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**Guidelines for performance evaluation  
of treatment technologies for water  
reuse systems —**

**Part 7:  
Advanced oxidation processes  
technology**

*Lignes directrices pour l'évaluation des performances des techniques  
de traitement des systèmes de réutilisation de l'eau —*

*Partie 7: Technologie des processus d'oxydation avancés*



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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see [www.iso.org/directives](http://www.iso.org/directives)).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: [www.iso.org/iso/foreword.html](http://www.iso.org/iso/foreword.html).

This document was prepared by Technical Committee ISO/TC 282, *Water reuse*, Subcommittee SC 3, *Risk and performance evaluation of water reuse systems*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at [www.iso.org/members.html](http://www.iso.org/members.html).

## Introduction

Global warming and climate change have become worldwide concerns as many countries suffer from water shortages. There has been global investment to develop alternative water resources and secure water supplies. One of such efforts is water reclamation/reuse since it is readily available. At the same time, the implementation of the water reuse technology raises public and regulatory concerns on potential human health, environmental, and its social impacts. The water reclamation/reuse technology vendors and technology users have increased needs for defining various aspects of water reuse projects, for regulation and for international standardization. Without ISO water reuse standards, many opportunities for sustainable development based on water reuse could be lost.

Standardization of water reuse should include objective specifications, assessments of service level and water reuse system performance dependencies such as safety, environmental protection, resilience, and cost-effectiveness. Therefore, appropriate methods are needed to evaluate the performance of the reuse system.

Varying amounts of persistent organic pollutants (POPs) can be found dependent on the biological activity of the surrounding watershed and the geochemical circulation. POPs are organic compounds that are resistant to degradation. POPs typically are halogenated organic compounds which exhibit high lipid solubility, thus bioaccumulate in fatty tissues. Polyhalogenated organic compounds are of particular concern because of the stability and lipophilicity which are often correlated to their halogen content. Since POPs accumulate and are persistent, they can adversely affect human health and the environment as a result.

The performance of the treatment technology for water reuse should be properly evaluated in order to select the most appropriate technology to achieve the objectives of the water reuse project. Despite considerable research and development on therapeutic techniques, such scientific knowledge is largely depending on the scope of commercial interests. This document establishes a specific performance evaluation method for advanced oxidation processes (AOPs) for water reuse systems based on ISO 20468-1 as a generic standard. To address these issues, this document provides the evaluation of the performance of water reuse systems in many applications by providing methods that most stakeholders can accommodate.

At the ISO TC282/SC3 meeting, a general standard for performance evaluation based on the discussion entitled "Guidelines for Performance Evaluation of Processing Technologies for Water Reuse Systems - Part 1: General" in ISO 20468-1 was discussed. Technology, and combinations, thereof, and descriptions of representative technologies should be included in the individual standards submitted in accordance with ISO 20468-1. In this context, this document establishes a specific performance evaluation method for advanced oxidation processes (AOPs) for water reuse systems based on ISO 20468-1 as a generic standard.

AOP technologies represent a group of treatment processes (e.g., hydrogen peroxide/ozone, hydrogen peroxide/UV, ozone/UV, pH elevated ozonation, etc.) that rely on the production of hydroxyl radicals as a strong oxidant capable of the complete oxidation of most organic compounds.

In water reuse systems, AOP technologies are mainly applied for disinfection and for removing total organic carbon (TOC) including persistent organic pollutants (POPs) that are barely decomposed by conventional oxidation processes, as indicated in [Table A.1 \(Annex A\)](#). For instance, direct oxidation of chlorobenzene by ozone is known to occur very slowly; this reaction's second-order kinetic rate constant is less than  $1 \text{ M}^{-1}\text{s}^{-1}$ . On the other hand, the oxidation of chlorobenzene by  $\cdot\text{OH}$  is extremely rapid (up to  $4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ).

AOPs as an advanced level treatment are generally applied to tertiary treated water, as shown in Figure 1 of ISO 20468-1.

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# Guidelines for performance evaluation of treatment technologies for water reuse systems —

## Part 7: Advanced oxidation processes technology

### 1 Scope

This document provides a performance evaluation method of treatment technology using advanced oxidation processes (AOPs) for water reuse treatment. It introduces a system of evaluating water quality to validate AOP performance through typical parameters such as the concentration of hydroxyl radicals.

### 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 20670:2018, *Water reuse — Vocabulary*

### 3 Terms, definitions, and abbreviated terms

For the purposes of this document, the terms and definitions given in ISO 20670 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

#### 3.1 Terms and definitions

##### 3.1.1

##### **persistent organic pollutant (POP)**

chemical substances that persist in the environment, bio-accumulate through the food web, poses a risk of causing adverse effects to human health and the environment, and can be subject to long range transport away from its original source

Note 1 to entry: Substances are classified as POPs according to either The Protocol to the regional UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) on POPs, opened for signatures in June 1998 and entered into force on 23 October 2003 or the global Stockholm Convention on POP, opened for signatures in May 2001 and entered into force on 17 May 2004.

