

Treatment of mature landfill leachate by electrocoagulation followed by Fenton or UVA-LED photo-Fenton processes

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ABSTRACT

The main objective of this study is to optimize a two-step treatment for mature landfill leachate consisting of electrocoagulation (EC) followed by Fenton or UVA-LED photo-Fenton processes aiming to provide a more efficient and feasible alternative treatment strategy that also increases biodegradability and decreases conductivity. Although 5 mA cm⁻² EC is cheaper than 10 mA cm⁻² EC per kg of removed COD (0.63 vs. 0.89 € kgCOD⁻¹), it achieved the half total COD removal (13% compared to 26%), and the low residual iron concentration (100 mg L⁻¹) that remained at the end of the process made necessary a long treatment time to perform the posterior Fenton (48 h) or UVA-LED photo-Fenton (6 h) process. When EC was performed at 10 mA cm⁻², the residual iron concentration (220 mg L⁻¹) was high enough to reduce treatment time by one half for both Fenton processes. Consequently, treatment cost decreases from 5.91 to 3.48 € kgCOD⁻¹ for the EC + UVA-LED photo-Fenton ([H₂O₂]/COD = 1.063) treatment combination; whereas it slightly decreases from 1.68 to 1.61 € kgCOD⁻¹ for the alternative EC + conventional Fenton combination. In both cases, total COD removal was around 87%. In addition, SUVA removal was >40%, conductivity was reduced about 20–30%, and biodegradability (BOD₅/COD) increased over 0.3.

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1. Introduction

Landfill leachate (LL) is considered an extremely harmful wastewater, resulting from the percolation of rainwater through landfill waste [1], and physicochemical and biological reactions during that percolation [2]. Decades after closing a landfill, leachate is still a problem for the environment, requiring treatment to meet regulatory requirements [3,4]. After decades of research, there is not an agreement on the optimum treatment yet due to both, the complexity and variety of leachate, and the drawbacks of the applied technologies.

The characteristics of LL can widely vary depending on the origin of waste in the landfill, climate conditions, and the age of the landfill [5,6] being the latter the most important one [7,8]. Based on this, LL is classified as young, intermediate, and mature. A young LL (age 0–10 years) is highly biodegradable (high biochemical oxygen demand to chemical oxygen demand ratio, BOD₅/COD ≈ 0.5–1), and it has low ammonia nitrogen content (< 400 mg L⁻¹), high COD content (> 4000 mg O₂ L⁻¹), and a pH below 6.5. On the other hand, a

mature LL (age > 20 years) shows BOD₅/COD < 0.1, high ammonia nitrogen content (> 400 mg L⁻¹), low COD content (< 4000 mg O₂ L⁻¹), and pH > 7.5. An intermediate LL holds intermediate characteristics between them [7,9–11].

Biological treatment is adequate for young LL because of its high biodegradability. However, mature LL needs to be treated by physical or chemical technologies, such as coagulation/flocculation, chemical precipitation, membrane treatments, or advanced oxidation processes (AOPs); as well as by combinations of these processes followed by biological treatment when a strict discharge legislation is in force [11,12].

The treatment sequence of coagulation/flocculation followed by Fenton or photo-Fenton processes has received some attention for the treatment of mature LL [12–15]. Li et al. [12] proposed a sequencing batch reactor with polyferric sulfate coagulation followed by Fenton treatment and a pair of up-flow aerated biofilters as tertiary treatment. They achieved the removal of 97% of the COD and 99% ammonia; although a significant increase of the content of sulfate (from 200 to 1100 mg L⁻¹) was also produced as its main drawback. Amor et al. [14], reported a 63% COD removal after coagulating LL with 2 g L⁻¹ of ferric chloride at pH = 5, and a final 89% COD removal

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after a Fenton process. In this case, the main disadvantage was adding 750 mg L⁻¹ of chloride. In this work, the treatment of LL by a single photo-Fenton process removed 43% of the COD, increasing to 83% when it was combined with a coagulation/flocculation pretreatment. Vedrenne et al. [15], reported the removal of the 56% of the COD and 64% of ammonia nitrogen from mature LL by a treatment with 300 mg L⁻¹ of ferric chloride followed by a solar photo-Fenton process with FeCl₂·4H₂O and H₂O₂ as reagents ([H₂O₂]/[Fe²⁺] = 114). Total chloride addition was 1.7 g L⁻¹ which results in being more toxic for a final biological process. The main drawback of these dual treatments is, therefore, the increased conductivity of the final effluent due to the counterion content that is added with the coagulants (chloride or sulfate). Furthermore, all these trials reported very large sludge production and implied a high cost associated to the addition of the coagulant. On the cost side, solar photo-Fenton has a large footprint and still requires a high cost of investment. UV photo-Fenton using conventional lamps also results in a high cost in terms of power consumption and investment, and produces residues with mercury at the end of the lamp life. In addition, the use of solar radiation in a compound parabolic concentrator requires a large area to be deployed and a high initial investment cost. In short, it is necessary to conduct further research on the development of more efficient and feasible treatment alternatives for mature LL.

Electrocoagulation (EC) maybe an attractive alternative. It has successfully been applied for the treatment of greywater [16], printing ink wastewater [17], drilling site wastewater [18], starch wastewater [19], for the removal of metals [20], and LL in some cases [21–23]. EC involves the electro dissolution of metal ions responsible for the destabilization of colloidal material. Several authors have reported good results for the treatment of LL (COD removal ≈ 60%). For example, Huda et al. [23] achieved the removal of the 47% of the COD and 82.7% of color at pH = 7.73 (electrode distance of 1.16 cm and 2 g L⁻¹ of NaCl as supporting electrolyte).

A combination of treatments has mainly been proposed in the previous related literature on this topic. Dia et al. [21] reported a COD removal of the 70% and 65% for aluminum and iron electrodes, respectively, at a current density of 8–10 mA cm⁻², for the treatment of bio-filtrated LL. Li et al. [22] reported a 94% COD removal when EC was combined with a two stage microfiltration plus a biofilter, which ended in membrane fouling problems after several working cycles. Le and Le [24] combined EC, obtaining a 73% COD removal, with an electro-Fenton treatment providing an additional 77.2% COD removal; thus, the final COD value was 130.9 mg L⁻¹. Ding et al. [25] addressed the removal 50%–60% of the COD and 100% of ammonia nitrogen by an electrooxidation-electrocoagulation-electroreduction process applying an electric charge of 1.5 A h L⁻¹. This treatment sequence holds the disadvantages of generating free chlorine during the electrooxidation stage, and its high power consumption (15 kWh m⁻³).

In summary, previous studies show that EC can provide an efficient pre-treatment. Our hypothesis is that it may have additional advantages and a synergic effect when it is combined with a Fenton process, because the residual iron remaining in the solution after EC can serve as the catalyst for the Fenton reaction. Consequently, the addition of more iron would not be necessary in the oxidation step, less chemicals would be used, and the amount of sludge that will be generated would be reduced to the lowest level. Therefore, the main objective of this manuscript is to assess the viability of the treatment of mature LL by EC and Fenton processes focusing on its efficiency in the reduction of the COD, the increase of biodegradability, the decrease of the conductivity of the final effluent, the reduction of sludge production, and the optimization of the global cost; as well as avoiding the above addressed drawbacks related to other treatment strategies for mature landfill leachates.

The initial EC step was investigated considering current density, electrodes distance, and initial pH as process variables to optimize.

For the second step, the supernatant was treated by both conventional Fenton and UVA-LED photo-Fenton processes to optimize the [H₂O₂]/COD concentration ratio with the objective of improving the treatment efficiency regarding COD removal and biodegradability enhancement (as BOD₅ ratio) at the lowest economic cost.

2. Material and methods

2.1. Chemicals

Sulfuric acid (H₂SO₄, 96–98%) was added for pH adjustment. Hydrogen peroxide (35%, w/w) was used in Fenton processes. Both products, and all the used chemicals during the experimental work were purchased from Sigma-Aldrich (Saint Louis, Missouri, USA).

2.2. Analytical determinations

All analyses were performed according to the Standard Methods for the Examination of Water and Wastewater [26]. Conductivity and pH were measured using a SensionTM+ MM374 pH-meter (Hach, Colorado, USA) equipped with pH and conductivity probes. H₂O₂ concentration was determined by the titanium sulfate spectrophotometric method [27]. Chemical oxygen demand (COD) was measured following the Nanocolor[®] test method (Macherey-Nagel GmbH, Düren, Germany) using an Aquamate UV-Vis spectrophotometer (Thermo Fisher Scientific, Waltham, USA) to perform measurements. BOD₅ was determined following the standard methods 5210B. Total organic carbon (TOC) and total nitrogen bound (TN_b) were determined by the combustion-infrared method using a Multi N/C[®] 3100 TOC/TN analyzer (Analytik Jena AG, Jena, Germany) with catalytic oxidation on cerium oxide at 850°C. UV-254 absorbance was measured using a Varyan Cary 50 UV-visible spectrophotometer (Varian, California, USA) using 1 cm pathway quartz cuvettes (Hellma, Müllheim, Germany). Specific UV absorbance (SUVA) was calculated as SUVA = 100·UV-254/TOC. Color was determined by measuring absorbance at 405 nm using a filter photometer (PF-11 from Macherey-Nagel, Düren, Germany). Dissolved iron was measured by atomic absorption spectrometry (3111B, 3111E) with a Varian SpectraAA 220 spectrophotometer (Varian, California, USA). Iron (II) was measured by the phenanthroline method.

