Treatment of landfill leachate from Fez city (Morocco) using Fenton and photo-Fenton processes

I El Mrabet1, M Kachabi1, M Nawdali1, A Harrach1, F Khalili2, M Ijjaali1, M Benzina3 and H Zaitan1,*

1Laboratoire de Chimie de la Matière Condensée, Faculté des Sciences et Techniques, Université Sidi Mohamed BenAbdellah. B.P. 2202, Fès, Maroc
2Laboratoire de Chimie Appliquée, Faculté des Sciences et Techniques, Université Sidi Mohamed BenAbdellah. B.P. 2202, Fès, Maroc
3Laboratoire Eau Environnement Energie, Ecole National d’Ingénieurs de Sfax, B.P. 1173, Route de Soukra, 3038 Sfax, Tunisie

*Email: hicham.zaitan@usmba.ac.ma

Abstract. In the present work, the treatment of a leachate from Fez city urban sanitary landfill (Morocco) was evaluated using different advanced oxidation processes (AOPs), such as, Fenton (Fe²⁺/H₂O₂), photo-Fenton (Fe²⁺/H₂O₂/UV-A), UV-A and UV-A/H₂O₂. The leachate was characterized by high chemical oxygen demand (COD), low biodegradability and intense dark color. The treatment efficiency was evaluated as a function of different operation variables ([H₂O₂], [Fe²⁺], UV-A irradiance), resulting in COD removals between 30% and 77%. Removal efficiencies decreased in the following order: photo-Fenton > Fenton > UV-A/H₂O₂ > UV-A. Thus, a detailed experimental analysis was carried out to analyze the effect of hydrogen peroxide and iron concentration in the photo-Fenton process. It was observed that: (a) COD removal ranged from 4% to 84% depending on the H₂O₂ dose, (b) COD removal increased by adding the H₂O₂ dose in multiple steps (84%) and (c) iron concentration corresponding to a Fe²⁺/COD mass ratio = 0.35 was found to be the most favorable. At optimum conditions, COD removal was 70% and 84% for Fenton and photo-Fenton processes, respectively. In addition, the optimum contact time for both processes was 1 hr. Finally, the results of this study showed that the Fenton and photo-Fenton process is capable of achieving high levels of COD removal.

1. Introduction
Landfill of Fez (Morocco) receives a large urban and industrial waste amount (about 800 tons per day), generating high volume of leachates (around 400-450 m³ per day). Landfill leachate is considered a potential contamination source of water resources, as they may percolate through soils and subsoils, causing serious environmental damage if they are discharged without any kind of treatment [1]. The leachate contains large quantities of organic compounds, heavy metals, a complex variety of materials, and many other hazardous chemicals. The composition and concentration of such effluents is variable,
depending on the type of deposited waste, the origin and composition of the wastes, and the structure, management and age of the landfill.

Additionally, leachate may cause malodors and aerosols, though these effects tend to be temporary and local. Therefore, it becomes necessary to treat landfill leachate and remove pollutants before it is discharged into water resources and land.

Various treatment technologies based on biological treatment, physical-chemical process such as chemical precipitation, coagulation–precipitation, ultrafiltration and reverse osmosis have been applied successfully for the treatment of landfill leachates [2-6]. On the other hand, combined processes including two or three physical–chemical methods have been widely used including ozonation-activated carbon adsorption [7-8], coagulation–ozonation [9], and precipitation–reverse osmosis [10].

Recently, conventional, Fenton and photo-Fenton processes have been investigated for landfill leachate treatment. In the Fenton process, hydrogen peroxide is added to wastewater in presence of ferrous salt, generating a large amount of free radicals such as “hydroxyl” (•OH) which can remove both organic and oxidizable inorganic components due to their ability to change in the chemical structure of the pollutants.

This work presents a study of the remediation of a mature landfill leachate applying several AOPs which include \( \text{H}_2\text{O}_2, \text{Fe}^{2+}, \) \( \text{UV-A} \) and their combination.

This study aims (a) to characterise the leachates of Fez landfill and (b) to examine the efficiency of different advanced oxidation processes (AOPs), such as, Fenton (\( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \)), photo-Fenton (\( \text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV-A} \)), \( \text{UV-A} \) and \( \text{UV-A}/\text{H}_2\text{O}_2 \) in terms of the removal of COD and colour.

