

Fenton's oxidation as post-treatment of a mature municipal landfill leachate

Susana Cortez, Pilar Teixeira, Rosário Oliveira, and Manuel Mota

Abstract—Mature landfill leachates contain some macromolecular organic substances that are resistant to biological degradation. Recently, Fenton's oxidation has been investigated for chemical treatment or pre-treatment of mature landfill leachates. The aim of this study was to reduce the recalcitrant organic load still remaining after the complete treatment of a mature landfill leachate by Fenton's oxidation post-treatment. The effect of various parameters such as H_2O_2 to Fe^{2+} molar ratio, dosage of Fe^{2+} reagent, initial pH, reaction time and initial chemical oxygen demand (COD) strength, that have an important role on the oxidation, was analysed. A molar ratio $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 3$, a Fe^{2+} dosage of $4 \text{ mmol}\cdot\text{L}^{-1}$, pH 3, and a reaction time of 40 min were found to achieve better oxidation performances. At these favorable conditions, COD removal efficiency was 60.9% and 31.1% for initial COD of 93 and $743 \text{ mg}\cdot\text{L}^{-1}$ respectively (diluted and non diluted leachate). Fenton's oxidation also presented good results for color removal. In spite of being extremely difficult to treat this leachate, the above results seem rather encouraging on the application of Fenton's oxidation.

Keywords—Fenton's oxidation, mature landfill leachate, recalcitrant organic matter.

I. INTRODUCTION

THE sanitary landfill method for ultimate disposal of municipal solid wastes continues to be the most used and accepted around the world. Its major disadvantage is the generation of leachates, defined as the aqueous effluent produced as a consequence of rainwater percolation through wastes, biochemical processes in waste cells and the inherent water content of wastes themselves. Thus, leachates are a complex mixture of organic and inorganic contaminants including, among others, volatile fatty acids, humic and fulvic compounds, heavy metals, xenobiotic organic substances and other inorganic salts [1], [2]. The composition and concentration of contaminants are influenced mainly by the type of waste and the age of the landfill [3], [4].

Proper treatment of landfill leachates has been a challenge and several processes have been applied. Biological processes have shown to be very effective when applied to relatively young leachates, rich in volatile fatty acids. However, such methods are not effective for treating mature leachates (i. e.,

from landfills older than 5-10 years), due to their low biochemical oxygen demand measured after 5 days (BOD_5)/chemical oxygen demand (COD) ratios (normally less than 0.3) and high fraction of recalcitrant organic substances. Hence, further processing is required to treat the effluent that is released by biological reactions [5], [6].

In recent years, among other advanced oxidation processes (AOP), Fenton's oxidation has been intensely studied for the treatment of mature landfill leachates, either as a post- or a pre-treatment step. It is considered to be one of the most cost-effective options for treating this kind of effluent (70). The Fenton oxidation process, in which iron (Fe^{2+}) reacts with hydrogen peroxide (H_2O_2) to generate the hydroxyl radical ($\cdot\text{OH}$) – a powerful oxidizer, has been proved to enhance the biodegradability of recalcitrant contaminants [7], [8] to increase the removal of organic load [8], [9] and to reduce color [6], thus helping to comply with the increasingly stringent discharge standards in different countries.

There are some recent reports about mature landfill leachate treatment by Fenton's oxidation [2], [5]. A particular feature of the leachate that is used in this work is that it was already treated by the existing plant. In other words, the leachate was collected before being discharged. In spite of that, the leachate still does not meet the maximum allowable nitrate and organic matter concentrations for direct or indirect discharge. In previous studies with this complex wastewater we developed a method to remove nitrate. However, this method was not able to remove the recalcitrant organic compounds. So, the purpose of this study is to apply and evaluate the effect of major operative parameters on Fenton's oxidation, with the aim of reducing its recalcitrant organic load. These parameters include H_2O_2 to Fe^{2+} molar ratio, dosages of Fenton reagents, initial COD strength, initial pH and reaction time.

II. MATERIALS AND METHODS

A. Landfill Leachate

Landfill leachate before being discharged to the municipal sewer treatment plant, was collected from a municipal landfill in the North of Portugal. This landfill has been in operation since 1998. The collected leachate was stored in closed containers at $4 \text{ }^\circ\text{C}$ until use. The composition of the tested landfill leachate is listed in Table I. Taking into account the low value of the BOD_5/COD ratio (0.01) and the high content of nitrogen-ammonium (N-NH_4^+) ($714.3 \text{ mg}\cdot\text{L}^{-1}$), it can be inferred that this leachate is mature and extremely rich in recalcitrant compounds. Another important characteristic of

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this leachate is the high nitrogen-nitrate (N-NO₃⁻) (1824.1 mg·L⁻¹) content.

