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Review article

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Advanced oxidation processes for water and wastewater treatment – Guidance for systematic future research

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ABSTRACT

Advanced oxidation processes (AOPs) are a growing research field with a large variety of different process variants and materials being tested at laboratory scale. However, despite extensive research in recent years and decades, many variants have not been transitioned to pilot- and fullscale operation. One major concern are the inconsistent experimental approaches applied across different studies that impede identification, comparison, and upscaling of the most promising AOPs. The aim of this tutorial review is to streamline future studies on the development of new solutions and materials for advanced oxidation by providing guidance for comparable and scalable oxidation experiments. We discuss recent developments in catalytic, ozone-based, radiationdriven, and other AOPs, and outline future perspectives and research needs. Since standardized experimental procedures are not available for most AOPs, we propose basic rules and key parameters for lab-scale evaluation of new AOPs including selection of suitable probe compounds and scavengers for the measurement of (major) reactive species. A two-phase approach to assess new AOP concepts is proposed, consisting of (i) basic research and proof-of-concept (technology readiness levels (TRL) 1–3), followed by (ii) process development in the intended water matrix including a cost comparison with an established process, applying comparable and scalable parameters such as UV fluence or ozone consumption (TRL 3-5). Subsequent demonstration of the new process (TRL 6-7) is briefly discussed, too. Finally, we highlight important research tools for a thorough mechanistic process evaluation and risk assessment including screening for transformation products that should be based on chemical logic and combined with complementary tools (mass balance, chemical calculations).

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1. Introduction

Advanced oxidation processes (AOPs) are generally defined as processes that use in situ generated highly reactive radicals for the oxidative degradation of contaminants [1]. The major radical formed in most AOPs is the hydroxyl radical (•OH) [2]. Besides the •OH, reactive oxygen species (ROS) including singlet oxygen and superoxide, radicals derived from persulfate, carbonate or nitrate, other dissolved inorganic constituents, and solvated electrons may be involved in AOPs and affect process kinetics, reaction mechanisms, and product formation [3,4]. Sulfate and chlorine radical-induced oxidations are often also referred to as AOP-like processes [5]. AOPs can be applied during drinking water and wastewater treatment, water reuse applications, brine and leachate treatment, and groundwater remediation, mostly to degrade organic contaminants but also for reduction of natural organic matter, disinfection or as pre-treatment to improve performance of downstream treatment processes [2,6–14]. Radicals for AOPs in water, including •OH, can be generated in many ways, while AOPs can be broadly classified into four categories that include ozone-based, radiation-driven, catalytic, and other AOPs. The latter encompass a range of different, often high-energy, physical methods for AOP generation.

Given the diversity of AOPs and the wide range of possible applications, research activity and interest into AOPs has been considerably increasing. Beyond AOPs established at full scale, various processes have been tested at pilot scale, while other AOPs are being explored and developed at lab scale (see Fig. 1). For instance, research has been conducted on the development of new materials for catalytic and electrolytic oxidation [15,16]. Similarly, new advanced oxidation processes such as vacuum UV, plasma treatment as well as new oxidants and radical promoters have been proposed and investigated [17–20]. Various alternative process combinations, from centralized treatment approaches to point-of-use-scale, but also reactor designs for catalytic or radiation-driven AOPs have been developed [15,21,22]. A large array of water contaminants, including so-called emerging contaminants, has been investigated to a

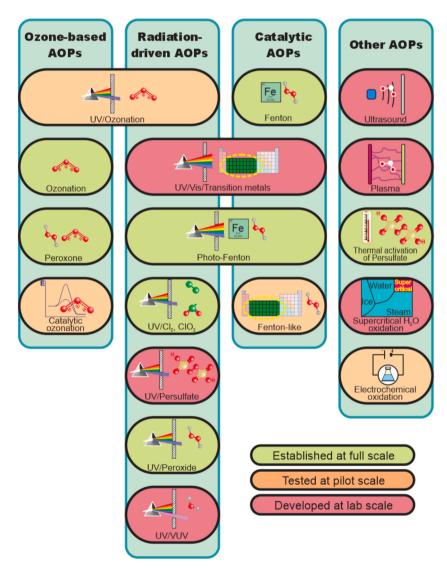


Fig. 1. Broad overview and classification of different AOPs and AOP-like processes.

great extent for their degradability by AOPs [2,23].

Despite several recent reviews on AOPs [2,5,24-26], it can be challenging for individual researchers to obtain a comprehensive insight and to keep track with the most recent developments in AOP research, given the large number of studies published. One needs to be critical when it comes to the prospective applicability of newly developed AOPs [27,28]. Despite extensive research and development, only a few established AOP variants have been developed from lab-to pilot- and full-scale implementation. The suitability of many novel AOPs for water treatment is debatable e.g., due to the utilization of materials with concerning toxicity, lack of long-term stability, or high energy demand [29-31]. Besides such obvious limitations, we hypothesize that flaws in experimental design and planning often hinder the assessment of new solutions and thereby the translation to pilot- and full-scale demonstration. AOP studies with new materials or new radical generation mechanisms often lack critical information that would allow a sound evaluation of the efficiency in real water matrices, including chemical and energy demand. One example are time-based reaction rate constants of target contaminants only but without further information on energy input, oxidant dose, or chemical reactivity of the target contaminant. Another issue can be the choice of adequate reference processes and treatment objectives. For instance, ozonation has been used as reference process to compare oxidative mineralization efficiency. However, a typical treatment target for ozonation is partial oxidation of target contaminants, followed by biofiltration, which has a significantly lower ozone dosage and, thus, energy demand [32,33] and mineralization is not required in most applications. Many studies combine the assessment of new materials and processes with the simultaneous investigation of new emerging contaminants, screening for transformation products, and the analysis of possible toxicological effects. While these aspects provide important information for a detailed understanding and assessment of the process itself, they do not enable an initial evaluation on the applicability and efficiency of the investigated process at larger scale. To streamline research efforts, systematic approaches are needed for an objective assessment of new AOPs for oxidation of emerging contaminants.

This tutorial review aims to guide researchers in developing innovative solutions and materials for advanced oxidation. The document is divided into five sections, allowing readers to separately explore specific aspects ranging from the current state of established and emerging AOPs to experimental design and the demonstration of novel AOPs.

- Section 2: We review the status, potential, and research needs for various AOPs, including ozone-based, radiation-driven, and catalytic methods, as well as emerging technologies like electrochemical oxidation, ultrasound, and non-thermal plasma.
- Section 3: This section evaluates the electrical energy per order (EEO) concept as a metric to assess and compare efficiency of AOPs.
- Section 4: Readers are directed to this section for guidance on selecting appropriate probe compounds and scavengers for oxidation experiments.
- Section 5: Describes experimental methodologies for systematic evaluation of AOPs at the laboratory scale.
- Section 6: Outlines a systematic approach for evaluating novel AOPs, from basic proof of concept to demonstration at approximately technology readiness levels (TRL) 6–7. It is structured to guide research from initial exploration (section 6.1, TRL 1–3), through process development and economic assessment (section 6.2, TRL 3–5), to pilot or full-scale application (section 6.3, TRL 6–7). The final section, 6.4, provides guidance on additional research needed to ensure that novel processes do not introduce new water quality hazards.

2. Status and perspectives for conventional and emerging oxidation processes

There is an immense variety of AOPs proposed and tested to generate radicals in water. Fig. 1 lists and categorizes various AOPs giving an indication of their respective technology readiness level. Established AOPs operating at full scale comprise mostly ozone- and UV -based approaches. In addition, Fenton-based processes are widely established for industrial wastewater treatment. Besides the long history applying ozone and UV irradiation in drinking water treatment [27], these most widely applied AOPs typically also provide the highest energy efficiencies among AOPs [25]. However, less efficient AOPs might still provide suitable solutions for specific applications, such as groundwater remediation, industrial wastewater treatment, degradation of otherwise recalcitrant contaminants, or decentralized water treatment applications with relatively small volumes of water, including specialized applications such as ballast water treatment [28,34,35]. In this section, we briefly address the current state of the art for different AOPs and provide references to studies with more detailed mechanistic discussion. We highlight advantages and limitations of individual AOPs, discuss future research needs, and identify potential areas for application. This section will review current advances in catalytic AOPs, novel concepts and materials for ozone-based and radiation-driven AOPs, and new alternative solutions for in situ radical generation.

