

Optimization of the landfill leachate treatment by the Fenton process

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biodegradability; Fe^{2+} dosage; Fenton process; H_2O_2 dosage; landfill leachate

Abstract

The Fenton process was used with the objective of improving the biodegradability of the leachate pretreated biologically up to a value compatible with a subsequent biological treatment. The optimum reaction and settlement pH was 3, both for the organic matter removal and for the improvement of the biodegradability. The chemical oxygen demand (COD) removal increased at increasing Fe^{2+} dosages, from 75.6% for 300 mg/L to 89.0% for 1400 mg/L. The most significant enhancement (84.8%) was obtained with 800 mg Fe^{2+} /L. However, the biological oxygen demand/chemical oxygen demand ratio (BOD/COD) was almost the same at all the Fe^{2+} dosages, around 0.29. Moreover, varying the H_2O_2 concentration between 600 and 3600 mg/L, COD removal percentages were between 85.9 and 89.0%. However, the BOD/COD ratio increased at increasing H_2O_2 dosage up to 3000 mg/L, from 0.12 at 600 mg/L to 0.29 at 3000 mg/L.

Introduction

Landfill leachates are considered one of the types of wastewater with the greatest environmental impact. There are many factors affecting the quality of leachates, i.e. waste type and composition, landfilling technique, seasonal weather variation, age of the landfill, etc. Leachates are normally classified depending on the age of the landfill into young, medium or mature leachates. Young leachates have high organic matter content and high biodegradability. However, mature leachates show the lowest values of organic matter and the lowest biodegradability properties, with biological oxygen demand/chemical oxygen demand (BOD/COD) ratios below 0.1.

There is a wide range of different approaches and technologies available for efficient treatment of leachates. The biological treatments, including aerobic and anaerobic processes, are the most economically efficient method for the removal of biodegradable organic compounds. Biological processes have been shown to be very effective when the BOD/COD ratio is high, but this ratio generally decreases with the age of the landfill because most of the organic compounds in the stabilized leachate are inhibitory, toxic or refractory to biological treatment (Wiszniewski *et al.* 2006). Traditionally, the removal of recalcitrant compounds can be achieved by advanced oxidation processes (AOP).

AOP involve the generation of the hydroxyl radical, which has a very high oxidation potential and is able to oxidize almost all organic pollutants. Researches about AOP reported in the literature demonstrate their high efficiency on the organic matter removal from the leachate. Nevertheless, AOP aiming at complete mineralization might become extremely cost-intensive as a unique process because the highly oxidized end products formed during chemical oxidation tend to be refractory to total oxidation by chemical means (Mantzavinos & Psillakis 2004). A significant decrease of overall leachate treatment cost could be obtained by the combination of AOP with a biological process and/or with other physical-chemical technologies, once the efficiency of these combinations has been proved (Lopes de Morais & Peralta Zamora 2005; Rivas *et al.* 2005; Primo *et al.* 2008).

The Fenton process is one of the most common AOP applied to the degradation of a great variety of industrial wastewaters, including pharmaceutical, textile, chemical, paper pulp, food processing, cork processing, oil shale semicoke leachate, landfill leachate, etc. (Bautista *et al.* 2008; Trapido *et al.* 2009). This technology is defined as the catalytic generation of hydroxyl radicals resulting from the chain reaction between ferrous iron and hydrogen peroxide, and the oxidation of organic compounds (RH) by Fenton reagents can proceed by the following chain reactions (Kang & Hwang 2000; Neyens & Baeyens 2003).

- $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH}$ (1)
- $\text{Fe}^{2+} + \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^-$ (2)
- $\text{RH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{R}$ (3)
- $\text{R} + \text{Fe}^{3+} \rightarrow \text{R}^+ + \text{Fe}^{2+}$ (4)
- $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$ (5)

The Fenton process is simple and easy to operate; it can be performed at ambient temperature, energy input is not necessary and commonly requires a relatively short reaction time compared with other AOP. Moreover, the reagents are readily available, easy to store and relatively safe to handle (Primo *et al.* 2008). As well, it is considered to be one of the most cost-effective options for treating landfill leachate (Deng 2007; Hermosilla *et al.* 2009; Wang *et al.* 2009).