[SOURCE: ISO 26367-2:2017, 3.8<sup>[1]</sup>]

##### 3.1.2

##### **advanced oxidation process (AOP)**

process that generates hydroxyl radicals in sufficient quantity to remove organics by oxidation

### 3.1.2.1

#### hydrogen Peroxide/Ozone ( $\text{H}_2\text{O}_2/\text{O}_3$ )

combination of  $\text{H}_2\text{O}_2$  and ozone which is able to generate  $\cdot\text{OH}$

Note 1 to entry: When ozone is dissolved in water, it causes a complex chain of reactions that result in the formation of radicals including  $\cdot\text{OH}$  and superoxide radicals. The addition of hydrogen peroxide to ozone also generates  $\cdot\text{OH}$  radicals. The typical stoichiometry of hydrogen peroxide and ozone based on the mass ratio is from 0,35 to 0,45 because 0,5 moles of  $\text{H}_2\text{O}_2$  are required to every mole of  $\text{O}_3$  for the complete reaction of  $\cdot\text{OH}$  production.

### 3.1.2.2

#### hydrogen Peroxide/UV ( $\text{H}_2\text{O}_2/\text{UV}$ )

combination of  $\text{H}_2\text{O}_2$  and UV light which is able to generate  $\cdot\text{OH}$  through UV photolysis of  $\text{H}_2\text{O}_2$

Note 1 to entry: The oxidation of organics can occur by either direct photolysis or reactions with  $\cdot\text{OH}$  in  $\text{H}_2\text{O}_2/\text{UV}$  system.

### 3.1.2.3

#### ozone/UV ( $\text{O}_3/\text{UV}$ )

combination of ozone and UV light which is able to generate  $\cdot\text{OH}$  through UV photolysis of ozone

Note 1 to entry: UV photolysis of ozone where  $\text{H}_2\text{O}_2$  is generated as an intermediate, which then decomposes to  $\cdot\text{OH}$ . Due to the relatively high molar extinction coefficient of ozone ( $\epsilon_{254\text{ nm}} = 3\,300\text{ M}^{-1}\text{ cm}^{-1}$ ), ozone/UV radiation can generally produce more  $\cdot\text{OH}$  than  $\text{H}_2\text{O}_2/\text{UV}$  radiation.

### 3.1.2.4

#### Fenton reaction

reaction between iron(II) and hydrogen peroxide to yield  $\cdot\text{OH}$

Note 1 to entry: Fenton reaction can occur either in homogeneous systems with dissolved ferrous iron or in heterogeneous systems in the presence of complexed iron. The by-product, ferric iron, in turn reacts with peroxide or superoxide radical to reproduce ferrous iron. The reaction cycle of iron between the ferrous and ferric oxidation states continuous until the  $\text{H}_2\text{O}_2$  is fully consumed, producing  $\cdot\text{OH}$  in the process. As in other AOPs, the destruction of organics is primarily due to oxidation reactions initiated by the  $\cdot\text{OH}$ . Similar reactions can occur with copper (II) in place of iron (II).

### 3.1.2.5

#### hydroxyl radical scavengers

non-target substances that react to high degree of reactivity of hydroxyl radical

Note 1 to entry: Hydroxyl radical can oxidize a broad range of organic pollutants quickly and non-selectively. A drawback resulting from such a high degree of reactivity is that the hydroxyl radical also reacts with "non-target" materials in solution such as chloride, nitrite, bromide, carbonate, bicarbonate, and NOM, all of which are referred to as radical "scavengers".

Note 2 to entry: see [Annex D](#)

### 3.1.2.6

#### UV/ $\text{TiO}_2$

semiconductor photocatalysts that absorb light and involve the generation of oxidants (e.g.,  $\cdot\text{OH}$  and  $\text{O}_2\cdot^-$ ) for the destruction of organic pollutants

Note 1 to entry: When  $\text{TiO}_2$ , a semiconductor photocatalyst, is illuminated by UV light ( $\leq 400\text{ nm}$ ), valence band electrons are excited to the conduction band, resulting in the production of electron and hole pairs. These generated electron and hole pairs are capable of initiating a wide range of chemical reactions (e.g., direct oxidation/reduction, oxidants generation). Among them,  $\cdot\text{OH}$  oxidation is the primary mechanism for the destruction of POPs. The production of  $\cdot\text{OH}$  can occur via several pathways but, as with many of the other AOPs analysed, is readily formed from hydrogen peroxide.

**3.1.3****hydroxyl radical ( $\cdot\text{OH}$ )**

neutral form of hydroxide ion ( $\text{OH}^-$ ) which possesses an unpaired electron

Note 1 to entry: The unpaired electron makes it a powerful and non-selective chemical oxidant, which acts very rapidly with most organic compounds.

**3.1.4****redox potential**

potential of a reversible oxidation-reduction reaction in a given electrolyte recorded on a standard hydrogen electrode scale

[SOURCE: ISO 8044:2020, 6.1.37<sup>[2]</sup>]

**3.1.5** **$\cdot\text{OH}$  concentration**

molar concentration of  $\cdot\text{OH}$  in a unit volume of liquid

**3.1.6** **$\cdot\text{OH}$  monitor**

instrument capable of measuring  $\cdot\text{OH}$  concentration (3.1.5) in samples

**3.1.7****electrical energy per order**

electrical energy in kWh which required to degrade a contaminant by one order of magnitude in  $1\text{m}^3$  of contaminated water

Note 1 to entry: Electrical energy per order as a Figure-of-merit for AOPs has been accepted by the International Union of Pure and Applied Chemistry (IUPAC) in 2001<sup>[3]</sup>.

