Advanced Oxidation Processes (AOPs) in Wastewater Treatment

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Abstract Advanced oxidation processes (AOPs) were first proposed in the 1980s for drinking water treatment and later were widely studied for treatment of different wastewaters. During the AOP treatment of wastewater, hydroxyl radicals (OH·) or sulfate radicals ($SO_4^{·-}$) are generated in sufficient quantity to remove refractory organic matters, traceable organic contaminants, or certain inorganic pollutants, or to increase wastewater biodegradability as a pre-treatment prior to an ensuing biological treatment. In this paper, we review the fundamental mechanisms of radical generation in different AOPs and select landfill leachate and biologically treated municipal wastewater as model wastewaters to discuss wastewater treatment with different AOPs. Generally, the treatment efficiencies rely heavily upon the selected AOP type, physical and chemical properties of target pollutants, and operating conditions. It would be noted that other mechanisms, besides hydroxyl radical or sulfate radical-based oxidation, may occur during the AOP treatment and contribute to the reduction of target pollutants. Particularly, we summarize recent advances in the AOP treatment of landfill leachate, as well as advanced oxidation of effluent organic matters (EfOM) in biologically treated secondary effluent (BTSE) for water reuse.

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Introduction

Advanced oxidation processes (AOPs) utilizing powerful hydroxyl or sulfate radicals as a major oxidizing agent were first proposed in the 1980s for potable water treatment. Later, AOPs were broadly applied for treatment of different types of wastewaters because the strong oxidants can readily degrade recalcitrant organic pollutants and remove certain inorganic pollutants in wastewater. The objective of this study was to review the fundamentals of and recent advances in the advanced oxidation processes for wastewater treatment. In particular, AOPs for treatment of landfill leachate are discussed in detail.

Advanced Oxidation Processes

Advanced oxidation processes (AOPs) were first proposed for potable water treatment in the 1980s [1, 2], which are defined as the oxidation processes involving the generation of hydroxyl radicals (OH·) in sufficient quantity to effect water purification. Later, the AOP concept has been extended to the oxidative processes with sulfate radicals ($SO_4^{·-}$). Different from common oxidants such as chlorine and ozone that have a dual role of decontamination and disinfection, AOPs are applied primarily for destruction of organic or inorganic contaminants in water and wastewater. Although AOP inactivation of pathogens and pathogenic indicators have been studied [3, 4], they are rarely employed for disinfection because these radicals

have too short half-life (on the order of microseconds), so that the required detention times for disinfection are prohibitive due to extremely low radical concentrations [5]. When AOPs are applied for wastewater treatment, these radicals, as a powerful oxidizing agent, are expected to sufficiently destruct wastewater pollutants, and transform them to less and even non-toxic products, thereby providing an ultimate solution for wastewater treatment [6].

Hydroxyl Radical-Based AOPs

Hydroxyl radical is the most reactive oxidizing agent in water treatment, with an oxidation potential between 2.8 V (pH 0) and 1.95 V (pH 14) vs. SCE (saturated calomel electrode, the most commonly used reference electrode) [5]. OH· is very nonselective in its behavior and rapidly reacts with numerous species with the rate constants on the order of 10^8–10^{10} M^{-1} s^{-1}. Hydroxyl radicals attack organic pollutants through four basic pathways: radical addition, hydrogen abstraction, electron transfer, and radical combination [7]. Their reactions with organic compounds produce carbon-centered radicals (R· or R·–OH). With O_2, these carbon-center radicals may be transformed to organic peroxyl radicals (ROO·). All of the radicals further react accompanied with the formation of more reactive species such as H_2O_2 and super oxide ($O_2^{\cdot-}$), leading to chemical degradation and even mineralization of these organic compounds. Because hydroxyl radicals have a very short lifetime, they are only in situ produced during application through different methods, including a combination of oxidizing agents (such as H_2O_2 and O_3), irradiation (such as ultraviolet light or ultrasound), and catalysts (such as Fe^{2+}) [6]. Hydroxyl radical generation mechanisms of the major AOPs for wastewater treatment are briefly summarized below.

