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# Treatment of a sanitary landfill leachate using combined solar photo-Fenton and biological immobilized biomass reactor at a pilot scale

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ABSTRACT

A solar photo-Fenton process combined with a biological nitrification and denitrification system is proposed for the decontamination of a landfill leachate in a pilot plant using photocatalytic (4.16 $m^2$ of Compound Parabolic Collectors – CPCs) and biological systems (immobilized biomass reactor). The optimum iron concentration for the photo-Fenton reaction of the leachate is 60 mg $Fe^{2+}$ $L^{-1}$. The organic carbon degradation follows a first-order reaction kinetics ($k = 0.020$ L $kJ_{UV}^{-1}$, $r_0 = 12.5$ mg $kJ_{UV}^{-1}$) with a $H_2O_2$ consumption rate of 3.0 mmol $H_2O_2$ $kJ_{UV}^{-1}$. Complete removal of ammonium, nitrates and nitrites of the photo-pre-treated leachate was achieved by biological denitrification and nitrification, after previous neutralization/sedimentation of iron sludge (40 mL of iron sludge per liter of photo-treated leachate after 3 h of sedimentation). The optimum C/N ratio obtained for the denitrification reaction was 2.8 mg $CH_3OH$ per mg $N{-}NO_3^-$, consuming 7.9 g/8.2 mL of commercial methanol per liter of leachate. The maximum nitrification rate obtained was 68 mg $N{-}NH_4^+$ per day, consuming 33 mmol (1.3 g) of NaOH per liter during nitrification and 27.5 mmol of $H_2SO_4$ per liter during denitrification. The optimal phototreatment energy estimated to reach a biodegradable effluent, considering Zahn–Wellens, respirometry and biological oxidation tests, at pilot plant scale, is 29.2 $kJ_{UV}$ $L^{-1}$ (3.3 h of photo-Fenton at a constant solar UV power of 30 W $m^{-2}$), consuming 90 mM of $H_2O_2$ when used in excess, which means almost 57% mineralization of the leachate, 57% reduction of polyphenols concentration and 86% reduction of aromatic content.

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## 1. Introduction

The overall aim of the Landfill Directive (Council Directive, 1999/31/EC of 26 April 1999) on the landfill of MSW (Municipal Sludge Wastes) is "to prevent or reduce as far as possible negative effects on the environment, in particular the pollution of surface water, groundwater, soil and air, and on the global environment, including the greenhouse effect, as well as any

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resulting risk to human health, from the landfilling of waste, during the whole life-cycle of the landfill" (1999/31/EC, 1999). Leachate production is inevitable due to rainwater percolation through the landfill and wastes decomposition, so a leachate treatment plant is required in a sanitary landfill. The high variability of leachate composition and quantity (Tatsi and Zouboulis, 2002; Kulikowska and Klimiuk, 2008), reinforced by the presence of high recalcitrant substances, such as humic and fulvic acids (Kang et al., 2002), xenobiotics and pesticides (Baun et al., 2004), heavy metals and inorganic macro-constituents ($Ca^{2+}$, $Mg^{2+}$, $K^+$, $Na^+$, $NH_4^+$, $Cl^-$, $HCO_3^-$, $SO_4^{2-}$, etc.) (Christensen et al., 2001; Öman and Junestedt, 2008), depending on the age of the landfill, climatic conditions, soil properties, waste type and composition (Christensen et al., 2001), is nowadays recognized as one of the greatest environmental problems in terms of water pollution.

Normally, old landfill leachates (>10 years), present a low $BOD_5$/COD ratio (<0.1), indicating low biodegradability due to the release of high molecular weight recalcitrant organic molecules and high concentration of $NH_3$–N, which makes difficult being treated by conventional biological processes (Chian and DeWalle, 1976; Calace et al., 2001; Renou et al., 2008). The main source of ammoniacal nitrogen in leachate results from the slow anaerobic hydrolysis of proteins present in the solid wastes, resulting in a slow release of ammonia, which can reach high concentrations in stabilized landfill leachates (Jokela and Rintala, 2003). Normally, for concentrations higher than 100 mg $L^{-1}$ (Burton and Watson-Craik, 1998), untreated $NH_3$–N is highly toxic to aquatic organisms, as confirmed by toxicity tests using *Brachydanio rerio* (Silva et al., 2004), *Daphnia magna* (Assmuth and Penttilä, 1995) and *Vibrio fischeri* luminescent bacteria (Nohava et al., 1995).

Due to its ability to enhance the biodegradability of recalcitrant compounds in the leachate, advanced oxidation processes (AOPs), using the combination of strong oxidants, e.g. $O_3$, $H_2O_2$, irradiation, e.g. ultraviolet (UV) (Kurniawan et al., 2006), ultrasound (US) (Gonze et al., 2003) or electron beam (EB) (Deng and Englehardt, 2007), and catalysts, e.g. $Fe^{2+}$ (Primo et al., 2008) and photocatalysts, e.g. $TiO_2$ (Weichgrebe et al., 1993), to produce hydroxyl radicals, have been considered as one of the most promising options for leachate treatment, which can be improved through the use of renewable solar energy, as UV/Vis photon source.

It has been demonstrated that the photo-Fenton reaction is more efficient for the treatment of the leachates (Rocha et al., 2011) than $TiO_2$, since the reaction rate is much higher and very low iron concentrations is enough for promoting leachate treatment. 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.

Biological nitrogen removal requires a two-step process: aerobic nitrification of ammonia to nitrite (Eq. 1) and then nitrite is converted to nitrate (Eq. 2); anoxic denitrification of nitrate to nitrogen gas (Eq. 3).

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO_2^- + H_2O + 2H^+ \text{ (ammonia oxidizing bacteria)} \quad (1)$$

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^- \text{ (nitrite oxidizing bacteria)} \quad (2)$$

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \quad (3)$$

Denitrification occurs in the absence of oxygen, where nitrate or nitrite is the electron acceptor and requires a carbon source as electron donor. Normally, methanol is used as substrate when an external carbon source is necessary (Eqs. 4 and 5), however acetic acid, methane and others can be used (Randall et al., 1992).

$$6NO_3^- + 5CH_3OH + CO_2 \rightarrow 3N_2 + 6HCO_3^- + 7H_2O \text{ (nitrate removal process)} \quad (4)$$

$$6NO_2^- + 3CH_3OH + CO_2 \rightarrow 3N_2 + 6HCO_3^- + 3H_2O \text{ (nitrite removal process)} \quad (5)$$

Complete nitrification requires 2 mol of oxygen per mol of ammonia to be nitrified (Eqs. 1 and 2). If denitrification is to be considered after a nitrification process, partial nitrification to nitrite implies 25% less oxygen demand compared to complete nitrification, and this shortcut of the nitrate would mean a reduction in the total carbon source required for denitrification because carbon is needed for conversion of nitrate to nitrite, which can yield up to 40% savings in methanol consumption (Eqs. 4 and 5). Approximately 7.14 mg of alkalinity (as $CaCO_3$) are consumed per mg N–$NH_4$ oxidized and 3.57 mg (as $CaCO_3$) of alkalinity production per mg of N–$NO_3$ reduced, meaning that for nitrogen biological elimination in a nitrification–denitrification cycle, 3.57 mg of alkalinity (as $CaCO_3$) is consumed.