**3.1.8****UV transmittance**

the fraction of photons in the UV spectrum transmitted through a material such as water or quartz. It is preferable that an online UVT sensor be installed and used to verify UVT

Note 1 to entry: The wavelength of the UVT (unit %) should be specified, often using a path-length of 1 cm. The measurement is calibrated compared to ultra-pure water (ISO 3696 grade 1 or equivalent).

Note 2 to entry: UVT is related to the UV absorbance (A) by the following equation (for a 1- cm path length): % UVT =  $100 \times 10^{-A}$ .

**3.2 Abbreviated terms**

|                       |                              |
|-----------------------|------------------------------|
| AOP                   | advanced oxidation process   |
| $E_{\text{EO}}$       | electrical energy per order  |
| LCC                   | life cycle cost              |
| NOM                   | natural organic matter       |
| $\text{O}_2^{\cdot-}$ | superoxide anion radical     |
| $\cdot\text{OH}$      | hydroxyl radical             |
| $\text{OH}^-$         | hydroxide ion                |
| O&M                   | operation & maintenance      |
| POP                   | persistent organic pollutant |

|     |                             |
|-----|-----------------------------|
| ROS | reactive oxygen species     |
| SCE | saturated calomel electrode |
| TOC | total organic carbon        |
| UVT | ultraviolet transmittance   |

## 4 System components

AOP technologies generally follow tertiary treatment for the purpose of attaining higher quality treated wastewater for specific water reuse applications. AOPs involve the following two stages of oxidation: 1) the formation of strong radical oxidants (e.g.,  $\cdot\text{OH}$ ) and 2) the reaction of these radical oxidants with the water contaminants. However, the term AOPs refer specifically to processes in which oxidation of organic contaminants occurs primarily through reactions with  $\cdot\text{OH}$ . The ability of an oxidant to initiate chemical reactions can be measured in terms of its redox potential and  $\cdot\text{OH}$  is one of the most reactive oxidants in an aqueous phase with an oxidation potential of 2,8 V (pH 0) vs. NHE (normal hydrogen electrode). In water treatment applications, AOPs usually refer to a specific subset of processes that involve  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , and/or UV light. All of these processes can produce  $\cdot\text{OH}$  as non-selective oxidant enable to rapidly destroy a wide range of organic contaminants. Although a number of the processes noted above may have other mechanisms for destroying organic contaminants, in general, the effectiveness of AOPs is proportional to its ability to generate  $\cdot\text{OH}$ .

Established AOP systems include two representative cases:

- 1) one system produces  $\cdot\text{OH}$  based on the combination of chemical sources only (e.g.,  $\text{H}_2\text{O}_2/\text{O}_3$ , etc.); and
- 2) the other system produces  $\cdot\text{OH}$  based on the combination of chemical sources and UV light ( $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{UV}$ , etc.)

### 4.1 Chemical source feed unit

The chemical source unit supplies the generation/contact unit (e.g., combinations of  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , UV, etc.).

### 4.2 UV unit

A UV unit has simple components including an irradiation vessel and a power control panel. UV units may be categorized into closed and open systems, based on the configuration of UV units in the irradiation vessel. The closed system has a UV unit, comprised of a UV lamp and its sleeve, placed in the flow chamber. Meanwhile, the open system has a UV unit immersed in an open channel or tank.

### 4.3 $\cdot\text{OH}$ generation/contact unit

The  $\cdot\text{OH}$  generation/contact unit typically is a unit to produce  $\cdot\text{OH}$  using feeds, and directly applies the generated  $\cdot\text{OH}$  to the water, due to the high reactivity of  $\cdot\text{OH}$ . The unit normally includes jet injector for feeds or/and mechanical agitation for an even distribution of  $\cdot\text{OH}$ . The  $\cdot\text{OH}$  generation/contact unit occasionally includes a UV lamp for systems employing photons (e.g.,  $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{UV}$ ).

### 4.4 $\cdot\text{OH}$ monitoring point

The  $\cdot\text{OH}$  monitoring unit monitors the concentration of  $\cdot\text{OH}$  at the  $\cdot\text{OH}$  generation/contact unit either by ex-situ sampling and in-situ detecting.

## 5 Performance requirements and evaluation methods

The purpose of performance requirements and evaluation methods for AOP technology is to assess whether the performance of AOP processes meets specific requirements for attaining reclaimed water which satisfy the reclaimed water quality standards for the specific purposes of water reuse. Performance requirements and evaluation methods include specific performance evaluation procedures (e.g., water quality test,  $\cdot\text{OH}$  quantification test, monitoring protocol), safety requirement, and environmental/energy performance as functional and non-functional requirements, respectively<sup>[4],[5]</sup>.

### 5.1 Functional requirements

#### 5.1.1 General

The design of AOPs is governed by the influent contaminant concentration, target effluent contaminant concentration, desired flow rate, and background water quality parameters such as pH, bromide concentration, alkalinity, etc. The key design parameters for AOPs include: chemical dosages and ratios with other chemicals, reactor contact time, and reactor configuration. The optimum dosages, ratios, and contact time are water-specific and treatment scenario-specific and are often determined through pilot studies using the water matrix of interest. As can be expected, higher chemical dosages and contact times are typically expected to result in higher removal rates; however, increasing dosages results in higher O&M costs and possible by-product formation (e.g., bromate aldehydes, chlorate, etc.). However, in some cases, the formation of by-products can be limited by higher chemical ratios. While AOPs have been found to be effective for a wide variety of organic contaminants, this analysis will focus on the practical implementation of AOPs in water reclamation, specifically for the treatment of tertiary treated wastewaters. As previously mentioned, there are many water quality parameters that may impact the effectiveness of any particular AOP. For example, nearly all dissolved organic compounds present in the source water can negatively affect the removal efficiency of the target compound by consuming  $\cdot\text{OH}$ . Below is a brief discussion of each of these water quality parameters and the mitigation measures that can be taken to limit the adverse impact of these parameters on AOPs effectiveness. Regarding the indirect parameters to judge whether AOP technology fulfills the requirements,  $\cdot\text{OH}$  concentration in the treatment system can be used.

