Elsevier Editorial System(tm) for Chemical Engineering Journal
Manuscript Draft

Manuscript Number: CEJ-D-13-04923R2

Title: Detailed treatment line for a specific landfill leachate remediation. Brief economic assessment.

Article Type: SI:JEP-2013

Keywords: Leachate treatment; solar photo-Fenton; wastewater treatment strategy

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Response to Reviewers: We have rewritten Highlights, attending to referee 1.

Detailed treatment line for a specific landfill leachate remediation. Brief economic assessment.

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Abstract

Landfill leachate is regarded as a great threat to environment and its remediation is very complicated task due to its recalcitrant nature.. Consequently, strategies based on integrated physic-chemical–biological techniques must be evaluated. This work propounds a combined treatment line for a particular landfill leachate, consisting of a preliminary physic-chemical stage followed by an Advanced Oxidation Processes (AOPs) by means of solar photo-Fenton and a final conventional biotreatment. Additionally, an economic evaluation of the proposed treatment line is presented. The results obtained for a landfill leachate sample containing a high organic load (landfill leachate of around 40 g/L as COD and 15 g/L as DOC) revealed that this technologies combination is effective reducing recalcitrant organic content after the conditioning step (17% DOC removal), requiring then a solar photo-Fenton (Fe 1 mM) treatment time of 11 h that generates a non-toxic and biodegradable effluent Mineralization percentage needed to achieve an appropriate biodegradability was 27%, requiring a consumption of 22 g H_2O_2 /L. Totals costs have been assessed in around 40 €/m^3.

Introduction

Landfilling is the most widespread method for municipal solid waste (MSW) disposal, receiving up to 95% solid residues worldwide [1]. As a result of percolation of rainfall combined with degradation of the organic fraction and other compounds transfer, deposits of wastewaters are generated. Such effluents are considered to be highly threatening to environment and human health due to the presence of highly hazardous substances. In addition to leachate's inherent complexity, its quality is greatly dependent on diverse factors such as age, precipitation, seasonal weather variation, waste type and surrounding population [2]. Thus, it is understandable that strict

legislation is required to guarantee proper waste disposal and landfill management. In this sense the Council Directive 1999/31/EC of 26 April 1999 aims to prevent or reduce as far as possible adverse effects of the landfill waste on the environment, in particular on surface water, groundwater, soil, air and human health [3].

Conventional biological treatments and classical physic-chemical methods were regarded as the most appropriate technologies for landfill leachate management [2, 4, 5]. However, biological treatment is hampered by toxic substances, the presence of biorefractory compounds and the limited amount of biodegradable organics (especially in the case of stabilized landfills) [2, 4, 5]. On the other hand, traditional leachate treatment methods, such as air stripping, coagulation, flocculation and settling, are often costly in terms of initial outlay of plant equipment, energy requirements and frequent use of additional chemicals. For instance, coagulation–flocculation has some disadvantages such as the production of a consistent volume of sludge and an increase in the aluminum or iron concentration in the liquid phase [4]. Other methods, such as reverse osmosis or active carbon adsorption, only transfer the pollution and do not solve the environmental problem [5]. In recent years, Advanced Oxidation Processes (AOPs) have been proposed as an effective alternative for mineralization of recalcitrant organics in landfill leachate. For instance, solar photo-Fenton process was tested at pilot-plant scale achieving mineralization levels of 40%, as well as reductions of polyphenols concentration and aromatic content of 82% and 83%, respectively [6]. Fenton oxidation was also used for mature, heavily polluted landfill leachate achieving COD removals of 60-86% [7-9]. Additionally, a recent review has been published regarding the trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate [10].

Another reported treatment is ozone under different conditions: alone, in combination with hydrogen peroxide and O_3/UV. In these cases landfill leachate's biodegradability was enhanced because toxic compounds were decomposed by means of ozonation as a pre-treatment step [11,12]. Electrochemical oxidation was successfully tested for landfill leachate remediation attaining high Chemical Oxygen Demand elimination [13] (73% of COD removal). Finally, it has been also reviewed that the use of membrane technologies (nanofiltration and ultrafiltration and, more especially, reverse osmosis (RO)), either as a main step in a landfill leachate treatment chain or as a single post-treatment step has shown to be an indispensable means of achieving purification [14].

However, these treatments are not economically acceptable for application to large-scale effluents treatment. Hence, strategies based on integrated chemical–physical–biological processes must be studied as they can ameliorate the drawbacks of individual processes, improving the overall treatment efficiency. For example, a significant decrease in overall leachate treatment costs could be achieved by combining AOPs with a biological process [15]. Other reported combinations are solar photo-Fenton and biological treatment [6, 16]. In both cases, solar photo-Fenton process enhanced landfill leachate's biodegradability enabling a later biological oxidation. Vilar et al. [17-19] have recently published interesting papers dealing with highly biorecalcitrant leachates coming from an aerated lagoon in which the effluent had been previously biotreated. No physicochemical pre-treatment was applied before solar photo-Fenton and therefore, a substantial mineralization (>70%) was needed to reach the biodegradability threshold. The main drawback was that this point was reached after a very long adaptation period (more than 20 days) which is too long for the implementation of a biodegradation process. Besides, solar photo-Fenton carries high operation costs and treatment times must be reduced. However, solar photo-Fenton carries high operation costs and

treatment times must be reduced. In this sense, this work presents a combined treatment line for a particular landfill leachate consisting of a preliminary physic-chemical stage followed by an oxidation process by means of solar photo-Fenton and a final step based on a toxicity and biodegradability assessment, with the aim of coupling those processes with a conventional biological oxidation. As far as we know, a three-step remediation strategy based on pilot scale studies has not been yet reported. Additionally, real wastewaters have a variable nature and, in any case, preliminary studies are necessary when combining several technologies for decontamination or reuse of a specific industrial wastewater in order to prove their compatibility. Consequently, bench-scale and pilot-plant studies are required to develop these technologies and generate information on new industrial wastewater treatment processes.

