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# A Comparative Study of Landfill Leachate Treatment Using Advanced Oxidation Photochemical Processes (AOPs)

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*Abstract:* Landfill leachate is a harmful liquid, a highly concentrated mixture of organic and inorganic contaminants, including ammonia nitrogen, heavy metals, inorganic salts, and pollutant waste. Leachate is made up of rain that passes through a landfill site and liquids that are generated by the breakdown of the waste within the landfill, their quantity and quality depending on the age and type of substances in the landfill. Landfill leachate has high chemical oxygen demand (COD), total dissolved solids (TDS), ammonia and other toxic wastes, and, eventually, high biochemical oxygen demand (BOD5). Leachate can be an important source of contamination for groundwater and soil and must be appropriately treated before being discharged to eliminate or minimize the adverse impact of the waste on the surrounding environment. Conventional biological processes are time consuming and inefficient methods to treat leachate directly. Consequently, physicochemical processes are frequently utilized before biological action in treatment plants to pretreat this liquid waste. In this study, advanced oxidation processes (AOPs), including Fenton,  $UV/H_2O_2$ , and photo-Fenton processes, were investigated in laboratory-scale experiments as an effective alternative for municipal leachate treatment. A modified photo-Fenton process was found to be the most effective method, with percentage COD removal of 87.95 % and colour removal of 96.32% up to 360 min.

Keywords: Advanced Oxidation Photochemical Processes (AOPs); Treatment; Landfills; Leachate.

# 1. INTRODUCTION

Landfill leachate is a harmful liquid, a highly concentrated mixture of organic and inorganic contaminants, including ammonia nitrogen, heavy metals, inorganic salts, and pollutant waste, Leachate is made up of rain that passes through a landfill site and liquids that are generated by the breakdown of the waste within the landfill, their quantity and quality depending on the age and type of substances in the landfill. Landfill leachate is characterized by high chemical oxygen demand (COD), total dissolved solids (TDS), ammonia and other toxic wastes, and, eventually, high biochemical oxygen demand (BOD5), Leachate can be an important source of contamination for groundwater and soil and must be appropriately treated before being discharged to eliminate or minimize the adverse impact of the waste on the surrounding environment, (Hagman, Heander, Jansen, 2008).

The inorganic and organic content of leachate is related to environmental risk because of limited biodegradation, severe bioaccumulation, and potential health damage, (Papastavrou, Mantzavinos, Diamadopoulos, 2009) The most employed and studied methods in landfill leachate pretreatment are chemical or electrochemical, coagulation, precipitation, oxidation, and advanced oxidation processes (AOPs), which are methods able to convert nonbiodegradable organic pollutants into nontoxic biodegradable compounds, (Meunier, et al., 2006) by the production of highly oxidizing hydroxyl radical species that oxidize organic pollutants by a broad range of actions, (Rivas, et al., 2004).

The biological method of nitrification/denitrification is probably the most efficient and cheapest process to eliminate nitrogen from leachate, (Bashir, Isa, Kutty, 2009) The efficiency of denitrification is reduced in particular in stabilized landfills due to the limited level of biodegradable organics and/or the presence of specific toxic substances (such as

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polyaromatic hydrocarbons [PAHs], adsorbable organic halogens [AOXs], and polychlorinated biphenyls [PCBs]) and/or by the presence of bio refractory organics such as surfactants, (Khan, et al. 2005).

Conventional leachate treatment methods are often costly in terms of initial outlay of plant equipment, energy requirements, and frequent use of additional chemicals, (Catalkaya, Kargi, 2008) Other methods such as reverse osmosis or active carbon adsorption only transfer the pollution and do not solve the environmental problem, (Kurniawan, Lo, Chan, 2006).