TABLE I
AVERAGE COMPOSITION OF THE INVESTIGATED LEACHATE

Parameter	Mean Value
pH	3.5
Conductivity (mS·cm ⁻¹)	4.45
COD (mg·L ⁻¹)	743
BOD ₅ (mg·L ⁻¹)	10
TOC (mg·L ⁻¹)	283.6
N-NO ₃ ⁻ (mg·L ⁻¹)	1824.10
N-NO ₂ ⁻ (mg·L ⁻¹)	0.001
N-NH ₄ ⁺ (mg·L ⁻¹)	714.3
P-PO ₄ ³⁻ (mg·L ⁻¹)	0.479
VSS (mg·L ⁻¹)	79.2

B. Fenton's Oxidation Procedure

Fenton's oxidation of landfill leachate was carried out at room temperature (22 ± 1 °C) and atmospheric pressure in magnetically stirred beakers. The tests were performed with non diluted leachate and diluted to 93 mg·L⁻¹ of COD. At the beginning, the pH was adjusted to 3 using H₂SO₄ 95-97% (w/w). The planned Fe²⁺ dosage was achieved by adding the necessary amount of solid FeSO₄·7H₂O. A known volume of 35% (w/w) H₂O₂ solution was added in a single step. After the fixed reactor time (2 h), sodium hydroxide was added to increase the pH up to the neutral range and mixed for 10 min. Stirring was turned off and the sludge was allowed to settle for one hour. Finally the supernatant was centrifuged for 10 min at 10 000 rpm and the samples were analysed. Different dosages were used in order to find the optimum H₂O₂ to Fe²⁺ molar ratio. This was achieved by maintaining the concentration of Fe²⁺ constant, while the dosage of H₂O₂ was progressively increased. After fixing the optimized H₂O₂/Fe²⁺ ratio other parameters were changed and studied.

C. Analytical Methods

Samples were analysed for various parameters such as pH, conductivity, chemical oxygen demand (COD), total organic carbon (TOC), nitrate, nitrite, ammonium and color. COD, nitrite-nitrogen and ammonium-nitrogen concentrations were determined according to Standard Methods [10]. Nitrate concentration was measured by high-performance liquid chromatography (HPLC), using a Varian Metacarb column (type 67H, 9 μm, 300 mm long, 6.5 mm internal diameter) and a mobile phase of 0.005 M sulphuric acid (H₂SO₄) at 0.7 mL·min⁻¹. Ultraviolet-visible (UV-VIS) spectra were obtained with a Jasco V-560 spectrophotometer. TOC analyses were performed using a Dohrmann DC-190 TOC Analyser.

III. RESULTS AND DISCUSSION

A. Effect of H₂O₂ to Fe²⁺ Molar Ratio and Fe²⁺ Dosage

In Fenton's oxidation neither H₂O₂ nor Fe²⁺ must be overdosed, so that the maximum amount of ·OH radicals is

available for the oxidation of organic compounds [11]. Thus, H₂O₂ to Fe²⁺ molar ratio is a very important operational parameter of the Fenton process. The effect of the H₂O₂/Fe²⁺ molar ratio on COD and TOC removal efficiencies was examined for the two tested COD strengths (93 and 743 mg·L⁻¹) under Fe²⁺ dosages of 1, 2, and 4 mmol·L⁻¹. For both cases, the maximum oxidative COD removal efficiency always occurred at H₂O₂/Fe²⁺ = 3.0. At this ratio, COD and TOC removal efficiencies were significantly higher at the maximum dosage of Fe²⁺ tested (4 mmol·L⁻¹).

The changes of COD removal efficiencies (for initial 743 mg·L⁻¹ of COD) are shown in Fig. 1. COD removal efficiency increased almost linearly with the increase of H₂O₂/Fe²⁺ until a molar ratio of 3. Further increase in this ratio did not show significant removal improvement. This result can be attributed to the scavenging effect of peroxide on the hydroxyl radicals, which presumably became stronger as the ratio H₂O₂/Fe²⁺ rapidly increased.

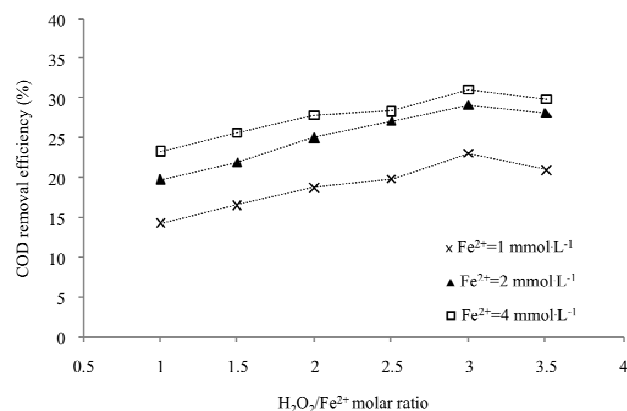


Fig. 1 Effect of H₂O₂/Fe²⁺ molar ratio and Fe²⁺ dosage on COD removal efficiencies in Fenton's oxidation of a mature landfill leachate (conditions: initial pH 3; reaction time = 2h; initial COD = 743 mg·L⁻¹)

Fig. 2 shows the UV-VIS spectra of the landfill leachate before and after treatment by Fenton's oxidation at different H₂O₂/Fe²⁺ molar ratios. It is clear from Fig. 2 that between and 225 and 500 nm there is a color reduction, more pronounced when H₂O₂/Fe²⁺ = 3 was used.

