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Treatment of Landfill Leachate via Advanced Oxidation Process (AOPs) - A Review.

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ABSTRACT

The landfill is a primary method used to dispose of solid waste around the world. Leachate has toxic and refractory organic matter that originated from the ground and surface waters. The landfill leachate treatment is mainly focused on the removal of organic matter, which contributes to the Chemical Oxygen Demand (COD) and toxic nitrogenous substances during treatment. Formation of leachate poses a serious problem closely related to the use of landfill sites and it is formed through the permeated mineral and organic compounds from the landfill bed. Due to its diverse chemical composition, it is necessary to purify the leachate before it is discharged into the drains or a natural receiver. The current review mainly discusses the Advanced Oxidation Processes (AOPs) which is used for the treatment of landfill leachate, especially the refractory organic compounds present in the wastewater. The application of AOPs represents the advancement in water and wastewater treatment which enables conversion of non-biodegradables to biodegradable compounds.

Keywords: Landfill Leachate, Advanced Oxidation Processes (AOPs), Biodegradability, BOD/COD ratio

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INTRODUCTION

In general pollutants were created by wastes that migrate to real environment [1,2]. Some events (precipitation, surface run-off, infiltration or intrusion of groundwater through landfill, biochemical processes) in the environment create leachate. Leachate can be produced by landfill that have ceased in operation and can stay for 30 to 50 years. The presence of ammoniacal-nitrogen, heavy metals (e.g. copper, iron, zinc, lead, and manganese), organic and inorganic salts (e.g. chloride, sulfate, sodium) in leachate should be evaluated and treated before discharge to the environment [3,4]. Leachate characteristic varies based on landfill age, the composition of the soil, rain fall and nature [5, 6].

When untreated leachate is directly disposed of to the natural environment; it severely contaminates the water sources. Thus, treatment of landfill leachate is essential prior disposal to the natural environment [7]. Biological treatment, adsorption using various adsorbents, precipitation, ion exchange, coagulation-flocculation, chemical and electrochemical oxidation, and reverse osmosis are the common treatment processes for the leachate [3, 7 - 9]. Obtaining an effluent with high quality by any single method is hard. Thus, the combinations of these parameters are used for the treatment [10, 11].

By comparing the different type of physical-chemical treatment methods, AOPs is one of the efficient ways to degrade the refractory compound available in leachate [12]. The AOPs were considered as one of the important alternatives for the incineration of wastes. The conventional incineration may cause a serious problem by releasing different toxic compounds such as polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) onto the environment [13].

Rainfall is the main contributor of leachate generation. The precipitation percolates through, and gains dissolved and suspended components from the biodegrading waste through several physical and chemical reactions [2]. The groundwater inflow, surface water runoff and biological decomposition and the liquid fractions present in the waste will be converted to leachate [2]. The production of leachate is greater whenever waste is less compacted because compaction reduces the filtration rate. The other factors involved in affecting the quality of leachates include i.e., age, precipitation, seasonal weather variation, waste type and composition. Mostly, the composition of landfill leachates varies depends on the age of the landfill [2].

There are three types of leachates that have been defined according to the landfill age. The relationships between the characteristics of landfill leachate versus age of landfill were summarized in Table1 [15,16]. The young landfill leachate have high Biochemical Oxygen Demand (BOD) (4000–13,000 mg/L) and Chemical Oxygen Demand (COD) (30,000–60,000 mg/L) which contains larger amount of biodegradable organic matter. The complex organic compounds are anaerobically fermented, thus producing soluble organic acids like free volatile fatty acids (VFAs), amino acids, low molecular weight compounds and gases (H_2, CO) [14].The concentration of VFAs can be found significant, thus representing 95% of TOC, leading to lower pH of 5. High BOD/COD ratio values (0.5 to 0.7) indicate the presence of a larger amount of biodegradable organic matter [14].

