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

Part 7: Advanced oxidation processes technology

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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.

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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.

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 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^[1]]

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 (H_2O_2/O_3)

combination of H_2O_2 and ozone which is able to generate $\cdot OH$ radicals

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 $\cdot OH$ and superoxide radicals. The addition of hydrogen peroxide to ozone also generates $\cdot OH$ 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 H_2O_2 are required to every mole of O_3 for the complete reaction of $\cdot OH$ production.

3.1.2.2

hydrogen Peroxide/UV (H_2O_2/UV)

combination of H_2O_2 and UV light which is able to generate $\cdot OH$ through UV photolysis of H_2O_2

Note 1 to entry: The oxidation of organics can occur by either direct photolysis or reactions with $\cdot OH$ in H_2O_2/UV system.

3.1.2.3

ozone/UV (O_3/UV)

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

Note 1 to entry: UV photolysis of ozone where H_2O_2 is generated as an intermediate, which then decomposes to $\cdot OH$. Due to the relatively high molar extinction coefficient of ozone ($\epsilon_{254\text{ nm}} = 3\ 300\ M^{-1}\ cm^{-1}$), ozone/UV radiation can generally produce more $\cdot OH$ than H_2O_2/UV radiation.

3.1.2.4

Fenton reaction

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

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 H_2O_2 is fully consumed, producing $\cdot OH$ in the process. As in other AOPs, the destruction of organics is primarily due to oxidation reactions initiated by the $\cdot OH$. 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/ TiO_2

semiconductor photocatalysts that absorb light and involve the generation of oxidants (e.g., $\cdot OH$ and $O_2\cdot^-$) for the destruction of organic pollutants

Note 1 to entry: When 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, $\cdot OH$ oxidation is the primary mechanism for the destruction of POPs. The production of $\cdot OH$ 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 (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^[2]]

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 C by one order of magnitude in 1m^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^[3].

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 = 100×10^{-A} .

3.2 Abbreviated terms

AOP	advanced oxidation process
E_{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
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 oxidant 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 O_3 , H_2O_2 , and/or UV light. All of these processes can produce $\cdot\text{OH}$ as nonselective 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 (O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, etc.)

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4.1 Chemical source feed unit

The chemical source unit supplies the generation/contact unit (e.g., combinations of O_3 , H_2O_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., $\text{H}_2\text{O}_2/\text{UV}$, O_3/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, $\cdot\text{OH}$ radical quantification test, monitoring protocol), safety requirement, and environmental/energy performance as functional and non-functional requirements, respectively^{[4],[5]}.

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 (O_3/UV); and
- 3) Hydrogen Peroxide/UV ($\text{H}_2\text{O}_2/\text{UV}$)

Emerging Technologies includes:

- 1) Fenton Reaction; and
- 2) UV/ 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 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