

Solar photocatalytic treatment of landfill leachate using a solid mineral by-product as a catalyst

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Highlights

- A solid industrial by-product containing Ti and Fe was used as photocatalytic agent. - The by-product studied acts coupling photo-Fenton and TiO₂ catalysis reactions.
- The TiO₂ by-product promoted degradation of MSW using solar energy.
- The photocatalytic process developed increased landfill leachate biodegradability.

ABSTRACT

The treatment of municipal solid waste landfill leachate in a pilot plant made up of solar compound parabolic collectors, using a solid industrial titanium by-product (WTiO₂) containing TiO₂ and Fe(III) as a photocatalyst, was investigated. In the study evidence was found showing that the degradation performed with WTiO₂ was mainly due to the Fe provided by this by-product, instead of TiO₂. However, although TiO₂ had very little effect by itself, a synergistic effect was observed between Fe and TiO₂. The application of WTiO₂, which produced coupled photo-Fenton and heterogeneous catalysis reactions, achieved a surprisingly high depuration level (86% of COD removal), higher than that reached by photo-Fenton using commercial FeSO₄ (43%) in the same conditions. After the oxidation process the biodegradability and toxicity of the landfill leachate were studied. The results showed that the leachate biodegradability was substantially increased, at least in the first stages of the process, and again that WTiO₂ was more efficient than FeSO₄ in terms of increasing biodegradability.

Keywords: Industrial by-product, Landfill leachate, Photo-Fenton, Solar collector, Titanium dioxide.

1. Introduction

Landfill leachate (LL) is generated when municipal solid waste (MSW) is disposed of, essentially due to the percolation of rainwater through the landfill layers and waste

decomposition (Renou et al., 2008; Puig et al., 2011). LL may contain large amounts of hardly-biodegradable organic matter, where humic acid-type constituents are an important group, as well as other pollutants. It has been reported that one of the most important aspects related to the planning, design, operation and long-term management of a MSW landfill is the management of leachate (Halim et al., 2010). LL may be characterized as an aqueous solution of four groups of contaminants: dissolved natural organic matter (including recalcitrant compounds), inorganic macrocomponents (common cations and anions including sulfate, chloride, iron, aluminum, zinc and ammonia), heavy metals (Pb, Ni, Cu, Hg), and xenobiotic organic compounds such as halogenated organics, (PCBs, dioxins, etc.) (Vilar et al., 2011a). Therefore, MSW leachate discharge may cause serious pollution problems to groundwater and surface waters.

Technologies commonly used for leachate treatment, whether physico-chemical or biological, depend on the age and leachate composition, but none of them alone are efficient enough for suitable depuration of LL (Xu et al., 2010). Consequently, it is still necessary to develop new technology which allows the proper elimination of the pollutants commonly found in LL. For mature LL, due to its high level of recalcitrant organic compounds, treatment options are reduced to physical or chemical processes. Recently, reverse osmosis has been used to treat this kind of leachate, but although this process is very efficient, it leads to high investment costs and energy consumption. Membrane fouling, which requires extensive pre-treatment or chemical cleaning of the membranes, results in a short membrane lifetime and decreases process productivity. Finally, the treatment also results in the generation of large volumes of concentrate, which is normally recycled to landfill (Renou et al., 2008). Another promising option for LL treatment is related to the use of advanced oxidation processes (AOPs), since with the use

of these technologies, the organic matter present in water, including recalcitrant compounds can be reduced. This objective is achieved through the hydroxyl radical action, generated by several processes such as Fenton, photo-Fenton (both using Fe and H₂O₂), O₃/UV, and heterogeneous photocatalysis by TiO₂, among others (Weichgrebe et al., 1993; Gonze et al., 2003; Kurniawan et al., 2006; Deng and Englehardt, 2007; Primo et al., 2008), which enhance the biodegradability of recalcitrant compounds in the leachate. However, it has been reported that the greatest disadvantage of AOPs is also the high demand for electric power and the consumption of expensive chemicals, which increase the operation costs of the process (Lopez et al., 2004; Matilainen and Sillanpää, 2010). For this reason, there is a growing interest in developing AOP applications using solar energy (e.g. photocatalysis with TiO₂ or photo-Fenton) along with low-cost catalysts (Malato et al., 2009; Vilar et al., 2011a,b). According to the literature, LL is more efficiently treated by the photo-Fenton reaction than by TiO₂, since the reaction rate is much higher and the Fe concentrations needed is very low (Rocha et al., 2011; Vilar et al., 2011b). Therefore, in order to improve the photocatalytic process, a new TiO₂ catalyst doped with Fe has recently been developed to increase the production of H₂O₂ during the AOP (Araña et al., 2011).