Power consumption was calculated by the product of the kW that were consumed by each equipment and their hours of use. Samples were filtered through 0.45 μm, and dilution was applied when necessary, prior to analytical determinations. All analyses were carried out in triplicate.

2.3. Landfill leachate (LL)

LL samples were collected from the municipal solid waste landfill located in Golmayo (Soria, Spain), which began operations in 1997. Table 1 shows the main properties of the sampled mature LL. Although the content of COD is not very high, its treatment would be

Table 1
Landfill leachate characteristics.

Parameter	Value
pH	8.30 ± 0.10
Conductivity, mS cm ⁻¹	19.80 ± 0.80
UV-254, cm ⁻¹	51 ± 1
Color, mg Pt L ⁻¹	18,800 ± 1082
COD, mg O ₂ L ⁻¹	4897 ± 650
BOD ₅ , mg O ₂ L ⁻¹	58 ± 10
BOD ₅ /COD	0.01 ± 0.01
TOC, mg C L ⁻¹	1802 ± 50
SUVA, mg C ⁻¹ L cm ⁻¹	2.83 ± 0.30
NH ₄ ⁺ , mg L ⁻¹	1500 ± 100
TN _b , mg N L ⁻¹	1734 ± 50

complex because of its very low biodegradability ($BOD_5/COD = 0.01$) and high conductivity (19.8 mS cm^{-1}).

2.4. Electrocoagulation (EC)

EC was carried out in a 600 mL beaker filled with 500 mL of LL using iron anode and cathode ($20 \times 5 \text{ cm}$) with 50 cm^2 of submerged area each. LL was magnetically stirred at 100 rpm at room temperature. Iron electrodes were selected to use the dissolved iron ions in the EC process as catalyst for the posterior Fenton or photo-Fenton processes that were designed as a second treatment step; thus, avoiding further addition of an external iron source to perform the Fenton step. The amount of dissolved iron was measured by atomic absorption and corroborated by weighing the anode. Experiments were carried out setting current intensity in the power supply (GLPS 3010, 0–30 V and 0–10 A, from Geti, Czech Republic). An intensity range of 0.25–1 A was tested to optimize EC pretreatment. The distance between iron electrodes was studied over the range between 1 and 5 cm, as well as the initial pH value of the process ranging from 4 to 8.

2.5. Fenton and UVA-LED photo-Fenton processes

All Fenton experiments were carried out in a 250 mL beaker (9 cm of diameter) with 100 mL of pre-electrocoagulated LL that were magnetically stirred at room temperature with or without further pH adjustment. Three $[H_2O_2]/COD$ concentration ratios were tested,

namely: 2.125, 1.063, and 0.531, representing the stoichiometric optimum of the process [11], the half, and the quarter of this value, respectively, to determine its effect on the efficiency of the treatment in terms of COD removal and enhancement of LL biodegradability. Control trials without adding H_2O_2 were also carried out. No more iron was added besides the remaining one after EC. A 4 W UVA-LED lamp, made up of 10 LED emitters at 365 nm (CUN6GB1A, Seoul Viosys, Asan, North Korea) that were uniformly disposed, was located at 4.5 cm from LL surface. A total photon flux of $4.15 \cdot 10^{20} \text{ photon s}^{-1} \text{ m}^{-2}$ (measured by potassium ferrioxalate actinometry [28,29]) was generated with the application of 125 mA of current intensity.

3. Results and discussion

3.1. Electrocoagulation (EC)

3.1.1. Current density

Current density is one of the most important parameters to take into account in EC treatment, which is directly correlated to electrode dissolution, as it is expected from the Faraday's laws of electrolysis [30]. Iron concentrations of 1, 2, and 4 g L^{-1} were produced by electro-dissolution of the iron electrodes during 2 h of application of respective current densities of 5, 10, and 20 mA cm^{-2} (whilst keeping other process variables constant, namely: $\text{pH} = 8.30$ and electrode distance = 5 cm) to respectively achieve a COD removal of the 13%, 26%, and 38% (Fig. 1a). It is important to remark that Fe^{2+} is the first species that appears in the solution during the electro-dissolution of

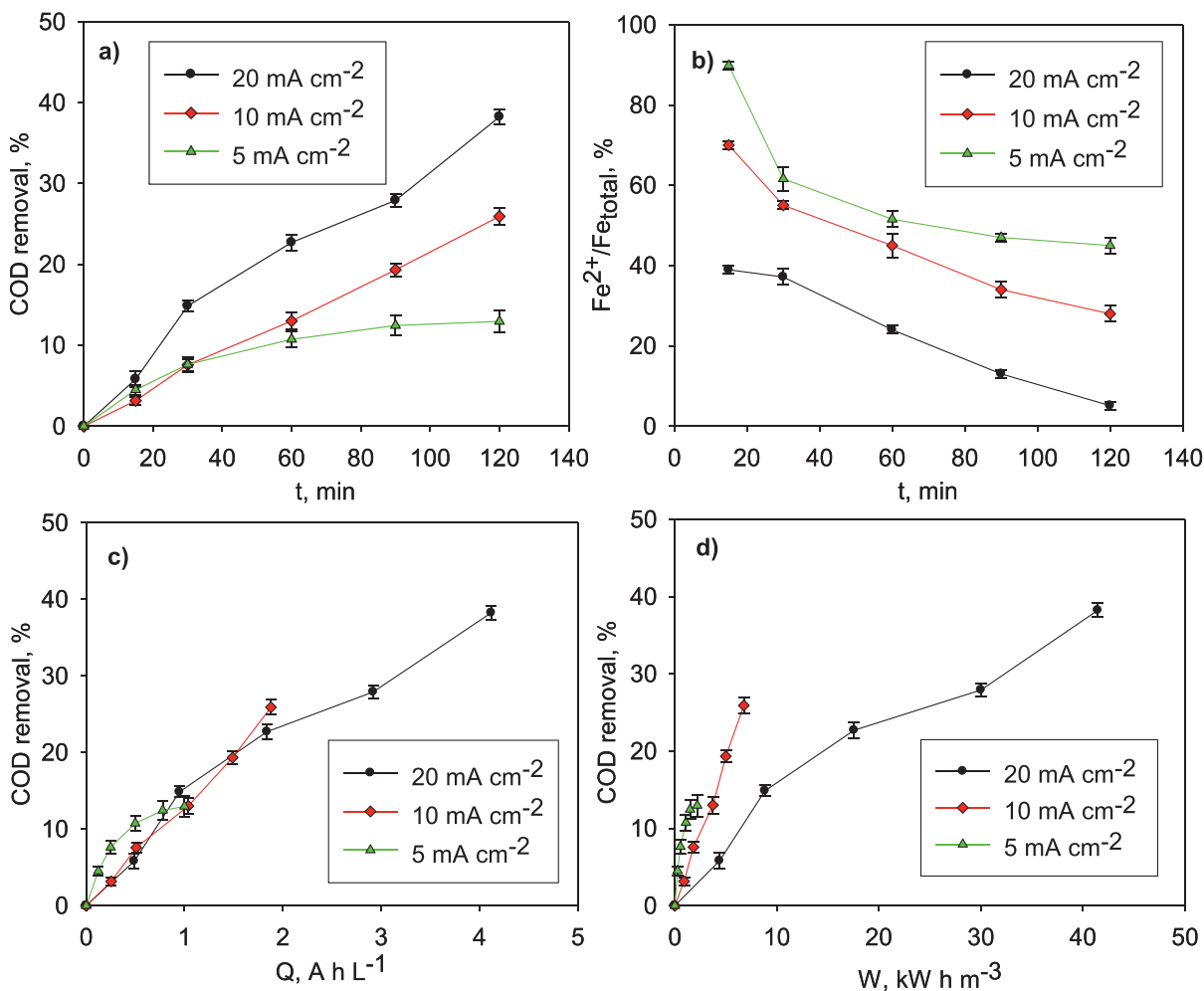


Fig. 1. Electro-coagulation (EC) performance applied to mature landfill leachate (LL) at different current densities (initial pH = 8.30; electrode distance = 5 cm): (a) COD removal evolution along treatment; (b) distribution of iron species; (c) COD removal versus applied charge; and (d) COD removal in relation to power consumption.