2.1. Emerging materials and concepts for catalytic AOPs

In catalytic oxidation, various homogenous and heterogeneous catalysts can be used to generate reactive species by activating radical precursors such as hydrogen peroxide (H_2O_2), sodium percarbonate ($Na_2CO_3 \times 1.5H_2O_2$), peroxydisulfate ($S_2O_8^{2-}$), and monochloramine (NH_2Cl) or increase radical formation from oxidants such as ozone [36–39]. This section focuses on dark catalytic processes, i.e., those without light as radical initiator, while light-induced AOPs are discussed in the section on radiation-driven AOPs. The most widely studied and applied homogeneous catalytic oxidation system is the Fenton reaction, in which H_2O_2 reacts with dissolved ferrous iron (Fe(II)) to generate **•**OH [40]. Although the traditional iron-based Fenton reaction is an established method-of-choice for the treatment of complex industrial wastewaters, critical aspects for its application include a narrow operation range determined by a maximum catalytic activity at pH = 2.8–3.0, rapid consumption of free radicals by excess Fe(II), and costs for iron-containing sludge disposal [29,40]. To avoid these bottlenecks, the application of chelating agents including humic substances,

polycarboxylates, aminopolycarboxylic acids, and polyoxometalates, as well as iron-free Fenton-like systems have been explored using other transition metal ions (e.g., copper or cobalt) that can activate H₂O₂ at near-neutral pH conditions, but only work under well-defined reaction conditions with careful consideration of catalyst toxicity [29,41,42]. A great deal of attention has been paid to both natural and synthetic solid catalysts such as iron-, manganese-, or cobalt-based materials [43-45], engineered nanomaterials [46–49], metal-free polymers [50,51], carbonaceous materials [52,53], layered double hydroxides [54], metal-organic frameworks [55], and single-atom catalysts [56,57]. Many of these materials possess high catalytic activity at the laboratory bench scale and promise AOP operation under neutral pH conditions. However, translation of catalytic AOPs into pilot- and full-scale water treatment has been slow [46,58]. To overcome obstacles that prevent catalytic water treatment technologies from commercialization and implementation, efforts should be directed not only towards producing standardized, regenerable, cost-effective, and sustainable catalysts with high physical and chemical stability, but especially towards testing their suitability and long-term performance for well-defined water treatment applications [46,58]. Standardized (high throughput) testing procedures of catalytic materials should be developed that could allow to rank different materials and support the selection of the best technology for specific applications [58]. Moreover, challenges concerning reactor design need to be addressed to allow for high contaminant-to-surface mass transfer and contaminant degradation efficiency, while at the same time minimizing catalyst loss and operational costs [46]. While there are important efforts needed to bridge the gap between laboratory-scale and implementation of catalytic AOPs at industrial scale, innovative catalysts show promise to broaden AOP applications towards enhanced in situ chemical oxidation or decentralized point-of-use water treatment, and tackle specific treatment goals for the removal of recalcitrant contaminants [46,58].

2.2. Ozone-based advanced oxidation

In every process involving ozonation, ${}^{\circ}OH$ are produced by the interaction of ozone with the water matrix, particularly with organic matter [59,60]. The oxidation of contaminants by ${}^{\circ}OH$ is often referred to as "indirect" reaction compared to the "direct" reaction of ozone with contaminants. However, the formation of ${}^{\circ}OH$ is typically uncontrolled, which is why ozonation is not often classified as an AOP. The production of ${}^{\circ}OH$ can be enhanced by the addition of H_2O_2 in the peroxone process, pH elevation, catalytic ozonation, or ozone photolysis [61–66]. UV/O₃ is considered in the next section.

In the peroxone process, ozone swiftly reacts with the H_2O_2 anion (HO_2^-) (k = 9.6 × 10⁶ M⁻¹ s⁻¹) yielding 0.5 mol °OH for every mol reacted ozone [61,64]. This process is frequently employed to reduce formation of undesired bromate [67,68] or to neutralize excess ozone which further leads to additional °OH formation [69].

At elevated pH, ozone may react with hydroxide ions to produce $^{\circ}$ OH. However, this reaction is slow ($k = 70 \text{ M}^{-1} \text{ s}^{-1}$) [70,71]. The associated costs for adding bases, especially in highly buffered waters, coupled with increasing risk of bromate formation, restrict ozonation at elevated pH towards a limited range of source and wastewaters [72].

In ozonation homogeneous and heterogenous catalysis relies on the breakdown of ozone by transition metal ions or solid metal oxide catalysts with a preference for iron- and manganese-based materials, as well as activated carbon and other carbon-based materials [65,73,74]. Heterogeneous catalytic ozonation can remove pollutants through interfacial reactions at the catalyst surface after the absorption of either gaseous or dissolved ozone and/or the pollutant. In the aqueous phase, [•]OH generated from the decomposition of ozone at the catalyst surface can also participate in pollutant removal [73,75]. This could potentially be more advantageous than homogeneous catalysis as it does not necessitate additional metal ions to be added and subsequently eliminated. However, it may face mass-transfer limitations since [•]OH are formed at the catalyst surface.

Understanding of the driving mechanisms for catalytic ozonation is still limited. For example, varying catalytic activity has been reported for different forms of MnO_2 , with some causing ozone decay without significant [•]OH production [65,76]. Likewise, the mechanisms of catalytic ozonation with activated carbon-based materials are still under investigation [73]. Some studies suggest that radical formation might be linked to specific reactions with the carbon's functional groups, which lead to its gradual consumption [77]. The lack of standardized experimental procedures often complicates the direct comparison of different research findings. Therefore, future studies on catalytic ozonation should adhere to standardized procedures that allow for a proper assessment of the benefits of radical generation in comparison to sole ozonation (see section 5), as well as the mid-to long-term stability of the catalytic process.

2.3. New solutions in radiation-driven AOPs

In radiation-driven AOPs, the energy of electromagnetic radiation is utilized to form radicals [78,79]. The applied wavelengths range from >170 (VUV) to 700 nm (visible light) [80]. UV water treatment has been applied for several decades for water disinfection using mercury (Hg) lamps. Solar radiation and other lamp technologies exist with a small market share. Recently, light emitting diodes (LEDs) have quickly evolved in the UV range and show promise to increasingly replace Hg-containing irradiation sources [81].

2.3.1. Homogeneous AOPs

Analogous to dark catalytic AOPs, radiation-driven AOPs can be distinguished into homogeneous and heterogeneous processes, utilizing a similar array of radical precursors for homogeneous processes including H_2O_2 , chlorine and chlorine dioxide, peroxydisulfate ($S_2O_8^{2^-}$), ozone, and the photo-Fenton process. Photolysis and radical generation mechanisms in these processes are widely established and well-described in literature [82–88].

The most commonly employed processes are UV/H_2O_2 and UV/chlorine [88–93]. The UV/H_2O_2 process is used in drinking water treatment and potable reuse schemes to remove trace contaminants that are difficult to remove otherwise [94] and can be

advantageous when ozone-based processes would result in undesired bromate formation from naturally occurring Br^- [68]. However, the UV/H₂O₂ demands a higher energy input compared to conventional ozonation and the peroxone process [95].

In full-scale potable reuse schemes, UV/chlorine (HOCl) is increasingly used with and without the addition of chloramines [89,88]. Thereby, the photolysis of HOCl results in the formation of *****OH and chlorine atoms [96], the photolysis of chloramines gives rise to formation of aminyl radicals and chlorine atoms [97]. Reactions of these reactive species in water are discussed in more detail elsewhere [98–100]. UV/chlorine is mostly applied as the last treatment step for simultaneous degradation of pollutants and the provision of disinfectant residuals, with limited application in organic-rich and ammonia-containing waters due to formation of toxic by-products [101].

Sulfate radicals react more substrate specific than $^{\circ}$ OH [5]. Therefore the UV/S₂O₈²⁻ process benefits from reduced oxidant scavenging by the water matrix, but less reactive compounds are more difficult to eliminate compared to the UV/H₂O₂ process [102]. Therefore, the UV/S₂O₈²⁻ process may provide tailored solutions towards individual substances or substance groups rather than broadband treatment envisioned in most AOP applications [5]. In addition, residual sulfate ions can be undesirable in some applications.

Compared to H_2O_2 [$\epsilon_{H2O2,\lambda = 254nm}$, = 18.6 M⁻¹ cm⁻¹] [103] and $S_2O_8^{2^-}$ [$\epsilon_{S2O82-,\lambda = 254nm}$ = 22 M⁻¹ cm⁻¹] [104], ozone has a high molar absorption coefficient of $\epsilon_{O3,\lambda = 254nm}$ = 3300 M⁻¹ cm⁻¹ [60], resulting in an efficient photolysis into [•]OH [87] that is 20 times more efficient than H_2O_2 photolysis at the same dissolved molar concentration. However, due to the combination of two energy-intensive processes, namely ozonation and UV irradiation, the UV/O₃ process is typically not competitive with alternative solutions.

The photo-Fenton process is based on the absorption of light by Fe(III)–HO₂-complexes ($\varepsilon = (450 \text{ nm}) \approx 450 \text{ M}^{-1} \text{ cm}^{-1}$) [87]. Thereby, the complex cleaves into HO₂ and Fe(II), and Fe(II) reacts with H₂O₂ to form °OH. The major obstacle of the photo-Fenton process is that Fe(III) precipitates in water at pH > 5 and, hence Fenton processes need to be operated at acidic conditions, to avoid excessive iron sludge formation and to improve process efficiency. Review articles on photo-Fenton, including solar photo-Fenton are available [105,106]. Other developments are related to using complexing agents to operate at pH 7 and using less costly reactor designs [107–110].

2.3.2. Heterogeneous photocatalytic AOPs

Research on photocatalysis for degradation of refractory pollutants has been intense since the discovery of photocatalytic water splitting [111]. Heterogeneous photocatalysis employs a range of semiconducting catalysts, of which TiO_2 and ZnO are the most widely researched materials [30,112]. Despite much research on photocatalysis in the last decades, including large-scale demonstration on the use of solar spectrum UV-A and UV-B radiation [105], photocatalysis is rarely applied in water treatment beyond lab and pilot scale [28]. There is an ongoing quest for new photocatalysts, with a broad variety of synthesis approaches taken, with the aim to either increase quantum efficiency or to expand the useable wavelength range to access a larger part of the electromagnetic spectrum [105]. Limitations and barriers for industrial uptake of photocatalysis comprise low energy efficiency, including low quantum efficiency of photocatalysts, complex reactor design, catalyst immobilization and process integration [28,113]. In a critical analysis of the technology and market prospects of photocatalysis, Loeb et al. [28] suggest to overcome the barriers to implementation of photocatalysis by focusing on niche applications and emphasizing the unique advantages of photocatalysis over competing technologies. One example is the ability to generate reductive conditions to treat oxyanions (e.g., nitrate) or certain heavy metals such as chromate. The ability to work largely chemical-free can be a valuable competitive advantage for small-scale and remote applications. One such promising example relevant to achieving the United Nations Sustainable Development Goals is the photocatalytic enhancement of solar disinfection (SODIS) [114].

