ELSEVIER

Chemical Engineering Journal 125 (2006) 35–57

Chemical Engineering Journal

www.elsevier.com/locate/cej

Radicals-catalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate

Tonni Agustiono Kurniawan, Wai-hung Lo*, G.Y.S. Chan*

Department of Applied Biology and Chemical Technology, State Key Laboratory of Chinese Medicine and Molecular Pharmacology,
The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

Received 24 January 2006; received in revised form 6 July 2006; accepted 18 July 2006

Abstract

This article reviews the technical applicability and the treatment performance of various advanced oxidation technologies (AOTs) for landfill leachate. A particular focus is given to ozonation, homogeneous systems without irradiation (Fe^{2+}/H_2O_2, O_3/H_2O_2) and homogeneous systems with irradiation (UV/O_3, UV/H_2O_2, $UV/O_3/H_2O_2$, photo-Fenton oxidation). Their advantages and limitations in application are evaluated. The formation of $^{\bullet}OH$ radicals in enhancing oxidation reactions is also elaborated. Selected information such as the pH, the dose of oxidants required, the characteristics of leachate in terms of COD and NH_3-N concentration and treatment performance is presented. It is evident from a review of 167 papers (1976–2005) that none of the individual AOTs is universally applicable or highly effective for leachate treatment. Among the individual AOTs reviewed, ozonation and/or Fenton oxidation are the most frequently studied and widely applied for leachate treatment. Both treatments are effective for 40–89% of COD removal with its concentrations ranging from 560 to 8894 mg/L. By combining the Fenton oxidation and coagulation–flocculation process, about 69–90% of COD removal with its concentrations ranging from 417 to 7400 mg/L was achieved. An almost complete COD removal (98%) was attained by combining the activated sludge (AS) and the Fenton oxidation (COD: 7000 mg/L) and/or the AS and wet air oxidation (WAO) (COD: 4140 mg/L). In general, the selection of the most suitable AOT for leachate treatment depends on the leachate characteristics, technical applicability and potential constraints, effluent discharge standard, cost-effectiveness, regulatory requirements and long-term environmental impacts.

Keywords: Advanced oxidation process (AOP); Catalytic oxidation; Fenton process; Hydroxyl radicals; Landfill leachate management; Municipal solid waste; Ozone

1. Introduction

Landfill is one of the most widely employed methods of disposing of municipal solid waste (MSW) [1]. More than 150,000 landfills have been built worldwide with over 55,000 sites located in the USA [2]. In the USA, about 57% of the 218 million tonnes of the MSW generated in 2000 was disposed of in landfills [3]; while in China, over 80% of the 160 million tonnes of the MSW generated in the same year was buried in 668 landfills [4].

After being landfilled, the solid waste decomposes through a series of combined physico-chemical and biological processes. With naturally present bacteria, the decomposition of the MSW occurs in four major stages: (a) an initial aerobic phase; (b) an anaerobic acid phase; (c) an initial methanogenic phase; (d) a stable methanogenic phase [5]. Due to the limited amount of oxygen present in the landfill, aerobic decomposition process predominates for the first few weeks only [6]. As soon as the oxygen is depleted by microbes, anaerobic conditions occur in the leachate and dominate until all the remaining organics of the waste have been decomposed [7].

During the decomposition process, highly contaminated wastewater called "leachate" is generated by rainwater percolating through the waste layer in the landfill [8]. The main sources of percolating water are precipitation, irrigation and run off that cause infiltration through the groundwater [9]. Depending on the rainfall conditions, the color of leachate varies from black to brown. A brownish color in the leachate is generated by dissolved organic materials such as humic substances [10].

With the increasing age of a landfill, the characteristics of the leachate vary from one landfill site to another [11]. Some factors affecting the composition of the leachate include the type and the composition of the MSW, the stage of the MSW decomposition, the age of the landfill, climate, seasonal variations [12], the

---

* Corresponding authors. Tel.: +852 3400 8724; fax: +852 2364 9932.
E-mail addresses: bctlo@polyu.edu.hk (W.-h. Lo), bcyschan@polyu.edu.hk (G.Y.S. Chan).

1385-8947/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2006.07.006

degree of the MSW stabilization [13], hydrology and geology sites, landfill design and operation, conditions within the landfill such as its pH and moisture content [14].

As water interacts with the refuse while seeping through a landfill, it becomes contaminated with waste components containing various organic and inorganic pollutants in dissolved or suspended forms [15]. Of the pollutants present in the leachate such as adsorptive organic halogen (AOX) [16], heavy metals [17], chlorinated organic [18] and xenobiotic compounds such as benzene, toluene and xylenes [19], ammoniacal nitrogen (NH_3-N) has been identified not only as a major long-term pollutant [20], but also as the primary cause of acute toxicity [21]. With a concentration of higher than 100 mg/L [22], NH_3-N is highly toxic to aquatic organisms, as confirmed by toxicity tests using zebrafish (*Danio rerio*) [23], freshwater fish (*Sarotherodon mossambicus*) [24], *Daphnia magna* [25] and luminescent bacteria [26].

In a study of 43 Finnish landfills conducted by Assmuth and Strandberg [27], the NH_3-N concentration tended to increase (500–1500 mg/L) even 30 years after the landfill closure. If allowed to migrate, NH_3-N that seeps from a landfill can infiltrate and contaminate the groundwater. Once the leachate enters the groundwater, it is difficult and expensive to control and clean it up, posing potentially serious threats not only to aquatic organisms, but also to public health in the long-term. In most cases, it is extremely difficult to restore the polluted groundwater to its former state. Therefore, the risk of groundwater pollution due to leachate seepage has become a major environmental concern worldwide in recent years.

A sound engineering design of a landfill can prevent or minimize the leakage of leachate from reaching the groundwater table. Measures include diverting the surface run off from the site, proper soil cover, proper vegetation and a proper means for leachate interception and collection systems such as synthetic/natural liners, piping and pumping the leachate to a treatment facility [28,29]. However, most of these precautions can only be applied to newly designed landfills. Some old landfills generate huge quantities of leachate daily, which must be treated prior to discharge.

To achieve a satisfactory removal of refractory pollutants from landfill leachate, several types of treatments have been adopted. Due to its cost-effectiveness, biological process is the most commonly employed method to remove the bulk of organic pollutants from landfill leachate [30]. This treatment employs microbes to break down the organic constituents of the leachate. Biological process is effective for the treatment of young leachate, which contains a high concentration of volatile fatty acids (VFA) [31]. The high strength of VFA, which accounts for the bulk of chemical oxygen demand (COD) in the young leachate, results in a pH value as low as 4. This acidic environment promotes an increasing concentration of heavy metals in the leachate [32]. With a molecular weight of less than 120 Da, VFA compounds such as acetic acid, propionic acid and butyric acid are biodegradable organic matter [33]. Young leachate is commonly characterized by a high biochemical oxygen demand (BOD) (4000–13,000 mg/L), high concentrations of COD (30,000–60,000 mg/L), a moderately high strength of NH_3-N (500–2000 mg/L) and a high ratio of BOD/COD ranging from 0.4 to 0.7 [34–39] (Table 1).

Table 1
Comparison of young and stabilized leachate [35–39]

Parameters	Young leachate	Stabilized leachate
Age	Less than 5 years	Older than 10 years
Composition	Low molecular weight compounds such as volatile fatty acids (acetic acid, propionic acid and butyric acid)	High molecular weight compounds such as humic acid and fulvic acid
pH	4	7–9
NH_3-N (mg/L)	500–2000	3000–5000
BOD (mg/L)	4000–13,000	<2000
COD (mg/L)	30,000–60,000	5000–20,000
BOD_5/COD	0.4–0.7	<0.1
COD/TOC	Higher than 2.8	<2.0

With the increasing age of a landfill, methane-forming bacteria degrade the VFA compounds, thus decreasing the organic strength in the leachate [40]. As a result, the pH rises to higher than 7 and some organic materials in the leachate are no longer readily degradable [41]. Due to the increasing population of *methanogenic* bacteria during the long methanogenic phase [42], the anaerobic decomposition process becomes dominant over a period of 20–50 years [43], resulting in the generation of a more stable leachate, which is commonly characterized by a high strength of NH_3-N (3000–5000 mg/L), a moderately high strength of COD (5000–20,000 mg/L) and a low BOD/COD ratio of less than 0.1 (Table 1). Typically, most of the organic materials present in the stabilized leachate have a high molecular weight and are refractory compounds such as humic substances and fulvic-like fractions, which are not easily degradable [44]. Many of these compounds such as 4-chlorophenol and benzyl succinic acid are on the US EPA list of priority pollutants [45]. As a result, stabilized leachate cannot be effectively treated either by using biological processes such as activated sludge (AS), anaerobic filtration and anaerobic lagoons [46] or by natural systems such as leachate recirculation [47] or constructed wetland [48]. Moreover, biological treatment is prone to toxic compounds that inactivate waste-degrading microbes, thus inhibiting biomass activity in the biological process [49].

Due to its ability to enhance the biodegradability of the recalcitrant compounds in the leachate, advanced oxidation technology (AOT) is considered as one of the most promising options for leachate treatment. Over the past three decades (1976–2005), an increasingly scholarly interest has been shown in the application of AOT such as ozonation and Fenton oxidation to transform toxic pollutants into less toxic molecules [50]. Such a phenomenon is evident from the increasing number of publications during the period between 1995 and 2000 [51]. In the early 1980s, there were less than 50 AOT-related articles published annually. By the turn of the 21st century, the number in the Chemical Abstract Database (1975–2000), however, significantly rose to over 5000 articles [52].

Although numerous studies of the technical applicability of AOT for leachate treatment have been undertaken worldwide in recent years, few attempts have been made to obtain a comprehensive overview on AOTs in terms of the optimum conditions required to achieve the maximum removal of recalcitrant compounds (as indicated by a decreasing COD value) and/or NH_3-N from the landfill leachate.

This article presents an overview with critical analysis of the technical applicability and the treatment performance of all AOTs such as ozonation, homogeneous systems without irradiation (Fe^{2+}/H_2O_2, O_3/H_2O_2), homogeneous systems with irradiation (UV/O_3, UV/H_2O_2, $UV/O_3/H_2O_2$, photo-Fenton oxidation) and heterogeneous system with irradiation (UV/TiO_2) for landfill leachate. Their advantages and limitations in application are compared. The formation of $^{\bullet}OH$ radicals in enhancing oxidation reactions is elaborated. To evaluate their removal performances for organic compounds and NH_3-N, selected information on the pH, the dose of oxidants required, the strength of wastewater in terms of COD and NH_3-N concentration, as well as their treatment efficiency is presented.

2. Various AOTs for degradation of recalcitrant compounds from landfill leachate

Among the various types of physico-chemical treatments, AOT has been reported as one of the most powerful methods to degrade a variety of refractory compounds from stabilized leachate [52]. This can be attributed to the role of a highly reactive radical intermediate such as hydroxyl free radical ($^{\bullet}OH$) as an oxidant. The radicals can be produced using UV/O_3, UV/H_2O_2, O_3/H_2O_2, UV/TiO_2, or Fe^{2+}/H_2O_2 [53].

With an oxidation potential (E^o) of 2.80 V (Table 2), the $^{\bullet}OH$ radical can rapidly degrade recalcitrant organics such as aromatic, chlorinated and phenolic compounds [54]. Once a reaction of the free radical is initiated by the 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 AOT depends on the concentration of radical and pollutant, temperature as well as the presence of scavengers such as bicarbonate ion [55]. During the treatment, the organic compounds in the leachate are oxidized by the free radicals and then mineralized to CO_2 and H_2O or transformed to less harmful compounds, which can be subsequently removed using a biological process.

Various AOTs that are commonly employed for leachate treatment are presented as follows:

Table 2
Oxidizing potential of some oxidizing agents [54]

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

2.1. Ozonation

Apart from Fenton oxidation, ozonation is one of the most frequently studied and widely applied methods for leachate treatment as a polishing step after a biological process [56]. As one of the most powerful oxidants with an oxidation potential (E^o) of 2.07 V (Table 2), ozonation alone can transform recalcitrant organic compounds in the leachate into lower molecular weight compounds within a short period, thus avoiding a deposit of toxic residue as special waste [57].

Once dissolved in water, the ozone reacts with a great number of non-biodegradable compounds. In this case, the nature of the compounds present in the leachate will determine the degree of reactivity with ozone and the efficiency of ozonation. Compounds with specific functional groups such as aromatic ring and C=C bonds are prone to ozone attack, which results in carbonyl compounds [58]. With organic compounds that have aromatic rings, O_3 is known to rupture the ring, yielding aliphatic acids [18].

Depending on the pH, which plays major roles in the ozone decomposition, ozone oxidation follows the two main pathways: either a direct electrophilic attack of the ozone molecule to the recalcitrant pollutants or a generation of $^{\bullet}OH$ radicals due to the ozone decomposition process and followed by a subsequent attack of the radicals on the pollutants [59].

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 rings [60] and decomposes them into carboxylic acid and aldehydes as the end products [61]. However, when exposed to a pH ranging from 8 to 9 (Table 3), in the presence of OH^- ions, the ozone rapidly decomposes into the more reactive $^{\bullet}OH$ radicals [54], which have an oxidation potential of 2.80 V, as shown in Eq. (1):

$$O_3 + H_2O \rightarrow O_2 + 2^{\bullet}OH \tag{1}$$

In an alkaline environment, many organic compounds that are slow to oxidize with the ozone can rapidly oxidize with the $^{\bullet}OH$ radicals, which rapidly attack most of the target molecules with a kinetic rate ranging from 10^6 to $10^9\ M^{-1}\,s^{-1}$ [62]. The $^{\bullet}OH$ radical is a highly reactive species, which can oxidize the organic compounds to a complete mineralization with carbonates as the end products. Such a phenomenon indicates that an alkaline environment is the key parameter in any AOT-based ozonation [63].