A potentially attractive alternative to complete oxidation by AOP is the use of a chemical oxidation pretreatment step to convert initial biorecalcitrant organics to more readily biodegradable intermediates, followed by biological oxidation of these intermediates to biogas, biomass and water (Lopez *et al.* 2004; Mantzavinos & Psillakis 2004; Lopes de Morais & Peralta Zamora 2005; Barnes *et al.* 2007). However, it should be taken into account that the application of AOP to wastewater with high biodegradability could oxidize not only the recalcitrant compounds but also the biodegradable organic matter, which would increase the cost of the treatment. Therefore, an appropriate option could be the combination of the biological treatment followed by an AOP, and a subsequent biological treatment or the recirculation to the previous biological process. This combination is the one proposed in this research in order to improve the treatment of landfill leachate.

The aim of this study was to optimize the treatment of the landfill leachate by the Fenton process. This process was used with the objective of improving the biodegradability of the leachate pretreated biologically up to a value compatible with a subsequent biological treatment. In order to optimize this process, different pH, iron dosages, hydrogen peroxide dosages and reaction times were assayed.

Materials and methods

Analytical methods

In this study, two different leachates were used, both collected from a landfill of urban solid wastes in the province of A Coruña (Spain) after being biologically treated. Leachate samples were taken with polyethylene bottles and were preserved in refrigerator at 4°C. The characterization of the landfill leachates was undertaken measuring the following parameters.

COD was analysed by the closed reflux method (*Standard Methods*, APHA 1998). Dissolved organic carbon (DOC) was determined by the combustion infrared method using a TOC-5050A Shimadzu (Shimadzu, Kyoto, Japan) (*Standard Methods*, APHA 1998). Total suspended solids, volatile suspended solids (VSS) and pH were also evaluated according to *Standard Methods* (*Standard Methods*, APHA 1998). BOD was determined using BOD systems (Velp Scientifica, Usmate Velate Monza e Brianza, Italy) in which the internal pressure is translated by a microprocessor directly into BOD. The BOD values used in this study are the ultimate BOD because the used sludge was not acclimatized to the leachate.

Ammonium was analysed by a colorimetric method based in the reaction of ammonium anion with hypochlorite and phenol. The absorbance of the compound obtained was determined at 635 nm using an ultraviolet/visible (UV/VIS) spectrophotometer (Lambda 11, Perkin Elmer, Waltham, MA, USA). Nitrate was determined by capillary

electrophoresis using a Hewlett Packard ^{3D}CE system (Palo Alto, CA, USA) with a microcapillary tube of fused silica [40 cm × 50 µm internal diameter (ID)]. A sodium phosphate solution was employed as the electrolyte and UV detection was undertaken at a wavelength of 214 nm. The concentration of residual hydrogen peroxide was calculated using the iodometric method (Vogel 1989).

Experimental procedure

The Fenton assays were performed in duplicate in batch mode using non-diluted landfill leachate after being biologically treated. They were undertaken using different pH, iron dosages, hydrogen peroxide dosages and reaction times in order to optimize the operational conditions of the Fenton process. The experiments were carried out at a temperature around 20°C in a conventional jar-test apparatus, equipped with six beakers of 500 mL volume. At the beginning of the assays, the pH of the leachate was adjusted to 3 (except for the reaction pH experiments), and there was no control of the pH during the Fenton reaction. After that, ferrous sulphate (Fe²⁺) was added and the reaction was initiated by adding hydrogen peroxide (H₂O₂). The reaction took place at 250 rpm during 2 h, except for the time assays.

Afterwards, the excess of hydrogen peroxide was removed by heating the samples at 50°C during 1 h (Barnes *et al.* 2007; Deng 2007). Then, the beakers were stirred at 50 rpm during 10 min for the coagulation. In some assays, aliquots were taken to adjust the pH at different values and study its effect on the coagulation. Finally, the samples were allowed to settle and the supernatants were analysed in order to evaluate the efficiency of the Fenton process.