Ozone-Based AOPs

Ozone (O_3) is a strong oxidant itself with an oxidation potential of 2.07 V vs. SCE. However, direct O_3 oxidation is a selective reaction, with typical reaction rate constants of 1.0×10^0–10^3 M^{-1} s^{-1} [8], in which O_3 preferentially reacts with the ionized and dissociated form of organic compounds, rather than the neutral form. Under certain conditions, OH· is produced from O_3 to initiate the indiscriminate oxidation (indirect mechanisms). Different detailed mechanisms have been proposed to explain the complex OH· generation, and the overall reaction involving OH· generation is expressed as below [8].

$$3O_3 + H_2O \rightarrow 2OH\cdot + 4O_2 \tag{1}$$

In the presence of other oxidants or irradiation, the OH· yield can be significantly improved. For example, in the so-called peroxone (O_3/H_2O_2) system, the O_3 decomposition and OH· production are enhanced by hydroperoxide (HO_2^-) produced from H_2O_2 decomposition.

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{2}$$

$$HO_2^- + O_3 \rightarrow OH\cdot + O_2^- + O_2 \tag{3}$$
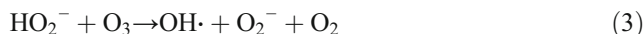
In the O_3/ultraviolet (UV) irradiation, H_2O_2 is generated as an additional oxidant primarily through O_3 photolysis (Eq. 4)

$$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2 \tag{4}$$
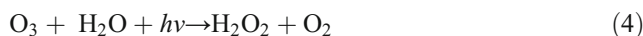
As a consequence, OH· can be generated, at a minimum, through three pathways: (1) ozonation (Eq. 1); (2) O_3/H_2O_2 (Eqs. 2 and 3); and (3) photolysis of H_2O_2, as shown in Eq. 5.

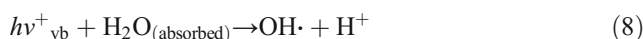$$H_2O_2 + hv \rightarrow 2OH\cdot \tag{5}$$

UV-Based AOPs

Hydroxyl radicals can be initiated by photons in the presence of catalysts or oxidants. The most common catalyst is titanium dioxide (TiO_2), a RO-type semiconductor. TiO_2 particles are excited to produce positive holes in the valence band (hv^+_{vb}) with an oxidative capacity, and negative electrons at the conduction band (e^-_{cb}) with a reductive capacity, as follows:

$$TiO_2 + hv \rightarrow e^-_{cb} + hv^+_{vb} \tag{6}$$

With the reactions of OH^-, H_2O, and $O_2^{\cdot-}$ at the surface of TiO_2, these holes and electrons can further form hydroxyl radicals [9].

$$hv^+_{vb} + OH^-_{(surface)} \rightarrow OH\cdot \tag{7}$$

$$hv^+_{vb} + H_2O_{(absorbed)} \rightarrow OH\cdot + H^+ \tag{8}$$

$$e^-_{cb} + O_{2\ (absorbed)} \rightarrow O_2^{\cdot-} \tag{9}$$

In the presence of oxidants such as H_2O_2 or O_3, additional OH· may be yielded under the UV irradiation. For example, a H_2O_2 molecule is cleaved by UV irradiation to generate two OH·.

$$H_2O_2 + hv \rightarrow 2OH\cdot \tag{10}$$

In addition, at a wavelength less than 242 nm, OH· can also be produced possibly through photolysis of H_2O.

$$H_2O + hv \rightarrow OH\cdot + H\cdot \tag{11}$$

Fenton-Related AOPs

Among these metals that are able to activate H_2O_2 and produce hydroxyl radicals in water, iron is the most frequently used. In the so-called Fenton process, H_2O_2 reacts with Fe^{2+} to generate strong reactive species. The reactive species

produced are traditionally recognized as hydroxyl radicals, though other substances such as ferryl ions are proposed. The Fenton-related chemistry for water and wastewater treatment has been discussed in detail elsewhere [10]. The classical Fenton radical mechanisms primarily involve the following reactions:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \tag{12}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \tag{13}$$

$$OH\cdot + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \tag{14}$$

$$OH\cdot + Fe^{2+} \rightarrow Fe^{3+} + OH^- \tag{15}$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2H^+ \tag{16}$$