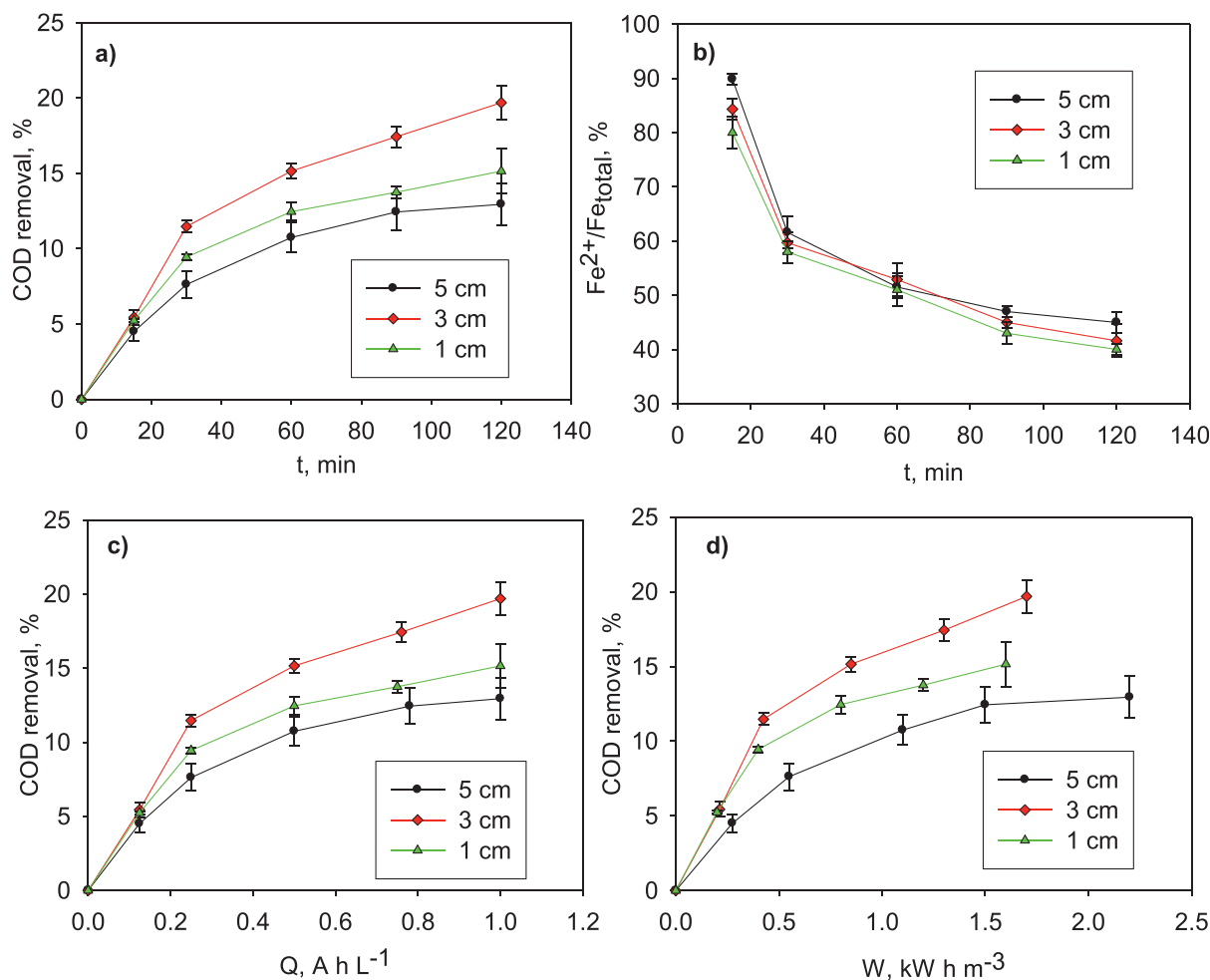


Fig. 2. Electro-coagulation (EC) performance applied to landfill leachate (LL) considering different electrodes distance (initial pH = 8.30; current density, $j = 5 \text{ mA cm}^{-2}$): (a) COD removal evolution along treatment; (b) distribution of iron species; (c) COD removal along applied charge; and (d) COD removal as a function of power consumption.

iron electrodes, and it is thereafter oxidized to Fe^{3+} [31], which is the most important species for the coagulation process.

Fig. 1b shows the percentage of iron species (ratio $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$). As expected, higher current densities and longer treatment time favored the oxidation of Fe^{2+} to Fe^{3+} ; thus, the COD removal efficiency is improved when the ratio $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ decreases. It is also relevant to comment that all the generated Fe^{2+} is rapidly oxidized to Fe^{3+} at the initial pH value of LL, even at lower current densities. These results are in agreement with Huda et al. [23], who reported COD removal values in the range of 15–45% when using iron electrodes for the treatment of a similar LL. Li et al. [31] also reported to achieve a 40% COD removal when applying 5.95 mA cm^{-2} at pH = 6.5 to a LL with half of the COD of the herein sampled.

Fig. 1c and 1d shows COD removal as a function of the applied charge (Q) and power consumption (W). Increments in Q were beneficial to COD removal (Fig. 1c), although the higher the applied charge, the higher power consumption and cost. In fact, increasing current density from 5 to 10 mA cm^{-2} triplicates power consumption (from 2.2 kWh m^{-3} to 6.8 kWh m^{-3}), and increasing current density to 20 mA cm^{-2} produces a twenty fold increase. Therefore, a current density of 5 mA cm^{-2} was initially chosen to proceed with the investigation of the other factors affecting the performance of EC. It is worth noting that the choice of the current density value that yielded the lowest COD removal by EC was preferred because of the subsequent process optimization based on minimizing the economic cost. In addition, although the lower total iron content that remained in the solution after the 5 mA cm^{-2} EC pre-treatment may limit the

overall efficiency of the posterior Fenton treatment, the higher relative Fe^{2+} iron content that was produced (Fig. 1b) may favor the initial triggering of the Fenton reaction.

3.1.2. Electrode distance

Three electrode distances were tested at the selected 5 mA cm^{-2} value of current density, namely: 1, 3, and 5 cm; producing COD removal results of 15%, 20% and 13%, respectively (Fig. 2a). This may be related with the small change in the distribution of iron species that is shown in Fig. 2b, besides small electrode distance (1 cm for example) produces repulsion, and large distance (5 cm) decreases electrostatic attraction [23]. Consequently, the applied current intensity, which was the same ($j = 5 \text{ mA cm}^{-2}$) for the three considered distance gaps between electrodes, was more efficient providing the best COD removal results at 3 cm of distance between electrodes (Fig. 2c).

Differences in power consumption efficiency removing the COD showed the same trend (Fig. 2d). The highest power consumption (2.2 kWh m^{-3}) was demanded when a 5 cm electrode distance was set because of the greater material resistance existing between electrodes. The total power consumption for the achieved COD removal results was 1.7 and 1.6 kWh m^{-3} for 1 and 3 cm distances between electrodes, respectively. Considering these results, a 3 cm distance between electrodes, together with the previously selected current density of 5 mA cm^{-2} , were selected to carry out next experiments investigating the effects of the initial pH on the performance of EC as a pre-treatment for LL.

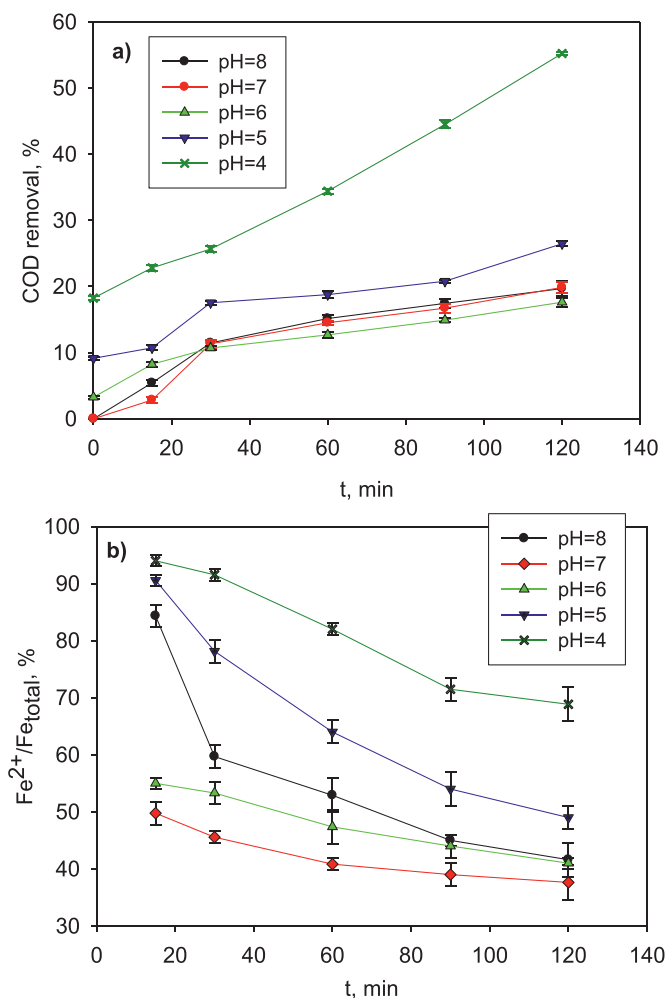


Fig. 3. pH optimization for an electro-coagulation (EC) pre-treatment of landfill leachate (LL) at a constant current density of $j = 5 \text{ mA cm}^{-2}$ and 3 cm of distance between electrodes: (a) COD removal results, and (b) iron species distribution.