Results and discussion

Two different leachates were used in the present research, both collected after the biological treatment of leachates of a landfill of urban solid wastes. Initially, the characterization of the landfill leachates was undertaken and their composition is presented in Table 1. Both leachates are characterized by high organic matter concentrations but very low biodegradability, which was expected because the biodegradable organic matter was removed in the previous biological treatment. The biodegradability is one of the parameters commonly used to select the best process for the treatment. In this study, the BOD/COD ratios are very low; therefore, the Fenton process could be adequate to remove the recalcitrant organic matter and increase the biodegradability of the leachates. This process was used with the objective of improving the overall leachate biodegradability, evaluated in terms of BOD/COD ratio, up to a value compatible with biological treatment. In order to optimize the Fenton process, different pH, iron dosages, hydrogen peroxide dosages and reaction times were assayed.

Table 1. Characterization of the landfill leachates (all parameters in mg/L, except pH)

	Leachate I	Leachate II
pH	7.4	7.2
COD	13782	6629
BOD	45	156
BOD/COD	0.02	0.02
DOC	5277	3330
N-NH ₄ ⁺	41.6	11.2
N-NO ₃ ⁻	1220.4	754.0
TSS	2335.7	1520.3
VSS	1692.9	1280.1

COD, chemical oxygen demand; BOD, biological oxygen demand; DOC, dissolved organic carbon; TSS, total suspended solids; VSS, volatile suspended solids.

Effect of pH

At the beginning of the assays with leachate I, when the pH was being adjusted, the variation of the aspect of the supernatant at decreasing pH was observed. The brown colour of the raw leachate was changing to yellow (Fig. 1a). Part of the organic matter present in the leachate precipitated with the decrease of the pH, as the COD and DOC concentrations showed (Fig. 1b). Percentages around 69 and 75% of COD and DOC, respectively, were removed of the supernatant by only adjusting the pH at 3. However, the pH reduction did not affect the BOD/COD ratio, which was kept at 0.02.

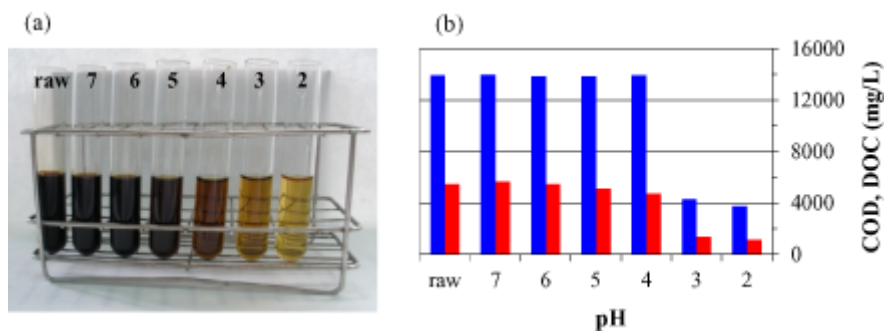


Figure 1. (a) Visual aspect of the leachate supernatant with the pH decrease from the raw leachate to pH 2; (b) evolution of the chemical oxygen demand (COD, ■) and dissolved organic carbon (DOC, ■) concentrations at decreasing pH values.

These results are according to those reported by Rivas *et al.* (2005), who evaluated several combinations of different processes for the landfill leachate treatment. A COD reduction around 60% was reached after carrying out both the previous acidic precipitation and the further coagulation-flocculation at pH 3.5 after addition of ferric ion 0.01 mol/L. The precipitation of the fraction of the humic substances was undertaken with sulphuric acid at pH 2, removing around 33% of COD. The acidic precipitation of the humic substances together with the coagulation favoured by the iron present in the leachate could explain our results.

The same effect was observed when the pH was increased after carrying out the Fenton reaction under the same conditions, such as pH 3, 900 mg Fe²⁺/L, 3180 mg H₂O₂/L and 2 h of reaction time. The pH of the different beakers was adjusted between 2 and 7 to carry out the coagulation-flocculation process and the settlement. As it is shown in Fig. 2, the COD and DOC concentrations decreased at decreasing pH values. Final COD values around 8450 and 2350 mg/L were obtained at pH 7 and 2, respectively. These facts guess that the neutralization at pH 7 is not only unnecessary but also damaging for the efficiency of the treatment. Taking into account these results, the coagulation and settlement were carried out at pH 3 in the following assays.

