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Solar photo-Fenton as a pre-oxidation step for biological treatment of landfill leachate in a pilot plant with CPCs

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ABSTRACT

A solar photo-Fenton process, without iron addition, is proposed for the decontamination of a landfill leachate in a pilot plant with CPCs, after a preliminary pre-treatment in aerated and non-aerated lagoons.

The solar photo-Fenton reaction leads to 60% mineralization (DOC_{final} = 1200 mg L^{-1}) and 90% reduction of aromatic content of the leachate after 5 sunny clear days (165 kJ_{UV} L^{-1}), consuming 275 mM of H_2O_2.

Photo-Fenton kinetics comprises a "lag period" after the acidification until approximately 68.7 kJ_{UV} L^{-1} in which less oxidized compounds are converted into more oxidized ones but without significant CO_2 release, followed by a first-order kinetic behaviour (k = 0.007 L $kJ_{UV}{}^{-1}$, r_0 = 20.2 mg $kJ_{UV}{}^{-1}$) until 136 kJ_{UV} L^{-1}, with a H_2O_2 consumption rate in both periods of $k_{H_2O_2} = 2.1\ \ \text{mmol}\ \ H_2O_2\ kJ_{UV}^{-1}$.

According to activated sludge respirometry and Zahn–Wellens biodegradability tests, BOD_5/COD ratio, polyphenols concentration and COS (carbon oxidation state), the biodegradability of the leachate was enhanced during the photo-Fenton treatment. From the kinetic results, the optimal amount of UV solar energy required for photo-treatment to reach a biodegradable effluent is 100 kJ_{UV} L^{-1} (10.5 h of photo-Fenton at a constant solar UV power of 30 W m^{-2}), consuming 180 mM of H_2O_2 when used in excess, which means almost 40% mineralization of the leachate, 82% reduction of polyphenols concentration and 83% reduction of aromatic content.

1. Introduction

A landfill, also known as a dump (and historically as a midden), is a site for the disposal of waste materials, and has been the most common method of organized waste disposal [1,2]. The generation of leachates is caused principally by precipitation percolating through the waste deposited in the landfill and during the decomposition of carbonaceous material, through the successive aerobic, acetogenic, methanogenic and stabilization stages, producing a wide range of compounds including methane, carbon dioxide and a complex mixture of organic acids, aldehydes, alcohols and simple sugars [3]. Landfill leachate composition varies widely with regard to the age of the landfill, climatic conditions, and the type of the stored waste [4] and may be characterized as a water-based solution of four groups of contaminants: dissolved organic matter (including recalcitrant compounds), inorganic macro components (common cations and anions including sulphate, chloride, iron, aluminum, zinc and ammonia), heavy metals (Pb, Ni, Cu, Hg), and xenobiotic organic compounds such as halogenated organics, (PCBs, dioxins, etc.) [5,6]. The physical appearance of leachate when it emerges from a typical landfill site is a strongly-odoured dark- or yellow-coloured cloudy liquid. The smell is acidic and offensive and may be very pervasive because of hydrogen, nitrogen and sulfur rich organic species such as mercaptans [3].

According to the characteristics of the leachates and the implementation of more strict regulations, conventional treatment technologies, including biological (aerobic and anaerobic treatment) and physical/chemical (flotation, coagulation–flocculation) processes may not be effective enough, principally for old leachates, to reach the level of purification needed to fully reduce the negative impact of landfill leachates on the environment [3]. Thus, in order to fulfil the standards of discharge and/or reutilization of wastewaters, advanced oxidation processes (using the combination of strong oxidants, e.g. O_3 or H_2O_2 with high energy sources, as ultraviolet (UV), ultrasound (US) or electron beam (EB), and catalysts, e.g. Fe^{2+} and photocatalysts, e.g. TiO_2, to produce hydroxyl radicals) [7–16], membrane based technologies (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) [17–21] and adsorption processes (activated carbon, resins) [22,23] have been investigated. The main disadvantages of the membrane technologies, beyond the high investment costs and energy consumption, are the membrane fouling (which requires extensive pre-treatment or chemical

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cleaning of the membranes, results in a short lifetime of the membranes and decrease process productivity) and the generation of a large volume of concentrate (which is normally recycled to landfill) [3]. The main drawback of the adsorption processes is the need for frequent regeneration of columns or an equivalently high consumption of adsorbent [3]. The main disadvantage of AOPs is their high cost associated with UV radiation generation or ozone production. So, future applications of these processes could be improved through the use of renewable solar energy.

Photo-Fenton combines the Fenton reaction ($H_2O_2 + Fe^{2+}$) and UV–Vis light. Photolysis of Fe^{3+} complexes allows Fe^{2+} to be regenerated producing additional radicals. Under these conditions, iron can be considered a real catalyst. It has been demonstrated that the photo-Fenton reaction is more efficient for the treatment of different recalcitrant pollutants [24,25] than TiO_2, since the reaction rate is much higher and very low iron concentrations are enough for promoting wastewater treatment. This is very helpful because removal of iron at low concentrations will not be necessary before disposal. The advantage of the photo-Fenton process is the higher light sensitivity up to 580 nm, corresponding to 35% of solar radiation spectrum, when compared with ≈5% for TiO_2 photocatalysis.