3.1.3. Initial pH

The initial pH of the sample plays an important role in EC processes [32]. Thus, initial pH = 8.30 was adjusted to lower values to study the behavior of the EC treatment under acid conditions. Fig. 3a shows that some COD was already removed before beginning the EC pre-treatment because acid pH values promote the precipitation of humic acids [8]. COD removal results of 18%, 9%, 3% and 0% were just achieved when LL was acidified to pH = 4, 5, 6, and 7, respectively, without beginning the EC treatment (Fig. 3). These results corroborate our previous findings on coagulation pre-treatments [11].

A total COD removal (acidification + EC) of just 17–20% was achieved for initial pH values between 6 and 8 after 120 min of EC. Although the oxidation of Fe^{2+} to Fe^{3+} has been reported faster at higher pH values [33], favoring coagulation efficiency, results show that COD removal results increased to 26% and 55% when the pH was respectively decreased to 5 and 4. This could have been caused by the fact that a higher electro-dissolution of iron is produced at lower pH values; as well as to the higher EC efficiency removing fulvic acids and hydrophilic compounds than humic acids [19]. Humic acids precipitate below pH = 5; thus, there is no competition between humic acids and fulvic acids or hydrophilic substances when the coagulation process is performed at pH = 4. In addition, the overall removal of COD, including both humic and fulvic acids, can further be promoted thanks to oxidative processes and the formation of chlorine and

Table 2

Characteristics of landfill leachate (LL) after being subjected to the designed EC pre-treatment (5 mA cm^{-2} of current density, 3 cm of distance between electrodes, and initial pH = 4).

Parameter	Value	Removal (%)
Final pH	7.20 ± 0.10	-
Conductivity, mS cm^{-1}	14.20 ± 0.60	28.28
Color, mg Pt L^{-1}	7332 ± 680	61.00
UV-254, cm^{-1}	24.49 ± 5	51.98
COD, $\text{mg O}_2 \text{ L}^{-1}$	2204 ± 210	54.99
BOD_5 , $\text{mg O}_2 \text{ L}^{-1}$	23 ± 5	60.34
BOD_5/COD	0.01 ± 0.01	-
TOC, mg C L^{-1}	924 ± 30	48.72
SUVA, $\text{mg C}^{-1} \text{ L cm}^{-1}$	2.65 ± 0.40	06.36
NH_4^+ , mg L^{-1}	1500 ± 100	-
TN_b , mg N L^{-1}	1734 ± 50	-

sulfate radicals. In conclusion, the optimal pH value to perform the designed EC pre-treatment with Fe^{3+} as coagulant is close to 4 [11].

3.1.4. Overall performance of the designed 5 mA cm^{-2} EC pre-treatment

Although a 55% COD removal was achieved, the biodegradability of LL (as estimated by the BOD_5/COD ratio) was not enhanced by EC (Table 2), as it was expected from previous results [21,22]. The pH increased along the EC treatment from 4.0 to 7.2, as it has already been addressed by other authors [33–35]; whereas conductivity decreased a 28% down to 14.20 mS cm^{-1} . This is a significant improvement with respect to other conventional coagulation processes, which have been reported to increase the conductivity of the solution. For example, ferric chloride coagulation increased conductivity by a 7.5% from the initial value of other sampled landfill leachate in a recent study [11]. In addition, a 61% color removal was also achieved, which is also very important because color may directly limit the penetration of irradiation in the next UVA-LED photo-Fenton treatment step. Thus, lower LL color would reduce power consumption and would increase treatment efficiency in terms of COD removal.

A better COD removal result (68%) was reported in a previous study applying chemical coagulation (2 g L^{-1} of ferric chloride at pH = 5), [11]. However, the main disadvantage of conventional coagulation with respect to EC is the addition of chloride to the solution, which significantly increases conductivity. Therefore, EC is still an alternative to consider as pre-treatment, particularly when there may be room to further optimize the process supplying higher current density values, even if the partial cost of pre-treatment would be more expensive.

3.2. Fenton or UVA-LED photo-Fenton alternative treatment

3.2.1. Conventional Fenton process

The amount of iron (100 mg L^{-1}) remaining in the solution after EC was used as the catalyst of the posterior Fenton reaction; therefore, no further iron addition was required. The resulting $\text{H}_2\text{O}_2/\text{Fe}$ molar ratios were 77, 38, and 19 for the tested $[\text{H}_2\text{O}_2]/\text{COD}$ ratios of 2.125 (stoichiometric optimum), 1.063, and 0.531, respectively. Fenton treatment was performed at the final pH value of EC (7.2), and no further pH adjustment being carried out.

61% and 43% COD removal efficiencies were achieved after 48 h of treatment at the $[\text{H}_2\text{O}_2]/\text{COD}$ ratios of 2.125 and 1.063, respectively (Fig. 4a). The very long treatment time that was required is attributable to the low kinetics of the reduction of Fe^{3+} to Fe^{2+} that was carried out by the remaining H_2O_2 or the radical species present in the solution [36]. In short, the time required to spend all the added hydrogen peroxide logically increased as the $\text{H}_2\text{O}_2/\text{Fe}$ molar ratios increased as well [37]. Only a 5% of the COD was removed after 12 h

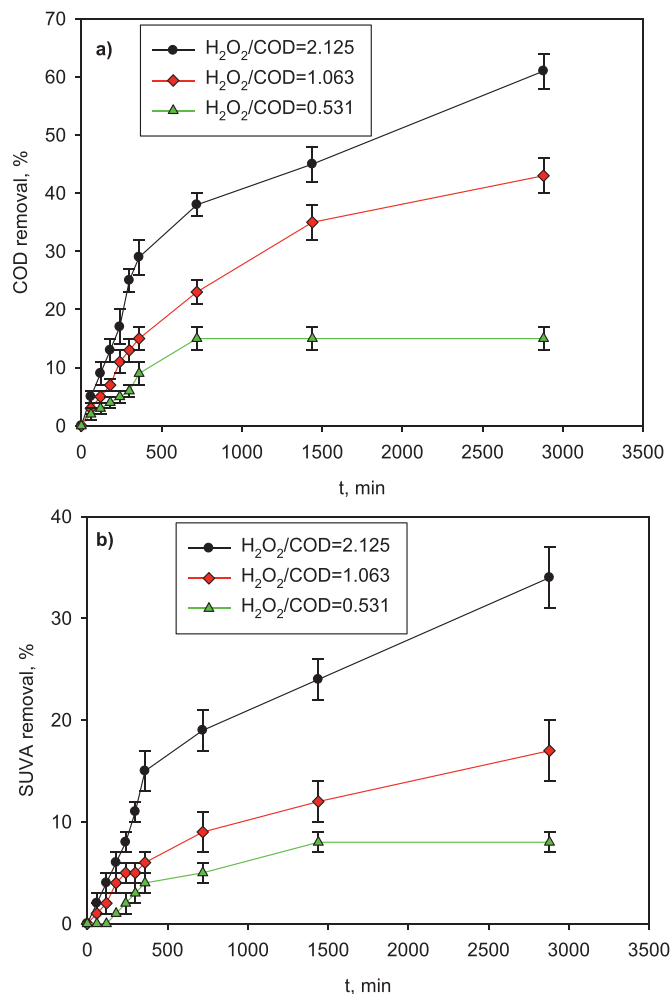


Fig. 4. Evolution of the removal of COD (a) and SUVA (b) along the conventional Fenton treatment of pre-electro-coagulated landfill leachate (LL) at a current density of 5 mA cm⁻².

of the treatment applying the lowest [H₂O₂]/COD ratio of 0.531. In addition, a 34% SUVA removal was achieved at the 2.125 [H₂O₂]/COD ratio; whereas it was much reduced for lower [H₂O₂]/COD ratios (Fig. 4b), following the same trend of the removal of the COD.

3.2.2. UVA-LED photo-Fenton treatment

The application of light irradiation to the Fenton process results in shortening the time of treatment because the reduction cycles of Fe³⁺ to

Fe²⁺ are produced much faster than in the conventional version of the treatment [38] 63% of the COD and 52% of the SUVA were removed after 6 h of pre-electro-coagulated LL treatment at the stoichiometric [H₂O₂]/COD ratio of 2.125. Lower COD and SUVA removal results were obtained at lower [H₂O₂]/COD ratios, namely: a COD removal of the 45% (in 4 h of treatment) and 17% (3 h) were respectively addressed for 1.063 and 0.531 ratios; whereas SUVA removal values of 28% (4 h) and 12% (3 h) were correspondingly achieved. In short, slightly higher COD removal results were addressed by the conventional and the UVA-LED photo-Fenton processes; whereas SUVA removal was significantly enhanced with the assistance of radiation (an 18% in the best case). This improvement is attributable to the faster reaction dynamics and the higher oxidation success with certain compounds, such as carboxylates.

