

Review Article

Removal of Organic Matter from Landfill Leachate by Advanced Oxidation Processes: A Review

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Received 15 January 2010; Accepted 12 April 2010

Academic Editor: Josiane Nikiema

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In most countries, sanitary landfill is nowadays the most common way to eliminate municipal solid wastes (MSWs). However, sanitary landfill generates large quantity of heavily polluted leachate, which can induce ecological risk and potential hazards towards public health and ecosystems. The application of advanced oxidation processes (AOPs) including ozone-based oxidation, Fenton oxidation, electrochemical oxidation, and other AOPs to treatment of landfill leachate was reviewed. The treatment efficiency in term of chemical oxygen demand (COD) of various AOPs was presented. Advantages and drawbacks of various AOPs were discussed. Among the AOPs reviewed, Fenton process should be the best choice, not only because it can achieve about 49~89% of COD removal with COD ranging from 837 to 8894 mg/L, but also because the process is cost-effective and simple in technological aspect, there is no mass transfer limitation (homogeneous nature) and both iron and hydrogen peroxide are nontoxic.

1. Introduction

Due to rapid economic development in recent years, the excessive generation of municipal solid wastes (MSWs) has been identified as one of the most serious environmental problems in the world which needs to be addressed urgently for environmental protection. Up to 95% total MSW collected worldwide is disposed using the landfilling method [1]. After landfilling, solid waste undergoes a series of physicochemical and biological changes. Consequently, the degradation of the organic fraction of the wastes in combination with percolating rainwater leads to the generation of a highly contaminated liquid called "leachate". Leachate may contain large amount of organic matter (biodegradable, but also refractory to be biodegraded), ammonia-nitrogen, heavy metals, and chlorinated organic compounds and inorganic salts.

The characteristics of landfill leachate are affected by many factors, such as age, precipitation, weather variation, and waste types and compositions. In particular, the composition of landfill leachate varies greatly depending on the age

of the landfill [2]. According to the landfill age, the leachate can be classified into three types: young, intermediate, and old, and the relationship of the characteristics of landfill leachate versus the age of landfill is summarized in Table 1 [3, 4]. The young landfill leachate is commonly characterized by high biochemical oxygen demand (BOD) (4000–13,000 mg/L) and chemical oxygen demand (COD) (30,000–60,000 mg/L), moderately high content of ammonium nitrogen (500–2000 mg/L), high ratio of BOD/COD (ranging from 0.4 to 0.7), and low pH values (as low as 4.0), with biodegradable volatile fatty acids (VFAs) appear to be its major constituents [5]. With an increase in the landfill age and decomposing of VFAs in the landfill leachate by anaerobic bacteria over a period of 10 years, the old leachates are catalogued as stabilized and characterized by a relatively low COD (<4000 mg/L), slightly basic pH (7.5–8.5), low biodegradability ($BOD_5/COD < 0.1$), and high molecular weight compounds (humic substances) [6].

Toxicity analysis carried out using various test organisms such as *Vibrio fischeri*, *Daphnia similis*, *Artemia salina*, and *Brachydanio rerio* has confirmed that the potential dangers

TABLE 1: Landfill leachate classification versus age [3, 4].

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

of landfill leachate [7–10] and the necessity to treat is so as to meet the standards for discharge in receiving waters. Laboratory studies to determine the effectiveness of various biological, physical, and chemical treatment processes on landfill leachate have been investigated since the early 1970s. Biological treatment processes, including anaerobic and aerobic processes, are quite effective for leachate generated in the early stage with a high BOD₅/COD. However, they generally fail to treat a leachate with a rather low BOD₅/COD, or high concentration of toxic metals [11]. Hence, physical-chemical processes are mostly used for pretreatment or full treatment for this type of landfill leachate.

Among the various types of physical-chemical treatments, advanced oxidation processes (AOPs) has been reported as one of the most effective method to degrade a variety of refractory compounds in landfill leachate [12]. This can be attributed to the role of a highly reactive radical intermediate such as hydroxyl radical ($\bullet\text{OH}$) as an oxidant. The radicals can be produced in ozone oxidation, Fenton oxidation, and electrochemical oxidation systems.