Temperature, pH and dissolved oxygen are the main parameters that control the nitrification and denitrification processes efficiency (Randall et al., 1992). Alleman (1984) showed that the optimal pH values are between 7.9 and 8.2 for nitrification and between 7.2 and 7.6 for denitrification. Ruiz et al. (2003) studied the nitrification of synthetic wastewater with high ammonia concentration (10 g N–$NH_4^+$ $L^{-1}$) at a temperature of 30 °C and concluded that for pH values lower than 6.45 and higher than 8.95 complete inhibition of nitrification takes place. Setting a DO concentration in the reactor at 0.7 mg $L^{-1}$, it was possible to accumulate more than 65% of the loaded ammonia nitrogen as nitrite with a 98% ammonia conversion, representing a reduction of 20% in the oxygen consumption. Below 0.5 mg $L^{-1}$ of DO, ammonia was accumulated and over a DO of 1.7 mg $L^{-1}$ complete nitrification to nitrate was achieved.

Different methanol demands, as external carbon source, for denitrification process of landfill leachates have been reported: 2.43 g $CH_3OH$/g N–$NO_3$ (3.6 g COD/g N–$NO_3$) (Kulikowska and Klimiuk, 2004), 2.8–3.0 g $CH_3OH$/g N–$NO_3$ (4.5–4.1 g COD/g N–$NO_3$) (Christensson et al., 1994), which are more than 2 times higher than the stoichiometric mass ratio between consumed methanol-C and nitrate-N (C/N = 0.46). Modin et al. (2007) studied the denitrification using methane as external carbon source, showing a C/N ratio of 7.1 g C–$CH_4$/g N–$NO_3$, approximately seven times higher than the stoichiometric mass ratio, according to Eq. (6) (Randall et al., 1992).

$$8NO_3^- + 5CH_4 \rightarrow 4N_2 + 8HO^- + 6H_2O + 5CO_2 \quad (6)$$

The objective of this study is to evaluate the possibility of combining a solar photo-Fenton process, as pre-oxidation step, to enhance the biodegradability of a landfill leachate, with a biological oxidation treatment (nitrification and denitrification) for nitrogen and residual DOC removal.

## 2. Experimental methodology

### 2.1. Sanitary landfill leachate samples

Leachate samples were collected at MSW sanitary landfill nearby Porto. Table 1 presents the main chemical–physical characteristics of the leachate used in this work.

### 2.2. Solar CPC pilot plant

The photo-Fenton experiments were carried out under sunlight in 100-L pilot plant installed at the roof of the Chemical Department, Faculty of Engineering, University of Porto (FEUP), Portugal. The pilot plant consists of a photocatalytic system, constituted by compound parabolic collectors (CPCs) (4.16 $m^2$), mounted on a fixed platform tilted 41° (local latitude), two polypropylene storage conic tanks (50 and 100 L), two recirculation pumps (20 L $min^{-1}$) (ARGAL model TMB), two flowmeters (Stübe, model DFM 165-350), polypropylene valves (FIP) and connecting tubing, being operated in batch mode. The pilot plant has also a sedimentation tank and a biological reactor system, consisting in a conditioner tank and an immobilized biomass reactor. The solar collectors are made-up of four CPC units (1.04 $m^2$) with 5 borosilicate tubes each (Schott-Duran type 3.3, Germany, cut-off at 280 nm, internal diameter 46.4 mm, length 1500 mm and thickness 1.8 mm) connected by polypropylene junctions. The pilot plant can be operated in two ways: using the total CPCs area (4.16 $m^2$) or using 2.08 $m^2$ of CPCs area individually, giving the possibility of performing two different experiments at the same time and at the same solar radiation conditions.

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. (7) 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 $\Delta t$:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV}_{G,n} \frac{A_r}{V_t}; \quad \Delta t_n = t_n - t_{n-1} \quad (7)$$

where $t_n$ is the time corresponding to $n$-water sample, $V_t$ total reactor volume, $A_r$ illuminated collector surface area and $\overline{UV}_{G,n}$ average solar ultraviolet radiation measured during the period $\Delta t_n$. All experiments were done from April to December 2009 during cloudy and sunny days.

**Table 1 – Landfill leachate characterization.**

| Parameters | Values |
|---|---|
| pH | 7.6 |
| T (°C) | 21.5 |
| Redox Potential (mV) | −98 |
| Conductivity (mS $cm^{-1}$) | 20.7 |
| Volatile Suspended Solids (mg $L^{-1}$) | 235 |
| Total Suspended Solids (mg $L^{-1}$) | 337 |
| COD (mg $O_2$ $L^{-1}$) | 4505 |
| $BOD_5$ (mg $O_2$ $L^{-1}$) | 300 |
| $BOD_5$/COD | 0.07 |
| Total Dissolved Carbon (mg C $L^{-1}$) | 1158 |
| Inorganic Carbon (mg C $L^{-1}$) | 60 |
| DOC (mg C $L^{-1}$) | 1098 |
| Polyphenols (mg caffeic acid $L^{-1}$) | 93.0 |
| Dissolved Iron (mg ($Fe^{2+}$ + $Fe^{3+}$) $L^{-1}$) | 8.5 |
| Absorbance at 254 nm (diluted 1:25) | 1.07 |
| Nitrite (mg N–$NO_2^-$ $L^{-1}$) | 469 |
| Nitrate (mg N–$NO_3^-$ $L^{-1}$) | 85.9 |
| Ammoniacal nitrogen (mg N–$NH_4^+$ $L^{-1}$) | 167 |
| Total Nitrogen (mg N $L^{-1}$) | 1780 |
| Phosphates (mg $PO_4^{3-}$ $L^{-1}$) | 3.2 |
| Total Phosphorous (mg P $L^{-1}$) | 10.8 |
| Sulfate (mg $SO_4^{2-}$ $L^{-1}$) | 374 |
| Chloride (mg $Cl^-$ $L^{-1}$) | 3823 |
| Sodium (g $Na^+$ $L^{-1}$) | 2.6 |
| Potassium (g $K^+$ $L^{-1}$) | 2.8 |
| Copper (mg $Cu^{2+}$ $L^{-1}$) | 0.1 |
| Total chromium (mg Cr $L^{-1}$) | 2.2 |
| Manganese (mg $Mn^{2+}$ $L^{-1}$) | 0.9 |
| Arsenic (μg As $L^{-1}$) | 95.6 |
| Lead (μg $Pb^{2+}$ $L^{-1}$) | 36.4 |
| Zinc (mg $Zn^{2+}$ $L^{-1}$) | 1.2 |
| Cadmium (μg $Cd^{2+}$ $L^{-1}$) | 0.4 |
| Nickel (mg $Ni^{2+}$ $L^{-1}$) | 0.8 |