Finally, an economic evaluation of the associated costs based on main operation parameters is presented for the proposed treatment line.

Materials and methods

1. Landfill leachate characterization. Reagents and chemicals

Two different samples, collected from the same landfill site, have been studied (LL1 and LL2). The leachate's samples characterization provided the results shown in table 1. In general, this real wastewater presents quite high values of Chemical Oxygen Demand (COD) and Dissolved Organic Carbon (DOC), and small amounts of total iron, which could help in a previous physic-chemical pre-treatment. While LL1 is a little toxic and it presents a low biodegradability, LL2 cannot be considered toxic but it was not biodegradable. Although both fractions seemed to have similar characteristics, important differences in toxicity and biodegradability were observed. This is probably

due to the fact that the samples were collected at different seasons, and landfill leachate's nature is strongly dependent of the mentioned factors. In addition, the organic nature of DOC and COD was unknown, but the results pointed out that it was more biorecalcitrant in the case of the second sample.

Table 1. Landfill leachates characterization (samples were not diluted for analytical determinations).

	LL1	LL2
pH	7.6	7.4
Conductivity (mS/cm)	40	77
COD (g O_2/L)	34	43
DOC (g/L)	13	15
Total iron (mg Fe/L)	5.0	5.0
Na^+ (g/L)	30	32
NH_4^+ (mg/L)	960	440
K^+ (g/L)	5.0	5.7
Cl^- (g/L)	33	40
SO_4^{2-} (g/L)	15	16
Toxicity (% Inhibition)	62	50
Biodegradability (COD_b/COD)	0.2	0

Experiments were performed using reagent-grade ferric chloride ($FeCl_3 \cdot 6H_2O$) and hydrogen peroxide (30% w/v, reagent-grade), sulphuric acid and sodium hydroxide (for physic-chemical pre-treatment and pH adjustment), all provided by Panreac and Merck.

2. Experimental methodology

2.1. Analytical determinations

A Shimadzu TOC-V_{CSN} analyser, equipped with an autosampler ASI-5000A and coupled with a TNM-1 unit, was used for Dissolved Organic Carbon (DOC) determinations of the filtered samples (0.2μm syringe-driven filters). Anion concentrations were analysed with a Dionex DX-600 ion chromatograph system equipped with an autosampler (Dionex AS40), a quaternary gradient pump (Dionex

GP50), a thermostatic column oven (Dionex LC30) and a conductivity detector (Dionex ED50) using a Dionex Ionpac AS11-HC 4×250 mm column. The gradient program for anion determination was pre-run for 5 min with 20 mM NaOH, an 8-min injection of 20 mM of NaOH, and 7 min with 35 mM of NaOH, at a flow rate of 1.5 mL/min. Cationic concentrations were determined with a Dionex DX-120 ion chromatograph equipped with a Dionex Ionpac CS12A 4 mm×250 mm column. Isocratic elution was done with H_2SO_4 (10 mM) at a flow rate of 1.2 mL/min.

COD was determined using Merk Spectroquant kits (ref: 1.14541.0001). Total iron concentration was measured using the 1,10-phentranoline method following ISO 6332, and hydrogen peroxide concentration was analysed by using titanium (IV) oxysulfate following DIN 38402H15. Turbidity was measured in a Hach 2100N turbidimeter. Total suspended solids (TSS) and volatile suspended solids (VSS) were determined according to the American Standard Methods [20]. Conductivity was measured using a conductivity meter Crison GLP31.

2.2. Biodegradability and toxicity assays

Acute toxicity and short term biodegradability assays on conventional activated sludge were carried out in a BM-T respirometer (Surcis S.L.), which consists of a 1L capacity vessel, equipped with temperature and pH control system. It also has an oxygen probe (Stratos 2402 Oxy, Knick Elektronische Messgeräte GmbH & Co., Germany) for measurement of the activated sludge activity based on the oxygen uptake rate (OUR). Conventional activated sludge was provided by the municipal wastewater treatment plant of El Bobar (Almería). After reception, the sludge was characterized through concentrations of DOC, ammonium, nitrate and nitrite determinations, and TSS and VSS measurements, and it was left with aeration until achieving endogenous phase

For toxicity measurements, the respirometer was loaded with 1L of endogenous activated sludge containing 3-4 g VSS/L. Temperature was controlled at 20ºC and the system was continuously aerated and agitated. This analysis compares maximum bacteria oxygen uptake rate (OUR_{max}) in a reference with the target sample. The reference was 30 mL of distilled water with ½ g sodium acetate/g VSS. Then 30 mL of each sample were added to obtain the $OUR_{max\text{-}sample}$. When the sample contained ammonium, and in order to avoid nitrification, Allyl Thiourea (3mg/g VSS) was added 30 minutes before the beginning of the bioassay. The inhibition percentages were calculated using (Eq. 1)

$$\text{Inhibition (\%)} = 100x(1- OUR_{max\text{-}sample} / OUR_{max\text{-}ref}) \quad \text{(Eq. 1)}$$

For biodegradability assays, 1L of endogenous activated sludge was poured into the reactor and once temperature (20ºC) and dissolved oxygen values (saturated conditions) were stable, a volume of 50 mL of the sample was added. No other substances were necessary. Just in the case sludge had nitrifying activity, Allyl Thiourea was used as a nitrification inhibitor. The ratio COD/COD_b (total chemical oxygen demand/easily biodegradable chemical oxygen demand) allows assessing the percentage of COD_b removed from the total COD and, thus, the biodegradable character of the sample can be established. A sample is considered to be very biodegradable when COD/COD_b is greater than 0.8; biodegradable, when it is comprised between 0.7 and 0.8; slightly biodegradable when the ratio is 0.3-0.7 and non-biodegradable when it is lower than 0.3.