2. Materials and methods
2.1. Materials
Leachate samples were collected from a municipal landfill in Sidi Hrazem, located at 11 km from the city of Fez, Morocco (Figure 1). This site (about 100 ha) has been in activity since 2004, receiving approximately 365 000 ton household wastes per year from different areas of Fez and generates about 350–450 m³ leachate per day. Raw leachate samples were collected in 25 L plastic containers directly from the landfill site. Then, samples were transported to the laboratory and preserved in a refrigerator at 4 °C in the dark in order to minimise leachate decomposition due to microbial activity.

![Figure 1. Leachate from the urban sanitary landfill of Fez city (Morocco).](image)

The materials used in the experiments were \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \) as source of catalyst, \( \text{H}_2\text{SO}_4 \) 96% and \( \text{NaOH} \) 5 M to adjust pH value and (\( \text{H}_2\text{O}_2, 30\% \ (w/w) \)) as oxidant reagent. All reagents used were analytical grade a, except as noted.
2.2. Fenton’s and Photo-fenton Reaction

All tests were carried out at ambient temperature in batch mode according to the following sequential steps. Initially, the leachate to be treated with a volume of 200 mL was introduced into a pyrex reactor and magnetically stirred; pH was adjusted to fixed value (3) by adding H₂SO₄ (0.1N). Then, mass of ferrous sulfate was added and the solution was stirred for 5 min using a magnetic plate to obtained a homogeneous solution. This was followed by the addition of oxidant solution (H₂O₂) under vigorous stirring to start Fenton reaction. This moment was considered to be the starting point (tₒ) of the dark (no radiation) reaction. The reaction mixture was kept away from any light source for the entire duration of each experimental run. Afterwards, the samples (5 mL) were withdrawn every 5 min during the initial 15 min of the reaction and every 15 min during the following 120 min. The sample was centrifuged for 5 min at 2000 rpm to collect the supernatant for the analysis of COD and the UV₃₂₅ nm. Once each sample was obtained, the reaction was followed until COD analysis showed no significant further variation in concentration or until the 60 min reaction time was completed. These experiments were repeated using different ratios of H₂O₂/COD and H₂O₂/Fe²⁺ values.

When applying the photo-Fenton process, all experimental procedures were the same except that a UV-A lamp of three (20 W, 365 nm) was used. Effluents collected were irradiated with the tubular-shaped photoreactor. Photoreactor (See Figure 2) consists of a three UV lamp located vertically at a distance of about 10 cm from the preserved leachate sample in a Pyrex glass reactor. The working volume of the sample was 0.1 L exposed to UV lamps. The entire assembly was placed in an aluminum cylinder to reflect any UV-A light dispersed in the photoreactor) on a magnetic stirrer to maintain a uniform concentration. The system was continuously cooled with a permanent fan maintained at a very proximal distance from the reactor.

Hydrogen peroxide was added as the lamp was turned on, and this moment was considered to be the start of the degradation process. The effect of different ratios of H₂O₂/COD and H₂O₂/Fe²⁺ values were also tested for the Photo-Fenton reaction. Samples were taken at regular time intervals, centrifuged at 2000 rpm for 5 min to remove suspended solids and analyzed by UV–visible spectrophotometer and analysis and COD measured.

![Figure 2. Schematics of photoreactor with suspended UV lamp](image)

2.3. Analytical determinations

Leachate samples were characterised before and after the Fenton and Photofenton treatment. Physical-chemical parameters such as pH, conductivity, turbidity, apparent color at 465nm were measured using respectively a pHmeter (JENCO – Electrocinics LTD), a conductivity meter (WTW
inoLab, Cond. Level 1), a turbidimeter HI 88713 - ISO HANNA-Instruments and a spectrophotometer (VWR UV-6300PC), after calibration with standard solutions. Chemical oxygen demand (COD), biological oxygen demand (BOD₅), total suspended solids (TSS), nitrate, nitrite, sulfate were quantified according to the Standard Methods for Water and Wastewater Examination [11]. Colour number (CN) was determined using the method described by Tizaoui et al. [12]. UV–visible absorption measurements were performed using a spectrophotometer VWR UV-6300PC. Inductively coupled plasma atomic emission spectroscopy analysis ICP-AES (Activa, JobinVyon) was used to quantify the concentration of metals after samples were filtered through 0.45 μm filter. Chloride was quantified by the Mohr method.

The COD removal efficiencies were obtained using the following equation:

\[
\text{Removal} \, (\%) = \frac{(C_i - C_f)}{C_i} \times 100
\]

Where \( C_i \) and \( C_f \) refer to the initial and final COD concentrations in leachate.