In this study, advanced oxidation processes (AOPs) such as Fenton, ultraviolet light and hydrogen peroxide (UV/H<sub>2</sub>O<sub>2</sub>), and photo-Fenton processes were investigated in laboratory scale experiments as an effective alternative for municipal leachate treatment (Tikhe, Gidde, 2014). The study showed that the photo-Fenton process was the most effective treatment process under acidic conditions at pH 2.5–3.5 and produced a higher percentage of COD removal and colour removal. Although these techniques are not economically acceptable for the treatment of large-scale effluents, the combination of AOPs with a biological process could significantly decrease the overall cost of leachate treatment (Neyens, Baeyens, 2003, Deng, Englehardt, 2006).

# 2. MATERIAL AND METHODS

Municipal leachate wastewater samples were collected from a local dump site area nearly 350 fed, old over 15 years and Contains accumulations of solid waste over a period of more than twenty years by about 13 million tons and a height of up to 25 meters, the El Waffa Wa El Amal landfill, Cairo. Raw leachate was collected from the landfill and the samples were stored in a cold room in the laboratory at  $4^{\circ}$ C to minimize biological and chemical reactions. Before the experiment, the samples were consists (preliminary coagulation) which in the separation of the sediment of humic substances precipitating after pH decrease and produce a necessary step in this process for 4 h. The characteristics of the raw and settled (4 h) leachate are presented in Table 1.



Location local dump site, the El Waffa Wa El Amal landfill, Cairo.



Pollution due to Landfill leachate

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Parameter	Raw	Settled
pH	8.2-8.6	8.0-8.7
Colour (PtCo)	2,173–2,572	1,998–2,194
Turbidity (NTU)	312-319	218-276
BOD <sub>5</sub> (mg/L)	98–164	83–144
COD (mg/L)	1,954–2,870	1,350-2,740
Total solids (mg/L)	6,424–6,623	6,410–6,620
Total suspended solids (mg/L)	172–196	123–172
Total dissolved solids (mg/L)	6,225–6420	6,214–6,411
Total phosphorus (mg/L)	146–169	142-168
Ammonia-nitrogen (mg/L)	725–975	650-890

Tuble It characteristics of Rail and Sectica Ecachate	Table 1:	Characteristics	of Raw	and Settled	Leachate
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All experiments were performed in a batch reactor with a cooling jacket. The reactor was cylindrical with 1.5 L volume and the internal part is made of quartz glass which was available for the transfer of the radiation and the outer part is made of Pyrex glass. Irradiation was achieved by using UV lamp (medium pressure mercury lamp UVOX 300 of 300 W, 245-265 nm, which was immersed in the glass tube. The reactor was equipped with a cooling water jacket system, The reactor was filled with the reaction mixture. Mixing was accomplished by the use of a magnetic stirrer.

For each experiment, synthetic aqueous solution of phenol was prepared in double distilled water as solvent For runs using  $UV/H_2O_2$  system, hydrogen peroxide at different amounts was injected in the reactor before the beginning of each run. For runs, using the photo-Fenton process, the pH value of the solution was set at the desired value by the addition of a H2SO4 solution before startup, then a given weight of iron salt was added. The iron salt was mixed very well before the addition of a given volume of hydrogen peroxide. The time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment which was taking place simultaneously with the addition of hydrogen peroxide.

Samples were taken at appropriate time intervals from the reaction vessel and pipetted into (5 ml) glass vials. The vials were filled so as to leave no headspace and sealed with Teflon-lined silicon septa and screw caps. The samples were immediately analyzed to avoid further reaction. Concentration changes of phenol were determined by a spectrophotometer (DR 2500, HACH) according to the standard methods, (Cortez S, et al. 2011) The initial and treated solutions were determined by the standard methods procedure, (Primo, Rivero, Ortiz, 2008) The pH measurements were carried out with a pH meter, (Shu Y, et al. 2006 Sun, Li, Feng, Tian, 2009).