Table 1: Landfill leachate classification versus age [18, 16]

Type of leachate	Young	Intermediate	Old
Age (years)	<5	5-10	>10
pH	<6.5	6.5-7.5	>7.5
COD (mg/L)	>10,000	4000–10,000	<4000
BOD_5/COD	0.5-1.0	0.1–0.5	<0.1
Organic compounds	80% volatile fatty acids (VFA)	5%–30% VFA + humic and fulvic acid	Humic and fulvic acids
Ammonia nitrogen (mg/L)	<400	N.A	>400
TOC/COD	<0.3	0.3–0.5	>0.5
Kjeldahl nitrogen (g/L)	0.1-0.2	N.A	N.A
Heavy metals (mg/L)	Low to medium	Low	Low
Biodegradability	Important	Medium	Low

Lower pH was associated with VFAs, and high concentration of metal ions like Fe, Mn, Ni and Zn [14]. Moderately high content of ammonium nitrogen (500–2000 mg/L), high ratio of BOD/COD (ranging from 0.4 to 0.7), with biodegradable volatile fatty acids (VFAs) also contributes to low pH values (as low as 4.0) [17]. The characteristics of matured or stabilized landfill leachate include low COD (<4000 mg/L), slightly basic pH (7.5-8.5), low biodegradability (BOD/COD < 0.1), and high molecular weight compounds (humic substances) and the lower concentration of VFAs [14].

This is mainly because of their conversion to CH4 and CO2 during the fermentation period. As the contents of VFA and other biodegradable organic compounds in the leachate decrease, the organic matter present in the leachate becomes dominated with refractory compounds such as humic substances [14].The humic substances give out a dark color formation as to stabilize the leachate. The decrease of VFA results in the increase of pH and typically stabilized leachate contains a pH of 8.

The concentration of metal ions is generally low due to the decreasing solubility of many different metal ions with the increasing pH whereas Lead is an exception, because it forms a very stable complex with humic acids [14]. Besides the effect of the shifting pH on metal ions, there is a reduction of sulphate to sulphide during this phase, which increases the precipitation of metals ions [14]. Table 2 summarizes the typical characteristics of leachate according to the age of landfill [13,14]. As the landfill age increases, the organic concentration (COD) present in leachate decreased and resulted in the increase of ammonia and nitrogen concentration [18].

Table 2: Typical concentrations of landfill leachate in comparison to sewage and groundwater [13,14]

Parameters	Young leachate Concentration	Old leachate concentration	Typical sewage concentration	Typical groundwater concentration
COD	20,000-40,000	500-3,000	350	20
BOD_5	10,000-20,000	50-100	250	0
TOC	9,000-25,000	100-1,000	100	5
Volatile fatty acids	9,000-25,000	50-100	50	0

Volumetric flow rate and composition are the two main characteristics of leachate and flow rate changes from site to site. The condition of every site depends on the season. Three important factors that specify the flow rate are the design of the tip, climate (rainfall and evaporation) and the nature of the waste (moisture content and liquid entering the landfill) [19]. Biological, chemical and physical processes happen in the landfill and affect the composition of leachate and gas production. Leachate contains natural organic substances that are in various forms, such as suspended or colloidal particles, macro polymers or simple low molecular substances and only a part of these organic substances remains dissolved.

The organic content of leachate is often measured in terms of COD, BOD, and TOC and dissolved organic carbon. The composition of landfill leachate, the amount generated and extraction of potential pollutants resulting from the waste depends on several factors. These includes solid waste composition, degree of compaction, absorptive capacity of waste and its age, seasonal weather variations, level of precipitation, temperature, size, hydro geological conditions present in the vicinity of landfill site, engineering and other operational factors (pH, landfill chemical and biological activities) [20,5,14]. A simplified water balancing equation taking into consideration all of these above factors allow designers to predict the amount of leachate that will be produced by the landfill [14]:

$$L = P - R - DUs - ET - Duw \quad (1)$$

Where L = leachate production
P = precipitation
R = surface run-off
Us= change in soil moisture
ET=actual evaporative losses from the bare-soil/evapotranspiration losses from a vegetated surface
Uw = change in the moisture content of the refuse components

Leachate generation in a landfill involves processes such as aerobic, acidogenesis, methanogenesis and stabilization. The first step is the aerobic process to reduce the organic matter. The second step is the anaerobic reaction that is divided into two processes; acidogenesis and methanogenesis. The function of acidogenic phase is to produce young leachate with high biodegradability whereas, in the end of methanogenesis, matured leachate with low biodegradability is produced. Organic matter was broken down during the fermentation to form simple compound [14].