The effect of H₂O₂/Fe²⁺ molar ratio and Fe²⁺ dosage on TOC removal efficiency was also measured and it was slightly lower than COD removal efficiency under the same tested operating conditions (result not shown).

Based on the removal efficiencies, the molar ratio H₂O₂/Fe²⁺ = 3 was chosen for further experiments. Deng [5] also found an optimal H₂O₂/Fe²⁺ molar ratio of 3 for Fenton's oxidation of a mature landfill leachate, although as a pre-treatment.

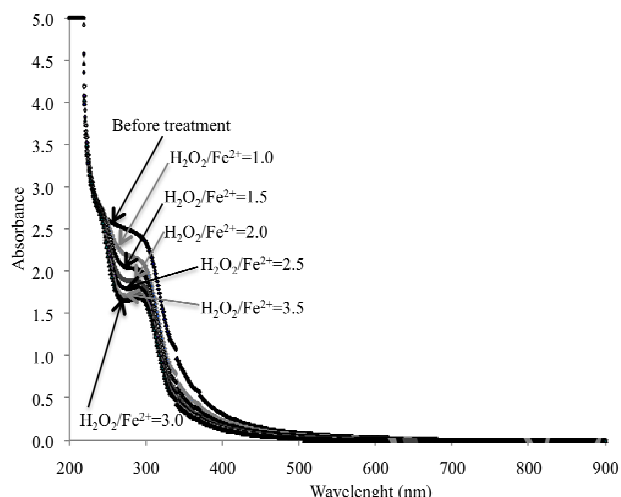


Fig. 2 UV-VIS spectra of the landfill leachate before and after treatment by Fenton's oxidation at different $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratios (conditions: initial pH 3; reaction time = 2h; initial COD = 743 $\text{mg}\cdot\text{L}^{-1}$; $\text{Fe}^{2+} = 4 \text{ mmol}\cdot\text{L}^{-1}$)

B. Effect of Initial pH

The effect of the initial pH on COD and TOC removal efficiencies and COD residual concentrations can be observed in Fig. 3. With $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 3$ and $4 \text{ mmol}\cdot\text{L}^{-1}$ the maximum COD oxidation-based removal efficiency occurred at pH 3, and the COD removal efficiency was about 32.6% for an initial COD strength of $743 \text{ mg}\cdot\text{L}^{-1}$ of COD strength and 64.6% when diluted to $93 \text{ mg}\cdot\text{L}^{-1}$ of COD strength. An optimum initial pH of 3 is also described by Deng [5] and Lopez *et al.* [8] in Fenton's oxidation of a mature municipal landfill leachate. At lower pH (<3) value the COD removal efficiency decreased sharply. One of the reasons may be the increased scavenging of $\cdot\text{OH}$ by H^+ [11]. On the other hand, COD removal efficiency dropped significantly when pH was higher than 3. That can be attributed to the increasing rate of self decomposition of H_2O_2 , deactivation of iron ions into iron oxyhydroxides, the increased scavenging effect of carbonate and bicarbonate on $\cdot\text{OH}$, and the decreased oxidation potential of $\cdot\text{OH}$. Therefore, COD removal efficiency depends strongly on the initial pH of the solution.

As it can be seen in Fig. 3, the effect of pH on TOC removal efficiency, is similar to that on COD removal efficiency, although slightly lower, under the same tested operating conditions. In terms of color removal, pH=3 also presented the best results (not shown).

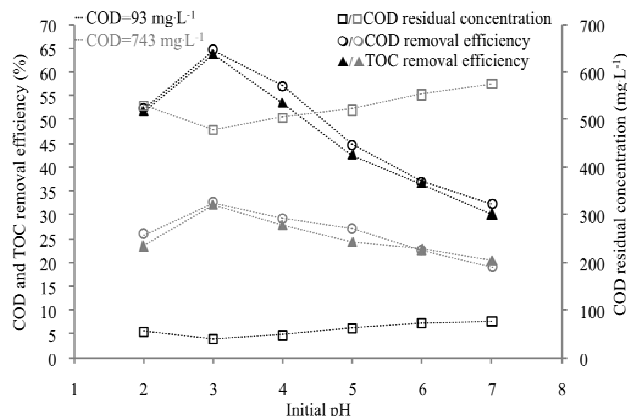


Fig. 3 Effect of initial pH on COD and TOC removal efficiencies and COD residual concentrations in Fenton's oxidation of a mature landfill leachate (conditions: reaction time = 2h; $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 3$; $\text{Fe}^{2+} = 4 \text{ mmol}\cdot\text{L}^{-1}$)