Long term biodegradability analyses were also performed by Zahn-Wellens test. Samples obtained during solar photo-Fenton treatment experiments were analysed by Zahn-Wellens according to the modified EC protocol, Directive 88/303/EEC (1992). In

this test, activated sludge from El Bobar (Almería), mineral nutrients and test material as sole carbon source were placed together in 0.25-L glass vessels equipped with agitation and aeration. Biomass concentration is marked by the protocol, as a function of the DOC value for the sample to be tested. The test lasted around 28 days and temperature was kept at 20–25ºC under diffuse illumination. Blanks were prepared using distilled water, mineral nutrients and a concentration of bacteria representative of the inoculum present in the test solutions. A vessel containing glucose (a well-known biodegradable substance recommended as a reference) was used to run a parallel test in order to check the activity of the activated sludge. Degradation was monitored by DOC determination of the filtered solution, daily or at others appropriate regular time intervals. The initial DOC was determined 3 hours after the test's beginning in order to detect adsorption of contaminants on the activated sludge.

Biodegradation percentage (D_t) was determined by Eq. (2)

$$D_t = \left(1 - \frac{C_t - C_B}{C_A - C_{BA}}\right) \cdot 100 \qquad \text{(Eq. 2)}$$

Where C_A and C_{BA} are the DOC values (mg C/L) in the mixture and in the blank measured 3 hours after de beginning of the experiment; and C_t and C_B are the DOC values (mg C/L) in the mixture and in the blank at the sampling time. The samples are considered to be biodegradable when D_t is higher than 70%.

2.3. Experimental equipment for photo-Fenton assays

Preliminary photo-Fenton tests for landfill leachate treatment were performed in a solar radiation simulator SUNTEST XLS+ Heraeus (ATLAS, Germany), equipped with a xenon lamp of 2.2 KW and a filter which allows radiation transmission between 290 and 750 nm. Lamp's power values can be adjusted from 250 to 765 W/m^2 (9% of this

radiation corresponds to UV-radiation comprised between 290 and 400 nm). During the experiments, radiation emission was kept at 765 W/m^2 (which corresponds to a radiation intensity of 69 W/m^2 in the UV range). Temperature was kept around 35ºC inside the solar simulator chamber.

Solar photo-Fenton treatment of landfill leachates at pilot plant scale were performed in a CPC solar photo-reactor installed in Plataforma Solar de Almería (PSA), using natural sun radiation. This prototype has an irradiated surface of 3 m^2. The CPC reflector is made of highly anodized aluminium. The CPC module has 12 borosilicate glass tubes and it is mounted on a metal frame tilted 37° (latitude of the PSA) and facing south. This pilot plant operates in batch mode. It has a total volume of 35 L (V_T) and a total illuminated volume inside the absorber tubes of 22 L (V_i). Wastewater was added to the recirculation tank of the CPC unit. If effluent's pH is not 2.8-2.9 it must be adjusted. Homogenisation is performed in darkness by turbulent recirculation during 15 min. Once checked that initial iron concentration (Fe^{3+}) was 1 mM or 2 mM, depending on the assay, hydrogen peroxide (30% w/v) was periodically added trying to maintain a relatively constant concentration throughout the experiment (700-1000 mg/L). Finally, the CPCs were uncovered and the photo-Fenton process started. Samples were taken at pre-defined times to evaluate the degradation process.

In addition, and with the objective of performing toxicity and biodegradability tests to partially treated samples only, a solar photo-Fenton experiment was performed by adding fixed doses of H_2O_2 and taking samples once this reagent was completely consumed.

Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3) mounted on a platform tilted 37º (the same angle as

the CPCs). With eq. (3), combination of the data from several days' experiments is possible.

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \cdot \frac{UV}{30} \cdot \frac{V_i}{V_T} \qquad \text{(Eq. 3)}$$

$$\Delta t_n = t_n - t_{n-1}$$

Where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation (λ<400 nm) measured between t_{n-1} and t_n, and t_{30W} is a "normalized illumination time". In this case, t_{30W} refers to a constant solar UV power of 30 W/m^2 (typical solar UV power on a perfectly sunny day around noon).

3. Results and discussion

3.1. Physic-chemical pre-treatment

Application of photo-Fenton process requires the lowest quantities of suspended solids as possible so that radiation penetration is favoured, and efficiency and operating costs could be highly reduced. Accordingly, a preliminary physic-chemical treatment of the received landfill leachates based on acidic pH and $FeCl_3$ additions was performed. Firstly, H_2SO_4 (96%) was added to decrease pH from 7 to 2.8-2.9 (optimal for photo-Fenton process). It provoked the coagulation of part of suspended solids and a change in the colour of the sample. Then, settled solids were removed and an initial amount of 2 mM Fe^{3+} (as $FeCl_3 \cdot 6H_2O$) was added, so a second coagulation took place and it was accompanied with COD, DOC and iron decrements. The same procedure was repeated and after several coagulation steps the final concentration of COD, DOC and dissolved iron (56-57 mg/L) were stable. Other tests were performed with flocculants as Ridexfloc 7408C (cationic) and Ridexfloc 7150A (anionic) of RIBA without any improvement in DOC removal (10 and 8%, respectively) compared with ferric chloride. Therefore, the intention was to remove as much organic matter along with suspended solids as

possible, finalizing with enough and stable dissolved iron (1 mM) to continue with the photo-Fenton process. Table 2 shows landfill leachates characterization after the application of the entire pre-treatment.