3.2.3. Comparison of results between treatment alternatives consisting of a 5 mA cm⁻² EC pre-treatment and a conventional Fenton or a UVA-LED photo-Fenton process

Besides producing better overall results, significantly reducing the time of treatment as well, the photo-Fenton process implies other important advantages in comparison with its conventional version, such as the almost null generation of iron sludge [36], or the feasibility of the treatment of great amounts of LL, for which conventional Fenton requires very slow flow rates and very big reactors. The main parameters measured at the end of the assessed oxidation treatments are included in Table 3.

The general trend attributing better COD and SUVA removal results to the UVA-LED photo-assisted version of the Fenton process (Figs. 4 and 5) is also verified for the removal of color and biodegradability enhancement in terms of BOD₅/COD ratio (Table 3). For example, the BOD₅/COD ratio increased from an initial value of 0.01 to 0.32 and 0.38 after the conventional and UVA-LED photo-Fenton treatments were respectively carried out at the 2.125 value for the [H₂O₂]/COD ratio. In addition, the final COD value resulted lower than 1000 mg L⁻¹ and a very high color removal (97–99%) was also achieved under these treatment conditions (Table 3). In general, these results are in accordance with our previously reported study [11] in which the BOD₅/COD ratio was increased up to 0.32 by coagulation with ferric chloride followed by a photo-Fenton process with a conventional mercury vapor immersion lamp. Furthermore, Amor et al. [14] reported in their earlier study to achieve an 89% COD removal by the treatment of LL applying ferric chloride coagulation followed by a 96 h-long solar photo-Fenton treatment.

3.3. First economic assessment approximation of the integral treatment proposal

The cost of both oxidation approaches essayed in this study can be compared, together with the EC pre-treatment, in terms of their main

Table 3
Comparison of results between the conventional Fenton and the UVA-LED photo-Fenton treatment of pre-electro-coagulated landfill leachate (LL).

	Conventional Fenton		UVA-LED photo-Fenton		Conventional Fenton		UVA-LED photo-Fenton	
[H ₂ O ₂]/COD	2.125		1.063		0.531			
Final pH	5.10 ± 0.10	5.15 ± 0.10	5.47 ± 0.10	5.42 ± 0.10	5.85 ± 0.10	5.90 ± 0.10		
Conductivity mS cm ⁻¹	15.00 ± 0.60	15.15 ± 0.60	14.80 ± 0.60	14.65 ± 0.60	14.35 ± 0.60	14.25 ± 0.60		
Oxidation time, min	2880	360	1440	240	720	180		
Color*	587 ± 100	147 ± 50	1100 ± 150	953 ± 75	1613 ± 200	1466 ± 200		
mg Pt L ⁻¹	(97%)	(99%)	(74%)	(76%)	(62%)	(63%)		
COD*	860 ± 80	815 ± 90	1256 ± 100	1212 ± 120	1873 ± 170	1829 ± 180		
mg O ₂ L ⁻¹	(82%)	(84%)	(74%)	(76%)	(62%)	(63%)		
BOD ₅ /COD	0.32 ± 0.05	0.38 ± 0.05	0.24 ± 0.05	0.32 ± 0.05	0.10 ± 0.05	0.13 ± 0.05		
SUVA*	1.75 ± 0.25	1.27 ± 0.20	2.20 ± 0.25	1.91 ± 0.15	2.44 ± 0.40	2.33 ± 0.30		
mg-C ⁻¹ L cm ⁻¹	(38%)	(56%)	(22%)	(33%)	(14%)	(18%)		
NH ₄ ⁺ mg L ⁻¹	1500	1500	1500	1500	1500	1500		

* Removal % after the electro-coagulation + Fenton treatment of mature landfill leachate (LL) is shown in brackets.

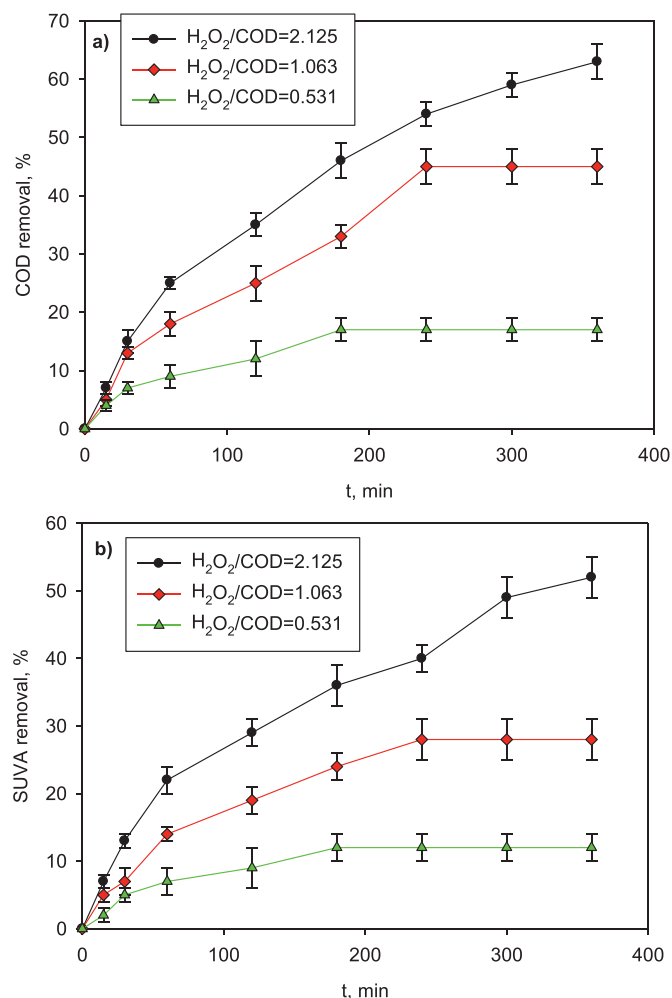


Fig. 5. Evolution of the removal of COD (a) SUVA (b) along the UVA-LED photo-Fenton treatment of pre-electro-coagulated landfill leachate (LL) at a current density of 5 mA cm^{-2} .

operational costs, namely the cost of chemicals and power consumption. In order to make this economic assessment (Table 4) we have assumed the following costs (prices for industrial grade chemicals at www.alibaba.com): 350 € ton^{-1} of hydrogen peroxide (35% wt.); 130 € ton^{-1} of concentrated sulfuric acid; 500 € ton^{-1} of iron bars; and 0.11 € kW h^{-1} , which is the average cost of power in Spain.

Power consumption is the highest contributor to the cost of the UVA-LED photo-Fenton treatment per m^3 of treated LL (Table 4);

although this value could be reduced much by further optimizing the use of radiation in full-scale applications [11]. The conventional Fenton process, which is only evaluated in terms of reagents consumption without energy use, reactor size, sludge disposal, labor cost, etc. was 3.5 times cheaper ($1.68 \text{ € kgCOD}^{-1}$) than the UVA-LED photo-Fenton process ($5.91 \text{ € kgCOD}^{-1}$), even considering a more conservative alternative configuration for energy use in this case, which was the 1.063 value for the $[\text{H}_2\text{O}_2]/\text{COD}$ ratio, which also implies the cost of half the hydrogen peroxide as well. This option just required 4 h of treatment to reach its top COD removal result (76%), whereas the 2.125 $[\text{H}_2\text{O}_2]/\text{COD}$ ratio continued to oxidize the solution even after 6 h of treatment (Fig. 5), which leads to a much higher power cost per m^3 of treated LL.

Although the UVA-LED photo-Fenton treatment alternative has several advantages (namely: the faster reaction time (4–6 h vs 24–48 h of treatment, which enable the treatment of higher water volume vs. time; a higher enhancement of biodegradability (BOD_5/COD); and a higher color and SUVA removal for the same H_2O_2 use), there is still room for the development of more efficient lamps aiming to turn this technology into more feasible for its wider application in the wastewater treatment sector. It should also be noted that further improvement of the conventional Fenton process could be achieved as well aiming to reduce reaction time by the addition of more iron, or by a higher electro-dissolution rate of iron, in the EC step. Finally, the reported results were obtained at laboratory scale; therefore, it is expected that the scale-up of the process will imply a lower overall treatment cost thanks to synergic effects enhancing the more efficient use of the input resources (chemicals and energy, for example) [11].

The herein essayed EC pre-treatment followed by conventional Fenton treatment shows improved results in the treatment of LL compared to our previous results included in Tejera et al. [11], in which 1.56 € per kg of COD removed were similarly addressed for the treatment of the same LL by coagulation with ferric chloride followed by homogeneous photo-Fenton treatment; but the advantage in the herein included case is that LL conductivity is reduced when using EC followed by conventional Fenton, in comparison with conventional coagulation, where conductivity increases because of the counterions of the coagulant that are added. In addition, this alternative will be cheaper in the waste management cost party because it will produce less iron sludge. Power consumption in UVA-LED photo-Fenton treatment has herein been addressed as the highest reported treatment cost (Table 4).