$$Fe^{2+} + HO_2^{\cdot} + H^+ \rightarrow Fe^{3+} + H_2O_2 \tag{17}$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \tag{18}$$
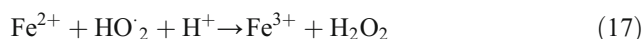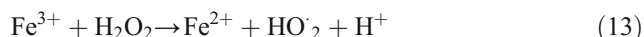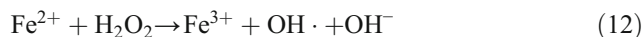
OH· is generated from Eq. 12 through electron transfer. However, OH· produced can be scavenged by either of Fenton reagents as shown in Eqs. 13 and 14. Therefore, the optimal molar ratio of iron ion to hydrogen peroxide needs to be experimentally determined for minimization of the unwanted scavenging. Although Eq. 13 indicates that the produced Fe^{3+} from Eq. 12 can be reduced to Fe^{2+}, the iron cannot be a catalyst in the Fenton system because the rate constant in Eq. 13 is several orders of magnitude less than that in Eq. 12. Consequently, Fe^{3+} forms iron sludge at typical water and wastewater treatment conditions. The sludge needs to be separately disposed of, thus increasing the treatment complexity and operational costs. Of note, the generation of hydroxyl radicals during the Fenton reaction is the most effective only at an acidic pH condition. As a result, the application of Fenton reaction for wastewater treatment is restricted in practice.

Based on the classical Fenton treatment scheme, three modified Fenton processes are proposed, including the Fenton-like system, photo-Fenton system, and electro-Fenton system. In the Fenton-like reaction, Fe^{2+} is replaced by ferric ion (Fe^{3+}), namely, the series of reactions in the Fenton system are initiated from Eq. 13 in the Fenton-like system, rather than from Eq. 12 in the traditional Fenton treatment. In the photo-Fenton reaction, UV irradiation is applied with the traditional Fenton system with a major purpose of enhancing the UV-induced reduction of dissolved Fe^{3+} to Fe^{2+}. In the electro-Fenton reaction, either or both of the Fenton reagents may be generated through electrochemical methods.

Other AOPs

A few other AOPs have been studied for different wastewater treatment, such as ultrasound (US) irradiation and electronic-beam irradiation. Under the US irradiation (16 kHz–100 MHz), alternate compression and rarefaction cycles of the sound waves can lead to three successive stages of cavities (i.e., nucleation, growth, and implosive collapse) that are made of vapor and gas-filled microbubble. The microbubble collapse can immediately generate a high temperature (4200–5000 K) and a high pressure (200–500 atm). Under such extreme conditions, water molecules in the form of gas within microbubbles are fragmented to generate hydroxyl radicals.

$$H_2O \rightarrow OH\cdot + H\cdot \tag{19}$$

Electronic-beam irradiation generates various free radicals in water through splitting water.

$$H_2O + e^- \rightarrow 2.7\,OH\cdot + 2.7\,H_3O^+ + 2.6\,e^- + 0.7\,H_2O_2$$
$$+ 0.6\,H\cdot + 0.45\,H_2 \tag{20}$$
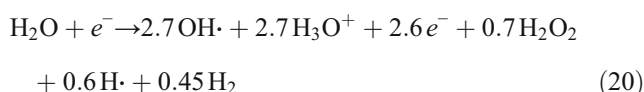
The coefficients in Eq. 20 are the G values that are defined as the number of excited states, radicals, or other products formed or lost in a system, when 100 eV of energy is absorbed [6]. Besides OH·, the AOP generates also strong reducing species—e^- and H·.
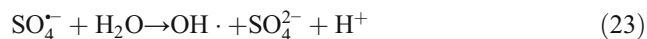
Sulfate Radical-Based AOPs

$S_2O_8^{2-}$ itself is a strong oxidant with a standard oxidation potential (E^o) of 2.01 V [11, 12]. Once activated by heat, ultraviolet (UV) irradiation (Eq. 21), transitional metals (Eq. 22), or elevated pH, $S_2O_8^{2-}$ can form more powerful sulfate radicals ($SO_4^{\cdot-}$, E^o=2.6 V) to initiate sulfate radical-based advanced oxidation processes [13, 14].