2.3.3. Lamp technology

UV-light emitting diodes or UV-LEDs are radiation sources based on semiconductors such as gallium nitride (GaN), indium nitride (InN), and aluminum nitride (AlN). Pilot- and full-scale application in water treatment has been tested primarily for disinfection and photocatalysis in the UV-A range [115], although large UV-C disinfection systems are being already tested, too [116]. So far, it has been possible to produce LEDs with an emission wavelength as short as 210 nm [117]. The acquisition costs of UV LEDs with wavelengths <300 nm are currently still high, while the service life, the radiant power, and energy efficiency are limited compared to visible spectrum LEDs [117]. The small size and control of individual LEDs enables an innovative reactor design and a larger range of applications [118,119]. UV LED development is a fast-paced research field, and it is likely that UV LED will soon become the lamp option of choice for many applications, not least because of anticipated regulatory pressures regarding the use of mercury. For a comprehensive outlook on the development of UV emitters based on LED technology see Amano et al. [81].

Alternative lamp technologies have been explored to generate vacuum UV (VUV) radiation (i.e., <200 nm) that can be used to photochemically split water into [•]OH and solvated electrons [120]. The lamps employed include Xe Excimer lamps with a peak emission at 172 nm emission and, more recently, LP-Hg arcs at 185 nm emission, with the latter having a photon conversion efficiency of 4–8% for the electricity invested [120,121]. The main challenge to implement the VUV process relates to the low penetration depth of VUV into water. At 185 nm, the decadic absorption coefficient of pure water is 1.8 cm^{-1} ($\epsilon_{H2O,\lambda} = 185 \text{ nm}$, = 0.032 M⁻¹ cm⁻¹) [122] meaning that almost 90 % of the photons are absorbed in the first 5 mm of the optical pathlength. Therefore, the treatment of large volumes of water requires the development of reactors that go beyond thin-film reactors and enable efficient use of 185 nm photons (and ideally also exploit 254 nm photons) without excessive pumping energy or reactor construction costs. Note that in most water matrices, other than reverse osmosis permeate, penetration depth will be substantially lower due to the competing light absorption of common inorganic anions, specifically chloride [123]. VUV absorption by chloride in real water matrices raises similar concerns as the

UV/chlorine process regarding the formation of halogenated oxidation by-products. Analogously, in waters with high nitrate concentrations, nitrate photolysis may generate potentially harmful nitrogenous oxidation by-products [124,125]. This is an aspect that has not yet been thoroughly investigated for the VUV process.

2.4. Other AOPs

The term "other AOPs" encompasses a broad and diverse array of processes designed to generate radicals in water for treatment purposes. Other than heat-activated persulfate activation and electrochemical oxidations, these methods generally require a higher energy input compared to the other three groups of AOPs (namely, ozone-based, radiation-driven and catalytic AOPs, as highlighted in Fig. 1) [25]. Despite their comparably high energy demand, these processes may offer distinctive features such as operating chemical-free making them appealing for specific niche applications like small and decentralized systems. Furthermore, techniques like ultrasound, plasma treatment, supercritical water oxidation, and electrochemical oxidation are presently being explored for the removal of resistant poly- and perfluoroalkyl substances (PFAS) [126–129]. However, PFAS exhibit considerable resilience to [•]OH attack and their breakdown is associated to different mechanisms, such as pyrolysis during ultrasound treatment [130], or direct electron transfer at the anode surface [127].

Application of ultrasound in water with frequencies of 20–1000 kHz generates oscillating gas bubbles. During the growth of these bubbles, expansion gas is drawn inside the bubble. Subsequent collapse of the bubbles leads to locally high temperatures (>4000 K) at the microscale [131]. The resulting pyrolysis of water vapour inside the bubbles yields **•**OH and H**•** radicals, which do not readily recombine due to the high temperature [87]. Hence, **•**OH diffuse outside the bubble and accumulate at the bubble surface. The local accumulation of reactive species results in comparably high energy demand for contaminant removal [25]. To the best of our knowledge, this process has never been tested at pilot or full scale.

Plasma is a gas-like state of matter in which a significant portion of molecules or atoms are ionized. This makes plasma highly conductive and a potential initiator of reduction and oxidation reactions. Plasma has been frequently proposed for water treatment [132]. Hot thermal or equilibrium plasma states occur at high temperatures, for example in lightnings or plasma arcs, where the ionized plasma gas molecules eject electrons. Substantial energy input is required for hot plasma formation and such plasmas are therefore unsuitable for engineering energy-efficient water treatment. Non-thermal non-equilibrium or cold plasma consists of positively charged molecule ions at ambient temperature and highly energized electrons [133]. Ionization is induced by strong electric fields such as dielectric barrier or corona discharge, rather than thermal energy input. Potentially, this leads to a much-improved ratio of reactive species generated to energy invested compared to hot plasma.

The cascading effects of accelerated electrons impacting on carrier gas molecules and water matrix compounds leads to a plethora of reactive species that include **•**OH, reactive oxygen species (ROS), but also nitrogen-containing radicals and related species such as different peroxides. Furthermore, the relaxation of excited states may generate photons across the UV range [134]. All these species can be involved in the degradation of a pollutant [135] but the contribution of each reactive species is highly substance and system specific.

The engineering challenges inherent to these processes are significant, and they bear some resemblance to those encountered in, for example, electrochemical processes. One of these challenges is the limited active reaction volume, which refers to the small area where the plasma comes into contact with the water that has to be treated [134]. As a result, it is crucial to design efficient reactors to ensure sufficient mass transfer and to create feasible solutions [136]. Another hardware-related challenge lies in the need to develop cost-effective and high-performance plasma generation systems specifically designed to meet the unique needs of water treatment.

The thermal activation of persulfate is a viable method for in situ chemical oxidation, typically employed to remediate contaminated groundwater and soil [86]. Due to the small bond dissociation energy of the peroxide bond (120 kJ mol^{-1}) [137], even moderate temperatures (>40 °C) are sufficient to split persulfate into sulfate radicals [138]. It has also been shown that slow reactions with high activation energies can become more important/feasible at the elevated temperatures of thermal activation of persulfate [139]. A disadvantage of using persulfate is a pronounced drop in pH and robust radical scavenging effects, particularly when chloride and bicarbonate are concurrently present [98].

Supercritical water oxidation (SCWO) has proven to be an effective method for degrading various types of waste at both laboratory and full-scale levels [140]. However, its use beyond demonstration sites has been limited. This is primarily due to the simpler alternatives available, such as incineration and disposal [140]. SCWO involves heating and pressurizing the water to reach a supercritical state, typically within a temperature range of 400–650 °C and at supercritical pressures [140]. In this state, water can mix with nonpolar compounds, while polar and ionic compounds may still remain soluble [141]. Conversely, inorganic compounds such as salts can precipitate and be treated as solid waste. This has enabled the separation of radioactive elements in nuclear power plant waste during bench-scale experiments, potentially reducing the volume required for radioactive waste storage [142]. The SCWO process is characterized by high gas phase diffusion rates and high liquid phase collision rates, which favor the oxidation process. Oxygen, typically used as an oxidant, can be derived from hydrogen peroxide, which decomposes into oxygen upon thermal decomposition [140].

In electrochemical advanced oxidation processes, [•]OH are directly generated from water oxidation at the electrode surface [31]. Among numerous used electrode materials, boron-doped diamond (BDD) and mixed metal oxides (MMO) are mostly applied for the removal of organic compounds in water treatment [143]. BDD electrodes are mainly applied at smaller scale for water treatment, e.g., for the removal of chemical oxygen demand (COD) in industrial wastewaters or the disinfection of ballast water [144,145]. Due to the efficient conversion of electrical energy into [•]OH and secondary oxidants (H₂O₂, O₃) and the chemical-free operation, electrical AOPs are often considered as environmentally-friendly treatment solutions [146]. However, additional energy is required to facilitate

transfer of contaminants to reactive species generated at the electrode surface. In addition, chloride is oxidized to active chlorine, which can be rapidly oxidized to chlorate and perchlorate [145]. Current research is focused on new electrode design to optimize mass transfer and measures to mitigate by-product formation [143,147].

3. Comparison and benchmarking of AOPs using the electrical energy per order (EEO)

The most important figure-of-merit for comparing AOPs is electric energy per order (EEO) proposed by Bolton et al. (1996) and subsequently published as an IUPAC Technical Report [148,149]. Given that ultimately most AOPs are electrically driven, the EEO employs electric energy required to decrease the concentration of a target contaminant by 90 %, i.e., by one order of magnitude. It applies to treatment conditions where contaminant decay follows pseudo-first order kinetics and therefore most AOP applications for water treatment. There are variations of the EEO for systems with high contaminant concentration (zero-order kinetics) using electric energy per mass (EEM) and for solar-driven systems using solar collector area instead of electric energy [148]. For light-induced AOPs, the EEO has been further elaborated to use fluence-based rate constants depending on fundamental photochemical probe compound characteristics i.e., quantum yield and molar absorption coefficients, for both single wavelengths and polychromatic light [150,151]. In contrast, the electrical energy dose (EED) defined as "electrical energy (kWh) consumed per unit volume [...] of water treated", which is sometimes used as operational metric, is not applied to compare different AOPs [94].