### 2.3. Biological oxidation system

The biological oxidation system is composed by a neutralization/sedimentation conic-bottom tank (75 L), a conditioner flat-bottom tank (50 L) and an immobilized biomass reactor (IBR) (50 L). The neutralization/sedimentation tank is equipped with a pH meter (CRISON) and a mechanical stirrer (TIMSA). The conditioner tank is equipped with a pH control unit (CRISON, electrode and PH27P controller) for pH adjustment using either $H_2SO_4$ or NaOH dosed by means of two metering pumps (DOSAPRO MILTON ROY, GTM series, model A) and a mechanical stirrer (TIMSA). The IBR is a flat-bottom container packed with 25–30 L of propylene rings (nominal diameter 50 mm), colonized by activated sludge from a municipal wastewater treatment plant (Freixo WWTP). The bioreactor is also equipped with a dissolved oxygen control unit (CRISON, electrode and OXI49P controller) and air is supplied by a blower (compressor-HAILEA model V-20; ceramic air diffuser) for maintaining the oxygen in the system in the selected range.

### 2.4. Analytical determinations

Evaluation of $H_2O_2$ concentration during experiments was performed by the metavanadate method, based on the reaction of $H_2O_2$ 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.

The total polyphenols concentration was measured by spectrophotometry at 765 nm using the reagent Folin-Ciocalteau (Merck) (Folin and Ciocalteau, 1927). The polyphenols content is expressed as mg $L^{-1}$ of caffeic acid.

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 programme for anions determination comprises a 20 min run using 9 mM $Na_2CO_3$ 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., 2005).

Dissolved organic carbon (DOC) was measured in a TC–TOC–TN analyzer (Shimadzu, model TOC-$V_{CSN}$) provided with an NDIR detector. UV–Vis spectrum between 200 and 700 nm, absorbance at 450 nm (vanadate method), 510 nm (phenantroline method), 765 nm (Folin-Ciocalteau 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, conductivity and ORP were measured using a pH meter HANNA HI 4522. Metal ions concentrations ($K^+$, $Na^+$, $Cu^{2+}$, total Cr, $Mn^{2+}$, total As, $Pb^{2+}$, $Zn^{2+}$, $Cd^{2+}$ and $Ni^{2+}$) were obtained, after a previous digestion of the leachate according to Standard Methods (Clesceri et al., 2005), by atomic absorption spectrometry (GBC 932 Plus Atomic Absorption Spectrometer and GBC GF 3000 graphite furnace system).

### 2.5. Biodegradability assays

Before biological tests and other analysis involving chemical oxidation, excess $H_2O_2$ present in samples was removed using a small volume of 0.1 g $L^{-1}$ solution of catalase (2500 U $mg^{-1}$ bovine liver) after adjusting the sample pH to 6.5–7.5.

Biochemical oxygen demand ($BOD_5$) was determined according to OECD-301F test using an OxiTop (manometric respirometry), described in Standard Methods (Clesceri et al., 2005). Respirometric 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, and continuously magnetically stirred. 1 mL of activated sludge suspension from a WWTP of Porto (Portugal) was added to the sample, and the oxygen consumption (OUR) measured during 30 min.

A 28 days biodegradability Zahn–Wellens test was performed according to the EC protocol, Directive 88/303/EEC (EPA, 1996). 250 mL of the pre-treated samples at different photo-Fenton times, without hydrogen peroxide, were added to an open glass vessel, magnetically stirred and kept in the dark at 25 °C. Activated sludge from a WWTP in Porto, 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, and was also added the mineral nutrients and activated sludge. The percentage of biodegradation ($D_t$) was determinate by the following equation:

$$D_t = \left[1 - \frac{C_t - C_B}{C_A - C_{BA}}\right] \times 100 \quad (8)$$

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

### 2.6. Experimental procedure

A volume of 50 or 105 L of sanitary landfill leachate was added to the recirculation tank of the CPC units (2.08 or 4.16 $m^2$) and homogenized by turbulent recirculation during 15 min in darkness (a first control sample was taken to characterize the wastewater). pH was adjusted with $H_2SO_4$ (Pancreac, 98% purity) to 2.6–2.9 (2 mL $H_2SO_4$ $L^{-1}$) to avoid iron hydroxide precipitation and another sample was taken after 15 min to confirm the pH. Afterward, iron salt (60 mg $Fe^{2+}$ $L^{-1}$) was also added ($FeSO_4.7H_2O$, 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 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 supplementing 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 a new dose 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 liter of leachate.

The pre-treated leachate by photo-Fenton reaction was pumped into the neutralization tank, where pH was neutralized with NaOH to a pH around 7 under stirring (1 mL NaOH 50% per L pre-treated leachate), leading to iron precipitation as $Fe(OH)_2$, followed by a period of 3 h for sedimentation of iron sludge (40 mL of iron sludge per liter of leachate photo-treated). A very small concentration of iron (<0.1 mg $L^{-1}$, analyzed by AAS after preliminary acid digestion) was detected in the supernatant after iron precipitation. Following this preliminary step, the neutralized photo-treated effluent was pumped to the conditioner tank, and afterward to the IBR previously colonized by activated biomass, which operates as an up-flow reactor at a recirculation of 4 L $min^{-1}$ (EHEIM

pump) between the conditioner tank and the IBR and pH is controlled in a range of 6.5–7.5.

## 3. Results and discussion

### 3.1. Leachate characterization

Table 1 presents the main chemical/physical characteristics of the leachate after a pre-treatment in a reception/equalization lagoon with pure oxygen injection, an activated sludge reactor with an anoxic and aerobic zone and a secondary clarifier. The pre-treated effluent presents a strong dark-brown colour associated with a high organic charge (DOC = 1098 mg C $L^{-1}$; COD = 4505 mg $O_2$ $L^{-1}$), high nitrogen content (1780 mg N $L^{-1}$), high polyphenols concentration (93.0 mg caffeic acid $L^{-1}$) and a low $BOD_5$/COD (0.07) ratio, indicating the low biodegradability of the leachate. The leachate presents also a high aromatic content measured as absorbance at 254 nm (the wavelength at which the aromatic compounds present maximum absorption) (Mrkva, 1983). Another relevant point is the high conductivity attributed to the high concentration of chloride, sulfate, ammonium ions, potassium and sodium. The effluent contains also a high concentration of suspended, dissolved and volatile solids. Heavy metals were relatively low, except total chromium.

### 3.2. Solar photo-Fenton process

Rocha et al. (2011) showed that the photo-Fenton reaction is faster than the Fenton reaction and the heterogeneous photocatalysis with $TiO_2$, $TiO_2/H_2O_2$/UV or homogeneous with $H_2O_2$/UV. The optimum iron concentration for the photo-Fenton treatment of this leachate is 60 mg $Fe^{2+}$ $L^{-1}$ (Fig. 1). The photo-Fenton kinetics shows a slow initial reaction rate, followed by a first-order kinetic behavior ($k$ = 0.020 L $kJ_{UV}^{-1}$, $r_0$ = 12.5 mg $kJ_{UV}^{-1}$), with a $H_2O_2$ consumption rate of 3.0 mmol $H_2O_2$ $kJ_{UV}^{-1}$, and finally, a reaction period characterized by a lower DOC degradation and $H_2O_2$ consumption until the end of the experiment, presumably due to formation of low-molecular carboxylic groups (Kavitha and Palanivelu, 2004).