AOPs can be divided into established and emerging technologies based on the existing literatures. Emerging technologies are defined here as technologies that have very limited, if any, full-scale applications for water reuse system.

Established Technologies includes:

- 1) Hydrogen Peroxide/Ozone ( $\text{H}_2\text{O}_2/\text{O}_3$ );
- 2) Ozone/UV ( $\text{O}_3/\text{UV}$ ); and
- 3) Hydrogen Peroxide/UV ( $\text{H}_2\text{O}_2/\text{UV}$ )

Emerging Technologies includes:

- 1) Fenton Reaction; and
- 2) UV/ $\text{TiO}_2$

#### 5.1.2 Performance evaluation procedures

Established AOPs technologies can be divided into two cases: one is based on a coupling between chemical oxidants and the other is based on a combination of chemical oxidants and UV light ([Annex B](#)).

##### **CASE 1: AOPs based on the combination of chemical sources only ( $\text{H}_2\text{O}_2/\text{O}_3$ )**

When  $\text{O}_3$  is added to water, it participates in a complex chain of reactions that result in the formation of radicals such as the  $\cdot\text{OH}$  and the  $\text{O}_2\cdot^-$ . Unlike ozone, these radical products could effectively destroy POPs. For instance, direct oxidation of chlorobenzene by ozone is known to occur very slowly; this

reaction's second-order kinetic rate constant is less than  $1 \text{ M}^{-1}\text{s}^{-1}$ . On the other hand, the oxidation of chlorobenzene by  $\cdot\text{OH}$  is extremely rapid (up to  $4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ). The addition of hydrogen peroxide enables the initiation of the decomposition of ozone, leading to the formation of  $\cdot\text{OH}$ . The typical stoichiometry of hydrogen peroxide and ozone based on the mass ratio is from 0,35 to 0,45 because 0,5 moles of  $\text{H}_2\text{O}_2$  are required to every mole of  $\text{O}_3$  for the complete reaction of  $\cdot\text{OH}$  production.

Two  $\text{O}_3$  and hydrogen peroxide contact configurations are continuously stirred basins and plug flow reactors.

In an  $\text{O}_3$  unit,  $\text{O}_3$  is bubbled or injected through the base of the unit and allowed to diffuse through the unit until it either escapes through the top or is completely reacted. These units are typically covered so that excess  $\text{O}_3$  can be collected and directed to an off-gas decomposer.  $\text{H}_2\text{O}_2$  can be added either as a single slug dose or at multiple points in the system. Automatic monitoring and control systems are used to regulate chemical feed rates, pH, and other parameters. In addition, a variety of safety, monitoring, and control systems are included to facilitate operation. A schematic of an  $\text{H}_2\text{O}_2/\text{O}_3$  system is shown in [Figure 1](#) (upper).

The major components of both a continuously stirred tank reactor and a plug flow reactor include a  $\text{H}_2\text{O}_2$  storage tank, a  $\text{H}_2\text{O}_2$  injection system, an  $\text{O}_3$  generator, a liquid oxygen or oxygen from a concentrator, in-line static mixers and mechanical agitation,  $\text{O}_3$  injector, an  $\text{O}_3$  contactor, an  $\text{O}_3$  decomposer and/or off-gas recycling device, supply and discharge pumps and piping, monitoring and control systems.

#### **CASE 2: AOPs based on the combination of chemical sources and UV light ( $\text{O}_3/\text{UV}$ and $\text{H}_2\text{O}_2/\text{UV}$ )**

A simplified schematic diagram of case 2 system is shown in [Figure 1](#) (bottom).

For  $\text{O}_3/\text{UV}$  applications,  $\text{O}_3$  is introduced into the system at the bottom of each chamber by a stainless steel sparger or injector. The  $\text{O}_3$  generator employed in the system can electrically generate  $\text{O}_3$  from either air or liquid oxygen. Any  $\text{O}_3$  that is present in the off-gas is put through a decomposer and/or recycling device such as activated carbon, catalyst media and heat, or combination of heat and catalyst media<sup>[6]</sup>.