The pH adjustment and settling was performed using 250 mL of leachate sample. The pH of the leachate sample was adjusted to 2.5, 3, and 3.5 using sulphuric acid and mixed for 15 min using a magnetic stirrer. The pH was tested every 5 min using a pH meter. When the pH became constant, the sample was settled for 1 h. Supernatant samples were taken for measurement of COD and turbidity.

# Fenton Process (H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>)

Figure 1 shows changes of COD (percentage removal) and colour removal during the process. The main steps involved in the Fenton process are oxidation, neutralization, flocculation, and sedimentation. Degradation of organic matter was found to be most effective at pH 2.5–3.5, with optimum pH = 3. The samples to be analyzed were rapidly stirred at 80–400 rpm for 30 s to 60 min followed by increase in pH to neutral point. Neutralization was followed by flocculation prior to sedimentation. After sedimentation, COD of the supernatant was analyzed to measure the treatment performance. COD value decreased relatively quickly up to 60 min then the process started to slow down. The optimal effect of treatment was obtained for H<sub>2</sub>O<sub>2</sub>/Fe(II) doses of 3500/500 and 3000/1000 mg/L. The COD percentage removal varied between 70.42%, 72.36, 75.21, and 78.85%, respectively, for different reaction times of 60, 120, 240, and 360 min. The leachate samples were tested with various dosages of Fenton reagent for color removal. Consistently higher percentage color removal was observed, varying between 90.32%, 91.83%, 92.20%, and 93.72%, respectively, for 60, 120, 240, and 360 min of reaction time.

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## Figure 1: Percentage Chemical Oxygen Demand (COD) and Colour Removal as a Function of Reaction Time: Fenton Process

The advantages and disadvantages of the Fenton Process are as follows (Zhang, Choi, Huang, 2005, Zhang, Choi, Huang, 2006).

#### Advantages

- Improves biodegradability
- Removes odour and colour
- Efficient on COD

#### Disadvantages

- Treatment efficiency is dependent on the initial leachate quality and waste composition
- Treatment performance is highly variable and not reproducible
- Limited effectiveness on ammonia
- Limited effectiveness on inorganics
- Limited effectiveness on BOD<sub>5</sub>
- Does not address TDS and conductivity
- Pretreatment required (pH adjustment)
- Post-treatment required (pH adjustment and filtration)
- Long retention times or storage requirements
- Chemical addition
- Potential chemical storage risks

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#### **Photo-Fenton Process**

Figure 2 shows the percent removal of COD and color removal during the photo-Fenton process, which was observed to be similar to the Fenton process, until 60 min after which a rapid drop in COD occurred. The efficiency of COD removal varied between 85.68%, 85.90%, 86.80%, and 87.95%, respectively at reaction times 60, 120, 240, and 360 min. A decrease in UV light intensity was observed which reduces the photolysis of ferric-oxalate complexes and decreases the photoregeneration rates, while a higher concentration of Fe<sup>2+</sup> leads to quicker consumption of H<sub>2</sub>O<sub>2</sub>, thus decreasing the production of hydroxyl radicals. UV irradiation showed no increase in degradation of organic compounds. The photo-Fenton process was also studied for the removal of color from landfill leachate. Consistently higher color removal was observed, varying between 93.82%, 94.63%, 96.10%, and 96.32%, respectively, for reaction times 60, 120, 240, and 360 min. Slightly better results appeared at doses of 4000/150 and 4000/200.





#### The advantages and disadvantages of the photo-Fenton process are as follows (Rabelo, et al., 2014).

#### Advantages

- Improves biodegradability
- Some disinfectant action
- Efficient on COD

#### Disadvantages

- Treatment efficiency is dependent on the initial leachate quality and waste composition
- Treatment performance is highly variable and not reproducible
- Prefiltration necessary for the UV light to work more efficiently
- Limited effectiveness for ammonia
- Limited effectiveness for inorganics
- Limited effectiveness for TDS and conductivity
- Potentially large energy requirements
- Chemical addition

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- Potential chemical storage risks
- Post-treatment often required