Apart from developments increasing the reaction rate of the photocatalytic process, the most important progress in solar photocatalysis in recent years has been related to its combination with biological treatment techniques, which proved to be successful in decreasing treatment time (i.e. plant size) and consequently increasing the overall process efficiency [26–28].

The objective of the present work is to study the solar photo-Fenton process, as a pre-treatment step, to enhance the biodegradability of a landfill leachate after a secondary lagoon, allowing the subsequent treatment by conventional biological processes, reducing the photo-treatment time, plant size and costs.

2. Experimental methodology

2.1. Solar CPC pilot plant

The photo-Fenton experiments were carried out in 30-L pilot plant installed at the Faculty of Engineering, University of Porto (FEUP), Portugal. The pilot plant, operated in batch mode, consists of a photocatalytic system equipped with compound parabolic collectors ($0.59\,m^2$ of CPCs, irradiated volume = 6.1 L, dark tubing volume = 3.9 L), with four borosilicate glass tubes (Schott-Duran type 3.3, Germany, cut-off at 280 nm, external diameter 50 mm, length 1000 mm and thickness 1.8 mm), one storage tank (20 L), one recirculation pump ($15\,L\,min^{-1}$), two polypropylene valves for flow rate regulation and sample collection, connecting tubing and an electric board for process control and UV data acquisition, being operated in batch mode.

The intensity of solar UV radiation is measured by a global UV radiometer (ACADUS 85-PLS) mounted on the pilot plant at the same inclination, which provides data in terms of incident $W_{UV}\,m^{-2}$. Eq. (1) allows to calculate 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:

$$Q_{UV,n} = Q_{UV,n-1} + t_n \overline{UV}_{G,n} \frac{A_r}{V_t}; \quad t_n = t_n - t_{n-1} \tag{1}$$

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

A more detailed description of the pilot plant can be found in Gomes et al. [29].

2.2. Analytical determinations

Evaluation of H_2O_2 concentration during experiments was performed by the vanadate method [30]. The method is based on the reaction of H_2O_2 with ammonium metavanadate in acidic medium, which results in the formation of a red-orange colour peroxovanadium cation, with maximum absorbance at 450 nm. Colorimetric determination of dissolved iron concentration was done with 1,10-phenantroline according to ISO 6332.

The total polyphenols concentration was measured by spectrophotometry at 765 nm using the reagent Folin–Ciocalteau (Merck) [31]. The polyphenols content is expressed as $mg\,L^{-1}$ of caffeic acid.

Sulphate, chloride, nitrate and nitrite were measured by ion chromatography (Dionex DX-120), using a Dionex Ionpac AS9-HC 4 mm × 250 mm column. The programme for anions determination comprises a 20 min run with 9 mM Na_2CO_3 at a flow rate of $1.0\,mL\,min^{-1}$. Ammonium, phosphates, total phosphorous, total nitrogen were determined by Merck®Spectroquant kits.

Total suspended solids, volatile suspended solids, total dissolved solids and volatile dissolved solids were carried out according to Standard Methods [32].

Dissolved organic carbon (DOC) was measured in a TC-TOC analyzer (Shimadzu, model 5000A) calibrated with standard solutions of potassium phthalate and provided with a NDIR detector. COD concentration was measured by Merck ®Spectroquant kits (ref: 1.14541.0001). UV–Vis absorbance (200–700 nm) was 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/conductivity meter HANNA HI 4522.

2.3. Biodegradability assays

Biochemical oxygen demand (BOD_5) was carried out according to Standard Methods using an OXITOP® system [32]. Respirometry activated sludge tests were performed using a YSI Model 5300 Biological oxygen monitor and a YSI Model 5301B thermostatic bath, allowing to measure the oxygen uptake rate (OUR) by the active sludge in the presence of the partially photo-treated samples. The respirometer cell was loaded with 5 mL of the sample saturated with air, which was continuously magnetically stirred. One millilitre of activated sludge suspension from a municipal wastewater treatment Plant (WWTP) of Freixo (Porto, Portugal) was added to the sample, and the oxygen consumption was measured during 30 min.