In a previous study, an industrial titanium by-product (WTiO₂), containing not only TiO₂ but also Fe(II) and mainly Fe(III), was used as a catalyst to degrade p-cresol, humic acids and LL using a UV photo-reactor (Poblete et al., 2011). The potential of WTiO₂ as a catalytic agent in AOPs was demonstrated since this catalyst showed an enhanced removal percentage of organic matter and therefore much higher activity in the degradation of humic acids or LL under UV light irradiation than commercial TiO₂. Soluble Fe(III) compounds may well have had a synergistic effect on the catalytic activity of TiO₂ when WTiO₂ was used.

The aim of the present work was to enhance the efficiency of the conventional UV photo-Fenton treatment of LL by using the same industrial by-product (WTiO₂) as a low-cost photocatalyst together with H₂O₂, applying solar UV irradiation in a pilot plant based in a solar compound-parabolic collector (CPC) photoreactor. The purpose was to produce a combination of solar photo-Fenton (or photo-Fenton like) and heterogeneous photocatalysis, due to the presence in WTiO₂ of Fe(II), (or Fe(III)) and TiO₂, respectively. In addition, the leachate biodegradability was studied before and after the oxidation process to know the degree of improvement achieved. This work intends to establish a technological basis, to analyze the possible use of this by-product in LL treatment plants, completing the treatment scheme.

2. Experimental

2.1. Landfill leachate and photocatalyst

Leachate was collected from a storage unit with a capacity of 12000 m³ situated in the integrated MSW plant Mancomunidad de La Vega, Seville, Spain, which produces a leachate flow rate of 7000 m³ yr⁻¹. The main characteristics of LL are presented in Table 1.

The by-product tested as a catalyst (WTiO₂) is a solid waste product obtained from the concentrated sulfuric acid digestion of ilmenite at 150–220 °C, where titanium separates in the form of titanyl sulfate which, after hydrolysis, precipitation, and calcination, is transformed into TiO₂. The main components of WTiO₂ (wt%) are TiO₂ (50.6), Fe₂O₃ (19.1), SiO₂ (11.1), Al₂O₃ (1.7), CaO (0.28), and MgO (0.13) (Vilches et al., 2003). Fe was found in its trivalent state, mainly in oxy-hydroxide form (FeOOH), and very small changes in the Fe chemical environment were produced after the use of WTiO₂ as a photocatalyst (Poblete et al., 2011). Before use, WTiO₂ was dried at 105 °C

for 2 d and milled, selecting particle sizes in the range of 63-75 μm . A conventional Fenton photocatalyst was used in the form of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Panreac) along with H_2O_2 (30% w/v, Panreac) for photo-Fenton treatment.

2.2. Experimental setup

Photocatalytic experiments were carried out in a CPC specifically developed for photo-Fenton applications, installed at the Plataforma Solar de Almeria, using solar energy as a UV light source (Kositzki et al., 2004). The reactor, with a total volume (V_T) of 21 L, consists of five borosilicate glass tubes of 50 mm external diameter, 142 cm length and 1.4 mm thickness, with a transmissivity between 0.900 and 0.915 ($\lambda \geq 350$ nm of wavelength). The irradiated volume (V_i) and area were 11 L and 5.1 m^2 , respectively. The CPC reactor is provided with a tank where some parameters such as pH or temperature were measured and different reagents were added, such as FeSO_4 , WTiO_2 , H_2O_2 , H_2SO_4 or NaOH . Solar UV radiation was measured by a global UV radiometer (KIPP&ZONEN, Model CUV 3) on a platform tilted 37° (the same as the CPCs), which provides data in terms of incident irradiance (W m^{-2}). This gives an idea of the energy reaching any surface in the same position with regard to the sun. Using Eq. (1), a combination of the data from several days' experiments and a comparison with other photocatalytic experiments was possible (Malato et al., 2003).

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30} \frac{V_i}{V_T}, \quad \Delta t_n = t_n - t_{n-1} \quad (1)$$

where t_{30W} is a normalized illumination time (min), t_n is the experimental time for each sample and UV is the average solar ultraviolet radiation measured during Δt_n . In this case, time refers to a constant global UV irradiance of 30 W m^{-2} (typical solar UV

irradiance on a perfectly sunny day around noon). The starting point of the process, $t_{30W} = 0$, was considered when LL was exposed to the sunlight.

In order to obtain optimal oxidation conditions for the solar photocatalysis application, the LL was pre-treated. Firstly, its pH was adjusted to 3 using H₂SO₄ (98%) (Panreac) and NaOH (50%) (J.T. Baker) since the original leachate pH was alkaline (pH = 8.3). A pH value of 3 was chosen because it has been reported that an acid pH favors conventional Fenton leachate treatment (Hermosilla et al., 2009). Moreover, in preliminary tests we did not find a significant difference in COD removal rates in the pH range between 2 and 4. Furthermore, the pH 3 value was very adequate to effectively flocculate organic colloids and improve their filtration. In a second step, the supernatant of the LL pH adjustment was subjected to a coagulation-flocculation process with the addition of FeCl₃ (Merck) in order to remove the nonsettleable suspended solids (SS) remaining. To optimize the process, a representative LL sample was tested first, at laboratory scale using jar-test experiments, with the purpose of determining the exact amount of FeCl₃ necessary to clarify LL and settle most of the SS. Finally, and prior to the solar photo-oxidation process, the pre-treated effluent was filtered using a 5 μm pore size filter.