## Ultraviolet Light and Hydrogen Peroxide (UV/H<sub>2</sub>O<sub>2</sub>)

Figure 3 shows the changes in COD and color removal during the UV/H<sub>2</sub>O<sub>2</sub> process., A rapid drop in percent COD occurred at 30 min. The efficiency of COD removal varied between 67.97%, 68.97%, 69.88%, and 70.30%, respectively, for reaction times 60, 120, 240, and 360 min. A decrease in UV light intensity decreased the photoregeneration rates, leading to faster consumption of H<sub>2</sub>O<sub>2</sub>, thus decreasing the production of hydroxyl radicals. No increase in organic compound degradation was observed due to UV radiation. The leachate was also studied for removal of colour and consistently higher color removal was found, at 87.33%, 88.23%, 89.40%, and 90.59%, respectively for reaction times 60, 120, 240, and 360 min.



Figure 3: Percentage COD and Colour Removal as a Function of Reaction Time: UV/H<sub>2</sub>O<sub>2</sub> Process

The advantages and disadvantages of the UV/H2O2 process are as follows (Tuhkanen, 2004).

#### Advantages

- Improves biodegradability
- Strong disinfectant action
- Efficient on COD
- Lower detention times compared to the H<sub>2</sub>O<sub>2</sub> process

#### Disadvantages

- Treatment efficiency is dependent on the initial leachate quality and waste composition
- Treatment performance is highly variable and not reproducible
- Prefiltration required for the UV to work efficiently
- Does not address ammonia
- Does not address inorganics
- Does not address TDS and conductivity
- Potentially large energy requirements
- Chemical addition
- Potential chemical storage risks

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## **Comparison of Performance for Various Advanced Oxidation Processes**

A preliminary analysis of the influence of operation variables in the AOPs considered was carried out following a factorial experimental design that combined the use of four relevant operational variables:  $H_2O_2$ ,  $Fe^{2+}$ , and UV light, at room temperature, (Deng, Ezyske, 2011).

The efficiency of the advanced oxidation processes was evaluated regarding the removal of COD. The results, shown in Figure 4 demonstrated that the COD content can be removed in less than 120 min of reaction time (87.95%) under the conditions of this study. The order of efficiency of the AOPs applied was photo-Fenton >  $UV/H_2O_2$ .

In the photo-Fenton process, when COD reduction reached its highest value (87.95%), the final value for colour removal was 96.32%, as shown in Figure 5.

The final value corresponded to organic acids that were the final products of the oxidation while when the COD reduction was lower, there were more complex organic molecules that had not been identified but should correspond to the original composition of the landfill leachate. The characterization of these compounds could help to design a combined treatment to achieve total removal of the organic matter.

After the neutralization step, the oxidation process produced large amounts of small flocs that contained iron hydroxide as a precipitated byproduct, which had to be discarded. Removal of organic compounds could occur by the mechanism of floc formation, (Rivas, et al., 2004).

This suggested that the combination of Fenton or photo-Fenton process and coagulation may increase the treatment efficiency, (Krzysztoszek, Naumczyk, 2012) Some precipitates could be observed after the preliminary acidification (Khan, et al., 2005). Therefore, the penetration depth of UV light is limited in the leachate solution, resulting in a low efficiency of the photolysis process, (Haapea, Korhonen, Tuhkanen, 2002) When hydrogen peroxide was added at varying doses, higher COD removal was obtained than with a single dose of  $H_2O_2$ . The same result was found in Fenton treatments, (Shu et al., 2006).

The degradation efficiency of the oxidation process could be accelerated by including UV radiation in the Fenton process, (Lopez, Pagano, Volpe, Pinto, 2004., Calli, Mertoglu, Inanc, 2005).

This alternative  $(UV/Fe^{2+}/H_2O_2)$  is known as the photo-Fenton process. UV radiation leads to faster regeneration of Fe<sup>2+</sup> ions in the solution. Fe<sup>3+</sup> complexes are photoreactive and photolysis generates Fe<sup>2+</sup> ions in acidic conditions, (Córdova et al., 2019).