A 28 days biodegradability test (Zahn–Wellens test) was performed according to the EC protocol, Directive 88/303/EEC [33]. A volume of 250 mL of the pre-treated samples (diluted two times), obtained at different photo-Fenton times, without hydrogen peroxide, and after pH correction to 6.5–7.5 by the addition of NaOH, was added to an open glass vessel, magnetically stirred and kept in the dark inside a thermostatic refrigerator at 25 °C. Activated sludge from a WWTP, previously centrifuged, and mineral nutrients (KH_2PO_4, K_2HPO_4, Na_2HPO_4, NH_4Cl, $CaCl_2$, $MgSO_4$ and $FeCl_3$) 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. The percentage of biodegradation (D_t) was determined by the following equation:

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

where C_A and C_{BA} are the DOC ($mg\,L^{-1}$) in the mixture and in the blank experiment, measured 3 h after the beginning of the experiment, C_t and C_B are the DOC ($mg\,L^{-1}$) in the mixture and in the blank experiment, measured at the sampling time t. The photo-

Table 1
Landfill leachate characterization at different pre-treatment steps and days.

Parameters	a_1	a_2	b	c	c	Discharge limits
Day/month/2009	17/02	17/02	17/02	17/02	07/03	
pH	7.6	7.4	8.3	8.4	8.1	6.0–9.0
Temperature (°C)	21.4	15.5	16.9	12.4	–	
Conductivity (mS/cm)	25.0	23.6	36.2	43.5	–	
Dissolved Oxygen (mg O_2 L^{-1})	8.8	0.25	2.50	0.25	–	
Turbidity (NTU)	210	–	–	–	–	
Total dissolved carbon (mg L^{-1})	8424	7565	5287	5175	5505	
Inorganic carbon (mg L^{-1})	2117	2027	2467	2353	2556	
Dissolved organic carbon (mg L^{-1})	6307	5538	2822	2821	2949	
COD (mg O_2 L^{-1})	12,930	10,748	6857	6810	8260	150
BOD_5 (mg O_2 L^{-1})	–	8580	1346	1259	1346	40
BOD_5/COD	–	0.80	0.20	0.18	0.16	
Nitrite (mg NO_2^- L^{-1})	1.0	–	–	–	17.1	
Nitrate (mg NO_3^- L^{-1})	<1	–	–	–	88.6	50
Ammonium (mg NH_4^+ L^{-1})	–	–	–	–	3320	10
Total nitrogen (mg N L^{-1})	–	–	–	–	2500	15
Phosphates (mg PO_4^{3-} L^{-1})	2.5	–	–	–	2.3	
Total phosphorous (mg P L^{-1})	10.5	–	–	–	13.9	10
Sulphates (g SO_4^{2-} L^{-1})	2.0	–	–	–	2.3	2
Chlorides (g Cl^- L^{-1})	2.4	–	–	–	5.8	
Polyphenols (mg caffeic acid L^{-1})	286	–	–	579	518	
Dissolved iron (mg L^{-1})	61.4	–	–	5.1	3.4	2[a]
Absorbance at 254 nm (1:25 diluted)	–	–	–	–	1.9	
Total suspended solids (mg L^{-1})	1260	–	–	–	–	
Volatile suspended solids (mg L^{-1})	760	–	–	–	–	
Total dissolved solids (g L^{-1})	20.2	–	–	–	–	
Volatile dissolved solids (g L^{-1})	10.2	–	–	–	–	
AOS	−1.2	−1.5	0.4	−0.4	−0.2	

a_1 and a_2 – raw leachate at different collection points from the sanitary landfill; b – primary aerated lagoon; c – secondary lagoon.

[a] Total iron.

Fenton pre-treated samples are considered biodegradable when D_t is higher than 70% [34].

2.4. Experimental procedure

A volume of 20 L of sanitary landfill leachate was added to the recirculation tank of the CPC units and homogenized by turbulent recirculation during 15 min in darkness (a first control sample was taken to characterize the wastewater). The pH was adjusted with H_2SO_4 (Panreac, 98% purity) to 2.6–2.9 (6 mL H_2SO_4 L^{-1} of leachate), which is the suitable pH range for the photo-Fenton reaction, avoiding iron hydroxide precipitation, and another sample was taken after 15 min to confirm the pH value. Finally, the first dose of hydrogen peroxide (30% w/v, Panreac) was added, the CPCs were uncovered, and samples were taken at pre-defined times to evaluate the degradation process. In the kinetic study, the hydrogen peroxide concentration was maintained in excess, between 200 and 500 mg L^{-1}, by the addition of small amounts of H_2O_2 as consumed. For the biodegradability tests, a new photo-Fenton experiment was performed maintaining all the parameters, with the exception of H_2O_2 dose. In this case, a small amount of H_2O_2 was added to the photoreactor, and after H_2O_2 total consumption, a sample was taken for bioassays and another amount of H_2O_2 was added. This procedure of “addition–total consumption–sample collection–addition” is very important since it prevents any reaction in dark conditions after sample collection, during the storage and possible interferences in the bioassays. Considering this procedure, the experimental data must be expressed in terms of H_2O_2 consumption and not accumulated UV energy per litre of leachate.