AOPs IN LANDFILL LEACHATE TREATMENT

Treatment of leachate can be performed by biological, physical and chemical processes [21]. However, the current method of treatment is a discharge into the municipal sewage system, and its treatment at a local sewage treatment plant using activated sludge process. Some are using a collection in a tank in landfills and periodical export to municipal biological treatment, recycling through the tip, and evaporation with heat from biogas combustion.

The treatment of leachate containing soluble organic, non-biodegradable and toxic substance requires chemical oxidation process [2]. Accordingly, the use of AOPs for the treatment of leachate has become more popular nowadays [21]. Oxidants such as chlorine, ozone, potassium permanganate and calcium hydrochloride have been used for the treatment of leachate. Most processes based on the direct reaction of oxidant (O3-selective) with contaminants or via generated hydroxyl radicals (OH) [2].Table 3 illustrated the capability of producing free radical (OH•) by various methods [22].

Table 3: Standard potential of some oxidant categories

Species	Reactions	E° (V vs NHE)
HO·	$OH + H^{+} + e = H_2O$	2.80
O_3	$O_3 + 2H^{+} + 2e= H_2O + O_2$	2.07
H_2O_2	$H_2O + 2H^{+} 2e = 2\ H_2O$	1.78
$HO_2^{°}$		1.70
ClO_2	$ClO_2 + e = Cl^{-} + O_2$	1.57
HOCl		1.49
Cl_2	$Cl_2 + 2e = 2Cl^{-}$	1.36

The shapes of hydroxyl radicals from the fission of a lone pair of the electron which result in separation of an electron to one hydroxyl radical each is given in Equation 2.

$$HO:OH \rightarrow HO^{°} + OH^{°} \qquad (2)$$

OH• is one of the powerful oxidants that can break compounds that could not be oxidized via conventional oxidants (e.g. oxygen and chlorine). Table 4 shows the oxidation potential of various oxidizing agents. The reaction between OH• and soluble compounds brings different oxidation reactions.

The organic compounds after oxidation are converted to water, carbon dioxide and inorganic molecules and this result in the mineralization of organic compounds. The mineralization of organic compounds is interfered by three factors; i) oxygen, ii) radicals, and iii) contaminant. The influential agents to the radical were pH, temperature, ions, contaminants and the presence of scavengers. The role of scavengers was to decrease the efficiency of AOPs [23, 24, and 25].

Table 4: Comparison of oxidizing potential of various oxidizing agents [24, 13]

Oxidizing species	Electrochemical oxidation potential (EOP), V [24]	EOP relative to chlorine [13]
Positively charged hole on titanium dioxide, TiO_2	3.02	2.35
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.06
Atomic oxygen	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

In general, AOPs can be classified according to the phase in which the process takes place. The categorization could be also evaluated in terms of variation of $OH^{º}$ manufacture. Thus, the photochemical and non-photochemical processes could be recognized [22]. The organization of AOPs as photochemical and non-photochemical process is shown in Table 5.

Table 5: Organization of some AOPs as photochemical and non-photochemical processes [22]

Non-photochemical processes	Photochemical processes
Ozonation in basic media (O_3/ HO^-)	O_3/UV ($\lambda \leq 320$ nm)
O_3/H_2O_2	H_2O_2/UV ($\lambda \leq 300$ nm)
O_3/Ultrasound	O_3/H_2O_2/UV ($\lambda \leq 320$ nm)
H_2O_2/Ultrasound	Photo catalytic ozonation ($\lambda \leq 320$ nm)
Electron Beam	Heterogeneous photo catalysis (TiO_2/UV) ($\lambda \leq 400$ nm)
Fenton (Fe^{2+}/H_2O_2)	Water photolysis in ultra-vacuum (UVV) ($\lambda \leq 190$)
Electro-Fenton	Photo-Fenton (Fe^{2+}/H_2O_2/UV) ($\lambda \leq 550$ nm) Photo electro-Fenton ($\lambda \leq 550$)

NON-PHOTOCHEMICAL METHODS

Hydrogen peroxide can be produced without the light energy. The following methods were the two ways to generate oxidants without the use of light energy, ozone reaction and using Fe2+ ions as catalyst [13].

Ozonation at elevated pH

The main use of ozone in treating wastewater is for disinfection and oxidation. The usage of oxidation via ozonation includes odor control, discoloration and elimination of micro pollutants. Ozone is unstable in water and can be dissolved in water [19]. The reaction between ozone and contaminants happens quickly. The solubility of ozone in water is low, and the lifetime of ozone is only a few minutes. Hence, ozone has to be produced in-situ [26].