After the pH adjustment, coagulation-flocculation and filtration steps, 21 L of the pre-treated LL was transferred to the CPC solar pilot plant to perform the corresponding solar photocatalytic treatment. The pilot plant was operated in batch mode with a LL flow rate of 20 L min⁻¹ using a recirculation pump during the experimental time (t_n) necessary to obtain the desired mineralization. All the experiments were carried out from October to December 2010, during cloudy and sunny days.

2.3. Biodegradability

In order to assess the biocompatibility of LL after the photocatalytic treatment, with the aim of studying the joint treatment of LL with urban wastewater, toxicity and biodegradability tests at different stages of the solar photo-Fenton treatment were carried out. With this purpose, photo-Fenton experiments were performed in a solar simulator (Suntest XLS + photoreactor, Atlas) equipped with a Xe lamp (765 W m^{-2}) and a thermostating unit to keep the temperature at $35 \text{ }^{\circ}\text{C}$. In these experiments H_2O_2 was added in several steps to the continuously stirred flask of 2 L of effective volume. This means that when H_2O_2 was exhausted, samples were taken for analysis, and another dose of H_2O_2 was added. As a result of this procedure, H_2O_2 did not affect bioassays. To assess the evolution of the treatment dissolved organic carbon (DOC) and COD were monitored during the process, which allowed direct comparison with the results obtained in the CPC photoreactor, and a subsequent connection of the results of bioassays with the kinetics calculated in the CPC photoreactor.

Toxicity evolution during the photocatalytic experiments was analyzed by respirometry using a BMT Respirometer (SURCIS, S.L), provided by an oxygen probe (Hamilton). The respirometer was loaded with the required amount of activated sludge (1 L, according to the manufacturer specifications) taken from a conventional municipal wastewater treatment plant (WWTP). Afterwards, in order to inhibit the nitrification process and measure the sample effect only on the heterotrophic bacteria, 3 mg of *N*-allylthiourea (Aldrich) g^{-1} of volatile solids (VS) was added to the activated sludge. For all the runs VS was 2.7 g L^{-1} . Then, continuous aeration to attain air saturation conditions and continuous agitation were applied to the respirometer reactor flask. The temperature was maintained at $20 \text{ }^{\circ}\text{C}$ during the experiment. Toxicity, expressed by means of the inhibition percentage, was measured comparing the activated sludge maximum respiration rate ($R_{S_{max}}$) in the presence of 50 mL of distilled water with 1 g L^{-1} of sodium

acetate (J.T. Baker), added to avoid the absence of substrate, with respect to the activated sludge respiration rate (R_s) obtained in the presence of 50 mL of a partially treated LL sample (after adjusting the pH to 6.5 – 7.5, filtered and aerated) with 1 g L⁻¹ of sodium acetate. The percentage of inhibition, % I , was calculated by Eq. (2).

$$\%I = \left(1 - \frac{R_s}{R_{s_{max}}}\right) 100 \quad (2)$$

where R_s and $R_{s_{max}}$ are expressed in terms of mg O₂ L⁻¹ h⁻¹.

For those samples which presented non-significant toxicity values, biodegradability assays based on respirometry were also carried out with the same BM-T respirometer. For the biodegradability tests, the respirometer was also loaded with 1 L of activated sludge taken from a conventional WWTP (VS = 2.7 g L⁻¹). The nitrification process was also inhibited and continuous aeration and agitation were applied to the reactor flask. Finally, 100 mL of the partially treated LL (after adjusting the pH to 6.5 – 7.5, filtered and aerated) was added to the respirometer reactor and the oxygen consumption was monitored automatically during the assay. At the end of the test, the respirometer software gave the readily biodegradable fraction of the filtered COD (rbCOD) according to the total oxygen consumption registered by the equipment.

The rbCOD/DCOD ratio shows the sample biodegradability (where DCOD is the dissolved COD of the sample), taking into account that values higher than 0.3 mean that the sample can be classified as highly biodegradable, values higher than 0.1 as slowly biodegradable, while values lower than 0.05 indicate that the sample is not biodegradable (values between 0.05 and 0.1 are considered samples with low biodegradability).