In basic conditions, both OH^- and $^{\bullet}OH$ act as the catalysts for the ozone decomposition process into intermediate compounds that are also highly reactive such as superoxide ions ($O_2{}^-$) and $HO_2{}^{\bullet}$ radical, as shown in the following mechanisms [64]:

Initial reactions:

$$O_3 + OH^- \rightarrow {}^{\bullet}O_2{}^- + HO_2{}^{\bullet}, \quad k_1 = 70\ M^{-1}\,s^{-1} \tag{2}$$

Propagation:

$$O_3 + {}^{\bullet}O_2{}^- \rightarrow {}^{\bullet}O_3{}^- + O_2, \quad k_2 = 1.6 \times 10^9\ M^{-1}\,s^{-1} \tag{3}$$

$$\text{At pH} < 8,\ {}^{\bullet}O_3{}^- + H^+ \leftrightarrow HO_3{}^{\bullet}, \quad pK_a = 6.2 \tag{4}$$

Table 3
Ozonation for treatment of hazardous leachate

Location of landfill	Ozone dose (g/L)	Ozone consumption (mg O_3/mg COD)	Initial concentration in leachate (mg/L)		BOD/COD	pH	Removal efficiency (%)		References
			COD	NH_3-N			COD	NH_3-N	
Roche-la-Moliere (France)	0.8	1.6	1400	NA	0.05	8.3	80	NA	[57]
Braunschweig (Germany)	2.5	3.0	1200	5	0.01	7	80	NA	[59]
Mustankorkea (Finland)	0.09	0.5	920	220	0.4	NA	80	NA	[67]
Finland	5.0	0.5	560	NA	0.30	10.0	40	NA	[100]
Gramacho (Brazil)	3.0	NA	3945	800	0.3	4.5	48	NA	[23]
Clover Bar (Canada)	3.6	NA	1090	455	0.04	8.3	70	67	[71]
Komurcuoda (Turkey)	2.8	NA	5850	1380	0.6	9	85	NA	[87]

NA: unavailable.

$$\text{At pH 8, } HO_3^{\bullet} \rightarrow {}^{\bullet}OH + O_2, \quad k_3 = 1.1 \times 10^8\,M^{-1}\,s^{-1} \tag{5}$$

$$\begin{aligned} &{}^{\bullet}OH + O_3 \rightarrow HO_2^{\bullet} + O_2 \rightarrow HO_4^{\bullet}, \\ &k_4 = 2.0 \times 10^9\,M^{-1}\,s^{-1} \end{aligned} \tag{6}$$

$$HO_4^{\bullet} \rightarrow HO_2^{\bullet} + O_2, \quad k_5 = 2.8 \times 10^4\,s^{-1} \tag{7}$$

$$HO_2^{\bullet} \leftrightarrow {}^{\bullet}O_2^{-} + H^{+}, \quad pK_a = 4.8 \tag{8}$$

Termination:

$$HO_4^{\bullet} + HO_4^{\bullet} \rightarrow H_2O_2 + 2O_3 \tag{9}$$

$$HO_4^{\bullet} + HO_3^{\bullet} \rightarrow H_2O_2 + O_3 + O_2 \tag{10}$$

However, oxidation through the formation of $^{\bullet}OH$ radical is limited by the presence of ozone-resistant compounds or $^{\bullet}OH$ radical scavengers [65]. If pH is higher than 9, bicarbonate ions are converted to carbonate ions, which are the scavengers for $^{\bullet}OH$ radicals that slow down the kinetic rate of the oxidation reaction [66] (Eqs. (11)–(13)).

$${}^{\bullet}OH + P \rightarrow \text{end products} \tag{11}$$

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:

$$\begin{aligned} &\text{(a)} \quad {}^{\bullet}OH + CO_3^{2-} \rightarrow OH^{-} + CO_3^{\bullet -}, \\ &k = 4.2 \times 10^8\,M^{-1}\,s^{-1} \end{aligned} \tag{12}$$

$$\begin{aligned} &\text{(b)} \quad {}^{\bullet}OH + HCO_3^{-} \rightarrow OH^{-} + HCO_3^{\bullet}, \\ &k = 1.5 \times 10^7\,M^{-1}\,s^{-1} \end{aligned} \tag{13}$$

In general, the treatment performance of ozonation is comparable to that of Fenton oxidation (Tables 3 and 4). With COD concentrations ranging from 560 to 5850 mg/L, about 85% of COD removal could be achieved by using ozonation alone (Table 3). In this case, a pH ranging from 8 to 9 is strongly recommended for ozonation, as in an alkaline environment, the

Table 4
Fenton oxidation process for leachate treatment

Location of landfill	Oxidants	Dose (g/L)	H_2O_2/Fe(II) mass ratio	Initial concentration in leachate (mg/L)			BOD/COD	COD/TOC	pH	Removal efficiency (%)		References
				COD	NH_3-N	BOD				COD	NH_3-N	
Delaware (USA)	Fe(II)SO_4 + H_2O_2	1.00 1.00	1.00	1000	NA	NA	NA	2.53	2–3	85	NA	[75]
Sandtown (USA)	Fe(II)SO_4 + H_2O_2	0.05 0.15	3.00	8894	NA	NA	NA	1.93	2.5	89	NA	[82]
Sandtown (USA)	Fe(II)SO_4 + H_2O_2	2.80 2.55	0.91	1000	NA	NA	NA	4.03	2.5	60	NA	[83]
Kimpo (Korea)	Fe(II)SO_4 + H_2O_2	1.75 1.65	0.94	1500	1300	30	0.02	NA	2.5–4.0	75	NA	[79]
Chonju (Korea)	Fe(II)SO_4 + H_2O_2	2.00 1.50	0.75	1900	NA	280	0.15	NA	3	52	NA	[86]
Italy	Fe(II)SO_4 + H_2O_2	0.83 10.00	12.05	10540	5210	2300	0.22	2.70	3	60	NA	[80]
Komurcuoda (Turkey)	Fe(II)SO_4 + H_2O_2	1.00 2.00	2.00	5850	1380	28680	0.6	NA	3–4	85	NA	[87]

NA: unavailable.

ozone is decomposed into free radicals ($^{\bullet}O_2^-$ and $HO_2^{\bullet}$) and subsequently produces $^{\bullet}OH$, leading to an ultimate mineralization of the compounds and thus enhancing the degradability of the treated effluents prior to another subsequent treatment [67].

The application of ozone for leachate treatment has many advantages. In addition to organic contaminants, ozonation is capable of removing color, taste and odor-producing organic compounds without the generation of odor [68]. Moreover, ozone can rapidly decay in water, thus avoiding any undesirable residual effects [69]. Unlike chlorination, ozonation does not create any secondary pollutants in the environment such as the chlorinated by-products, as the ozonation of organic matter leads to the formation of a low molecular weight compound such as acetic acid [70].

In spite of being a powerful oxidant, ozone reacts slowly with certain toxic compounds such as inactivated aromatics and NH_3-N, causing an incomplete oxidation of the compounds [71]. Another limitation of using ozonation alone is a high energy consumption coupled with a short half-life period (15–25 min) [72]. Due to the high cost of ozone production, the application of high ozone dosage may not be economically feasible. This is attributed to the fact that the remaining organic compounds may become less and less reactive to ozone oxidation when the ozone dose for COD abatement increases [60].

Although various efforts have been devoted to improve the ozone transfer efficiency, the ozone consumption rate is low (Table 3), since some of the residing ozone in the exhaust gas of the reactor is lost. For a high strength of leachate, ozonation alone is not enough to meet the effluent limit of discharge standard unless a higher ozone dose is applied [72]. Therefore, other subsequent treatment using a biological process such as activated sludge and nitrification is necessary to complement the degradation of the leachate with a high strength of COD [73].

2.2. *Homogeneous systems without irradiation*

2.2.1. *Fe^{2+}/H_2O_2 (Fenton oxidation)*

With an oxidation potential (E^{o}) of 1.80 V, H_2O_2 is theoretically effective as an oxidizing agent for leachate treatment. However, its effectiveness for the removal of organic pollutants depends on an intermediate association to yield OH^- and $HO_2^{\bullet -}$ radicals [74]. Due to its slow reaction rates with organics and slow self-decomposition rate, H_2O_2 alone is not effective to degrade recalcitrant compounds present in a high strength of stabilized leachate [75].

To overcome such problems, the oxidation of most recalcitrant pollutant requires H_2O_2 to be activated with catalysts such as Fe(II) salts. H_2O_2 acts as a reductant when reacting with a strong oxidizing agent and generates free oxygen with decomposition by itself [76]. This system is based on the electron transfer between H_2O_2 and Fe^{2+} (Reactions (14)–(16)) that acts as a homogenous catalyst to yield $^{\bullet}OH$ radicals. The H_2O_2 catalyzation by Fe(II), which induces its decomposition into $^{\bullet}OH$, enhances its effectiveness for degradation [77]. Radicals produced in this way degrade organic compounds, as shown in the following mechanisms [78]:

Initial reactions:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH, \quad k_1 = 70\,M^{-1}\,s^{-1} \tag{14}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe(OOH)^{2+} + H^+ \leftrightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \tag{15}$$

$$OH^- + Fe^{3+} \rightarrow Fe(OH)^{2+} \leftrightarrow Fe^{2+} + {}^{\bullet}OH \tag{16}$$

Propagation:

$${}^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O, \quad k_2 = 3.3 \times 10^7\,M^{-1}\,s^{-1} \tag{17}$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow {}^{\bullet}OH + H_2O + O_2 \tag{18}$$

$$HO_2^{\bullet} + HO_2^- \rightarrow {}^{\bullet}OH + OH^- + O_2 \tag{19}$$

Termination:

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-, \quad k_2 = 3.2 \times 10^8\,M^{-1}\,s^{-1} \tag{20}$$

$$HO_2^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2 \tag{21}$$

$${}^{\bullet}OH + HO_2^{\bullet} \rightarrow H_2O + O_2 \tag{22}$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{23}$$

The Fenton process dissociates the oxidant, leading to $^{\bullet}OH$ formation [79]. The radicals react with the organic compounds that abstract one electron from Fe(II) and results in Fe(III). The rate of $^{\bullet}OH$ formation is enhanced through the reaction of Fe(II) with H_2O_2. Since organic species are prone to auto-oxidation [77], when Fe(II) is added into the system, the initiation of the chain reactions by $^{\bullet}OH$ will lead to an effective degradation of the organic pollutants, as indicated by a decreasing COD value.

When the recalcitrant compounds in the leachate are oxidized by the Fenton reagents, the compounds undergo either one of these three processes: primary degradation, a structural change in the parent compound where its biodegradability may be improved, or degradation to the extent that reduces toxicity, an ultimate degradation to CO_2 and H_2O [80].

Like other AOTs, the Fenton oxidation process is also affected by many factors such as the concentration of Fe(II) and H_2O_2, the ratio of organic materials to the Fenton reagents, the pH, reaction by-products and temperature [81]. Zhang et al. [82] reported that when the temperature increased from 13 to 37 °C, the COD removal slightly improved from 90 to 94% with its initial concentration of 1000 mg/L. In a separate study [83], at the same COD concentration of 1000 mg/L, they also found that COD removal increased from 42 to 56% at the same range of temperature. This indicated that higher temperature conditions improved the degradation rate of organic pollutants in the leachate [84].

Such a phenomenon might be attributed to the fact that a higher temperature could accelerate the reaction between H_2O_2 and Fe^{2+}, thus increasing the generation rate of oxidizing species such as $^{\bullet}OH$ radical [85].

Although the degree of organic degradation improves with an increasing dose of H_2O_2, care needs to be taken when selecting the optimum dose, since the presence of H_2O_2 is harmful to living organisms. In addition, the presence of H_2O_2 in a large quantity can act as a scavenger for the formed $^{\bullet}OH$ radicals, thus reducing the kinetic rate of the Fenton oxidation [86].

Although a higher concentration of Fe(II) accelerates the kinetic rate of the Fenton oxidation reaction, since the Reactions (14)–(16) are a chain process, only a small amount of Fe(II) is required to catalyze the process of H_2O_2 decomposition. A mass molar ratio of 2.0–3.0 for H_2O_2/Fe(II) has been found to be ideal to achieve a rapid oxidation and an effective degradation of the recalcitrant compounds in the leachate [82,87]. Calli et al. [87] also found that a maximum oxidation efficiency (85% of COD removal with an initial COD concentration of 5850 mg/L) was attained when neither H_2O_2 nor Fe(II) was overdosed so that the maximum amount of $^{\bullet}OH$ radicals was available not only for oxidizing the organic compounds, but also for minimizing the scavenging effects in the solutions.

In addition to Fe(II) ions, the presence of H^+ is required for the H_2O_2 decomposition process [88]. This indicates the need for an acidic environment to generate a maximum amount of $^{\bullet}OH$. Since it affects the activity of the oxidant and the substrate, the speciation of iron and H_2O_2 decomposition [89], pH is the key parameter to optimize the treatment efficiency of Fenton oxidation. When the operating pH is low, the addition of H_2O_2 can increase the oxidation efficiency of the Fenton reaction. A pH range from 2.5 to 3 is optimum for the Fenton oxidation process [82,87] (Table 4). When the pH is higher than 4, the kinetic rate of the H_2O_2 decomposition decreases due to the formation of Fe(II) complexes with the buffer, inhibiting the formation of $^{\bullet}OH$ radicals [88]. The Fenton reaction slows down due to the precipitation of ferric oxyhydroxides, which inhibits the regeneration of Fe(II) ions [90,91]. On the other hand, at a pH lower than 3.0, the formation of $Fe(OOH)^{2+}$ occurs, which reacts slowly with H_2O_2, thus producing fewer $^{\bullet}OH$ radicals [92].

In general, the key features of the Fenton system lay on the reagent conditions and the reaction characteristics such as pH, temperature and the amount of constituents in the solution [74]. The ideal conditions for Fenton oxidation is pH 2.5–3 and a peroxide to catalyst ratio of 2:1 (w/w). With 89% of COD removal, Fenton oxidation has been found to be satisfactory for leachate treatment with a high strength of COD ranging from 1 to 9 g/L (Table 4). Fenton oxidation is not only able to achieve a complete degradation of the recalcitrant pollutants, but it is also able to convert toxic materials to less harmful compounds, thus reducing the toxicity and enhancing the biodegradation of the leachate. In addition, due to its homogeneous catalytic nature, the Fenton process is simple and no form of energy is involved as a catalyst, thus reducing energy consumption [80].

In spite of its advantages, some major drawbacks of the Fenton process are its high operational costs due to the chemicals required and the sludge disposal cost [93]. Since the Fenton reagent, especially H_2O_2, is very aggressive, corrosion can be a potentially serious problem [83]. In addition, the homogeneous catalyst added as Fe(II) salts cannot be retained during the degradation, because the oxidation process produces sludge that contains iron hydroxide as a precipitated by-product, thus requiring further disposal of the sludge. In this case, the cost of sludge disposal has to be taken into consideration when evaluating the cost-effectiveness of the process. Another limitation is that a continuous supply of feeding chemicals is required to prevent stagnation in the Fenton process [94].

2.2.2. O_3/H_2O_2

The capability of ozone in oxidizing organic pollutants by using direct electrophilic attack on double bonds such as C=C or aromatic rings may be enhanced in the presence of H_2O_2 through the generation of $^{\bullet}OH$. Like other AOTs, ozone decomposition in this process is controlled by radical-type chain reactions, as shown in the following mechanisms [95]:

Initial reaction:

$$H_2O_2 \leftrightarrow H^+ + HO_2^- \quad -pK_a = 11.8 \tag{24}$$

$$O_3 + HO_2^- \rightarrow O_2 + O_2^{-\bullet} + {}^{\bullet}OH, \quad k_2 = 2.8 \times 10^6\,M^{-1}\,s^{-1} \tag{25}$$

$$O_3 + O_2^{-\bullet} \rightarrow O_3^{-\bullet} + O_2, \quad k_3 = 1.6 \times 10^9\,M^{-1}\,s^{-1} \tag{26}$$

Propagation:

$$O_3^{-\bullet} + H^+ \rightarrow HO_3^{\bullet}, \quad k_4 = 5.2 \times 10^{10}\,M^{-1}\,s^{-1} \tag{27}$$

$$HO_3^{\bullet} \rightarrow O_2 + {}^{\bullet}OH, \quad k_5 = 1.1 \times 10^6\,M^{-1}\,s^{-1} \tag{28}$$

$${}^{\bullet}OH + O_3 \rightarrow HO_2^{\bullet} + O_2, \quad k_6 = 2.0 \times 10^9\,M^{-1}\,s^{-1} \tag{29}$$

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}, \quad k_7 = 2.7 \times 10^7\,M^{-1}\,s^{-1} \tag{30}$$

$${}^{\bullet}OH + HO_2^- \rightarrow OH^- + HO_2^{\bullet}, \quad k_8 = 7.5 \times 10^9\,M^{-1}\,s^{-1} \tag{31}$$

Termination:

$${}^{\bullet}OH + P \rightarrow \text{end products}, \quad k_9 = 1.6 \times 10^9\,M^{-1}\,s^{-1} \tag{32}$$

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

$$\text{(a)} \quad {}^{\bullet}OH + HCO_3^- \rightarrow OH^- + HCO_3^{\bullet}, \quad k_{11} = 8.5 \times 10^6\,M^{-1}\,s^{-1} \tag{33}$$

Table 5
Homogenous system without irradiation for treatment of stabilized leachate

Location of landfill	Type of treatment	Dose (g/L)	Energy (kW/m^3)	Reaction time (min)	O_3 consumption (mg O_3/mg COD)	Initial concentration in leachate (mg/L)			BOD/COD	pH	Removal efficiency (%)		References
						COD	NH_3-N	BOD			COD	NH_3-N	
Finland	O_3 + H_2O_2	5.0 15.0	NA	NA	NA	560	NA	34	0.13	3.0	50	NA	[100]
Flanders (Belgium)	O_3 + H_2O_2	0.90 0.25	15	NA	2.7	1090	455	NA	0.14	3–4	28	NA	[102]

NA: unavailable.

$$\text{(b)}\quad CO_3^{-\bullet} + H_2O_2 \rightarrow HCO_3^- + HO_2^\bullet,\quad k_{12} = 4.3\times10^5\,M^{-1}\,s^{-1} \tag{34}$$

The most important factor that plays a major role in the O_3/H_2O_2 treatment is the operating pH. Different from the Fenton oxidation process where H_2O_2 reacts immediately with Fe(II) at acidic conditions, in the O_3/H_2O_2 treatment, however, H_2O_2 reacts very slowly with the ozone under the same conditions [93], resulting in a low COD removal from leachate (Table 5). While at a pH higher than 7.0, H_2O_2 dissociates into HO_2^- as its conjugate base [96]. In basic conditions, both OH^- and HO_2^- initiate the ozone decomposition more rapidly and more effectively into $^\bullet OH$ radicals than the OH^- alone [97]. Therefore, to enhance the effectiveness of the O_3/H_2O_2 performance for leachate treatment, the pH should vary, ranging from 8 to 9. This is in agreement with Nelieu et al. [98], who reported that the basic conditions are preferable for O_3/H_2O_2 to degrade organic compounds. Such a phenomenon indicates that $^\bullet OH$ radical is also the major pathway in the O_3/H_2O_2 process.