C. Effect of Reaction Time

Tests were also carried out to assess whether reaction times smaller than 2 h, i.e. the time fixed during the whole investigation, would reduce the extent of leachate oxidation. For that, along the experiments samples were taken at pre-selected time intervals and immediately neutralized with sodium hydroxide to stop the reaction. Fig. 4 reports the results of such experiments. It is possible to see that organic matter was rapidly degraded by Fenton's oxidation. Most organic removal (COD and TOC) occurred in the first 40 min. After that time, the change of residual COD became insignificant. Therefore, 40 min of Fenton's oxidation for this mature landfill leachate would be enough to obtain the same results than in two hours.

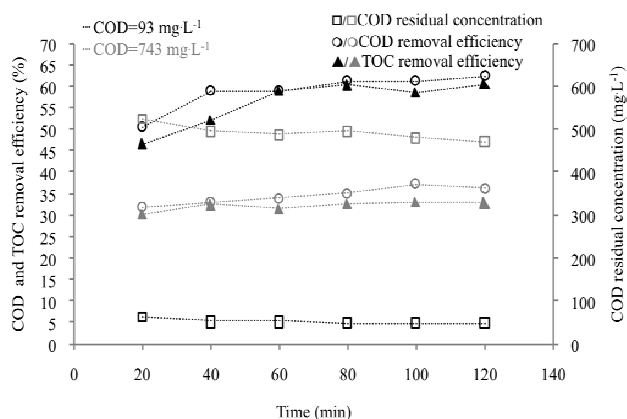


Fig. 4 Effect of reaction time on COD and TOC removal efficiencies and COD residual concentrations in Fenton's oxidation of a mature landfill leachate (conditions: pH 3; $\text{H}_2\text{O}_2/\text{Fe}^{2+} = 3$; $\text{Fe}^{2+} = 4 \text{ mmol}\cdot\text{L}^{-1}$)

D. Effect of Initial COD Strength

In order to ascertain the effect of initial COD strength, the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio, Fe^{2+} dosage, pH, and reaction time were fixed at 3, $4 \text{ mmol}\cdot\text{L}^{-1}$, 3, and 2 h, respectively. Fig. 5

shows that it is possible to observe that more COD (and TOC) was removed at higher COD strength.

For example, COD removal efficiency was 60.9% and 31.1% when initial COD was 93 and 743 mg/L respectively, corresponding to 57 and 231 mg/L respectively.

It is important to note that for all assayed parameters, in all experiments, nitrogen compounds, namely, nitrate, nitrite and ammonium were also measured. However, in all cases nitrogen compounds concentration remained unchanged.

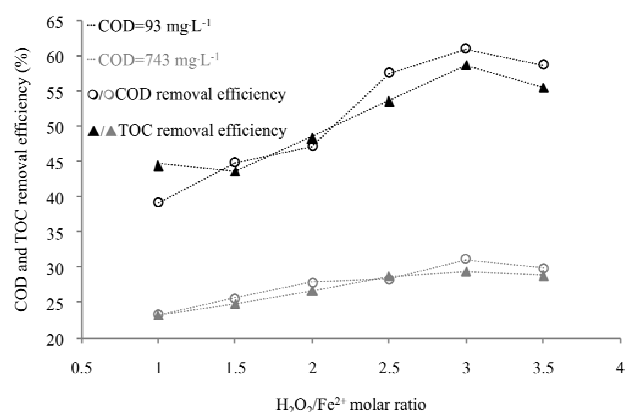


Fig. 5 Effect of initial COD strength on COD and TOC removal efficiencies in Fenton's oxidation of a mature landfill leachate (conditions: reaction time = 2 h; pH 3; H₂O₂/Fe²⁺ = 3; Fe²⁺ = 4 mmol·L⁻¹)

IV. CONCLUSION

The optimal conditions for the Fenton's oxidation process studied were as follows: H₂O₂ to Fe²⁺ molar ratio of 3, Fe²⁺ dosage of 4 mmol·L⁻¹, initial pH 3, and reaction time of 40 min. Under these conditions, COD removal efficiency was 60.9% and 31.1% when initial COD was 93 and 743 mg/L respectively. Fenton's oxidation also presented good color removal results.

This work shows that the recalcitrant organic load of a pre-treated mature landfill leachate can be significantly reduced by Fenton's oxidation. It can be expected that the remaining organic load will be degraded during a subsequent denitrification process, which will be needed to remove the high nitrate load.

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