2.4. Analytical determinations

Mineralization of the organic matter was followed by measuring the DOC by direct injection of filtered samples (PTFE 0.22 μm , Millipore Millex1GN) into a Shimadzu 5050A TOC analyzer with an NDIR detector and calibrated with standard solutions of potassium phthalate. Total Fe and H_2O_2 were both determined spectrophotometrically (UNICAM 2 spectrophotometer). Fe was determined with 1,10-phenanthroline (Merck), at 510 nm, following ISO 6332 and H_2O_2 was analyzed using Ti(IV) oxysulfate (Fluka) (DIN 38 402, H15 method) at 410 nm wavelength and using Peroxid-Test (Merckoquant). COD was measured with Merck Spectroquant test kits following the Standard Methods (APHA, 2005). The absorbance was measured with a Merck Spectroquant1 NOVA 30 photometer (an external calibration curve was used).

The Average Oxidation State (AOS) has been used as a useful parameter to estimate the level of oxidation and to get indirect information on wastewater biodegradability. From DOC and COD the AOS of each sample was determined (Scott and Ollis, 1995).

3. Results and discussion

3.1. Solar photocatalytic treatment of landfill leachate

In previous studies it was verified that 1 g L^{-1} of WTiO_2 contained approximately 56 mg L^{-1} of soluble Fe representing a molar concentration of 1 mM, being the optimum Fe concentration for the AOP carried out using UV irradiation ($\lambda = 350 \text{ nm}$) and WTiO_2 as a catalyst for the degradation of humic acids and diluted LL (Poblete et al., 2011). A similar result (60 mg L^{-1}) has been described for the optimal Fe concentration in solar photo-Fenton treatment of LL (Vilar et al., 2011a).

Fig. 1a shows the results of DOC depletion and consumption of H_2O_2 during the photo-Fenton process with FeSO_4 , using a Fe concentration of 1 mM (the same amount

of Fe solubilized when WTiO_2 was used) and two different concentrations of H_2O_2 : approximately 0.3 and 1 g L^{-1} , regularly measured and added to in order to maintain the desired concentration taking into account the literature (Hermosilla et al., 2009). The H_2O_2 concentrations chosen were high enough to get a good level of removal efficiency and low enough to be an attractive option from both environmental and economic points of view. In comparison, Fig. 1b shows the results obtained from two different experiments, both with 1 g L^{-1} of H_2O_2 , one carried out with 1 g L^{-1} of WTiO_2 (which contains approximately 56 mg L^{-1} of solubilized Fe) and the other with a mix of 0.5 g L^{-1} of WTiO_2 combined with FeSO_4 to attain a final soluble Fe concentration of 56 mg L^{-1} . The results of LL pretreatment (average values), after the pH adjustment, coagulation/flocculation and filtration are shown in Table 1. As can be seen in Fig. 1a, DOC degradation and H_2O_2 consumption were accelerated after a certain time, probably due to the mineralization of organic intermediates that were only partially oxidized during the first stages of the treatment. Fe concentration and temperature were measured during the process, observing that the concentration of Fe remained stable around the desired concentration (1 mM), thus demonstrating that no Fe was lost due to any coagulation/flocculation provoked in the LL by the addition of H_2O_2 . The temperature oscillated drastically between 17 and $49 \text{ }^\circ\text{C}$ due to solar irradiation changes during the experiment, but temperature did not affect the final results significantly. Removals of DOC (ΔDOC) at the end of the test were 41% and 54% using 0.3 or 1 g L^{-1} H_2O_2 , respectively. H_2O_2 consumed/ ΔDOC ratios were 6.7 and 9 mg mg^{-1} for 0.3 and 1 g L^{-1} H_2O_2 , respectively, demonstrating that H_2O_2 was consumed less efficiently when the higher concentration was used. These experiments were considered the basis for comparing the rest of the experiments performed with WTiO_2 in order to elucidate the efficiency of this photocatalyst compared with the well-known photo-Fenton process.

The procedure to which the results shown in Fig. 1b refer was devised to ascertain if the Fe present in WTiO₂ was as active as the dissolved Fe from commercial FeSO₄. Results show that using 1 g L⁻¹ of WTiO₂ in an irradiation time $t_{30W} = 406$ min, a DOC elimination of 67% (from 2540 to 844 mg L⁻¹) was attained, while the experiment carried out using 0.5 g L⁻¹ WTiO₂ and FeSO₄ achieved a DOC elimination of 50% (from 1850 to 930 mg L⁻¹) in an irradiation time $t_{30W} = 328$ min. Evolution of DOC and consumption of H₂O₂ were within the same range in both approaches and were also quite similar to the results obtained using 1 mM Fe from FeSO₄ which are shown in Fig. 1a. The H₂O₂ consumed/ Δ DOC ratio was about 7 and 12 mg mg⁻¹ for 1 g L⁻¹ of WTiO₂ and 0.5 g L⁻¹ of WTiO₂ (with FeSO₄), respectively, demonstrating the similarity between both approaches and, therefore, the high efficiency of the Fe content of WTiO₂ in the photo-Fenton process. This result could be attributed to the presence of Fe in WTiO₂ in its trivalent state, since Fe(III) complexes formed with some organic compounds present in LL (Poblete et al., 2011) may have a synergistic effect on the catalytic activity of TiO₂ (Rodríguez et al., 2009; Araña et al., 2011). Therefore, the presence of both Fe and TiO₂ in WTiO₂ particles resulted in a combination of photo-Fenton and TiO₂ photocatalysis. Figure SM-1 of Supplementary Material (SM) shows a photograph of LL before and after the photo-Fenton process using WTiO₂ as a catalyst, in which a marked difference in LL appearance can be appreciated.