### 3.3. Evaluation of combined biological and photo-Fenton treatment

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 (Amat et al., 2007; Arques et al., 2007):

$$AOS = 4 - 1.5\frac{COD}{DOC} \tag{9}$$

$$COS = 4 - 1.5\frac{COD}{DOC_0} \tag{10}$$

where DOC is the dissolved organic carbon at time $t$ (mg of C $L^{-1}$), $DOC_0$ is the initial dissolved organic carbon of the solution (mg of C $L^{-1}$) and COD is the chemical oxygen demand at time $t$ (mg of $O_2$ $L^{-1}$). 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. In COS calculation, $CO_2$ eliminated from the solution (with an oxidation state +4) is also taken into account (Amat et al., 2007; Arques et al., 2007).

The COD concentration decreases 89% (from 4348 to 477 mg $O_2$ $L^{-1}$), showing a strong oxidation of the organics, which is well correlated with the COS parameter, which increased from −1.9, indicating the presence of rather reduced

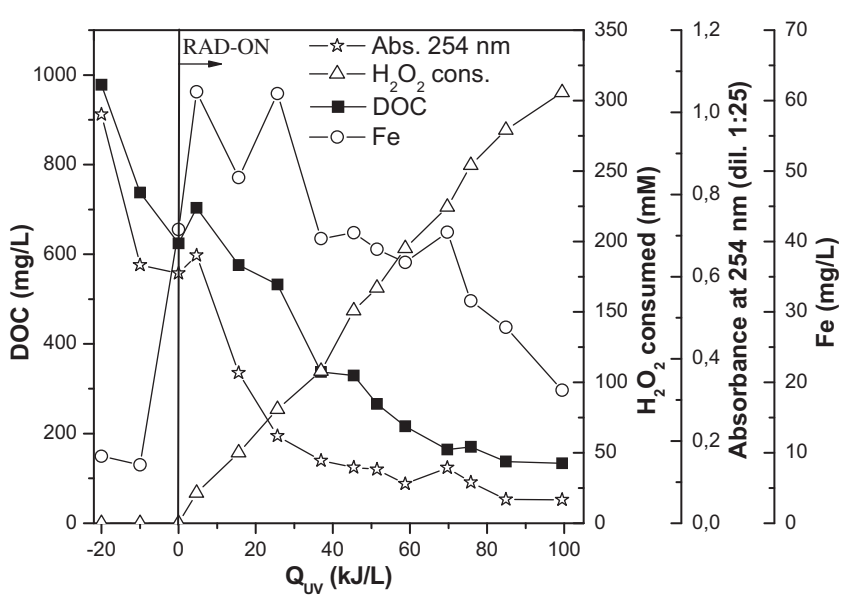


**Fig. 1 – DOC degradation of landfill leachate, $H_2O_2$ consumed, iron concentration and aromatic content (absorbance at 254 nm) during the photo-Fenton reaction as a function of amount of accumulated UV energy per liter of effluent.**

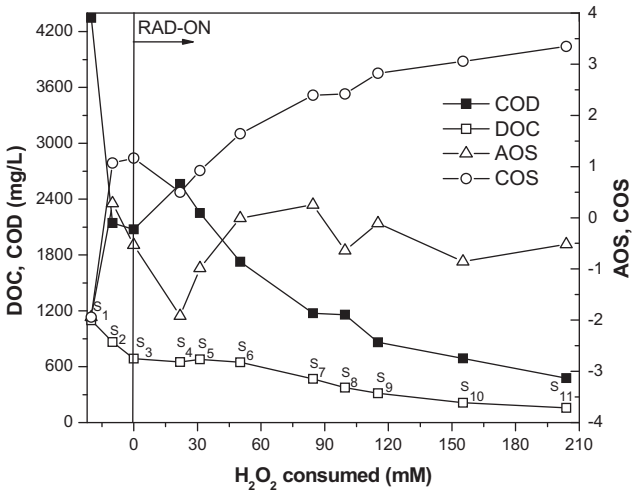


**Fig. 2 – DOC, COD, AOS, and COS evolution as a function of the hydrogen peroxide consumption during the photo-Fenton process.**

organic compounds, to +3.4, which means strong mineralization and generation of highly oxidized intermediates. Fig. 2 also shows that AOS starts at −1.9, increases rapidly to approximately 0.28 due to acidification, decreasing again to the initial value and then increases to 0.25 and remains almost constant during the phototreatment. 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 (Sarria et al., 2002).

The $BOD_5$/COD ratio has been established as a more reliable parameter to evaluate the biodegradability (Marco et al., 1997; Esplugas et al., 2004; Metcalf and Eddy, 2005), as it is not affected either by the amount or by the oxidation state of organic matter (Amat et al., 2009). Fig. 3 shows a very important increase of $BOD_5$/COD ratio (from 0.07 to 0.44), suggesting that photo-oxidation enhanced significantly the biodegradability. The OUR/$OUR_0$ profile shows also the same trend, showing a high increase after 155 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 six times when compared with the raw leachate ($OUR_{raw\ leachate} = 1.04 \times 10^{-3}$ mol $O_2$ $mol^{-1}$ C $h^{-1}$), 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. 4), shows a similar profile, leading to 78% reduction after 155 mM of $H_2O_2$ consumed, and only more 12% until the end of the experiment (204 mM).

According to the Zahn–Wellens test (Fig. 5), which involves longer periods of contact (28 days) of the sample with microorganisms to allow some adaptation of the biomass, the first four samples (non-treated, after pH adjustment, after iron addition and after 22 mM $H_2O_2$ consumed) present a poor biodegradation level, between 14 and 20%. However, as expected, the biodegradability of the leachate was enhanced during the photo-Fenton treatment and a value higher than 70% biodegradation after 28 days was achieved for sample 10. Although sample 10 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 $H_2O_2$ consumption of 54%, 47% and 22%, relatively to sample 10.