3. Results and discussion

3.1. Landfill leachate characterization

Leachate was collected from Planalto Beirão sanitary landfill located at the centre of Portugal, covering an area of 14 ha and receiving 350 tons of wastes every day since 1999. The landfill leachate, extracted from various locations in the landfill site, is drained to a wastewater treatment plant, which includes a reception/equalization lagoon with air injection, a sedimentation lagoon and a reverse osmosis system (see supplementary data). The aerated lagoon, with a capacity of 5000 m^3, promotes a biological oxidation of the leachate, leading to 84%, 49% and 39% elimination of the biochemical oxygen demand (BOD_5), dissolved organic carbon (DOC) and chemical oxygen demand (COD) (Table 1), which indicates that the biodegradable fraction of the organic carbon is almost completely removed. At this point, the pre-treated leachate presents a low BOD_5/COD ratio, which means that the remaining organic carbon is recalcitrant and possibly inhibitory to microbial metabolism of a biological oxidation system. A non-aerated lagoon with the same capacity is used downstream for the clarification of the leachate and sludge sedimentation. The tertiary treatment of the leachate is performed in two parallel reverse osmosis modules. The concentrate is recirculated to the sanitary landfill. The two reverse osmosis modules have a treatment capacity of approximately 217 m^3 per day, and generate a concentrate of 96 m^3 per day, corresponding to an efficiency of 44%. Finally, the leachate passes through a stripper to remove H_2S and NH_3 gas. This treated wastewater is retained in a final lagoon, and can be used for irrigation, facilities cleaning and the excess is drained to the Vale river.

Table 1 presents the main chemical/physical characteristics of the leachate at different treatment steps and in different days. The effluent presents a strong dark-brown colour associated with a high organic load (DOC = 5500–6300 mg C L^{-1}; COD = 10,000–13,000 mg O_2 L^{-1}), high nitrogen content (2500 mg N L^{-1}) and high polyphenols concentration (≈500 mg caffeic acid L^{-1}). The leachate presents also a high aromatic content measured in terms of absorbance at 254 nm (as absorption at this wavelength has been usually associated with the presence of aromatics). Another relevant point is the high conductivity attributed to the great concentrations of chloride, sulphate, ammonium,