According to the results presented in Fig. 1b, it is not clear whether the TiO₂ content of WTiO₂ is relevant for the measured efficiency of the photocatalyst or not. Therefore, in order to know the individual effect of the TiO₂ present in WTiO₂ particles, it was decided to test WTiO₂ after removing its Fe content in soluble form. To separate Fe from WTiO₂ it was necessary to attack the solid in an acid medium adjusted to pH = 3 using H₂SO₄ (98%) for 24 h to obtain all the solubilized Fe in the liquid phase. Then,

the solid was filtered and the particles trapped in the filter were used as the heterogeneous photocatalyst. After this treatment, the characteristics of the catalyst are not greatly changed (except for the Fe loss) since in previous work (Poblete et al., 2011) the stability of WTiO₂ was determined by using the product in consecutive photocatalytic experiments at pH = 2. In those experiments, the activity of the catalyst was not lost but decreased and this decrease could be attributed, to some extent, to the Fe that was washed out from the catalyst during the first run.

The tests were performed using 1 g L⁻¹ of WTiO₂ without Fe and 200 mg L⁻¹ of H₂O₂. The objective of adding H₂O₂ was to maintain similar conditions to those used in previous experiments. As an electron acceptor, H₂O₂ could react with conduction band electrons formed during the illumination of WTiO₂ to generate additional hydroxyl radicals (Eqs. (3)-(5)).



The effect of this electron acceptor deserves further comment. The improvement achieved depends on the H₂O₂ concentration, generally showing an optimum range of concentration. At higher concentration values the positive effect starts to lessen and an inhibition effect appears. The beneficial effect can easily be explained in terms of prevention of electron/hole recombination and additional •OH production through Eqs. 3-5, whereas inhibition could be explained in terms of TiO₂ surface modification by H₂O₂ adsorption, scavenging of photo-produced holes and reaction with hydroxyl radicals (Achilleos et al., 2010).

Taking into account the high content of TiO_2 in WTiO_2 (about 50%), it was decided not to use such a high H_2O_2 concentration as 1 g L^{-1} to avoid inhibition of the reaction rate due to an excessive oxidant concentration. Results are presented in Fig. 2. As can be seen, the removal of DOC reached 37% after an irradiation time of 480 min (t_{30W}) when WTiO_2 without Fe was used. Consequently, it was demonstrated that WTiO_2 without Fe was, to some extent, able to degrade the LL studied in this work. Notwithstanding, some doubts persisted when these results were compared with those presented in Fig. 1, taking into consideration that LL contains 7.0 mg L^{-1} of Fe and 10.2 mg L^{-1} after the pretreatment (see Table 1). Thus, it might be possible that the degradation of LL could be ascribed to the Fe present in the leachate when Fe from WTiO_2 was removed and not to the TiO_2 in WTiO_2 . Therefore, Fig. 2 also shows the results obtained using LL directly, without adding any catalyst, just H_2O_2 (blank test). In this case, less DOC degradation (30%) was obtained as compared to WTiO_2 without Fe under the same conditions. The consumption of H_2O_2 was also quite similar in both experiments but lower in the blank test. Therefore, it was demonstrated that TiO_2 in WTiO_2 particles was responsible for part of the efficiency of the catalysts. In consequence, we can interpret that the degradation of DOC in the experiments carried out with WTiO_2 was mainly due to the Fe provided by the catalyst's particles, but also to the TiO_2 content and a synergic effect could potentially exist. There are two possible reasons for the low contribution of TiO_2 to the degradation process. First, the high salinity of LL usually reduces TiO_2 photoactivity and secondly, the photo-Fenton efficiency under solar light is much higher, compared to TiO_2 action, because the process is active up to 600 nm due to the possible formation of Fe complexes with some of the organic components of LL (Pignatello et al., 2006).

3.2. Toxicity and Biodegradability

Toxicity and biodegradability tests at different stages of the LL treatment were carried out as described in Section 2.3. The results in this case are presented as a function of H₂O₂ consumption, instead of illumination time.

