Emerging advanced oxidation processes for water and wastewater treatment

– guidance for systematic future research

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Abstract

Advanced oxidation processes (AOPs) for water treatment are a growing research field with a large variety of different concepts and materials being tested at laboratory scale. However, only few
concepts have been translated into pilot- and full-scale operation recently. One major concern are the inconsistent experimental approaches applied across different studies that impede identification, comparison, and upscaling of the most promising concepts. 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, radiation-driven, and other mostly physical AOPs, and outline future perspectives and research needs. Suitable figures-of-merit for comparison and benchmarking of AOPs are reviewed. Since standardized experimental procedures are not available for the majority of AOPs, we propose basic rules and key parameters for lab-scale evaluation of new AOPs including selection of suitable probe compounds, model compounds, and scavengers for the measurement of (major) reactive species. A two-phased approach to assess new AOP concepts is proposed, consisting of (i) a feasibility-of-concept study phase with validation of major radical species and comparison to suitable reference processes and materials, followed by (ii) a benchmarking phase conducted in the intended water matrix for the process, applying comparable and scalable parameters such as UV fluence or ozone consumption. Screening for transformation products should be based on chemical logic and combined with complementary tools (mass balance, chemical calculations) to advance mechanistic understanding of the process.

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.\textsuperscript{2,6–14} Radicals for AOPs in water, including \textsuperscript{\textbullet}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 Figure 1). For instance, research has been conducted on the development of new materials for catalytic and electrolytic oxidation.\textsuperscript{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.\textsuperscript{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.\textsuperscript{16,21,22} A large array of water contaminants, including so-called emerging contaminants, has been investigated to a great extent for their degradability by AOPs.\textsuperscript{2,23} Despite several recent reviews on AOPs,\textsuperscript{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.\textsuperscript{27,28} The suitability of many novel AOPs for water treatment is debatable e.g., due to the utilization of materials with concerning toxicity or lack of long-term stability.\textsuperscript{29–31} 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\textsuperscript{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 concepts for oxidation of emerging contaminants.

With this tutorial review, we aim to provide guidance for researchers that work on the development of new solutions and materials for advanced oxidation. We briefly discuss status, potential and future research needs for emerging AOPs, summarize available concepts to assess and compare different AOPs, and outline basic rules for conducting oxidation experiments and selecting probe compounds and scavengers. Finally, we propose a systematic approach for the assessment of novel concepts and materials for advanced oxidation.

2 Status and perspectives for “emerging” oxidation processes

There is an immense variety of different approaches proposed and tested to generate radicals in water. Figure 1 summarizes various AOPs with indicated degree of application (lab-scale vs. pilot- and full-scale). Established AOPs operating at full scale comprise mostly UV- and ozone-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,\textsuperscript{27} these most widely applied AOPs typically also provide the highest energy efficiencies among AOPs.\textsuperscript{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.\textsuperscript{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 concepts, 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.

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

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$_2$O$_2$), sodium percarbonate (Na$_2$CO$_3$ x 1.5 H$_2$O$_2$), peroxysulfate (S$_2$O$_8^{2-}$), and monochloramine (NH$_2$Cl) or increase radical formation from oxidants such as ozone. 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$_2$O$_2$ 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 as well as iron-free Fenton-like systems
have been explored using other transition metal ions (e.g., copper or cobalt), which can activate
H$_2$O$_2$ 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,$^{46,47}$ metal-free polymers,$^{48,49}$ carbonaceous materials,$^{50,51}$ layered double
hydroxides,$^{52}$ metal-organic frameworks,$^{53}$ and single-atom catalysts.$^{54,55}$ 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 full-scale water treatment has
been slow.$^{46}$ To overcome obstacles that prevent catalytic systems 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.$^{46}$ These desirable attributes and testing requirements also apply to photocatalysts (see
section on radiation-driven AOPs). 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.$^{46}$ Innovative
catalysts may 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.$^{46}$
2.2 Recent progress in ozone-based advanced oxidation

In every ozonation process, ‘OH are formed from the reaction of ozone with the water matrix, especially with organic matter.\textsuperscript{56,57} However, since the formation of ‘OH is “uncontrolled”, ozonation is often not defined as an AOP. ‘OH formation can be enhanced by the addition of H\textsubscript{2}O\textsubscript{2} (either as solution or by electrochemical in situ production) in the peroxone process, pH elevation, catalytic ozonation, or ozone photolysis.\textsuperscript{58–63} UV/O\textsubscript{3} is discussed as a UV-based AOP in the next section.

In the peroxone process, ozone reacts fast with the H\textsubscript{2}O\textsubscript{2} anion (HO\textsubscript{2}\textsuperscript{-}) (k = 9.6 × 10\textsuperscript{6} M\textsuperscript{-1} s\textsuperscript{-1}) with a yield of 0.5 mol ‘OH per mol reacted ozone.\textsuperscript{58,61} The peroxone process is often applied to mitigate formation of undesired bromate\textsuperscript{64,65} or to quench excess ozone with the advantage of further ‘OH formation.\textsuperscript{66} At elevated pH, ozone may react with hydroxide ions to form ‘OH. However, this reaction is rather slow (k = 70 M\textsuperscript{-1} s\textsuperscript{-1})\textsuperscript{67,68} and the costs for adding bases, especially in strongly buffered waters, as well as increasing risk of bromate formation may limit ozonation at elevated pH towards a narrow range of source and wastewaters.\textsuperscript{69}