Theoretically, the addition of H_2O_2 before the ozonation of the leachate should accelerate the ozone decomposition and subsequently enhance the production of $^\bullet OH$ radicals, as shown in the following reaction:

$$2O_3 + H_2O_2 \rightarrow 2^\bullet OH + 3O_2 \tag{35}$$

According to the stoichiometric concepts, the two molecules of the ozone in the Reaction (35) are eliminated by each peroxide molecule, thus giving two $^\bullet OH$ radicals. These situations should be sufficient for the radicals to degrade the organic compounds in the leachate [99]. However, Haapea et al. [100] found that the treatment performance of the O_3/H_2O_2 alone for organic compounds was low (Table 5). With an initial COD concentration of 560 mg/L, they found that only 50% of COD removal was attained. This might be due to the fact that H_2O_2 acted not only as an $^\bullet OH$ generator, but also as $^\bullet OH$ scavenger during the oxidation process, as shown in the following reactions:

$$H_2O_2 + ^\bullet OH \rightarrow H_2O + HO_2^\bullet \tag{36}$$

$$HO_2^- + ^\bullet OH \rightarrow OH^- + HO_2^\bullet \tag{37}$$

The presence of a high concentration of radical scavengers in the solution in the basic conditions can slow down the reaction rate, as they interrupt the chain reactions (Reactions (33) and (34)) [101].

In another study, Geenens et al. [102] reported that 28% of COD removal with an initial COD concentration of 1090 mg/L was achieved using this treatment. This result was slightly higher than that of the photo-assisted Fenton process, which attained 20% of COD removal at an initial COD concentration of 895 mg/L (Tables 5 and 6). Although the increasing dose of H_2O_2 did not significantly improve the COD removal, it is found to improve the biodegradability of the leachate, as indicated by the increase of BOD_5/COD ratio from 0.04 to 0.14.

In general, as compared to the Fenton process, the O_3/H_2O_2 process is less intensively investigated. For O_3/H_2O_2, COD removal can be as high as 50% with COD concentrations ranging from 560 to 1090 mg/L, and the mass ratio of H_2O_2 to O_3 is 3 (Table 5). Theoretically, the stoichiometric mass ratio of H_2O_2 to O_3 should be 0.354. Low COD removal efficiency may be caused by an improper H_2O_2 to O_3 ratio [103]. It is therefore recommended that pH ranging from 8 to 9 be employed for the O_3/H_2O_2 process, since under an alkaline environment, ozone rapidly decomposes into some intermediate compounds such as $^\bullet O_2^-$ and $HO_2^\bullet$, that are also reactive to subsequently produce $^\bullet OH$ radicals.

After oxidation, O_3 and/or H_2O_2 residue may be left in the leachate. The presence of such residue may hinder the biological process in another subsequent treatment [101]. Therefore, it must be removed by the aeration of the ozonated leachate for 15 min before subsequent treatments. Due to its low cost, aeration may be a better method than the application of inert gas such as He.

2.3. Homogeneous system with irradiation

In recent years, photochemical technology such as UV irradiation has received considerable attention for leachate treatment [104,105]. UV irradiation is employed to initiate the production of $^\bullet OH$ radical either through a direct photolysis of H_2O_2 or through photo-induced processes like that in the photo-Fenton reaction [106]. Direct photolysis involves the interaction of light with target molecules to dissociate them into fragments with the following mechanism pathways:

$$X + h\nu \rightarrow \text{intermediates} \tag{38}$$

$$\text{Intermediates} + h\nu \rightarrow CO_2 + H_2O \tag{39}$$

Table 6
Homogenous system with irradiation for degradation of recalcitrant compounds

Location of landfill	Type of treatment	Dose (g/L)	Energy (kW/m^3)	Reaction time (min)	H_2O_2 consumption (mg H_2O_2/mg COD)	UV wavelength (nm)	Initial concentration in leachate (mg/L)		BOD/COD	pH	Removal efficiency (%)		References
							COD	NH_3-N			COD	NH_3-N	
NA	$Fe(II)SO_4$ + H_2O_2 + UV	0.056 0.034	80	120	2.13	300	1150	NA	0.004	3	70	NA	[120]
Flanders (Belgium)	$Fe(II)SO_4$ + H_2O_2 + UV	0.56 0.25	15	NA	NA	254	895	626	0.09	3–4	20	NA	[102]
Curitiba (Brazil)	$Fe(II)SO_4$ + H_2O_2 + UV	0.01 2.00	NA	60	NA	400	5200	NA	0.37	3–4	58	NA	[38]
Curitiba (Brazil)	H_2O_2 + UV	3.00	NA	60	NA	400	5200	NA	0.42	3–4	56	NA	
Braunschweig (Germany)	H_2O_2 + UV	0.50	2×10^5	NA	2.10	254	1200	5	0.01	3–4	90	NA	[59]
Shalu (Taiwan)	H_2O_2 + UV	7.91	NA	300	NA	254	3750	NA	NA	NA	65	NA	[114]
Stutgart (Germany)	H_2O_2 + UV	2.10	675	480	NA	254	1280	NA	0.08	2	59	NA	[109]
	O_3 + UV	3.00	NA	480	NA	254	1280	NA	0.08	2	54	NA	
	O_3 + H_2O_2 + UV	3.00 2.10	1100	480	NA	254	1280	NA	0.08	2	89	NA	
Clover Bar (Canada)	O_3 + H_2O_2 + UV	2.60 0.63	NA	NA	NA	254	1090	455	0.04	NA	72	78	[71]

NA: unavailable.

If UV is applied, some oxidizing agents such as ozonation and/or H_2O_2 can form a homogenous AOT system with irradiation such as UV/O_3, UV/H_2O_2 and $UV/O_3/H_2O_2$. Each of these processes is elaborated as follows:

2.3.1. UV/O_3 (photolytic ozonation)

Since ozonation alone cannot transform recalcitrant compounds into CO_2 and H_2O, some remaining intermediate products in the leachate may be as toxic as the initial compounds [107]. To complete the ozone oxidation of the organic compounds, UV irradiation can be employed.

In the UV/O_3 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 [108]. The initial step of the radical mechanism in this process is the direct photolysis of the ozone to produce $^\bullet OH$, as shown in the following reactions [109]:

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \quad (40)$$

$$\underline{H_2O_2 + h\nu \rightarrow 2\ {}^\bullet OH \qquad\qquad (41)}$$

$$\text{Net reaction:}\quad O_3 + H_2O + h\nu \rightarrow 2\ {}^\bullet OH + O_2 \quad (42)$$

The reactions involved are very complex in the AOT, since the organic compounds can be degraded either by direct ozonation, photolysis reactions or $^\bullet OH$ oxidation [109].

During oxidation, the ozone catalyzed by UV oxidizes organic substances and breaks down the saturated bonds of the contaminants. In basic conditions, UV/O_3 is reported to be more reactive than UV/H_2O_2 for two reasons: (a) the remarkably higher light-absorbing potential of the ozone is in the UV band (2850 and 19 $M^{-1}\,cm^{-1}$) at 254 nm; (b) the diversity of the chain reactions that involves the reactive $^\bullet OH$ radicals and the intermediate products [110]. The radicals then participate in the numerous steps of oxidative reaction, leading to an ultimate oxidation of the organics. For this reason, UV/O_3 technique is more effective than either UV photolysis or ozonation alone for leachate treatment.

Among the various AOTs surveyed in this paper, UV/O_3 is less intensively investigated for leachate treatment due to its high operational cost. To optimize the UV/O_3 process, the operating pH should be adjusted to alkaline conditions (pH 8–9). Ince [109] suggested that UV/ozone treatment should not be conducted in acidic conditions. With an initial COD concentration of 1280 mg/L, only 54% of COD removal was attained at pH 2.0 (Table 6).

Compared to UV/H_2O_2 process, there are also some limitations of the UV/O_3 process. First, O_3 is an unstable gas that must be generated and used on-site immediately. Second, an ozone-water contacting device to transfer the gaseous ozone into the liquid phase has to be available. Third, this process requires special technical expertise to enable ozone transfer into the liquid as effectively as possible, as UV can play a major role in the process if both the background of the absorbance and the particle concentration of the leachate are low. Fourth, foaming in the leachate due to the ozone bubble blocks the UV transmittance/penetration inside the leachate, resulting in a low COD removal by the UV/O_3 process [111].

In spite of these limitations, a major advantage of using the UV/O_3 process is that after oxidation, no trihalomethane (THM) compounds can be found in the treated effluent [112]. Unlike the UV/H_2O_2 process, all oxidants can be degraded in the UV/O_3 process and the system does not require any waste disposal, as the contaminants in the leachate have already been destroyed.

2.3.2. UV/H_2O_2

When compared to the ozone with an oxidation potential (E^o) of +2.08 V, the oxidizing strength of H_2O_2 is slightly weaker with an oxidation potential (E^o) of +1.78 V [54]. However, in the UV/H_2O_2 process, the addition of UV irradiation enhances the strength of the H_2O_2 oxidation on organic compounds through the formed $^\bullet OH$ radicals [112]. First, many organic contaminants that absorb the UV light undergo transformation in their molecular structure to be more reactive with the oxidants. Second, UV irradiation catalyzes the breakdown of H_2O_2 into two $^\bullet OH$ radicals. The radicals are formed by the hemolytic splitting of the O=O bonds of H_2O_2 by the UV light [113], as seen in the following mechanisms:

Initial reactions:

$$H_2O_2 + UV \rightarrow 2^\bullet OH \quad (43)$$

$$H_2O_2 \rightarrow H_2O + 1/2O_2 \quad (44)$$

Propagation:

$$^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O, \quad k_2 = 2.7\times 10^7\,M^{-1}\,s^{-1} \quad (45)$$

$$HO_2^\bullet + H_2O_2 \rightarrow {}^\bullet OH + H_2O + O_2, \quad k_2 = 0.5\,M^{-1}\,s^{-1} \quad (46)$$

$$HO_2^\bullet + HO_2^- \rightarrow {}^\bullet OH + OH^- + O_2 \quad (47)$$

Termination:

$$^\bullet OH + HO_2^\bullet \rightarrow H_2O + O_2, \quad k_2 = 10^{10}\,M^{-1}\,s^{-1} \quad (48)$$

$$^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \quad (49)$$

Since the first introduction of the UV/O_3 process, other types of AOT such as UV/H_2O_2 have been explored [38,59,109,114]. Ince [109] investigated the treatment of leachate from the Stuttgart landfill (Germany) using the UV/H_2O_2 process. The researcher found that with an initial COD concentration of 1280 mg/L, 59% of COD removal was achieved. The result was lower than that of Steensen [59], who employed the same process of leachate treatment in the Braunschweig landfill (Germany). With an initial COD concentration of 1200 mg/L, 90% of COD removal was attained. These differences might be due to the fact that Steensen employed more UV lamps to activate organic molecules, thus enabling them to be more prone to the oxidation process. Steensen [59] also consumed a higher energy of 2×10^5 kW/m^3, compared to Ince [109], who applied only 675 kW/m^3. The significantly higher amount of energy consumption for UV irradiation has improved the degradation of the recalcitrant compounds from the leachate, as indicated by the higher COD removal (90%).

It is important to note that the oxidation process in the UV/H_2O_2 systems is dependent on some reaction conditions that can affect its treatment performance for COD removal. The variables include the type and the concentration of organic contaminants, the total organic substances present in the leachate, the light transmittance in the solution (as indicated by turbidity or color), the type and concentration of dissolved inorganic substances (such as carbonates and iron), the H_2O_2 dose and pH [115]. For COD removal, pH ranging from 3 to 4 has been found to be ideal for the UV/H_2O_2 process.

As a whole, the performance of the UV/H_2O_2 process for COD removal is higher than that of UV/O_3. With COD concentrations ranging from 1200 to 1280 mg/L, 90% of COD removal could be achieved by the UV/H_2O_2 systems at a pH ranging from 3 to 4, while at the same COD concentration range and at pH 2.0, less than 55% of COD removal was attained by the UV/O_3 systems (Table 6). Since H_2O_2 easily splits into two $^\bullet$OH radicals through UV irradiation, the ability to degrade organic contaminants or to transform them into innocuous constituents is another major advantage of UV/H_2O_2 over other AOT processes such as ozonation [109].

In spite of its advantages, UV/H_2O_2 has some limitations. Due to the small molar UV absorption of H_2O_2 within 200–300 nm, a high dose of H_2O_2 and a longer UV exposure time with a strong output with a wide range of wavelengths are required, thus requiring more energy consumption than the UV/O_3 process [116]. In addition, the UV/H_2O_2 process is sensitive to the scavenging effects of carbonate in the basic conditions (pH 8–9). A high concentration of H_2O_2 acts as radical scavengers that slow down the kinetic rate of the oxidation process [116], while a low concentration of H_2O_2 generates insufficient $^\bullet$OH in the leachate, which leads to a slower rate of oxidation [115].