The ozone is considered as a strong oxidizing agent capable of reacting with organic and inorganic compounds. There are two oxidizers that have a higher oxidation potential than ozone, hydroxyl and fluorine ion [27]. Thus, ozonation can be categorized as AOP, and the decomposition of ozone can be initiated by the presence of transition metal cations [28].

The decomposition rate of ozone in water increases along with the increased pH [28, 13]. Organic compounds which have C=C double bonds and aromatic ring were attacked by ozone radicals at acidic pH to decompose and produce carboxylic acid and aldehydes [29]. However, pH in alkalinity phase from 8 to 9; the OH−ions react with ozone and produce superoxide anion radicals (•O2−) as follow:

Initiation $O_3 + OH^- \rightarrow \bullet O_2^- + HO_2^\bullet$ (3)
Radical chain-reaction $O_3 + {}^\bullet O_2^- \rightarrow \bullet O_3^{-1} + O_2$ (4)
$\bullet O_3^{-1} \rightarrow {}^\bullet OH + O_2$ (5)
${}^\bullet OH + O_3 \rightarrow HO_2^\bullet + O_2 \rightarrow HO_4^\bullet$ (6)
$HO_4^\bullet \rightarrow {}^\bullet O_2^- + O_2$ (7)
$HO_2^\bullet - \rightarrow {}^\bullet O_2^- + H^+$ (8)
Termination $HO_4^\bullet + HO_4^\bullet \rightarrow H_2O_2 + 2O_3^\bullet$ (9)
Overall, 1mol of O_3 yields 1 mol of •OH

The oxidation through the formation of •OH radical is limited by the presence of ozone resistant compounds or •OH radical scavengers when the pH is higher than 9.0. Consequently, carbonate ions were produced by bicarbonate ions, and the oxidation rate is slowed by the scavengers of •OH radicals [30]. The corresponding equation is listed below:

$$\bullet OH + {}^*P \rightarrow \text{end products} \quad (10)$$

*P could be HCO_3^- and CO_3^{2-} as per the example below:

$$^{\bullet}OH + CO_3^{2-} \rightarrow OH^{-} + CO_3^{\bullet -} \tag{11}$$

$$^{\bullet}OH + HCO_3- \rightarrow OH^{-} + HCO_3^{\bullet} \tag{12}$$

Ozonation is not an efficient process for the treatment of leachate due to the complexity of leachate. Thus, high dose of ozone is required for the treatment of leachate and consume more time; therefore economically it's not favorable [30]. The amount of °OH radicals attack is between 106 to 109 times faster than the corresponding reaction rate for the molecular ozone. The disadvantages of ozonation were electricity cost, pure oxygen cost [13] and generation of inorganic compounds like ammoniacal nitrogen [19].

The removal efficiency of biological treatment was limited by the recalcitrant compound in leachate. Ozonation is able to increase biodegradability of wastewater [31]. Thus, combining biological treatment with ozonation promotes better removal efficiency. Marttinen et al. [32] evaluated an ozone dose of 0.5 mg O_3/ mg to convert slowly biodegradable COD (SBCOD) to biodegradable form [19]. Cortez et al. [33] evaluated Fenton and ozone-based AOPs for the treatment of mature landfill leachate. They found that high COD removal and an increase in biodegradability at elevated pH, solely or combined with H_2O_2, confirming enhanced production of hydroxyl radical under such conditions. After 60 min of ozonation at 5.6 g O_3 h^{-1}, initial pH 7, and 400 mg L^{-1} of hydrogen peroxide, COD removal efficiency was 72% and BOD_5/COD increased from 0.01 to 0.24 [33].

In addition, Cortez et al. [34] studied the treatment of matured landfill leachate using ozonation. They reported a COD removal efficiency of 40% at an ozone concentration of 112 mg L^{-1}, ozone flow rate of 0.83 $Lmin^{-1}$, contact time of 60 min and pH of 11.The BOD_5 increased to 180% at 112 mg O_3 L^{-1}. The BOD_5/COD ratio increased with the increase in the ozone concentration [34].