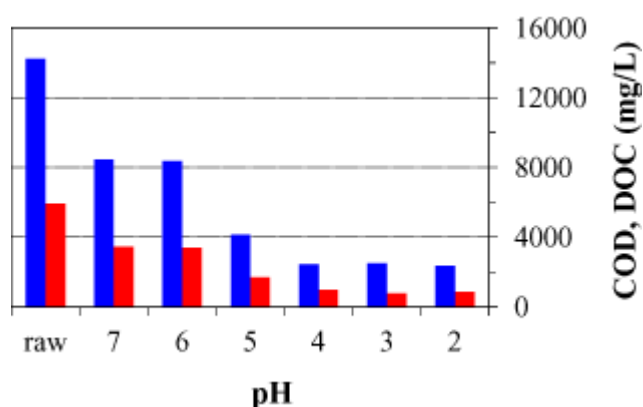


Figure 2. Evolution of the chemical oxygen demand (COD, ■) and dissolved organic carbon (DOC, ■) concentrations at decreasing pH values for coagulation-flocculation, after carrying out the Fenton reaction at the same conditions (900 mg Fe²⁺/L and 3180 mg H₂O₂/L).

This is in concordance with the results obtained for other authors studying the effect of the pH on the COD removal by coagulation. Gau & Chang (1996) observed that the optimum pH for the coagulation was 4. Kang & Hwang (2000) tested the pH range from 2 to 9, obtaining an optimum pH range 3–6 to maximize the COD removal efficiency by coagulation, lower than the pH range of 6–9 generally showed in literature.

After the coagulation-flocculation process at pH 3, the time for solid–liquid separation by settlement was of several hours. In the literature, settlement periods from some minutes to several days are reported (Deng & Englehardt 2006; Hermosilla *et al.* 2009). Some authors state alternatives to settlement such as sand-filtration or membrane processes, in order to reduce the space requirements and increase the efficiency of the separation process (Bautista *et al.* 2008; Primo *et al.* 2008).

Effect of reaction pH

In order to optimize the reaction pH, the Fenton assays were carried out with leachate I adding 800 mg Fe²⁺/L and 3000 mg H₂O₂/L. According to the literature, low pH favours Fenton oxidation (Deng & Englehardt 2006), so the reaction pH was varied between 2 and 7. The reaction time was 2 h and the coagulation and the settlement took place at pH 3 in order to maintain the same conditions. COD and DOC concentrations and BOD/COD ratios are shown in Fig. 3. Both the lowest COD concentration and the highest BOD/COD ratio were obtained at reaction pH 3. Therefore, the optimum reaction pH was 3, both for the organic matter removal and for the improvement of the biodegradability. The COD and DOC concentrations in raw leachate were 13 890 and 5450 mg/L, respectively, COD and DOC removal percentages were both around 90.0% for the reaction pH 3. Therefore, the following Fenton assays were carried out at a reaction pH of 3 according to several authors such as Deng (2007) and Primo *et al.* (2008).

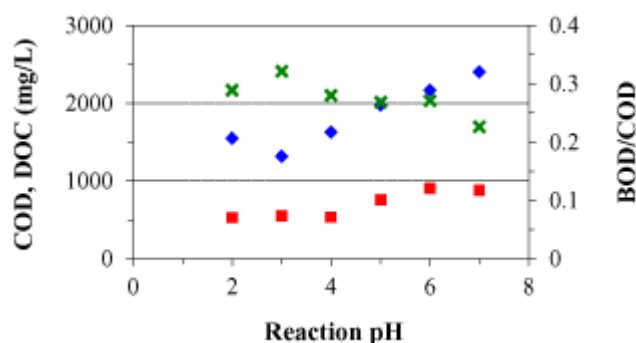


Figure 3. Chemical oxygen demand (COD, ◆) and dissolved organic carbon (DOC, ■) concentrations and biological oxygen demand (BOD)/COD ratios (×) obtained at different reaction pH, after carrying out the Fenton reaction at the same conditions (800 mg Fe²⁺/L and 3000 mg H₂O₂/L).