The EEO has been extensively applied on most AOPs, including ozonation and peroxone [6,66,95], electro-chemical [145,152], ultrasound-based [153], and both homogeneous and heterogeneous UV-based AOPs [95,154,155]. Thereby, the EEO has proven useful for the initial assessment and comparability of the energy efficiency across different AOPs. However, within each class of AOP, additional relevant experimental and water quality parameters are required to allow for appropriate comparison between different target compounds, water matrices, and reactors. For example, UV/H_2O_2 requires knowledge on target compounds' molar absorption coefficients, second-order reaction rate constants with $^{\circ}OH$ (k_{OH}), and direct phototransformation rates to determine EEO values. In addition, the water matrix pH, UV absorbance, and $^{\circ}OH$ scavenging capacity (see details in section 5) should be reported [156]. To extrapolate upscaling from bench to pilot and full scale, changes in reactor fluid dynamics, mixing and mass transfer, light distribution, including transmittance and path lengths need to be considered [156]. The variance of literature data within individual AOPs indicates the difficulty to compare processes at different scale and in different water matrices [25].

While the EEO serves as a solid factor in benchmarking the power efficiencies of various AOP-systems, it falls short as a reactor design parameter or for scale-up. This is primarily due to the variations in energy efficiencies across AOP systems. Consider two given AOP systems, A and B, both reaching the same treatment objective. However, owing to distinct equipment properties such as UV light distribution, efficiency of ozone generation, or hydraulic conditions within each reactor, the EED and EEO of both A and B can diverge. As a result, with an identical EED, system B might either underperform or outperform in reaching the treatment target as compared to system A.

4. Characterization of reactive species in oxidation processes

The characterization of reactive species formed in radical-based processes is hampered by their short life-time, which is typically in the range of microseconds (μ s) (°OH and SO₄⁽⁻⁾) to milliseconds (ms) (e.g., carbonate radicals and superoxide radicals) [157,158]. Short-lived reactive species can in principle be measured and characterized directly by laser flash photolysis and pulse radiolysis hyphenated with fast UV–vis spectroscopy, which has resulted in comprehensive data sets of reaction rates for radicals in aqueous solutions [78,79]. However, these methods require considerable expertise and expensive, non-portable specialized instrumentation that is not readily available to most researchers. Alternatively, chemical probes can serve a central role as diagnostic tools in AOP research [3]. Chemical probes can be used for various purposes (e.g., determination of radical exposures or formed reactive species) and can be divided into three groups with the following aims.

- (i) To investigate the types of reactive species and their exposures in the water matrix, chemical compounds (so called probe compounds) should be dosed in low concentrations, so that less than 5 % of the reactive species under study are scavenged [159, 160,161].
- (ii) To quantify reactive species and to study their effect on the water matrix, chemical compounds (scavengers) are dosed in higher concentrations to significantly scavenge the reactive species of interest. For instance, scavenging of individual reactive species under study indicates their effect on by-product formation or contaminant degradation. In addition, complete scavenging (e.g., >95 %) allows their quantification by quantifying the removal of the scavenger or product. Note the difference between scavengers, which react with reactive species, and quenchers, which deactivate excited states [162].
- (iii) To quantify excited triplet states, quenchers are used. Upon direct photochemical interactions, molecules are photoexcited and can form stable products. Quenching (e.g., by NOM) intercepts the excited states under reformation of the starting material [162].

There is a wide range of probe compounds and scavengers available for reactive species in water. Recent reviews have summarized probe compounds used to detect reactive oxygen species in AOPs [163], aqueous environments [157], during photocatalysis [164] or in UV-based advanced reduction processes [161], to assess the photochemical activity of dissolved organic matter [165], and the contribution of reactive nitrogen species to compound transformation [166]. Here, we briefly discuss the requirements for suitable probe compounds and provide some examples of frequently employed compounds for the most relevant reactive species in AOPs.

There are several requirements for suitable probe compounds and scavengers in AOP research. A probe compound/scavenger should react selectively with the reactive species of interest with a known second-order reaction rate constant. This is especially important in AOPs with more than one significant reactive species. E.g., in case of ozone or UV-based processes, probe compounds/ scavengers must not react with ozone or absorb UV-radiation. To elucidate and distinguish between different radicals in one process, a suite of probe compounds may be required that exhibit a wide-ranging selectivity toward the relevant individual oxidants present [99, 163,167–169]. An exemplary procedure for a sulfate radical-based process in the presence of chloride is provided by Lutze et al. [98].

Probe compounds or their reaction products should be straightforward to measure with available analytical equipment. UV/Visspectrophotometry has been often the analytical method of choice for initial assessment of AOPs due to its accessibility and availability of portable devices. As a non-separating analytical method, UV/Vis has disadvantages due to possible signal interference with reaction products and water matrix components, especially when working with dyes [170]. Other analytical techniques typically employed for probe compounds in AOP research include fluorescence spectroscopy, HPLC-UV/Vis or HPLC/MS, and to a lesser extent ion chromatography.

The •OH is the reactive species of highest interest for most AOPs. Probe compounds for •OH can be dyes such as rhodamine B, methylene blue, and fluorescein. For a summary of different approaches for UV/H_2O_2 , including assessment of an external standard calibration method using methylene blue, see Wang et al. [171]. Typical probe compounds for •OH that can be readily measured via HPLC include *para*-chlorobenzoic acid (*p*CBA) and *para*-nitrobenzoic acid (*p*NBA) [95,98,172,173]. These compounds can be readily used for ozone-based processed but also for UV-based ones, as the quantum yield for their direct photooxidation is rather low (<0,008 E^{-1} at 254 nm) [174].

It is important to distinguish between scavengers and quenchers present in real water matrices, such as organic matter and inorganic ionic species, which have significant effects on AOP treatment performance [171,175–178], and those employed for diagnostic purposes. Scavengers can be used to indicate and quantify the presence of radicals, non-radical reactive species, and excited states in AOPs by suppressing reactions [163]. In principle, any suitable probe compound can serve as a scavenger, but in contrast to its role as a probe, it must be added in sufficiently high concentration to outcompete the radical reactions with the matrix constituents. To adjust the dosing of the scavenger, the reaction rate constants of the reactive species of interest with all matrix components and with the scavenger must be known. Typical scavengers for 'OH include tert-butanol and dimethyl sulfoxide (DMSO) [163,179]. The reaction of $^{\circ}$ OH with *tert*-butanol and DMSO leads to the formation of formaldehyde (yield ≈ 25 %) and methanesulfinic/methanesulfonic acid (yield of the sum of each \approx 98 %), respectively [179]. Quantification of these transformation products allows calculation of the [•]OH formed [179]. While a large variety of substances can be used to scavenge different reactive species [180], many scavengers are non-specific and do not unequivocally indicate the presence of a single reactive species only. In such cases, in addition to matrix reactions, reaction rate constants with all relevant reactive species should be considered to avoid misinterpretation of the results. Working at relatively high concentrations, often in the millimolar range, poses additional challenges. Scavenger reactions may lead to the formation of secondary reactive species or the formation of unexpected products that may affect reaction mechanisms, pathways, and kinetics [181]. The use of scavengers, thus, requires appropriate control experiments to assess the reactivity of the scavenger with the oxidants, target compounds, and matrix. For heterogenous AOPs, reconsideration of solubility and adsorption of scavengers onto materials may be required to assess the impact on dissolved and surface-bound reactive species.

5. Set-ups and methodologies for laboratory-scale AOP experiments

Knowledge transfer from many recent AOP studies is limited because experiments were operated with set-ups that are not adequately characterized or comparable. Requirements regarding the experimental design and operation depend on the objective of the study. Initial feasibility tests to confirm the formation of reactive species or the removal of selected probe compounds can be conducted in pure or synthetic water matrices using non-standardized experimental set-ups in the laboratory (see section 6.1 for details). In contrast, for a sophisticated comparison of costs and energy demand, lab-scale experiments should provide comparable and scalable information from standardized experimental set-ups. Ideally, these experiments are conducted in real waters to account for the strong impact of the water matrix on process efficiency (see section 6.2). So far, standard experimental procedures have been described only for UV-based processes [182], and such equipment may not be accessible for researchers or may be unsuitable especially for newly developed treatment processes. This section provides recommendations for the systematic selection of experimental procedures, when standardized set-ups are undefined, unavailable or unsuitable for the process at study.

5.1. General aspects

Requirements for experimental set-ups of AOPs are highly process specific and discussed separately in the following sections. As already briefly outlined in section 3 (comparison and benchmarking), the water matrix needs to be well-defined, and possible matrix effects on the oxidation process reported.

Broadly, the matrix has three impacts. First, the matrix can compete with radical precursors, e.g., absorbing photons (inner filter effect) or consuming ozone [60,183]. In some cases, this can generate secondary reactive species [60,184]. Second, matrix components can scavenge radicals terminating radical chain reactions in non-productive ways towards treatment targets [183]. Third, upon scavenging of highly reactive radicals, less reactive and longer-lived radical species such as carbonate radicals, superoxide, or dichloride anion radicals can be produced [4]. Depending on their respective reactivity with a target compound and their tendency to accumulate at higher concentrations due to their persistence compared to other radical species, such secondary reactive species can contribute significantly to the degradation of a target compound [185,186]. Probe compounds (see section 4) can be used to estimate

the contribution of different radicals. Depending on the target application, matrix components that contribute to scavenging may include organic matter (typically measured as dissolved or total organic carbon, DOC/TOC), inorganic carbon or alkalinity, and nitrogen species (nitrate, nitrite, ammonia). In addition, process-specific reporting of additional water quality parameters affecting the radical generation might be needed (see details in sections 5.2-5.5), e.g., bromide for its potential in by-product formation. Similarly, the pH must be recorded and reported at least before and after, and preferably during the experiment, as it can affect acid-base-equilibria and reactivity of reactive species, matrix and target contaminants [187–189]. In experiments with synthetic waters, buffer effects should be considered as for example carbonate and phosphate buffers may scavenge radicals, form secondary radicals or interact with catalysts [75,190,191]. Furthermore, concentrations of any added chemicals need to be listed.