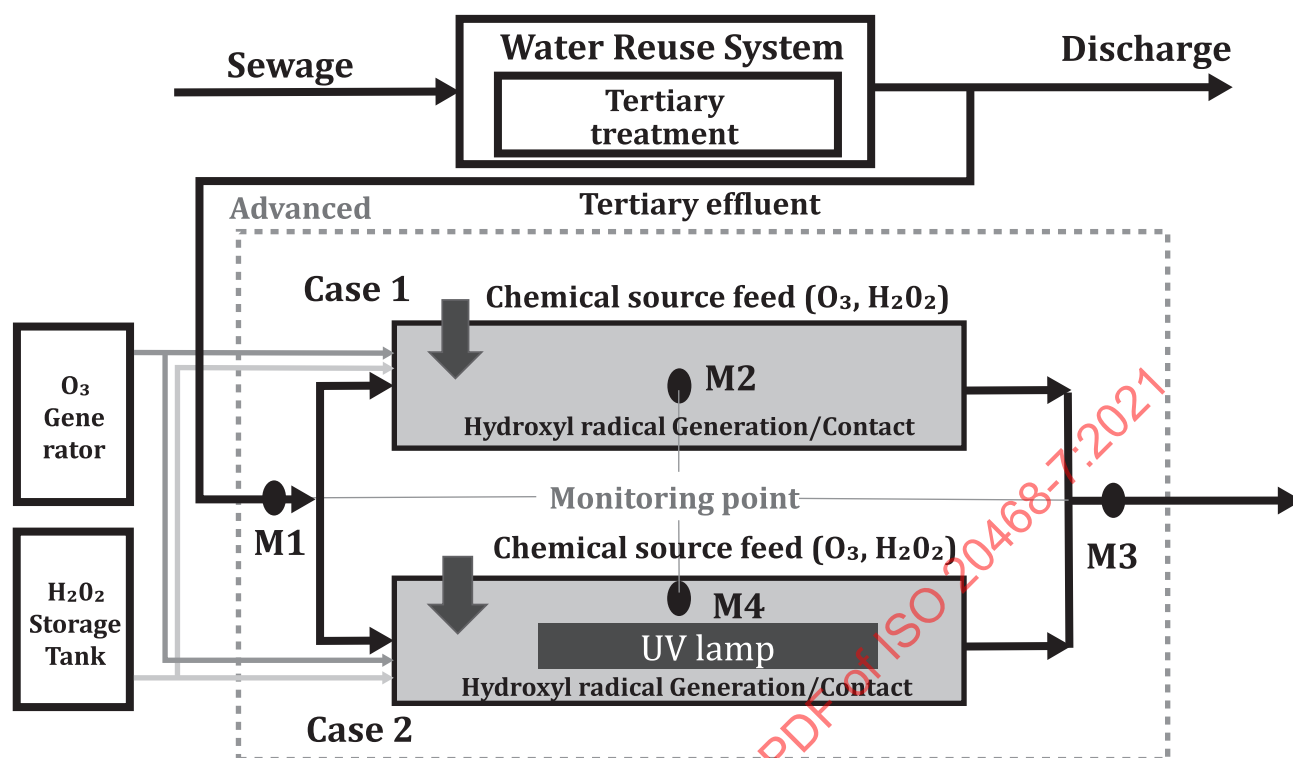
The major components of an  $\text{O}_3/\text{UV}$  system include UV lamps, sleeves, and cleaning system, an  $\text{O}_3$  generator and injectors, an  $\text{O}_3$  contactor, an  $\text{O}_3$  off-gas decomposer, an liquid oxygen or oxygen from a concentrator, supply and discharge pumps and piping, monitoring and control systems with appropriate sensors (UV intensity and UVT), and data recording and reporting utilities.

In case of  $\text{H}_2\text{O}_2/\text{UV}$  system, the key design and operating parameters include the  $\text{H}_2\text{O}_2$  dose, the UV lamp type and intensity, the reactor contact time, and the control systems (pH and temperature).  $\text{H}_2\text{O}_2$  can be added either as a single slug dose or at multiple points in the system. The optimum dose of  $\text{H}_2\text{O}_2$  should be determined for each water source based on bench and pilot-scale testing, but is commonly estimated as twice the TOC and not less than 1,0 to 2,0 mg/l.

The major components of a  $\text{H}_2\text{O}_2/\text{UV}$  system include UV lamps, sleeves, and cleaning system,  $\text{H}_2\text{O}_2$  storage and injection system, a reactor chamber, in-line mixer, supply and discharge pumps and piping, monitoring and control systems with appropriate sensors (UV intensity and UVT) and data recording and reporting utilities.

AOP systems are expected to further improve water quality parameters of tertiary treated wastewater, as an example, by removing remaining TOC including POPs. Performance of AOP systems should be evaluated by regularly measuring water qualities as direct parameters in which water quality shall satisfy the reclaimed water quality standards for the specific purposes of water reuse. In order to attain this, water quality parameters can be periodically evaluated at both inlet (M1, before treatment) and outlet (M3, after treatment) points.

As a complimentary evaluation method, the monitoring of  $\cdot\text{OH}$  concentration as indirect parameters should be utilized to evaluate the performance of AOP systems.  $\cdot\text{OH}$  concentration at M2 and M4 points (at  $\cdot\text{OH}$  generation/contact units) can be monitored. If at least one of water quality parameters does not meet standard value, AOP systems can have failure in the equipment. The possible failure may be  $\cdot\text{OH}$  production decrease or degradation of mass transfer efficiency.



## NOTE

Case 1 includes 1) Injection system (O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>), 2) liquid oxygen or oxygen from a concentrator, 3) O<sub>3</sub> contactor, 4) In-line static mixers and mechanical agitation, 5) O<sub>3</sub> decomposer and/or off-gas recycling device, 6) Supply and discharge pumps and piping, 7) Monitoring and control system, and 8) data recording and reporting utilities.

Case 2 includes all the components of case 1, and additionally includes 1) H<sub>2</sub>O<sub>2</sub> reactor chamber and 2) UV lamps, sleeves, and cleaning system.