Table 2. Main parameters values after pre-treatment

	LL1 PRE-TREATED	**LL2 PRE-TREATED**
pH	2.9	2.9
COD (g O_2/L)	27	39
DOC (g/L)	11	13
Initial total iron (mg/L)	5.0	5.0
Added total iron (mg/L)	237	190
Total iron lost (mg/L)	186	133
Final dissolved iron (mg/L)	56	57
Toxicity (%Inhibition)	62	50
Biodegradability (COD_b/COD)	0.2	0

As a summary, after this physic-chemical pre-treatment, initial COD was reduced to an extent of 19 % and 8 %, and DOC removals were 17 % and 15 %, with associated iron consumption in coagulation-flocculation of 186 and 133 mg/L, for LL1 and LL2, respectively. Additionally, toxicity and biodegradability enhancements were not observed after the conditioning step, showing that the it did not substantially changed the composition of the dissolved phase which is the main responsible of toxicity and biodegradability..

3.2. Landfill leachate treatment at bench scale

To monitor the degradation of the first sample of the pre-treated landfill leachate (LL1) and analyze the toxicity and biodegradability evolution through the solar photo-Fenton process, H_2O_2 additions between 1.5 and 3 g/L were performed taking the sample after complete consumption of this reagent for permitting stability of the main parameters,

avoiding reactions in the dark with remaining H_2O_2. These experiments were performed at bench scale in a solar simulator at 35ºC. The main objective was to determine if a solar photo-Fenton process was able to substantially improve the biocompatibility of the partially oxidized landfill leachate, to gain experience in H_2O_2 and Fe dosing in relation to important COD changes during photo-Fenton, to assess if AOS evolved to higher and more stable values, etc. These preliminary experiments should be done at bench scale as they are quicker, more stable (constant irradiation power) and easier to repeat than at pilot plant scale. Figure 1 shows the evolution of COD, DOC and the Average Oxidation Stage (AOS), as well as changes in toxicity and biodegradability during the assay, based on the amount of hydrogen peroxide consumed during the solar photo-Fenton treatment of LL1. AOS is used to assess the wastewater oxidation degree achieved at different times of the photocatalytic treatment and to have an initial qualitative idea of the degradation mixture biocompatibility [21, 22]. It is calculated by using Eq. (4), where DOC and COD are expressed in mol C/L and mol O_2/L, respectively.

$$\mathrm{AOS} = 4 \cdot \left(\frac{\mathrm{DOC} - \mathrm{COD}}{\mathrm{DOC}} \right) \qquad \text{(Eq. 4)}$$

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.

Throughout the solar photo-Fenton test, a progressive decline of both the COD and the DOC and substantial discoloration took place. After physic-chemical pre-treatment, the final concentration of dissolved iron was 1 mM, so it was necessary to add 56 mg Fe^{3+}/L more to reach a concentration equal to 2 mM Fe^{3+} at the beginning of the treatment. The concentration of dissolved iron and the pH remained stable throughout the assay (data not shown). At the end of this preliminary experiment, a DOC reduction

of 59 % and 68 % of COD with a total consumption of 26 g H_2O_2/L was obtained, indicating a consumption of 4 g H_2O_2 per g of DOC. Initial AOS increment and increasing H_2O_2 consumption indicate that the chemical nature of the generated intermediates was continuously changing to more oxidized compounds and, therefore, the biodegradability of the sample was expected to vary. From 15 g H_2O_2/L on, AOS was almost stabilized, but, variations for COD_b/COD ratio were observed when sample biodegradability was supposed not to change significantly.