$$S_2O_8^{2-} \xrightarrow{\Delta/UV} 2SO_4^- \tag{21}$$

$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^- + SO_4^{2-} + M^{n+1} \tag{22}$$
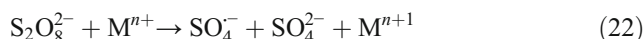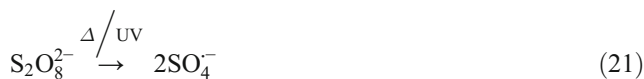
Elevated pH can also activate persulfate, but the relevant mechanisms are still unclear [15]. In a thermally activated persulfate method, the temperature applied broadly ranges within 35 and 130 °C [15]. As seen in Eqs. 21 and 22, with the same molar persulfate concentration, the metal activation method only generates 50 % of a sulfate radical yield produced from the heat or UV-activated persulfate method. Therefore, the metal activation method is not theoretically efficient. The most frequently used metals include ferrous (Fe(II)) and ferric (Fe(III)) ions, though other metals have been demonstrated to have an activation capability, such as Cu(I) and Ag(I) [16].

Similar to hydroxyl radicals, sulfate radicals are highly reactive species with a short lifespan, though both radical species have different reaction patterns. Hydroxyl radicals

preferably add to C=C bonds or abstract H from C–H bonds during their reactions with organic compounds [17]. In contrast, sulfate radicals tend to remove electrons from organic molecules that are subsequently transformed to organic radical cations [18]. It would be noted that hydroxyl radicals can also be produced from sulfate radicals through Eqs. 23 and 24 [19].

$$SO_4^{\bullet-} + H_2O \rightarrow OH \cdot + SO_4^{2-} + H^+ \qquad (23)$$

$$SO_4^{\bullet-} + OH^- \rightarrow OH \cdot + SO_4^{2-} \qquad (24)$$

Particularly, Eq. 24 shows that more hydroxyl radicals can be generated from sulfate radicals at an alkaline condition.

Multiple Mechanisms Occurring During AOPs for Wastewater Treatment

Besides OH· or $SO_4^{\bullet-}$-based oxidation, other mechanisms simultaneously occurring during the AOP treatment may remove target pollutants in wastewater. The contribution of the non-radical oxidative mechanisms in the contaminant removal may be dominant or insignificant, depending on the AOP type and reaction conditions. Mechanisms concurrently occurring in different AOP treatments are summarized in Table 1.

AOPs for Treatment of a High-Strength Wastewater—Landfill Leachate

Since the concept of AOPs was proposed in the 1980s, different advanced oxidation technologies have been widely studied and applied for treatment of municipal wastewater and various industrial wastewaters. The treatment efficiency relies heavily upon chemical properties of contaminants and operating conditions. It is impossible to cover all the investigations on the AOP treatment of wastewaters in this review. Rather, as an example, here, we review AOPs for treatment of a typical high-strength wastewater—landfill leachate.

Over the past five decades, landfilling has consistently remained the dominant disposal method of municipal solid wastes in the USA [20, 21]. A major environmental concern of landfills is continuous production of landfill leachate. Leachate is formed when water passes through solid waste in a landfill cell and the water content of solid waste is above field capacity (FC) of the deposited waste. Landfill leachate is a high-strength wastewater, exhibiting acute and chronic toxicity, with a variety of organic wastes and inorganic species [22–26]. Dissolved organic matters, ammonia, heavy metals, and xenobiotic organic compounds are major contaminants in landfill leachate [22]. If not properly managed or treated, these contaminants may cause serious pollution to groundwater,

Table 1 Major mechanisms for organics removal during wastewater treatment by different AOPs

AOP types	Oxidant for advanced oxidation	Other occurring mechanisms
O_3	OH·	Direct O_3 oxidation
O_3/H_2O_2	OH·	Direct O_3 oxidation
		H_2O_2 oxidation
O_3/UV	OH·	UV photolysis
UV/TiO_2	OH·	UV photolysis
UV/ H_2O_2	OH·	UV photolysis
		H_2O_2 oxidation
Fenton reaction	OH·	Iron coagulation
		Iron sludge-induced adsorption
Photo-Fenton reaction	OH·	Iron coagulation
		Iron sludge-induced adsorption
		UV photolysis
Ultrasonic irradiation	OH·	Acoustic cavitation generates transient high temperatures (≥5000 K) and pressures (≥1000 atm), and produce H· and HO_2·, besides OH·
Heat/persulfate	$SO_4^{\bullet-}$	Persulfate oxidation
UV/persulfate	$SO_4^{\bullet-}$	Persulfate oxidation
		UV photolysis
Fe(II)/persulfate	$SO_4^{\bullet-}$	Persulfate oxidation
		Iron coagulation
		Iron sludge-induced adsorption
OH^-/persulfate	$SO_4^{\bullet-}$ / OH·	Persulfate oxidation

