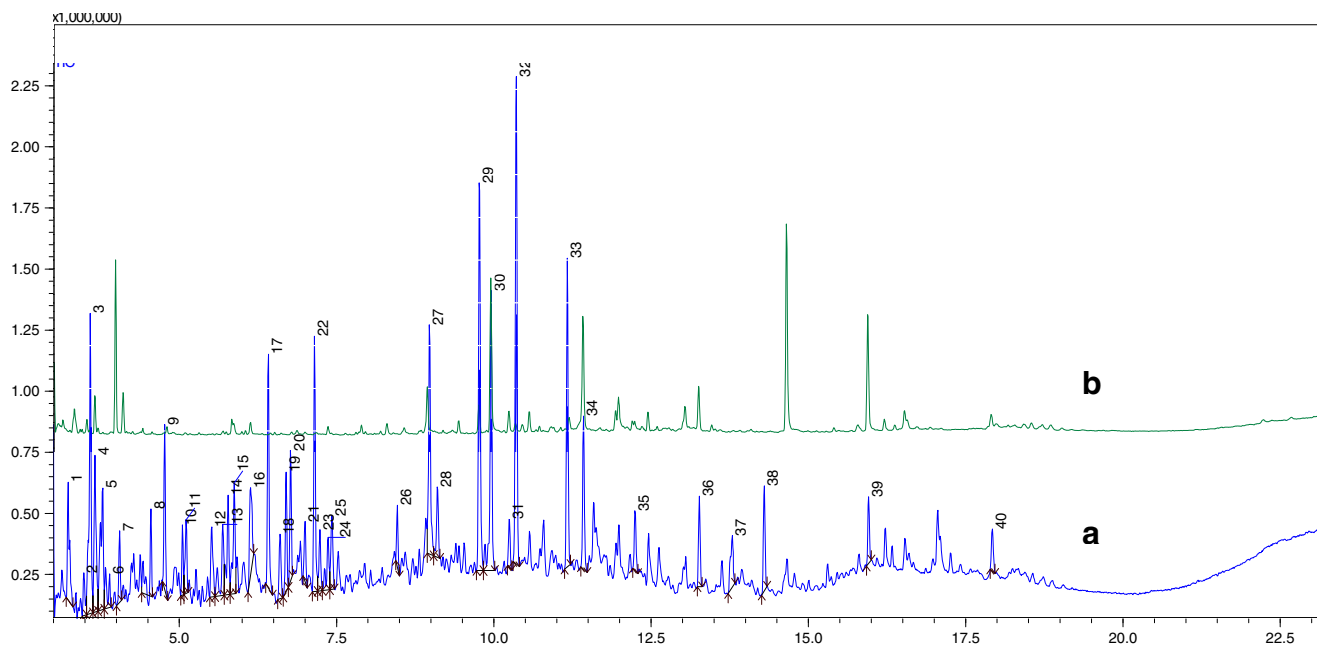


Fig. 2 GC-MS chromatograms of the raw (a) and photo-treated leachate (b)

Table 3 Compounds present in the raw and photo-treated leachate, fitting probabilities and peak areas