Effect of Fe²⁺ dosage

The influence of the Fe²⁺ dosage on the efficiency of the Fenton process was studied using both leachates. The assays were carried out at pH 3 maintaining the H₂O₂ concentration at 3500 mg/L and varying the Fe²⁺ dosage from 300 to 1400 mg/L, the reaction time was 2 h. The obtained COD concentrations and BOD/COD ratios are

shown in Fig. 4. The initial COD of leachate I was 13 332 mg/L and the BOD/COD ratio was almost nil, showing its low biodegradability. An organic matter removal of 68.2% was attained by only adjusting the pH at 3, obtaining a COD concentration of 4239 mg/L (Fig. 4a). After the Fenton reaction, the COD removal increased at increasing Fe^{2+} dosages, from 75.6% for 300 mg/L to 89.0% for 1400 mg/L. The most significant enhancement was until 800 mg/L, obtaining a COD removal percentage of 84.8% at this Fe^{2+} concentration. However, the BOD/COD ratio was almost the same at all the Fe^{2+} dosages, around 0.29.

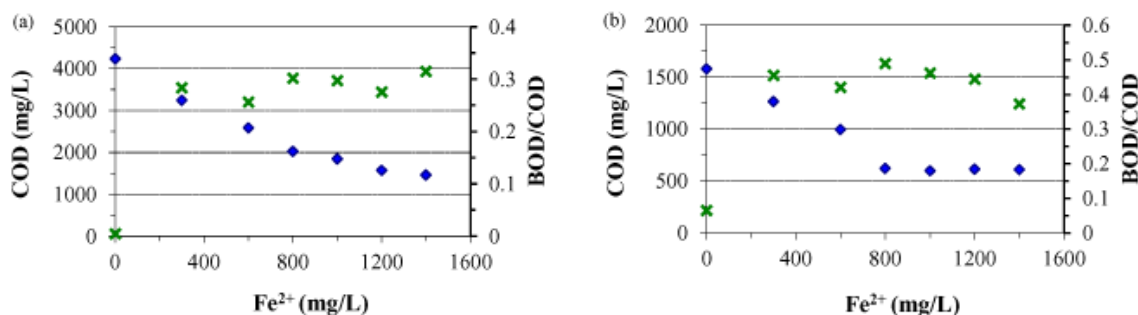


Figure 4. Chemical oxygen demand (COD, \blacklozenge) concentrations and biological oxygen demand (BOD)/COD ratios (\times) obtained after carrying out the Fenton reaction with leachate I (a) and leachate II (b), maintaining the H_2O_2 dosage at 3500 mg/L and varying the Fe^{2+} concentration from 300 to 1400 mg/L.

Although the organic matter was lower in leachate II, with an initial COD of 6629 mg/L, the results obtained are similar to the ones of leachate I. A removal organic matter of 76.2% was attained by only adjusting the pH at 3, achieving a COD concentration of 1578 mg/L (Fig. 4b). Until a Fe^{2+} dosage of 800 mg/L, the COD removal increased at increasing Fe^{2+} concentrations; while at Fe^{2+} dosages of 800 mg/L and higher, the COD removal was almost constant around 90.8%. The BOD/COD ratio was approximately the same at all the Fe^{2+} dosages, being the average value 0.44.

From the obtained results, it can be concluded that a Fe^{2+} dosage of 800 mg/L is sufficient to remove the organic matter and increase the biodegradability. Therefore, the following experiments were performed at an Fe^{2+} concentration of 800 mg/L because dosages of Fenton reagents determine the operating costs of the process. Moreover, excess iron salt contributes to an increase in effluent total dissolved solids and electrical conductivity, as well as in the amount of iron sludge that requires treatment.