Homogeneous and heterogenous catalysis in ozonation is based on the decomposition of ozone by transition metal ions or solid metal oxide catalysts (mostly iron- and manganese-based materials), and activated carbon or other carbon-based materials.\textsuperscript{62,70,71} In heterogeneous catalytic ozonation, pollutant removal can be achieved via interfacial reactions at the catalyst surface after sorption of ozone (gaseous or dissolved) and/or the pollutant, and in the aqueous phase through ‘OH, which is generated from ozone decomposition at the catalyst surface.\textsuperscript{70,72} The process may have an advantage over homogenous catalysis because no additional metal ions need to be dosed and subsequently removed. However, it may have mass-transfer limitations as ‘OH are formed at the catalyst surface. Knowledge about the driving mechanisms for catalytic ozonation is still limited. For example, different catalytic activity has been reported for various types of MnO\textsubscript{2}, with some types leading to ozone decay without significant ‘OH formation.\textsuperscript{62,73} Different mechanisms have been proposed for catalytic ozonation with activated carbon-based materials,\textsuperscript{70} with some studies indicating that radical formation may be related to finite reactions with functional groups of the carbon leading to a slow consumption of the “catalyst”.\textsuperscript{74} A direct comparison of different study results is
often hampered by the use of various experimental procedures with different mass transfers (gaseous ozone vs. injection of ozone stock solution), different design and duration of the experiments, and different active catalyst surface areas. Research on catalytic ozonation should therefore follow standardized experimental procedures (see section 5) that enable the assessment of benefits for radical generation compared to sole ozonation (which already contributes to considerable radical generation), as well as 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.\textsuperscript{75,76} The applied wavelengths range from $>170$ (VUV) to $700$ nm (visible light).\textsuperscript{77} 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 (see below).

Homogeneous AOPs. Analogous to dark catalytic AOPs, radiation-driven AOPs can be distinguished into homogeneous and heterogeneous processes applying a similar range of radical precursors for homogeneous processes including H$_2$O$_2$, chlorine and chlorine dioxide, peroxydisulfate (S$_2$O$_8^{2-}$), ozone, and the photo-Fenton process. Photolysis and radical generation mechanisms in these processes are widely established and well-described in literature.\textsuperscript{78–83} UV/H$_2$O$_2$ and UV/chlorine are the most widely applied processes.\textsuperscript{84–88} The UV/H$_2$O$_2$ process is used in drinking water treatment and potable reuse schemes to remove trace contaminants that are difficult to remove otherwise\textsuperscript{69} and can be advantageous when ozone-based processes would result in undesired bromate formation from naturally occurring Br.\textsuperscript{65} The energy demand of UV/H$_2$O$_2$ is higher compared to conventional ozonation and the peroxone process.\textsuperscript{90} In full-scale potable reuse schemes, UV/chlorine (HOCl) is increasingly used with and without the addition of chloramines.\textsuperscript{85} Thereby, the photolysis of HOCl results in the formation of •OH and chlorine atoms,\textsuperscript{91} the photolysis of chloramines gives rise to formation of aminyl radicals and chlorine atoms.\textsuperscript{92} Reactions of these reactive species in water are discussed in more detail elsewhere.\textsuperscript{93,94}
UV/chlorine is mostly applied as the last treatment step for simultaneous degradation of pollutants and disinfectant residuals, with limited application in organic-rich and ammonia-containing waters due to formation of toxic by-products.95 Sulfate radicals react more substrate specific than \( \cdot \)OH.\(^5\) Therefore the UV/S\(_2\)O\(_8\)\(^2\)⁻ process benefits from reduced oxidant scavenging by the water matrix, but less reactive compounds are more difficult to eliminate compared to the UV/H\(_2\)O\(_2\) process.\(^96\) The UV/S\(_2\)O\(_8\)\(^2\)⁻ process may provide tailored solutions towards individual substances or substance groups rather than broadband treatment envisioned in most AOP applications.\(^5\) Compared to H\(_2\)O\(_2\) [\( \varepsilon_{\text{H}_2\text{O}_2,\lambda=254\text{nm}} = 18.6 \text{ M}^{-1} \text{ cm}^{-1} \)]\(^97\) and S\(_2\)O\(_8\)\(^2\)⁻ [\( \varepsilon_{\text{S}_2\text{O}_8,\lambda=254\text{nm}} = 22 \text{ M}^{-1} \text{ cm}^{-1} \)]\(^98\), ozone has a high molar absorption coefficient of \( \varepsilon_{\text{O}_3,\lambda=254\text{nm}} = 3300 \text{ M}^{-1} \text{ cm}^{-1} \),\(^57\) resulting in an efficient photolysis into \( \cdot \)OH\(^82\) that is 20 times more efficient than H\(_2\)O\(_2\) photolysis at the same dissolved molar concentration. However, due to the combination of two energy-intensive processes, namely ozonation and UV irradiation, the UV/O\(_3\) process is typically not competitive with alternative solutions.

The Photo-Fenton process is based on the absorption of light by Fe(III)-HO\(_2\)⁻-complexes (\( \varepsilon = (450 \text{ nm}) \approx 450 \text{ M}^{-1} \text{ cm}^{-1} \)).\(^82\) Thereby, the complex cleaves into HO\(_2\)⁻ and Fe(II), and Fe(II) reacts with H\(_2\)O\(_2\) to form \( \cdot \)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.\(^99,100\) Recent developments are related to using complexing agents to operate at pH 7 and using less costly reactor concepts.\(^101,102\)

**Heterogeneous photocatalytic AOPs.** Research on photocatalysis for degradation of refractory pollutants has been intense since the discovery of photocatalytic water splitting.\(^103\) Heterogeneous photocatalysis employs a range of semiconducting catalysts, of which TiO\(_2\) and ZnO are the most widely researched materials.\(^31,104\) 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,\(^99\) 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. 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. In a critical analysis of the technology and market prospects of photocatalysis, Loeb et al. (2019) 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 or arsenate. 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).