Figure 3 shows the evolution of DOC, COD and AOS during the photo-Fenton treatment of LL with commercial FeSO₄ (Fig. 3a) or WTiO₂ (Fig. 3b) as catalysts. In the Fig. 3a we can observe that DOC showed a significant decrease (50%), when 5 g L⁻¹ of H₂O₂ were consumed and a final removal of 67% when 13 g L⁻¹ were consumed. COD removal was 43% and 72% for 5 and 13 g L⁻¹ of H₂O₂, respectively, which indicated that the carbon remaining had been partially oxidized. This was accompanied by a significant increase of the AOS during the first steps of the process until 4 g L⁻¹ of H₂O₂ were consumed. After that moment, AOS did not increase any more, and fluctuated between 0.44 and 0.62 until a consumption of 13 g L⁻¹ of H₂O₂ was reached. The increase of AOS only until 4 g L⁻¹ of H₂O₂ were consumed suggests that although more oxidized organic intermediates are formed during the photo-Fenton process, the composition of the intermediates generated did not vary significantly regarding biodegradability with this treatment and, therefore, it might not be worth increasing the reaction time with commercial FeSO₄ beyond a certain time period. Similar results in the treatment of LL have been published elsewhere (Vilar et al., 2011a). In the WTiO₂ case, the maximum dose used of H₂O₂ was 5 g L⁻¹ since this dose was enough to attain a substantial mineralization 64 and 86%, expressed as DOC and COD removal, respectively (Fig. 3b). This was also enough to reach AOS values higher than those obtained by the commercial FeSO₄ treatment (1.5 vs. 0.5). This H₂O₂ consumption was lower than that needed by other authors describing the mineralization of benzene sulfonic acid (Ting et al., 2008), nalidixic acid (Sirtori et al, 2009), and LL (Vilar et al., 2011b), who used 19, 7.5 and 6.4 g L⁻¹ of H₂O₂ and obtained 70%, 100% and 89% of DOC removal, respectively.

Both photo-Fenton photocatalytic processes using FeSO_4 or WTiO_2 showed an increase of AOS which could be representative of a toxicity decrease and an improvement in biodegradability (Fig. 3). AOS increase was quicker and required a lower H_2O_2 dose when the catalysis used was WTiO_2 (Fig. 3b).

Figure 4 shows inhibition and biodegradability percentages achieved in the course of the photo-Fenton with FeSO_4 or photocatalysis with WTiO_2 treatments of LL. As can be observed, in both cases toxicity measurements achieved 0% of inhibition just after the beginning of the process. However, after a consumption of 5 g L^{-1} of H_2O_2 during photo-Fenton treatment, toxicity increased up to 30% and then decreased until 0% at the end of the process. This behavior could be due to the generation of highly toxic intermediates (González et al., 2007; Trovo et al., 2009; Arslan-Alaton et al., 2010) which are later eliminated in the process. Concerning the biodegradability results, raw LL biodegradability was enhanced due to the oxidation process from 3% to 64% or 12-89% by photo-Fenton or photocatalysis with WTiO_2 , respectively. The enhancement of biodegradability fits well with the observed continuous increase in AOS.

4. Conclusions

In this work the removal of organic matter from a MSW landfill leachate was accomplished using the WTiO_2 by-product in a CPC reactor at pilot plant scale. One of the main conclusions of the work was that the use of WTiO_2 produced a higher organic matter removal rate (86%) than photo-Fenton using commercial FeSO_4 (43%). The proposed solar photocatalytic integrated treatment of LL using WTiO_2 was more efficient than photo-Fenton using FeSO_4 in terms of treatment time, COD removal and H_2O_2 consumption. The main reason for the high WTiO_2 efficiency in LL depuration appeared

to be its Fe content, since the use of the iron-free by-product resulted in a DOC removal efficiency lower than 37%.

Biomass from activated sludge produced in a municipal WWTP has the ability to utilize the LL studied, without a previous adaptation time, but only to a certain extent, because extensive biodegradation is usually restricted by the high level of recalcitrant compounds in LL. Process integration of Solar photo-catalyst and aerobic degradation seem conceptually advantageous to treat LL, since AOPs can transform the refractory compounds into more readily biodegradable organic matter. The idea has been proved experimentally, demonstrating that LL biodegradability improved after the two AOPs studied.

In summary, the results obtained show that the treatment proposed offers many advantages for potential industrial use in MSW landfills such as, low-cost catalysts, energy savings and lower equipment costs, as compared with the UV lamp oxidation process.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version.