In the literature, there are large discrepancies in the reported optimum dosages and organic matter removals ascribed to variations in leachate quality (Deng & Englehardt 2006). Lopez *et al.* (2004) studied the Fenton process as pretreatment for the leachate from a municipal landfill to find the optimum conditions for the improvement of the biodegradability. The organic matter concentration of the leachate was similar to our study, being the COD 10 540 mg/L. The maximum COD removal was about 60%, using a similar iron dosage (830 mg/L) but a higher hydrogen peroxide concentration (10 000 mg/L).

Effect of H₂O₂ dosage

After optimizing the iron dosage, the effect of the hydrogen peroxide was studied using leachate I. The assays were undertaken during 2 h at pH 3 with 800 mg Fe²⁺/L, varying the H₂O₂ concentration between 600 and 3600 mg/L. The coagulation and the settlement took place at the same pH than the Fenton reaction. COD and DOC concentrations and BOD/COD ratios are shown in Fig. 5(a). The initial COD and DOC concentrations in the leachate were 13 137 and 5110 mg/L, respectively. The 70.9% of the COD and the 73.5% of the DOC were removed only because of the adjustment of the pH at 3. COD and DOC removals were between 85.9 and 89.0% and between 87.0 and 91.1%, respectively, at all H₂O₂ dosages. However, the BOD/COD ratio increased at increasing H₂O₂ dosage up to 3000 mg/L, from 0.12 at 600 mg/L to 0.29 at 3000 mg/L. At higher hydrogen peroxide dosages, the BOD/COD ratio maintained constant around 0.29. Therefore, a H₂O₂ concentration of 3000 mg/L to increase the biodegradability of the leachate is necessary.

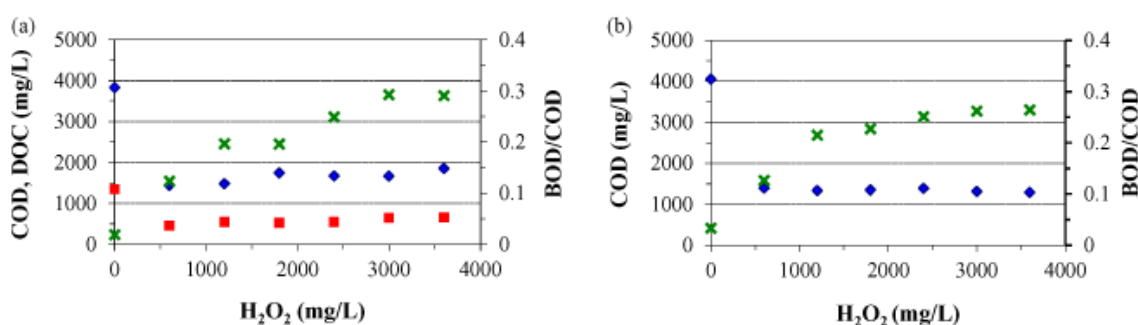


Figure 5. Chemical oxygen demand (COD, ♦) and dissolved organic carbon (DOC, ■) concentrations and biological oxygen demand (BOD)/COD ratios (✖) obtained after carrying out the Fenton reaction with raw leachate (a) and the supernatant at pH 3 (b) maintaining the Fe²⁺ dosage at 800 mg/L and varying the H₂O₂ concentration between 600 and 3600 mg/L.

In the previous assays, after adjusting the leachate pH at 3, a high percentage of the organic matter was removed from the supernatant. Taking into account this fact, these assays were repeated using the supernatant obtained when adjusting pH at 3, once it was separated from the formed precipitate. In order to compare the efficiency of the Fenton process, the assays with the supernatant at pH 3 were performed at the same conditions as the previous assays with the raw leachate. As it can be observed in Fig. 5(b), the obtained results were very similar in both cases. The COD removal percentage was almost constant at all H₂O₂ dosages, around 89.9%. While, the BOD/COD increased at increasing H₂O₂ dosage up to 3000 mg/L, from 0.13 at 600 mg/L to 0.26 at 3000 mg/L. At higher hydrogen peroxide dosages, the BOD/COD ratio maintained constant around 0.26. From these results, it can be concluded that the presence of the organic matter susceptible to coagulation had not influence on the Fenton reaction. Therefore, the previous separation of the supernatant improved neither the efficiency of the Fenton process according to COD removal and biodegradability nor the reagents' consumption.

