

Advanced Oxidation Handbook

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**American Water Works
Association**

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Introduction

WHAT IS ADVANCED OXIDATION?

Advanced oxidation technologies (AOTs) involve the use of powerful oxidizing intermediates (e.g., the hydroxyl radical $\cdot\text{OH}$) that can oxidize and degrade primarily organic pollutants from contaminated air and water. The term *advanced* is used because the chemical reactions involved are essentially the same (except billions of times faster) as the reactions that would occur if these pollutants were exposed in a natural environment. AOTs oxidize a broad range of contaminants, including those that are not readily removed with other advanced technologies (e.g., reverse osmosis or granular activated carbon).

Most of the commercially viable AOTs use either ozone or photochemical processes [i.e., ultraviolet (UV) or visible light] to generate $\cdot\text{OH}$ radicals. Although conventional ozone treatment relies on oxidation, ozone treatment alone is not considered an AOT. Ozone-based AOTs would include ozone combined with hydrogen peroxide or UV to form hydroxyl radicals. This handbook will present a range of AOTs, but the focus is limited to UV and ozone-based AOTs as they are the most commonly used AOTs in municipal treatment applications.

Treatment with AOTs leads not only to the destruction of the target pollutants susceptible to oxidation but also, given sufficient treatment time, to complete mineralization (i.e., the only products are CO_2 , H_2O and mineral acids [e.g., HCl , HNO_3 , H_2SO_4 , etc.] for any Cl, N, S, etc. present in the pollutants) of the pollutants and their by-products. However, because the intermediate products of AOT reactions are often nontoxic and/or readily biodegradable with biological treatment (Linden et al. 2015), treatment to complete mineralization, in most cases, is not necessary nor cost-effective.

This handbook provides a brief introduction (with examples) to the concepts related to the fundamentals, design, and operation of AOTs. It is designed to help the beginner and to provide important reference material for those experienced with AOTs; however, this handbook is not intended to be an exhaustive review of all concepts related to AOTs. The following are recommended references for additional information:

- AOT reviews
 - Bolton and Cater (1994)
 - Legrini et al. (1993)
 - Ikehata and Gamal El-Din (2006)
- AOT books
 - Braun et al. (1991)
 - Oppenländer (2003)
 - Tarr (2003)
 - Parsons (2004)
- UV light fundamentals and photochemistry
 - Wayne and Wayne (1996)
 - Bolton and Cotton (2008)
 - Bolton (2010)

WHAT ARE POSSIBLE APPLICATIONS OF ADVANCED OXIDATION?

AOTs may be considered for treatment of many source waters to oxidize contaminants. However, there are three principal applications where AOTs provide effective treatment and are cost-effective when compared to other treatment technologies (e.g., granular activated carbon, membranes, etc).

Micropollutant Treatment

Micropollutants are pollutants present in water at microgram-per-liter ($\mu\text{g/L}$) or lower concentrations. These include volatile organic compounds (VOCs), pesticides, herbicides, endocrine-disrupting compounds, personal care products, pharmaceuticals, and so on. Most micropollutants are not easily treated in conventional water treatment processes, and there is concern about their potential health effects. For example, endocrine-disrupting compounds, at certain doses, are known to interfere with the hormone system of mammals and can cause cancerous tumors, birth defects, or developmental disorders. The solvent stabilizer 1,4-dioxane is an example of a micropollutant that is not readily removed or oxidized with other treatment technologies.

Treatment of Taste-and-Odor Compounds

During warmer months, some drinking water sources are subject to algal blooms that generate taste-and-odor compounds, such as geosmin and 2-methylisoborneol (MIB). Although these compounds do not represent a health hazard, they are detectable to customers at concentrations in the nanogram-per-liter range (ng/L) because they give drinking water an unpleasant taste and odor. Algal blooms may also be accompanied by the presence of algal toxins (e.g., microcystin) that do have known health effects.

Table 1-1 Advanced oxidation history

Date	Development	Reference
1894	Description of decomposition of tartaric acid by the addition of hydrogen peroxide (H ₂ O ₂) to solutions containing ferrous ion (Fe ²⁺) at a pH of about 3. This is now known as the <i>Fenton reaction</i> .	Fenton 1894
1900	H ₂ O ₂ observed to be decomposed by light.	Kistiakowsky 1900
1929	Proposed that the UV photolysis of H ₂ O ₂ yields ·OH radicals.	Urey et al. 1929
1956	Described the photolysis of ozone in solution, determined the quantum yield, and identified O ₂ and H ₂ O ₂ as the products.	Taube 1956
1957	Determination that the quantum yield of H ₂ O ₂ photolysis is 1.0.	Baxendale and Wilson 1957
1968	Description of products of the vacuum UV (VUV) photolysis of water.	Getoff and Schenck 1968
1975	Proposal of a mechanism for the decay of ozone that involved a pathway for the generation of ·OH radicals.	Hoigné and Bader 1975
1979	Introduction of the O ₃ / H ₂ O ₂ process.	Nakayama et al. 1979
1982	Description of the UV/O ₃ oxidation of trichloroethylene	Peyton et al. 1982
1987	First comprehensive reviews of advanced oxidation processes involving ozone, hydrogen peroxide, and ultraviolet light. Introduction of the term <i>advanced oxidation technologies</i> (AOTs).	Glaze et al. 1987
1996, 2001	Introduction of the energy efficiency concepts of electrical energy per order and electrical energy per mass.	Bolton et al. 1996, 2001
2012	Introduction of UV dose scale-up approach for UV-based AOTs.	Bircher et al. 2012