| Peak | Compound | Precursor ion m/z | Fitting probability (%) | Area | |
|-------------------------|---|-------------------|-------------------------|-----------|---------------|
| | | | | Raw | Photo-treated |
| Carboxylic acids | | | | | |
| 2 | Nonanoic or pelargonic acid | 117 | 77 | 2,199,085 | nd |
| 3 | 3-Butenoic acid | 82 | 69 | 3,945,845 | 121,012 |
| 5 | 3-Butenoic acid | 82 | 64 | 2,450,783 | nd |
| 6 | Azelaic acid | 73 | 63 | 910,215 | nd |
| 7 | Mandelic acid | 73 | 76 | 1,035,147 | nd |
| 18 | Cinnamic acid | 235 | 74 | 1,606,871 | 894,908 |
| 19 | Benzoic acid | 251 | 63 | 1,697,717 | nd |
| 22 | Dodecanoic or lauric acid | 73 | 81 | 1,040,661 | nd |
| 26 | Alpha-linolenic acid | 73 | 65 | 4,687,516 | 2,754,915 |
| 38 | Alpha-linolenic acid | 73 | 63 | 1,231,574 | 1,615,230 |
| 28 | Phthalic acid or benzene-1,2- dicarboxylic acid | 149 | 96 | 4,576,494 | 5,464,057 |
| 32 | Hexadecanoic or palmitic acid | 117 | 92 | 1,789,376 | 3,223,332 |
| 33 | 2-propenoic or acrylic acid | 147 | 66 | 1,699,439 | 5,666,216 |
| 36 | Octadecanoic or stearic acid | 117 | 92 | 1,008,551 | 3,496,031 |
| 37 | Hexanoic or caproic acid | 73 | 60 | 995,481 | nd |
| Esters | | | | | |
| 1 | 2,2-Dimethyl-3-ester oxobutyric | 73 | 72 | 890,523 | nd |
| 14 | 2,4,6-trimethyl-ester benzoate | 147 | 88 | 2,070,041 | 903,469 |
| 21 | Ibuprofen ester | 73 | 94 | 3,282,277 | 1,661,179 |
| 34 | 9-Octadecenoic acid (Z)-, methyl ester | 55 | 86 | 1,402,997 | nd |
| 39 | Mono(2-ethylhexyl) phthalate (MEHP) | 149 | 92 | 888,686 | 5,125,851 |
| Monosaccharides | | | | | |
| 8 | 2-Deoxyribose | 73 | 73 | 2,591,386 | 1,639,551 |
| Others | | | | | |
| 4 | Ether of glycerol | 73 | 83 | 2,248,502 | nd |
| 9 | Propane | 73 | 64 | 1,663,115 | nd |
| 10 | 3,6,10,13-Tetraoxa-2,14-disilapentadecane, 2,2,14,14-tetramethyl- | 73 | | 1,421,347 | nd |
| 11 | Diisopropylbenzene | 43 | 89 | 1,011,168 | nd |
| 12 | Ethanone, 1-[4-(1-hydroxy-1-methylethyl)phenyl]- | 163 | 78 | 1,239,815 | nd |
| 13 | Ethanone, 1 - [3 - (5-clorooxazolo [4,5-H] hidroxi-2-ilsulfanilmethyl)-4-metoxifenil] | 163 | 68 | 1,021,956 | nd |
| 15 | 1(2H)-Pentalenone, hexahydro-4-methylene-5-(trimethylsilyl)- | 73 | 64 | 3,186,648 | nd |
| 16 | Etane, 1,2-bis (di-isopropylpospinil) | 161 | 65 | 3,114,071 | nd |
| 17 | Propanediamide | 235 | 70 | 1,394,378 | nd |
| 20 | Bicycle [4.2.1] nona-2 ,4,7-triene | 73 | 74 | 1,050,753 | nd |
| 23 | 4-Hydroxyphenylacetic acid di(t-butyl)dimethylsilyl) | 323 | 66 | 1,084,296 | 2,197,529 |
| 24 | 3H-Benz[e] indene | 180 | 64 | 1,246,478 | nd |
| 25 | 2-octenal, 2-butyl | 112 | 62 | 864,549 | nd |
| 27 | 2-Propanol, 1-chloro-, phosphate (3:1) | 125 | 91 | 1,086,325 | 32,388 |
| 29 | 4-tert-butyl-o-phenylene diacetate | 166 | 57 | 3,577,198 | nd |
| 30 | 7,9-Di-tert-butyl-1-oxaspiro (4,5) deca-6 ,9-diene-2 ,8-dione | 57 | 82 | 5,517,916 | 6,128,829 |
| 31 | 3,5-Di-terc-butyl-4-trimetilsiloxi-toluene | 293 | 59 | 3,283,697 | nd |
| 35 | 2,2,5-trimethyl-6-trimethylsilylmethylenecyclohex-4-eno-1 ,3-dione | 221 | 62 | 1,232,683 | nd |
| 40 | Cholesterol | 295 | 59 | 1,312,063 | 3,745,707 |

Nd not detected

Table 4 Chemical structure of the compounds detected in the raw and photo-treated leachate and their respective biodegradabilities

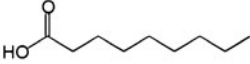
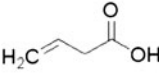
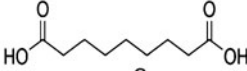
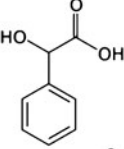
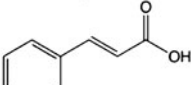
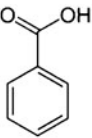
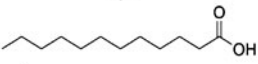
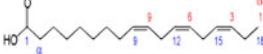
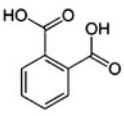
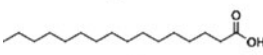
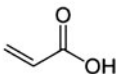