5.2. UV-based processes

5.2.1. Fluence-based evaluation

As outlined in the previous section on benchmarking, scale and geometry importantly affect EEO and EED. That situation is generally exacerbated for laboratory-scale set-ups, which are rarely designed for optimal energy efficiency. At laboratory scale, it is therefore preferable to focus on using set-ups that allow assessing photochemical reactions as function of the fluence [162] in the reactor as basis for comparing photochemical studies.

Determining fluence allows to model the fundamental reactions i.e., radical formation rate, direct photolysis and it can be used to determine fundamental photochemical characteristics such as quantum yields of photochemical reactions. These fluence-based parameters such as reaction rate constants can be translated in time-based parameters by simple calculations with the apparent fluence rate at hand when needed [95].

5.2.2. Light source and its impact on process evaluation

The choice of light source is usually intrinsically related to the goal of the study, but the experimenter needs to be aware that the choice of photon source will impact the process evaluation procedure. There are quasi-monochromatic light sources (e.g., low-pressure Hg lamps, and, with a slightly broader emission peak, excimer lamps and LEDs) and polychromatic light sources (e.g., medium- and high-pressure mercury lamps, Xenon arc lamps, or sunlight). Fundamental photochemical properties such as molar absorption coefficients and quantum yields of photochemical reactions depend on wavelength. Consequently, radiation propagation throughout any photoreactor is strongly wavelength dependent. How this can be considered for the determination of fluence and fluence rates has been extensively discussed for UV disinfection processes [192]. The same approach has been transferred also to AOPs [193].

5.2.3. Fluence rate determination

There are several methodologies to determine the photon-fluence rate. First, there are numerous chemical actinometers, most of which have been conveniently described in an IUPAC Technical Report [194], some of which have been reviewed recently [195]. Among them we can distinguish opaque actinometers, e.g., the iodide/iodate actinometer [196,197] and non-opaque actinometers such as the uridine actinometer, both photochemically active towards 254 nm radiation [195]. The first type essentially determines the incident fluence rate (full absorption of UV radiation at the interface with the actinometer solution, no penetration of light into the reactor) yielding a value for irradiance. The actinometer solution in the second type has high transmittance. By that means an average photon-fluence rate is measured. It should be noted that actinometers provide information different from biodosimetry. The latter is suited to identify deficient mixing and radiation fields in reactors leading to a broadened distribution of applied UV dose [198]. This is an aspect particularly important in disinfection, where several orders of magnitude of microorganism inactivation are typically envisaged. As long as required removal is <90 %, this tends to be of lesser relevance for AOPs, except perhaps in processes prone to mass transfer limitations. Finally, radiometers and spectroradiometers, calibrated against an absolute standard, are commonly applied to measure irradiance at a chosen location in the experimental set-up [182].

When choosing the way to measure fluence-rate, the experimenter must be aware that using opaque actinometers and radiometer measurements may require a complex mathematical post-processing to obtain a reliable fluence-rate (depending on the geometry of the photochemical reactor). This issue can be circumvented by using a simplified geometry such as a quasi-collimated beam apparatus (see below). Also, using polychromatic light sources can complicate the use of actinometers for this purpose, although wavelength-dependent quantum yields have been reported for several commonly used actinometers [195].

Finally, on a very practical level, for experimentation with quasi-collimated beam apparatuses it is recommended to use radiometry on a routine-basis to determine irradiance and chemical actinometry periodically to verify that the calibration of the radiometer is still accurate and does not suffer from drifts.

5.2.4. Advantages and disadvantages of different laboratory set-ups

From a chemical engineering point of view, we can distinguish batch experiments in continuously stirred tank reactors (CSTR) and experiments in flow-through reactors. Among CSTRs, the most referred to and most standardized approach is the quasi-collimated beam apparatus (qCB) [182]. In flow-through reactors, we can distinguish single-pass and multiple-pass systems, i.e., where treated fluid is fed back to a feed tank and recycled multiple times through the photoreactor.

A qCB consists of a (i) light source, (ii) an optical system, most typically a tube of a certain length rough-black painted on the inside, that eliminates non-parallel radiation and (iii) a shallow, typically round photoreactor whose surface is homogeneously illuminated with the resulting parallel rays. Guidance on system design and acceptable deviations from ideality (therefore quasi-collimated beam) have been reported [182] and recently complemented with additional guidance on evaluation [192]. The key advantage of this

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geometry is that due to its simplicity the pathlength of photons and its attenuation by absorption through the treated solution is well-defined. Hence all chemical actinometers as well as radiometry are suitable to determine fluence rate without complex mathematical processing. qCB systems have been extensively used in research using mercury lamps but with modern LEDs with comparably higher power outputs, it is straightforward to construct a qCB with multiple LEDs to satisfy qCB design criteria (e.g., APRIA Systems [199]).

Other CSTRs include similar photoreactors, in its simplest form a beaker, exposed to light, often used when working with solar light or solar simulators only. In such geometries, measuring fluence rates accurately is more challenging due to the complex direction and optical pathlength of rays through the treated solution. Actinometers that directly estimate fluence rate are preferable rather than opaque actinometers and radiometers to avoid the complex post-processing to obtain fluence rate from the actinometry result [182]. Radiation evaluation methods and processes for matching wavelength-dependent responses apply in analogy to action spectra for different pathogens and irradiation sources in disinfection [200].

The second type of photoreactor are flow-through systems, either single pass or multi-pass, including plug-flow reactors. Radiation input into such systems is characterized by biodosimetry (often provided by the manufacturer) or actinometry (often conducted in the research laboratory). When using such systems measured fluence rates and radiation distribution are not transferable across optically different solutions e.g., clear water vs. wastewater. Actinometry must be conducted separately for each solution. Similarly, when using radiometry or opaque chemical actinometers geometric complexities and hydraulic flow fields need to be considered. For multi-pass systems, choice of sampling points, recirculation velocity, feed tank volume, and mixing are important to obtain meaningful results. Such considerations are especially important for upscaling to pilot systems, for more details see Ref. [105].

5.3. Ozone-based processes

5.3.1. Ozone consumption, mass transfer and radical formation efficiency

This section primarily discusses pitfalls for evaluating experimental results with ozone-based AOPs. For a more detailed guide on conducting ozonation experiments, refer to the manual by Gottschalk [75]. Like UV-based operations, lab-scale ozonation can be carried out using CSTRs. The reactors may involve injecting gaseous ozone in semi-batch operations or a concentrated ozone solution in batch experiments. Mass transfer observed in lab-scale experiments can be highly variable [75] and does not align with that of larger-scale operations, where pilot- and full-scale ozone injection systems typically provide mass transfer of >95 % gaseous ozone into solution. Consequently, enhanced performance observed for ozone-based AOPs compared to using ozone alone may be partially attributed to enhanced mass transfer and ozone consumption in inefficient lab reactors. Therefore, to generate transferable and scalable data for ozone-based AOPs, it is recommended to report the amount of consumed (reacted) ozone as a reliable figure of merit [201]. In batch ozonation experiments, monitoring of ozone decay over time can provide useful complementary data.

In pure water at circumneutral pH, ozone decomposes slowly (OH⁻, $k = 70 \text{ M}^{-1}\text{s}^{-1}$) leading to the creation of °OH [70]. Ozone-based AOPs may aim to: (i) actively enhance the rate of radical formation through accelerated ozone decomposition via "quenching" (residual) ozone with a radical promoter, and/or (ii) boost the overall generation of radicals compared to conventional ozonation. However, in complex water matrices, including secondary effluents, the benefits of AOPs may be limited due to the interfering reactions of ozone with organic matter, which already produce significant amounts of °OH [184,202].

Therefore, the yield of [•]OH in the AOP under test should always be evaluated against conventional ozonation. Researchers conducting experiments with gaseous ozone should also consider potential biases owing to effects on mass transfer, as previously discussed.

The R_{CT} -concept, which defines the ratio between [•]OH exposure and ozone exposure [203], often comes into play when assessing the efficiency of ozone-based AOPs. However, this concept was not designed for this purpose but rather to compare different types of waters. Therefore, R_{CT} values should be interpreted with caution, as enhanced ozone decomposition skews the values towards seemingly high [•]OH exposure [204]. Hence, it is recommended to compare radical yields (or exposures) from ozonation and the tested AOP as a function of the consumed ozone, which is independent on ozone decomposition kinetics, as detailed in Hübner et al. [184].

5.3.2. Lab set-ups for ozone and ozone-based AOP experiments

For most experiments with ozone, batch experiments with an ozone stock solution generated in ultrapure water and injected into the water sample are recommended as the easiest and best characterized approach. Concentration of the stock solution can be controlled by adjustment of ozone gas concentration, pressure, and temperature [205,206], and easily measured photometrically prior to injection [207]. Consumed ozone is then determined as the difference between the diluted stock solution and the residual at the end of the experiments. Previous comparison experiments confirmed good agreement between contaminant oxidation in CSTR batch experiments and experimental set-ups using gas/liquid mass transfer in the sample [201].

Experiments involving gaseous ozone necessitate a comprehensive ozone mass balance. This includes constant monitoring of gas flow, in-gas and off-gas ozone, and the remaining ozone in the water to determine the consumed ozone. Lab-scale experiments are mostly operated in semi-batch mode with gaseous ozone injected into a batch reactor. For an accurate determination of consumed ozone in such experiments, it is important to include all residual ozone in off-gas pipes into the mass balance [75,201]. Time-resolved sampling from these experiments is generally discouraged due to inaccuracies in describing the consumed ozone at various times, often referred to as "transferred ozone dose".