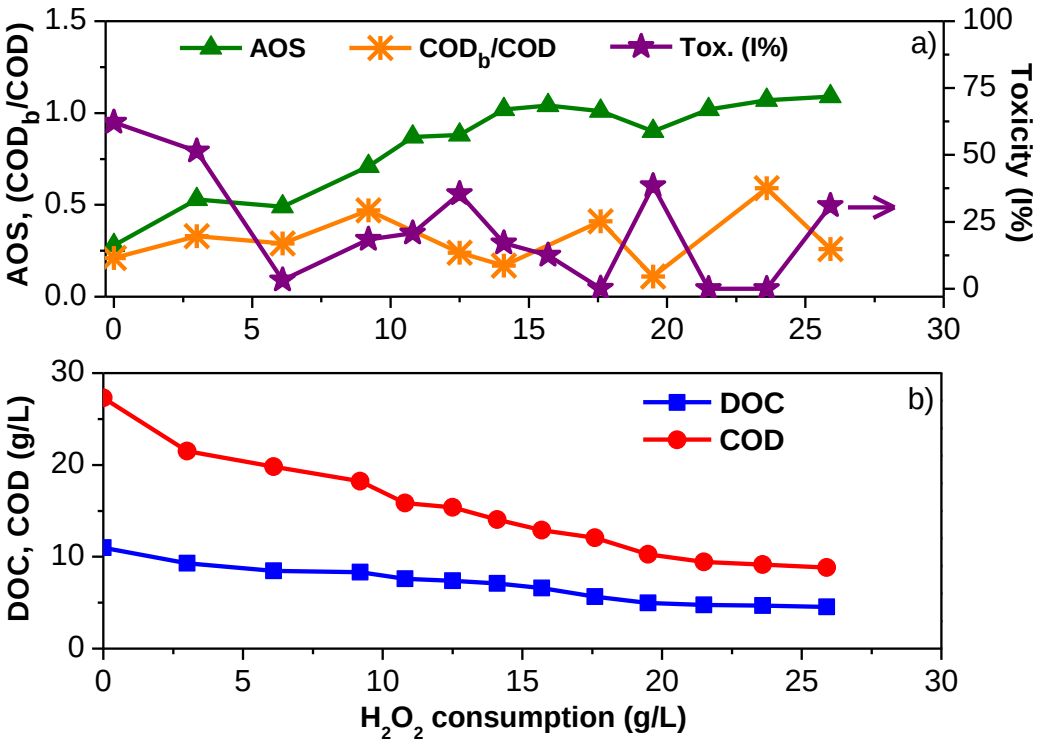

Figure 1. Evolution of the main parameters throughout LL1 treatment with solar photo-Fenton process in the solar simulator: **a)** AOS, biodegradability (COD_b/COD) and toxicity**; b)** COD and DOC.

Toxicity evolution throughout solar photo-Fenton treatment of LL1 was studied. As it can be seen in figure 1-a), inhibition percentages ranged randomly from 62 to 0%, observing the most important descent after the second addition of H_2O_2. In all the

analyzed samples, the inhibition percentage was lower than that of the initial sample (62%). Additionally, biodegradability assessment of several photo-treated samples was performed. When the COD_b/COD ratio is greater than 0.3, the sample is regarded as biodegradable, so it can be stated that most of the partially photo-treated wastewater was easily biodegradable. A second sample of pre-treated landfill leachate (LL2) was also tested, giving similar results than LL1: a progressive decline of both COD and DOC, substantial discoloration, concentration of dissolved iron and the pH remained stable throughout the assay, an important DOC reduction with a very similar H_2O_2 consumption in both cases, AOS increment followed by a final stabilization, and variations for CODb/COD ratio. Results were similar to those presented in the following section for LL2 when working at pilot plant scale. However this information was not enough to perform an economic assessment as pilot plant scale experiments with solar irradiation were needed.

3.3. Landfill leachate treatment at pilot plant scale

A second sample of pre-treated landfill leachate (LL2) was finally tested in a solar CPC pilot plant by photo-Fenton, taking into account the solar simulator's previous results with LL1 and LL2. LL2 was selected for pilot plant study because it was more difficult to treat due to higher COD content and conductivity. Therefore, the obtained results are considered to be more conservative in terms of hydrogen peroxide consumption, treatment time, etc. Several tests were conducted at different concentrations of Fe^{3+} (1 mM and 2 mM) to evaluate the effect on degradation kinetics and to determine the most favourable one. In both cases the concentration of hydrogen peroxide was maintained between 0.7 and 1.0 g/L to ensure an excess of reagent in order to avoid reaction rate limitation. In addition, a final experiment was carried out in order to take enough sample volumes for long term biodegradability analyses by Zahn-Wellens test.

First, experiments with an initial concentration of Fe^{3+} equal to 1 mM were performed in order to test whether a lower concentration of this reagent could provide good results, given that at pilot plant scale the usage of reagents is usually more efficient. These tests were extended until attaining a DOC reduction of approximately 37% (it had been previously demonstrated with LL1 that AOS was stabilized at this treatment point). To reach this mineralization percentage, 21 g H_2O_2/L and 11.4 hours of illumination time (117 kJ/L of accumulated energy) were required (figure 2), and a COD elimination of 52% was achieved (data not shown), indicating a consumption of 4.4 g H_2O_2 per g of DOC. Iron concentration was stable throughout the test. It is important to remark that temperature measured in the reactor varied between 20ºC (sometimes lower, but it is not relevant as it occurred during very short moments) and 43 ºC (average value was 34.7

ºC) due to solar irradiation evolution during the assay (figure 2). Therefore, this fact should be taken into account for economical and design calculations because temperatures affects photo-Fenton rate and H_2O_2/L consumption. In any case, 30-35 ºC is a typical average temperature in a CPC photoreactor [23].

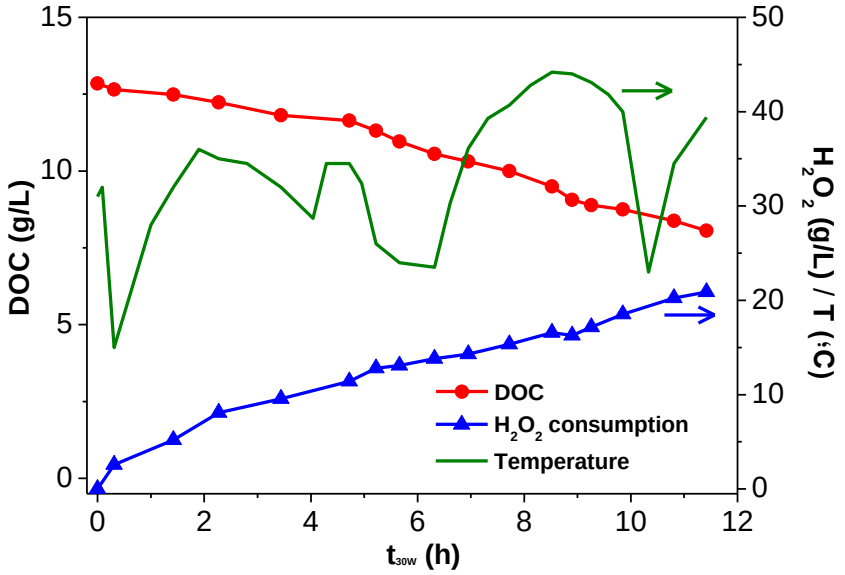

Figure 2. Solar photo-Fenton treatment of LL2 with 1 mM of Fe^{3+} at CPC pilot plant scale.

