



## Research article

## Insights into solar photo-Fenton reaction parameters in the oxidation of a sanitary landfill leachate at lab-scale



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## ABSTRACT

This work evaluates the effect of the main photo-Fenton (PF) reaction variables on the treatment of a sanitary landfill leachate collected at the outlet of a leachate treatment plant, which includes aerated lagooning followed by aerated activated sludge and a final coagulation-flocculation step. The PF experiments were performed in a lab-scale compound parabolic collector (CPC) photoreactor using artificial solar radiation. The photocatalytic reaction rate was determined while varying the total dissolved iron concentration (20–100 mg Fe<sup>2+</sup>/L), solution pH (2.0–3.6), operating temperature (10–50 °C), type of acid used for acidification (H<sub>2</sub>SO<sub>4</sub>, HCl and H<sub>2</sub>SO<sub>4</sub> + HCl) and UV irradiance (22–68 W/m<sup>2</sup>). This work also tries to elucidate the role of ferric hydroxides, ferric sulphate and ferric chloride species, by taking advantage of ferric speciation diagrams, in the efficiency of the PF reaction when applied to leachate oxidation. The molar fraction of the most photoactive ferric species, FeOH<sup>2+</sup>, was linearly correlated with the PF pseudo-first order kinetic constants obtained at different solution pH and temperature values. Ferric ion speciation diagrams also showed that the presence of high amounts of chloride ions negatively affected the PF reaction, due to the decrease of ferric ions solubility and scavenging of hydroxyl radicals for chlorine radical formation. The increment of the PF reaction rates with temperature was mainly associated with the increase of the molar fraction of FeOH<sup>2+</sup>. The optimal parameters for the photo-Fenton reaction were: pH = 2.8 (acidification agent: H<sub>2</sub>SO<sub>4</sub>); T = 30 °C; [Fe<sup>2+</sup>] = 60 mg/L and UV irradiance = 44 W<sub>UV</sub>/m<sup>2</sup>, achieving 72% mineralization after 25 kJ<sub>UV</sub>/L of accumulated UV energy and 149 mM of H<sub>2</sub>O<sub>2</sub> consumed.

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## 1. Introduction

Leachate treatment plant (LTP) design constitutes nowadays a challenge for environmental engineers, mainly due to the recalcitrant character of leachates with high organic (e.g. humic and fulvic acids) and inorganic contaminants concentration (e.g. ammonium nitrogen, heavy metals) (Christensen et al., 2001; Öman and Junestedt, 2008). Normally, resulting in a complex LTP to achieve a final wastewater with quality enough to be discharged into

receiving water bodies, at comfortable costs, without the generation of further wastes. LTP normally combines different processes, as: (i) conventional combined treatment with domestic sewage or recycling back the treated effluent to the landfill; (ii) aerobic and anaerobic biological processes; (iii) chemical and physical methods (flotation, coagulation/flocculation, adsorption, chemical precipitation, chemical oxidation, ammonium stripping and ion exchange); (iv) membrane filtration (microfiltration, ultrafiltration, nanofiltration and reverse osmosis); (v) advanced oxidation processes – AOPs (TiO<sub>2</sub>/UV, H<sub>2</sub>O<sub>2</sub>/UV, Fenton (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>)/photo-Fenton (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV)/electro-Fenton/electro-photo-Fenton, ozone (O<sub>3</sub>, O<sub>3</sub>/UV, and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>), etc.) (Abu Amr and Aziz, 2012; Deng and Englehardt, 2008; Hermosilla et al., 2009; Panizza and Martinez-Huitle, 2013; Renou et al., 2008; Rocha et al., 2011; Umar et al.,

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2010; Wu et al., 2004).

The photo-Fenton reaction has been proposed as a good option for biodegradability enhancement of old recalcitrant leachates from sanitary landfills, being possible to couple it with a further biological process to achieve the discharge limits (Cortez et al., 2011; de Morais and Zamora, 2005; Li et al., 2009; Umar et al., 2010; Vilar et al., 2011b, 2012b).

Vilar and co-workers (Silva et al., 2013a, 2013b, 2013c) presented the first results at pre-industrial plant scale for the treatment of leachates after lagooning, by combining a solar photo-Fenton oxidation process using 39.52 m<sup>2</sup> of compound parabolic collectors (CPCs) and an aerobic/anoxic biological system (3.5 m<sup>3</sup> capacity). According to the results obtained, two of the main observed drawbacks were related to: (i) the inner filter effect consisting in the absorption of photons by other absorbing species, mainly humic acids, associated with the dark-brown colour intrinsic to leachates; and (ii) the high amount of suspended solids generated during the acidification step required by the photo-Fenton reaction, due to the precipitation of some organic compounds with ferric ions. The high amount of suspended solids decreases the light penetration, competes with H<sub>2</sub>O<sub>2</sub> and iron species as photons absorbers, and leads to a high consumption of H<sub>2</sub>O<sub>2</sub> during the phototreatment due to the oxidation of particulate organic matter. Considering these aspects, a preliminary physico-chemical process can be a good option to significantly reduce the organic load (through the sludge production) and the light absorption species, boosting the phototreatment efficiency.