2.3.3. O_3/H_2O_2/UV

Theoretically, as a strong oxidizing agent, O_3 can oxidize organic compounds to their highest stable oxidation states. However, ozonation alone is not enough to degrade the recalcitrant compounds in the leachate [117]. In combination with UV irradiation and H_2O_2, ozone can oxidize more refractory compounds present in the leachate. The addition of H_2O_2 in the UV/O_3 system can accelerate the ozone decomposition process, which subsequently increases the rate of $^\bullet$OH generation, as shown in the following reactions [118]:

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \tag{50}$$

$$H_2O_2 + h\nu \rightarrow 2^\bullet OH \tag{51}$$

In their study of leachate treatment in the Stuttgart landfill (Germany), Ince [109] reported that the O_3/H_2O_2/UV process was better than either UV/O_3 or UV/H_2O_2, as indicated by its removal performance for COD (Table 6). At the same COD concentration of 1280 mg/L, the O_3/H_2O_2/UV systems could achieve 89% of COD removal compared to the UV/O_3 (54%) and/or the UV/H_2O_2 (59%). This might be due to the synergistic effects of H_2O_2 and ozone to form $^\bullet$OH radical to degrade the recalcitrant compounds in the leachate. They also found that the COD in the treated effluent was less than 140 mg/L, the effluent limit for local COD discharge standard. In terms of energy consumption, the O_3/H_2O_2/UV system is an attractive alternative, provided that the cost of ozone generation is low [105].

Overall, the optimum operating pH for the process with H_2O_2 is recommended to be 2–3 and 8–9 for the process involving ozone [82,87]. The major advantage of employing the O_3/H_2O_2/UV system is that no pollution from the photo-reactor takes place. Therefore, there is no interruption during the oxidation process [119].

2.3.4. H_2O_2/Fe^{2+}/UV (photo-Fenton oxidation)

The Fenton process has attracted great interest in recent years due to its effectiveness to generate $^\bullet$OH radicals through H_2O_2 decomposition by Fe(II) in acidic conditions. However, the introduction of UV irradiation into the Fenton process (Reactions (52) and (53)) may be able to improve the COD removal.

$$H_2O_2 + Fe^{2+} + h\nu \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \tag{52}$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + {}^\bullet OH + H^+ \tag{53}$$

To enhance the oxidation power of the Fenton process, the photolysis of Fe(III) oxalate complexes takes place under UV irradiation, thus generating Fe(II), as indicated by the following reactions:

$$Fe(C_2O_4)_3{}^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4{}^{2-} + {}^\bullet C_2O_4{}^- \tag{54}$$

$${}^\bullet C_2O_4{}^- + Fe(C_2O_4)_3{}^{3-} \rightarrow Fe^{2+} + 3C_2O_4{}^{2-} + 2CO_2 \tag{55}$$

$${}^\bullet C_2O_4{}^- + O_2 \rightarrow {}^\bullet O_2{}^- + 2CO_2 \tag{56}$$

The Fe(II) ions formed by the photo-reduction of Fe(III) complexes (Reaction (54)) carry out further the Fenton process. In addition to the reaction of intermediate oxalate radicals with Fe(III) oxalate complex (Reaction (55)), additional Fe(II) ions are generated from the interaction of UV irradiation and $Fe(OH)^{2+}$ (Reaction (57)). Subsequently, the generated Fe(II) ions react immediately with H_2O_2, leading to the formation of $^\bullet$OH radicals (Reactions (58) and (59)) [120].

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^\bullet OH \tag{57}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \tag{58}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2{}^\bullet + H^+ \tag{59}$$

The $^\bullet$OH radicals formed in the photolysis system are highly reactive and initiate the oxidation of pollutants (RH) in the leachate, leading to a mineralization of the organic pollutants (Reactions (60) and (61)).

$${}^\bullet OH + RH \rightarrow R^\bullet + H_2O \tag{60}$$

$$R^\bullet + O_2 \rightarrow RO_2{}^\bullet \tag{61}$$

The organic radical ($R^\bullet$) generated in the Reaction (60) reacts immediately with dissolved oxygen to yield peroxyl radicals ($RO_2{}^\bullet$), which subsequently initiate radical-controlled chain reactions and lead to another oxidation reaction [120].

The operating pH is the most crucial factor that affects the degradation rate of the photo-Fenton oxidation. For the photo-Fenton involving H_2O_2, acidic conditions ranging from pH 2 to 4 have been used in the majority of studies. In addition to the pH, the radiation intensity and the dose of H_2O_2 and Fe(II) play important roles in the formation of $^{\bullet}OH$. With an initial COD concentration ranging from 1150 to 5200 mg/L, 70% of COD removal was attained (Table 6). This result was slightly higher than that (59%) of the UV/H_2O_2 systems at the same COD concentration range (Table 6). The biodegradability ratio of the leachate was significantly enhanced [38], indicating that the photo-Fenton process had broken down the molecular structures of the organic matter and converted the compounds to a more degradable form.

Photo-Fenton offers some advantages in terms of cost-effectiveness. To reduce the treatment cost of another subsequent biological process, it is possible to use sunlight instead of UV [109], thus facilitating the development of a low-cost treatment. However, in acidic conditions, the treatment performance of photo-Fenton oxidation for COD removal is not as good as that of UV/H_2O_2 (Table 6). Similar to the Fenton process, sludge resulting from iron hydroxide precipitation is also generated from the photo-Fenton process, which requires further disposal for the sludge [102].

Other drawbacks are that soluble oxalates due to the interference of carbonate and bicarbonate ions as the radical scavengers will form a solid layer on the UV lamps if UV is employed in the photo-Fenton process. The solids will hinder UV transmittance into the solution, causing its poor transmission into the leachate [102]. A full-scale application of UV lamps for irradiation requires high energy consumption, thus increasing the operational cost of the photo-Fenton process [59].

2.4. *Miscellaneous AOTs*

Wet air oxidation (WAO), UV/TiO_2 (heterogeneous AOT systems with radiation), UV/TiO_2/O_3 (heterogeneous AOT systems with irradiation) and electro-Fenton (heterogeneous systems without irradiation) are less intensively applied for leachate treatment in part due to their high operation cost of UV irradiation.

2.4.1. *Wet air oxidation*

WAO is an oxidation process of organic matter in the liquid phase with oxygen (either in pure form or as air) at an elevated temperature of 100–350 °C and at pressure ranging from 5 to 200 bar [121]. The resulting gas phase passes through an air purifier and is vented to the atmosphere, while the liquid phase is recycled into the heat exchanger. The capacity of WAO to transform recalcitrant compounds in a high strength of contaminated wastewater is the major reason for its development.

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 [122]. 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 [123]. 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.

2.4.2. *UV/TiO_2*

Due to its stability and a lack of toxicity, TiO_2 is the most widely accepted catalyst for AOT. It is a semiconductor that absorbs light at a wavelength of less than 385 nm and requires 1 W/m^2 of light [124]. TiO_2 is employed in combination with UV irradiation to initiate the generation of $^{\bullet}OH$ radicals.

The band gap energy of TiO_2 is wide enough ($E = 3.2$ eV) to promote reduction–oxidation reactions upon the UV irradiation at 400 nm [125]. This excitation leaves a positively charged vacancy called a hole. The hole itself is a powerful oxidizing agent that can generate $^{\bullet}OH$ radicals [126]. The photocatalysis with TiO_2 can be explained by the following reactions:

$$TiO_2 + h\nu \rightarrow TiO_2\,(e^-/h^+) \tag{62}$$

$$TiO_2(OH^-) + H_2O_2 + h\nu \rightarrow TiO_2(OH)_{adsorbed} + OH^- + {}^{\bullet}OH \tag{63}$$

So far, this treatment is less intensively investigated for leachate treatment due to its high operational cost caused by high energy consumption.

2.4.3. *TiO_2/O_3*

In addition to UV, TiO_2 can be employed in heterogeneous photocatalytic oxidation with the ozone. In photocatalytic ozonation, in the presence of TiO_2 and under illumination, the ozone can generate $^{\bullet}OH$ radicals through the formation of an ozonide radical ($^{\bullet}O_3{}^-$), as shown in the following reactions:

$$TiO_2 + h\nu \rightarrow e^- + h^+ \tag{64}$$

$$O_3 + e^- \rightarrow {}^{\bullet}O_3{}^- \tag{65}$$

The $^{\bullet}O_3{}^-$ species rapidly reacts with H^+ in the solution to give $HO_3{}^{\bullet}$ and then $^{\bullet}OH$.

$${}^{\bullet}O_3{}^- + H^+ \rightarrow HO_3{}^{\bullet} \tag{66}$$

$$HO_3{}^{\bullet} \rightarrow O_2 + {}^{\bullet}OH \tag{67}$$

In the presence of oxygen, the photocatalytic process requires three electrons to generate a single $^{\bullet}OH$ species, which is less favored compared to the requirement of one electron through the $^{\bullet}O_3{}^-$ pathway. The electron transfer from TiO_2 to oxygen slows down the formation of $^{\bullet}OH$ radical by TiO_2/O_3 [127].

2.5. *Combined AOT and other physico-chemical treatment*

Although AOT alone can degrade the recalcitrant contaminants from landfill leachate, a complete degradation cannot be carried out if the organic matter in the leachate is refractory to the applied oxidants [128]. Therefore, it is necessary to develop a more effective process to maximize the removal performance of the recalcitrant compounds.

In this case, a combination of two AOTs/AOT and physico-chemical technique into an integrated treatment may synergize the advantages of their treatment performance, while overcoming their respective limitations. Generally, the combination of two AOTs may enhance the formation of $^{\bullet}$OH radicals. The efficacy of the integrated AOT process depends not only on the enhancement in the number of $^{\bullet}$OH radicals formed, but also on the presence of radical scavengers such as carbonate, as well as on the reactor conditions to maximize contact between $^{\bullet}$OH radicals with the target compounds in the solution [129].

Some combinations of AOT and other physico-chemical techniques that have been commonly employed for leachate treatment are presented as follows:

2.5.1. Ozone–GAC adsorption

Due to its synergistic effects, some researchers have integrated ozonation and granular activated carbon (GAC) adsorption as one of the most promising options for leachate treatment [130,131]. Ozone is capable of oxidizing organic substances to their highest stable oxidation states and subsequently produces CO_2 and H_2O, while GAC accelerates the kinetic rate of the ozone decomposition process through the formation of $^{\bullet}$OH radicals [61]. Through the $^{\bullet}$OH radicals, the ozone rapidly reacts with the target compounds in the leachate for an ultimate degradation.

To promote the ozone oxidation of organic compounds in the leachate, the surface of GAC initiates the chain reactions of ozone decomposition. In this case, the ozone may attack the pyrrolic groups of the graphenic layers in the GAC (basal plane electron) that act as Lewis bases to generate N-oxide-type groups and hydroperoxide radical ($HO_2^{\bullet}$) [132]. Since the presence of pyrrol groups on the surface of GAC improves the electronic density on its basal plane, $^{\bullet}O_2^-$ (superoxide radical) concentration in the system also increases [133]. The electron transfer from $^{\bullet}O_2^-$ radicals to O_3 results in the formation of $^{\bullet}O_3^-$ (ozonide radical) as an intermediate and then generates $^{\bullet}$OH radicals [134], which subsequently have a rapid reaction with most of the target compounds in the leachate ($k = 10^8$–$10^{11}\ M^{-1}\ s^{-1}$).

There are some steps for the formation of $^{\bullet}$OH radicals, resulting from GAC catalytic ozonation. In the solution, the reduction of ozone on the surface of GAC was reported to generate OH$^-$ ions (Reaction (68)) [133]:

$$O_3 + H_2O + 2e^- \leftrightarrow O_2 + 2OH^-, \quad k_2 = 1.1 \times 10^{-4}\ M^{-1}\ s^{-1} \tag{68}$$

Due to its electrophilic properties, ozone has a higher affinity towards the Lewis basic group on the surface of GAC, specifically on the aromatic compounds, which is a π electron-rich region [133]. For the aromatics substituted with electron donor groups such as −OH, the initial attack of the ozone occurs at an *ortho*- and *para*-position [135], resulting in the ozone decomposition into $^{\bullet}$OH radicals. The increase in the π electron of the GAC due to the presence of pyrrol groups increases the interaction between the GAC and the water molecules to form OH$^-$ ions, as indicated in the following Reaction (69) [136].

$$C_\pi + 2H_2O \leftrightarrow C_\pi{-}H_3O^+ + OH^- \tag{69}$$

Combination of the two Eqs. (68) and (69) gives the overall reaction of GAC catalytic ozonation as follows:

$$O_3 + C_\pi + 3H_2O + 2e^- \rightarrow C_\pi{-}H_3O^+ + O_2 + 3OH^- \tag{70}$$

The Eq. (70) suggests that the number of OH$^-$ ions in the solution increased for combined ozone–GAC adsorption treatments, compared to that of individual ozonation or GAC treatment alone. As indicated by the stoichiometric ratio of their reaction coefficients (Reactions (71)–(75)), both the OH$^-$ ions and $^{\bullet}$OH radicals have the same corresponding ratio of mole. Therefore, the number of OH$^-$ ions produced in the Reaction (70) also represents the amount of $^{\bullet}$OH radicals that would be generated in the Reaction (75). Such a phenomenon indicates the synergistic effects between the two physico-chemical treatments in the formation of $^{\bullet}$OH radicals. As the solution pH increased to 9 or the concentration of H$^+$ ions decreased (to 10^{-9} M), the reaction equilibrium shifted from left to right, resulting in the production of more OH$^-$ ions in the solution, thus leading to the generation of more $^{\bullet}$OH radicals (Eqs. (71)–(75)). In this case, the OH$^-$ ions facilitated the formation of $^{\bullet}$OH radicals through its reaction with ozone as reported elsewhere [64]:

Initial reactions:

$$O_3 + OH^- \rightarrow {}^{\bullet}O_2^- + HO_2^{\bullet}, \quad k_2 = 70\ M^{-1}\ s^{-1} \tag{71}$$

$$O_3 + {}^{\bullet}OH \rightarrow O_2 + HO_2^{\bullet}, \quad k_2 = 70\ M^{-1}\ s^{-1} \tag{72}$$

Propagation:

$$HO_2^{\bullet} \rightarrow H^+ + {}^{\bullet}O_2^-, \quad pK_a = 4.8 \tag{73}$$

$${}^{\bullet}O_2^- + O_3 \rightarrow {}^{\bullet}O_3^- + O_2, \quad k_2 = 1.6 \times 10^9\ M^{-1}\ s^{-1} \tag{74}$$

$${}^{\bullet}O_3^- + H^+ \rightarrow {}^{\bullet}OH + O_2, \quad k_2 = 5.2 \times 10^{10}\ M^{-1}\ s^{-1} \tag{75}$$

Termination:

$${}^{\bullet}OH + P \rightarrow \text{end products} \tag{76}$$

where P represents the organic compounds in the leachate.

As seen from the above reactions, $^{\bullet}$OH radicals are the responsible species for GAC catalytic ozonation. For this reason, it is suggested that ozone/GAC is also another kind of AOT controlled by a free radical mechanism, in which GAC functions as the initiator that enhances the transformation of the ozone into $^{\bullet}$OH radicals [137,138].

In addition to the GAC surface, solution pH also plays a major role in the ozone decomposition process. In basic conditions (pH 8–9), with the increasing OH$^-$ ions that initiate the chain reactions, the kinetic rate of ozone decomposition is significantly enhanced in the presence of $^{\bullet}$OH radicals. The ozone attacks the polar bonds of GAC, causing bond breaking, thus subsequently leading to the formation of $^{\bullet}$OH radicals as an oxidant

[132], which are free to react in the liquid phase. In this process, the delocalized π electron systems in the basic group of GAC and the oxygenated basic groups (chromene and pyrone) acting as Lewis bases play a major role as the catalytic center of the reaction, reducing the ozone molecules to OH^- and H_2O_2 [139].

