Treatment of landfill leachates by advanced oxidation processes and phytotoxicity assessment

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Keywords: landfill leachates, AOPs, phytotoxicity, Sorghum saccharatum.
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The generation of leachate, from the disposal of waste in sanitary landfills, is a major socioeconomic and environmental problem that deserves special attention. The reasons for this must be sought to the particularly complex composition which includes not only organic matter and inorganic species but also xenobiotic organic compounds (XOCs). Given the hazardous nature of the constitutes, treatment processes must be developed in order to purify these liquids. Fenton-based processes seem to be an attractive choice due to their strong points as high reaction rates and simplicity. In this study, UV/Fe^{2+}/H_2O_2 and Fe^{2+}/H_2O_2 processes were applied in the treatment of a stabilized (L2) and a medium (L1) landfill leachate. The experimental conditions applied to all photocatalytic experiments were as follow: COD: [H_2O_2] = 1:1, [Fe(II)]: [H_2O_2] = 1:10, pH = 3, treatment time = 60 min. For the stabilized leachate, UV/Fe^{2+}/H_2O_2 process achieved greater removals (54.62 % COD, 74.2 % TOC) than Fe^{2+}/H_2O_2 process. The same trend was observed in the case of the medium leachate, in which UV-Fenton treatment process caused reductions 52.5 % and 67.47 % of COD and TOC, respectively. In addition to above data, phytotoxicity tests were performed using *Sorghum saccharatum* seeds and estimating the germination index (GI). Both untreated non-diluted leachates L1, L2 were toxic (GI of 0). Fenton treatment was more effective in reducing the phytotoxicity of both non-diluted leachates (GI=30 % and 85 % for L1 and L2, respectively), compared to UV-Fenton treatment (GI=10 % and 60 % for L1 and L2, respectively), supporting the hypothesis that more toxic byproducts are produced by UV-Fenton treatment. The results of the study show that *Sorghum saccharatum* seeds respond differently to Fenton and UV-Fenton treated, as well as to stabilized and medium landfill leachates.

The formation of landfill leachate in municipal landfills is one of the most important issues of the dominant waste disposal method. These highly contaminated fluids are produced through various routes with the main one being the percolation of the rainwater through the wastes placed in a landfill. Therefore, leachate samples contain a variety of pollutants like organic matter (fulvic, humic and fatty acids), inorganic species, metals and xenobiotic organic substances (Vaccari, Tudor and Vinti, 2019). Especially, the latter subcategory is of major concern since it includes a plethora of chemicals like pesticides, herbicides, pharmaceuticals, personal care products and plasticizers. The concentration of each component depends mainly on waste composition and weather conditions. Given the particularly negative effects that these compounds can cause to living organisms and humans, efficient treatment methods must be developed and applied. Advanced oxidation processes (AOPs) constitute a particularly attractive option for processing wastewaters, as can be observed from the literature. Their popularity, already since the 1980s, is due to their noteworthy characteristics and advantages like high reaction rates, high efficiencies and non-selectivity (Linden and Mohseni, 2014). Among AOPs, classical Fenton process occupy a central position, as is based on the well-known reaction between dissolved ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2), resulting to production of hydroxyl radicals (E = 2.8 eV). The produced oxidative radicals react with the organic contaminants of the sample, leading to their destruction or transformation. The process becomes even more efficient when combined with UV irradiation as a result of the enhanced production of hydroxyl radicals (Ma *et al.*, 2021).

Two different leachate samples were collected and used for the experiments (Figure 1A, 1B, Table 1).

Table 1. Characteristics of leachate samples used in the present study.

Leachate	COD (mg/L)	TOC (mg/L)	CI	pH
L1	6030	2190	3.56	7
L2	3350	1392		8

The photocatalytic experiments were conducted using a glass cylindrical reactor and a UV-lamp (125W) (Figure 1C). A multi-parameter photometer (Hanna) and a TOC analyzer (Shimadzu) were utilized for the measurements. *Sorghum saccharatum* seeds were used for the phytotoxicity test using Plant Growth Incubator (MRC, PGI-550RH) and estimating the germination index (GI). Distilled water was used for positive control. Four (4) ml of each leachate sample was added to a petri dish containing five pieces of blotting paper onto which 20 seeds were evenly placed. Petri dishes were incubated for 72 h at 25 ºC. After the incubation period, sprouted seeds and GI was estimated.

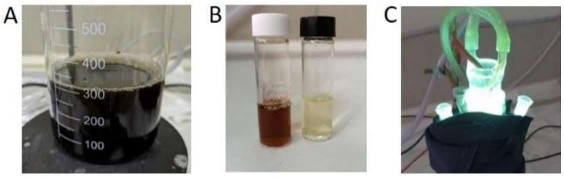

Figure 1. A. Untreated leachate sample, B. Leachate samples L1, L2 after treatment, C. glass cylindrical reactor.

The following experimental conditions were selected: COD: $[H_2O_2]$ = 1:1, [Fe(II)]: $[H_2O_2]$ = 1:10, pH = 3, treatment time = 60 min.

Table 2. COD, TOC and CI removal percentages after the treatment of leachate sample L1.

Leachate sample L1	COD removal (%)	TOC removal (%)	CI removal (%)
Fe^{2+}/H_2O_2	32.17	57	85.49
$UV/Fe^{2+}/H_2O_2$	52.5	67.47	92.75

Table 3. COD, TOC and CI removal percentages after the treatment of leachate sample L2.

Leachate sample L2	COD removal (%)	TOC removal (%)	CI removal (%)
Fe^{2+}/H_2O_2	45.67	69.49	91.6
$UV/Fe^{2+}/H_2O_2$	54.62	74.2	94.11

Table 4: Overall Data.

L1	$UV/Fe^{2+}/H_2O_2$	2840	712.2
	Fe^{2+}/H_2O_2	4090	941.4
L2	$UV/Fe^{2+}/H_2O_2$	1520	359
	Fe^{2+}/H_2O_2	1820	424.6

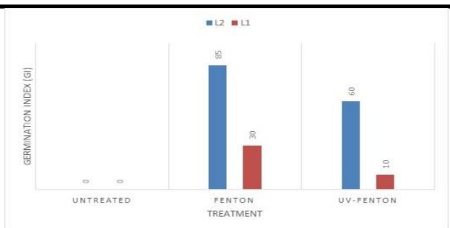

Figure 2. Germination Index (GI) of untreated, Fenton and UV-Fenton treated non-diluted leachate samples L1, and L2.

Under the experimental conditions applied to all photocatalytic experiments of the present study, $UV/Fe^{2+}/H_2O_2$ process achieved greater removals of COD and TOC for both medium (L1) and stabilized (L2) landfill leachates, while Fe^{2+}/H_2O_2 process was more effective in reducing the phytotoxicity of both non-diluted leachates, as was assessed by phytotoxicity tests using *Sorghum saccharatum* seeds. In the case of the stabilized leachate (L2), a GI value of 85% could be achieved after Fe^{2+}/H_2O_2 treatment, indicating non phytotoxicity, while the $UV/Fe^{2+}/H_2O_2$ treatment resulted in moderate phytotoxicity (GI=60%). The treatment of medium (L1) landfill leachate with both processes resulted in GI values of 30% and 10%, respectively, for Fe^{2+}/H_2O_2 and UV/Fe2+/H2O2 processes, indicating high phytotoxicity.

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Acknowledgements

This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: Project code: T2EDK-00137