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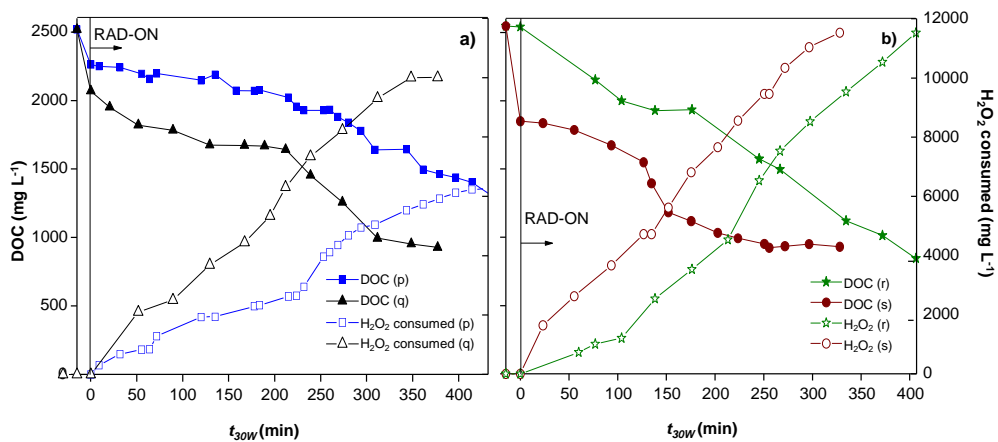


Fig. 1

Fig. 1. Organic matter degradation achieved in LL by photo-Fenton process in a CPC photoreactor vs. H_2O_2 consumption using a) 1 mM FeSO_4 and two different H_2O_2 constant concentrations (p) $0,3 \text{ g L}^{-1}$ or (q) 1 g L^{-1} and b) two different catalyst (r) 1 g L^{-1} WTiO_2 or (s) $0,5 \text{ g L}^{-1}$ $\text{WTiO}_2 + 0,5 \text{ g L}^{-1}$ FeSO_4 . Both, (r and s) used 1 g L^{-1} of H_2O_2 .

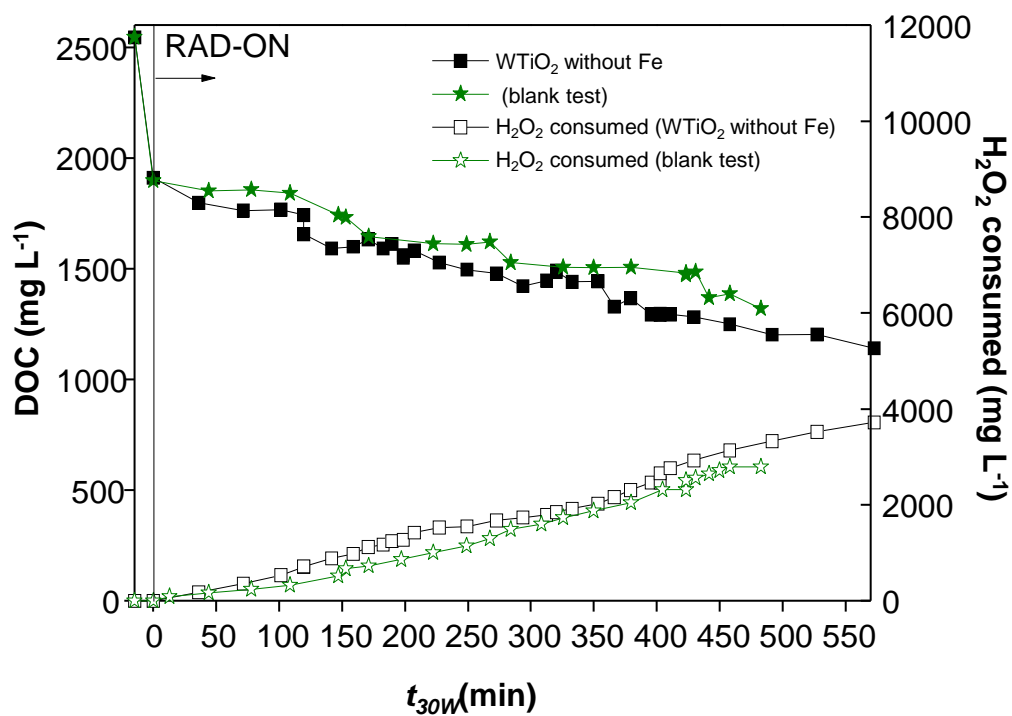


Fig. 2

Fig 2. Organic matter degradation achieved in LL in a CPC photoreactor using WTiO₂ (1 g L⁻¹) without Fe or without a catalyst (blank test). Both reactors used 200 mg L⁻¹ of H₂O₂.