In order to further reduce the cost of the integral treatment, we look for a more synergic effect between the two treatment steps. Therefore, a second treatment combination alternative was assessed considering EC at a higher current density of 10 mA cm^{-2} , followed by a posterior Fenton or UVA-LED photo-Fenton treatment, in which

Table 4

Operational cost assessment approximation of the optimized combination of the developed EC pre-treatment with the posterior conventional Fenton or UVA-LED photo-Fenton treatment.

EC cost	EC @ pH=4 and 5 mA cm^{-2} for 2h			
H_2SO_4 , € m^{-3}	1.04			
Iron electrode, € m^{-3}	0.50			
EC power consumption, € m^{-3}	0.16			
EC total cost, € m^{-3}	1.70			
EC total cost, € kg^{-1} of COD removed	0.63			
Oxidation cost	Conventional Fenton $[\text{H}_2\text{O}_2]/\text{COD}$, time	UVA-LED photo-Fenton $[\text{H}_2\text{O}_2]/\text{COD}$, time		
H_2O_2 , € m^{-3}	2.125, 48h	1.063, 24h	2.125, 6h	1.063, 4h
Oxidation power consumption, € m^{-3}	4.90	2.45	04.90	02.45
Oxidation total cost, € m^{-3}	0.00	0.00	26.40	17.60
Oxidation total cost, € kg^{-1} of COD removed	4.90	2.45	31.30	20.05
Total process cost, € m^{-3}	3.65	2.58	23.75	20.21
Total process cost, € kg^{-1} of COD removed	6.60	4.15	33.00	21.75
Total process cost, € kg^{-1} of COD removed	1.68	0.86	6.47	05.91

the higher EC cost that is assumed might be balanced by a further reduction of the power consumption cost of the Fenton process. The hypothesis is that the higher investment in EC will enhance COD removal in the pre-treatment step (Fig. 1) and will provide enough residual iron content to reduce the hydrogen peroxide and the power required for the Fenton and UVA-LED photo-Fenton processes (Table 4). Thus, the increase of efficiency in the second step would reduce the treatment time and the overall cost for the integral treatment without adding counter ions to the wastewater.

3.4. An integral treatment alternative considering the EC pre-treatment at a current density of 10 mA cm^{-2} plus a posterior Fenton or UVA-LED photo-Fenton treatment

3.4.1. EC optimization at 10 mA cm^{-2}

The initial pH of EC was optimized for a 3 cm electrode distance, as in the case of $j = 5 \text{ mA cm}^{-2}$. COD removal results of the 26%, 34%, 54%, 62%, and 59% were achieved at initial pH values of 8, 7, 6, 5, and 4, respectively, after 2 h of treatment (Fig. 6a). These results enhance the best reported one of the 55% addressed by EC performed at 5 mA cm^{-2} and an initial pH = 4. In addition, the maximum efficiency of the 62% was achieved at an initial pH = 5 in the case of 10 mA cm^{-2} , and not 4, thanks to a higher iron dissolution amount the electrode, which would also imply a lower addition of sulfate to the media to adjust the pH. This is particularly relevant because of the savings that are implied to potential full-scale applications.

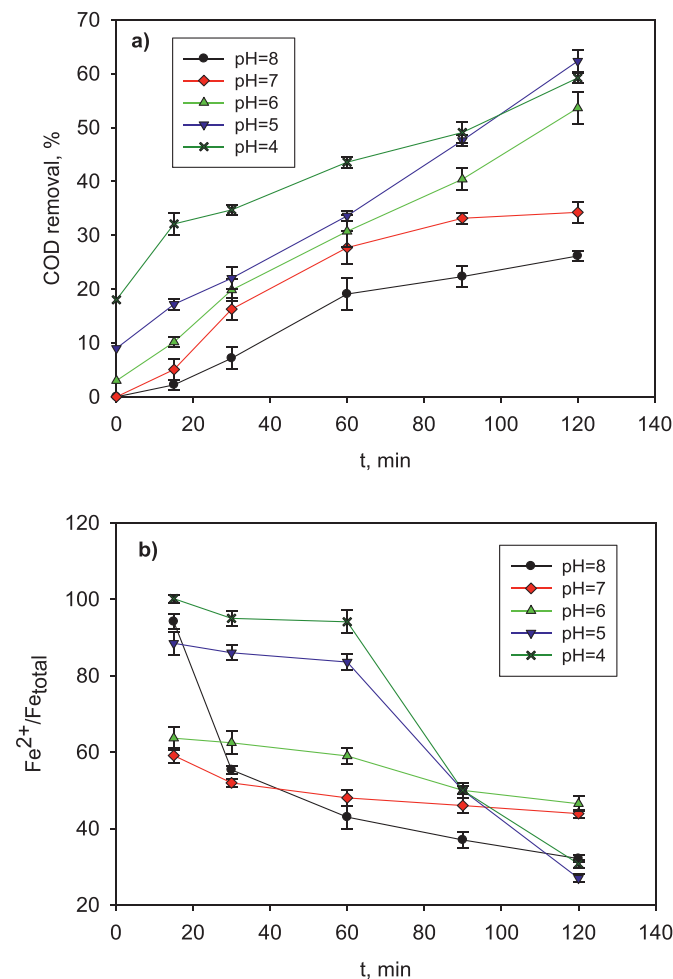


Fig. 6. pH optimization for an electro-coagulation (EC) pre-treatment of mature landfill leachate (LL) at a constant current density of 10 mA cm^{-2} and 3 cm of distance between electrodes: a) COD removal results, and b) iron species distribution.

Table 5
Characteristics of landfill leachate (LL) after being subjected to the designed alternative EC pre-treatment (10 mA cm^{-2} of current density of, 3 cm of distance between electrodes, and initial pH = 5).

Parameter	Value	Removal (%)
Initial pH	5.00 ± 0.10	-
Final pH	7.10 ± 0.10	-
Conductivity, mS cm^{-1}	15.30 ± 0.60	22.73
COD, $\text{mg-O}_2 \text{ L}^{-1}$	1861 ± 210	62.00
BOD_5/COD	0.01 ± 0.01	0-
SUVA, $\text{mg-C}^{-1} \text{ L cm}^{-1}$	2.40 ± 0.40	15.19
Color, mg Pt L^{-1}	6204 ± 680	67.00

More than the double amount of iron was dissolved at the end of the EC treatment (220 mg L^{-1}) when applying a current density of 10 instead of 5 mA cm^{-2} , which is also expected to improve the performance of the posterior Fenton oxidation processes; even though a higher pH value promotes a faster oxidation rate from Fe^{2+} to Fe^{3+} , which may counter effect an overall slower kinetics of the process. In this case, little difference in the iron speciation dynamics was observed between performing the designed EC pre-treatment at pH = 4 or 5. Nevertheless, the final EC pH was close to neutral for any of both current density values (Tables 2 and 5), which in neither case is particularly favorable to the performance of Fenton processes [36]. Furthermore, the higher dissolved iron content just implied a slight lower reduction of conductivity in the solution (14.20 for 5 mA cm^{-2} , whereas 15.30 for 10 mA cm^{-2}).

Finally, the removal of color (Fig. 7) was also higher when applying 10 mA cm^{-2} (67%; Table 5) than when EC was performed at 5 mA cm^{-2} (61%; Table 2). This is of particular interest for a more efficient transmission of the light in the posterior trialed UVA-LED photo-Fenton treatment; moreover considering that the removal of SUVA increased over the double (15.19%; Table 5) in the case of applying a current density of 10 mA cm^{-2} for the performance of EC with respect to 5 mA cm^{-2} (6.36%; Table 2).

3.4.2. Conventional Fenton treatment after 10 mA cm^{-2} EC

65% of the COD and 40% of the SUVA were removed from the 10 mA cm^{-2} electro-coagulated LL at after 24 h of conventional Fenton treatment at an $[\text{H}_2\text{O}_2]/\text{COD}$ ratio of 2.125 (Fig. 8). Thus, slightly better treatment results were achieved (61% COD and 34% SUVA removal after 5 mA cm^{-2} EC; Fig. 4), and the time of conventional Fenton treatment required to achieve such results was reduced to the half when current density was raised up from 5 to 10 mA cm^{-2} to perform the previous EC treatment step. This reduction in the time of treatment can be explained by the higher total iron concentration present in the electro-coagulated LL at 10 mA cm^{-2} (220 mg L^{-1}) than in the case of 5 mA cm^{-2} (100 mg L^{-1}), which implies a lower $\text{H}_2\text{O}_2/\text{Fe}_{\text{mol}}$ ratio, as explained in Section 3.2.1.