**Lamp technology.** New UV radiation sources in water treatment have been tested, primarily for disinfection and photocatalysis in the UV-A range. 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). So far, it has been possible to produce LEDs with an emission wavelength as short as 210 nm. 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. The small size and control of individual LEDs enables an innovative reactor design and a larger range of applications. 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. (2020).

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 \( \cdot \)OH and solvated electrons. Lamps employed for AOP development include Xe Excimer lamps 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.\textsuperscript{112} The main challenges to implement the VUV process relate to the low penetration depth of VUV into water and possible by-product formation by inorganic ions. At 185 nm, the decadic absorption coefficient of pure water is $1.8 \text{ cm}^{-1}$ ($\varepsilon_{\text{H}_2\text{O}, \lambda=185\text{nm}} = 0.032 \text{ M}^{-1} \text{ cm}^{-1}$)\textsuperscript{113} 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 reactor concepts 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.\textsuperscript{114} VUV absorption by chloride in real water matrices raises similar concerns as the UV/chlorine process regarding the formation of halogenated oxidation byproducts. Analogously, in waters with high nitrate concentrations, nitrate photolysis may generate potentially harmful nitrogenous oxidation byproducts.\textsuperscript{115,116} This is an aspect that has not yet been thoroughly investigated for the VUV process.

### 2.4 Other AOPs

Here, “other AOPs” include a broad and diverse range of approaches to generate radicals in water for treatment applications. Apart from heat-activated persulfate activation, these approaches largely are more energy intensive treatment solutions compared to the other three groups of AOPs (i.e., ozone-based, radiation-driven and catalytic AOPs, Figure 1).\textsuperscript{25} Despite comparably high energy demand, these processes may have unique features (e.g., chemical-free operation) that make them attractive for specific niche applications (e.g., in small and decentralized systems). In addition, ultrasound, plasma treatment, supercritical water oxidation, and electrochemical oxidation have been discussed for the removal of highly refractory poly- and perfluoroalkyl substances (PFAS).\textsuperscript{117-120} However, PFAS are highly persistent to \textsuperscript{•}OH attack and breakdown is related to different mechanisms, e.g., pyrolysis during ultrasound treatment,\textsuperscript{121} or direct electron transfer at anode surface.\textsuperscript{118}
Application of ultrasound in water with frequencies of 20-1,000 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 (> 4,000 K) at the microscale. The resulting pyrolysis of water vapour inside the bubbles yields ·OH and H· radicals, which do not readily recombine due to the high temperature. 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. 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. 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. 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. All these species can be involved in the degradation of a pollutant but the contribution of each reactive species is highly substance and system specific.

Regarding the engineering challenges of the process, it is clear that similar to e.g., electrochemical processes, the active reaction volume, i.e., where plasma contacts with water to be treated, is small. Consequently, efficient reactor engineering is key to ensure adequate mass transfer and
to develop practicable solutions.\textsuperscript{127} Another hardware-related challenge is the development of economic and efficient plasma generation systems tailored to specific needs of water treatment.  

Thermal activation of persulfate has been used for in situ chemical oxidation to remediate contaminated groundwater and soil.\textsuperscript{83} Due to the small bond dissociation energy of the peroxide bond (120 KJ mol\textsuperscript{-1}),\textsuperscript{128} even moderate temperatures (> 40 °C) suffice to cleave persulfate into sulfate radicals.\textsuperscript{129} 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.\textsuperscript{130}  

A disadvantage of using persulfate is a strong drop in pH and strong radical scavenging effects in the concomitant presence of chloride and bicarbonate.\textsuperscript{93}  

Supercritical water oxidation (SCWO) has been shown to be applicable for the degradation of various wastes in laboratory scale and full scale.\textsuperscript{131} However, applications other than demonstration sites are very rare or hardly exist so far. The reason is that alternative treatment options such as incineration and dumping are less complex.\textsuperscript{131} In supercritical water oxidation, the water under treatment is heated and pressurized to reach the critical state (temperature range 400-650°C at supercritical pressures).\textsuperscript{131} In the super critical state, water becomes mixable with nonpolar compounds, while polar and ionic compounds may still remain soluble.\textsuperscript{132} However, inorganic compounds such as salts can precipitate and be treated as solid waste. In this way, it has been possible, e.g., to separate radioactive elements from bulky non-flammable material of artificial nuclear power plant wastes in bench-scale experiments, which may reduce the volume needed for radioactive waste storage.\textsuperscript{133} Under conditions of SCWO the oxidation process is favoured by high (gas phase) diffusion rates combined with high liquid phase collision rates. Oxygen is typically used as oxidant and as a source of oxygen, H\textsubscript{2}O\textsubscript{2} can be used, which decomposes into oxygen upon its thermal decomposition.\textsuperscript{131}  

In electrochemical advanced oxidation processes, ‘OH are directly generated from water oxidation at the electrode surface.\textsuperscript{30} 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.\textsuperscript{134} 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.\textsuperscript{135,136} Due to the efficient conversion of electrical energy into •OH and secondary oxidants (\textit{H}_2\textit{O}_2, \textit{O}_3) and the chemical-free operation, electrical AOPs are often considered as environmentally-friendly treatment solutions.\textsuperscript{137} 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.\textsuperscript{136} Current research is focused on new electrode design to optimize mass transfer and concepts to mitigate by-product formation.\textsuperscript{134,138}