surface water, and soil [21]. For example, New Jersey is the US state with the most Superfund sites, and approximately 25 % of these contaminated sites were polluted by landfill leachate [27]. Recently, leachate management has become an increasingly important component in integrated and sustainable solid waste management as a result of gradually tightened regulations and significant associated expenses. In the solid waste industry, leachate management has a typical capital cost ranging between $750K and $14M, accounting for 20–33 % of operating costs in landfills (no. 1 single landfill operating expense) [28, 29].

The earliest leachate treatment began in the 1970s [30–32]. The initial efforts were focused on application of the biological and physical/chemical treatment technologies that have been widely used in treatment of municipal wastewater. However, limited success was accomplished because leachate contaminants are typically more complex and recalcitrant than sewage. In the 1990s, AOPs were first applied for treatment of landfill leachate, particularly mature or biologically stabilized leachate [33–36]. The primary purpose of AOP application includes the following: (1) to increase the biodegradability of organics for following biological treatment, (2) to directly remove organic constituents, or (3) to further degrade organics as a post-treatment unit for other technologies [37, 38].

Treatment Efficiency

Deng [37] summarized the treatment efficiencies of different AOPs for treatment of landfill leachate. *Ozonation* of landfill leachate removed 6–88 % of chemical oxygen demand (COD) with an average value of 53 % and a standard deviation of 24 %. The major operational parameters include pH and O_3 dosage. As mentioned before, the oxidation mechanism shifts toward direct O_3 oxidation under acidic conditions, whereas OH· oxidation becomes dominant at an alkaline condition, particularly above pH 10.0. O_3 preferentially attacks aromatics, olefins, phenols, and S-containing organics, but slowly reacts with acetylenes, aldehydes, ketones, alcohols, alkanes, and carboxylic acids [9], while OH· almost reacts with most organic molecules, except organic compounds such as carbon tetrachloride, chloroform, tetrachloroethane, and trichloroethane in landfill leachate [39, 40]. Moreover, the COD removal efficiencies in the O_3/H_2O_2 treatment of landfill leachate range from 18 to 78 %, with an average value of 43 % and a standard deviation of 23 %. The COD removal efficiency in the O_3/UV treatment of landfill leachate varies between 31 and 83 %, with an average value of 52 % and a standard deviation of 19 %. And, the UV/H_2O_2 treatment of landfill leachate removed 57 and 92 % of the initial COD, with an average value of 77 % and a standard deviation of 11 %.

The *Fenton processes*, whether the traditional or modified, constantly exhibit a strong capacity for leachate treatment. Based on 24 data from 17 literatures, Deng

[37] reported that the COD removal efficiencies of Fenton treatment for landfill leachate range between 35 and 90 %, with an average COD removal efficiency of 71 % and a standard deviation of 13 %. Singh and Tang [41] reviewed 30 publications on the Fenton treatment of landfill leachate and found that the COD removal varied between 31 and 95 %. Englehardt et al. [42] made preliminary cost analysis of different physical/chemical treatment technologies for landfill leachate and concluded that the Fenton process is the most cost-effective. However, solid iron sludge, as the iron reduction by-product, is continuously produced accompanied with the mitigation of organic pollutants. The undesirable sludge needs to be disposed of, thereby increasing the operational treatment costs [43]. Moreover, the Fenton process is only effective at an acidic pH (typically 3.0–4.0) [43]. As a consequence, the pH adjustment significantly increases the treatment costs and risks in the storage, transportation, and handling of strong acid.