3.4.3. UVA-LED photo-Fenton treatment after 10 mA cm^{-2} EC

The UVA-LED photo-Fenton treatment of 10 mA cm^{-2} electro-coagulated LL also achieved better COD (68%) and SUVA (56%) removal results (Fig. 9) than after a 5 mA cm^{-2} EC (63% and 52%, respectively; Fig. 5); as well as the required time of treatment was comparatively reduced by one half (Fig. 9), namely: 180, 120, and 60 min for the $[\text{H}_2\text{O}_2]/\text{COD}$ ratio values of 2.125, 1.063, and 0.531, respectively. This reduction in the time of required treatment is explained as well by the higher total iron concentration remaining in the solution after EC at 10 mA cm^{-2} compared to 5 mA cm^{-2} (220 mg L^{-1} vs. 100 mg L^{-1}). In addition, 46% of the COD were removed from the 10 mA cm^{-2} electro-coagulated LL at after 2 h of UVA-LED photo-Fenton treatment at an $[\text{H}_2\text{O}_2]/\text{COD}$ ratio of 1.063 (Fig. 8), which was previously selected for comparison with the conventional Fenton process as a balance between results and cost of the treatment. This

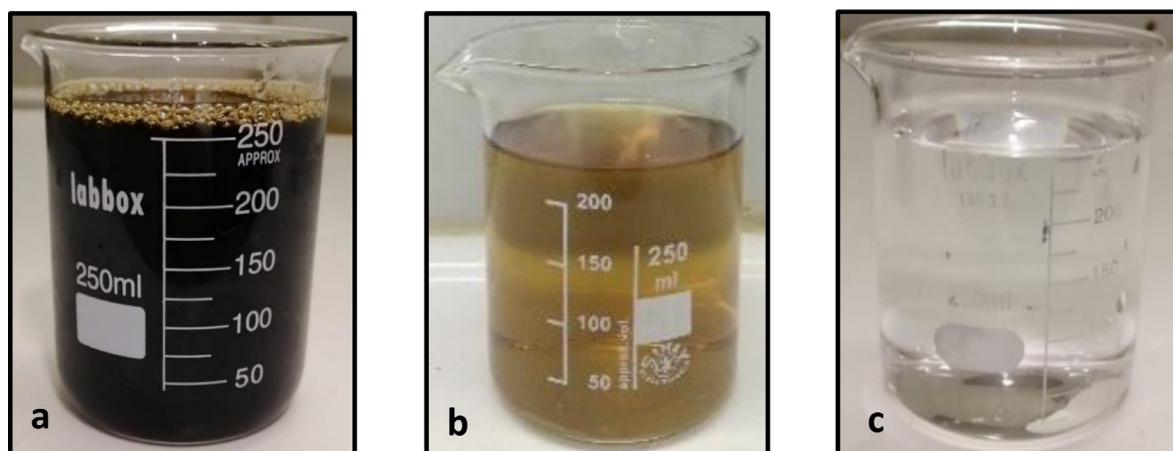


Fig. 7. Color removal display: Raw mature landfill leachate, LL (a), electro-coagulated LL (b), and Fenton ($[H_2O_2]/COD = 2.125$) oxidized electro-coagulated LL (c).

is also an enhancement in comparison to the 4 h that were needed to remove a 45% of the COD from 5 mA cm^{-2} electro-coagulated LL (Fig. 5).

Control tests without the addition of hydrogen peroxide were complementarily carried out as well (Figs. 8 and 9) to get further understanding of the mechanisms implied in the essayed Fenton processes. In this case, no COD, nor SUVA, removal was achieved. Thus,

the oxidation of organic matter was not addressed by the sole presence of UVA light in the case of the photo-Fenton process; or by side coagulation aid mediated by the presence of iron in the conventional Fenton process. The generation of hydroxyl radical from hydrogen peroxide in the solution was addressed to be necessary to degrade organic compounds.

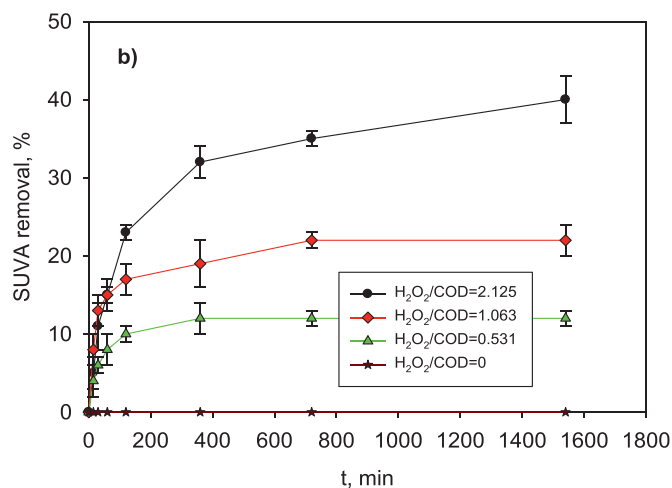
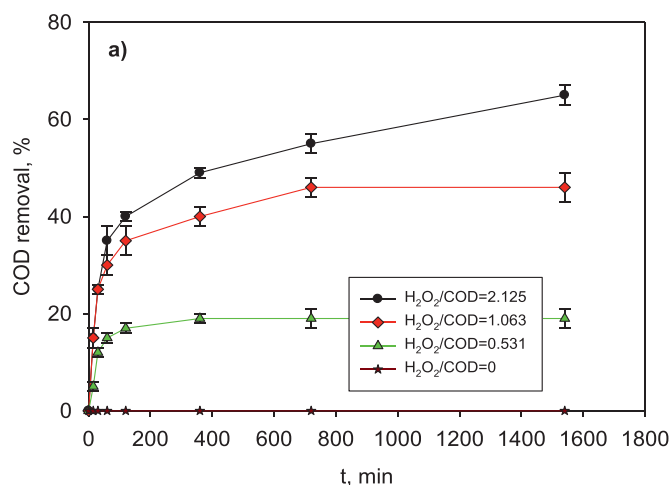


Fig. 8. Evolution of the removal of COD (a) and SUVA (b) along the conventional Fenton treatment of pre-electro-coagulated landfill leachate (LL) at a current density of 10 mA cm^{-2} .

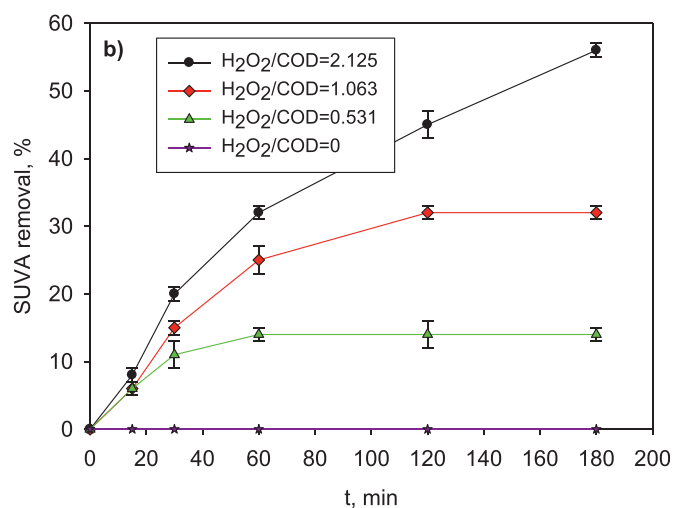
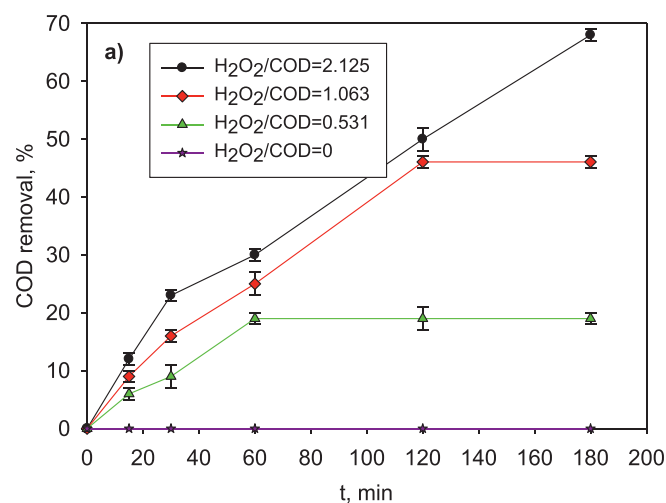


Fig. 9. Evolution of the removal of COD (a) and SUVA (b) along the UVA-LED photo-Fenton treatment of pre-electro-coagulated landfill leachate (LL) at a current density of 10 mA cm^{-2} .

Table 6
Comparison of results between the conventional Fenton and the UVA-LED photo-Fenton treatment of pre-electro-coagulated (10 mA cm⁻²) landfill leachate (LL).