3 Comparison and benchmarking of AOPs

One of the first concepts for figures-of-merit for comparing AOPs was proposed by Bolton et al. (1996) and subsequently published as an IUPAC Technical Report.\textsuperscript{139,140} Given that ultimately most AOPs are electrically driven, the concept employs electric energy required to decrease the concentration of a target contaminant by 90\%, i.e., by one order of magnitude. The electric energy per order (EEO) concept applies to AOP systems with dilute (low) concentration of contaminants and therefore most water treatment applications. There are variations of the concept for systems with high contaminant concentration using electric energy per mass (EEM) and for solar-driven systems using solar collector area instead of electric energy.\textsuperscript{140} For light-induced AOPs, the EEO concept 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.\textsuperscript{141,142} The EEO concept has been extensively applied on most AOPs, including ozonation and peroxone,\textsuperscript{13,63,90} electro-chemical,\textsuperscript{136,143} ultrasound-based,\textsuperscript{144} and both homogeneous and heterogeneous UV-based AOPs.\textsuperscript{90,145,146} Thereby, the EEO concept 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\textsubscript{2}O\textsubscript{2} requires reporting of probe compound concentration, molar absorption coefficients, second-order reaction rate constants
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with \( \cdot \text{OH} \) \((k_{\text{OH}})\), observed reaction rate constants \((k_{\text{obs}})\), and direct phototransformation rates. In addition, the water matrix pH, light absorbance, and \( \cdot \text{OH} \) scavenging rates by non-target compounds, e.g., natural organic matter should be reported.\(^{147}\) 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.\(^{147}\) The variance of literature data within individual AOPs indicates the difficulty to compare processes at different scale and in different water matrices.\(^{25}\)

In addition, the electrical energy dose (EED) of a treatment process can be determined. The EED is defined as “electrical energy (kWh) consumed per unit volume […] of water treated”.\(^{89}\) For example, for a given UV-AOP it is the UV-reactor’s energy demand divided by the flow rate for a specific treatment target or for a defined percentage lamp ballast power (regulating supplied voltage and current). This factor is independent from the water matrix and allows a direct comparison of different treatment processes. However, it requires a precise definition of the system boundaries to allow a direct comparison of different processes. Scaling effects need to be considered, because large-scale systems are often more efficient than lab-scale processes.\(^{89}\) While the EED and EEO have their eligibility as sound factors benchmarking the power efficiencies of different AOP-systems, they are lacking qualification as AOP design parameters. This is because of the difference in energy efficiencies of different AOP systems. For example, two given AOP systems, A and B, may achieve the same treatment target. However, due to different equipment properties such as differences in the efficiency of ozone generation, UV light distribution, or different hydraulic conditions inside each reactor, both EED and EEO of A and B may differ. Therefore, at the same EED or EEO, system B might under- or overachieve the treatment target in comparison to system A.

In the UV-AOP business for instance, the market is currently shifting away from use of EED and EEO as design parameters for micropollutant abatement towards the Reduction Equivalent Dose (RED), similar to the RED defined by the Ultraviolet Disinfection Guidance Manual UVDGM for pathogen reduction\(^{148}\) (personal conversation, Xylem). As rule of thumb, disinfection requires less than 10% of energy demand compared to micropollutant reduction to achieve the same RED value.
Chemical probe compounds, including scavengers and quenchers, serve a central role as diagnostic tools in AOP research.\textsuperscript{3} Probe compounds are selective, typically low molecular weight, molecules that allow kinetic and mechanistic investigation of an AOP. Scavengers are compounds that react with or trap reactive species. Quenchers deactivate excited states by energy transfer, electron transfer, or a chemical mechanism.\textsuperscript{149} However, they are used for very similar objectives and therefore jointly named scavengers in the following. AOP literature does not always clearly distinguish between probe, indicator, and model compounds. Here, we define model compounds as actual contaminants or representatives that occur in a specific treatment scenario. The term indicator is synonymous and not used in this paper. In contrast, probe compounds also include compounds that are rarely encountered in water treatment and are only used for diagnostic purposes.

Ultimately, both probe and model compounds (if selected based on similar criteria than probe compounds) can be used to gain information on the efficiency of AOPs and to determine reactive species concentration and process performance, including under full-scale conditions.\textsuperscript{150,151} There is a wide range of probe compounds available for reactive species in water. Recent reviews have summarized probe compounds used to detect reactive oxygen species in aqueous environments\textsuperscript{152}, during photocatalysis\textsuperscript{153} or in UV-based advanced reduction processes,\textsuperscript{154} to assess the photochemical activity of dissolved organic matter,\textsuperscript{155} and the contribution of reactive nitrogen species to compound transformation.\textsuperscript{156} Here, we briefly discuss the requirements for suitable probe compounds and provide a few examples for frequently employed compounds for the most relevant reactive species in AOPs.

The use of probe compounds in AOP research is imposed by the difficulty to measure reactive species directly given their short lifetime. The half-life ($t_{1/2}$) of reactive species produced in AOPs and AOP-like processes in pure water is typically in the range of microseconds (µs) as for "OH and SO$_4$\textsuperscript{-}, to milliseconds (ms) for less reactive species such as carbonate radicals and superoxide radicals.\textsuperscript{152,157} Non-radical oxidants such as ozone and H$_2$O$_2$ are more stable with half-lives in the range of minutes to hours.\textsuperscript{158,159} In real water matrices, the lifetimes of most reactive species may
be much shorter due to the presence of reactants, including scavengers (see below). Generally, short-lived reactive species in water can be measured and characterized directly by laser flash photolysis and pulse radiolysis hyphenated with fast UV-vis spectroscopy, and by electron spin resonance after scavenging with a spin trap, which has resulted in comprehensive datasets of reaction rates for radicals in aqueous solutions. However, these methods require expensive, non-portable specialized instrumentation and considerable expertise with limited availability to most researchers.