Besides solution pH and Fenton reagents' doses, the molar ratio of Fenton reagents (i.e., Fe(II) and H_2O_2) is an essential operating factor to determine the COD removal efficiency. Because either of the two chemicals can scavenge the OH·, the optimal molar ratio of Fe(II) to H_2O_2 should be experimentally determined to minimize their scavenging effects. Of note, both oxidation and iron sludge-induced coagulation during the Fenton treatment can reduce organics [44–48]. Their relative contributions to the COD removal rely heavily upon solution pH, as well as the molar ratio and absolute doses of Fenton reagents [48].

Treatment Issues

Two critical issues have been proposed for hydroxyl radical-based AOPs for treatment of landfill leachates [37]. Firstly, though a major purpose of AOP application is to increase leachate biodegradability for subsequent biological treatment reactors, the improvement in the leachate biodegradability is very poor in practices. The leachate effluent BOD_5/COD after AOP treatment is below 0.50 in most cases [49]. Therefore, AOPs appear not to be a suitable pre-treatment option for biological treatment. Secondly, hydroxyl radical-based AOPs difficultly remove ammonia nitrogen, the other major leachate pollutant, because hydroxyl radicals have a very slow reaction rate with ammonia [50].

Recent Studies

Over the past 5 years, AOPs have remained a research focus as a leachate treatment option, and the knowledge of the AOP treatment of landfill leachate has been advanced.

Sulfate Radical-Based AOPs for Leachate Treatment

Deng and Ezyske [51] first attempted to apply a heat-activated persulfate system for treatment of a mature landfill leachate. They found that the SR-AOP could simultaneously oxidize refractory organic matters and ammonia nitrogen, advantageous over traditional hydroxyl radical AOPs that was unable to remove ammonia nitrogen. In the thermally activated persulfate system, the treatment efficiency was primarily influenced by solution pH, temperature, and persulfate dose. An acidic condition (pH 3.0–4.0), higher temperature, and higher chemical dose favored the treatment. Up to 100 % ammonia and 91 % COD could be finally removed by the sulfate radical AOPs. Later, different sulfate radical-based AOPs (SR-AOPs) have been studied. Zhang et al. [52] tested an electro/Fe^{2+}/peroxydisulfate process and found that oxidation and coagulation both contributed to the COD reduction. The treatment was highly affected by pH, current density, and chemical dose, and an optimal ferrous concentration existed for the treatment. Amr et al. [53, 54] optimized a combined ozonaton and persulfate oxidative system for treatment of a stabilized landfill leachate. The maximum removal values of COD, color, and NH_3-N were 72, 93, and 55 %, respectively, and BOD_5/COD was increased from 0.05 to 0.29.

AOPs for Mitigation of UV-Quenching Organic Matters in Landfill Leachate

Discharge of leachate to publicly owned treatment works (POTWs) is a common and preferred leachate management practice in the USA, due to the lowest treatment cost and the least management complexity as compared to other strategies. However, the benefits of this option have diminished in many cases due to adverse impacts from the leachate discharged to POTWs, as it can significantly interfere with UV disinfection performance after the introduction of strongly UV-quenching substances in the leachate [55]. The emerging issue is seriously challenging the solid waste industry because a regulatory trend toward less chlorination disinfection by-products (DBPs), but with the same pathogen inactivation requirement, is forcing POTWs to turn from traditional chlorination to alternative UV disinfection. POTWs with UV disinfection that receive in excess of approximately 3 % by volume of leachate are susceptible to ineffective disinfection and may reduce or eliminate leachate acceptance or require pre-treatment to remove UV-absorbing materials. Recent interests have been focused on AOPs for mitigation of the leachate-induced UV absorbance. For example, the Fenton process has been attempted as a polishing treatment for biologically treated leachate with a purpose of the UV-absorbing reduction. More than 90 % of UV_{254} in raw leachate can be removed after the Fenton treatment. Particularly, Fenton oxidation targets bio-refractory UV-quenching humic substances that are mainly >1 kDa [56, 57].

Role of Inorganic Species in the AOP Treatment of Landfill Leachate

Although hydroxyl radicals are the most powerful oxidants in engineering systems, hydroxyl radical AOPs typically achieve a moderate COD removal efficiency in treatment of a landfill leachate. Deng et al. [58] investigated the effects of inorganic species abundantly existing in landfill leachate on the Fenton treatment efficiency. Results showed that nitrate did not significantly affect the COD removal rate. In contrast, sulfate (SO_4^{2-}) and chloride (Cl^-), particularly the latter, inhibited Fenton oxidation, because their competition with target organic pollutants for OH· as well as their competition with H_2O_2 to form Fe(III) complexes prevented the Fe(II) regeneration from Fe(III) reduction.