The high concentration of nitrogen in landfill leachates constitutes, beyond the presence of recalcitrant carbon compounds, a big environmental concern that must be solved. The concentration profiles of nitrate, nitrite, ammonium and total nitrogen during the photo-Fenton reaction are shown in Fig. 6. The total nitrogen concentration, after a first decrease

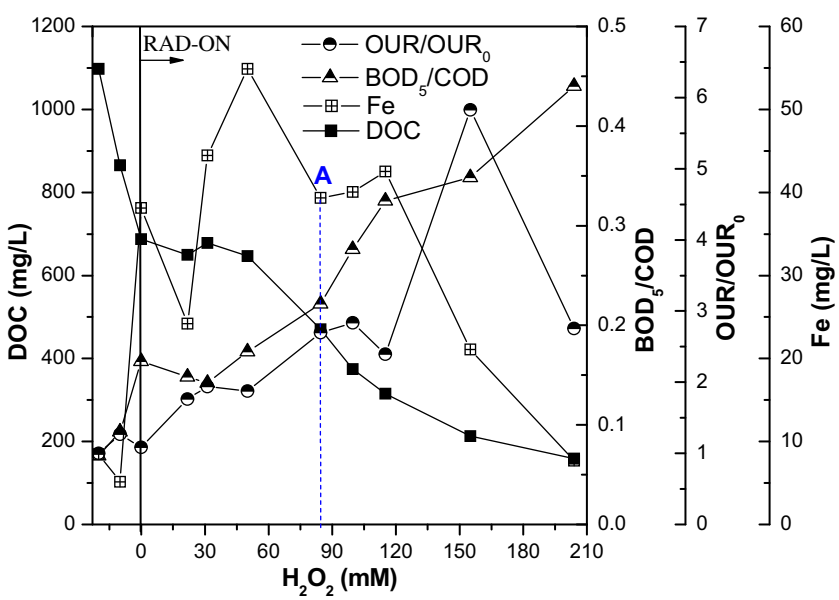


**Fig. 3 – DOC, $BOD_5$/COD ratio, OUR/$OUR_0$ and Fe concentration evolution as a function of the hydrogen peroxide consumption during the photo-Fenton process.**

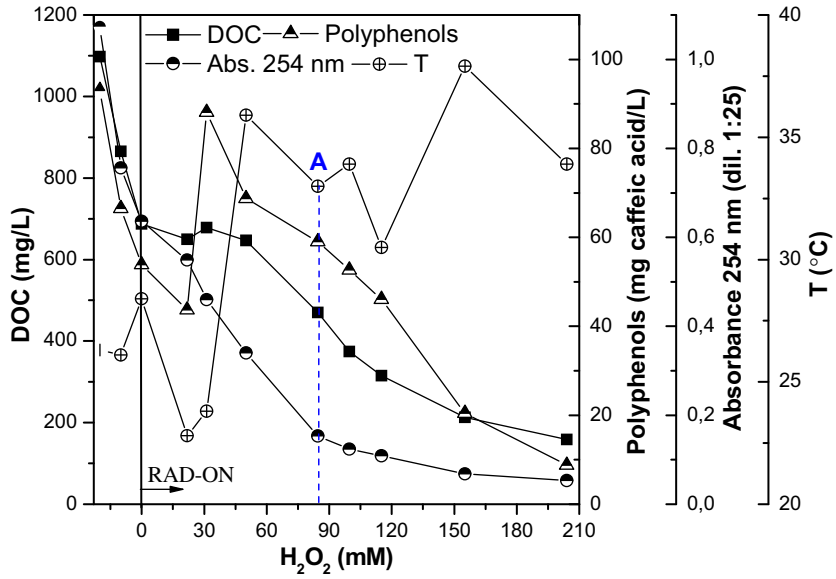


**Fig. 4 – DOC, polyphenols concentration, absorbance at 254 nm and temperature evolution as a function of the hydrogen peroxide consumption during the photo-Fenton process.**

during the acidification process, maybe due to retention of nitrogenated compounds in the foam formed, returned to the initial value (between sample 4 and 5) and remained approximately constant during the photo-Fenton reaction (≈1.7 g N $L^{-1}$).

The high concentration of nitrite (≈469 mg N–$NO_2^-$ $L^{-1}$) can be justified by the nitrification/denitrification stages in the biological system installed in the sanitary landfill, taking into consideration that leachate samples used for the experiments performed in this work were collected after the biological process. However, almost all nitrite were easily oxidized to nitrate after acidification. The leachate presents initially a low concentration of nitrates (86 mg N–$NO_3^-$ $L^{-1}$) that increased abruptly to ~1178 mg N–$NO_3^-$ $L^{-1}$ at sample 4 (22 mM of $H_2O_2$ consumed) and remained approximately constant until the end of the experiment. This behavior is explained by the nitrite conversion into nitrate and by the conversion of organic nitrogen into ammoniacal nitrogen, which remained approximately constant between 115 and 154 mg N–$NH_4^+$ $L^{-1}$, and then into $NO_3^-$. The oxidation of ammonia to nitrate was also observed during the photo-Fenton process applied to a bio-recalcitrant industrial compound, α-methylphenylglycine (Oller et al., 2007).

After sample 6, the organic nitrogen remained approximately constant (360 mg N $L^{-1}$), which corresponds to the

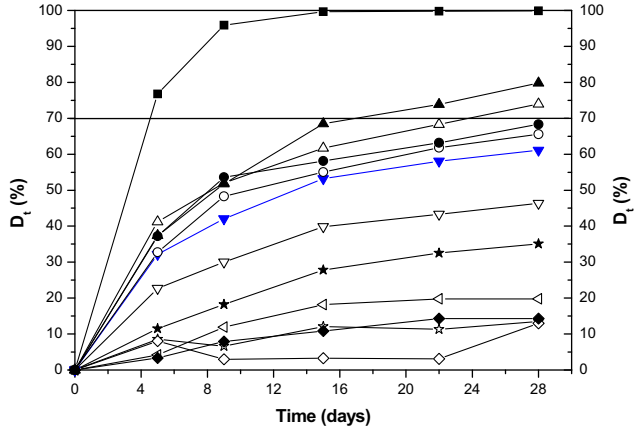


**Fig. 5 – Zahn–Wellens test for samples taken during the photo-Fenton process (initial sample is also showed, as the reference): ☆ – $S_1$, DOC = 1098 mg $L^{-1}$; ◁ – $S_2$, DOC = 865 mg $L^{-1}$; ◇ – $S_3$, DOC = 688 mg $L^{-1}$; ◆ – $S_4$, DOC = 650 mg $L^{-1}$; ★ – $S_5$, DOC = 678 mg $L^{-1}$; ▽ – $S_6$, DOC = 647 mg $L^{-1}$; ▼ – $S_7$, DOC = 470 mg $L^{-1}$; ○ – $S_8$, DOC = 374 mg $L^{-1}$; ● – $S_9$, DOC = 315 mg $L^{-1}$; △ – $S_{10}$, DOC = 213 mg $L^{-1}$; ▲ – $S_{11}$, DOC = 158 mg $L^{-1}$; ■ – Reference.**

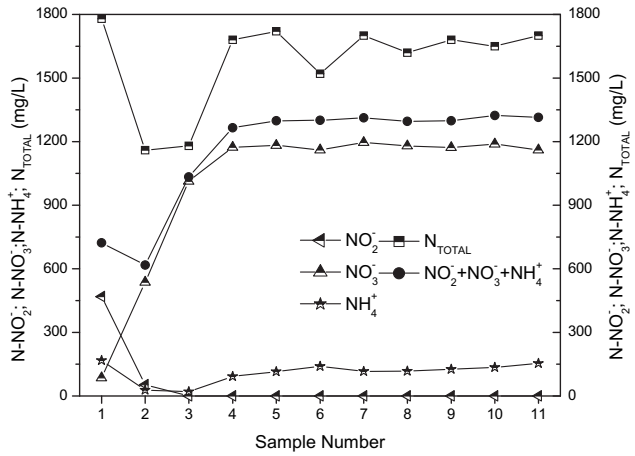


**Fig. 6 – Profile of nitrate, nitrite, ammoniacal nitrogen and total nitrogen concentration during the photo-Fenton process.**

difference between the total nitrogen and the sum of nitrites, nitrates and ammoniacal nitrogen. It seems that between sample 1 and 6 (50.2 mM of $H_2O_2$ consumed), 700 mg of organic nitrogen per liter was converted into ammonia, and then into nitrite and nitrate. Approximately 90% of the organic nitrogen converted to ammonia was due to leachate acidification to pH 2.8.