There are several requirements for a suitable probe compound in AOP research. A probe compound should react fast and selectively with the reactive species of interest with a known second-order reaction rate constant. The reaction of the probe compound with the reactive species should be specific and well-defined, preferably with a known reaction mechanism. A probe compound should not physically interact with the system under investigation, for example via adsorption onto solids in heterogeneous processes or electrodes in electrochemical AOPs. Ideally, probe compounds should react only via one clearly defined transformation pathway. This is especially important in combined AOPs with more than one significant reactive species. Particularly, ozone- or UV-based AOPs require the selection of probe compounds that are insensitive to ozone and photolysis, respectively. To elucidate and distinguish between different radical sources (e.g., HOCl, H$_2$O$_2$, and persulfate in UV-based AOPs), a suite of probe or model compounds may be required that exhibit a wide-ranging selectivity toward the relevant individual oxidants present. Similarly, the study of complex systems involving the formation of secondary and tertiary radicals may require a combination of probe compounds and selective scavengers. An exemplary procedure for a sulfate radical-based process in the presence of chloride is provided by Lutze et al. (2015). Preferably, probe compounds should be inexpensive, non-toxic, non-carcinogenic, and readily dissolvable in water at a desired concentration without the need for co-solvents. To determine oxidant exposures, probe compounds are used at low concentrations to not significantly lower the concentration of reactive species by acting as scavengers themselves. Probe compounds or reaction products should be straightforward to measure with available analytical equipment. UV/Vis-
spectrophotometry 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. 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 \( \cdot \text{OH} \) is the reactive species of highest interest for most AOPs. Treatment concepts based on \( \cdot \text{OH} \) can be adequately evaluated through spectrophotometric monitoring of the removal of chromophores, often dyes such as rhodamine B, methylene blue, and fluorescein. For a summary of different approaches for UV/H\(_2\)O\(_2\), including assessment of an external standard calibration method using methylene blue, see Wang et al. (2020). Typical probe compounds for \( \cdot \text{OH} \) that can be readily measured via HPLC include \( \text{para} \)-chlorobenzoic acid (\( \text{pCBA} \)), \( \text{para} \)-nitrobenzoic (\( \text{pNBA} \)) acid, and atrazine. For UV-only probe compounds, including actinometry, see section 5.2 for fluence rate determination.

It is important to distinguish between the various scavengers present in real water matrices, such as organic matter and inorganic ionic species, which have significant effects on AOP treatment performance, and those employed for diagnostic purposes. Diagnostic scavengers can be used to indicate and quantify the presence of radicals, non-radical reactive species, and excited states in AOPs by suppressing reactions. 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. As a rule of thumb, a scavenger should trap more than 95% of the reactive species, which can be determined by competition kinetics calculations as described before. Typical scavengers for \( \cdot \text{OH} \) include \( \text{tert} \)-butanol and dimethyl sulfoxide (DMSO). The reaction of \( \cdot \text{OH} \) with \( \text{tert} \)-butanol and DMSO leads to the formation of formaldehyde (yield \( \approx \) 25%) and methanesulfinic/methanesulfonic acid (yield of the sum of each \( \approx \) 98%), respectively.
Quantification of these transformation products allows calculation of the \textsuperscript{•}OH formed.\textsuperscript{172} While a large variety of substances can be used to scavenge different reactive species,\textsuperscript{173} 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.\textsuperscript{174} 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 Basic rules for oxidation 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,\textsuperscript{175} and such equipment may not be accessible for researchers or may be unsuitable especially for newly developed treatment concepts. 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 the section on 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. In some cases, this can generate secondary reactive species. Second, matrix components can scavenge radicals terminating radical chain reactions in non-productive ways towards treatment targets. 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. Depending on their respective reactivity with a target compound and their tendency to accumulate at higher concentrations due to their persistance compared to other radical species, such secondary reactive species can contribute significantly to the degradation of a target compound.

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).

Similarly, the pH must be recorded and reported at least before and after, and if possible during the experiment, as it can affect acid-base-equilibria and reactivity of matrix and target contaminants. 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.

Furthermore, concentrations of any added chemicals need to be listed.

5.2 UV-based processes

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-
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scale set-ups, which are rarely designed for optimal energy efficiency. At laboratory scale, it is preferable to focus on directly evaluating the photochemical processes only, i.e., direct photolysis of contaminants and photolysis of radical precursor species such as $\text{H}_2\text{O}_2$. This is done by using set-ups that allow assessing photochemical reactions as function of the fluence rate in the reactor as basis for comparing photochemical studies.

The fluence rate 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 rates can be translated in time-based parameters by simple calculations with the apparent fluence rate at hand when needed.

**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, excimer lamps, and LEDs with a slightly broader emission peak) 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. How this can be addressed has been extensively discussed for UV disinfection processes. The same approach has been transferred also to AOPs.

**Fluence rate determination.** There are several methodologies to measure the photon flux. These can rely on different principles, which affects how the information obtained can be used to determine fluence rate. First, there are numerous chemical actinometers, most of which have been conveniently described in an IUPAC Technical Report, some of which have been reviewed recently. Among them we can distinguish opaque actinometers, e.g., the iodide/iodate actinometer frequently used to determine 254 nm radiation and non-opaque actinometers such as the uridine actinometer, also used to determine 254 nm radiation. The first type essentially determines the incident fluence rate (full absorption after contacting the reactor, no penetration of...
light into the reactor) yielding a value for irradiance, whereas with the second type allows photons to fully move through the reactor (vanishing absorption). By that means an average fluence rate of photons available for photochemical reactions 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. This is an aspect particularly important in disinfection, where several orders of magnitude of microorganism inactivation are typically envisaged. For AOPs it tends to be of lesser relevance, except perhaps in processes prone to mass transfer limitations. Finally, radiometers and spectroradiometers are commonly applied to measure by means of an electronic device, calibrated against an absolute standard, the photon flux at a chosen location in the experimental set-up.