**Figure 1 — AOP systems and monitoring points**

Evaluating the concentration of  $\cdot\text{OH}$  in the whole system would be difficult, so the evaluation can be conducted by sampling a small amount of water at the monitoring points. Evaluation can be done by using probe molecules (e.g., terephthalic acid, 5,5-dimethyl-1-pyrroline-1-oxide) (see [Annex C](#)), which are molecules that only react with  $\cdot\text{OH}$ . The concentration of the chemicals produced from the reaction with  $\cdot\text{OH}$  will be an indicator of the amount of  $\cdot\text{OH}$  occurring in the system.

Although the monitoring of  $\cdot\text{OH}$  concentration is necessary to evaluate AOPs, the in-situ measurement of  $\cdot\text{OH}$  may have difficulty since  $\cdot\text{OH}$  is a powerful, non-selective chemical oxidant reacting with most organic compounds rapidly. As an alternative method, the  $\cdot\text{OH}$  generation capability of the system can be evaluated by using ex-situ testing.

### **In-situ testing**

In-situ testing monitors the concentrations of  $\cdot\text{OH}$  by using probe molecules during the treatment of wastewater at a water treatment plant. (i.e., on-site).

### **Ex-situ testing**

Ex-situ testing evaluates the capability of  $\cdot\text{OH}$  generation in laboratory conditions. Samples are tested in the presence of probe molecules only (e.g., terephthalic acid, 5,5-dimethyl-1-pyrroline-1-oxide) (see [Annex C](#)). After a specified reaction time, the sample is analysed to determine the  $\cdot\text{OH}$  concentration as a function of chemical dose or/and UV dose.

### 5.1.3 UV transmittance

UVT functions as an index of UV demand. Monitoring of UVT can be used to feed data to the system controller to adjust the power of the lamp to assure that the required dose is provided. The UV dose achieved, and the amount of energy needed for AOP processes is impacted by the UV absorbing substances (e.g., TSS, TOC, etc.) which reduce UVT and thereby affect the treatment effect. UVT should be measured as often as needed at M4 point to attain specific OH radical concentration.

UVT can be assessed from a sample, but that due to the potential for variation in constituent presence and concentrations that can interfere with UVT, it is preferable that an online UVT sensor be installed and used to verify UVT<sup>[2]</sup>.

### 5.1.4 Monitoring procedure

Monitoring is a planned observation or measurement sequence where AOP is controlled and used to assess water quality stability. These observations are necessary for creating accurate records and for future verification.

Measurement or observation is typically monitored to indicate that AOP is operating within critical limits such as temperature, flow rate, glass breakage, etc. Workers shall be trained to accurately measure, read and record information using the appropriate tools. The monitoring period determines the amount of product affected by the critical limit deviation. Continuous monitoring is usually performed by a device that generates continuous records. If continuous monitoring is not possible, non-continuous (intermittent/periodic) monitoring is required. Non-continuous monitoring frequency can be affected by past history and knowledge of products and processes. Examples include visual inspection and sensory evaluation.

### 5.1.5 Safety requirement

Safety measurements are needed when the process requires UV light and ozone. The use of UV light can affect vision, and the use of ozone can impact lungs for people and animals. Cases when the process requires UV ( $O_3$ /UV and  $H_2O_2$ /UV), both UV radiation and high voltage supply interlocks on UV units shall be installed to protect personnel.

All potential outlets of ozone gas in AOPs process into the occupied areas or external atmosphere should be identified and contained and passed through an ozone destruction system with an effective ventilation system commensurate with the rate of ozone production and other risk factors. Where ozone is applied to liquids, it is important to consider that ozone will escape from solutions under most conditions. Precautions include ensuring all vessels containing ozonated liquids are air-tight or under negative pressure to prevent escape of ozone. After AOPs treatment, the discharge should be via close pipe work to close drains.

## 5.2 Non-functional requirements

### 5.2.1 General

The following three performance characteristics are provided:

1. Environmental performance;
2. Economic performance;
3. Dependability performance.

### 5.2.2 Environmental performance

Key factors of environmental performance:

— Energy consumption

Elevated levels of POPs will require greater energy due to increased recycling and increased oxidation to reduce the POP concentration.

$E_{EO}$  (Electrical energy per order) is an evaluation method to compare various types of AOPs as a function of energy consumption, which enables a rapid determination of the AOP system cost.

Calculations of  $E_{EO}$  are based on [Formula \(1\)](#);

$$E_{EO} = \frac{P \times t \times 1000}{V \times \lg \left( \frac{c_i}{c_f} \right)} \quad (1)$$

where

$P$  is the rated total power consumption [kW] of all components of the AOP system

$V$  is the volume in litres of the treated water

$t$  is the time in hours required to achieve a reduction by one order of magnitude in the concentration of a contaminant

$\lg$  is the symbol for the decadic logarithm

$c_i, c_f$  are the initial (or influent) and final (or effluent) concentrations of the contaminant [M or mol l<sup>-1</sup>]

Calculated  $E_{EO}$  values of AOP vary since there are several parameters that impact the  $E_{EO}$  values. In the cases using UV, there are parameters such as unit design, water quality, contaminant characteristics, lamp type, and design flow rate. These factors should be considered when comparing different types of AOPs<sup>[8]</sup>.

— Chemical consumption

To assess the chemical consumption several treatment scenarios to evaluate a typical range of reuse water production rates, influent POPs concentrations, and effluent treatment goals.