Fenton Treatment of Landfill Leachate

Singh and Tang [41] recently completed statistical analysis of optimum Fenton oxidation conditions for landfill leachate. Based on this study, the optimal pH ranges at 2.5–4.5 with a median pH of 3.0 for raw and coagulated landfill leachate and varies within 2.5–6.0 with a median pH of 4.2 for biologically treated leachate. Moreover, a median optimum molar ratio of ferrous ion to hydrogen peroxide is 3.0, much lower than the theoretically calculated ratio. Furthermore, they found a universal Fenton oxidation relationship between COD removal efficiency (η) and COD loading factor (L_{COD}), which is defined as the initial COD (COD_0) of leachate with respect to available O_2 for oxidation, for landfill leachate treatment [59], as follows:

$$H = 0.733 L_{COD} - 0.182 \quad (L_{COD} = 0.03 - 72.0) \quad (25)$$

AOPs for Treatment of Effluent Organic Matters in Biologically Treated Secondary Effluent

Rapidly expanding population, escalating water consumption, and dwindling water resources have severely aggravated the water shortage problem on a global scale, particularly in arid and water-stressed areas, making water reuse a strategically important approach to meet the current and future water demand [60, 61]. Water reclamation has been long practiced for non-potable urban, industrial, and agricultural scenarios, as well as to augment potable water supplies through indirect or direct reuse [60]. Among various reclaimed water sources, biologically treated secondary effluents (BTSE) produced from wastewater treatment plants (WWTPs) represent a stable

non-seasonal source, generally meeting 87 of the 93 numerical primary and secondary drinking water standards without further treatment [62]. Effluent organic matters (EfOM) in BTSE, similar to other BTSE pollutants such as nutrients, play an essential role in tertiary wastewater treatment and water reuse. EfOM is a complex mixture primarily comprised of extracellular polymeric substances (EPS), soluble microbial products (SMPs), and natural organic matter (NOM) derived from drinking water sources [63, 64]. Detailed information regarding the EfOM characteristics is available elsewhere [65, 66]. Despite a few benign effects in limited cases, EfOM has, at least, five adverse impacts on physical, chemical and biological treatment of BTSE [65], including the following:

1) Potential precursor for disinfection by-product formation
2) Fouling adsorbents and membranes
3) Increasing the dose of coagulant or oxidant
4) Causing corrosion
5) Supporting biomass growth as substrate in water distribution networks

Many US states have their own guidelines to limit the maximum organic content in reclaimed water (e.g., $BOD_5 \leq 10$ mg/L in urban unrestricted reclaimed water in New Jersey). Different treatment options are considered to remove EfOM in treated wastewater, among which AOPs have increasingly attained great attention.

AOPs have been well demonstrated to effectively reduce UV_{254} of EfOM (removal efficiency >90 %) [65, 67]. However, the reported DOC removal varies broadly within a range of 15–70 % [67–72]. Here, reaction kinetics and thermodynamics information and reaction pathways on hydroxyl radical oxidation of EfOM are discussed. And, different AOP technologies for the removal of EfOM is described in detail elsewhere [66].

Electron pulse radiolysis techniques and ozonation tests are employed to determine absolute bimolecular reaction rate constants ($k_{OH\cdot\text{-}EfOM}$) for the reactions between OH· and EfOM (or certain EfOM isolates) [73–77]. The rate constants broadly range between 0.27 and 35.0×10^8 $M_c^{-1} s^{-1}$ (Table 2). The disparity among the measured data is principally due to the different EfOM compositions. COD, retention onto NH_2 extraction medium, TOC, and fluorescence index (FI) are recognized as major parameters, accounting for approximately 62 % of the variability among the various $k_{OH\cdot\text{-}EfOM}$. The temperature dependence of the reactions between OH· and EfOM allows for the determination of key Arrhenius activation energies (E_a) and thermodynamic parameters. A recent study indicates that E_a of three EfOM samples, which were calculated from kinetics tests at 8–41 °C, were 15.16 ± 1.32, 10.71 ± 2.02, and 16.95 ± 1.67 kJ mol^{-1}, respectively [78].