Ozone + hydrogen peroxide (O_3/H_2O_2)

The following equations illustrate the decomposition of hydrogen peroxide and ozone for the formation of °OH radicals [28].

$$H_2O_2 \rightarrow HO_2^{-} + H^{+} \tag{13}$$

$$HO_2^{-} + O_3 \rightarrow HO_2^{\circ} + O_3^{-\circ} \tag{14}$$

$$2O_3 + H_2O_2 \rightarrow 2OH^{\circ} + 3O_2 \tag{15}$$

Tizaoui et al. [35] demonstrated that the combination of ozone and hydrogen peroxide produces excellent treatment system for leachate [35]. The COD reduction was up to 48%, 0.7 biodegradability and 94% color removal were achieved in the treatment system. Hydrogen peroxide proved to enhance the treatment process when combined with ozone as compared to ozone alone or hydrogen peroxide alone.

Cortez et al. [34] observed efficiency of ozonation varies due to reaction time, pH, ozone and hydrogen peroxide concentrations [34]. The combination of O_3/H_2O_2 obtained the highest decomposition of compound and biodegradability at 600 mg $H_2O_2L^{-1}$(COD removal, 63%, TOC, 53% and biodegradability increased from 0.01 to 0.17). Combination of O_3/H_2O_2 reduced recalcitrant organic matter and improved the BOD_5/COD ratio. Based on the observation of Cortez et al. [34], ozone of 5.6 g O_3h^{-1} in combinations with hydrogen peroxide of 400 mg L^{-1}, contact time of 60 min and initial pH of 7 was found to be the best oxidation approach tested. COD removal reached 72% and BOD_5/COD ratio increased from 0.01 to 0.24.

Ozone + Catalyst (O_3/CAT)

Usage of heterogeneous or homogeneous catalysts (Fe_2O_3, Al_2O_3–Me, MnO_2, Ru/CeO_2, TiO_2–Me, Fe^{2+}, Fe^{3+},Mn^{2+}) increased rate of ozonation. However, the reaction mechanism in most of cases still remains unclear [13].

$$C \rightarrow C\ (e^{-} + h^{+}) \tag{16}$$

$$h^{+} + Red_2 \rightarrow Ox_2 \quad \text{(Heterogeneous reaction)} \tag{17}$$

$$e- + Ox_1 \rightarrow Red \tag{18}$$

$$C \rightarrow C^{\circ} \tag{19}$$

$$C^{\circ} + R \rightarrow RE^{\circ} + C^{\circ} \tag{20}$$

$$R^{\circ} \rightarrow P \tag{21}$$

Fenton System (H_2O_2/FE^{2+})

The role of iron in this process can be considered as a catalyst and the reaction of ferrous ion with H_2O_2 produces high rate constant. Transmission of electron happens among H_2O_2 and Fe^{3+}. The oxidation Fe^{2+} to Fe^{3+} occurs in few seconds till few minutes if there is excess amount of H_2O_2. Hydroxyl radicals were produced by splitting H_2O_2 catalytically with Fe^{3+}. Fenton reaction cascade is shown below [36]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \tag{23*}$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{\bullet}_2 + H^{+} \tag{24}$$
$$\bullet OH + H_2O_2 \rightarrow HO^{\bullet}_2 + H_2O \tag{25}$$
$$\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \tag{26}$$
$$Fe^{3+} + HO^{\bullet}_2 \rightarrow Fe^{2+} + O_2H^{+} \tag{27}$$
$$Fe^{2+} + HO^{\bullet}_2 + H^{+} \rightarrow Fe^{3+} + H_2O_2 \tag{28}$$
$$2HO^{\bullet}_2 \rightarrow H_2O_2 + O_2 \tag{29*}$$

The reaction of (23*)–(29*) considered as H_2O_2 decomposition into water and O_2 catalyzed by iron summarized as follow:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{30}$$

The oxidation of Fenton involves four intermediate steps; pH adjustment, oxidation reaction, neutralization, coagulation and precipitation. In the oxidation and coagulation steps the organics substances were removed [16]. Oxidation of organic compounds by Fenton's reagent results in a reduction of the COD from 45 to 75%. The dependence of Fenton process to pH is too high. When the pH is between 2 to 4, the Fenton oxidation is efficient especially at pH of 2.8 due to the formation of ferric oxyhydroxide [36].