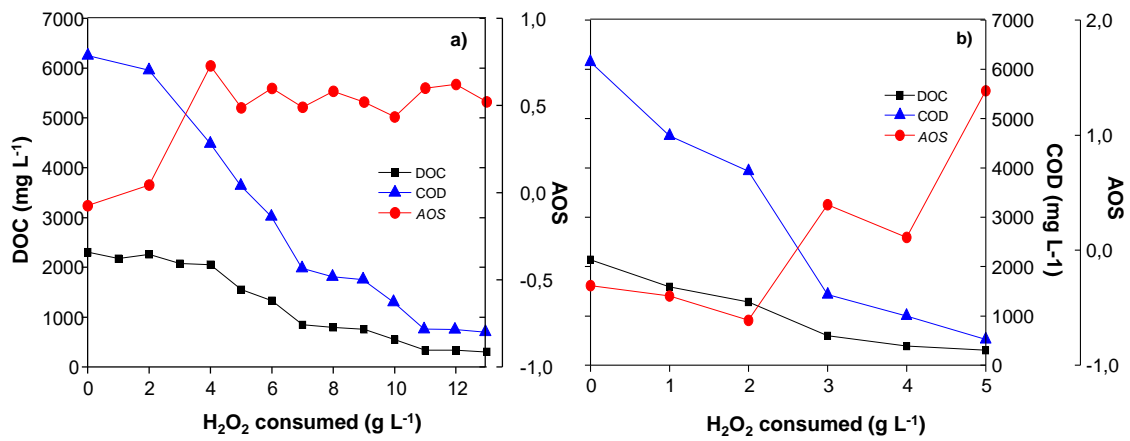


Fig. 3

Fig. 3. DOC, COD and AOS evolution, and H₂O₂ consumption for LL in a photo-Fenton process using (a) FeSO₄ and (b) WTiO₂.

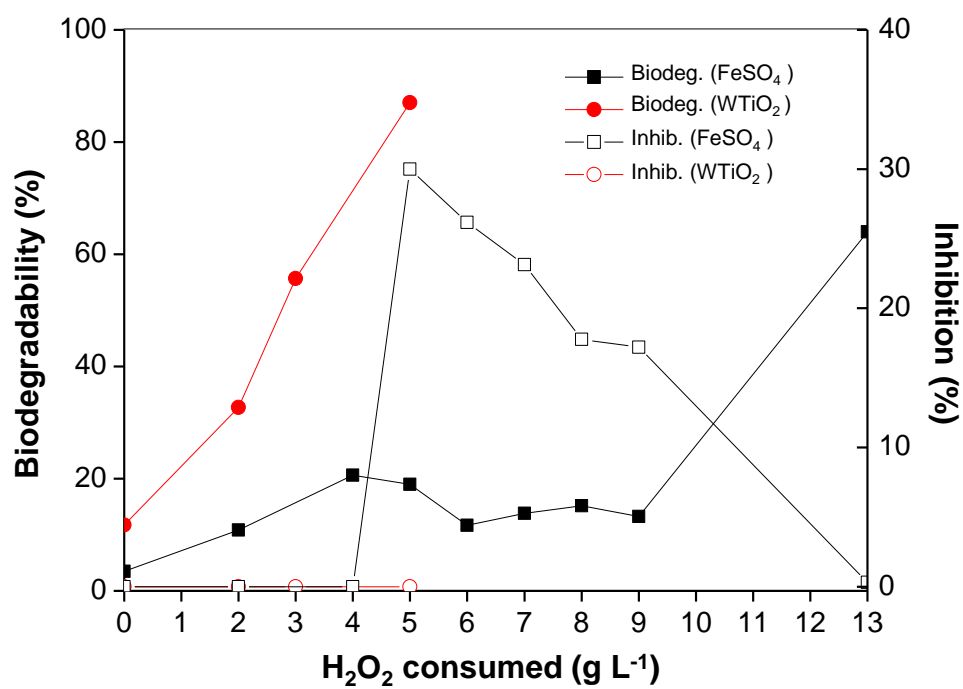


Fig. 4

Fig. 4. Biodegradability (%) and Inhibition (%) achieved at different landfill leachate treatment stages using FeSO₄ or WTiO₂ as a catalyst.

Table 1. Main characteristics of Landfill Leachate before and after pre-treatment (mean values).

Leachate parameter /units	Raw leachate	Leachate after pH adjustment	Leachate after coagulation/flocculation	Leachate after filtration
pH	8.3	3.0	3.2	3.2
DOC/mg L ⁻¹	4,780	2,359	2,174	2,046
COD/mg L ⁻¹	13,646	7,390	6,553	6,262
TN/mg L ⁻¹	1,932	1,635	1,439	1,238
Total Fe/mg L ⁻¹	7.0	7.9	34.6	10.2
Na ⁺ /mg L ⁻¹	2,993	2,990	2,683	1,486
NH ₄ ⁺ /mg L ⁻¹	2,010	2,012	2,003	1,992
K ⁺ /mg L ⁻¹	1,940	1,936	1,910	1,900
Ca ²⁺ /mg L ⁻¹	1,249	1,233	1,204	1,197
SO ₄ ²⁻ /mg L ⁻¹	9,130	16,340	12,934	8,923
Cl ⁻ /mg L ⁻¹	4,630	4,600	4,284	4,194