In basic conditions, OH^- ions facilitate the formation of $^\bullet OH$ through an indirect route. The OH^- ions react with the ozone to form hydroperoxide ion (HO_2^-) (Eq. (77)), which is the conjugate base of H_2O_2 [78]. At a pH lower than 11.6 (the pK_a of H_2O_2), HO_2^- would be converted to H_2O_2 (Reaction (78)). Therefore, the increasing concentration of OH^- also facilitates the formation of H_2O_2, which is a source of $^\bullet OH$ radicals. The overall process is presented in Reaction (79):

$$OH^- + O_3 \rightarrow HO_2^- + O_2 \qquad (77)$$

$$HO_2^- + H_2O \rightarrow H_2O_2 + HO^- \qquad (78)$$

$$\text{Net reaction:}\quad O_3 + H_2O \rightarrow H_2O_2 + O_2 \qquad (79)$$

As a whole, GAC play two important roles both as an adsorbent and as a promoter in the overall degradation process. As an adsorbent, GAC adsorbs the organic matter on its surface, while as a promoter, GAC promotes ozone transformation through the formation of $^\bullet OH$ radicals. The $^\bullet OH$ radicals catalyze the ozone to break down the recalcitrant compounds into oxidation by-products that have a smaller molecular size than the initial compounds. As a result, the by-products become more easily degradable, enabling GAC to adsorb the remaining organic materials unchanged by the ozone oxidation [62]. The other advantage of using this process is that the spent GAC could be restored after becoming saturated through regeneration by using ozone for multiple uses, thus improving the cost-effectiveness of this combined method.

In general, the combination of ozonation and GAC adsorption into an integrated process is an attractive option for leachate treatment. With an initial COD concentration of 8000 mg/L and at pH 8, this integrated treatment could remove 86% of COD. This result [131] was higher than that of Rivas et al. [130], who reported 90% of COD removal with an initial COD concentration of 4970 mg/L and at the same pH (Table 7).

2.5.2. *Ozone–coagulation*

Due to the complexity of leachate, a high dose of ozonation alone is not enough for its treatment. In this case, another treatment using coagulation process can be applied as a pre-treatment or as a polishing step before or after ozonation to improve COD removal from leachate.

Principally, the coagulation process destabilizes colloidal particles by the addition of a coagulant. The process is followed by the flocculation of the unstable particles into bulky floccules, which can settle more easily. This technique facilitates the removal of suspended solids and colloidal particles from the leachate. The general approach for this technique includes a pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between the particles [140].

As a micro-flocculation aid, ozone is usually added during or before a rapid mixing step to improve the particle flocculation. Through pH adjustment, ozonation affects the coagulation of the organic matter by altering the electrostatic interactions between the coagulant flocs and the organic molecules rather than altering the affinity of the organic compounds for the floc surface sites [141].

In recent years, both ozonation and coagulation–flocculation were employed as an integrated treatment to transform the recalcitrant compounds from stabilized leachate. Monje-Ramirez and Velásquez [142] found that at pH 4–5, the combined treatment with ozonation gave 78% of COD removal with an initial concentration of 5000 mg/L (Table 7). The result was slightly higher than that of Wu et al. [143], who applied the same type of integrated treatment for stabilized leachate from the Chen Shi Li landfill (Taiwan). About 72% of COD removal with an initial COD concentration of 6500 mg/L was achieved at pH 8.6. Wu et al. [143] found that coagulation–flocculation could remove a variety of large organic molecules in raw leachate to complement the degradation by ozone-based AOT.

In another study conducted by Silva et al. [23], the ammonium stripping treatment was employed after coagulation–flocculation and ozonation for leachate from the Gramacho landfill (Brazil). They found that the integrated treatment could completely remove NH_3-N with an initial concentration of 800 mg/L. When 3 mg/L of ozone alone was applied, 48% of COD removal was attained with an initial COD concentration of 3460 mg/L. This result was comparable to that of Bila et al. [68], who achieved 40% of COD removal with an initial COD concentration of 3945 mg/L for leachate from the Gramacho landfill (Brazil).

Other findings were also reported for the leachate treatment in the Thessaloniki landfill (Greece) [141]. The researchers found that coagulation–flocculation followed by ozonation could not reduce the COD of the treated leachate to less than 200 mg/L, the effluent limit of COD in Greece. About 78% of COD removal with an initial COD concentration of 1010 mg/L was attained at pH 4.5.

In general, the combined coagulation–flocculation is one of the most frequently studied and widely employed methods for leachate treatment, in addition to the integrated ozone–GAC. With COD concentration ranging from 3945 to 6500 mg/L, about 85% of COD removal could be attained at pH 8–9. This result is lower than that of ozone–GAC adsorption, which could remove 90% of COD with an initial COD concentration of 8000 mg/L at the same pH range [131].

2.5.3. *Fenton oxidation–coagulation*

In general, the Fenton oxidation consists of four stages: pH adjustment, oxidation reaction, neutralization as well as coagulation and precipitation. Because iron salt cannot be retained during the degradation, the Fenton process produces large amounts of small flocs that contain iron hydroxide as a precipitated by-product, which has to be discarded [144]. The coagulation treatment can be employed to complete the removal process. Two removal mechanisms using coagulation–flocculation are postulated for organic compounds that mostly constitute of humic

Table 7
Combined AOT and physico-chemical technique for leachate treatment

Location of landfill	Type of combined treatment	Coagulant/ oxidant	Dose (g/L)	Ozone consumption (mg O_3/COD)	Initial concentration in leachate (mg/L)		BOD/ COD	pH	Removal efficiency (%)		References
					COD	NH_3-N			COD	NH_3-N	
Lubna (Poland)	Coagulation + ozonation + hydrogen peroxide	$FeCl_3$ O_3 H_2O_2	2.52 0.29 0.15	–	3960	1360	0.60	8.0	89	NA	[146]
Bordo Poniente (Mexico)	Coagulation + ozonation	Fe(II)SO_4 O_3	2.4 1.7×10^{-3}	1.7	5000	NA	0.02	4–5	78	NA	[142]
Gramacho (Brazil)	Coagulation–flocculation + ozonation + ammonia Stripping	$Al_2(SO_4)_3$ O_3	0.7 3.0	NA	3460	800	0.04	8.5	48	100	[23]
Gramacho (Brazil)	Coagulation–flocculation + ozonation	$Al_2(SO_4)_3$ O_3	0.7 3.0	NA	3945	800	0.3	4.5	40	NA	[68]
Thessaloniki (Greece)	Coagulation–flocculation + ozonation	$FeCl_3$ O_3	0.78	NA	1010	NA	0.17	4.5	78	NA	[141]
Chen Shi Li (Taiwan)	Coagulation + ozonation	$FeCl_3$ O_3	0.9 1.2	NA	6500	5500	0.5	8.6	72	NA	
Chen Shi Li (Taiwan)	Coagulation + ozonation + UV irradiation	$FeCl_3$ O_3 UV	0.9 1.2	NA	6500	5500	0.5	8.6	85	NA	[143]
Chonju (Korea)	Coagulation + Fenton oxidation	$FeCl_3$ Fe(II)SO_4 + H_2O_2	1.5 0.6 0.5	NA	1900	NA	0.45	3	69	NA	[86]
Metropolitan (Korea)	Coagulation + Fenton oxidation	$FeCl_3$ Fe(II)SO_4 + H_2O_2	0.8–1.0 1.0	NA	417	NA	NA	5	89	NA	[91]
Badajoz (Spain)	Coagulation–flocculation + Fenton oxidation	$FeCl_3$ Fe(II)SO_4 + H_2O_2	0.8 0.28	NA	7400	NA	0.06	8.5	90	NA	[145]
Wuhan (China)	Coagulation + photooxidation	$FeCl_3$ UV-VIS	0.5	–	5800	NA	0.07	7.6	64	NA	[119]
Badajoz (Spain)	Ozonation + adsorption	O_3 GAC	1.5×10^{-3} 5	1.5	4970	700	0.17	8–9	90	NA	[130]
NENT (Hong Kong)	Ozonation + adsorption	O_3 GAC	3×10^{-3}	1.8	8000	2620	0.09	8	86	92	[131]
Futekeng (Taiwan)	Fenton oxidation + adsorption	Fe(II)SO_4 H_2O_2 PAC	0.8 0.5 0.5	NA	2020	3400	0.13	4.0	92	NA	[150]

NA: unavailable.

acid: (1) the binding of cationic metal species to anionic sites, resulting in the neutralization of humic substances and the reduction of their solubility; (2) the adsorption of humic substances onto the produced amorphous metal hydroxide precipitates [144]. This suggests that the combination of Fenton oxidation and coagulation–flocculation may synergize the advantages of their treatment performance, while overcoming their respective limitations.

The technical applicability of the combined Fenton oxidation and coagulation was investigated to see if colloidal particles present in the leachate could be removed. Rivas et al. [145] found that 90% of COD removal with an initial concentration of 7400 mg/L was attained at pH 8.5. The result was higher than that of a previous study carried out by Kim et al. [86] for leachate treatment in the Chonju landfill (Korea). They reported that 69% of COD removal with an initial COD concentration of 1900 mg/L was achieved at pH 3. This result was more effective than those of coagulation alone (41%) and/or Fenton oxidation alone (52%) at the same concentration, suggesting that the synergistic effects of Fenton oxidation–coagulation have improved its removal for organic compounds.

Such a phenomenon is also in agreement with Yoon et al. [91], who studied the characteristics of coagulation–Fenton oxidation for leachate treatment in the Metropolitan landfill (South Korea). With an initial COD concentration of 417 mg/L, they reported that the removal of organic compounds (with molecular weights of higher than 500 Da) improved from 48% (by using coagulation alone) to 89% (after combined treatments at pH 5.0).

Other important findings of the effect of the combined Fenton oxidation and coagulation treatments on the toxicity reduction in the treated leachate were reported [146]. Although 89% of COD removal with an initial concentration of 3960 mg/L could be attained, the researchers found that this integrated treatment did not bring a significant reduction in the toxicity level in the treated leachate. This phenomenon suggests that the combined treatment did not improve the quality of the treated effluent.

In general, the performance of the combined Fenton oxidation–coagulation treatment for COD removal is satisfactory (about 69–90% of COD removal with an initial COD concentration ranging from 417 to 7400 mg/L). This result is comparable to that of either the integrated ozone–GAC adsorption or combined ozone–coagulation (Table 7).

One benefit of using AOT over conventional coagulation is that it produces less residue than the coagulation process, thus reducing the operational cost for its disposal. However, the presence of radical scavengers in the leachate during AOT treatment can reduce COD removal, as their presence interrupts the chain reactions in the liquid phase [101]. Another limitation of this combined treatment is that AOT prefers an acidic environment for organic degradation, while the coagulation process using $FeCl_3$ as the coagulant works better at pH 4–6.

2.5.4. Fenton oxidation–GAC adsorption

In addition to coagulation, GAC adsorption is also employed as another subsequent treatment after Fenton oxidation. Basically, adsorption is a process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and chemical interactions [147]. Due to its physical properties and a large surface area, GAC has received considerable attention for the removal of organic pollutants from contaminated wastewater [148].

Some interesting results were reported by Zamora et al. [149], who compared the treatment performance of Fenton oxidation alone to coagulation–flocculation in combination with GAC for leachate in a local landfill (Mexico). The Fenton pre-treatment was found to significantly improve the adsorption capacity of GAC for COD (443 mg COD/g GAC) at pH 4.0, compared to coagulation–flocculation (193 mg of COD/g GAC) at pH 5.7. This might be due to the different pH levels applied. At acidic pHs ranging 3–4, Fenton could effectively transform organic compounds into oxidation by-products that had a smaller molecular size than the initial compounds. After Fenton oxidation, GAC adsorbed the remaining by-products on its surface.

Other significant findings were obtained by Gau and Chang [150], who employed the same combined treatments for leachate in the Futekeng landfill (Taiwan). They reported that the addition of activated carbon reduced COD in the treated effluent to 170 mg/L, thus improving COD removal from 60 to 92% with an initial COD concentration of 2020 mg/L. This result suggests that the treated effluent could comply with the COD effluent limit of less than 200 mg/L. This combined treatment cost about US$ 1.5 per m^3 of the treated effluent, excluding the cost of sludge management and other costs for transportation and maintenance.

2.6. Combined AOT and biological process

Since AOT alone is not enough, biological treatment can also be employed to complement the degradation of organic compounds in the leachate through a microbial process [122]. If the presence of recalcitrant compounds does not trigger toxic effects on the microbes during the treatment, a combination of AOT as a pre-treatment followed by a biological process may be an attractive option from an economic point of view.

Among biological processes, activated sludge (AS) is the most frequently studied method to complement the degradation of leachate after AOT [151,152] (Table 8). Encouraging findings were reported for leachate treatment in a local landfill (in Finland) using combined ozonation and AS [100]. About 95% of COD removal with an initial COD concentration of 560 mg/L at pH 9.5 could be achieved with the overall treatment cost of US$ 0.41/kg of COD removed. This cost was lower than that (US$ 1.61/kg of COD removed) reported by Geenens et al. [153]. This might be due to the difference in the strength and the quantity of the leachate, the conditions of the landfill site, the amount and the composition of the impurities and the extent of purification.

AS was also employed after other AOTs such as Fenton oxidation, UV/H_2O_2 and wet air oxidation. Some promising results of the combined Fenton oxidation and AS were reported for leachate treatment in the Kimpo landfill (Korea) [154]. They found that with initial COD and NH_3-N concentrations of 7000 and 1800 mg/L, respectively, about 98% COD removal and 89% NH_3-N removal could be attained. These results are comparable to those achieved by integrated WAO and AS for leachate treatment in the Fossalta landfill (Italy). They found that the

Table 8
Combined AOT and biological process for biodegradation of leachate

Location of landfill	Type of combined treatment	Coagulant/Precipitant Adsorbent/Oxidant	Dose (g/L)	Ozone consumption (mg O_3/mg COD)	Initial concentration in leachate (mg/L)		BOD/COD	pH	Removal efficiency (%)		References
					COD	NH_3-N			COD	NH_3-N	
Taiwan	Coagulation + electro-Fenton + SBR	Fe(II)SO_4/ H_2O_2	0.75	–	1941	151	0.3	4	95	81	[157]
Kimpo (Korea)	Fenton oxidation + activated sludge	Fe(II)SO_4/ H_2O_2	0.9 0.9	NA	7000	1800	0.15	3.5	98	89	[154]
Germany	Photochemical + activated sludge	UV/ H_2O_2	1 4	–	920	NA	0.005	4.0	89	NA	[155]
Fossalta (Italy)	Wet oxidation + activated sludge	–	–	–	4140	998	0.46	7.8	98	NA	[122]
Flanders (Belgium)	Ozone + activated sludge	O_3	2.8	3.7	895	626	0.05	8.2	81	NA	[153]
–	Ozone + activated sludge	O_3	0.05	2.0	2800	250	0.54	6	97	NA	[73]
Finland	Ozone + activated sludge	O_3	5.00	0.3	560	NA	0.06	9.5	95	NA	[100]
Teuftal (Switzerland)	Ozone + nitrification	O_3	0.03	NA	1500	600	0.23	7.0	98	NA	[156]
Kemerburgaz (Turkey)	MAP + Fenton oxidation + UASB	$MgNH_4PO_4$ Fe(II)SO_4/ H_2O_2	NA NA	–	4024	2240	NA	9.2 4.0	82	85	[159]

NA: unavailable.

combined treatments improved the extent of COD removal from 83% (using WAO alone) to 98% (after integrated treatments) at the same COD concentration of 4140 mg/L. This result suggests that WAO have played a major role in the COD removal.