The percentage of removal of COD is still not satisfactory, however. As leachate contains different organic and inorganic ligands, a variety of  $Fe^{3+}$  complexes could be formed by scavenging the available iron in the solution and slowing down

the OH<sup>•</sup> formation due to the slow production of  $Fe^{2+}$  from  $Fe^{3+}$ , (Neyens, Baeyens, 2006) The analytical measurements showed that the initial Fe2<sup>+</sup> concentration was converted to  $Fe^{3+}$  ion at the end of the oxidation process. Ferrous ions were consumed quickly, but reproduced slowly during the reaction. Therefore,  $Fe^{3+}$  ions were accumulated in the system and when Fe2<sup>+</sup> ions were consumed, the reaction practically stopped, (Deng, 2007).

Traditionally, Fenton reagent incorporates  $Fe2^+$  as catalyst, but some studies have shown that it is not possible to remove all the intermediate compounds of the degradation reactions using only  $Fe2^+$ , (Morais, Zamora, 2005) Other transition metals appeared as an alternative to achieve higher rates and efficiencies and the complete mineralization of the organic molecules, (Dandauthiya, 2012)

That group of AOPs are the so-called Fenton-like processes. Copper also undergoes a Fenton-type reaction and can lead to the oxidation of different compounds, (Lau I.W.C., Wang P., Fang H.H.P, 2007).

A new experimental design was performed to analyse the influence of initial hydrogen peroxide concentration, the number of  $H_2O_2$  dosages, and the iron concentration, in the reduction of organic matter by the photo-Fenton process, (Kang, Hwang, 2000).

 $H_2O_2$  dose was a critical variable in the process. A low concentration of  $H_2O_2$  did not generate enough  $OH^{\bullet}$  in solution. In addition, increasing  $H_2O_2$  concentration had two opposite effects on the reaction yield. On the one hand, higher initial

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hydrogen peroxide concentration enhanced the oxidation process, leading to an increase in the concentration of  $OH^{\bullet}$  radicals up to a certain concentration, when hydrogen peroxide started to react with hydroxyl radicals, acting as a free-radical scavenger itself and decreasing the hydroxyl radical concentration and generating  $HO_2^{\bullet}$  radicals, which are much less reactive, (Jonsson, et al., 2003), (Wu, Zhou, Qin, Zheng, Ye, 2010). So there was an optimum  $H_2O_2$  concentration to achieve the maximum percentage of removal although the definition of the concentration range varies for different contaminated wastes, (Wu, et al., 2011).

Photochemical oxidation processes involve the fragmentation of large organic compounds into smaller ones, (Godala, Nowicki, 2002).



The experimental error in duplicate experiments was on average lower than 5%.



Figure 4: Percentage COD Removal as a Function of Reaction Time for all Processes.

Figure 5: Percentage Colour Removal as a Function of Reaction Time for all Processes.

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## 3. DISCUSSION

The aim of this study was to compare the efficiency of treatment of leachate from the el Wafaa Wa el Amal landfill using the Fenton, photo-Fenton, and ultraviolet light and hydrogen peroxide processes. The leachate in this study is described as medium stabilized and characterized by BOD5/COD values in the range 0.22–0.24, which have four operational variables:  $H_2O_2$ ,  $Fe^{2+}$ ,  $Cu^{2+}$ , and UV light, at room temperature The response corresponded to the COD reduction after 60 min of reaction time. BOD5 values also decreased during these processes.