The concentration profile of $Cl^-$, $SO_4^{2-}$, $PO_4^{3-}$ ions and total phosphorous are presented in Fig. 7. The chloride concentration in solution decreased sharply from 3.8 g $L^{-1}$ to 2.2 g $L^{-1}$, after the acidification process, possible due to the retention in the foam formed, but it was gradually released into the solution, remaining almost constant during the photo-Fenton reaction at 3.2 g $L^{-1}$.

The sulfate concentration increased drastically after the addition of sulfuric acid for the acidification of leachate to pH ≈ 2.8 and addition of iron sulfate, and remained constant during the reaction (2.6 g $L^{-1}$).

The concentration of total phosphorous and phosphates remained approximately constant during the photo-Fenton treatment at 1 mg P–$PO_4^{3-}$ and 11.6 mg P $L^{-1}$, respectively.

### 3.4. *Evaluation of biological nitrification and denitrification*

In order to evaluate the optimal phototreatment time to reach a biodegradable effluent and nitrogen removal by a biological nitrification–denitrification system, another photo-Fenton experiment was carried out in order to get a photo-treated leachate with a residual organic carbon of 446 mg $L^{-1}$, 324 mg $L^{-1}$ and 220 mg $L^{-1}$, which corresponds to the more biodegradable samples, 7, 9 and 10 of the Zahn–Wellens test. After the pre-oxidation, the pre-treated leachate was neutralized to pH 7, leading to iron precipitation as $Fe(OH)_2$, and after iron sludge removal, the wastewater was introduced into the biological system constituted by a conditioner tank and IBR previously colonized by activated sludge from a municipal WWTP. A volume of 60 L of the pre-treated leachate (DOC = 324 mg $L^{-1}$) and 10 L of suspended biomass resulted from the inoculation suspension (DOC = 1150 mg $L^{-1}$, resulting from the use of methanol during the adaptation period), were added to the biological reactor.

Fig. 8 presents the evolution of DOC, $NH_4^+$, $NO_3^-$ and total nitrogen concentration during the denitrification process. It can be seen an increase in DOC due to the addition of 10 L of suspended biomass and a decrease of total nitrogen and nitrates due to dilution and adsorption of nitrogenated organic compounds on the biomass. During the first three days, almost no denitrification was observed, but almost all the DOC present initially in the pre-treated leachate was consumed. After the first addition of methanol (370 mL, 0.96 g $cm^{-3}$) on the third day (point a), a decay ratio of 312 mg C $day^{-1}$ and 175 mg N–$NO_3^-$ $day^{-1}$, which is equivalent to 4.75 mg $CH_3OH$ per mg N–$NO_3^-$ (2.48 mg $NO_3^-$ per mg C), was observed. Fig. 8 also shows a small decay of ammonia along the denitrification process. Between the 9th and 14th days the DOC remained almost constant, meaning that this residual organic carbon (120 mg C $L^{-1}$) is not biodegradable by this kind of biomass. Another addition of methanol (25 mL, point b) was enough to eliminate all the nitrates present in the photo-treated leachate.

The second experiment was performed with a photo-treated leachate (446 mg $L^{-1}$, point 7), in order to study the denitrification and nitrification processes and to evaluate the biodegradability of all organic carbon. In this case, the mass ratio between methanol and nitrate obtained was to 3.6 mg $CH_3OH$ per mg N–$NO_3^-$ achieving the same final residual DOC of 120 mg $L^{-1}$.

After complete removal of nitrates (1st denitrification step), aeration was promoted in order to have sufficient oxygen to perform a nitrification cycle. This test was performed in winter, at an average temperature of 13 °C. In these conditions almost no nitrification occurred during 20 days. So, it was decided to collect 4 L of the wastewater and perform the study at controlled temperature (23 °C) and aeration conditions.

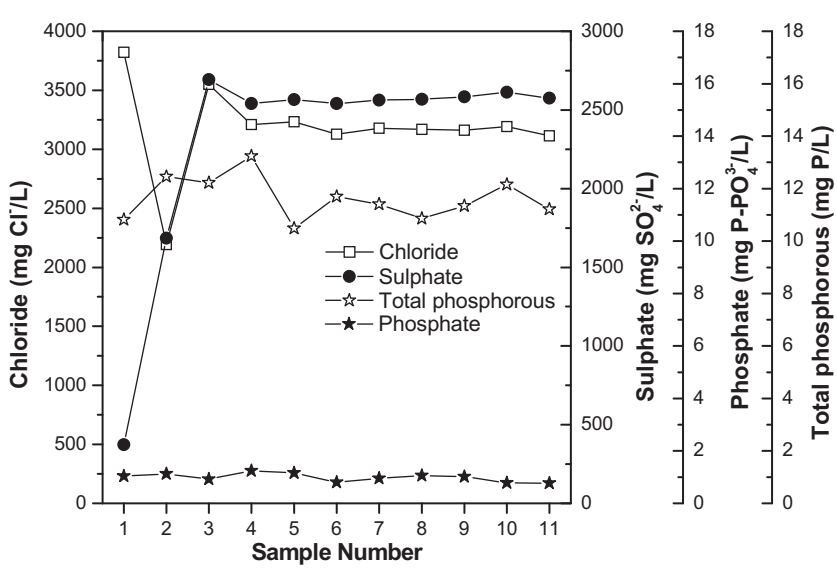


**Fig. 7 – Profile of chloride, sulfate, phosphate and total phosphorous concentration during the photo-Fenton process.**