### 5.2.3 Economic performance

The Life Cycle Cost (LCC) consists of capital costs and operating costs, and is analysed by measuring the costs to purchase, install, operate (including energy costs and chemicals' costs), maintain, and dispose of all system components. Capital and Operation costs for each AOP process should be developed as a function of water quality, flow rate, influent indicator concentration, and required removal efficiency. These cost evaluations shall be performed under uniform design criteria (e.g., required removal efficiency) and operational assumptions (e.g., power rate). A unified costing approach will enable a direct comparison of the various AOPs for specific water qualities.

#### 5.2.4 Dependability performance

Key factors of dependability performance include:

- Production of required amounts of  $\cdot\text{OH}$

Hydroxyl radicals from AOPs that involve UV light and  $\text{H}_2\text{O}_2/\text{O}_3$  can react with and destroy a wide range of organic contaminants. In general, the effectiveness of an AOP is proportional to its ability to generate hydroxyl radicals. The dose of UV light and  $\text{H}_2\text{O}_2/\text{O}_3$  required per unit volume of water treated may vary the amount of hydroxyl radicals from one type of water to another.

- Assessing and addressing scavenging capacity

Since the oxidation through  $\cdot\text{OH}$  is the main mechanism of POP removal for each AOP discussed above, the presence of the hydroxyl radical scavenger (e.g., chloride, nitrite, bromide, carbonate, bicarbonate, NOM, etc.) affects the treatment performance independently of the selected AOP(s).

- Water quality

AOP treatment of POPs shall independently evaluate the impact of each water quality parameter such as pH, alkalinity, NOM, TOC, turbidity, and concentration of other interfering compounds.

- Equipment safety and operating requirements

AOPs ( $\text{H}_2\text{O}_2/\text{O}_3$ ,  $\text{O}_3/\text{UV}$ , and  $\text{H}_2\text{O}_2/\text{UV}$ ) are required to operate within the range of maximum to minimum allowable flow rates.

In addition, appropriate safety measures, which may include emergency shutdown, shall be implemented when the process requires ozone ( $\text{H}_2\text{O}_2/\text{O}_3$  and  $\text{O}_3/\text{UV}$ ). In order to confirm the ozone leakage in these cases, exhaust ozone concentration ( $\text{M}^3$ ), as shown in [Figure 1](#), shall be measured.

## Annex A (informative)

### Main treatment technologies and target constituents for water reuse

Table A.1 indicates main treatment technologies and target constituents after BOD removal for water reuse systems. It is summarized by focusing on typical technologies for advanced treatment and disinfection described in ISO 20468-1<sup>[9]</sup> with related functions required for water reuse.

**Table A.1 — Main treatment technologies and target constituents for water reuse (after BOD removal)**

| Functions required  |                     | Separation                    | Disinfection |                                |          | Desalination        | Oxidation or others |      |      |
|---------------------|---------------------|-------------------------------|--------------|--------------------------------|----------|---------------------|---------------------|------|------|
| Technologies        | Target Constituents | Turbidity or TSS              | Pathogens    |                                |          | Conductivity or TDS | Color               | Odor | POPs |
|                     |                     |                               | Bacteria     | Virus                          | Protozoa |                     |                     |      |      |
| Membrane filtration | MF                  | √                             | √            |                                | √        |                     |                     |      |      |
|                     | UF                  | √                             | √            | √                              | √        |                     |                     |      |      |
|                     | NF/RO               |                               | √            | √                              |          | √                   | √                   | √    | √    |
| Ion Exchange        | Resin               |                               |              |                                |          | √                   | √                   |      |      |
|                     | Membrane            |                               |              |                                |          | √                   |                     |      |      |
| UV                  |                     |                               | √            | √                              | √        |                     |                     |      |      |
| Ozone               |                     |                               | √            | √                              | √        |                     | √                   | √    | √    |
| AOPs                |                     |                               | √            | √                              | √        |                     | √                   | √    | √    |
| (Note)              |                     | Typical monitoring parameter* |              | Additional target constituents |          |                     |                     |      |      |

\* Reference: ISO 20468-1

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## Annex B (informative)

### Classification of AOPs

The AOPs can be roughly divided into non-photochemical methods and photochemical methods, which are shown in [Table B.1](#).