The measure of COD of the settled sludge gives the contribution of coagulation/flocculation to removal of organics. Leachate quality can be significantly improved with regard to organic content and colour by the Fenton process. The Fenton reaction is probably for the oxidation of maleic acid. Reagents used are generally hydrogen peroxide and ferrous iron. The process is the result of the catalytic action of ferrous ions (Fe<sup>2+</sup>) with hydrogen peroxide according to the following equations:

Initial reactions:

 $Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + HO^{\cdot} + H_2O$  (1)  $Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+ \longleftrightarrow Fe^{2+} + HO_2^{\cdot} + H^+$  (2)

Propagation:

$$H_2O_2 + HO^{\cdot} \rightarrow HO_2^{\cdot} + H_2O$$
(3)  
$$H_2O_2 + HO_2^{\cdot} \rightarrow HO^{\cdot} + O_2 + H_2O$$
(4)

Termination:

 $Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^{-}$  (5)  $Fe^{3+} + HO_{2}^{\cdot} \rightarrow Fe^{2+} + H^{+} + O_{2}$  (6)

Propagation reactions in the  $H_2O_2/UV$  process are exactly the same as in the Fenton and photo-Fenton processes (Equations 3 and 4). Termination reaction follows according to Equations (7) and (8).

$$HO' + HO_2' \rightarrow H_2O + O_2 (7)$$
$$HO' + HO' \rightarrow H_2O_2$$
(8)

An increase in the hydrogen peroxide-to-substrate ratio results in more extensive degradation, while a higher concentration of iron leads to increased yield. The Fenton process improves biodegradability and removes odour and colour. Most importantly, the Fenton process can significantly remove recalcitrant and toxic organic compounds. Because of the use of iron, sludge residuals, mainly from ferric precipitates, can be generated in large quantities. An additional step, such as sedimentation, is generally required after the Fenton process to deal with these residuals.

This has the effect of generating the Fenton catalyst in situ and enhancing the production of hydroxyl radical through direct photolysis and also by reaction.

The photo-Fenton process has two main features:

(a) the reduction of  $Fe^{3+}$  to  $Fe^{2+}$  to produce more hydroxyl radicals via photolysis

(b) the photo-decarboxylation of ferric carboxylates.

Reduction in the amount of catalytic iron consequently reduces the final sludge volume. Moreover, some additional organic compounds (carboxylates) can also be treated efficiently.

For the photo-Fenton process, after pH adjustment to pH < 3.0, the optimum conditions for maximum degradation were:  $[Fe2+] = 1.0 \times 10-3 \text{ M} (56 \text{ mg/L})$  and a molar ratio of 1:1 COD:H2O2. The starting COD concentration was 1150 mg/L, and after 2.0 hours of treatment at 80 kW/m<sup>3</sup>, the observed removal was 70%. A medium-pressure mercury vapor lamp

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(160 kW/m<sup>3</sup>), an O<sub>2</sub> aeration system (Q = 45 mL/min), and reagent concentrations of 2000 mg H<sub>2</sub>O<sub>2</sub>/L and 10 mg Fe<sup>2+</sup>/L were used. The pH was adjusted to 2.8, and after 60 minutes, the initial COD concentration of 5200 mg/L as O<sub>2</sub> was reduced to 686 mg/L as O<sub>2</sub>, which equals a removal of 87 percent. The biodegradability of the leachate was also greatly improved by increasing the BOD5-to-COD ratio from 0.13 to 0.40. This confirms the general opinion that many AOPs enhance the biodegradability of landfill leachate.

Although UV radiation helped in recycling the  $Fe^{2+}$  and consequently aided in the formation of additional hydroxyl radicals, the brown turbidity observed in the solution due to the higher amount of  $Fe^{2+}$  severely hindered the UV light transmission through the media and thus made UV ineffective in enhancing further degradation. The additional cost related to UV radiation in the photo-Fenton process can be compensated for by the reduced concentration of  $Fe^{2+}$  needed in the photo-Fenton process, together with the decreased amount of sludge produced, which makes the photo-Fenton process competitive with the Fenton process in terms of overall treatment cost.