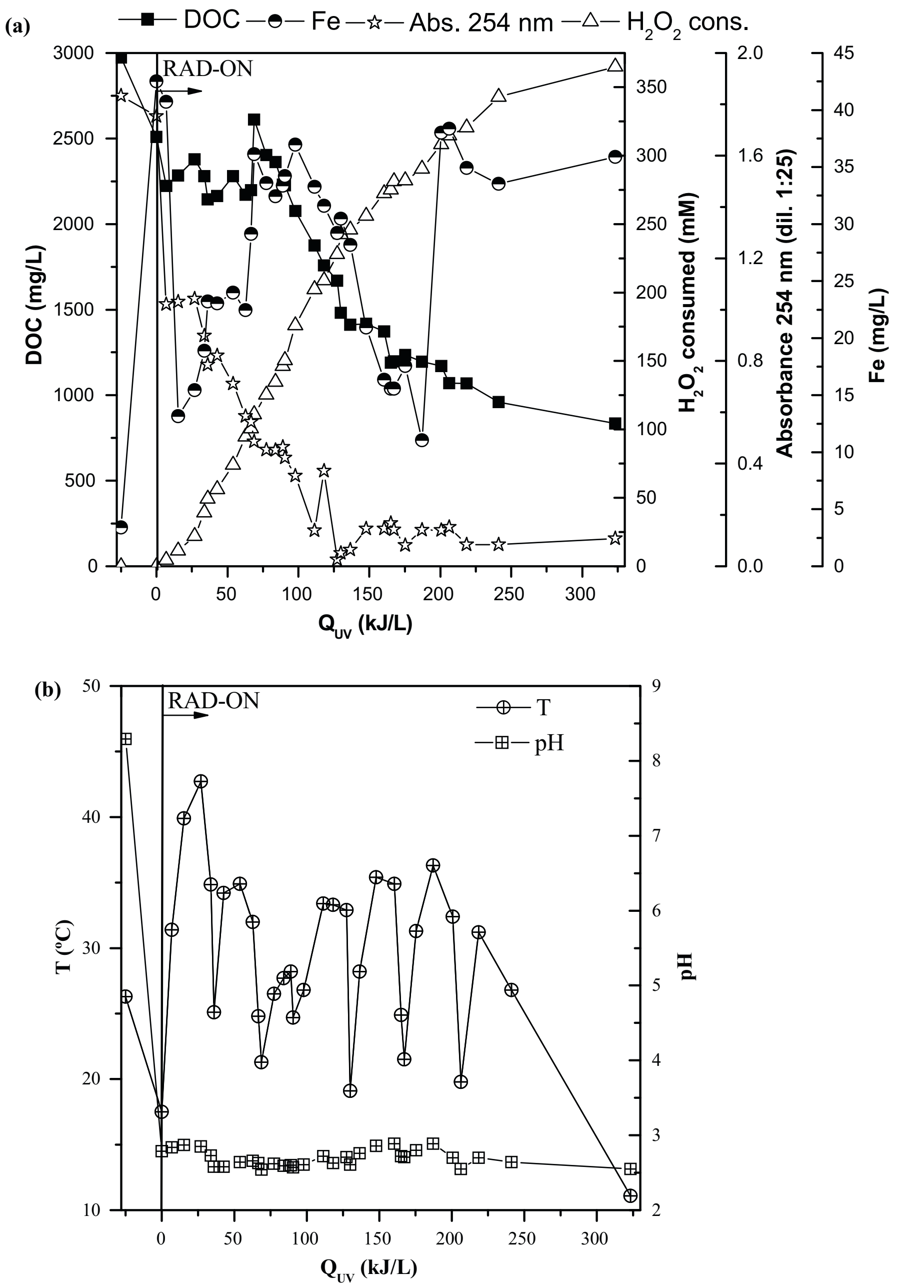

Fig. 1. DOC removal of landfill leachate, H_2O_2 consumed, iron concentration, aromatic content at 254 nm (a); pH and temperature, (b); during the photo-Fenton reaction as a function of the amount of accumulated UV energy per litre of effluent.

potassium, sodium, calcium and magnesium ions. The effluent also contains a high concentration of suspended, dissolved and volatile solids.

Considering the properties of the leachate, the AOP processes may be considered as alternative method to destroy the recalcitrant organic carbon instead of the use of expensive reverse osmosis technologies. So, the leachate samples used in this work were collected after the non-aerated lagoon.

3.2. Solar photo-Fenton treatment

Leachate was treated by a photo-Fenton reaction, using the solar energy as UV light source, in a pilot plant with CPCs. Fig. 1 (a and b) presents the mineralization results of the leachate, without the addition of iron, since it was observed that leachates could have enough iron for the reaction, decreasing reactants costs. From Fig. 1 (a) it can be seen that the initial dissolved iron concentration was 3.4 mg L^{-1}, however, after pH correction to approximately 2.8, the dissolved iron concentration increased abruptly to 42.5 mg L^{-1}, probably due to iron redissolution from organo-iron compounds. The abatement of DOC (25%) and absorbance at 254 nm (44%) after H_2SO_4 addition for pH correction could be attributed to the destruction of most oxidized organic compounds and to the formation of large amounts of foam originated by carbon dioxide bubbles and H_2S gas formation, which could retain large amounts of DOC. When foam disappears during the process, the DOC is redissolved.

Fig. 1 (a) shows a “lag period” after the acidification until approximately 68.7 $kJ_{UV}\,L^{-1}$ in which less oxidized compounds are converted into more oxidized ones but without signifi-

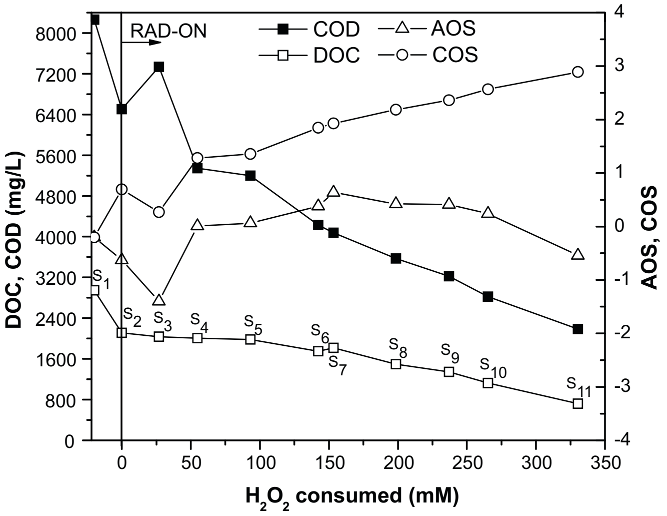

Fig. 2. DOC, COD, AOS, and COS evolution as a function of the hydrogen peroxide consumption during the photo-Fenton process.