Based on the studies of Cortez et al. [34] on the evaluation of Fenton and ozone-based AOPs; the treatment of mature landfill leachate at optimized experimental conditions removed 46% of COD and increased the BOD_5/COD ratio from 0.01 to 0.15.

PHOTOCHEMICAL METHODS

The degradation of harmful compound is not always effective by the chemical oxidation due to the formation of by-products with higher toxicity and lower biodegradation compared with initial composition. The efficiency of oxidation process can be improved by using the UV light [13]. In some reactions, the intermediate oxidation products in the solution may be more toxic than the initial compound [13]. Degradation of these compounds can be enhanced with sunlight or artificial light source. Photochemical processes (called also as UV-AOPs processes) depends on the •OH from water molecule in leachate and direct photolysis. The reaction below depicts radicals produced from water by light [31, 38].

$$H_2O + h\nu \rightarrow H^{\circ} + OH^{\circ} \tag{31}$$

The advantage of photochemical treatment is basically on the efficient removal of refractory compound. The drawback of photochemical treatment is the high cost of UV light which prevents industrial scale usage. Combination of H_2O_2 and/or O_3, (Photo-Fenton) or photo catalysis (TiO_2) [27] increase the rate of this process.

Ozone–UV Radiation (O_3/UV)

The photolysis of ozone to break down H_2O_2 and provide °OH becomes expensive due to the usage of mercury lamp at low pressure which produces 80% UV energy. However, the easiest method to generate °OH is photolysis of H_2O_2, but H_2O_2 at 254 nm ($\varepsilon 254nm = 18.6\ M^{-1}\ cm^{-1}$) is absorbed by low molecular and the production of °OH is limited in the solution. It can be seen from Table 6 that photolysis of ozone yields more radicals than the UV/H_2O_2 process [13].

Table 6: Formation of OH from photolysis of ozone and H_2O_2 [13]

Oxidant	ε254 nm, $M^{-1}cm^{-1}$	Stoichiometry	OH° formed per incident photon
H_2O_2	20	$H_2O_2 \rightarrow 2OH°$	0.009
O_3	3300	$3O_3 \rightarrow 2OH°$	2.00

H_2O_2 is a poor acid but strong oxidant and able to initiate the decomposition of ozone via a loop technique that is illustrated below [22].

$$H_2O_2 \leftrightarrow HO^-{}_2 + H^+ \tag{34}$$
$$HO^-{}_2 + O_3 \rightarrow O^-{}_3 + HO_2^\bullet \tag{35}$$
$$HO_2^\bullet \leftrightarrow O_2^- + H^+ \tag{36}$$
$$O2\text{-}\bullet + O_3 \rightarrow O_3^{-\bullet} + O_2 \tag{37}$$
$$O_3^{-\bullet} + H^+ \leftrightarrow HO_3^\bullet \tag{38}$$
$$HO_3^\bullet \rightarrow HO^\bullet + O_2 \tag{39}$$
$$O_3 + HO^\bullet \rightarrow O_2 + HO_2^\bullet \tag{40}$$

Qureshi et al. [40] studied on the UV-catalytic treatment of municipal solid-waste landfill leachate with hydrogen peroxide and ozonation. The TOC removal efficiency (61%), color (87.2%) and BOD/COD ratio (0.112to 0.323) of the effluent were increased when ozone dosage was increased [40].

Hydrogen Peroxide–UV Radiation (H_2O_2/UV)

The capability of a molecule to lose and gain electrons will be increased by the absorption of light [27]. By the photolysis of hydrogen peroxide, hydroxyl radicals were generated. The following reaction explains H_2O_2/UV process [13].

$$H_2O_2 \rightarrow 2OH° \tag{41}$$

HO_2^- (acid–base equilibrium with H_2O_2) also absorbs the UV radiation at 254 nm wavelength [13 and14].

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \tag{42}$$
$$HO_2^- \rightarrow OH° + O^{°-} \tag{43}$$

If the H_2O_2 dosage is higher than optimum value, reaction will be less effective. The reaction of radicals with H_2O_2 creates intermediate radicals as shown below [38].

$$OH° + H_2O_2 \rightarrow HO°_2 + H_2O \tag{44}$$
$$HO°_2 + H_2O_2 \rightarrow OH° + H_2O + O_2s \tag{45}$$
$$HO°_2 + HO°_2 \rightarrow H_2O_2 + O_2 \tag{46}$$

Pieczykolan et al. [41] studied on COD removal from landfill leachate using H_2O_2, UV radiation and combination of these processes. They concluded that the most effective process was the UV/H_2O_2 process. When oxidation was conducted under the most suitable conditions, the maximum COD removal efficiencies were 74.6%, 19.6% and 19.3% when the treatment was performed by H_2O_2/UV, H_2O_2 and UV radiation, respectively [41].