This study mainly focuses on the optimization of sanitary landfill leachate treatment, collected at the outlet of a LTP, which includes biological oxidation and physico-chemical processes, by a photo-Fenton reaction mediated by artificial solar radiation, taking into account the (i) total dissolved iron (TDI) concentration, (ii) solution pH, (iii) operating temperature (T), (iv) type of acid used in the acidification, and (v) UV irradiance (I). Simultaneously, the role of ferric hydroxides, ferric sulphate and ferric chloride complexes, in the PF reaction efficiency, was assessed through the use of ferric ion speciation diagrams, taking into account the solution pH, temperatures and acid type used in the acidification step.

## 2. Experimental

### 2.1. Sanitary landfill leachate samples

Leachate samples were collected at the outlet of a LTP, from a Municipal Solid Waste Sanitary Landfill located in northern Portugal, receiving on average 150 m<sup>3</sup> of leachate per day, which comprises the following treatment units: (i) an aerated lagoon with pure oxygen injection (15,000 m<sup>3</sup>); (ii) an anoxic and an aerobic activated sludge reactors (150 m<sup>3</sup> each); (iii) a coagulation/flocculation tank (27 m<sup>3</sup>) and (iv) a final retention lagoon (3000 m<sup>3</sup>). The treated leachate is transported to a municipal WWTP since it does not meet the Portuguese discharge regulations into sewerage systems and water bodies (Decree-Law no. 236/98 – Table 1). Table 1 presents the main physico-chemical characteristics of the leachate used for the photo-Fenton oxidation tests.

### 2.2. Chemicals

Photo-Fenton experiments were performed using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, Quimitecnica SA, 50% (w/v), 1.10 g/cm<sup>3</sup>), iron (II) sulphate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O, Panreac), as iron source, sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, Pronalab, 96%, 1.84 g/cm<sup>3</sup>), hydrochloric acid (HCl, Merck, 37%, 1.16 g/cm<sup>3</sup>) and sodium hydroxide (NaOH, Merck).

### 2.3. Analytical determinations

All the analytical methods employed in this work are detailed described in the [Supplementary Material \(SM\) \(Table SM-1\)](#).

### 2.4. Lab-scale photoreactor

The photo-Fenton experiments were carried out in a lab-scale photoreactor equipped with a sunlight simulator. A schematic representation of the prototype and its detailed description can be seen in [Soares et al. \(2014\)](#) and in the [Supplementary Material \(Fig. SM-1\)](#). The UV radiation intensity was measured by a broadband UV radiometer (Kipp & Zonen B.V., model CUV5) placed inside the sunlight simulator at the same level as the photoreactor center. The radiometer was plugged to a handheld display unit (Kipp & Zonen B.V., model Meteon), in order to record the incident irradiance (W/m<sup>2</sup>). The total amount of accumulated UV energy ( $Q_{UV,n}$  kJ/L) can be calculated using [Eq. \(SM-1\)](#).

### 2.5. Photo-Fenton experimental procedure

Regarding the photo-Fenton reactions experimental procedure, the recirculation glass vessel of the lab-scale prototype (see [Fig. SM-1](#)) was filled with 1-L of pre-treated leachate, which was homogenized (magnetic stirrer) and recirculated through the CPC unit during ca. 30 min in the darkness. Then, a first sample was taken. Meanwhile, the temperature set-point of the refrigerated thermostatic bath was adjusted to keep the leachate in the intended temperature (10, 20, 30, 40 or 50 °C). After that, the SUNTEST was switched on (keeping the photoreactor covered with an aluminium sheet) and the irradiance was set at 250, 500 and 750 W/m<sup>2</sup>, which is equivalent to 22, 44 and 68 W<sub>UV</sub>/m<sup>2</sup>, measured in the wavelength range 280–400 nm. Then, the leachate was acidified with H<sub>2</sub>SO<sub>4</sub>, HCl or H<sub>2</sub>SO<sub>4</sub> + HCl until the desired pH (2.0, 2.4, 2.8, 3.2 and 3.6) and ferrous sulphate was added to achieve the concentrations of 20, 40, 60, 80 and 100 mg/L, taking into account its initial content of dissolved iron. After about 10 min, a second sample was taken for TDI concentration control. Finally, the CPC was uncovered and the first dose of H<sub>2</sub>O<sub>2</sub> was added to start the photo-Fenton reaction. Additional samples were taken at pre-defined times, in order to follow-up the degradation process. The concentration of H<sub>2</sub>O<sub>2</sub> was maintained in excess, between 200 and 500 mg/L, during the entire reaction, by adding the amounts required to compensate the consumed ones, as indicated by the analyses performed throughout the experiments. The operational conditions used in the experiments are presented in [Table SM-2](#).

### 2.6. Ferric ion speciation diagrams

The iron (III) speciation diagrams were obtained from the chemical equilibrium modelling system MINEQL+ ([Schecher and McAvoy, 2007](#)), taking into account (i) the formation of Fe(OH)<sub>3</sub> (s) and (ii) the equilibrium constants related to the complexes iron–water, iron–sulphate and iron–chloride, as well as (iii) the respective reaction enthalpies.

## 3. Results and discussion

### 3.1. Leachate characterization

The leachate shows an intense yellow-brown colour associated to the high concentration of humic substances (HS), as reported in a previous study, achieving values near 1.2 g C<sub>HS</sub>/L for a raw leachate ([Silva et al., 2013c](#)). It is also characterized by a high organic content (DOC = 848–860 mg C/L, COD = 2.5–2.8 g O<sub>2</sub>/L), with low

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