Lab-scale experiments are typically not conducted at continuous water flow, since even the smallest commercially available generators (2–4 g O_3/h) provide ozone for considerable water flow rates (e.g., 1 m³/h can be treated with ozone doses of 2–4 mg/L) and their operation at <10 % of capacity is not recommended. Electrochemical ozone generation can provide a suitable solution for

continuous operation of ozonation at lab scale [33]. As an alternative approach, gaseous ozone can be injected into a side stream to generate a concentrated solution, which is then continuously mixed into the sample [208]. Continuous flow operation might be required for some applications, e.g., mid-to long-term stability testing of catalytic ozone decomposition or the continuous feeding into a post-treatment step.

5.3.3. Set-up modifications and important aspects for ozone-based advanced oxidation

Procedures for testing ozone-based AOPs depend on the objectives and conditions of the target application. In most studies, radical promoters or catalysts are dosed before ozonation. However, in certain applications, concurrent or subsequent dosing may prove more advantageous, for instance, to mitigate competition with ozone-reactive water constituents or to leverage the effectiveness of direct ozone reactions (such as disinfection) prior to rapid decomposition during the AOP [184].

For heterogeneous catalytic ozonation, the choice of reactor design should be carefully considered. In addition to the basic rules for catalytic AOPs (see section 5.4), experimenters need to account for ozone-related characteristics of the process including the potential variances in the interaction of gaseous and dissolved ozone with the catalyst, as well as ozone decay into [•]OH in the absence of a catalyst. Control experiments at identical conditions are crucial to evaluate effects of ozone alone (ideally with a non-catalytic reference material), as well as sorption of probe compounds onto the catalyst. Different probe compounds may be used to account for various affinity to the catalyst. Moreover, the experiments should provide information on the stability of catalytic activity, because [•]OH can also be generated by finite reactions, e.g., from the reaction of ozone with activated carbon [77].

5.4. Catalytic AOPs

5.4.1. Characterization of the dissolved compounds and the catalyst

In contrast to established ozone- or UV-based processes, experimental protocols for catalytic AOPs are much less standardized [209], which complicates the comparability between different studies and oxidation processes. In this case, the experimenter must carefully select and report a suitable set-up so that the research outcomes are not only repeatable but also transferrable.

Catalytic AOPs require consideration and thorough characterization of (i) the homogeneous (dissolved) and/or heterogeneous (solid) catalyst, and (ii) the water quality. While most homogeneous catalysts are straightforward to describe, the characterization of heterogeneous catalysts can be a research task in itself, requiring the use of sophisticated analytical techniques to determine, e.g., catalyst loading density for supported catalysts, particle size, surface area to volume ratio, surface charge, and other relevant quantities. In addition, the synthesis of the catalyst must be reported in detail. It must be considered that the properties of the catalyst may change in the application environment compared to the conditions during material characterization. For instance, the solution pH can change the surface charge of heterogeneous catalysts and affect their adsorptive properties as well as the formation of reactive species [58,75]. Water quality measurements should include the parameters listed in section 5.1.

5.4.2. Process evaluation

For catalytic reactions, catalytic activity can be normalized by combining observed kinetics with applied catalyst concentration to determine kinetics-related metrics such as turnover frequency [210], which denotes the number of reactions per catalytic reaction center or, alternatively, per catalyst mass or surface area. Note that the turnover frequency is sometimes used interchangeably with the turnover number, which describes the maximum number of reactions before catalytic activity is lost [210]. However, the applicability of this concept to catalytic oxidation is not trivial because the turnover frequency in catalytic processes in theory describes the catalytic reaction, i.e., the generation of short-lived radicals in an AOP. How many of these short-lived radicals actually react with a contaminant is affected by many parameters including the mixing efficiency, the water matrix, contaminant characteristics and reactivity, all of which do not depend on the catalyst activity. This creates the dilemma that we cannot directly determine the turnover frequency by measuring the contaminant degradation. In addition, catalytic oxidation often involves different reactive species and mechanisms, which we often do not fully understand [58].

Experimenters must therefore carefully report the experimental conditions, e.g., stirring velocity, temperature, and the chemical and catalyst concentrations used. Ideally, results are presented as kinetic rate constants at various chemical and catalyst doses. If the reaction follows pseudo-first order (i.e., rate constants correlate linearly with catalyst and chemical concentrations), rate constants normalized to catalyst concentration might be used for comparing catalysts. However, it should be noted that the selection of probe compounds can have a significant impact on the results. Standardized material testing protocols should, thus, focus on the same set of model compounds. In addition to compound removal, the process evaluation should also include consumption, stability, life cycle, catalyst poisoning and regeneration potential, as well as toxicity of the catalyst.

5.4.3. Advantages and disadvantages of different lab set-ups

Since the evaluation of catalytic systems is inherently nontrivial, we recommend batch experiments in CSTRs for initial feasibility testing of new catalyst materials. This is because CSTRs allow for straightforward control of the experimental environment and exclusion of mass transfer limitations for most catalytic systems. To directly compare the performance of new catalyst materials with that of established materials, contaminant or probe compound degradation kinetics with both catalysts should be determined using exactly the same experimental set-up (see section 6.1). The experimental set-ups or probe compounds can also be selected based on previous studies with promising catalysts to facilitate comparison. To elucidate the formation of different reactive radical species, an adequate system of probe compounds and radical scavengers can be employed, as described in section 4. Given the complexity of a catalytic system, control experiments are required for the reactions of the probe compounds with the oxidant and catalyst separately,

including possible physical interactions with the catalyst.

To generate scalable data for benchmarking of a catalytic AOP, the experimental design should consider the engineering of the entire process, including approaches for optimized mass transfer and subsequent catalyst separation. Continuously operated flow-through or flow-by reactors can provide information on process performance and mid-to long-term stability of the process and catalyst in different water matrices. In addition, process engineering may involve novel process configurations where the innovation is a novel catalyst (support) geometry itself, e.g., (photo)catalytic membranes and foams [211,212], or immobilized catalysts in filters [15,213]. However, the experimenter needs to consider process-related parameters such as the applicable transmembrane flow velocity or backwashing of filters in addition to evaluation of mid-to long-term performance of the process. Furthermore, control experiments are essential to characterize the removal of probe compounds in the process without catalyst or oxidant, e.g., to account for removal by adsorption. Furthermore, mass transfer-related parameters (such as surface area of catalyst, hydrophilicity) which control e.g., contacting of ozone with the heterogenous catalyst, require thorough characterization and reporting.

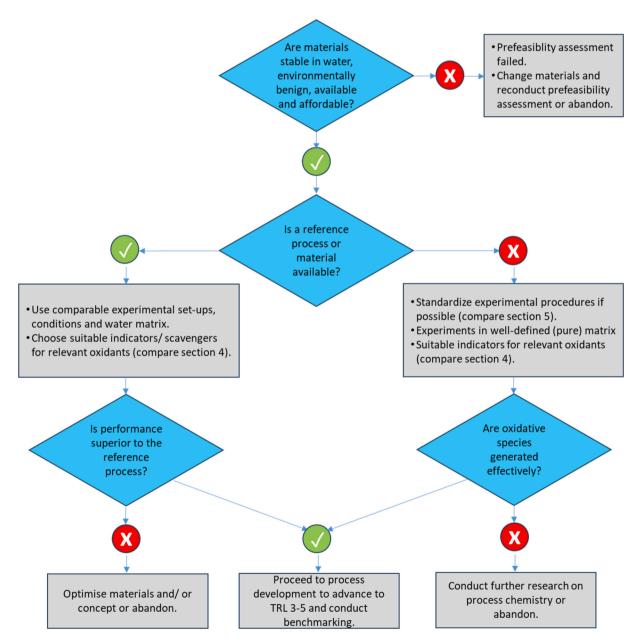


Fig. 2. Basic research for assessing the feasibility of new developments in advanced oxidation (TRL 1-3).

5.5. Other AOPs

The diverse range of other AOPs is challenging to evaluate because standardized set-ups are mostly not available and different treatment efficiency is observed with different lab reactors. For example, for plasma treatment, energy yield, which was defined as mass of pollutant degraded (grams) per unit of electrical energy invested (kWh) at a given percentage of degradation, was differing by up to five orders of magnitude among studied experimental systems [136]. Also results from sonolysis using slightly different reactor design at the same experimental conditions were not comparable [214].

Reactors for pilot- and full-scale operation are often not available, which further limits upscaling of costs and energy efficiencies to realistic treatment scenarios. In addition, mass transfer will play an essential role in practical application and hence, experimental setups will have to cope with this situation and with the related difficulties in reporting accurately transferrable knowledge. For instance, contaminant removal by electrochemical oxidation can be improved by increasing turbulent flow at the electrode, but this will also increase energy demand for pumping.

In summary, as advised previously for other processes, describing the reactor characteristics as well as the process conditions including the hydraulic conditions becomes even more critical for these processes. Ideally, this includes relevant parameters for the energy efficiency of the set-up (e.g., the calorimetric efficiency of transducers used for sonochemical treatment). A detailed review of this diverse set of processes goes beyond the scope of this manuscript and we kindly refer to review papers outlining reactor designs, e. g., for electrochemical oxidation [145], plasma [136], and cavitation processes [215].

6. Implications for future research: assessment of new concepts and materials for advanced oxidation

This section presents a systematic approach for feasibility testing (Fig. 2) and benchmarking of new concepts for advanced oxidation in water treatment (Fig. 3). New concepts in this context refer to the development of new AOPs, but also to new materials (e. g., catalysts) or reactor designs that improve the performance of an existing AOP.