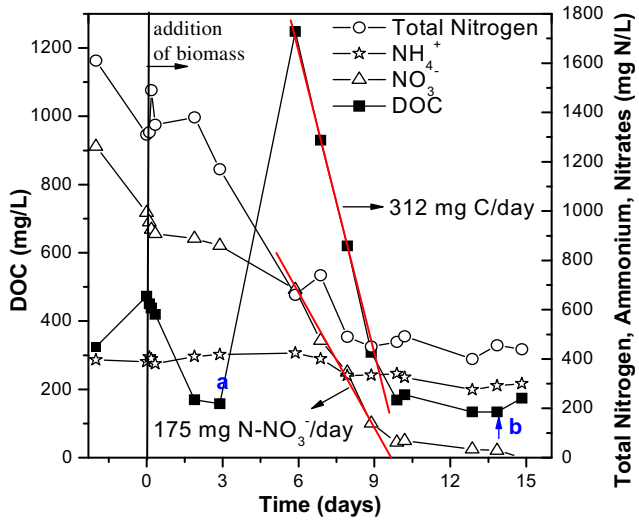


**Fig. 8 – Evolution of total nitrogen, nitrate, nitrite, ammonia and DOC concentration during the biological denitrification of the photo-treated leachate (initial DOC of 324 mg $L^{-1}$).**

Ilies and Mavinic (2001) showed that decreasing the temperature from 20 to 10 °C, nitrification and denitrification processes suffered major inhibition. Isaka et al. (2007) showed that using nitrifying bacteria entrapped in a gel carrier increased the nitrification rates at low temperatures (0.71 kg N $m^{-3}$ $day^{-1}$ at 10 °C, DO > 7 mg $L^{-1}$, 7.5 < pH < 8.0). However, ammonium nitrogen at low concentrations was detected in the effluent, showing that cultivated ammonium-oxidizing bacteria at low temperatures had low affinity for ammonium nitrogen.

Fig. 9 shows that after four days of adaption period, the ammonia removal rate was 87 mg $NH_4^+$ per day (68 mg $N–NH_4^+$ per day), converted into 90.1 mg $NO_3^-$ per day (20.3 mg $N–NO_3^-$ per day) and 33 mg $NO_2^-$ per day (10 mg $N–NO_2^-$ per day), which leads to the ratios 3.4 mg $N–NH_4^+$ $mg^{-1}$ $NO_3^-$ and 6.8 mg $N–NH_4^+$ $mg^{-1}$ $N–NO_2^-$. At the end of the nitrification reaction 305 mg $N–NH_4^+$ $L^{-1}$ were converted into 43 mg $N–NO_2^-$ $L^{-1}$ and 178 mg $N–NO_3^-$ $L^{-1}$, which means that approximately 170 mg N were converted into $N_2$, consuming 33 mmol of NaOH per liter (1.3 g NaOH per liter). After the nitrification cycle, a second denitrification cycle was performed adding 3.4 mL of methanol at point a and 0.2 mL of methanol at point b, obtaining a denitrification ratio of approximately 3 mg $CH_3OH$ per mg of ($N–NO_3^-$ + $N–NO_2^-$), which indicates that less carbon is needed for reduction of nitrites instead of nitrates. Canziani et al. (2006) studied the nitrification and denitrification of old landfill leachates (0.2–4 g $N–NH_4^+$ $L^{-1}$, $T$ = 33 °C, pH = 8.0) showing that for values of DO between 0.2 and 0.5 mg $L^{-1}$, 90% oxidation of ammonia to nitrite was achieved. The impact of organic carbon on nitrification performance performed by Ling and Chen (2005) showed that 60–70% nitrification rate reduction was observed when COD/N ration increased from 0 to 3 ($T$ = 20 °C).

During nitrification, DOC removal is very slow, however, some of the organic carbon from the photo-treated leachate is eliminated during denitrification, leading to a final DOC of 86 mg $L^{-1}$ and final COD of 227 mg $O_2$ $L^{-1}$. Denitrification of the leachate consumed 27.5 mmol $H_2SO_4$ per liter.

A last denitrification/nitrification experiment was performed in a 4 L- suspended biomass reactor at temperature (22 °C) and aeration controlled conditions, using a photo-treated leachate with a residual DOC of 240 mg $L^{-1}$, which is equivalent to sample 10 of the biodegradability tests (Fig. 10). In this case the C/N ratio obtained for the denitrification reaction was 2.8 mg $CH_3OH$ per mg $N–NO_3^-$ (points a, b, c and d indicate the addition of 15, 5, 5 and 2.5 mL of methanol), which is similar to the ratios reported by Kulikowska and Klimiuk (2004), 2.43 g $CH_3OH$ $g^{-1}$ $N–NO_3$ (3.6 g COD $g^{-1}$ $N–NO_3$), and Christensson et al. (1994), 2.8–3.0 g $CH_3OH$ $g^{-1}$ $N–NO_3$ (4.5–4.1 g COD $g^{-1}$ $N–NO_3$), although those values are more than 2 times higher than the stoichiometric mass ratio between consumed

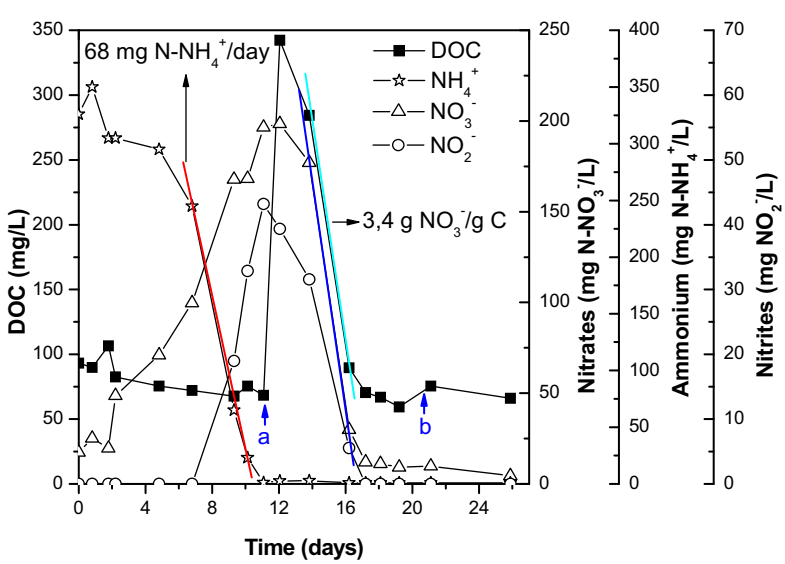


**Fig. 9 – Evolution of total nitrogen, nitrate, nitrite, ammonium and DOC concentration during the denitrification/nitrification of the photo-treated leachate (initial DOC of 446 mg $L^{-1}$).**