Solar Photo-Fenton treatment with Fe^{3+} 2 mM was performed until reaching a 33% reduction of DOC. At this treatment point, a COD removal of 48% (data not shown) was attained after 11.2 hours of illumination time (158 kJ/L of accumulative energy) and with a global H_2O_2 consumption of 25g/L (figure 3), indicating a consumption of 5.8 g H_2O_2 per g of DOC. Once again, the concentration of dissolved iron remained constant during the test (data not shown). Average temperature was 28.7ºC.

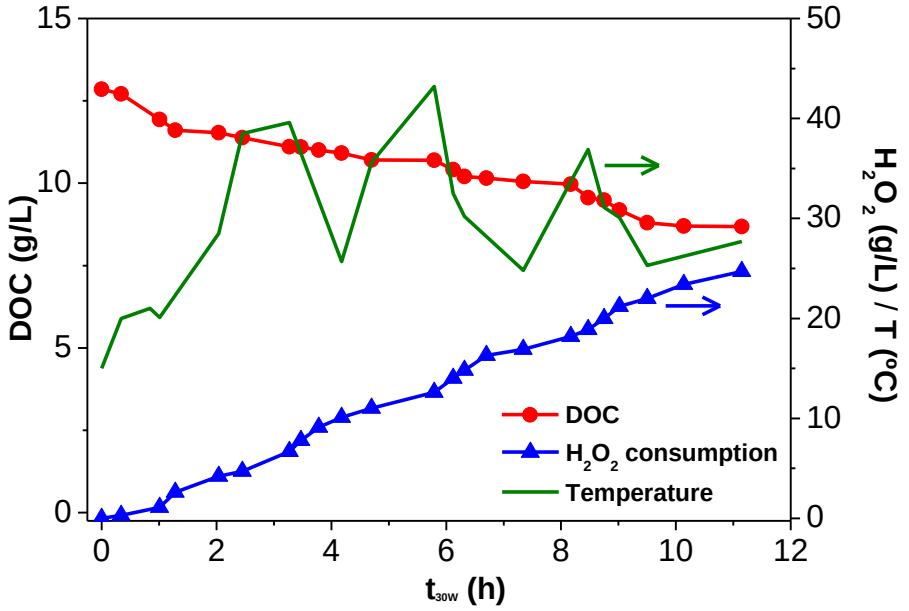

Figure 3. Solar photo-Fenton treatment of LL2 with 2 mM of Fe^{3+} at CPC pilot plant scale.

Comparing these results with those obtained at a Fe^{3+} concentration of 1 mM, it can be said that increasing the catalyst concentration did not improve the photo-Fenton efficiency for this kind of industrial wastewater.

Toxicity and biodegradability assessment

A final solar photo-Fenton experiment, at 1 mM of Fe^{3+}, was performed in order to study the evolution of acute toxicity and biodegradability during LL2 treatment. The aim of this test was verifying whether solar photo-Fenton was able to improve LL2 biodegradability (as in the case of LL1 in solar simulator), so that it may be completely treated in a subsequent conventional biological reactor. During the assay, a similar decline of DOC (40%), COD (49%) and a substantial discoloration were observed as doses of H_2O_2 were added (as it occurred in previous tests). Eight partially photo-treated samples were collected during the test for toxicity and biodegradability analyses.

Figure 4 shows the evolution of AOS, inhibition percentage and short term biodegradability of the samples taken during the photo-treatment. Biodegradability is measured by the COD_b (biodegradable COD fraction)/COD ratio. When it is higher than 0.1, a sample can be considered slowly biodegradable. The inhibition percentages (toxicity) measured by respirometry ranged from 30 to 50% randomly. These values indicated no significant toxicity changes and made it interesting to study long term biodegradability of each sample in order to find the best point for a possible combination with a subsequent biological treatment. Regarding AOS profile presented in figure 4, it can be said that more oxidized intermediates were formed from 14 g/L of H_2O_2 consumed to the end of the photo-treatment (AOS continuously increased). In addition, biodegradability ratio and AOS reached the maximum when 40% of mineralization was attained, involving a consumption of 35.5 g H_2O_2/L.