Qureshi et al. [40] studied on the UV-catalytic treatment of municipal solid-waste landfill leachate with hydrogen peroxide and ozonation. In UV/H_2O_2 oxidation experiment, with the increase of H_2O_2 dosage, removal efficiencies of TOC and color along with the ratio of BOD to COD of the effluent were increased and a better performance was obtained than H_2O_2 treatment alone. In UV/H_2O_2 oxidation, under the optimum condition of H_2O_2, removal efficiencies of TOC and color were 78.9% and 95.5%, respectively, and BOD/COD ratio was significantly increased from 0.112 to 0.366 [40].

Ozone–Hydrogen Peroxide–UV Radiation ($O_3/H_2O_2/UV$)

Further positive way for receiving more °OH was using combination of double process same as UV/ H_2O_2, O_3/UV and O_3/ H_2O_2 and also the tertiary system of O_3/UV/ H_2O_2. By utilizing those processes, fast decomposition rate for pollutant and mineralization in total carbon can be achieved. It is the most effective treatment for highly polluted effluents [27]. To accelerate the decomposition of ozone to °OH, H_2O_2 should be added to O_3/UV. The addition hydrogen peroxide at a reduced UV flux evaluated as cost effective. If direct photolysis of pollutants is not a major factor, O_3/H_2O_2 should be considered as alternative to photo oxidation processes. Table 7 presents a comparison of the operating costs of various AOPs [13].

Table 7: Comparative operating costs of some AOPs [42]

Process	Cost of oxidant	Cost of UV
O_3/UV	High	Medium
O_2/H_2O_2	High	0
H_2O_2/UV	Medium	High
Photo catalytic oxidation	Very low	Medium to high

Photo-Fenton and Fenton-like Systems

In Photo-Fenton process, Fe^{3+}ions added to H_2O_2/UV reaction to produce OH° and Fe^{2+} ions (ferrous ions) known as photo-Fenton process. The reaction is shown below [42].

$$Fe^{3+}+H_2O \rightarrow Fe^{2+}+H^{+}+OH^{\circ} \quad (47)$$

At acidic phase (pH 3) Fe $(OH)^{2+}$ was formed and then decomposed with UV irradiation. Thus, Fe^{2+} ions and hydroxyl radicals are produced [13].

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^{+} \quad (48)$$
$$Fe(OH)^{2+} \rightarrow Fe^{3+} + OH^{-} \quad (49)$$
$$Fe(OH)^{2+} \rightarrow Fe^{2+}+OH^{\circ} \quad (50)$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\circ} + OH^{-} \quad (51)$$

One of economical choice in the photo-Fenton process is using the solar light instead of UV light. It is clear that photo-Fenton-type reaction depends on UV irradiation to initiate the generation of °OH. If desired, the organic pollutants can be mineralized with UV/visible irradiation [13]. In comparison with other oxidants, hydrogen peroxide is not costly, not dangerous, and is easy to handle and does not poses no lasting environmental threat because it readily decomposes to water and oxygen. Also, iron is reasonably priced, safe and environmental friendly next to oxygen, silicon and aluminum [37]. The disadvantage of the photo-Fenton process is the requirement of pH adjustment [22]. Fenton and photo-Fenton process have been used with great success for the degradation of several organic and inorganic pollutants including pesticides [43]. The important disadvantage regarding to Fenton and photo-Fenton for treatment of wastewater is requirement to control of pH and issue of manufacture sludge [32]. Qureshi et al. [40] studied on UV-catalytic treatment of municipal solid-waste landfill leachate with hydrogen peroxide and ozonation which in $UV/H_2O_2/O_3$ system, color removal and BOD/COD ratio were improved further and TOC removal efficiency was found to be 30.4% higher than the system of UV/O_3 without H_2O_2 [40].