Other important findings were reported by Koh et al. [155], who combined UV/H_2O_2 and AS for leachate treatment in a local landfill (Germany). They found that the degradability of the leachate significantly improved from 0.005 to 0.25 after photo-chemical reactions that consumed 30 kW/m^3 of energy. With an initial COD concentration of 920 mg/L, COD removal improved from 64% (using UV irradiation alone) to 89% (after combined treatments with AS), enabling the treated effluent to be discharged into the receiving environment.

Other biological treatments such as nitrification, sequencing batch reactor (SBR) and an upflow anaerobic sludge blanket (UASB) were less intensively employed as a subsequent treatment after AOT. Karrer et al. [156] employed nitrification after ozonation. They found that at pH 7.0, 98% of COD removal with an initial COD concentration of 1500 mg/L was attained. This result was more satisfactory than that of Lin and Chang [157], who integrated coagulation, electro-Fenton oxidation, and SBR for leachate treatment in a local landfill (in Taiwan). With an initial COD concentration of 1941 mg/L, COD removal improved from 67% (using electro-Fenton alone) to over 95% (after a subsequent treatment with SBR), thus complying with the local discharge standard of less than 100 mg/L.

UASB is another biological process that uses a suspended growth type reactor with a high rate of anaerobic process [158]. Altinbaş et al. [159] applied UASB as a subsequent treatment after Fenton oxidation and struvite precipitation. The precipitation of struvite forms an insoluble compound, which can be easily separated from the liquid phase (Reaction (80)):

$$\begin{aligned} &MgCl_2{\cdot}6H_2O + Na_2HPO_4 + NH_4^+ \\ &\quad \leftrightarrow MgNH_4PO_4{\cdot}6H_2O \downarrow + 2NaCl + H^+, \\ &pK_a = 12.6\,(25\,^\circ C) \end{aligned} \tag{80}$$

With a 1:1:1 mole ratio of Mg^{2+}, NH_4^+ and PO_4^{3-}, 82% of COD removal with an initial COD concentration of 4024 mg/L could be achieved after its combination with a biological process.

In general, considering the extent of COD removal, a combination of AOT and biological process is preferred to that of AOT and another physico-chemical treatment. In addition to enhancing the biodegradability of leachate prior to another subsequent treatment, the biological process can help reduce the COD level in the treated effluent to comply with the required environmental legislation [155,157].

2.7. Comparison of outstanding performance among AOTs for COD removal

To evaluate the treatment performance of the AOTs presented in this article, a comparative study is made in terms of their pH, the dose of oxidants required (g/L), and the strength of leachate in terms of COD and NH_3-N (mg/L). Although it has a relative meaning due to different testing conditions (pH, temperature, the strength of leachate, seasonal climate and hydrology site), this comparison is still useful to evaluate the overall performance of each AOT.

Table 9 presents the outstanding treatment performance of various individual and/or combined AOTs for COD and/or NH_3-N removal from landfill leachate. Both ozonation and Fenton oxidation alone could achieve 40–89% of COD removal with COD concentration ranging from 560 to 8894 mg/L. Among the combined treatments surveyed, the integrated Fenton oxidation and AS gives a higher treatment performance (98% of COD removal with COD concentration of 7000 mg/L) than the Fenton oxidation combined with the coagulation process (90% of COD removal with CO concentration of 7400 mg/L). This suggests that the combination of AOT and a biological process has improved the leachate degradability than its integration with a physico-chemical treatment.

Table 10 summarizes the treatability of various AOTs for landfill leachate. Most of the AOTs presented in the table have a

Table 9
Summary of the highest reported COD removal of some AOTs

Location of landfill	Type of treatment	Coagulant/precipitant adsorbent/oxidant	Dose (g/L)	Initial concentration in leachate (mg/L)		BOD/COD	pH	Removal efficiency (%)		References
				COD	NH_3-N			COD	NH_3-N	
Sandtown (USA)	Fenton oxidation alone	Fe(II)SO_4 + H_2O_2	0.05 0.15	8894	NA	NA	2.5	89	NA	[82]
Komurcuoda (Turkey)	Ozonation alone	O_3	2.8	47800	3260	0.6	9	85	NA	[87]
Braunschweig (Germany)	Homogenous system with irradiation	H_2O_2 + UV	0.5	1200	5	0.01	3–4	90	NA	[59]
Badajoz (Spain)	Coagulation–flocculation + Fenton oxidation	$FeCl_3$ Fe(II)SO_4 + H_2O_2	0.8 0.6 0.5	7400	NA	0.06	8.5	90	NA	[145]
Kimpo (Korea)	Fenton oxidation + Activated sludge	Fe(II)SO_4 + H_2O_2	0.9 0.9	7000	1800	0.15	3.5	98	89	[154]

Table 10
Summary of the treatability of various AOTs for landfill leachate

Type of AOT	Major characteristics	Mechanism of the generation of $^{\bullet}OH$	COD removal (%)	COD concentration range (mg/L)	References
Ozonation alone	1. Compounds with specific functional groups are prone to ozone attack, resulting in carbonyl compounds 2. An alkaline environment is the key parameter in AOT-based ozonation	$O_3 + H_2O \leftrightarrow O_2 + 2^{\bullet}OH$	25–85	920–5850	[160]
Fe^{2+}/H_2O_2 (Fenton oxidation)	1. Fenton's reagent contains Fe^{2+}, which acts as a catalyst	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$	52–85	1000–8894	[74]
$H_2O_2/UV/Fe^{2+}$ (photo-assisted Fenton)	1. A combination of H_2O_2 and UV irradiation with Fe(II) oxalate 2. The oxidation process was enhanced by UV light	$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$	20–70	895–5200	[104]
Ozone/H_2O_2	1. Alkaline conditions alone is able to produce $^{\bullet}OH$ radicals 2. Reaction rate increases in the presence of H_2O_2	$2O_3 + H_2O_2 \rightarrow 2^{\bullet}OH + 3O_2$	28–50	560–1090	[160]
UV/H_2O_2	1. Reaction a direct cleavage of central O—O bond 2. Alkaline conditions increase $^{\bullet}OH$ formation	$H_2O_2 + UV \rightarrow 2^{\bullet}OH$	56–90	1280–5200	[113]
UV/ozone/H_2O_2	1. The photolysis of O_3 through a complex chain of reactions 2. An increase in pH increases $^{\bullet}OH$ formation 3. The process is enhanced by the presence of H_2O_2	$2O_3 + H_2O_2 \rightarrow 2^{\bullet}OH + 3O_2$	72–89	1090–1280	[118]
TiO_2/UV photocatalysis	1. Process reaction involves the excitation of electrons by the absorption of UV light 2. No chemical added, no residuals, short reaction times	(1) $TiO_2 + h\nu \rightarrow TiO_2(e^-/h^+)$ (2) $TiO_2(OH^-) + H_2O_2 + h\nu \rightarrow TiO_2(OH)_{\text{adsorbed}} + OH^- + {}^{\bullet}OH$	NA	NA	[55]
Ozone–GAC adsorption	1. GAC accelerates the kinetic rate of ozone decomposition through the formation of $^{\bullet}OH$ radicals in the solution 2. GAC plays roles as the adsorbent and as the promoter in the degradation process	(1) $O_3 + H_2O + 2\,e^- \leftrightarrow O_2 + 2OH^-$ (2) $C_\pi + 2H_2O \leftrightarrow C_\pi{-}H_3O^+ + OH^-$	86–90	4970–8000	[131]
Ozone–coagulation–flocculation	1. Coagulation–flocculation is applied as a pre-treatment or a polishing step before/after ozonation 2. Ozone is added during or before the rapid mix step to improve particle flocculation 3. Through pH adjustment, ozonation affects the coagulation of organic matter by altering the electrostatic interactions between the coagulant flocs and the organic molecules	$O_3 + H_2O \leftrightarrow O_2 + 2^{\bullet}OH$	72–85	3945–6500	[141]

wide range of COD removal with different COD concentration ranges. Such a wide range of COD removal among the AOTs may be due to the different dose of oxidants required, the strength of the leachate, the pH and the concentration of carbonate and bicarbonate as radical scavengers. Although many AOTs can be employed, the leachate characteristics, the technical applicability and the cost-effectiveness are the key factors that play important roles in the selection of the most suitable AOT for leachate treatment.

Some studies carried out in Hong Kong [39,131] found that the characteristics of the leachate in the local landfills were not affected by seasonal variations/rainfall. Although the climate in Hong Kong is markedly seasonal with a clearly defined wet season, the researchers [39,131] reported that there were no significant seasonal variations in the quality and the quantity of leachate between the dry and the rainy seasons. This indicates that the chemical compositions in the leachate may not be affected by rainfall, but by the hydrology site of the landfill [161]. This could explain why the effects of climatic conditions on the performance of each AOT for leachate treatment are rarely reported.

In spite of its effectiveness for COD removal, little attention has been directed toward evaluating the changes of NH_3-N concentration in the leachate after AOT treatment. It was reported that during ozonation the toxic NH_3-N was converted to the relatively harmless nitrate, as shown in the following reaction [71,162]:

$$NH_3 + 4O_3 \rightarrow NO_3^- + 4O_2 + H_2O + H^+ \qquad (81)$$

Gunten [60] further reported that $^{\bullet}OH$ radical rapidly reacted with most leachate constituents ($k = 10^8$–$10^{11}\ M^{-1}\ s^{-1}$), except NH_3-N. This compound is slowly oxidized by the radicals, as indicated by the low kinetic rate of the oxidation reaction. Consequently, the removal of NH_3-N was not effective enough. This could explain why the extent of NH_3-N removal after AOT treatment is rarely reported.

In general, AOT is a promising means for the treatment of stabilized leachate with a high strength of refractory compounds. This treatment technique offers some advantages such as the absence of secondary waste, the ability to handle varying compositions of leachate and most importantly, no generation of any harmful residuals.

2.8. Comparison of cost-effectiveness among various treatment methods

Basically, the treatment cost of landfill leachate varies depending on its strength and quantity, the process employed, the conditions of the landfill site, the amount and the composition of impurities, as well as the extent of purification [163]. The overall treatment cost includes the construction and the operational and maintenance costs (O&M). The construction costs depend on the effluent quality required and the capacity of the installation, while the O&M costs cover manpower, energy, chemicals and maintenance.

It is important to note that the operational cost for leachate treatment varies from time to time, as leachate quality and quantity would change due to seasonal variations. To cope with the temporal fluctuation in the strength and the composition of the leachate, the treatment facilities would need necessary upgrading, thus resulting in the increasing operational cost for landfill management. The operational cost is significant due to the long-term operation of landfills. If regulation requires a high standard of discharge, a significant increase in taxation related to waste management should be anticipated. Such investments should be evaluated periodically for their long-term operation. For this reason, information on the treatment cost of landfill leachate is rarely reported.

Nevertheless, some researchers have estimated the overall treatment cost of leachate using certain treatments. The treatment cost of leachate using combined ozone–GAC adsorption varies between US$ 2–4 per m^3 of the treated effluent [131]. The cost covered the chemicals required and energy consumption, but it did not take into account any costs associated with the regeneration of the spent GAC. Li et al. [164] reported that the treatment cost for NH_3-N removal using struvite precipitation was one-fifth more expensive than that of ammonium stripping. Depending on the type of precipitation and chemicals employed, the treatment cost of struvite precipitation varies (US$ 2–4 per m^3 of treated effluent).

Although many techniques can be employed, the most important aspect in the selection of AOT for leachate treatment is that the treated effluent can meet the effluent limit for COD and NH_3-N at an economical cost. Moreover, the selected treatment should be flexible enough to remain useful with changing technology, regulation, leachate characteristics and economic factors [165]. All these factors need to be considered when selecting the most effective and inexpensive treatment in order to protect the environment.

3. Concluding remarks

Over the past three decades, the application of AOTs such as ozonation, Fenton oxidation, O_3/H_2O_2, UV/O_3, UV/H_2O_2, $UV/H_2O_2/Fe^{2+}$ for leachate treatment has been reviewed. It is evident from the review of 167 papers (1976–2005) that none of the individual AOT is universally applicable or highly effective for leachate treatment.

Among the AOTs reviewed, ozonation and Fenton oxidation are the most frequently studied and widely applied methods for leachate treatment. Both techniques can achieve about 25–89% of COD removal with COD concentration ranging from 560 to 8894 mg/L. By integrating the Fenton oxidation and coagulation–flocculation process, about 69–90% of COD removal with its concentrations ranging from 417 to 7400 mg/L was achieved. A combination of AOT and biological process for leachate treatment has been found to be an economical option, as oxidation by-products resulting from AOT can be removed by an inexpensive biological process. An almost complete COD removal (98%) was attained by combining the AS and the Fenton oxidation (COD: 7000 mg/L) and/or AS and WAO (COD: 4140 mg/L).

Although many techniques can be employed, in general, the leachate characteristics such as the nature of the MSW and the concentration of organic pollutants to be removed, the effluent discharge alternatives, the treatment efficiency to be achieved, the technical applicability, and the economic factors (investment and operational costs) are the key factors that play important roles in the selection of the most suitable AOT for leachate treatment [166,167].

Acknowledgements

Mr. Tonni Agustiono Kurniawan thanks The Hong Kong Polytechnic University (PolyU) for the International Postgraduate Study Scholarship, which enables him to pursue a higher degree. The authors are also grateful for the support of PolyU Central Research Grant and the grant from the Research Grants Council (RGC) of The Hong Kong SAR (China) (Project No. PolyU 5224/05E).