With an oxidation potential (E^0) of 2.80 V (Table 2), the $\bullet\text{OH}$ radical can rapidly degrade recalcitrant organics such as aromatic, chlorinated, and phenolic compounds [13]. Once a reaction of the free radical is initiated by ozone or H_2O_2 , a series of oxidation reactions occurs in the solution and the radicals rapidly react with most of the target compounds. The kinetic rate of AOPs depends on the concentration of radicals and pollutants, temperature as well as the presence of scavengers such as bicarbonate ion [14].

2. Treatment of Landfill Leachate via AOPs

2.1. Ozone-Based Oxidation Processes. Ozonation processes are attractive means for the treatment of landfill leachates due to the high oxidative power that ozone possesses [15]. As one of the most powerful oxidants with an oxidation potential (E^0) of 2.08 V (Table 2), ozonation alters the molecular structure of refractory organic compounds in landfill leachate, turning them into compounds that are easily assimilated biologically [16].

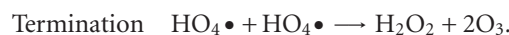
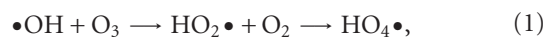
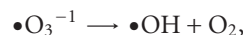
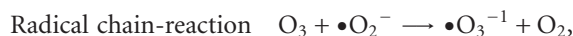
Depending on the pH values, which play major roles in the ozone decomposition, ozone oxidation follows the two

TABLE 2: Oxidizing potential of some oxidizing agents [13].

Type of oxidizing agents	Oxidation potential (E^0) (V)
Fluorine	3.06
Hydroxyl radical	2.80
Oxygen (atomic)	2.42
Ozone	2.08
Hypochlorite	1.49
Hydrogen peroxide	1.78
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen (molecular)	1.23

main pathways: either a direct electrophilic attack of the ozone molecule to the recalcitrant pollutants or a generation of $\bullet\text{OH}$ radicals due to the ozone decomposition process and followed by a subsequent attack of the radicals on the pollutants [17].

At an acidic pH range, ozone undergoes selective electrophilic attack on the specific part of the organic compounds that have C=C bonds and/or aromatic ring [18] and decomposes them into carboxylic acid and aldehydes as the end products [19]. When exposed to the pH values ranging from 8.0 to 9.0, in the presence of OH^- ions, the hydroxide ion reacts with ozone to yield superoxide anion radicals ($\bullet\text{O}_2^-$), which in their turn are involved in a series of reactions as follows:

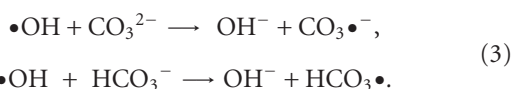


Overall, 1 mol of O_3 yields 1 mol of $\bullet\text{OH}$.

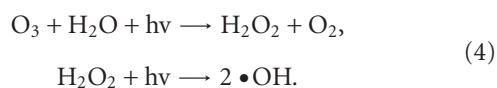
When pH is higher than 9.0, oxidation through the formation of $\bullet\text{OH}$ radical is limited by the presence of ozone-resistant compounds or $\bullet\text{OH}$ radical scavengers. Under such condition, bicarbonate ions are converted to carbonate ions, which are the scavengers for $\bullet\text{OH}$ radicals that slow down the kinetic rate of the oxidation reaction [17]. The corresponding equation is listed as follows:



where P represents the scavenger of hydroxyl radicals such as HCO_3^- and CO_3^{2-} . Some examples of the reactions are presented as follows:



As a single process, oxidation with ozone is not considered as very effective due to the complexity of leachate composition, high ozone doses are often required and the respective reaction may take longer time, rendering this process economically unfavorable [20]. Ozone processes can be made more effective by employing UV irradiation (O_3/UV) or the addition of hydrogen peroxide ($\text{O}_3/\text{H}_2\text{O}_2$). UV and H_2O_2 initiate a series of radical reactions that enhance ozone decomposition to yield $\bullet\text{OH}$ [21]. In the O_3/UV process, UV irradiation not only activates the ozone molecules by absorbing the UV light at 254 nm, but also makes other organic molecules susceptible to the oxidation process [22]. The initial step of the radical mechanism in this process is the direct photolysis of the ozone to produce $\bullet\text{OH}$, as shown in the following reactions [23]:



And the net reaction is



On the other hand, in the $\text{O}_3/\text{H}_2\text{O}_2$ system, the addition of H_2O_2 can accelerate the decomposition of ozone and subsequently enhance the production of $\bullet\text{OH}$ radicals, as (6):



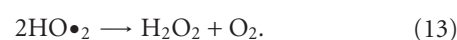
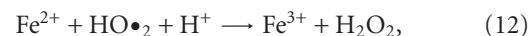
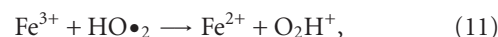
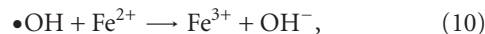
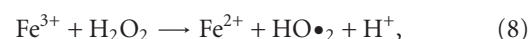
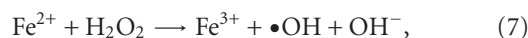
The reactions involved are very complex in the systems, since the organic compounds can be degraded either by direct ozonation, photolysis reaction, or $\bullet\text{OH}$ oxidation [17].

Performance of O_3 , $\text{O}_3/\text{H}_2\text{O}_2$, and O_3/UV process can be evaluated thanks to key parameters (COD, BOD, BOD/COD, and oxidant dose) summarized in Table 3. As previously mentioned, ozonation as a single process was not considered as very effective (COD reduction is about 15–50%) [15, 16, 24–29]. Thus, most researchers used ozonation process as pretreatment before biological treatment or tertiary treatment prior to discharge in the environment. COD reduction can be greatly enhanced via combining oxidants ($\text{H}_2\text{O}_2/\text{O}_3$) (Table 3). Wable et al. [28] and Schulte et al. [30] reported the

efficiency of organic matter removal can be up to 95% and 97%, respectively. However, adding an irradiation system ($\text{UV}/\text{H}_2\text{O}_2$) was not as efficient as $\text{H}_2\text{O}_2/\text{O}_3$ system, with COD reduction at a range between 40% and 63%.

The common drawback of ozone-based oxidation is the high demand of oxidant (O_3 or H_2O_2) and the electrical energy used by UV lamps, which results in rather high treatment costs. However, ozone-based oxidation can improve the biodegradability of landfill leachate (Table 3). Using ozone-based oxidation as pretreatment of biological treatment can lower the cost.

2.2. Fenton Oxidation. Fenton process has been extensively studied in recent years, and analyses indicate Fenton process to be one of the most cost-effective alternatives for this application [37]. In the Fenton process, hydrogen peroxide is added to wastewater in presence of ferrous salts, generating species that are strongly oxidative with respect to organic compounds. $\bullet\text{OH}$ is traditionally regarded as the key oxidizing species in the Fenton processes. The classical Fenton free radical mechanism in the absence of organic compounds mainly involves the sequence of reactions below [38]:



$\bullet\text{OH}$ radicals are rapidly generated through (7). In the above reactions, iron cycles between Fe^{2+} and Fe^{3+} , and plays the role of catalyst. The net reaction of (7)–(13) is the decomposition of H_2O_2 into water and O_2 catalyzed by iron as follows:



Generally speaking, Fenton's oxidation process is composed of four stages including pH adjustment, oxidation reaction, neutralization and coagulation, and precipitation. The organic substances are removed at two stages of oxidation and coagulation [39]. $\bullet\text{OH}$ radicals are responsible for oxidation, and coagulation is ascribed to the formation of ferric hydroxo complexes [40]. The relative importance of oxidation and coagulation depends primarily on the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio. Chemical coagulation predominates at a lower $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio, whereas chemical oxidation is dominant at higher $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratios [41]. Wang et al. [42] and Lau et al. [43] reported that oxidation and coagulation were responsible for approximately 20 and 80% of overall COD removal respectively, in Fenton treatment of biologically stabilized leachate.