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Based on the studies by Davinson [44] the percentage of TOC removal during the ozonation treatment increased because of addition of metal ions such as Fe^{2+}, Mn^{2+}, Ni^{2+} or Co^{2+} compared with ozonation alone. After using the combination of photo-Fenton and ozone the decomposition process increased because of increase in production of OHº.

In addition, ferrous ion is oxidized by ozone to ferric ion by different mechanisms which have been studied. Hart et al. [45] stated the first mechanism that evaluated transmission of an electron from the reduced metal to ozone, forming ferric ion and the radical ion O^{-}_{3} and then the formation of hydroxyl radical. Then, an idea suggested by Nowell and Hoigné [39] which reaction with ozone is a system that oxygen transferred from ozone to ferrous ion [39]. Recently, Logager et al. [46] evaluated that in acidic phase ferrous ion directly reacts with O_3 and produce $[FeO^{2+}]$ which emits hydroxyl radical as follows.

$$Fe^{2+} + O_3 \rightarrow [FeO]^{2+} + O_2 \tag{52}$$
$$[FeO]^{2+} + H_2O \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \tag{53}$$

Photo catalytic oxidation (UV/TiO_2)

The fundamental of photo catalysis with TiO_2 is the semiconductor photo-excitation. One of the highest photo catalysts in the process is Titanium dioxide (TiO_2) which utilized in industry. The preparation of TiO_2 is done by the high refractive index in the visible range and thin films. TiO_2 is utilized in the industry in the formation of anatase and rutile. Its high refractive index in the visible range permits for the preparation of thin films, and thus can be used as a pigment material. On the other hand, its use as a catalyst support or as a catalyst and photo catalyst itself is well known and it acts not only as a catalyst support, but also interacts with supported phase as promoter [13].The energy of TiO_2 (anatase) is 3.2 eV. This energy is between two bands [48]. It can be activated by UV irradiations with a wavelength up to 387.5 nm. TiO_2 photo catalysis can utilize of only 3–4% of solar irradiations that come the earth, because they begins at a wavelength of about 300 nm [13].

Absorbance of UV by semiconductor creates electron-hole pairs. When semiconductor illuminated by light the electron of the valence band of the semiconductor becomes excited. Transferring excited electron of the semiconductor enhances and makes the negative-electron (e^-) and positive-hole (h^+) pair [47].

$$TiO_2 \rightarrow h^+ + e^- \tag{53}$$

Hydrogen gas and hydroxyl radical were formed to water molecule by positive hole. The negative electron reacts with oxygen molecule and forms super oxide anion. Electrons and holes existence at the surface of the TiO_2 particle would react with absorbed species. The oxidation potential of holes was high. The reactions were explained as below [13].

$$h^+ + H_2O \rightarrow OH^\circ + H^+ \tag{54}$$
$$e^- + O_2 \rightarrow O_2^{-\circ} \tag{55}$$
$$h^+ + A^- \rightarrow A^\circ \tag{56}$$
$$h^+ + OH^- \rightarrow OH^\circ \tag{57}$$
$$OH^\circ + RH \rightarrow RHOH^\circ \tag{58}$$
$$OH^\circ + RH \rightarrow R^\circ + H_2O \tag{59}$$
$$h^+ + RH \rightarrow {}^\circ RH^+ \tag{60}$$

CONCLUSION

Landfill leachate varies widely in chemical composition. Leachate composition depends on numerous factors and undergoes changes during the operation of the landfill site. Leachate in young landfill sites are easily biodegradable compounds. When a landfill site is older, the leachate contains more degradable biochemical substances. These substances are mainly humic acids. Due to the differences in chemical composition of leachate, the treatment varies from biological to physic -chemical treatment. For the hardly decomposable impurities, contained in the leachate from stabilized landfill sites there apply any physico-chemical methods. To choose the appropriate purification method of municipal landfill leachate, an in-depth analysis should be carried out, considering waste storage technologies, landfill types, quality and quantity of leachate that arise and the size of the landfill site. AOPs were effective, but relatively expensive. Advanced oxidation methods can be divided into homogeneous and heterogeneous processes. Homogeneous processes can be carried out with or without power. However, it is the combined processes that are definitely more efficient. These methods can effectively remove or reduce the number of pollutants that could not be removed by conventional methods. It has the ability to break down hardly biodegradable compounds and they are regarded as an effective tool for the treatment of water from the persistent residue.

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