Since individual steps of this approach may be different and not exactly align with technology readiness levels (TRL), we apply the OECD approach to integrate several TRL into four stages of process development. The major focus is on basic research and proof of concept (TRL 1–3, section 6.1) as well as process development and cost estimation (TRL 3–5, section 6.2) [216,217]. Subsequent pilot-and full-scale demonstration (TRL 6–7) is briefly discussed in section 6.3. Finally, we outline scientific approaches to elucidate oxidation mechanisms, assist process design and operation, and assess the potential formation of currently unknown by-products.

6.1. Basic research and proof of concept (TRL 1-3)

The general feasibility is evaluated based on a thorough literature review and preliminary, (non-)standardized bench-scale experiments. The feasibility study elucidates the suitability of the applied materials and chemicals for water treatment and the general potential of the new concept for contaminant elimination. In addition, this phase may already provide initial information for subsequent cost and energy evaluation (TRL 3–5). In some cases (e.g., the synthesis of new catalytic materials), laboratory-scale experiments can already provide a direct comparison with established (reference) materials or processes.

6.1.1. Prefeasibility assessment

It is recommended to consider the fundamental applicability of a new process based on a literature study. These considerations include (i) stability and functionality of the new material or process under water treatment conditions, (ii) potential toxicity or risks of materials and their components, and (iii) availability and costs of required chemicals and materials. The major conditions to be considered in water treatment include pH, salinity, temperature, and matrix constituents. These treatment conditions have a wide span depending on the target application (e.g., municipal and industrial wastewater, seawater, or drinking water). A new process must be robust and materials must be durable or self-renewing under the prevailing conditions. For example, metal-based electrodes may corrode in waters with high salinity. New materials may increase the toxicity of water, for example by leaching heavy metals, which may require precautionary measures. Cobalt, for instance, is a potent catalyst to initiate sulfate radical formation from peroxymonosulfate. However, cobalt is a toxic heavy metal that should only be used after immobilization on a surface [218]. In general, researchers should ensure that the applied materials are approved for the intended application (e.g., drinking water directives).

The availability of chemicals and materials and the envisaged scale of application are important points to consider. For example, new iron-based materials may not be constrained by shortage of resources, but complex catalysts may have these limitations [139,219, 220]. Another example is ultrasound treatment, which is often tested in an artificial argon atmosphere, which would incur high costs in full-scale applications [221]. Robust materials that are nontoxic and not resource-limited can be used at large scale (e.g., for municipal wastewater treatment). More sophisticated catalysts, which require rare earth metals, for example, may be tailored to specific applications such as small-scale industrial wastewater treatment. Fundamental research on new materials in the context of water treatment is a highly important research field that should not be restricted by any boundary conditions. However, the recommended prefeasibility considerations are crucial and should be addressed prior to suggesting a new water treatment process.

6.1.2. Proof of concept

Initial laboratory-scale experiments test the suitability of the process for contaminant removal in well-defined (pure) water systems. The experiments should follow the basic rules for oxidation experiments as described in section 5. If a suitable reference material or treatment process can be identified, the proof of concept study should demonstrate at least similar, preferably better, performance of

the new development (i.e., more efficient pollutant degradation or less by-product formation) in comparison to the reference process or material. An ideal reference material or process would closely mimic the set-up and reaction conditions of the proposed new water treatment process. Note that a detailed comparison to a benchmark process (i.e., a process that is currently applied as state of the art for the envisioned application) regarding costs, energy efficiencies and other relevant aspects is highly case specific (involving target contaminants and water matrix) and, therefore, proposed at a later stage of the evaluation scheme. At this stage, experiments should be designed to provide a first estimate on process feasibility.

A direct comparison to a reference is often possible in case new materials are designed for a certain advanced oxidation. For example, new catalysts can often be directly compared to already established materials using the same experimental set-up. In this case, simple probe compounds (see section 4) can be used for a first assessment, but it is important that researchers ensure direct comparability of experimental results, e.g., by using normalized surface areas and similar reaction conditions (e.g., pH and temperature) compared to the reference process. For some new processes and reactor designs, direct comparison is also possible with wellstudied experimental set-ups described in section 5, e.g., for ozone- and UV-based AOPs. In such cases, transferable and up-scalable parameters (i.e., UV fluence rate, reacted ozone) are important for comparison. However, it has to be noted that ideal reference materials might not be available in all cases.

If a direct comparison to a reference process or material is not possible, initial feasibility tests should be conducted to (i) confirm that the process has indeed an oxidative effect on e.g., degradation of pollutants, (ii) identify major reactive species involved in the process, and (iii) provide first information on the stability of materials and formation of reactive species. Experiments should be designed to provide the required information for process development and cost comparison (section 6.2). Although different analytical approaches may be used to validate the presence of individual radical species, substantial generation of these radicals should be verified experimentally with selected probe compounds. In this case, a broader selection of probe compounds with different affinity to sorption, photolysis, ozone, and different radical species can provide a better assessment of process feasibility and involved mechanisms (compare section 4). The details for the feasibility tests are determined by the existing knowledge about the process at study. In some cases (e.g., the combination of UV-LEDs with H_2O_2), a general feasibility study may not be needed because the reaction

Select potential applications for new AOP, treatment goals and benchmark

- What contaminants can be targeted? Which water matrix can be treated? Which scale (centralized vs. decentralized) is applicable?
- Define treatment goal for specific application.
- Which established process is or would be applied for the application? Select a suitable benchmark AOP.

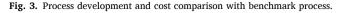
Optimize and assess performance in real water matrix of new AOP and benchmark

- Determine optimum treatment parameters (e.g., pH, oxidant dose, contact time, catalyst dose).
- Quantify residuals (e.g., leaching of heavy metals, residual chemicals).
- Assess by-product formation from water matrix.
- Evaluate performance of benchmark AOP in the same water matrix.

Compare energy and cost efficiency of new AOP and benchmark

- · Conduct theoretical/computational process design and scale-up for the new and the benchmark AOPs.
- Determine and compare the energy demand for both processes.
- Estimate & compare the total capital and operating costs (e.g., energy, chemicals) for both processes.





mechanism and major oxidants are already well-known. In such cases, the evaluation of the process would start directly with process development (TRL 3–5).

6.2. Development and cost comparison of new AOPs (TRL 3-5)

A detailed cost comparison and benchmarking of new processes against established solutions is typically conducted in the demonstration stage with on-site pilot- and/or full-scale testing (TRL 6–7). However, initial cost estimations based on lab-scale experiments can be beneficial to support the decision whether to proceed with process demonstration. We hypothesize that the lack of robust performance and cost data from thoroughly planned lab experiments impedes the transition of new AOPs to the demonstration stage.

Site-specific aspects including the type (and reactivity) of the contaminant, the water matrix, and the process scale strongly affect the suitability of individual AOPs for specific applications. Lab-scale experiments to benchmark new AOP solutions should therefore be conducted in real water matrices in direct comparison to an established process to account for matrix-specific efficiencies. Thereby, the new process has to be compared with an established or already applied process (benchmark process) under comparable reaction conditions (same water matrix, pH, etc). The benchmark process should represent a currently available solution for the selected application.

Therefore, the identification of suitable applications for a new AOP is a key step that has often been paid little attention in past studies. Here, we propose a cost comparison of new AOPs in a three-step procedure that includes theoretical considerations to select potential applications, lab-scale performance assessment in a real water matrix, and cost and energy comparison with a benchmark process (Fig. 3).

6.2.1. Theoretical consideration to select potential applications for new AOP

Current water research has a strong focus on the removal of trace organic chemicals from secondary effluents, but many AOPs are unsuitable for this application due to high energy demands (e.g., ultrasound, see section 2), potential by-product formation (e.g., electrochemical oxidation), or the required pH range (Fenton reaction). Unique features of these oxidative processes can still make them attractive for applications in different water matrices (industrial wastewater, mine water, drinking water, and water reuse), for different contaminants (e.g., individual chemicals from specific industries), and treatment targets (e.g., removal of COD instead of individual compounds). Alternatively, they may be more relevant for decentralized and small-scale systems, as they potentially offset higher costs by avoiding the need for storage and dosing of chemicals or the removal of residuals [15]. Before conducting the experiments to assess and optimize treatment efficiency in the selected water matrix, theoretical considerations are therefore needed to identify the most suitable application for an AOP. Researchers should carefully evaluate the available information on the process at study (i.e., data from feasibility tests, literature data) and translate it into the definition of potential applications. Criteria for the identification of suitable applications include substrate-specificity of the major reactive species, expected matrix effects on the generation and scavenging of radicals, potential by-product formation in the respective water matrix, as well as requirements for space, labor (for operation and maintenance), and infrastructure (chemicals, electricity). Example discussions on the identification of potential niche applications can be found in reviews on photocatalytic oxidation [28], ballast water treatment [34], and activation of persulfates [5].

The requirements for selected applications need to be characterized thoroughly, including the required steps for pre- and posttreatment. In addition, a specific treatment goal needs to be defined for the selected application. This goal may include percent elimination of a chemical or list of chemicals, but also the removal of alternative parameters such as TOC or COD. Treatment targets can be based on established figures-of-merit for comparison as discussed in section 3 (e.g., 90 % elimination following the EEO figureof-merit), regulatory requirements, or case-specific requirements (e.g., in industrial applications).

Finally, a suitable benchmark process needs to be identified for the selected application. Researchers should answer the following questions: Is a state-of-the-art process already applied? If not, which established processes would likely be used for the defined treatment targets? As an example, •OH-based processes would not be applied for the oxidation of compounds with electron-rich functional groups (e.g., phenols, anilines, amines), where more specific oxidants such as ozone (or potentially sulfate radicals) are more efficient. Similarly, ozonation alone is not an adequate benchmark for mineralization of a target chemical or COD removal, because the reaction typically stops after few individual transformation reactions.