TABLE 3: O₃, O₃/H₂O₂, and O₃/UV treatments of leachates (updated from Renou et al. [2]).

Initial characteristics of the leachate				BOD/COD	Removal efficiency (%)		O ₃ (a.g/l) or (b.gO ₃ /g COD)	H ₂ O ₂ /O ₃ (g/g)	UV(W)	Reference
COD (mg/L)	BOD (mg/L)	pH	Color (mgP tCo/l)	After treatment	COD	Color				
O ₃										
6500	500	8.1	12,000	0.5	15	90	1.2 ^a			[15]
3096	130	8.2	5759	0.2-0.3	25-50	—	3.0 ^a			[16]
3460	150	8.2	5300	—	48	87	3.0 ^a			[24]
4850 ± 100	520 ± 30	8.2	—	0.25	30	—	1.3-1.5 ^b			[25]
5000	20	—	8300	0.015	33	100	1.7 ^b			[26]
5230	500	8.7	—	0.1	27	—	—			[27]
4850	10	—	—	0.1	33	—	—			[29]
895	43	8.2	—	0.14	28	—	0.76 ^b			[31]
O ₃ /H ₂ O ₂										
5230	500	8.7	—	0.7	48	94	—	H ₂ O ₂ :2 g/L		[27]
2000	—	—	—	—	95	—	3.5 ^b	0.4		[28]
600	—	—	—	—	92	—	3.3 ^b	0.4		
2000	160	8.4	—	0.13	92	—	1.5 ^b	0.3		[32]
—	—	8	—	—	97	—	2.5 ^a	2		[30]
—	—	8	—	—	70	—	—	0.5		
1360	<5	8.4	—	0.32	93	—	1.5 ^b	0.3		[31]
480	25	7.7	—	0.13	40	—	0.05-0.5 ^b	0.25-1		[33]
O ₃ /UV										
1280	100	2	—	—	54	—	—	—	100	[34]
1280	100	2	—	—	47	—	—	—	500	
2300	210	8	—	—	40	—	1 ^b	—	15	[32]
430TOC	—	—	—	—	51TOC	—	0.1 ^a	—	300	[35]
26,000	2920	7.8	—	63	0.32	—	3.5 ^b	—	1500	[36]
26,000	2920	7.8	—	61	0.35	—	4.7 ^b	—	1500	

The introduction of UV irradiation into the Fenton process as well as electro-Fenton process may be able to improve the removal of COD. Many researchers studied the treatment efficiency of Fenton, photo-Fenton and electro-Fenton processes and the performances are summarized in Table 4. It indicated that leachate quality in terms of COD, odor, and color can be greatly improved following Fenton treatment.

The treatment efficiency of Fenton process depends on pH and the dosage of Fe²⁺ and H₂O₂. According to Table 4, the optimal pH was in a range 2.0-4.0. The pH value affects the activity of both the oxidant and the substrate, the speciation of iron, and hydrogen peroxide decomposition [44]. Higher •OH radical product yields in the pH range of 2.0-4.0 by a reaction involving in the organometallic complex where either hydrogen peroxide is regenerated or reaction rates are increased [45]. The dosage of Fe²⁺ and H₂O₂ are major operational cost items for wastewater treatment. The removal of organic contaminants is improved as the concentration of Fe²⁺ and H₂O₂ increases. However, the extent of increase becomes negligible when the dosage is increased above a certain threshold level. Most researches

indicated that the optimal molar ratio of H₂O₂ to Fe²⁺ was from 1.5 to 3.0 [44, 46-48].