The degradation efficiency of the oxidation process could be accelerated by including UV radiation in the Fenton process. This alternative  $(UV/Fe^{2+}/H_2O_2)$  is known as the photo-Fenton process. UV radiation leads to faster regeneration of Fe<sup>2+</sup> ions in the solution. Fe<sup>3+</sup> complexes are photoreactive and their photolysis generates Fe<sup>2+</sup> ions in acidic conditions.

Photo-Fenton experiments led to the maximum reduction of COD. A 59% of COD removal was obtained using 5000 mg/L of  $H_2O_2$ . This percentage increased to 77% when a higher hydrogen peroxide concentration (15,000 mg/L) was used. These results attest to the efficiency of the photo-Fenton oxidation process due to the higher production of hydroxyl radicals, compared with the Fenton process or UV/ $H_2O_2$ , as result of the combination of  $H_2O_2$  and a metallic catalyst in the presence of UV radiation.

Using UV and  $H_2O_2$  without iron for leachate treatment results in three modes of treatment: 1) direct photolysis by UV, 2) direct oxidation by  $H_2O_2$ , and 3) the indirect generation of OH• radicals. Direct photolysis of hydrogen peroxide also leads to the formation of OH• radicals by splitting the oxygen-oxygen bond [19]. The hydroxyl radical HO. characterized by high redox potential is produced (2.8 V). The oxidation of combined UV/ $H_2O_2$  processes is more effective at low pH = 3, which requires pH adjustment and reduction of alkalinity. The efficiency of the first experiments with  $H_2O_2$  was enhanced by adding four UV lamps. With this new setup, COD removal improved from 60% with they improved the alone to 65%. The formation of hydroxyl radical was greatly improved by the addition of UV energy. The results also demonstrated the importance of the initial COD concentration on process performance. Indeed, the COD removal increased as the initial COD concentration decreased, keeping the retention time constant at 120 min.

The effect of using  $Fe^{2+}$  or  $Cu^{2+}$  was similar. The additions of UV radiation and  $H_2O_2$  had positive effects on the final COD removal. In addition to the organic matter, another very important pollutant that has to be considered is the nitrogen content. The reduction of this pollutant was investigated during the study from the comparison between ammonium concentration in the raw leachate and in the final effluent of each experiment. These results showed that AOPs tested did not reduce the ammonium concentration. Therefore, additional treatments, such as biological processes, precipitation, or air stripping, are needed to resolve the environmental problem of ammonium in landfill leachate.

The composition of municipal landfill leachate exhibits noticeable temporal and site-specific variation in chemical and microbiological characteristics, attributable to a combination of factors, including landfill age, type of waste, moisture availability, temperature, pH, depth of fill, and compaction. As a result, reported concentrations of leachate contaminants range extensively, and often vary by several orders of magnitude. The internal biological and chemical transformations within landfills occurring as wastes decompose have a strong relationship with leachate characteristics.

In a study one of the primary parameters influencing the Fenton and photo-Fenton processes is the pH of the solution, which greatly influences the efficiency of the photo-Fenton reaction. The study indicated that pH 2.8 avoids  $Fe^{3+}$  precipitation, and the predominant iron-water species in solution is FeOH<sup>2+</sup>, which explained higher hydroxyl radical product yields in the pH range of 2–4 by a reaction involving the organometallic complex where either hydrogen peroxide is regenerated or reaction rates are increased and can absorb light up to 410 nm. which is the most photoactive ferric ion water complex since it the molar fraction of the iron-water complexes., iron-organic complexes (e.g. oxalic, formic, etc.) and iron-inorganic complexes (e.g. chlorides, sulphates, etc.),

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It was observed that the extent of degradation increased with increasing initial  $Fe^{2+}$  concentration. Particular attention must be paid to  $Fe^{2+}$  dosage to avoid the undesired HO. radicals scavenging reaction occurring in the presence of an excess of  $Fe^{2+}$ . Naturally, an excessive dosage of iron can contribute to a significant increase in total dissolved solids (TDS) and electrical conductivity in the effluent. Excessive iron salt dosing requires further treatment of the effluent before its discharge to the receiving water. The optimum iron concentration in the solar photo-Fenton process depends essentially on the light source, photo reactor configuration and dimensions, and the type of wastewater to be treated. In the photo-Fenton process, the presence of light-absorbing species such as fulvic acids and nitrates also affects the optimum iron concentration value.