**Table B.1 — Classification of AOPs**

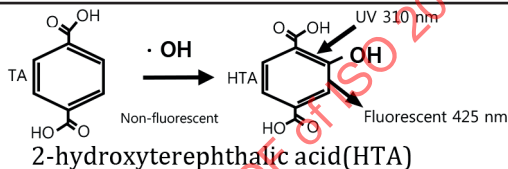
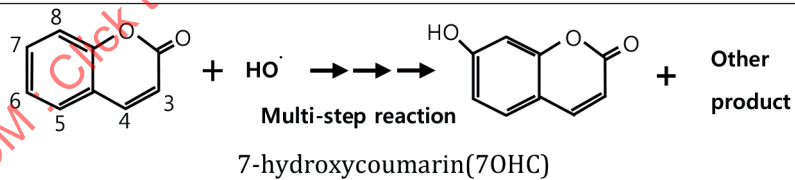
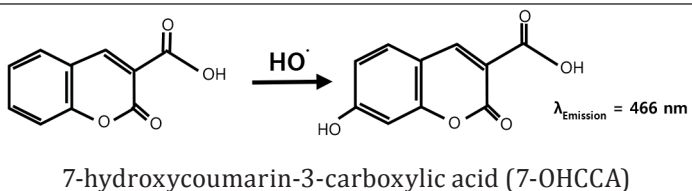
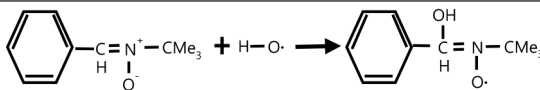
| Method                    | Type                     | Main reaction formula                                                                                                                                                                                                                                                       |
|---------------------------|--------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Non-photochemical methods | Ozonation at elevated pH | $3\text{O}_3 + \text{OH}^- + \text{H}^+ \rightarrow 2\text{HO}_2 + 4\text{O}_2$                                                                                                                                                                                             |
|                           | Hydrogen peroxide/Ozone  | $2\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow 2\text{HO}_2 + 3\text{O}_2$                                                                                                                                                                                                 |
|                           | Fenton                   | $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH}$ $\text{Fe}^{3+} + \text{H}_2\text{O}_2 \leftrightarrow \text{H}^+ + \text{Fe}-\text{OOH}^{2+}$ $\text{Fe}-\text{OOH}^{2+} \rightarrow \text{HO}_2 \cdot + \text{Fe}^{2+}$ |
| Photochemical methods     | Ozone/UV                 | $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1\text{D})$ $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 \rightarrow 2\text{HO} \cdot$                                                                                                 |
|                           | Hydrogen peroxide/UV     | $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{HO} \cdot$ $\text{H}_2\text{O}_2 \leftrightarrow \text{HO}_2^- + \text{H}^+$ $\text{HO}_2^- + h\nu \rightarrow \cdot\text{OH} + \text{O}^-$                                                                                 |
|                           | Photo-Fenton             | $\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})^{2+} + \text{H}^+$ $\text{Fe}(\text{OH})^{2+} \leftrightarrow \text{Fe}^{3+} + \text{OH}^-$ $\text{Fe}(\text{OH})^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \cdot\text{OH}$                            |
|                           | UV/TiO <sub>2</sub>      | $\text{TiO}_2 + h\nu \rightarrow (\text{h}^+ + \text{e}^-)$ $\text{e}^- + \text{O}_2 \rightarrow \text{O}_2 \cdot^-$ $\text{h}^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+$                                                                              |

## Annex C (informative)

### Reaction formulas and feature of indicator molecules capable of measuring $\cdot\text{OH}$

Table C.1 exemplifies methodologies (probe molecules and involved reactions) for measuring  $\cdot\text{OH}$ .

Table C.1 — Examples of methodologies for measuring  $\cdot\text{OH}$

| Indicator molecule                                      | Reaction                                                                                                                                                                                                                                                                                                                                     |
|---------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                                         | Feature                                                                                                                                                                                                                                                                                                                                      |
| Terephthalic acid (TA) <sup>[10]</sup>                  |  <p style="text-align: center;">2-hydroxyterephthalic acid (HTA)</p>                                                                                                                                                                                       |
|                                                         | <p><math>\cdot\text{OH}</math> can convert terephthalic acid to HTA, which can be detected by fluorescence measurement. When the solution containing TA and HTA molecules is irradiated by UV light (<math>\lambda = 310\text{nm}</math>), HTA molecules emit light at <math>\lambda = 425\text{nm}</math>, while TA molecules does not.</p> |
| 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) <sup>[11]</sup> | $\text{DMPO} + \cdot\text{OH} \rightarrow [\text{DMPO} - \text{OH}] \cdot$                                                                                                                                                                                                                                                                   |
|                                                         | <p>When the electron spin resonance (ESR) signal of the DMPO-OH adducts decreases or disappears, it can be concluded that the <math>\cdot\text{OH}</math> was scavenged.</p>                                                                                                                                                                 |
| Coumarin <sup>[12]</sup>                                |  <p style="text-align: center;">7-hydroxycoumarin (7OHC)</p>                                                                                                                                                                                             |
|                                                         | <p>Coumarin forms fluorescent 7OHC by reacting with <math>\cdot\text{OH}</math>. One advantage of using coumarin as the probe is that 7OHC fluoresces in the visible region fluorescence maximum around <math>\lambda = 456\text{nm}</math>. Disadvantage is that other hydroxycoumarins can be formed throughout the reaction.</p>          |
| Coumarin-3-carboxylic acid (CCA) <sup>[13]</sup>        |  <p style="text-align: center;">7-hydroxycoumarin-3-carboxylic acid (7-OHCCA)</p>                                                                                                                                                                        |
|                                                         | <p>CCA reacts with <math>\cdot\text{OH}</math> and produces 7-OHCCA which emits light at <math>\lambda = 446\text{nm}</math></p>                                                                                                                                                                                                             |
| Benzene <sup>[14]</sup>                                 | $\cdot\text{OH} + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{OH}(\text{phenol}) + \text{H}$                                                                                                                                                                            |
|                                                         | <p>Benzene reacts with <math>\cdot\text{OH}</math> and produces phenol, but there are some other products produced.</p>                                                                                                                                                                                                                      |
| Phenyl-tert-butyl nitron (PBN) <sup>[15]</sup>          |                                                                                                                                                                                                                                                          |
|                                                         | <p>PBN reacts with <math>\cdot\text{OH}</math> and produces PBN-<math>\text{HO}\cdot</math>. The PBN-<math>\text{HO}\cdot</math> can be detected by its fingerprint ESR signal.</p>                                                                                                                                                          |