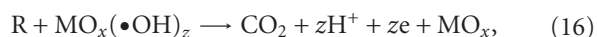
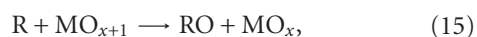
Fenton process can significantly remove recalcitrant and toxic organic compounds, and increase the biodegradability of organic compounds [49, 50, 52, 56]. There are four advantages of the Fenton's reagent: (i) both iron and hydrogen peroxide are relative cheap and nontoxic; (ii) there is no mass transfer limitation due to its homogeneous catalytic nature; (iii) there is no form of energy involved as catalyst; (iv) the process is technologically simple. However, Fenton process also shows drawback that large amounts of iron sludge may form, because Fe³⁺ is converted to ferric-hydroxo complexes.

2.3. Electrochemical Oxidation Processes. Electrochemical oxidation of pollutants in wastewater is fulfilled through two different approaches, as shown in Figure 1: indirect oxidation, where a mediator is electrochemically generated to carry out oxidation, and direct anodic oxidation, where pollutants are destroyed on the anode surface [57]. During indirect oxidation, the agents generated anodically, which are responsible for oxidation of inorganic and organic

TABLE 4: Fenton, photo-Fenton, and electro-Fenton treatments of leachates.

Initial characteristic of leachate			COD	BOD/COD	Optimal condition	Reference
COD (mg/L)	BOD (mg/L)	pH	Removal (%)	after treatment		
Fenton						
1300	30	8.7	—	—	pH: 3.5, Fe ₂ (SO ₄) ₃ : 500 mg/L, H ₂ O ₂ : 1650 mg/L	[39]
8298–8894	—	6.65–6.69	—	—	pH: 2.5, H ₂ O ₂ /Fe ²⁺ (molar ratio): 1.5, reaction time: 30 min	[44]
10540	2300	8.2	60	0.5	pH: 3, Fe ²⁺ : 275 mg/L, H ₂ O ₂ : 3300 mg/L, reaction time: 2h	[49]
837–6119	42.50–620.00	8.09–8.47	80 (young leachate) 60~70 (old leachate)	—	pH: 2.5, H ₂ O ₂ /Fe ²⁺ (molar ratio): 1.5, [H ₂ O ₂]: 0.075 M	[46]
1100–1300	—	8.18	61	—	pH: 3, [H ₂ O ₂]: 0.24 M, H ₂ O ₂ /Fe ²⁺ (molar ratio): 3	[47]
8894	—	6.65–6.69	89	—	pH: 2.5, [H ₂ O ₂]: 0.15 M, H ₂ O ₂ /Fe ²⁺ (molar ratio): 3	[48]
5700 ± 300	3600 ± 200	7.8 ± 0.3	66	0.88	pH: 3.5, H ₂ O ₂ : 650 mg/L, H ₂ O ₂ /Fe ²⁺ (molar ratio): 1 : 19	[50]
Photo-Fenton						
3824	680	7.94	86	—	Fe ²⁺ : 2000 mg/L, H ₂ O ₂ : 10000 mg/L	[51]
5200 ± 27	720 ± 81	8.4 ± 0.1	49	0.4	pH: 2.8, Fe ²⁺ : 10 mg/L, H ₂ O ₂ : 2000 mg/L	[52]
1150	4.6		70		pH: 3, Fe ²⁺ : 56 mg/L, H ₂ O ₂ : 34 mg/L, UV: 80 KW/m ³	[53]
Electro-Fenton						
5000	—	6.4	83.4	—	pH: 3, H ₂ O ₂ : 0.34 mol/L, Fe ²⁺ : 0.038 mol/L, I: 2 A, d = 2.1 cm	[54]
2350	—	2.36	72	—	pH: 3, H ₂ O ₂ : 2000 mg/L, I: 2 A, reaction time: 20 min	[55]
1941	195	8.1	69	0.29	pH: 4, H ₂ O ₂ : 750 mg/L	[56]