In addition,  $H_2O_2$  dose is a critical variable in the process. There was an optimum  $H_2O_2$  concentration to achieve the maximum percentage of removal although the definition of the concentration range varies for different contaminated wastes. Excessive application of  $H_2O_2$  generates gas bubbles, which inhibits sludge sedimentation. A low concentration of  $H_2O_2$  did not generate enough OH• in solution. Addition of  $H_2O_2$  above optimum will lead to decrease in hydroxyl radical concentration due to free radical scavenging by the excess  $H_2O_2$ . The photo-Fenton treatment was mediated by a  $[H_2O_2]/[Fe^{2+}]$  ratio of 115, and after a total irradiation of 95 kJ/L, it achieved 96.5% removal efficiency for TC, 63.0% for COD, and 75.9% for NH<sup>4+</sup>. Reaction time above an optimum does not give significant increase in pollutant removal efficiency. Optimum reaction time for the photo-Fenton process is 2 h with less sludge production.

It was observed that there was no significant increase in COD removal when temperature w the light and radiation intensity is strongly Effect dependent on the photochemical reaction The rate of initiation of photocatalysis and electron-hole formation While increasing the intensity of incident light, the probabilities of excitation of electrons as well as the reexcitation of recombined electrons increase, hence increase in the intensity of incident light will increase the rate of degradation in the Fenton process. In such a process, in fact, under acidic conditions, a  $Fe^{2+}/H_2O_2$  mixture produces OH radicals in a very effective way. The Fenton process seems to be the best compromise because the process is technologically simple, there is no mass transfer limitation (homogeneous nature), and both iron and hydrogen peroxide are relatively cheap and nontoxic. However, the Fenton process required low pH and a modification of this parameter is necessary.

Several reviews have been conducted with the goal of collecting information regarding leachate composition according to the location (i.e. the climate and especially the precipitation rate), the age of the landfill, or the type of wastes. Basically, the available leachate quality datasets lead to the same conclusion: the composition of leachate is highly variable and site specific. Differences can be as high as several orders of magnitude. Typically, the most environmentally significant parameters of leachate quality are ammonia, BOD5, COD, TDS, and heavy metals concentration, as increased from 25 to  $45^{\circ}$ C by the conventional Fenton process.

## 4. CONCLUSIONS

Landfill leachate is heavily polluted and thus detrimental to surface and subsurface sources, thus landfill leachate management is a major issue which has to be handled properly. In recent years, with the continuous hardening of the discharge standards in most countries and the ageing of landfill sites with more and more stabilized leachate, conventional treatments (biological or physico-chemical) are no longer sufficient to reach the level of treatment needed to fully reduce the negative impact of landfill leachate on the environment.

Most earlier work focused on the efficiency of removal of organic matter from landfill leachate. This study sought to explore suitable treatment options for leachate from the al Waffa Wa el Amal landfill of Cairo City, to develop an efficient leachate treatment system that complies with international standards. The photo-Fenton process  $(UV/Fe^{2+}/H_2O_2)$  was found to be the most efficient treatment compared with the Fenton treatment process and  $UV/H_2O_2$  treatment process, combining the use of iron as catalyst and hydrogen peroxide in the presence of UV radiation. Appropriate molar ratio of Fenton reagents which are the two most important factors to achieve maximum COD removal performance for treatment of medium-age landfill leachate, which gives an adequate percentage of COD removal (96.32%) and percentage of colour removal (87.95%) at reaction time 120 min, initial pH 2.5–3.5 with an optimum pH approximately 3. No residual H<sub>2</sub>O<sub>2</sub> was detected in the final effluent.

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