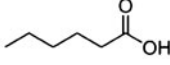
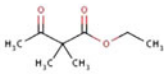
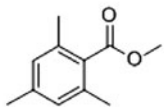
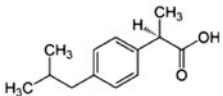
| Peak | Compound | Chemical Structure | Biodegradability |
|-------------------------|--|--|------------------------------------|
| Carboxylic acids | | | |
| 2 | Nonanoic or pelargonic acid |  | Moderate (Torpy et al. 1983) |
| 3, 5 | 3-Butenoic acid |  | High (Torpy et al. 1983) |
| 6 | Azelaic acid |  | Moderate (Torpy et al. 1983) |
| 7 | Mandelic acid |  | not found |
| 18 | Cinnamic acid |  | Low (Amat et al. 2003) |
| 19 | Benzoic acid |  | Low (Pariante et al. 2008) |
| 22 | Dodecanoic or Lauric acid |  | Moderate (Chipasa & Mdrzycka 2008) |
| 26, 38 | alpha-Linolenic acid |  | Moderate (Chipasa & Mdrzycka 2008) |
| 28 | Phthalic acid or Benzene-1,2-dicarboxylic acid |  | Low (Fan et al. 2004) |
| 32 | Hexadecanoic or Palmitic acid |  | Moderate (Chipasa & Mdrzycka 2008) |
| 33 | 2-propenoic or Acrylic acid |  | High (Larson et al. 1997) |
| 36 | Octadecanoic or Stearic acid |  | Moderate (Chipasa & Mdrzycka 2008) |
| 37 | Hexanoic or Caproic acid |  | High (Hongwei et al. 2004) |
| Esters | | | |
| 1 | 2,2-Dimethyl-3-oxo butyric |  | High (Torpy et al. 1983) |
| 14 | 2,4,6-trimethyl-benzoate |  | Not found |
| 21 | Ibuprofen Ester |  | High (Méndez-Arriaga et al. 2010) |

Table 4 (continued)


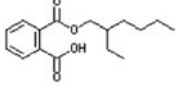
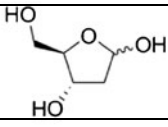
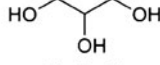
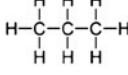
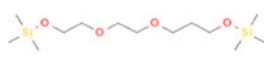

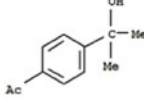
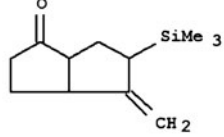
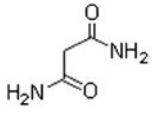
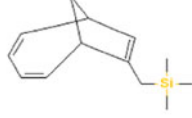
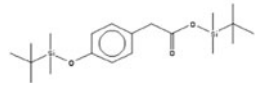
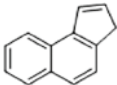
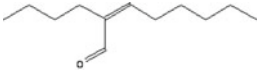
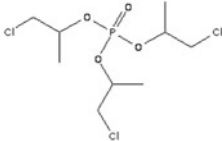
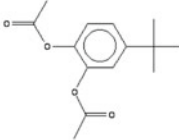
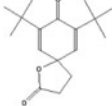
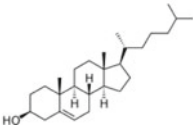
| Peak | Compound | Chemical Structure | Biodegradability |
|------------------------|--|--|------------------------------|
| 34 | 9-Octadecenoic acid (Z)-, methyl ester |  | Moderate (Torpy et al. 1983) |
| 39 | Mono(2-ethylhexyl) phthalate (MEHP) |  | Low (Wang et al. 1997) |
| Monosaccharides | | | |
| 8 | 2-Deoxyribose |  | not found |
| Others | | | |
| 4 | Ether of Glycerol |  | High (Hongwei et al. 2004) |
| 9 | Propane |  | High (Hongwei et al. 2004) |
| 10 | 3,6,9,13-Tetraoxa-2,14-disilapentadecane, 2,2,14,14-tetramethyl |  | Moderate (Torpy et al. 1983) |
| 11 | Diisopropylbenzene |  | not found |
| 12 | Ethanone, 1-[4-(1-hydroxy-1-methylethyl)phenyl]- |  | not found |
| 13 | Ethanone, 1 - [3 - (5-chlorooxazolo [4,5-H] hidroxi-2-ilsulfanilmethyl)-4-metoxifenil] | ----- | not found |
| 15 | 1(2H)-Pentalenone, hexahydro-4-methylene-5-(trimethylsilyl)- |  | not found |
| 16 | Ethane, 1,2-bis (di-isopropylpospinil) | ----- | not found |
| 17 | Propanediamide |  | not found |
| 20 | Bicycle [4.2.1] nona-2 ,4,7-triene |  | not found |
| 23 | 4-Hydroxyphenylacetic acid di(t-butylidimethylsilyl) |  | not found |