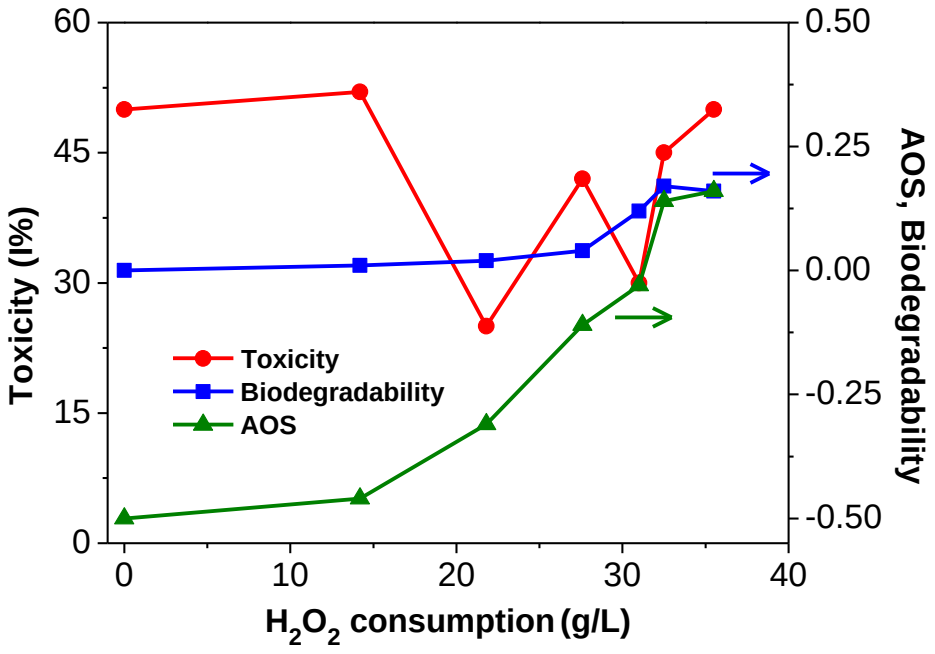

Figure 4. AOS, toxicity and short term biodegradability assessment during solar photo-Fenton treatment of LL2 performed at 1 mM of Fe^{3+}.

These biodegradability results give information about the immediate response of the activated sludge since each test has an approximated duration of 30 minutes. Nevertheless, and with the objective of having more information regarding the long term behavior of conventional biomass from a municipal wastewater treatment plant against this partially treated effluent, a Zahn-Wellens test was carried out using some of the samples which had been already evaluated by respirometry (figure 5). With this biological assay, more specific conclusions can be extracted regarding biomass adaptation, adsorption phenomena, sludge age and hydraulic retention time for the correct operation of a possible bioreactor. As it can be observed in figure 5, all the partially treated samples attained 70% of biodegradability after a quite low residence time (not higher than five days). This means that even less oxidized samples could be considered biodegradable after a very short adaptation period of the conventional activated sludge.

In addition, and as it happened for the respirometric assays, leachate biodegradability increased progressively as the photo-Fenton treatment took place, reaching higher biodegradability values in shorter times, at lower DOC concentrations.

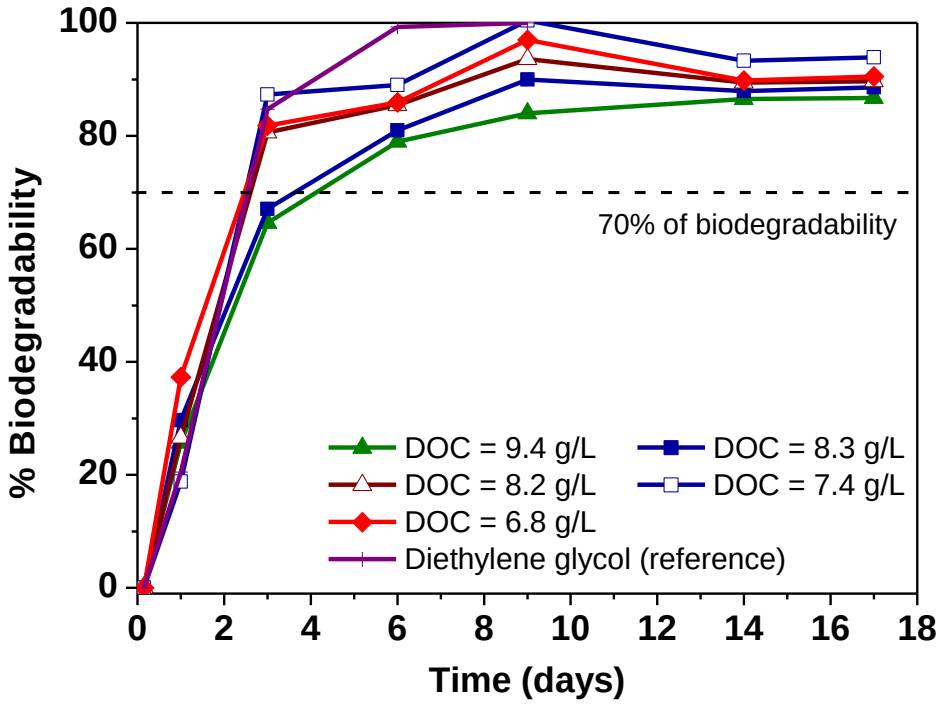

Figure 5. Zahn-Wellens test results for samples taken along the solar photo-Fenton treatment of LL2 performed at 1 mM of Fe^{3+}.

Although lowest oxidized samples showed high biodegradability percentages after four days of treatment, scaling-up to conventional biological reactors could require a previous biomass adaptation stage to reduce residence time and sludge age. Taking this consideration into account, a more conservative design point (end of photo-Fenton treatment prior to biotreatment) has been selected and solar photo-Fenton treatment is recommended to be maintained until achieving a mineralization percentage of 27% (final DOC of 8 g/L) and a 30% of COD elimination, with an associated global H_2O_2 consumption equal to 22 g/L (total accumulated energy required was 137 kJ/L). Afterwards, the partially oxidized effluent could be completely treated in a conventional biological treatment plant with the corresponding reduction in global operating costs.