From the obtained results, it can be concluded that a H₂O₂ concentration of 3000 mg/L is sufficient to increase the biodegradability of the leachate. Taking into account the

results shown in Fig. 5, it could be considered that higher hydrogen peroxide dosages could enhance the biodegradability. Nevertheless, the residual hydrogen peroxide values observed from 69 to 898 mg/L throughout the tested dosages from 600 to 3600 mg/L, respectively, indicated that no limitation by hydrogen peroxide took place. The high residual hydrogen peroxide could be attributed to radical chain reactions in which organic matter (RH) takes part. Some authors state that low molar ratios of $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0$ can lead to a predominant role of chemical oxidation versus coagulation (Neyens & Baeyens 2003; Primo *et al.* 2008). In our assays, the $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0$ molar ratio was from 0.81 to 0.14 throughout the tested dosages from 600 to 3600 mg/L, respectively. Neyens & Baeyens (2003) analysed different $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0$ molar ratios and the effect of the presence of t-BuOH and MeOH on the fate of $\cdot\text{OH}$ produced by Fenton reaction. The results were interpreted in terms of the known reaction mechanisms of the Fenton system. According to those authors, at $[\text{Fe}^{2+}]_0/[\text{H}_2\text{O}_2]_0$ molar ratios much lower than 1, the presence of RH has an impact on the behaviour of the hydrogen peroxide. No further H_2O_2 decomposition occurs just after the initial decrease because of Eq. (1), because the Eq. (3) of RH with $\cdot\text{OH}$ competes with Eq. (5) of H_2O_2 with $\cdot\text{OH}$. Moreover, the presence of excess RH can hinder Eq. (2) between $\cdot\text{OH}$ and Fe^{2+} . Organic radicals obtained by Eq. (3) are highly reactive and can be further oxidized, even initiate a radical chain propagation reaction.

Effect of reaction time

After optimizing the iron and hydrogen peroxide dosages, assays were performed with leachate II at different reaction times in order to determine the time necessary for the Fenton reaction to take place. The used conditions were 800 mg Fe^{2+}/L , 3000 mg $\text{H}_2\text{O}_2/\text{L}$ and pH 3. The COD of raw leachate was 6629 mg/L and the BOD/COD ratio was almost nil. A high percentage of the COD was removed and the biodegradability increased (Fig. 6). After 1 h of reaction, the organic matter removal was almost constant (90.7%), obtaining a COD concentration around 614 mg/L. The BOD/COD ratio increased at increasing reaction times, from 0.19 for 20 min to 0.33 for 120 min.

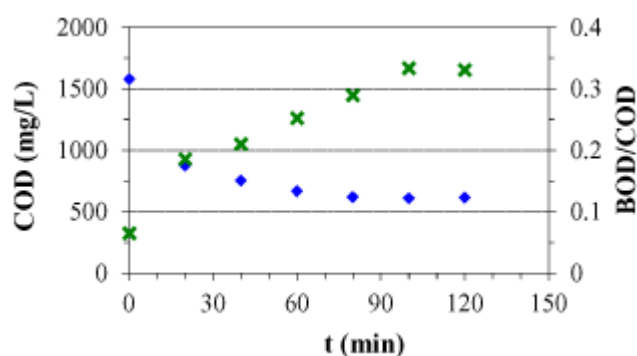


Figure 6. Chemical oxygen demand (COD, \blacklozenge) concentrations and biological oxygen demand (BOD)/COD ratios (\blacktimes) obtained at different reaction times after carrying out the Fenton reaction at the same conditions (800 mg Fe^{2+}/L and 3500 mg $\text{H}_2\text{O}_2/\text{L}$).