Recycled Water Treatment

There is increasing interest in the reuse and recycling of wastewater. Most wastewater contaminants can be removed from secondary effluents using membranes; however, many micropollutants cannot be completely removed by such treatments [e.g., 1,4-dioxane or *N*-nitrosodimethylamine (NDMA)]. Recycled water applications can also have a range of contaminants that are not typically found in most drinking water applications and AOTs can provide a broad treatment barrier for these contaminants, especially if the water is indirectly or directly augmenting potable water supplies.

HISTORY OF ADVANCED OXIDATION

The book by Oppenländer (2003) has a compilation of historical events related to the development of AOTs. Table 1-1 presents some important landmarks related to AOTs.

GOVERNMENT REGULATIONS

Ozone- and UV-based AOTs involve similar technologies and equipment as used for disinfection applications. Disinfection applications have well-defined standards and regulations that can be used to dictate equipment sizing. These standards include ozone concentration-detention time requirements (i.e., CT tables) and UV dose tables. Standard guidance for the design, operation, monitoring, and reporting of ozone and UV disinfection facilities can be found in the US Environmental Protection Agency (USEPA) guidance manuals. However, there are no USEPA guidance manuals available to aid in the design and operation of AOT facilities. The design of AOT systems are site-specific, dependent on the target contaminants and water quality, and vary by process and system manufacturer.

Water treatment at many utilities may be impacted by regulated or unregulated contaminants that can be effectively treated by AOTs. As part of the Safe Drinking Water Act, the USEPA has established maximum contaminant levels (MCLs) for a wide range of contaminants. Some of these contaminants are difficult to treat with conventional methods but can be effectively treated with AOTs (e.g., atrazine). For AOT applications targeting regulated contaminants, compliance is based on maintaining concentrations below the MCL based on the defined monitoring frequency. Therefore, the utility has flexibility in the design and operation of the AOT facility as long as concentrations are maintained below the MCL. For AOTs targeting unregulated contaminants (e.g., taste and odor), there is no USEPA required monitoring or reporting, and the system design and operation would then be based on utility preferences and any requirements of the governing agency.

State regulatory agencies may also develop notification levels, health advisory levels, or action levels for many micropollutants that do not have USEPA MCLs. For example, 1,4-dioxane, which is primarily treated with AOTs, has a USEPA health advisory level of 0.35 mg/L but does not have a drinking water MCL. Many states have adopted drinking water guidelines for 1,4-dioxane (Table 1-2). As with federally regulated contaminants, compliance with any US state notification or action levels would be based on maintaining concentrations below the required level based on the state required monitoring frequency.

The USEPA also regulates several potential by-products from AOTs as part of the Stage 1 and Stage 2 Disinfectant and Disinfection By-product Rules. These include bromate (ozone-based AOTs and UV/chlorine only) and disinfection by-products (DBPs) (total trihalomethanes and haloacetic acids). AOTs do not directly form regulated DBPs; however, depending on the site, specific water quality can increase the formation potential once chlorine is added to the water. AOT by-products are discussed in more detail in chapter 6.

In the United States, requirements for reuse or recycled water applications are typically more state-specific as many micropollutants found in wastewater are unregulated by the USEPA. Water reuse is defined as “the use of treated municipal wastewater (reclaimed water)” (USEPA et al. 2012) and is synonymous with water recycling. Reuse

Table 1-2 Example US state guidelines for 1,4-dioxane (as of June 2015)

State	Guideline	Description	Concentration ($\mu\text{g/L}$)
California	Notification Level	Health based advisory level with public notification requirements	1
Colorado	Interim Ground Water Standard	State groundwater regulation	0.35
Connecticut	Action Level	Level above which remedial action is recommended	3
Maine	Maximum Exposure Guideline	Non-enforceable recommendation for maximum concentrations	4
Massachusetts	Guideline	Non-regulatory limit set by state	0.3
North Carolina	Groundwater Quality Standard	State maximum allowable concentration	3

can be further divided into potable and nonpotable application. Potable reuse applications are ones where the treated water would be used for augmentation of drinking water supplies either directly or indirectly. Potable reuse applications often employ AOTs for treatment of a broad range of contaminants.