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.

Finally, on a very practical level, it is recommended to implement a combined approach of radiometry and actinometry in the laboratory, whereby on a routine-basis radiometry is used to determine irradiance and chemical actinometry is used periodically to verify that the calibration of the radiometer is still accurate and does not show drifts.

**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). 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 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\textsuperscript{175} and recently complemented with additional guidance on evaluation.\textsuperscript{184} The key advantage of this 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\textsuperscript{191}).

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 or biodosimetry are preferable rather than opaque actinometers and radiometers to avoid the complex post-processing to obtain fluence rate from the actinometry result.\textsuperscript{175} Radiation evaluation methods and processes for matching wavelength-dependent responses apply in analogy to action spectra for different pathogens and irradiation sources in disinfection.\textsuperscript{192}

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 is important to obtain
meaningful results. Such considerations are especially important for upscaling to pilot systems, for
more details see.  

5.3 Ozone-based processes

Ozone consumption and mass transfer. Transfer of results from lab-scale ozonation requires
coloration of injected or reacted (consumed) ozone, because mass transfer in lab-scale
experiments is not comparable to larger-scale operations. While pilot- and full-scale ozone injection
systems typically provide mass transfer of >95% gaseous ozone into solution, mass transfer in lab-

scale reactors can be highly variable. Standardized concepts to determine transfer efficiency of a
reactor (e.g. k_La) do not provide a reliable characterization for ozonation because the high reactivity
of ozone affects its transfer efficiency into water. Observed better removal of contaminants with
ozone-based AOPs compared to ozone alone may be a result of enhanced mass transfer (and
ozone consumption) in inefficient lab reactors and not only related to improved treatment efficiency.

To generate transferable data from lab- and pilot-scale ozonation, consumed ozone should be
reported as a reliable figure of merit. In batch ozonation experiments, monitoring of ozone decay
over time can provide helpful complementary information. This section discusses major aspects for
experiments with ozone-based AOPs. A detailed manual for ozonation experiments is provided by
Gottschalk (2010).

Determination of radical formation efficiency. In a pure water at neutral pH, ozone is slowly
decomposed by water (OH-, k = 70 M⁻¹s⁻¹) giving rise to the formation of •OH. In more complex
matrices such as secondary effluents, elevated ozone decay through reactions with organic matter
also leads to considerable •OH formation. Active enhancement of radical formation in ozone-

based AOPs can therefore have two objectives: i) to accelerate ozone decomposition kinetics into
radicals by “quenching” (often residual) ozone with a radical promoter, and/or ii) to enhance overall
radical generation compared to conventional ozonation. In complex water matrices, the benefits of
the AOP are often limited due to the competing reactions of organic matter with ozone that already
generate considerable amounts of •OH. The •OH yield in the tested AOP should therefore always
be assessed in comparison to conventional ozonation. In experiments with gaseous ozone,
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Researchers also need to account for potential bias caused by effects on mass transfer (see previous discussion).

The R\textsubscript{CT}-concept by Elovitz and von Gunten (1999),\textsuperscript{195} which defines the R\textsubscript{CT} as the ratio between \textsuperscript{1}OH exposure and ozone exposure, has often been applied to assess efficiency of ozone-based AOPs. However, this concept was not designed for this purpose and R\textsubscript{CT} values should be evaluated carefully because enhanced kinetics compared to conventional ozonation primarily reduce ozone exposure in the denominator.\textsuperscript{196} It is therefore recommended to compare radical yields (or exposures) from ozonation and the tested AOP as a function of the consumed ozone as for example described in Hübner et al. (2015).\textsuperscript{177}

**Advantages and disadvantages of different lab set-ups.** Like UV-based processes, lab-scale ozonation systems can be distinguished into CSTRs (with injection of gaseous ozone (semi-batch experiments) or as a concentrated ozone solution (batch experiments)), and continuously operating systems.

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,\textsuperscript{197,198} and easily measured photometrically prior to injection.\textsuperscript{199} 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.\textsuperscript{193}

For experiments with gaseous ozone, a full ozone mass balance including continuous monitoring of gas flow, in-gas and off-gas ozone, and residual ozone in the water is needed to determine the consumed ozone. Lab-scale experiments are mostly operated in semi-batch mode (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.\textsuperscript{72,193}
A time-resolved sampling from such experiments is not recommended because the consumed ozone at different times (often referred to as “transferred ozone dose”) is not accurately described. Lab-scale experiments are typically not conducted at continuous water flow, since even the smallest commercially available ozone generators (2-4 g O₃/h) would induce considerable water flow rates (or ozone doses). Electrochemical ozone generation can provide a suitable solution for continuous operation of ozonation at lab scale.\textsuperscript{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.\textsuperscript{200} 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.

**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, for some applications, parallel or later dosing might be more beneficial, e.g., to reduce competition with ozone-reactive water constituents or to utilize the efficiency of direct ozone reactions (e.g., for disinfection) before rapid decomposition during the AOP.

For heterogeneous catalytic ozonation, the reactor design should be carefully selected. In addition to the basic rules for catalytic AOPs (see section 5.4), the experimenter needs to account for ozone-related characteristics of the process including the potentially different interaction of gaseous and dissolved ozone with the catalyst and the ozone decay into ‘OH without catalyst. Reference experiments at identical conditions are needed to test 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.\textsuperscript{74}
5.4 Catalytic AOPs

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,\textsuperscript{201} 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 taken into account 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 reactivity.\textsuperscript{72} Water quality measurements should include the parameters listed in section 5.1.