3. Results and discussion

3.1. Landfill leachate

The dark colour of the liquid is related to the high values of COD (5653 mgO₂. l⁻¹), BOD₅ (600 mgO₂. l⁻¹) and to the high turbidity content (248 NTU), being all these parameters higher than the values of the Morocco Reject Requirements. The high concentration of COD is due to the presence of different kinds of dissolved organic matter. Another relevant point is the high conductivity (28 mS. cm⁻¹) that could be related to the high salinity value, principally due to the amount of chlorides (7100...
mg L$^{-1}$), nitrates (6.58 mg. L$^{-1}$), nitrites (6.56 mg. L$^{-1}$) and sulfates (140 mg. L$^{-1}$). The BODs/COD ratio is close to 0.1 with a pH of 8, indicating that this leachate may be defined as stabilised leachate and difficult to further biodegradation. In addition, the landfill leachate contains Cr, Cu, Fe, Mn and Zn with concentration of 1.74, 0.05, 1.83, 0.043 and 0.2 mg. L$^{-1}$ respectively. The total suspended solids are of the order of 15.77 g.L$^{-1}$.

3.2. **COD removal**

UV photolysis without addition of any catalyst or oxidant reagent showed very low degradation efficiency (<4%) so it is not a suitable treatment. This could be attributed to the low transmittance in the landfill leachate as indicated by the presence of turbidity and deep black colour. When the oxidation was carried out using only H$_2$O$_2$ oxidant reagent, the reduction of organic compounds concentration expressed as COD was less than 14% after 1 h of treatment (Table 2, Figure. 3).

| AOP                      | H$_2$O$_2$ (mg. l$^{-1}$) | Catalyst (mg. l$^{-1}$) | COD Removal (%) |
|--------------------------|---------------------------|--------------------------|------------------|
| Photolysis UV            | 0                         | 0                        | 2                |
| H$_2$O$_2$               | 10000                     | 0                        | 4                |
| UV/H$_2$O$_2$            | 2500                      | 0                        | 32               |
| UV/H$_2$O$_2$            | 10000                     | 0                        | 11               |
| Fenton Fe$^{2+}$/H$_2$O$_2$ | 2500                   | 2000                     | 58               |
| Fenton Fe$^{2+}$/H$_2$O$_2$ | 10000                   | 2000                     | 70               |
| Photo-Fenton (UV/Fe$^{2+}$/H$_2$O$_2$) | 2500                   | 2000                     | 75               |
| Photo-Fenton UV/Fe$^{2+}$/H$_2$O$_2$ | 10000                   | 2000                     | 84               |

The combination of UV radiation and hydrogen peroxide (UV/H$_2$O$_2$) enhanced the oxidation of organic compounds compared to direct UV photolysis through the formation of hydroxyl radicals. Two different concentrations of H$_2$O$_2$ were added in the presence of UV-A. Experiments using 2500 mg. L$^{-1}$ and 10000 mg. L$^{-1}$ H$_2$O$_2$ (H$_2$O$_2$/COD mass ratios = 0.37–1.48) were carried out achieving COD reductions of 32% and 11% respectively (Table 2). These results showed that the photochemical oxidation enhanced the organic matter removal, although the results should be improved to obtain a cleaner effluent before discharge. Possibly the intensive colour of the solution inhibited light transmittance and H$_2$O$_2$ photolysis was not effective enough.
Fenton oxidation experiments (Fe$^{2+}$/H$_2$O$_2$), with a residence time of 60 min and pH=3 using a fixed concentration of Fe$^{2+}$ of 2000 mg. L$^{-1}$ resulted in 58% of organic matter decrease, expressed as COD, using 2500 mg. L$^{-1}$ H$_2$O$_2$. Increasing the hydrogen peroxide concentration up to 10000 mg. L$^{-1}$, lead to better results (70%).

The degradation efficiency of the oxidation process could be accelerated including UV radiation in the Fenton process. This alternative (UV/Fe$^{2+}$/H$_2$O$_2$) is known as photo-Fenton. UV-A radiation leads to faster regeneration of Fe$^{2+}$ ions in the solution.

Fe$^{3+}$ complexes are photoreactive and its photolysis generates Fe$^{2+}$ ions in acidic conditions [13]. Photo-Fenton experiments led to the maximum reduction of COD. A 75% of COD removal was obtained using 2500 mg. L$^{-1}$ of H$_2$O$_2$. This percentage increased to 84% when the higher hydrogen peroxide concentration (10000 mg. L$^{-1}$) was used.