In order to evaluate reaction times longer than 2 h, another assay was performed under the same conditions (data not shown). This experiment was carried out with a mechanic stirrer coupled to a 10-L vessel and samples were periodically taken and analysed. Reaction times longer than 2 h improved neither organic matter removal nor the biodegradability. From the obtained results, it can be concluded that a time of 2 h is

sufficient for the Fenton reaction to take place. This is according with reaction times applied by other authors (Lopez *et al.* 2004; Deng 2007).

The optimum conditions obtained in this study were established as follows: pH 3 for reaction, coagulation and settlement, dosages of 800 mg Fe²⁺/L and 3000 mg H₂O₂/L, and reaction time of 2 h. Under these conditions, the biodegradability of the leachate I enhanced, increasing the BOD/COD ratio from 0.02 to 0.29. For initial COD and DOC concentrations of about 13 000 and 5000 mg/L, respectively, organic matter removal achieved values around 87% for both COD and DOC. Similar results were obtained with leachate II, the biodegradability enhanced, increasing the BOD/COD ratio from 0.02 to 0.33. For initial COD concentrations about 6600 mg/L, organic matter removal attained values around 91%. Nevertheless, the BOD/COD ratios slightly could improve if the seed sludge for BOD determination was acclimatized to the leachate. Therefore, better results could be obtained at the landfill leachate treatment plant where biomass is acclimatized to the leachate.

The obtained results confirm that the Fenton process could be useful to improve the biodegradability of the leachate pretreated biologically up to a level compatible with the biological treatment. This is in accordance with the results reported by Barnes *et al.* (2007) and Lopez *et al.* (2004). Consequently, our leachate after the Fenton reaction could be treated in a subsequent biological reactor or recirculated to the previous biological treatment. The second option would reduce the strength of organic matter and ammonia in the influent of the biological treatment as well as inhibitory effects because of their toxicity, according to Li *et al.* (2009).

The treatment of leachates with organic matter content close to this study was analysed by other authors, and similar Fe²⁺ and H₂O₂ dosages were obtained. Lopez *et al.* (2004) applied 830 mg Fe²⁺/L and 10 000 mg H₂O₂/L to leachate with 10 540 mg COD/L, reaching a maximum COD removal around 60%. Barnes *et al.* (2007) evaluated the Fenton process as pretreatment for old-intermediate landfill leachate (COD 4113–9257 mg/L). Operating with dosages of 437.5 mg Fe²⁺/L and 3500 mg H₂O₂/L, pH 4 and reaction time of 30 min, the biodegradability was improved. The BOD/COD ratio increased from 0.35 to 0.71 and the COD removal was about 76%. With dosages of 2000 mg H₂O₂/L, the biodegradability was sufficiently enhanced to a BOD/COD ratio of 0.54, suitable for biological post-treatment. Li *et al.* (2009) applied a combination of processes in a full-scale plant: biological treatment – coagulation – Fenton process – biological treatment. Using this combination of processes, the COD concentration was reduced from 3000 to 82 mg/L. In the Fenton step, the BOD/COD ratio was increased from 0.05 to 0.17 and subsequent upflow biological aerated filters were applied successfully.

In the literature, it is stated that the stepwise addition of Fenton reagents could increase the removal of COD and even reduce the total chemical consumption (Umar *et al.* 2010). However, this stepwise addition could affect in a negative way to the biodegradability of the treated leachate and its subsequent biological treatment, as suggested by other authors (Goi *et al.* 2010). Therefore, the effect of the reagent feeding mode on both the COD removal and the biodegradability improvement should be assessed in future studies in order to improve the efficiency of the treatment and reduce its cost.

Conclusions

- (1)

The optimum conditions obtained in this study were established as follows: reaction pH of 3, dosages of 800 mg Fe²⁺/L and 3000 mg H₂O₂/L, and reaction time of 2 h. Under these conditions, the biodegradability of the leachate enhanced, increasing the BOD/COD ratio from 0.02 to 0.33.

- (2)

The obtained results confirm that the Fenton process can be useful to improve the biodegradability of the leachate pretreated biologically up to a level compatible with the biological treatment.

- (3)

Consequently, the leachate after the Fenton reaction can be treated in a subsequent biological reactor or recirculated to the previous biological treatment.

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