	Conventional Fenton		UVA-LED photo-Fenton		Conventional Fenton		UVA-LED photo-Fenton	
[H ₂ O ₂]/COD	2.125		1.063		0.531			
pH	4.60 ± 0.10	4.75 ± 0.10	4.85 ± 0.10	4.90 ± 0.10	5.15 ± 0.10	5.65 ± 0.10		
Conductivity mS cm ⁻¹	15.80 ± 0.70	15.75 ± 0.70	15.20 ± 0.70	15.10 ± 0.70	14.85 ± 0.70	14.75 ± 0.70		
Oxidation t, min	1440	180	720	120	360	60		
Color*	250 ± 80	135 ± 80	985 ± 100	945 ± 90	1405 ± 250	1400 ± 150		
mg Pt L ⁻¹	(99%)	(99%)	(95%)	(95%)	(93%)	(93%)		
COD*	651 ± 90	596 ± 80	1005 ± 120	1005 ± 130	1507 ± 190	1507 ± 170		
mg O ₂ L ⁻¹	(87%)	(88%)	(80%)	(80%)	(69%)	(69%)		
BOD ₅ /COD	0.34 ± 0.05	0.40 ± 0.05	0.26 ± 0.05	0.33 ± 0.05	0.13 ± 0.05	0.15 ± 0.05		
SUVA*	1.44 ± 0.30	1.06 ± 0.25	1.87 ± 0.20	1.63 ± 0.20	2.11 ± 0.30	2.06 ± 0.35		
mg-C ⁻¹ L cm ⁻¹	(49%)	(63%)	(34%)	(43%)	(25%)	(37%)		
NH ₄ ⁺ mg L ⁻¹	1500 ± 100	1500 ± 100	1500 ± 100	1500 ± 100	1500 ± 100	1500 ± 100		

* Removal % including the electrocoagulation + Fenton treatment of landfill leachate are shown in brackets.

3.4.4. Results comparison between treatment alternatives including an EC pre-treatment at 10 mA cm⁻² and a conventional Fenton or UVA-LED photo-Fenton step

Table 6 shows the comparison of the characteristics of LL after being subjected to EC at 10 mA cm⁻² and a Fenton or UVA-LED photo-Fenton treatment performed at different [H₂O₂]/COD ratios. In all the cases, color removal was greater than 90% (Fig. 7), and results were better than when EC was performed at 5 mA cm⁻² (Table 3); with the exception of NH₄⁺ content, which remained unchanged at 1500 ± 100 mg L⁻¹, and conductivity, which final values were slightly higher in the range of about 15 mS cm⁻¹ than in the previous case, surely due to the higher iron content in the solution. Nevertheless, conductivity was also significantly reduced with respect to initial LL value (19.80 ± 0.80; Table 1).

The greater ratio [H₂O₂]/COD used, the greater COD and SUVA removals were obtained. In all cases, SUVA and COD removals followed the same behavior, indicating that a significant amount of refractory/non-biodegradable COD is removed with these treatments, as it is also observed by the increase in the BOD₅/COD ratio such as 0.13, 0.30 and 0.40 for [H₂O₂]/COD ratios of 0.531, 1.063 and 2.125, respectively.

In short, residual COD values were in the range of 600 mg O₂ L⁻¹ for [H₂O₂]/COD = 2.125 and about 1000 mg O₂ L⁻¹ for [H₂O₂]/COD = 1.063 for both Fenton processes; but the treatment time required to achieve these results was 6–8 times lower in the case of the UVA-LED photo-Fenton process. Moreover, the increase of biodegradability (BOD₅/COD over 0.3), together with an enhanced SUVA removal (30–60% range), and the reduced values of conductivity (≈ 15–16 mS cm⁻¹) lead to expect a high posterior treatment efficiency

by conventional biological processes whenever it would be necessary (for example, under strict limitations imposed by the legislation regulating discharge water quality limits to natural water bodies). This biological step may also include a nitrogen reduction step to contribute removing the high content of ammonium within, for which an alternative strategy should be designed.

3.4.5. First economic assessment approximation of the integral treatment considering the electro-coagulation (EC) pretreatment at 10 mA cm⁻²

The use of a higher current density (10 vs. 5 mA·cm⁻²) increased the overall operational cost of EC from 0.63 to 0.89 € kgCOD⁻¹ (Tables 4 and 7). However, the important shortening of the running time of the UVA-LED photo-Fenton oxidation process led to an important reduction in the total operational cost, namely: from 5.91 € kgCOD⁻¹ (Table 4) to 3.48 € kgCOD⁻¹ (Table 7) for the photo-Fenton treatment at an [H₂O₂]/COD = 1.063. On the other hand, the total cost of the combination with the conventional Fenton process at an [H₂O₂]/COD = 2.125 just decreased from 1.68 € kgCOD⁻¹ (Table 4) to 1.61 € kgCOD⁻¹ (Table 7).

Therefore, increasing EC current density from 5 to 10 mA cm⁻² reduced in a 41% the total treatment cost of EC + UVA-LED photo-Fenton reaction per kg of removed COD; but it was just a 4% lower for the combination with the conventional Fenton process at laboratory scale, although higher COD was removed. Nevertheless, further assessment considering other costs, such as waste and sludge management, pumping, or facilities implementation could be developed. In short, the conventional Fenton process was estimated as cheaper than the UVA-LED photo-Fenton, in first approximation at lab scale,

Table 7
Operational cost assessment approximation of the optimized combination of the developed EC pre-treatment ($j = 10 \text{ mA cm}^{-2}$) with the posterior conventional Fenton or UVA-LED photo-Fenton treatment.

EC cost	EC @ pH=5 and 10 mA cm ⁻² for 2h			
H ₂ SO ₄ , € m ⁻³	0.94			
Iron electrode, € m ⁻³	1.00			
EC power consumption, € m ⁻³	0.75			
EC total cost, € m ⁻³	2.69			
EC total cost, € kg ⁻¹ of COD removed	0.89			
Oxidation cost	Conventional Fenton	[H₂O₂]/COD, time	UVA-LED photo-Fenton	[H₂O₂]/COD, time
H ₂ O ₂ , € m ⁻³	2.125, 24h	1.063, 12h	2.125, 3h	1.063, 2h
Oxidation power consumption, € m ⁻³	4.14	2.07	04.14	02.07
Oxidation total cost, € m ⁻³	0.00	0.00	13.20	08.80
Oxidation total cost, € kg ⁻¹ of COD removed	4.14	2.07	17.34	10.87
Total process cost, € m⁻³	3.42	1.64	20.25	12.69
Total process cost, € kg⁻¹ of COD removed	6.83	4.76	20.03	13.56
	1.61	1.09	04.98	03.48

because it does not require power consumption for the application of radiation; but a treatment time of 24 h may not be feasible in the full scale when large volumes of LL are generated.

Conclusions

The proposed new integral treatment alternative for mature landfill leachate based on EC pretreatment followed by Fenton oxidation processes, successfully improve the results obtain in previous similar treatment alternatives, in terms of the removal of contaminants and overall treatment cost; as well as in reducing conductivity, and increasing biodegradability, so a biological treatment may further be considered when necessary.

EC optimization for a current density of 5 mA cm^{-2} (3 cm of distance between electrodes and $\text{pH} = 4$) addressed a 55% COD reduction standalone, for which a cost of $0.63 \text{ € kgCOD}^{-1}$ was estimated in a first approximation assessment at lab scale. Final iron concentration was only 100 mg L^{-1} , which implied a longer time of treatment in a posterior Fenton process; thus increasing the overall cost of treatment, especially in the case of the UVA-LED photo-Fenton process because of the derived power consumption related to the application of radiation.

At a current density of 10 mA cm^{-2} , the residual iron concentration increased up to 220 mg L^{-1} , and, consequently, the time required for the UVA-LED photo-Fenton stage was reduced by one half (2 h; $[\text{H}_2\text{O}_2]/\text{COD} = 1.063$). Although the cost of EC increased up to $0.89 \text{ € kgCOD}^{-1}$, the overall treatment cost was reduced from 5.91 to $3.48 \text{ € kgCOD}^{-1}$ (41% lower). Similarly, the required treatment time for the most efficient conventional Fenton posterior treatment ($[\text{H}_2\text{O}_2]/\text{COD} = 2.125$) was reduced from 48 to 24 h; but the first operational cost approximation was just reduced a 4%.

The application of Fenton processes (conventional or UVA-LED photo-Fenton) to pre-electrocoagulated landfill leachate addressed up to the 90% of COD removal and 60% reductions of SUVA. In addition, the biodegradability of mature LL increased from 0.01 to 0.3–0.4 BOD_5/COD ratio at the best tested conditions. Conductivity was reduced by a 20–30% after the overall EC+Fenton treatment in any case.

Although the application of UVA-LED photo-Fenton was assessed as 2–3 times more expensive than its conventional version in a preliminary cost assessment, because of the need of power consumption, it also required 6–8 times less time for treatment and it would require much less space for facilities to be implemented at a full industrial scale. These are very relevant issues to take into account considering the great volume of leachate that it is typically produced in landfills.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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All authors have equally contributed to this work.

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