References

[1] M. El-Fadel, A.N. Findikakis, J.O. Leckie, Environmental impacts of solid waste landfilling, J. Environ. Manage. 50 (1997) 1–25.
[2] K. Westlake, Landfill Waste Pollution and Control, Albion Publishing, Sussex, UK, 1995.
[3] US EPA, Municipal Solid Waste in the United States: 2000 Facts and Figures, Office of Solid Waste and Emergency Response, Washington, DC, 2002 (EPA 530-R-02-001).
[4] Z.Y. Feng, D. Na, L.J. Hong, X.C. Zhong, A new pyrolysis technology and equipment for treatment of municipal household garbage and hospital waste, Renewable Energy 28 (15) (2003) 2383–2393.
[5] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen, Present and long-term composition of MSW landfill leachate: a review, Crit. Rev. Environ. Sci. Technol. 32 (4) (2002) 297–336.
[6] D.R. Reinhart, T.G. Townsend, Landfill Bioreactor Design and Operation, CRC Press, Lewis Publishers, Boca Raton, FL, 1998.
[7] E.A. McBean, F.A. Rovers, G.J. Farquhar, Solid Waste Landfill Engineering and Design, Prentice Hall PTR, Englewood Cliffs, NJ, 1995.
[8] US EPA (Environmental Protection Agency), Urban Watershed Management Research Terminology, 2005 (http://www.epa.gov/ednnrmrl/terminology.html).
[9] S.R. Qasim, W. Chiang, Sanitary Landfill Leachate: Generation, Control and Treatment, Technomic Publishing, Lancaster, PA, 1994.
[10] R.D. Cameron, F.A. Koch, Toxicity of landfill leachates, JWPCF 52 (1980) 760–769.
[11] P. Kjeldsen, M. Christophersen, Composition of leachate from old landfills in Denmark, Waste Manage. Res. 19 (2001) 249–256.
[12] M. Åkesson, P. Nilsson, Seasonal changes of leachate production and quality from test cells, J. Environ. Eng. 123 (1997) 892–900.
[13] T.J. Bookter, R.K. Ham, Stabilization of solid waste in landfills, J. Environ. Eng. 108 (1982) 1089–1100.
[14] P. Kjeldsen, A.A. Grundtvig, P. Winther, J.S. Andersen, Characterization of an old municipal landfill (Grindsted, Denmark) as a groundwater pollution source: landfill history and leachate composition, Waste Manage. Res. 16 (1) (1998) 3–13.
[15] N. Paxeus, Organic compounds in municipal landfill leachates, Water Sci. Technol. 42 (7–8) (2000) 323–333.
[16] C. Grøn, J.B. Christensen, D.L. Jensen, P. Kjeldsen, O. Østfeld, Organic halogens in landfill leachates, Water Air Soil Pollut. 120 (2000) 331–345.
[17] H. Belevi, P. Baccini, Long-term behavior of municipal solid waste landfills, Waste Manage. Res. 7 (1989) 43–56.
[18] R. Manoharan, S.C. Harper, D.S. Mavinic, C.W. Randal, G. Wang, D.C. Marickovich, Inferred metal toxicity during the biotreatment of high ammonia landfill leachate, Water Environ. Res. 64 (1992) 858–865.
[19] A. Baun, A. Ledin, L.A. Reitzel, P.L. Bjerg, T.H. Christensen, Xenobiotic organic compounds in leachates from ten Danish MSW landfills—chemical analysis and toxicity tests, Water Res. 38 (2004) 3845–3858.
[20] W.R. Ernst, P. Hennigar, K. Doe, S. Wade, G. Julien, Characterization of the chemical constituents and toxicity to aquatic organisms of a municipal landfill leachate, Water Pollut. Res. J. Can. 29 (1994) 89–101.
[21] B. Clément, G. Merlin, The contribution of ammonia and alkalinity to landfill leachate toxicity to duckweed, Sci. Total Environ. 70 (1995) 71–79.
[22] S.Q. Burton, I.A. Watson-Craik, Ammonia and nitrogen fluxes in landfill sites: applicability to sustainable landfilling, Waste Manage. Res. 16 (1998) 41–53.
[23] A.C. Silva, M. Dezotti, G.L. Sant'Anna Jr., Treatment and detoxification of a sanitary landfill leachate, Chemosphere 55 (2004) 207–214.
[24] M.H. Wong, Toxicity test of landfill leachate using *Sarotherodon mossambicus* (freshwater fish), Ecotoxicol. Environ. Saf. 17 (1989) 149–156.
[25] J.W. Atwater, S. Jasper, D.S. Mavinic, F.A. Koch, Experiments using daphnia to measure landfill leachate toxicity, Water Res. 17 (1983) 1855–1861.
[26] M. Devare, M. Bahadir, Biological monitoring of landfill leachates using plants and luminescent bacteria, Chemosphere 28 (1994) 261–271.
[27] T. Assmuth, T. Strandberg, Groundwater contamination at Finnish landfills, Water Air Soil Pollut. 69 (1993) 179–199.
[28] J.P. Murray, J.V. Rouse, A.B. Carpenter, Groundwater contamination by sanitary landfill leachate and domestic wastewater in carbonate terrain: principal source diagnosis, chemical transport characteristics and design implications, Water Res. 15 (1981) 745–757.
[29] A. Bagchi, Design, Construction and Monitoring of Landfills, John Wiley & Sons, New York, 1994.
[30] P.N. Cheremisinoff, K.A. Gigliello, Leachate from Hazardous Wastes Sites, Technomic Publishing Co Inc., Lancaster, PA, 1983.
[31] H.J. Ehrig, Treatment of sanitary landfill leachate: biological treatment, Waste Manage. Res. 2 (1984) 131–152.
[32] A.S. Erses, M.A. Fazal, T.T. Onay, W.H. Craig, Determination of solid waste sorption capacity for selected heavy metals in landfills, J. Hazard. Mater. 121 (1–3) (2005) 223–232.
[33] B. Schults, P. Kjeldsen, Screening organic matter in leachate from sanitary landfills using gas chromatography combined with mass spectrometry, Water Res. 20 (8) (1986) 965–970.
[34] H.J. Ehrig, Leachate quality, in: T.H. Christensen, R. Cossu, R. Stegmann (Eds.), Sanitary Landfilling: Process, Technology and Environmental Impact, Academic Press, London, 1989, pp. 213–229.
[35] J.J. Wu, C.C. Wu, H.W. Ma, C.C. Chang, S.J. Masten, Treatment of landfill leachate by ozone-based advanced oxidation processes, in: Proceeding of the 15th IOA World Congress 2001, London, UK, 11–15 September, 2001, pp. 339–349.
[36] S. Baig, I. Coulomb, P. Courant, P. Liechti, Treatment of landfill leachates: lapeyhouse and satrod case studies, Ozone Sci. Eng. 21 (1999) 1–22.
[37] A.I. Zouboulis, M.X. Loukidou, K. Christodoulou, Enzymatic treatment of sanitary landfill leachate, Chemosphere 44 (2001) 1103–1108.
[38] J.L. Morais, P.P. Zamora, Use of advanced oxidation process to improve the biodegradability of mature landfill leachate, J. Hazard. Mater. B123 (2005) 181–186.
[39] I.M.C. Lo, Characteristics and treatment of leachates from domestic landfills, Environ. Int. 22 (4) (1996) 433–442.
[40] P.H. Chen, Assessment of leachates from sanitary landfills: impact of age, rainfall, and treatment, Environ. Int. 22 (2) (1996) 225–237.
[41] A.M. Martensson, C. Aulin, O. Wahlberg, S. Argen, Effect of humic substances on the mobility of toxic metals in a mature landfill, Waste Manage. Res. 17 (1999) 296–304.
[42] M.A. Barlaz, D.M. Schaefer, R.K. Ham, Bacterial population development and chemical characteristics of refuse decomposition in a simulated sanitary landfill, Appl. Environ. Microbiol. 55 (1989) 55–65.
[43] K.R. Gurijala, J.M. Suflita, Environmental factors influencing methanogenesis from refuse in landfill samples, Environ. Sci. Technol. 27 (6) (1993) 1176–1181.
[44] M. Weis, G. Abbt-Barun, F.H. Frimmel, Humic-like substances from landfill leachates—characterization and comparison with terrestrial and aquatic humic substances, Sci. Total Environ. 81/82 (1989) 343–352.

[45] A. Metry, F.L. Cross, Leachate Control and Treatment, Technomic Publishing, Connecticut, 1976.

[46] E.S. Venkataramani, R.C. Ahlert, P. Corbo, Biological treatment of landfill leachates, CRC Crit. Rev. Environ. Control 14 (4) (1986) 333–372.

[47] C.M. Lee, X.R. Lin, C.Y. Lan, S.C.L. Lo, G.Y.S. Chan, Evaluation of leachate recirculation on nitrous oxide production in the Likang landfill (China), J. Environ. Qual. 31 (2002) 1502–1508.

[48] M.J. Barr, H.D. Robinson, Constructed wetlands for landfill leachate treatment, Waste Manage. 17 (1999) 498–504.

[49] H.J. Ehrig, R. Stegmann, Biological process, in: T.H. Christensen, R. Cossu, R. Stegmann (Eds.), Landfilling of Waste: Leachate, E & FN SPON, London, 1992, pp. 65–88.

[50] S.K. Han, S.N. Nam, J.W. Kang, OH radical monitoring technologies for AOP advanced oxidation process, Water Sci. Technol. 46 (11–12) (2002) 7–12.

[51] H. Suty, C. De Traversay, M. Cost, Applications of advanced oxidation processes: present and future, Water Sci. Technol. 49 (4) (2004) 227–233.

[52] S.A. Parsons, M. Williams, Introduction, in: S.A. Parsons (Ed.), Advanced Oxidation Processes for Water and Wastewater Treatment, IWA Publishing, London, 2004, pp. 1–6.

[53] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment. I. Oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.

[54] A. Al-Kdasi, A. Idris, K. Saed, C.T. Guan, Treatment of textile wastewater by advanced oxidation processes—a review, Global Nest Int. J. 6 (3) (2004) 226–234.

[55] C.A. Murray, S.A. Parsons, Advanced oxidation processes: flowsheet options for bulk natural organic matter removal, Water Sci. Technol. 4 (4) (2004) 113–119.

[56] A. Chaturapruek, C. Visvanathan, K.H. Ahn, Ozonation of membrane bioreactor effluent for landfill leachate treatment, Environ. Technol. 26 (1) (2005) 65–73.

[57] S. Baig, P.A. Liechti, Ozone treatment for biorefractory COD removal, Water Sci. Technol. 43 (2) (2001) 197–204.

[58] P. Westerhoff, G. Aiken, G. Amy, J. Debroux, Relationship between the structure of organic matter and its reactivity towards molecular ozone and hydroxyl radicals, Water Res. 33 (10) (1999) 2265–2276.

[59] M. Steensen, Chemical oxidation for the treatment of leachate—process comparison and results from full-scale plants, Water Sci. Technol. 35 (4) (1997) 249–256.

[60] U. Gunten, Ozonation of drinking water. Part I. Oxidation kinetics and product formation, Water Res. 37 (2003) 1443–1467.

[61] K. Ikehata, M.G. El-Din, Degradation of recalcitrant surfactants in wastewater by ozonation and advanced oxidation process: a review, Ozone Sci. Eng. 26 (2004) 327–343.

[62] J. Rivera-Utrilla, M. Sánchez-Polo, Degradation and removal of naphthalenesulphonic acids by means of adsorption and ozonation catalyzed by activated carbon in water, Water Resources Res. 39 (9) (2003) 1232–1245.

[63] J. Hoigné, H. Bader, Ozonation of water: selectivity and rate of oxidation of solutes, Ozone Sci. Eng. 1 (1979) 73–85.

[64] J. Staehelin, R.E. Buhler, J. Hoigné, Ozone decomposition in water studied by pulse radiolysis. 2. OH and HO_4 as chain intermediates, J. Phys. Chem. 88 (24) (1984) 5999–6004.

[65] V. Camel, A. Bermond, The use of ozone and associated oxidation processes in drinking water treatment, Water Res. 32 (11) (1998) 3208–3222.

[66] Y. Takeuchi, K. Mochidzuki, N. Matsunobu, R. Kojima, H. Motohashi, S. Yoshimoto, Removal of organic substances from water by ozone treatment followed by biological activated carbon, Water Sci. Technol. 35 (7) (1997) 171–178.

[67] S.K. Marttinen, R.H. Kettunen, K.M. Sormunen, R.M. Soimasuo, J.A. Rintala, Screening of physical-chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachate, Chemosphere 46 (2002) 851–858.

[68] D.M. Bila, A.F. Montalvão, A.C. Silva, M. Dezotti, Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement, J. Hazard. Mater. 117 (2–3) (2005) 235–242.

[69] S. Bouland, J.P. Duguet, A. Montiel, Minimizing bromate concentration by controlling the ozone reaction in a full-scale plant, Ozone Sci. Eng. 26 (2004) 381–388.

[70] J. Fettig, H. Stapel, C. Steinert, M. Geiger, Treatment of landfill leachate by preozonation and adsorption in activated carbon columns, Water Sci. Technol. 34 (1996) 33–40.

[71] M.F. Wang, M.G. El-Din, D.W. Smith, Oxidation of aged raw landfill leachate with O_3 only and O_3/H_2O_2: treatment efficiency and molecular size distribution analysis, Ozone Sci. Eng. 26 (2004) 287–298.

[72] S.H. Lin, C.L. Lai, Kinetic characteristics of textile wastewater ozonation in fluidized and fixed activated carbon beds, Water Res. 34 (3) (2000) 763–772.

[73] I. Kamenev, L. Pikkov, S. Kamenev, J. Kallas, Landfill leachate under combined oxidation treatment, in: Proceedings of the 15th IOA World Congress 2001, London, UK, 11–15 September, 2001, pp. 345–351.

[74] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. B98 (2003) 33–50.

[75] R.M. Roddy, C.P. Huang, Landfill leachate treatment using an integrated Fenton process, in: Proceedings of the 7th International Waste Management and Landfill Symposium, Cagliari, Italia, 04–08 October, 1999.

[76] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constant for reaction of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/O^-) in aqueous solution, J. Phys. Chem. Ref. Data 17 (2) (1988) 513–586.

[77] R. Venkatadri, R.W. Peters, Chemical oxidation technologies: ultraviolet/hydrogen peroxide, Fenton's reagent, and titanium dioxide-assisted photocatalysis, Hazard. Waste Hazard. Mater. 10 (1993) 107–149.

[78] M. Pera-Titus, V. Garcia-Molina, M.A. Banos, J. Gimenez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B: Environ. 47 (2004) 219–256.

[79] Y.W. Kang, K.Y. Hwang, Effects of reaction conditions on the oxidation efficiency in the Fenton process, Water Res. 34 (2000) 2786–2790.

[80] A. Lopez, M. Pagano, A. Volpe, A.C. Di Pinto, Fenton's pre-treatment of mature landfill leachate, Chemosphere 54 (2004) 1005–1010.

[81] H.J. Choi, Evaluation of Fenton's Process for the Treatment of Landfill Leachate, Ph.D. Thesis, The University of Delaware, 1998.

[82] H. Zhang, H.J. Choi, C.P. Huang, Treatment of landfill leachate by Fenton's reagent in a continuous stirred tank reactor, J. Hazard. Mater. 136 (3) (2006) 618–623.

[83] H. Zhang, H.J. Choi, C.P. Huang, Optimization of Fenton process for the treatment of landfill leachate, J. Hazard. Mater. B125 (2005) 166–174.

[84] W.Z. Tang, Physicochemical Treatment of Hazardous Wastes, CRC Press, Lewis Publishers, FL, USA, 2004.

[85] J.H. Sun, S.P. Sun, G.L. Wang, L.P. Qiao, Degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process, Dyes Pigment (2006), in press.

[86] J.S. Kim, H.Y. Kim, C.H. Won, J.G. Kim, Treatment of leachate produced in stabilized landfills by coagulation and Fenton oxidation process, J. China Inst. Chem. Eng. 32 (5) (2001) 425–429.

[87] B. Calli, B. Mertoglu, B. Inanc, Landfill leachate management in Istanbul: applications and alternatives, Chemosphere 59 (2005) 819–829.

[88] M.E. Lindsey, M.A. Tarr, Quantitation of hydroxyl radical during Fenton oxidation following a single addition of iron and peroxide, Chemosphere 41 (3) (2000) 409–417.

[89] J.P. Duguet, E. Brodard, B. Dussert, J. Malleivalle, Improvement of the effectiveness of ozonation of drinking water through the use of H_2O_2, Ozone Sci. Eng. 7 (1985) 241–258.

[90] S.H. Lin, C.C. Lo, Fenton process for treatment of desizing wastewater, Water Res. 31 (1997) 2050–2056.

[91] J. Yoon, S. Cho, Y. Cho, S. Kim, The characteristics of coagulation of Fenton reaction in the removal of landfill leachate organics, Water Sci. Technol. 38 (2) (1998) 209–214.

[92] J.J. Pignatello, D. Liu, P. Huston, Evidence for additional oxidant in the photoassisted Fenton reaction, Environ. Sci. Technol. 33 (1999) 1832–1839.

[93] J. Kiwi, A. Lopez, V. Nadtochenko, Mechanism and kinetics of the OH-radical intervention during Fenton oxidation in the presence of a

significant amount of radical scavenger (Cl^-), Environ. Sci. Technol. 34 (2000) 2162–2168.

[94] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent, Water Res. 35 (9) (2001) 2129–2136.

[95] A.S. Amiri, O_3/H_2O_2 treatment of methyl-*tert*-butyl ether (MTBE) in contaminated waters, Water Res. 35 (15) (2001) 3706–3714.