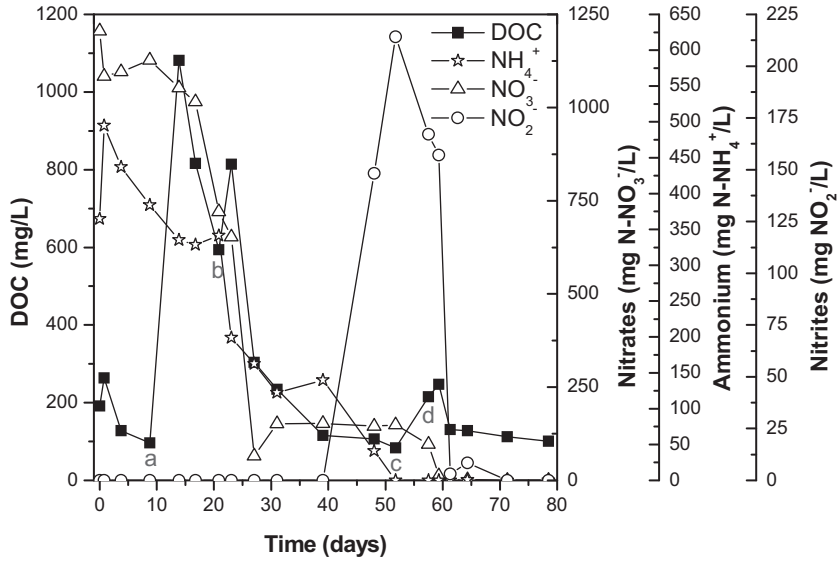


**Fig. 10 – Evolution of total nitrogen, nitrate, nitrite, ammonium and DOC concentration during the denitrification/nitrification of the photo-treated leachate (initial DOC of 220 mg $L^{-1}$).**

methanol-C and nitrate-N (C/N = 0.46) (Eqs. 4 and 5). Modin et al. (2007) showed that methane can be a potentially inexpensive carbon source for the denitrification of leachates, since methane is generated in landfills, although the use of methane for electricity generation, presence of hydrogen sulphide impurities and indirect methane oxidation when used for denitrification (Thalasso et al., 1997) can be negative points.

Considering the ratio above mentioned, the total denitrification of nitrates, considering the nitrates formed during the nitrification process, requires 4.4 g of methanol per liter of leachate or 4.6 mL of commercial methanol per liter of leachate.

It was observed a parallel nitrification reaction with a decay of 11.7 mg N–$NH_4^+$ per day even at very low oxygen concentrations (<0.2 mg $O_2$ $L^{-1}$). The absence of biodegradable carbon between days 30 and 50, stopped the denitrification reaction. Oxygen concentration was maintained between 0.5 and 2.0, and nitrification of the remaining ammonia is observed and consequently lead to the formation of nitrates and nitrites. After total elimination of ammonia, two more additions of methanol (points c and d), were sufficient for complete denitrification. In this experiment the lowest dissolved organic carbon concentration obtained was 83 mg $L^{-1}$.

According to these results, complete removal of ammoniacal nitrogen, nitrates and nitrites is possible for this pretreated leachate and sample 7 of the phototreatment can be considered the best one for the combination with a biological oxidation process. So, the optimal phototreatment energy estimated to reach a biodegradable effluent is 29.2 $kJ_{UV}$ $L^{-1}$ (3.3 h of photo-Fenton at a constant solar UV power of 30 W $m^{-2}$), consuming 90 mM of $H_2O_2$ when used in excess,

**Table 2 – Landfill leachate characteristics at the best phototreatment time and discharge limits (Decree n. 236/98).**

| Parameter | LOPT | LPBT | DLPL | DLBL | DLUL | DLCHL |
|---|---|---|---|---|---|---|
| pH | 2.9 | 7.0 | 6.0–9.0 | 6.0–8.5 | 6–9 | 5.5–8.5 |
| $BOD_5$, 20 °C (mg $O_2$ $L^{-1}$) | 260 | – | 40 | 120** | 220 | 20 |
| COD (mg $O_2$ $L^{-1}$) | 1174 | 227 | 150 | 360** | – | 60 |
| DOC (mg C $L^{-1}$) | 470 | 83 | – | – | – | – |
| Nitrite (mg N–$NO_2^-$ $L^{-1}$) | 0 | <0.5 | – | – | – | – |
| Nitrate (mg $NO_3^-$ $L^{-1}$) | 5300 | <5 | 50 | – | – | – |
| Ammoniacal nitrogen (mg N–$NH_4^+$ $L^{-1}$) | 149 | <1 | 10 | – | 10 | 12 |
| Total Nitrogen (mg N $L^{-1}$) | 1280 | <10 | 15 | 10 | – | 20 |
| Sulfate (g $SO_4^{2-}$ $L^{-1}$) | 2.6 | 2.6 | 2 | | – | – |
| Total phosphorous (mg P $L^{-1}$) | 11.4 | 7.0 | 10 | 1 | – | 1.5 |
| Phosphates (mg $PO_4^{2-}$ $L^{-1}$) | 2.9 | 2.0 | – | – | – | – |
| Polyphenols (mg caffeic acid $L^{-1}$) | 59 | – | – | – | – | – |
| Chloride (g $Cl^-$ $L^{-1}$) | 3.2 | 3.2 | – | – | – | – |
| Dissolved iron (mg $L^{-1}$) | 39.3 | <0.05* | 2* | 10 | – | 5 |

*Total iron; **Flow rates between 200 and 1000 $m^3$/day; LOPT-Leachate at the Optimum Phototreatment time; LPBT-Leachate Photo-Bio-Treated; DLPL-Discharge Limits in the Portuguese legislation (Decree no 236/98); DLUL-Discharge Limits in the Brazilian legislation (Portaria 05/89, 1989); DLUL-Leachate Discharge Limits in USA Legislation (EPA, 2000); DLCHL-Discharge Limits in Chinese Legislation (Bureau, 2002).

which means almost 57% mineralization of the leachate, 57% reduction of polyphenols concentration and 86% reduction of aromatic content.

Although total nitrogen removal was achieved using a nitrification/denitrification process, aeration and an external organic carbon source are needed. A promising process, called *Anammox*, can save up to 90% of operation costs as compared to the traditional nitrogen removal process (Jetten et al., 2001), since in this case microbial oxidation of ammonium with nitrite to nitrogen gas occurs under strict anoxic conditions, and no organic carbon source is needed (Graaf et al., 1996; Strous et al., 1998). Liu et al. (2010) used shortcut nitrification combined with *Anammox* for treating diluted effluent from an UASB reactor fed by landfill leachate and found an average total inorganic nitrogen removal efficiency of 87%.

Table 2 compares the characteristics of the photo-bio-treated leachate with the discharge limits according to the Portuguese, Chinese, Brazilian and USA Legislation. Sulfate ions concentration greatly exceeds the discharge limits imposed by Portuguese legislation. COD is also another parameter that exceeds the discharge limits imposed by Portugal and China, although accomplishes Brazilian regulations. However, considering the complex nature of leachates, higher discharge limits can be stipulated, as recommended by EPA, that allows $BOD_5$ values of 220 mg $O_2$ $L^{-1}$.

## 4. Conclusions

Leachate from landfills usually has high content of pollutants, especially recalcitrant organic compounds, as humic and fulvic acids, xenobiotics, pesticides, and other harmful substances, that result in environment pollution problems.

The solar photo-Fenton process was found to be very efficient in the treatment of leachates, enhancing the biodegradability of the leachate and making possible a subsequent treatment by a biological oxidation process. Biological nitrogen removal was achieved by a two-step process: aerobic nitrification of ammonia to nitrite and then to nitrate followed by anoxic denitrification of nitrate to nitrite, nitric oxide, nitrous oxide and nitrogen gas using an external carbon source.

## Acknowledgments

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