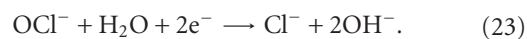
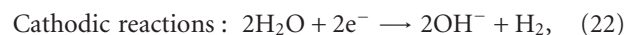
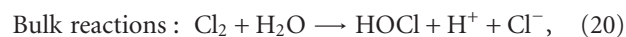
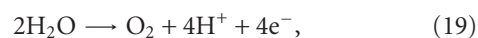
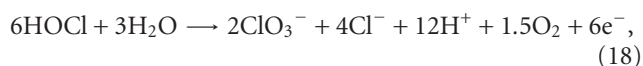
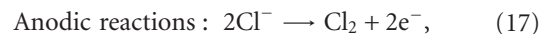
pollutants may be chlorine and hypochlorite, hydrogen peroxide, ozone and metal mediators such as Ag²⁺. Direct anodic oxidation is achieved through two different pathways: electrochemical conversion and electrochemical combustion [58]. During electrolysis, two species of active oxygen can be electrochemically generated on oxide anodes (MO_x). One is the chemisorbed “active oxygen” (oxygen in the oxide lattice, MO_{x+1}), responsible for the electrochemical conversion through (15). While the other is the physisorbed “active oxygen” (adsorbed hydroxyl radicals, •OH), responsible for electrochemical combustion through (16):



where R represents organic compounds; z represents the number of adsorbed •OH on anode.

During the electrochemical oxidation of landfill leachate, the removal of pollutants may be primarily attributed to

indirect oxidation, utilizing chlorine/hypochlorite formed by anodic oxidation of chlorine originally existing or added in the leachate [59]. However, direct anodic oxidation may to some extent destroy pollutants adsorbed on the anode surface [60]. A series of reactions involving indirect oxidation during electro-oxidation are shown in (17)–(23)



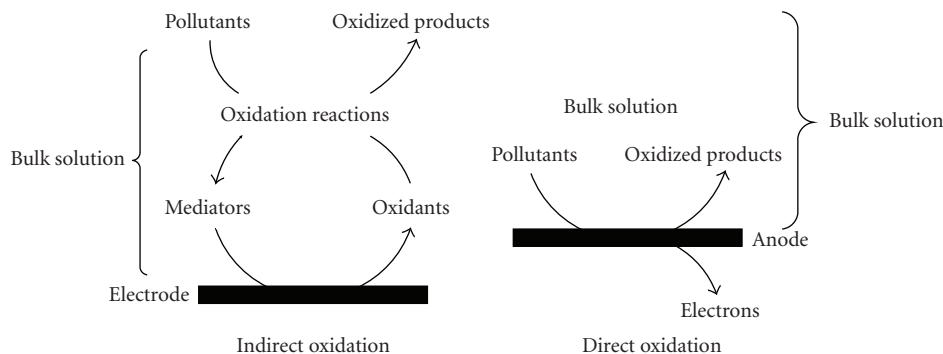


FIGURE 1: Pollutant removal pathways in electrochemical oxidation (indirect and direct oxidation) [57].

Hypochlorite (OCl^-) generated in (20) and (21) is a strong oxidant that can oxidize aqueous organic compounds. So, it can oxidize the organic matters in the leachate.

Some researchers have investigated the treatment efficiency of electrochemical oxidation in treating landfill leachate [59–63]. The pollutant removal efficiency was influenced by a number of operating factors, including anode materials, pH, current density, Cl^- concentration, and electrolytes added (Table 5). The common anode materials are ternary Sn-Pd-Ru oxide-coated titanium (SPR), binary oxide-coated titanium Ru-Ti oxide (DSA), PbO_2 -coated titanium (PbO_2/Ti), graphite, SnO_2 -coated titanium (SnO_2/Ti), iron (Fe) and aluminum (Al), and the COD removal efficiency when using the anode material followed the order of $\text{SPR} > \text{DSA} > \text{PbO}_2/\text{Ti} > \text{graphite}$ [59]. Moraes and Bertazzoli [61] found that the removal rates achieved were 73% for COD, 57% for TOC, 86% for color and 49% for ammonium at a current density of 116.0 mA/cm^2 , using oxide-coated titanium anode. Bashir et al. [63] used graphite carbon and got 70% BOD removal, 68% COD removal, and 84% color removal when the current density was 79.9 mA/cm^2 and reaction time was 2 hours.