cant CO_2 release. The second part of the DOC degradation curve shows a first-order kinetic behaviour ($k = 0.007\,\text{L}\,\text{kJ}_{\text{UV}}^{-1}$, $r_0 = 20.2\,\text{mg}\,\text{kJ}_{\text{UV}}^{-1}$) until $136\,\text{kJ}_{\text{UV}}\,\text{L}^{-1}$. The H_2O_2 consumption profile shows a linear correlation with the UV energy accumulated per unit of volume of wastewater during the first and second reaction periods ($k_{H_2O_2} = 2.1$ mmol $H_2O_2\,\text{kJ}_{\text{UV}}^{-1}$). A lower DOC degradation rate ($k = 0.002\,\text{L}\,\text{kJ}_{\text{UV}}^{-1}$, $r_0 = 5.1\,\text{mg}\,\text{kJ}_{\text{UV}}^{-1}$) and H_2O_2 consumption ($k_{H_2O_2} = 0.9$ mmol $H_2O_2\,\text{kJ}_{\text{UV}}^{-1}$) is observed after $141\,\text{kJ}_{\text{UV}}\,\text{L}^{-1}$, due to the disappearance of Fe in solution, presumably due to the iron complexation with end products, normally low-molecular-weight carboxylic groups and partly attributed to the precipitation of iron phosphate, which is in agreement with the decrease of total phosphorous concentration. However, after the addition of iron ($20\,\text{mg}\,\text{L}^{-1}$) at $187\,\text{kJ}_{\text{UV}}\,\text{L}^{-1}$ and consequently increase of dissolved iron concentration up to $35\,\text{mg}\,\text{L}^{-1}$, the DOC degradation rate remained low, which indicates that the photo-Fenton reaction is unable to degrade the last oxidized compounds, probably low-molecular carboxylic acids, which could contribute to the decrease in the pH from 2.8 to 2.5 at the end of the experiment, although the difference is not so significant (Fig. 1b). A total of 365 mM of H_2O_2 was consumed for attaining 72% mineralization ($\text{DOC}_{\text{final}} = 834\,\text{mg}\,\text{L}^{-1}$) and 94% reduction of the aromatic compounds content.

Temperature usually rises from morning start-up (15–20 °C) to an almost constant value for several hours until 14:00 h (42.7 °C was the maximum temperature achieved) and decreases again during the afternoon, depending on the sunlight intensity. It must be emphasized that experiments were performed in consecutive days (Fig. 1b).

3.3. Biodegradability tests

In order to assess the biocompatibility of the pre-treated effluent, different biodegradability tests, such as Zahn–Wellens and activated sludge respirometry, were performed at different stages of the solar photo-Fenton reaction.

Fig. 2 presents the evolution of DOC, COD and two parameters, AOS (average oxidation state) and COS (carbon oxidation state), which can be used to evaluate the oxidation degree and efficiency of the oxidative process, respectively [35,36]:

$$\text{AOS} = 4 - 1.5\frac{\text{COD}}{\text{DOC}} \tag{3}$$

$$\text{COS} = 4 - 1.5\frac{\text{COD}}{\text{DOC}_0} \tag{4}$$

where DOC is the dissolved organic carbon at time t (mg C L^{-1}), DOC_0 is the initial dissolved organic carbon of the solution (mg C L^{-1}) and COD is the chemical oxygen demand at time t (mg O_2 L^{-1}). AOS takes values between +4 for CO_2, the most oxidized state of C, and −4 for CH_4, the most reduced state of C. The AOS only takes into consideration the organic matter in the solution. Note that in COS calculation, CO_2 eliminated from the solution (with an oxidation state +4) is also considered in the calculation [35,36].

The COD concentration decreases 74% (from 8260 to 2185 mg O_2 L^{-1}), showing a strong oxidation of the organics, which is well correlated with the COS parameter, which increased from −0.2, indicating the presence of rather reduced organic compounds, to +2.9, related with strong mineralization and generation of highly oxidized intermediates. Fig. 2 also shows that AOS starts at −0.2, increases rapidly to approximately 0.69 and remains practically constant during the photo-treatment. The increase of AOS suggests that more oxidized organic intermediates are formed during the treatment and, after AOS reaches a plateau, the chemistry of the intermediates generated does not vary significantly [28]. The formation of more oxidized intermediates indirectly demonstrates that the treatment can improve biodegradability, although biological assays are needed to confirm this point. The same type of results was also obtained in solar photo-treatment of pesticides [37] in water and industrial pharmaceutical wastewater [38].

The BOD_5/COD ratio has been established as a more reliable parameter to evaluate the biodegradability [39–41], as it is not affected either by the amount or by the oxidation state of organic matter [42]. Fig. 3 (a) shows a very important increase from 0.16 to 0.37, suggesting that photo-oxidation enhanced significantly the biodegradability. The OUR/OUR_0 profile also shows the same trend, showing a high increase after 142 mM of H_2O_2 consumed (OUR_0 is the oxygen uptake rate for the raw leachate used in this work). At the end of the phototreatment the OUR increased approximately seven times when compared with the raw leachate ($\text{OUR}_{\text{raw leachate}} = 0.76 \times 10^{-3}$ mol O_2/mol C/h), indicating that photo-oxidation treatment leads to more biodegradable organic carbon, which can be assimilated by the activated sludge. Polyphenols concentration and aromatic content given by absorbance at 254 nm after dilution 1:25 (Fig. 3b), shows a similar profile, leading to 85% reduction after 142 mM of H_2O_2 consumed, and only 5% more until the end of the experiment (337 mM).