EfOM plays a key role in advanced oxidation of BTSE because it as a major water matrix component is able to rapidly react with OH·, as aforementioned. The OH· scavenging due to EfOM was greater than due to inorganic components such as ammonia and phosphorus. The relative reduction in the UV absorbance of EfOM during AOP treatment was strongly and unambiguously correlated with the removal of emerging micropollutants such as pharmaceutical and personal care products (PPCPs) [79]. Studies showed that these unselectively active radicals tend to attack more oxygen-rich, less hydrophobic, and more biodegradable EfOM molecules [80]. Meanwhile, OH· can react with fluorophores and consistently reduce EfOM fluorescence. Fluorescence excitation-emission matrix (EEM) analysis reveals that this fluorescence reduction is the most prominent in the EEM region associated with SMPs [71]. Of interest, a previous study compared ozonation and UV/H_2O_2 (a commonly used AOP) for degradation of EfOM. Results showed that direct O_3 oxidation and OH· produced from UV/H_2O_2 can both decompose biopolymers and effectively eliminate humics and other oxidation by-products. However, O_3 poorly oxidizes low molar mass (LMM) acids that are accumulated throughout the treatment, while OH· is capable to readily decompose the LMM acids,

Table 2 Absolute bimolecular reaction rate constants for the reaction between OH· and EfOM

$k_{OH\cdot\text{-}EfOM}$ ($\times 10^8$ $M_c^{-1} s^{-1}$)	EfOM type	Ref.
2.5	EfOM from 28 WWTPs	[76]
0.27~1.21 (average: 0.86 ± 0.35)	EfOM from 8 WWTPs	[77]
1.72 ± 0.13	Hydrophobic neutral EfOM isolate from a WWTP	[75]
3.62 ± 0.31	Transphilic acid EfOM isolates from a WWTP	[75]
4.53 ± 0.53	Transphilic neutral EfOM isolates from a WWTP	[75]
6.32~14.1	EfOM from 4 WWTPs	[74]
14.3~35.0	<1 kDa EfOM from 4 WWTPs	[74]
1.83 ± 0.25	<3 kDa EfOM from 4 WWTPs	[74]
1.32 ± 0.23	<5 kDa EfOM from 4 WWTPs	[74]
1.26 ± 0.35	<10 kDa EfOM from 4 WWTPs	[74]
2.3~2.8	EfOM from 2 WWTPs	[73]

suggesting that AOPs are advantageous over ozonation in terms of EfOM removal.

Identification of the oxidation products subsequent to advanced oxidation of EfOM is also of great interest. Fenton oxidation was tested to remove up to 30 % of the total carbon concentration, accompanied with the formation of oxidation products such as oxalic, formic, and acetic acids and, less prominently, formaldehyde, acetaldehyde, propionaldehyde, and glycolaldehyde [79]. Production of these EfOM oxidation products is also correlated with EEM changes [71]. Another study examined the OH· exposures and attendant changes of fluorescence-based parameters, which allowed for establishment of strong linear relationships between formation of the aldehydes and carboxylic acids and the relative changes of integrated fluorescence [81].

Conclusions

Traditional hydroxyl radical-based advanced oxidation processes have been studied for treatment of wastewaters over the past three decades. The major purpose of HR-AOP is to remove recalcitrant organic matters, traceable emerging contaminants, in addition to certain inorganic pollutants. The treatment efficiency relies primarily on the AOP types, physical/chemical properties of target pollutants, and operational conditions. Recently, SR-AOP has also attracted attention for wastewater treatment. Sulfate radicals have a similar strong oxidative capacity and a short lifespan but different reaction patterns from hydroxyl radicals. For example, SR-AOPs are able to readily oxidize ammonia nitrogen in wastewater, which can be rarely removed by HR-AOPs. Particularly, AOPs for treatment of landfill leachate and EfOM in BTSE have been reviewed. Previous studies have demonstrated that AOPs are a technically viable option for leachate treatment and water reuse. In the future research, the development of cost-effective AOPs needs to be investigated.

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