The results showed a high percentage of colour removal in all conditions (>90%). So, in the final solutions, colour was almost negligible. This change in colouration was probably due to changes in the nature of the compounds present in the leachate solution. AOPs were able to degrade aromatic or polymeric organic compounds, which were the main compounds responsible for colour, in much simple compounds. It is important to remark that the UV/H$_2$O$_2$ process achieved 60 % colour reduction just in one step as in this AOP sludge was not generated.

These results attest the efficiency of the photo-Fenton oxidation process due to the higher production of hydroxyl radicals, comparing to the Fenton process or UV/H$_2$O$_2$, as result of the combination of H$_2$O$_2$ and a metallic catalyst in presence of UV radiation.

The efficiency order of the applied advanced oxidation processes in this work regarding COD reduction was: photo-Fenton > Fenton > UV-A/H$_2$O$_2$ > UV-A.

**Figure 3.** COD removal in the different AOPs (H$_2$O$_2$ = 2500 mg. L$^{-1}$, H$_2$O$_2$ = 10000 mg. L$^{-1}$, Fe$^{2+}$ = 2000 mg. L$^{-1}$, oxidation time = 60 min).
3.2.1. Effect of hydrogen peroxide concentration

Hydrogen peroxide dose is the key factor in Fenton and Photo-Fenton process. The theoretical mass ratio of removable COD to that of H$_2$O$_2$ is 470.6/1000; that is 1000 mg. l$^{-1}$ H$_2$O$_2$ theoretically removes 470.6 mg. l$^{-1}$ COD by oxidation [14]. In this study different initial concentrations ranging from 2500 mg.L$^{-1}$ to 19000 mg L$^{-1}$ (H$_2$O$_2$/COD mass ratios= 0.44 to 3.22), were investigated in order to determine the optimum ratio for the treatment of initial COD leachate. pH was kept at 3 and constant Fe$^{2+}$ dosage of 2000 mg.L$^{-1}$ (H$_2$O$_2$/Fe$^{2+}$ mass ratio = 0.35). Aliquot of the sample was taken regularly from the reaction in order to determine the residual COD.

Fig. 3 shows the effect of initial H$_2$O$_2$ concentration on the final COD removal efficiency. It was observed that COD removal increased from 55% to 82% when H$_2$O$_2$ dosage increased up to 18214 mg.L$^{-1}$. This may be due to the fact that increased H$_2$O$_2$ dosage produces more OH radicals leading to higher substrate degradation [14]. H$_2$O$_2$ dosage from 7285 mg. L$^{-1}$ to 18214 mg L$^{-1}$ did not enhance significantly the yield of the process. This may be due to scavenging of •OH radicals by H$_2$O$_2$ as in the following reaction [15].

\[ \cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \]

This reaction leads to the production of hydroperoxyl radical (HO$_2^-$), a species with much weaker oxidizing power compared to •OH radical [16]. Besides, an excess amount of H$_2$O$_2$ can cause the auto decomposition of H$_2$O$_2$ to water and oxygen, and the recombination of •OH radicals as in the following reactions [17], thereby decreasing the concentration of •OH radicals and reducing degradation efficiency.

\[ 2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 \]
\[ \cdot \text{OH} + \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2 \]

The optimal concentration of H$_2$O$_2$ was obtained as 7285 mg. l$^{-1}$ for the Fenton process, and photoFenton processes. Thus a concentration of H$_2$O$_2$ of 7285 mg. l$^{-1}$ was selected in further experiments.

![Figure 4](image-url)

**Figure 4.** Effect of H$_2$O$_2$ concentration on %COD removal by Fenton and Photo-Fenton reaction ([COD]$_0$= 5653 mgO$_2$.L$^{-1}$, [Fe$^{2+}$]= 2000 mg.L$^{-1}$, pH= 3 and H$_2$O$_2$/COD mass ratios= 0.44 to 3.22).
3.2.2. Effect of Fe$^{2+}$ concentration

In order to investigate the effect of ferrous ion concentration on Fenton and Photo-Fenton treatment of leachate of COD$_0$ = 5653 mgO$_2$/L, H$_2$O$_2$ concentration was kept constant at 7285 mg. L$^{-1}$ (H$_2$O$_2$/COD weight ratio = 1.29) and pH = 3, while ferrous ion concentration has been changed from 200 to 3000 mgO$_2$/L which corresponds to Fe$^{2+}$/COD mass ratios 0.04 and 0.53, respectively. Fig. 4 shows the effect of initial Fe$^{2+}$/COD ratio on the final COD removal efficiency.