Table 4 (continued)

| Peak | Compound | Chemical Structure | Biodegradability |
|------|---|--|------------------------------|
| 24 | 3H-Benz[e] indene |  | not found |
| 25 | 2-octenal, 2-butyl |  | Moderate (Torpy et al. 1983) |
| 27 | 2-Propanol, 1-chloro-, phosphate (3:1) |  | Moderate (Torpy et al. 1983) |
| 29 | 4-tert-butyl-o-phenylene diacetate |  | not found |
| 30 | 7,9-di-tert-butyl-1-oxaspiro (4,5) deca-6,9-diene-2,8-dione |  | not found |
| 31 | 3,5-Di-tert-butyl-4-trimethylsiloxy-toluene | ----- | not found |
| 35 | trimethylsilylmethylenecyclohex-4-eno-1,3-dione | ----- | not found |
| 40 | Cholesterol |  | not found |

acid esters was, the faster the degradation process occurred (Fang et al. 2009; Stales et al. 1997).

The compounds with a fitting probability equal or superior to 90 % (library NIST05.LIB) were ibuprofen ester (R_f =7.150 min, peak 21), phthalic acid (R_f =9.767 min, peak 28), palmitic acid (R_f =11.425 min, peak 32), stearic acid (R_f =13.267 min, peak 36), and MEHP (R_f =15.958 min, peak 39). These compounds have also been identified in leachate samples by other authors (Chen et al. 2009; Martinen et al. 2003; Öman and Junestedt 2008).

Table 4 presents the chemical structure of the 40 compounds detected in the leachate samples, including their biodegradability, as reported by other researchers. The solar photo-Fenton oxidation process allowed the degradation of most recalcitrant high-molecular weight organic compounds, leading to an increase of leachate biodegradability by 60 %, according to the Zahn-Wellens test. The remaining fraction can be correlated with the moderate to high biodegradability of palmitic acid, stearic acid, alpha-linolenic acid, acrylic acid,

and other low-molecular carboxylic acids, certainly present as degradation by-products. Torpy et al. (1983) studied the biological oxidation of different organic compounds during water treatment process and their reduction by activated sludge treatment. Results demonstrated that higher carboxylic acids tend to be less resistant to biological oxidation (100, 96, and 83 % removal for C_1 - C_3 , C_4 - C_6 , and C_7 - C_{11} carboxylic groups, respectively). Benzoic and toluic acids, phenols, and cresols were also removed at greater than 90 % efficiency. Hongwei et al. (2004) assessed the anaerobic biodegradability of 47 kinds of aliphatic compounds and their qualitative structure biodegradability relationship. Integrated assessment indices were calculated and four laws of anaerobic biodegradability were drawn: a) Law of substituents (acids, alcohols, and aldehydes > esters and ketones > ethers), b) Law of chain length (caproic acid > valeric acid > butyric acid > propionic acid > acetic acid > formic acid), c) Law of branch (primary alcohols > secondary alcohols > tertiary alcohols), d) Law of substituent number (glycerol > propane-1,2-diol > *n*-propanol).

Vilar et al. (2011b) performed a biological treatment of the same photo-treated leachate used in this work, reaching a final effluent with a residual COD of 227 mgL⁻¹. This final COD can be attributed to the presence of cinnamic acid, phthalic acid, 2,4,6-trimethyl-ester benzoate, MEHP, DBP, DEHP, ibuprofen ester, and other compounds reported in Table 4, which shows low biodegradability (Amat et al. 2003; Fan et al. 2004; Méndez-Arriaga et al. 2010; Wang et al. 1997).

Conclusions

The quali-quantitative analysis of a raw sanitary landfill leachate allowed to identify more than 40 trace organic compounds, including benzene, trichlorophenol, phthalic acid, phthalates esters (DBP, BBP, DEHP, and MEHP), and high-molecular weight carboxylic acids, which can be considered responsible for the low biodegradability of the leachate. The photo-Fenton process was able to totally eliminate, below detection limit, 65 % of those trace compounds, including TCP and BBP. On the other hand, cinnamic acid and ibuprofen ester showed low removal efficiency between 37 and 56 %. Some of the identified trace compounds can be correlated with the increase of 60 % in biodegradability, according to the Zahn-Wellens test.

Acknowledgments This work was partially supported by project PEst-C/EQB/LA0020/2011, financed by FEDER through COMPETE—Programa Operacional Factores de Competitividade, and by FCT—Fundação para a Ciência e a Tecnologia. Financial support for this work was also provided by EFACEC Ambiente SA. E. Rocha acknowledges her Ph.D. scholarship by Coord. de Aperfeiçoamento de Pessoal de Nível Superior—CAPES Process 0340/09-0. V. Vilar's acknowledges Ciência 2008 Program.

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