Electrochemical oxidation of landfill leachate under appropriate conditions can remove most COD and significantly remove color. The important advantage of electrochemical oxidization is to oxidize organic pollutants into CO_2 and water to avoid a problem of contaminants shifting from one phase to another. Also, the operation at room temperature and atmospheric pressure prevents volatilization and discharge of unreacted wastes, and the reaction can be simply terminated in seconds by cutting off the power [64]. However, there are two drawbacks of electro-oxidation which may limit its wide application for landfill leachate treatment, one is high energy consumption, and the other is potential for formation of chlorinated organics. Especially because of its expensive operating costs compared with other available technologies (for example, biological processes), electro-oxidation will be favored as a finishing step in a combined process or an auxiliary unit in emergency situations, instead of a full treatment for landfill leachate [65].

2.4. Other AOP Processes. Wet air oxidation (WAO) is a useful treatment method for reduction of aqueous pollution

bound to heavily contaminated wastewater, in particular when it is necessary to treat low volumes. This process consists in the oxidation of dissolved or suspended aqueous solution of organic and inorganic substances by means of oxygen, at elevated temperature (450–590 K) and pressure (2–15 MPa), assuring wet conditions of reaction. Under these conditions organic waste streams too dilute to incinerate and too concentrated for biological treatment can be degraded to simpler, frequently more biodegradable, organic compounds or completely converted to CO_2 and H_2O [66]. Typically, WAO process has shown promising results (80%–99% of COD removal) for a complete mineralization of organic compounds or for their degradation into a less complex structure, which is more biodegradable [67]. This process is cost-effective for leachate treatment with COD concentrations ranging from 10,000 to 100,000 mg/L. If complete COD removal is not required, the operating conditions such as the air flow rate, temperature, and pressure can be lowered to reduce the operational cost [68]. Although WAO offers some advantages such as a small plant for operations and its ability to deal with varying flow rates and composition of the effluent, this process is not cost-effective for leachate treatment with a COD concentration of less than 5000 mg/L.

Ultrasonic process is considered as a possibility in wastewater treatment for several decades. It is able to remove pollutants through the production of radicals in the bubble of cavitation that can react with refractory compounds [69]. Ultrasonic irradiation is an effective method for the removal of organic matters and ammonia nitrogen from landfill leachate. After 180 minutes ultrasound irradiation (ultrasonic power input: 150 W, pH: 11) up to 96% ammonia nitrogen removal efficiency can be obtained [70]. Due to the high cost of ultrasonic, it is always used as pre- or posttreatment of the biological treatment. Ultrasound pretreatment of raw leachate can significantly improve the removal rates of COD and nitrogen compound (frequency: 20 kHz and amplitude: $12 \mu\text{m}$) [71].

It is obvious that WAO and ultrasonic show a better treatment efficiency of the landfill leachate. However, there are two drawbacks of the two AOPs. One is high energy consumption, and the other is the operation mode restrain its practical application. They are suitable for small quantity and high strength wastewater.

TABLE 5: Influence of operating factors in electro-oxidation of leachate [57].

Operating factor	Influence
Anode materials	Anode materials with high electrocatalytic activity and high anodic oxygen evolution potential cause a high COD and NH ₃ -N removal efficiency; usage of metal anode such as Fe and Al causes simultaneous electro-oxidation and electro-coagulation
pH	The influence of pH is unclear. Reported results are inconsistent
Current density	Increase in current density causes increase in removal efficiencies of COD and color
Chloride ion concentration	Increase in Cl ⁻ concentration improves removal of pollutants, but increase the hazard of formation of chlorinated organics
Additional electrolytes	Effects of additional electrolytes depend on their species and properties

TABLE 6: Summary of the highest reported COD removal of some AOPs.