**Figure 5.** Effect of Fe$^{2+}$ concentration on %COD removal by Fenton and Photo-Fenton reaction ([COD]$_0$ = 5653 mgO$_2$/L, [H$_2$O$_2$] = 7285 mg.L$^{-1}$, pH= 3 and Fe$^{2+}$/COD mass ratios= 0.04 to 0.53). Fig. 4 shows that an increase in Fe$^{2+}$/COD ratio over 0.13 did not lead to a significant improvement of final COD removals. Increasing Fe$^{2+}$/COD ratio above 0.33 did not enhance the efficiency or rate of the oxidation process. Moreover, when higher Fe$^{2+}$/COD mass ratios were used, several side reactions would occur decreasing the yield of the process [18-19]. The maximum COD reduction achieved in the Fenton and photo-Fenton processes were 78 and 87 respectively.

4. Conclusion

This study reports the comparison of advanced oxidation processes, photo-Fenton, Fenton and UV-A/H$_2$O$_2$, for removal of landfill leachates. UV photolysis required high time of irradiation and it did not result in a satisfactory COD removal (<13%). UV/H$_2$O$_2$ treatment increased considerably the reduction achieved by UV light alone (32%) and 60% of colour removal was obtained. With Fenton (Fe$^{2+}$/H$_2$O$_2$) process, result is were obtained with final COD reduction of 58%.

The photo-Fenton process (UV/Fe$^{2+}$/H$_2$O$_2$) was found to be the most efficient treatment, combining the use of iron as catalyst and hydrogen peroxide in presence of UV radiation, for reduction of COD (84%) in landfill leachates compared to the other processes investigated (UV/Fe$^{2+}$/H$_2$O$_2$ > Fe$^{2+}$/H$_2$O$_2$ > UV-A/H$_2$O$_2$ > UV-A).

An additional experimental analysis was carried out to find the most favorable operation conditions in the photo-Fenton process. Dosing 7285 mg/LH$_2$O$_2$ and using 2000 mg/L Fe$^{2+}$ leading to a 81% COD reduction at the end of the treatment process.
References

[1] Li W, Hua T, Zhou Q X, Zhang S G and Li F X 2010 Desalination 264 56-62
[2] Kurniawan T A, Lo WH and Chan G Y S 2006 J. Hazard. Mater. 129 80–100
[3] Chan G Y S, Chang J, Kurniawan T A, Fu C X, Jiang H and Je Y 2006 Desalination 202 310–317
[4] Zin N S M, Abdul Aziz H, Adlan M N, Ariffin A, Yusoff MS and Dahan I 2015 Desal. Water Treat. 54(11) 2951–2958
[5] Tatsi A A, Zouboulis A I, Matis K A and Samaras P 2003 Chemosphere 53 (2003) 737–744
[6] Chaouki Z, El Mrabet I, Khalil F, Ijjaali M, Rafqah S, Anouar S, Nawdali M, Valdés H and Zaitan H 2017 J. Mat. Environ. Sci. 8(8) 2781-2791
[7] Rivas F J, Beltran F, Gimeno O, Acedo B and Carvalho F 2003 Water Res., 37 4823–4834
[8] Chaouki Z, Khalil F, Ijjaali M, Valdés H, Rafqah S, Sarakha M and Zaitan H 2017 Desal. Water Treat 83 262–271
[9] Monje-Ramirez I and Orta de Velasquez M T 2004 Water Res. 38 2359–2367
[10] Renou S, Poulain S, Givaudan J G and Moulin P 2008 J. Hazard. Mater. 313 9–22
[11] Standard methods for the examination of water and wastewater. Washington, DC: American Public Health Association (APHA), 2012.
[12] Tizaoui C, Bouselmi L, Mansouri L, Ghrabi A 2006 J. Hazard. Mat. 140 316–324.
[13] Kavitha V and Palanivelu K 2004 Chemosphere 55 1235–1243
[14] Deng Y and Englehardt J D 2006 Wat. Res. 40 3683-3694
[15] Andreozzi R, Canterino M, Marotta R and Paxeus N 2005 J. Hazard. Mater. 122 243-250.
[16] Ting W P, Lu MC and Huang Y H 2008 J. Hazard. Mater. 161 1484-1490.
[17] Mandal T, Maity S, Dasgupta D and Datta S 2010 Desalination 250 87-94
[18] Zhang H, Choi H J and Huang C P 2005 J. Hazard. Mater. B125 166–174.
[19] Lopez A, Pagano M, Volpe A and Di Pinto C 2004 Chemosphere 54 1005–1010.

Acknowledgment
Authors are gratefully for the financial support provided from the Moroccan and Tunisian higher education ministries (Project 17/TM 12).