[96] J. Staehelin, J. Hoigné, Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide, Environ. Sci. Technol. 16 (1982) 676–681.

[97] W.H. Glaze, J.W. Kang, Advanced oxidation processes: test of a kinetic model for the oxidation of organic compounds with ozone and hydrogen peroxide in a semibatch reactor, Ind. Eng. Chem. Res. 28 (1989) 1580–1587.

[98] S. Nelieu, L. Kerhoas, J. Einhorn, Degradation of attrazine into ammeline by combined O_3/H_2O_2 treatment in water, Environ. Sci. Technol. 34 (2000) 430–437.

[99] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment. II. Hybrid methods, Adv. Environ. Res. 8 (2004) 553–597.

[100] P. Haapea, S. Korhonen, T. Tuhkanen, Treatment of industrial landfill leachates by chemical and biological methods: ozonation, ozonation + hydrogen peroxide, hydrogen peroxide and biological post-treatment for ozonated water, Ozone Sci. Eng. 24 (5) (2002) 369–378.

[101] B. Legube, N.K.V. Leitner, Catalytic ozonation: a promising advanced oxidation technology for water treatment, Catal. Today 53 (1999) 61–72.

[102] D. Geenens, D. Bixio, C. Thoeye, Advanced oxidation treatment of landfill leachate, in: Proceedings of the 7th International Waste Management and Landfill Symposium, Cagliari, Italia, 04–08 October, 1999.

[103] P. Schulte, A. Bayer, F. Kuhn, T. Luy, M. Volkmer, H_2O_2/O_3, H_2O_2/UV and H_2O_2/Fe^{2+} processes for the oxidation of hazardous waste, Ozone Sci. Eng. 17 (2) (1995) 119–134.

[104] S.M. Kim, A. Vogelpohl, Degradation of organic pollutants by the photo-Fenton process, Chem. Eng. Technol. 21 (1998) 187–191.

[105] A. Wenzel, A. Gahr, R. Niessner, TOC-removal and degradation of pollutants in leachate using a thin-film photoreactor, Water Res. 33 (4) (1999) 937–946.

[106] M.I. Stefan, UV photolysis: background, in: S.A. Parsons (Ed.), Advanced Oxidation Processes for Water and Wastewater Treatment, IWA publishing, London, 2004, pp. 7–48.

[107] W.S. Kuo, Synergistic effects of combination of photolysis and ozonation on destruction of chlorophenols in water, Chemosphere 39 (11) (1999) 1853–1860.

[108] G.R. Peyton, W.H. Glaze, Destruction of pollutants in water with ozone in combination with ultraviolet radiation. 3. Photolysis of aqueous ozone, Environ. Sci. Technol. 22 (1988) 761–767.

[109] N.H. Ince, Light-enhanced chemical oxidation for tertiary treatment of municipal landfill leachate, Water Environ. Res. 70 (6) (1998) 1161–1169.

[110] P.L. Yue, O. Legrini, Photochemical degradation of organics in water, Water Pollut. Res. J. Can. 27 (1992) 123–137.

[111] V. Bigot, F. Luck, H. Paillard, A. Wagner, Landfill leachate treatment: comparison of three oxidation processes using ozone, in: Proceedings of the Regional IOA Conference, Zurich, Switzerland, 31 August–02 November, International Ozone Association, 1994, pp. 219–228.

[112] F.J. Benitez, J.B. Heredia, J.L Acero, M.L. Pinilla, Simultaneous photodegradation and ozonation plus UV radiation of phenolic acids—major pollutants in agroindustrial wastewaters, J. Chem. Technol. Biotechnol. 70 (3) (1999) 253–260.

[113] J.R. Bolton, Ultraviolet Applications Handbook, Bolton Photosciences Inc., Ontario, 1999.

[114] H. Shu, H.J. Fan, M.C. Chang, W.P. Hsieh, Treatment of MSW landfill leachate by a thin gap annular UV/H_2O_2 photoreactor with multi-UV lamps, J. Hazard. Mater. 129 (1–3) (2006) 73–79.

[115] J.P. Müller, C. Gottschalk, M. Jekel, Comparison of advanced oxidation processes in flow-through pilot plants (Part II), Water Sci. Technol. 44 (5) (2001) 311–315.

[116] F.J. Benitez, J.B. Heredia, J.L. Acero, F.J. Rubio, Oxidation of several chlorophenolic derivatives by UV irradiation and hydroxyl radicals, J. Chem. Technol. Biotechnol. 76 (3) (2001) 312–320.

[117] C. Hofl, G. Sigl, O. Specht, I. Wurdack, D. Wabner, Oxidative degradation of AOX and COD by different advanced oxidation processes: a comparative study with two samples of a pharmaceutical wastewater, Water Sci. Technol. 35 (4) (1997) 257–264.

[118] K. Kusakabe, S. Aso, T. Wada, J. Hayashi, S. Marooka, K. Isomutta, Destruction rate of volatile organochlorine compounds in water by ozonation with ultraviolet radiation, Water Res. 25 (1991) 1199–1203.

[119] Z.P. Wang, Z. Zhang, Y.J. Lin, N.S. Deng, T. Tao, K. Zhuo, Landfill leachate treatment by a coagulation–photooxidation process, J. Hazard. Mater. B95 (2002) 153–159.

[120] S.M. Kim, S.U. Geissen, A. Vogelpohl, Landfill leachate treatment by a photoassisted Fenton reaction, Water Sci. Technol. 35 (4) (1997) 239–248.

[121] J.D. Enzminger, D. Robertson, R.C. Ahlert, D.S. Kosson, Treatment of landfill leachates, J. Hazard. Mater. 14 (1987) 83–101.

[122] F. Avezzu, G. Bissolotti, C. Collivignarelli, Combination of wet oxidation and activated sludge treatment, in: T.H. Christensen, R. Cossu, R. Stegmann (Eds.), Landfilling of Waste: Leachate, E & FN SPON, London, 1992, pp. 333–352.

[123] S.T. Kolaczkowski, P. Plucinski, F.J. Beltran, F.J. Rivas, D.B. McLurgh, Wet air oxidation: a review of process technologies and aspects in reactor design, Chem. Eng. J. 73 (2) (1999) 143–160.

[124] P. Navarro, J. Sarasa, D. Sierra, S. Esteban, J.L. Ovelleiro, Degradation of wine industry wastewaters by photocatalytic advanced oxidation, Water Sci. Technol. 51 (1) (2005) 113–120.

[125] M. Bekbolet, M. Lindner, D. Weichgrebe, D.W. Bahnemann, Photocatalytic detoxification with the thin-film fixed bed reactor (TFFBR): clean up of highly polluted landfill effluents using a novel TiO_2-photocatalyst, Solar Energy 56 (5) (1996) 455–469.

[126] S. Chiron, A. Fernandez-Alba, A. Rodriguez, E. Garcia-Calvo, Pesticide chemical oxidation: state-of-the-art, Water Res. 34 (2) (2000) 366–377.

[127] E. Gilbert, Influence of ozone on the photocatalytic oxidation of organic compounds, Ozone Sci. Eng. 24 (2) (2002) 75–82.

[128] E. Diamadopoulos, P. Samaras, X. Dabou, G.P. Sakellapoulos, Combined treatment of landfill leachate and domestic sewage in a sequencing batch reactor, Water Sci. Technol. 36 (2–3) (1997) 61–68.

[129] K. Ozekin, P. Westerhoff, G.L. Amy, M. Siddiqui, Molecular ozone and radical pathways of bromate formation during ozonation, J. Environ. Eng. 124 (5) (1998) 456–462.

[130] F.J. Rivas, F. Beltrán, O. Gimeno, B. Acedo, F. Carvalho, Stabilized leachates: ozone-activated carbon treatment and kinetics, Water Res. 37 (2003) 4823–4834.

[131] T.A. Kurniawan, W.H. Lo, G.Y.S. Chan, Degradation of recalcitrant compounds from stabilized landfill leachate using a combination of ozone–GAC adsorption treatment, J. Hazard. Mater. 137 (1) (2006) 443–455.

[132] U. Jans, J. Hoigné, Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH-radicals, Ozone Sci. Eng. 20 (1) (1998) 67–87.

[133] J. Rivera-Utrilla, M. Sánchez-Polo, Ozonation of 1,3,6-naphthalenetrisulphonic acid catalyzed by activated carbon in aqueous phase, Appl. Catal. B: Environ. 39 (2002) 319–329.

[134] B. Kasprzyk-Hordern, M. Ziolek, J. Nawrocki, Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment, Appl. Catal. B: Environ. 46 (2003) 639–669.

[135] F. Wang, D.W. Smith, G.M. El-Din, Application of advanced oxidation methods for landfill leachate treatment—a review, J. Environ. Eng. Sci. 2 (2003) 413–427.

[136] J. Rivera-Utrilla, M. Sánchez-Polo, Ozonation of naphthalenesulphonic acid in aqueous phase in the presence of activated carbon in aqueous phase, Langmuir 20 (2004) 9217–9222.

[137] C.A. Zaror, Enhanced oxidation of toxic effluents using simultaneous ozonation and activated carbon treatment, J. Chem. Technol. Biotechnol. 70 (1997) 21–28.

[138] F.J. Beltran, B. Acedo, F.J. Rivas, O. Gimeno, Pyruvic acid removal from water by the simultaneous action of ozone and activated carbon, Ozone Sci. Eng. 27 (2005) 159–169.

[139] M. Sanchez-Polo, U. Gunten, J. Rivera-Utrilla, Efficiency of activated carbon to transform ozone into •OH radicals: influence of operational parameters, Water Res. 39 (2005) 3189–3198.

[140] T.A. Kurniawan, W.H. Lo, G.Y.S. Chan, Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate, J. Hazard. Mater. 129 (1–3) (2006) 80–90.

[141] X. Ntampou, A.I. Zouboulis, P. Samaras, Appropriate combination of physico-chemical methods (coagulation/flocculation and ozonation) for the efficient treatment of landfill leachate, Chemosphere 62 (5) (2006) 722–730.

[142] I. Monje-Ramirez, O. Velásquez, Removal of transformation of recalcitrant organic matter from stabilized saline landfill leachate by coagulation–ozonation coupling process, Water Res. 38 (2004) 2359–2367.

[143] J.J. Wu, C.C. Wu, H.W. Ma, C.C. Chang, Treatment of landfill leachate by ozone-based advanced oxidation processes, Chemosphere 54 (2004) 997–1003.

[144] J. Yu, D.D. Sun, J.H. Tay, Characteristics of coagulation–flocculation of humic acid with effective performance of polymeric flocculant and inorganic coagulant, Water Sci. Technol. 47 (1) (2003) 89–95.

[145] F.J. Rivas, F. Beltrán, F. Carvalho, B. Acedo, O. Gimeno, Stabilized leachate: sequential coagulation–flocculation + chemical oxidation process, J. Hazard. Mater. B116 (2004) 95–102.

[146] B. Slomczynska, J. Wasowski, T. Siomczynski, Effect of advanced oxidation processes on the toxicity of municipal landfill leachates, Water Sci. Technol. 49 (4) (2004) 273–277.

[147] T.A. Kurniawan, W.H. Lo, G.Y.S. Chan, Removal of refractory contaminants from stabilized landfill leachate using ozone-oxidized granular activated carbon (GAC), in: Proceedings of the 5th International Symposium on Wastewater Reclamation and Reuse for Sustainability, Jeju, Korea, 08–11 November, 2005.

[148] T.A. Kurniawan, G.Y.S. Chan, W.H. Lo, S. Babel, Comparison of low-cost adsorbents for treating wastewater laden with heavy metals, Sci. Total Environ. 366 (2–3) (2006) 409–426.

[149] R.M.R. Zamora, A.D. Moreno, M.T.O. Velásquez, I.M. Ramírez, Treatment of landfill leachates by comparing advanced oxidation and coagulation–flocculation processes coupled with activated carbon adsorption, Water Sci. Technol. 41 (2000) 231–235.

[150] S.H. Gau, F.S. Chang, Improved Fenton method to remove recalcitrant organics in landfill leachate, Water Sci. Technol. 43 (1996) 315–322.

[151] M.X. Loukidou, A.I. Zouboulis, Comparison of two biological treatment processes using attached-growth biomass for sanitary landfill leachate treatment, Environ. Pollut. 111 (2) (2001) 273–281.

[152] H.D. Robinson, P.J. Maris, The treatment of leachate from domestic waste in landfill sites, JWPCF 22 (1) (1983) 30–38.

[153] D. Geenens, B. Bixio, C. Thoeye, Combined ozone-activated sludge treatment of landfill leachate, Water Sci. Technol. 44 (2–3) (2000) 359–365.

[154] J.H. Bae, S.K. Kim, H.S. Chang, Treatment of landfill leachate: ammonia removal via nitrification and denitrification and further COD reduction via Fenton's treatment followed activated sludge, Water Sci. Technol. 36 (1997) 341–348.

[155] I.O. Koh, X.L. Chen, K. Hicke, W. Thiemann, Leachate treatment by the combination of photochemical oxidation with biological process, J. Photochem. Photobiol. A: Chem. 162 (2004) 261–271.

[156] N.J. Karrer, G. Ryhiner, E. Heinzle, Applicability test for combined biological-chemical treatment of wastewaters containing biorefractory compounds, Water Res. 31 (5) (1997) 1013–1020.

[157] S.H. Lin, C.C. Chang, Treatment of landfill leachate by combined electro-Fenton oxidation and sequencing batch reactor method, Water Res. 34 (17) (2000) 4243–4249.

[158] R.L. Irvine, L.H. Ketchum, Sequencing batch reactor in biological wastewater treatment, Crit. Rev. Environ. Contr. 18 (1989) 255–294.

[159] M. Altinbaş, C. Yangin, I. Ozturk, Struvite precipitation from anaerobically treated municipal and landfill wastewaters, Water Sci. Technol. 46 (2002) 271–278.

[160] N.K. Shammas, L.K. Wang, Ozonation, in: L.K. Wang, Y.T. Hung, N.K. Shammas (Eds.), Physico-chemical Treatment Processes: Handbook of Environmental Engineering, vol. 3, Humana Press, Totowa, NJ, 2005, pp. 315–358.

[161] H.J. Fan, H.Y. Shu, H.S. Yang, W.C. Chen, Characteristics of landfill leachate in Central Taiwan, Sci. Total Environ. 361 (1–3) (2006) 25–37.

[162] W.R. Haag, J. Hoigné, H. Bader, Improved ammonia oxidation by ozone in the presence of bromide ion during water treatment, Water Res. 18 (9) (1984) 1125–1128.

[163] B. Weber, F. Holz, Combination of activated sludge pre-treatment and reverse osmosis, in: T.H. Christensen, R. Cossu, R. Stegmann (Eds.), Landfilling of Waste Leachate, Elsevier, Amsterdam, 1992, pp. 323–332.

[164] X.Z. Li, Q.L. Zhao, X.D. Hao, Ammonium removal from landfill leachate by chemical precipitation, Waste Manage. 19 (1999) 409–415.

[165] J. Kettern, R. Steegmans, C. Maurer, Optimization and cost reduction in biological-chemical oxidative landfill treatment, in: Proceedings of the 5th International Landfill Symposium, Sardinia, Italy, 1995, pp. 559–566.

[166] T.A. Kurniawan, G.Y.S. Chan, W.H. Lo, S. Babel, Physico-chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J. 118 (1–2) (2006) 83–98.

[167] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. 97 (1–3) (2003) 219–243.