AOPs	Optimal condition	Initial COD (mg/L)	COD removal efficiency (%)	Reference
O ₃	3 g/L	3460	48	[24]
O ₃ /H ₂ O ₂	O ₃ : 3.5 g/gCOD H ₂ O ₂ g/g O ₃	2000	95	[28]
O ₃ /UV	O ₃ : 3.5 g/gCODUV:1500 W	26,000	63	[36]
Fenton	pH: 2.5, [H ₂ O ₂]: 0.15 M, H ₂ O ₂ /Fe ²⁺ (molar ratio): 3	8894	89	[48]
Photo-Fenton	Fe ²⁺ : 2000 mg/L, H ₂ O ₂ : 10000 mg/L	3823.8	86	[51]
Electro-Fenton	pH: 3, H ₂ O ₂ : 0.34 mol/L, Fe ²⁺ : 0.038 mol/L, I: 2 A, d = 2.1 cm	5000	83	[54]
Electrochemical oxidation	Current density: 116.0 mA/cm ²	1855	73	[61]

3. Comparison of Various AOP's Performance

The outcomes of AOPs applied to treat the landfill leachate can be classified into two types: (i) oxidize organics substances to their highest stable oxidation states being carbon dioxide and water (i.e., to reach complete mineralization); (ii) improve the biodegradability of recalcitrant organic pollutants up to a value compatible with subsequent economical biological treatment. Thus, the comparison of various AOP's performance was evaluated from these two aspects.

Table 6 presents the outstanding treatment performance and optimum operate condition of various AOPs for COD removal from landfill leachate. The ozone-based process can achieve 40–95% of COD removal with COD concentration ranging from 2000 to 26,000 mg/L, while electrochemical oxidation process and Fenton process can achieve 70–90% of COD removal with COD concentration ranging from 1855 to 8894 mg/L. It should be noted that the treatment efficiency of Fenton process is better than ozone-based process and electrochemical oxidation. In term of biodegradability improvement, BOD/COD ratios are 0.29–0.88 [49, 50, 52, 56] and 0.1–0.5 (Table 3) were reported after oxidation by Fenton process and ozone-based oxidation, respectively.

Concerning the cost of various AOPs, electrochemical oxidation, wet air oxidation, and ultrasound oxidation are more expensive due to the high demand of electrical energy

for devices ozonizers, UV lamps, ultrasounds. The only exception is the Fenton's process. In such a process, in fact, under acidic condition, a Fe²⁺/H₂O₂ mixture produces •OH radicals in a very effective way [49]. Tizaoui et al. [27] estimated the treatment cost of O₃/H₂O₂ system was about 2.3 US\$/kg COD. Kurniawan et al. [17] showed that the treatment cost of leachate using ozone-GAC adsorption varies between US\$ 2 and 4 per m³ of the treatment effluent. While Rivas et al. [72] estimated the operational cost for Fenton treatment of leachate was 8.0 × 10⁻³ US\$ per m³ of leachate and ppm of COD removed. Based on the analysis and Lopez et al. [49], Fenton process seems to be the best compromise because the process is technologically simple, there is no mass transfer limitation (homogeneous mature) and both iron and hydrogen peroxide are relatively cheap and nontoxic. But Fenton's process required low pH and a modification of this parameter is necessary.

4. Conclusions

The application of AOPs including ozone-based oxidation, Fenton oxidation, electrochemical oxidation, wet air oxidation, and ultrasound oxidation to treatment of landfill leachate was reviewed. Among the AOPs reviewed, ozone-based oxidation and Fenton oxidation are the most frequently studied and widely applied methods for the

treatment of landfill leachate. Both techniques can achieve about 15~95% of COD removal with COD concentration ranging from 600 to 26,000 mg/L. In particular, Fenton process can improve BOD/COD ratio to close 0.5. Fenton process seems to be the best compromise because the process is technologically simple, there is no mass transfer limitation (homogeneous mature) and both iron and hydrogen peroxide are cheap and nontoxic. From the economic point of view, using Fenton process as the pretreatment of biological treatment can lower the cost and improve the treatment efficiency.

In the past, most of works were focused on the removal efficiency of organic matters from landfill leachate. Only a few researches considering the toxicity reduction were involved. However, the toxicity assessment of landfill leachate is very important, which determines the effect of the subsequent biological treatment or the influence on the environment. So, the toxicity reduction of AOPs should be evaluated in the future research.

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