Nine US states (as of 2012) have developed potable reuse rules, regulations, or guidelines for the design and operation of a reuse facility (USEPA et al. 2012). In 2012, the USEPA released the *Guidelines for Water Reuse* (USEPA et al. 2012), which provides general recommendations for treatment and water quality goals for wastewater reuse (Table 1-3). Advanced wastewater treatment, which includes advanced oxidation, is listed as a suggested treatment technology for indirect potable reuse with finished water quality recommended to meet drinking water standards. The reuse guidelines also recommend providing a multibarrier approach for microbiological and chemical contaminants and advanced technologies that address a broader variety of contaminants with greater reliability. AOTs can help to meet both of these recommendations. AOTs may also be useful in nonpotable reuse applications as well, depending on project goals and requirements.

ADVANTAGES AND DISADVANTAGES OF ADVANCED OXIDATION

Advantages and disadvantages for AOTs are described in the following section.

AOT Advantages

1. Degrades organic contaminants and does not transfer to another phase that must be treated or disposed of [e.g., reverse osmosis (RO) brine or granular activated carbon (GAC) media].

2. Converts most refractory organic contaminants (not treatable biologically) into forms that are biologically treatable.
3. Very effective in treating most micropollutants.
4. Nonselective and can treat a broad range of contaminants simultaneously.
5. Oxidizes taste-and-odor compounds from drinking water.
6. Complements other technologies in water reuse applications by providing a barrier for a broad group of microconstituents.
7. Reactions are very fast and contact times are in the range of a few seconds.
8. Provides simultaneous microbial disinfection while degrading contaminants.

AOT Disadvantages

1. Can be expensive in terms of capital and annual operations and maintenance (O&M) costs (i.e., power and chemical requirements).
2. Treated water should be tested for potential regulated and unregulated by-products.
3. Any hydrogen peroxide residual after treatment must be quenched if the water goes to a potable distribution system.
4. Most UV reactors contain mercury lamps, so breakage of UV lamps presents a possible mercury hazard. Site-specific evaluations can be completed to determine potential concentrations.
5. Power interruptions could inhibit effective system operation without expensive power conditioning equipment. This could result in some water not being treated unless the water is diverted to the influent of AOT process or waste.

Table 1-3 USEPA suggested guidelines for water reuse (USEPA et al. 2012)

Indirect Potable Reuse Category	Treatment	Reclaimed Water Quality
Groundwater recharge by injection into potable aquifers or Augmentation of surface water supply reservoirs	<ul style="list-style-type: none"> • Secondary • Filtration • Disinfection • Advanced wastewater treatment 	Includes, but not limited to, the following: <ul style="list-style-type: none"> • No detectable total coliform/100 mL • 1 mg/L Cl residual, minimum • pH = 6.5–8.5 • ≤2 NTU • ≤2 mg/L TOC of wastewater origin • Meets drinking water standards

AOT HANDBOOK ORGANIZATION

This handbook consists of twelve chapters and three appendices designed to provide basic technology background and important design and operational considerations for AOT. The handbook is organized as follows:

- **Chapter 2—Fundamentals of UV Light and Photochemistry.** Describes the fundamental principles of UV light generation and photochemical reactions as the basis of UV-based AOTs.
- **Chapter 3—Fundamentals of Advanced Oxidation.** Discusses radical formation, treatment mechanisms, and examples of AOTs applications.
- **Chapter 4—Advanced Oxidation Types.** Discusses the available AOTs and the general applications of each technology.
- **Chapter 5—Advanced Oxidation Equipment.** Summarizes the equipment required for the two most commonly used AOT systems in municipal applications (UV- and ozone-based AOTs)
- **Chapter 6—Effects of Water Quality on AOT Systems.** Discusses water quality parameters and by-products that should be considered when designing an AOT system.
- **Chapter 7—Possible Locations for AOT Facilities.** Discusses general applications where AOTs are an applicable technology.
- **Chapter 8—AOT System Design Considerations.** Discusses planning for AOT systems, including treatment goals, basic design parameters, hydraulics, electrical power considerations, treatability testing, and cost evaluations.
- **Chapter 9—Startup, Operations, and Maintenance.** Discusses startup and operation issues for AOT facilities, recommended monitoring, and maintenance tasks.
- **Chapter 10—AOT Case Studies.** Presents examples of AOT applications.
- **Chapter 11—Safety and Handling of AOT Equipment.** Discusses important health and safety concerns when designing and operating an AOT facility.
- **Chapter 12—Considerations for a Water Utility Manager.** Discusses important considerations for utilities considering the design of an AOT facility.
- **Appendix A Terms, Units, Symbols, and Definitions.**
- **Appendix B Rate Constants and Quantum Yields.**
- **Appendix C Calculation of Fraction of UV Absorbed for UV/H₂O₂ AOT.**

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