Nevertheless, a Zahn–Wellens test (Fig. 4), which involves longer periods of contact (28 days) of the effluent with the microorganisms to allow some adaptation of the sludge, was performed. The four first samples (non-treated, after pH adjustment, and after 27 and 55 mM H_2O_2 consumed) present a poor biodegradation (44–49%). However, as expected, the biodegradability of the leachate was enhanced during the photo-Fenton treatment, reaching 58%, 67%, 70%, 74%, 79%, 83% and 89%, corresponding to a hydrogen peroxide consumption of 93, 142, 153, 199, 237, 265 and 330 mM, respectively for samples 5–11. Considering that the photo-Fenton pre-treated samples are considered biodegradable when D_t is higher than 70%, sample 6 can be considered the optimal photo-treatment time, which corresponds to point A. These results are in agreement with OUR/OUR_0 and BOD_5/COD profile, since sample 6 corresponds to the starting point of a high increase in those ratios (Fig. 3 (a)).

According to these results, the optimal energy dose estimated for photo-treatment to reach a biodegradable effluent is

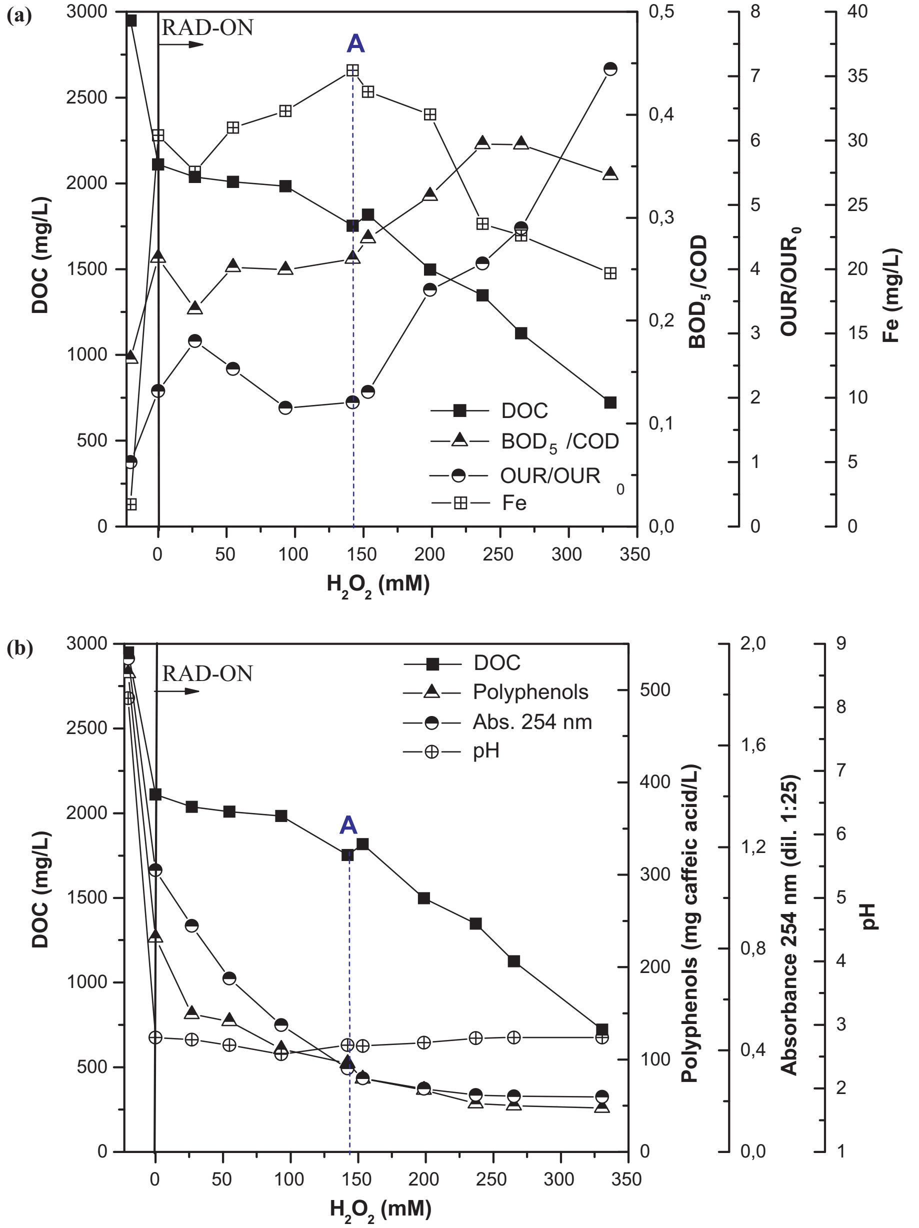

Fig. 3. DOC, BOD_5/COD ratio, OUR/OUR_0, Fe concentration (a); polyphenols concentration, absorbance at 254 nm and pH, (b); evolution as a function of the hydrogen peroxide consumption during the photo-Fenton process.