6.2.2. Performance assessment and optimization in real water matrix

Based on the selected treatment targets for the new process, studies to evaluate the treatment efficiency should be operated in a real water matrix with environmentally relevant concentrations of target pollutants and/or probe compounds. Lab-scale experiments should be designed according to the principles described in section 5 to generate results that are scalable and comparable to the benchmark process. They should (i) provide information on optimum treatment parameters for the performance of the process (e.g., pH, oxidant dose, contact time, catalyst dose), (ii) indicate toxic residuals, (iii) quantify residual chemicals, and (iv) assess by-product formation. In some cases, additional mechanistic studies might be needed to characterize and optimize the process. Screening of by-product formation potential should include the analysis of regulated contaminants (and their precursors) with respect to local regulations. In most cases, we would not expect a systematic analysis of transformation products or a screening for toxicological effects at this point (see discussion in section 6.4 for details). The performance of the benchmark process needs to be tested in the same water matrix to ensure comparability of both processes.

6.2.3. Energy and cost efficiency comparison with benchmark process

Because energy consumption data from lab-scale experiments (i.e., energy consumption of the laboratory apparatus) are barely scalable, we recommend using theoretical approaches to upscale both experimentally tested processes (AOP under study and benchmark process) to a representative full-scale operation. For standard processes such as activated carbon, ozonation or UV/H₂O₂, manufacturers can often provide energy and cost estimations based on system dimensions, UV transmittance of the treated water and scalable results from experiments (i.e., required UV fluence rates or ozone consumption). Some processes might be upscaled by implementation of individual modules (e.g., additional electrodes). However, for some innovative AOPs, upscaling of lab-scale results might not be straightforward because pilot- and full-scale applications are not (yet) established (e.g., high frequency ultrasound reactors). Process scale-up is an integral part of chemical engineering to anticipate the performance of a certain process at large scale based on available preliminary lab- or pilot-scale data, and to raise the analyzed process to a similar scale as other commercially available solutions. Traditional scale-up by construction of a pilot-scale plant is expensive and time consuming. Alternative approaches using predictive models and building information modeling based on laboratory data are increasingly used for planning and designing water treatment modules, a scale-up framework for chemical processes was recently proposed by Piccinno et al. [222]. At scale, a comparison of efficacy and efficiency to the benchmark process can provide an initial assessment of the competitiveness of the new process. In addition, data from upscaling may also be used for decision making, e.g., in a life cycle assessment inventory [223] or a triple bottom line (TBL, social, environmental, economic) assessment [220].

The cost and energy evaluation needs to consider the entire process including the dosing of chemicals and subsequent removal and treatment of residuals. In some AOPs, major energy consumption is not only related to the process of radical generation (ozonation, UV-light, or plasma), but also includes energy demand needed to run the desired hydraulics, for example to generate turbulent flow in electrolytic and catalytic AOPs.

6.3. Demonstration of new AOPs (TRL 6-7)

Even though laboratory experiments are conducted in real water matrices, some aspects such as the longevity of new treatment materials, the influence of changes in the water matrix, the effects of combining with other treatment processes, and unforeseen effects can only be revealed in pilot or demonstration tests that are ideally carried out directly at the planned site of operation. In case the pilot testing disproves the applicability of a new material or process, the new AOP must be revised. Considering the undesired effects revealed in the pilot tests, solutions can be developed through revisiting and revising the investigations in detail in previous phases. Successful pilot testing paves the way for full-scale application of new AOPs, which ideally complement the spectrum of well-characterized and ready-for-use AOPs to provide optimal treatment solutions for a wide spectrum of pollutants and scales. In addition, it provides the required information for process upscaling and detailed estimations of costs and environmental impacts.

6.4. Scientific approaches for mechanistic investigation and extended risk assessment

Experiments described in sections 6.1 - 6.3 are not designed to provide a detailed mechanistic understanding of the process at study. Nevertheless, there are several examples of detailed mechanistic information being useful to determine potentials for process optimization, identify and manage risks, and develop corrective actions. One example is the development of bromate mitigation strategies in ozonation processes (e.g., by addition of ammonia or H₂O₂) based on fundamental investigations on the formation mechanisms [72, 224]. Other examples in advanced oxidation include the characterization of nitrite as a scavenger or the identification of *N*-nitrosodimethylamine (NDMA) precursors and formation pathways [225].

Due to the very different approaches to develop new AOPs, studies on the understanding of main reactions in a new oxidative process are diverse and case specific. Experiments may address the whole range and variety of formed reactive species, the reactive sites in heterogeneous processes, transformation mechanisms for individual pairs of oxidant and contaminant, but also nonspecific toxicity and specific mixture effects caused by complex mixtures of products formed in waters treated with AOPs. Experimental approaches often combine various tools such as the use of (multiple) probe compounds and scavengers (see section 4), quantum chemical calculation, and the analysis of transformation products. Good example studies include the characterization of the heterogenous catalytic persulfate process by Zhang et al. [226] and the peroxone process by Merényi et al. [64]. Potential risks related to the formation of unknown by-products may be addressed through bioanalytical tools [227] or non-target screening methods for previously unknown and unregulated by-products [228].

High-resolution mass spectrometry (HRMS) can be a powerful method-of-choice to identify transformation products when it is combined with mechanistic considerations to corroborate reaction pathways. Except for specific industrial wastes, target contaminants in most water sources are not at concentrations that would result in formation of high levels of transformation products. Sources of problematic products are the major water constituents (organic matter, inorganic chemicals) and in some cases the oxidants themselves. However, the analysis of major transformation products can help to identify relevant reactive species and formation pathways [229], and substantiate or falsify results from identification of reactive species. The researcher should follow a systematic approach including available knowledge on transformation reactions of different oxidants from literature [230], and in-silico chemistry [231]. Ideally, product screenings are accompanied by mass-balances to assess the relevance of detected transformation products formed from the target pollutant. In addition, screening for unknown products can assist to elucidate relevant transformation pathways [232,233]]. It should be noted that these studies should be conducted according to a systematic experimental design that is based on existing knowledge (e.g., transformation mechanisms involving **°**OH and different functional groups are well-described) and provides transformation mechanisms involving **°**OH and different functional groups are well-described).

Quantum chemical calculation is an important tool to obtain a first estimate on conceivable reaction mechanisms and transformation products facilitating actual product identification using HRMS [231]. Further insights on the potential of these in-silico tools for mechanistic evaluation of oxidative processes and example applications are provided in literature [64,70,226,231,234].

Bioassays with suitable endpoints can be applied for indicating mixture toxicity effects after water treatment [233], identifying unknown toxic chemicals through effect-directed analysis [235], and monitoring certain classes of chemicals [234]. For instance, the estrogen receptor alpha ($ER-\alpha$) is activated in the presence of endocrine disruptors [236], which can be expressed as estradiol equivalent concentrations. Könemann et al. [236] identified most suitable bioassays to detect adverse effects generated during ozonation of secondary effluents, but these effects have never been attributed to specific unknown transformation products and oxidation by-products. In all cases, the relevance of effects for the aquatic environment and human health should be assessed carefully.

7. Conclusions

Extensive research has been conducted on the development of new materials for catalytic and electrolytic oxidation, the development of new advanced oxidation processes such as vacuum UV, plasma treatment as well as new oxidants and radical promoters. However, up-scaling to pilot- and full-scale operation is slow and evaluation and benchmarking of these advancements is often hindered due to limitations of experimental design and lack of analysis or reporting of relevant information. Typical shortcomings include the selection of contaminants that are not representative, limited reporting of operational (e.g. oxidant dose) and water quality data, or comparison to irrelevant processes. This tutorial review aims to guide researchers from different fields including chemists, physicists, material scientists, and chemical and environmental engineers on how to systematically plan, execute and report experiments on advanced oxidation that are scalable and comparable to benchmark processes. It includes recommendations from basic evaluation of a new concept (TRL 1–3) to pilot- and full-scale demonstration (TRL 6–7).

Following a critical review of the status, potential and future research needs for individual AOPs in section 2 and a discussion of the EEO concept for AOP benchmarking (section 3), the main tutorial chapters provide guidance for the selection of suitable probe compounds and scavengers (section 4), discuss basic rules and key parameters for lab-scale evaluation of different AOPs (section 5), and outline a systematic approach for proof of concept and development of novel AOPs (section 6). Section 6 outlines the major research objectives and tasks from initial exploration and proof of concept (section 6.1, TRL 1–3) through process development and economic assessment (section 6.2, TRL 3–5) to pilot- or full-scale demonstration (section 6.3, TRL 6–7). The final section, 6.4, highlights scientific approaches for the mechanistic evaluation and risk assessment of the process. These studies are not necessarily required during process development, but are recommended to accompany full-scale implementation to ensure optimum operation of a new AOP without introduction of new water quality hazards.

CRediT authorship contribution statement

Uwe Hübner: Writing – review & editing, Writing – original draft, Visualization, Conceptualization. **Stephanie Spahr:** Writing – review & editing, Writing – original draft, Conceptualization. **Holger Lutze:** Writing – review & editing, Writing – original draft, Conceptualization. **Arne Wieland:** Writing – review & editing, Writing – original draft, Conceptualization. **Steffen Rüting:** Writing – review & editing, Conceptualization. **Wolfgang Gernjak:** Writing – review & editing, Writing – original draft, Conceptualization. **Jannis Wenk:** Writing – review & editing, Writing – original draft, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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