3.4. Economic assessment

An economic assessment of the selected treatment line for landfill leachate, according to the experimental results presented in this work, was carried out. Most important operating parameters (reagents consumption, labour, electricity and investment costs) were used to estimate the costs associated to this process. The most suitable strategy selected for landfill leachate treatment would consist of a physic-chemical pre-treatment followed by a solar photo-Fenton process and, finally, a conventional biological treatment. Costs associated to physicochemical pre-treatment could be considered negligible as main expenses (acidification and $FeCl_3$) were already included within the photo-Fenton costs. Sludge generated during pre-treatment would be recycled to the landfill. The partially oxidized effluent, not requiring any previous biomass adaptation stage, could be completely treated in a conventional municipal biological treatment plant at negligible costs (less than 1 €/m3) compared with photo-Fenton costs. As it was previously stated, the design point was set in a mineralization degree of 27% (final DOC=8 g/L, at the end of the solar photo-Fenton process) provided that it reached 70% biodegradability threshold after less than five days of conventional biological treatment (according to Zahn-Wellens test results). This design point has the advantage of requiring a shorter photocatalytic treatment time (and so less accumulated energy) and lower reagents consumption than complete mineralisation, with a consequent reduction in operating costs. In addition, residence time in the final biological stage is highly dependent on activated sludge adaptation process. Therefore, for these leachates, when solar photo-Fenton is used, a substantial reduction in treatment time of subsequent biological treatment is achieved because ultimate biodegradability is sufficiently enhanced without requiring high mineralization percentages.

In solar-driven systems the most important investment cost is the CPC field, whose design directly depends on the required accumulated UV energy (Q_{UV}) for wastewater remediation. Experiments presented in this work showed that Q_{UV} necessary to achieve the selected design point was of 137 kJ/L. In addition, the target economic parameters have been calculated considering a leachate design flow of 40 m^3/day, 365 days/year of operation and industrial grade reagents prize of: sulphuric acid (96%), 0.10 €/L; $FeCl_3 \cdot 6H_2O$, 0.78 €/kg; and H_2O_2 (30% w/v), 0.41 €/L.

Considering Q_{UV} equal to 137 kJ/L, a CPC collector surface of 6850 m^2 has been calculated (with an associated cost of 349 €/m^2-collector, including auxiliary systems), involving treatment costs related to investment of 10.5 €/m^3 of leachate to be treated (considering a depreciation period of 15 years). On the other hand, labor requirement for plant's operation has been estimated on 3 h-man/batch (considering one batch per day and 18.8 €/h-man), and 1.6 kWh/m^3 of electricity consumption is expected. Finally, industrial grade reagents consumption would be: sulphuric acid (96%), 6.4 L/m^3; $FeCl_3 \cdot 6H_2O$, 0.9 kg/m^3; H_2O_2, 22 kg/m^3 (namely 73 L of 30% w/v /m^3 leachate treated).

Table 3 summarizes detailed operating and investment costs estimated for landfill leachate's partial oxidation by solar photo-Fenton, which would be the most expensive stage in the whole treatment line proposed and studied in this work.

Table 3. Solar photo-Fenton's estimated operating costs and corresponding percentages of each item over the total costs.

	Operating costs	**Percentage over the total costs**
	€/m^3	**%**
Total reagents consumption	31	72
Electricity consumption	0.1	0.2
Labour requirement	1.4	3.2
CPC solar field and auxiliary facilities	10	24
Total costs	**43**	**100**

Total costs for solar photo-Fenton partial treatment of this particular landfill leachate has been estimated in 43 €/m^3 or lower for LL1. It is important to highlight the strong contribution of reagents consumption costs over the whole process, meaning 72% of the total operating costs.

4. Conclusions

A treatment line for landfill leachate, by combining different processes, has been proposed and evaluated. Two different samples collected from a landfill site were studied in this work. Given that both of them exhibited high toxicity, it was deemed appropriate to include solar photo-Fenton process as a step of the global remediation strategy. Although only one of the samples was selected for the detailed feasibility study, the protocol would be very similar for the treatment of other landfill leachates.

During physic-chemical pre-treatment, change in sample's pH and ferric salt addition provoked a coagulation that carried significant COD and DOC reductions. It was

demonstrated that solar photo-Fenton process was substantially able to mineralize the organic content of the pre-treated leachate, by using a dissolved iron concentration of 1 mM, taking advantage of pre-coagulation also with iron. Additionally, significant improvements in toxicity and biodegradability values were attained.

The positive results obtained by Zahn-Wellens test pointed out that partially oxidized samples by solar photo-Fenton could be completely treated in a subsequent biological process, not requiring any previous biomass adaptation stage and therefore negligible costs.

Consequently, an appropriate treatment strategy for this type of water remediation would comprise a physic-chemical pre-treatment, followed by a solar photo-Fenton process (performed until an extent of initial DOC removal between 20 and 30%) and, the last step would consist of a conventional biological process.

Finally, a preliminary economic evaluation was developed in order to provide information about reagents, electricity and labor requirements associated to solar photo-Fenton process, which is considered the main responsible of increasing operating costs. Besides, total costs (including investment and operating costs) per m^3 of landfill leachate treated (30 % COD removal, around 12 g/L) was estimated on 43 €/m^3. It was noticed that the main operating cost comes from the reagent's consumption, especially of H_2O_2; while electricity requirement was found to be insignificant compared to the costs of other design parameters.

5. Acknowledgments

The authors wish to thank the Spanish Ministry of Economy and Competitiveness for financial support under AQUAFOTOX project (reference: CTQ2012-38754-C03-01).

Estefanía de Torres Socías would like to thank the University of Almeria and CIEMAT-PSA for her Ph.D. research grant.

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