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,\textsuperscript{202} 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.\textsuperscript{202} However, the applicability of this concept to catalytic oxidation is not trivial because the turnover in catalytic processes in theory describes the catalytic reaction, i.e., the generation of short-lived radicals in an AOP. The actually measured reaction of these radicals with a contaminant is affected by many parameters including the mixing efficiency, contaminant characteristics and reactivity, which do not depend on catalyst activity. In addition, catalytic oxidation often involves different reactive species and mechanisms.
Experimenters must 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), normalized rate constants might be used as a suitable figure of merit for comparison. However, it should be noted that the selection of probe compounds can have a significant impact on the results. In addition to compound removal, the process evaluation should also include consumption, stability, life cycle, regeneration potential, and toxicity of the catalyst.

**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 concepts where the innovation is a novel catalyst (support) geometry itself, e.g., (photo)catalytic membranes.
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and foams,\textsuperscript{203,204} or immobilized catalysts in filters.\textsuperscript{16} 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 sorption. 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.

### 5.5 Other AOPs

The diverse range of other AOPs is challenging to evaluate because standardized set-ups and suitable figures-of-merit 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.\textsuperscript{127} Also results from sonolysis using slightly different reactor design at the same experimental conditions were not comparable.\textsuperscript{205} Reactor concepts 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 set-ups will have to cope with this situation and with the related difficulties in reporting accurately. 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. 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 concepts for electrochemical oxidation,\textsuperscript{136} plasma,\textsuperscript{127} and cavitation processes.\textsuperscript{206}
6 Implications for future research: Assessment of new concepts and materials for advanced oxidation

Research on AOPs can be separated into two major research tasks: i) the development and assessment of new concepts and materials for advanced oxidation and ii) the selection of suitable oxidation processes for specific treatment targets. This section presents a systematic approach for feasibility testing (Figure 2) and benchmarking of new concepts for advanced oxidation in water treatment (Figure 3), which approximately corresponds to a technology readiness level (TRL) of 5, defined as a validated process in a relevant environment. Subsequent pilot- and full-scale implementation is briefly discussed, including a corresponding approach for systematically selecting a suitable process for specific treatment targets (Figure 4). Finally, we outline scientific approaches to elucidate oxidation mechanisms and assess the potential formation of currently unknown by-products.

6.1 Phase 1 – Feasibility study

In phase 1, the general feasibility of a concept is evaluated based on theoretical considerations and preliminary, (non-)standardized bench-scale experiments. The feasibility study elucidates the suitability of applied materials and chemicals for water treatment and the potential of the new concept for contaminant elimination. In addition, this phase provides initial information for the cost and energy evaluation in phase 2. In some cases (e.g., the synthesis of new catalytic materials), lab-scale experiments may already provide direct comparison to established (reference) materials or concepts.
Figure 2. Phase 1 - Assessing the feasibility of new developments in advanced oxidation (after positive evaluation the new concept will be benchmarked against established AOPs in Phase 2)

Prefeasibility assessment. It is recommended to consider the fundamental applicability of a new process on a theoretical basis. 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, e.g., by leaching heavy metals, which may require precautionary measures. Cobalt, for instance, is a potent catalyst to initiate sulfate radical formation. However, cobalt is a toxic heavy metal that should only be used after immobilization on a surface. 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.\textsuperscript{130,209} Another example is ultrasound treatment, which is often tested in an artificial argon atmosphere, which would incur high costs in full-scale applications.\textsuperscript{210} 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.

\textbf{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 concept 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 benchmark AOPs regarding 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 (phase 2). 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 well-studied 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 an “oxidation strength”, ii) identify major reactive species involved in the process, and iii) provide first information on process and material stability. Experiments should be designed to provide the required information for considerations in phase 2.

Although different analytical approaches may be used to validate the presence of individual radical species, relevant exposures 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 H₂O₂), a general feasibility study may not be needed because the reaction mechanism and major oxidants are already well-known. In such cases, the evaluation of the process would start directly with phase 2.

6.2 Phase 2 – Benchmarking new concepts for advanced oxidation

Individual AOPs have specific advantages and disadvantages depending on target contaminants, water matrix, and process scale. Lab-scale experiments to benchmark new AOP solutions should be conducted in real water matrices in direct comparison to an established AOP to account for matrix-specific efficiencies. Thereby, the new process has to be compared with the established or already applied AOP (benchmark AOP) under comparable reaction conditions (same water matrix, pH, etc). Unlike the reference process in phase 1, which is selected based on mechanistic similarity, the benchmark AOP should provide the most suitable 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 benchmarking 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
AOP (Figure 3).

Theoretical consideration to select potential applications for new AOP
- Identify potential application(s) for new process
  - What contaminants can be targeted? Which water matrix can be treated? Which scale
    (centralized vs. decentralized) is applicable?
- Define treatment goal for specific application
- Select a suitable benchmark AOP
  - Which established process is or would be applied for a specific application?

Performance assessment and optimization in real water matrix
- 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

Energy and cost efficiency comparison with benchmark AOP
- Theoretical/computational process design and scale-up for the new and the
  benchmark AOPs
- Determine and compare the energy demand for both full processes
- Estimate & compare the total capital and operating costs (e.g., energy, chemicals)
  for both processes

Figure 3. Phase 2 - Benchmarking new concepts for advanced oxidation

Theoretical consideration to select potential applications for new AOP. Before conducting the
experiments to assess and optimize treatment efficiency in the selected water matrix, theoretical
considerations are 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. 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.\textsuperscript{16} 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,\textsuperscript{28} ballast water treatment,\textsuperscript{35} and activation of persulfates.\textsuperscript{5}

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 concepts for comparison as discussed in section 3 (e.g., 90\% elimination following the EEO concept), regulatory requirements, or case-specific requirements (e.g., in industrial applications).