100 $kJ_{UV}\,L^{-1}$ (10.5 h of photo-Fenton at a constant solar UV power of 30 $W\,m^{-2}$), consuming 180 mM of H_2O_2 when used in excess, which means almost 40% mineralization of the leachate, 82% reduction of polyphenols concentration and 83% reduction of aromatic content, which corresponds to the sample 6.

The concentration of total nitrogen (2890 $mg\,N\,L^{-1}$), ammonium (2460 mg $N{-}NH_4{}^{+}\,L^{-1}$) and nitrate (15 mg $N{-}NO_3{}^{-}\,L^{-1}$) remained approximately constant (see supplementary data). Small variations can be due to the high complexity of the samples that can affect the chemical analysis. A small concentration of nitrite (5.2 mg $N{-}NO_2{}^{-}\,L^{-1}$) was detected in the non-treated leachate, however all nitrites were easily oxidized to nitrate after acidification.

The sulphate ion concentration increased drastically from 2.3 $g\,L^{-1}$ to 13.0 $g\,L^{-1}$ after the addition of sulphuric acid 98% (1.6 $g\,L^{-1}$ = 6 mL $H_2SO_4\,L^{-1}$) for the acidification of leachate to pH ≈2.8, and remained constant during the reaction. The chloride content remained almost constant during the photo-Fenton reaction at 5.7 $g\,L^{-1}$. The concentrations of total phosphorous and phosphates were around 14 $mg\,P\,L^{-1}$ and 15 mg $PO_4{}^{3-}\,L^{-1}$, respectively, until 142 mM of H_2O_2 consumption. After that, the concentrations decreased, maybe due to precipitation with iron, which concentration decreased from 34 to 19 $mg\,L^{-1}$. Li et al. [43] observed phosphate removal rates of 50–60% from secondary effluents at 1:1 molar addition of Fe^{2+}, and showed that the removal of phosphates is enhanced by the use of Fe^{2+}/H_2O_2 relatively to ferric coagulation alone, since phosphates have more affinity to the Fe^{3+} formed in the Fenton reaction.

In order to achieve the discharge limits (see supplementary data) in terms of pH and iron concentration, after the pre-oxidation using the solar photo-Fenton reaction, the effluent must be neutralized to pH ≈7, using lime or sodium hydroxide, which will also precipitate iron. Iron sludge generated must be disposed in

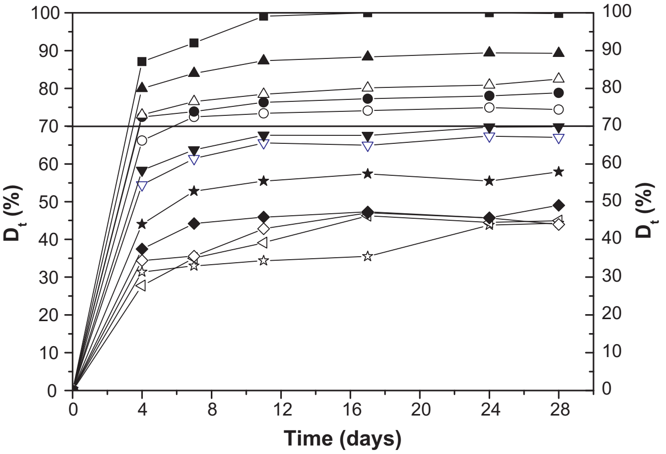

Fig. 4. Zahn–Wellens test for the selected samples during the photo-Fenton process (initial sample is also showed, as the reference): ☆ – S_1, DOC = 2949 mg L^{-1}; ◁ – S_2, DOC = 2110 mg L^{-1}; ◊ – S_3, DOC = 2038 mg L^{-1}; ♦ – S_4, DOC = 2008 mg L^{-1}; ★ – S_5, DOC = 1983 mg L^{-1}; ▽ – S_6, DOC = 1753 mg L^{-1}; ▼ – S_7, DOC = 1817 mg L^{-1}; ○ – S_8, DOC = 1497 mg L^{-1}; ● – S_9, DOC = 1346 mg L^{-1}; △ – S_{10}, DOC = 1125 mg L^{-1}; ▲ – S_{11}, DOC = 722 mg L^{-1}; ■ – Reference (DOC = 1297 mg L^{-1}). The samples were diluted two times.

a landfill, or it can be reused in a next cycle of photo-Fenton treatment.

4. Conclusions

Leachate from sanitary landfills presents a very complex composition, with an intense colour, high concentration of organics (biodegradable and recalcitrant), suspended solids, ammonium, chloride, sulphate and other ions. The complexity of leachates, principally old leachates, implies the search of more efficient and low cost treatment methods, in order to reduce the negative impact of landfill leachates on the environment.

The solar photo-Fenton process, without iron addition, was found to be very efficient in the treatment of leachates, enhancing the biodegradability of the leachate and making possible its combination with a biological oxidation process. The presence of iron in the leachate can be an important economic factor, since reactant consumption represents a considerable fraction of the treatment costs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2010.08.025.

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