Finally, a suitable benchmark AOP 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.

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 concentration 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 AOP. 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. 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 AOP needs to be tested in the same water matrix to ensure comparability of both processes.

**Energy and cost efficiency comparison with benchmark AOP.** 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 AOPs (AOP under study and benchmark AOP) to a representative full-scale operation. For standard processes such as ozonation or UV/H$_2$O$_2$, 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. (2016). At scale, a comparison of efficacy and efficiency to the benchmark AOP 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\textsuperscript{212} or a triple bottom line (TBL, social, environmental, economic) assessment.\textsuperscript{213}

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 Implementation of new AOPs

**Pilot-scale testing.** The functionality of a new treatment process under real conditions is typically tested at pilot scale. 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 tests. The latter 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 concept of 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 phase 2. 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.

**Selection of suitable oxidation processes for specific treatment targets.** New AOP concepts will be of particular interest in meeting new treatment targets triggered by revised regulatory requirements for specific chemicals and chemical classes, e.g., the recent regulations for poly- and perfluoroalkyl substances in drinking water.\textsuperscript{214} Moreover, the discovery of an ever-increasing number of new contaminants, such as persistent, mobile, and potentially toxic organic chemicals, will increase the need for novel and efficient mitigation processes.\textsuperscript{215} The selection of a suitable oxidation process for a specific treatment target depends on the reactivity of the target...
contaminant(s), but also on the composition of the water matrix, treatment scale, and other treatment objectives (e.g., disinfection). Based on these considerations, we propose a three-step approach to systematically identify a suitable AOP for a defined application (Figure 4).

**Figure 4. Systematic approach for the selection of a suitable oxidation process for mitigation of a contaminant S.**

In a first step, the reactivity of the target contaminant S with different oxidants (e.g., ozone, \( \cdot \)OH, or sulfate radicals) should be systematically evaluated, starting with a literature search for reaction rate constants and additional information on the fate of the contaminants in oxidative or photochemical processes. For compounds with unknown reactivity, reactivity could be estimated based on structural analogues\(^{216}\) or using in-silico tools based on quantitative structure-activity relationships\(^{217}\). Simple lab-scale kinetic experiments\(^{164}\) can be performed to complement existing knowledge. In case the chemicals cannot be removed effectively by oxidation, alternative solutions to oxidation need to be considered.

Second, the best-suited oxidative treatment for the prevailing conditions should be selected, taking into account information on water quality, process dimensions, and available infrastructure. Although different processes are often based on the same reactive species (e.g., \( \cdot \)OH), the activity of water matrix parameters as oxidant scavengers, promoters of radical chain reactions or precursors for by-product formation may strongly affect the applicability of individual processes.\(^{167}\) Additional treatment targets and potential process benefits should also be identified, such as the activity of the
oxidants as disinfectants or the formation of biodegradable products that may favor the combination of oxidation with biological processes.

A third step should address potential risks associated with the transformation of the target contaminant. Especially in waters with high pollutant concentrations (e.g., industrial wastewaters), significant amounts of potentially toxic transformation products may form. The identification of relevant transformation products should follow a systematic approach including available knowledge on transformation reactions of different oxidants from literature,\textsuperscript{218} and in-silico chemistry.\textsuperscript{219} Ideally, product screenings should be accompanied by mass-balances to assess the relevance of detected transformation products formed from the target pollutant. Alternatively, effect-directed analysis can be used as a powerful approach to first determine the toxicity of the overall chemical mixture in a sample, and then unravel individual toxicants through a combination of bioanalytical tools, fractionation steps, and chemical analyses.\textsuperscript{220} In both cases, relevance of effects for the aquatic environment should be assessed carefully, as toxic effects as well as transformation products are often removed in subsequent biological treatment steps.\textsuperscript{221}

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 H\textsubscript{2}O\textsubscript{2}) based on fundamental investigations on the formation mechanisms.\textsuperscript{69,222} Other examples in advanced oxidation include the characterization of nitrite as a scavenger or the identification of NDMA precursors and formation pathways.\textsuperscript{223}

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 using high-resolution mass spectrometry (HRMS). Good example studies
include the characterization of the heterogenous catalytic persulfate process by Zhang et al.
(2022), and the peroxone process by Merényi et al. (2010). Potential risks related to the
formation of unknown by-products may be addressed through bioanalytical tools or non-target
screening methods for previously unknown and unregulated by-products. HRMS can be a powerful method-of-choice to identify transformation products when it is combined
with mechanistic considerations to corroborate reaction pathways. The analysis of known
transformation products can help to identify relevant reactive species and formation pathways,
and substantiate or falsify results from identification of reactive species. In addition, screening for
unknown products can assist to elucidate relevant transformation pathways. 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 transferable knowledge.
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.
Further insights on the potential of these in-silico tools for mechanistic evaluation of oxidative
processes and example applications are provided in literature.
Bioassays with suitable endpoints can be applied for indicating mixture toxicity effects after water
treatment, identifying unknown toxic chemicals through effect-directed analysis, and
monitoring certain classes of chemicals. For instance, the estrogen receptor alpha (ER-α) is
activated in the presence of endocrine disruptors, which can be expressed as estradiol equivalent
concentrations. However, similar targeted approaches to monitor induced effects from oxidative
processes are not available. Könemann et al. (2018) 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.\footnote{230}

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