Emerging advanced oxidation processes for water and wastewater treatment

– guidance for systematic future research –

Uwe Hübner[a], Stephanie Spahr[b], Holger Lutze[c,d,e], Arne Wieland[f], Steffen Rüting[f], Wolfgang Gernjak[g,h], Jannis Wenk[i]

[a]Chair of Urban Water Systems Engineering, Technical University of Munich, Am Coulombwall 3, 85748 Garching, Germany

[b]Leibniz Institute of Freshwater Ecology and Inland Fisheries (IGB), Müggelseedamm 301, 12587 Berlin, Germany

[c]Department of Civil and Environmental Engineering, Institute IWAR, Chair of Environmental Analytics and Pollutants, Technical University of Darmstadt, Franziska-Braun-Straße 7, 64287 Darmstadt, Germany

[d]IWW Water Centre, Moritzstraße 26, 45476 Mülheim an der Ruhr, Germany

[e]Centre for Water and Environmental Research (ZWU), Universitätsstraße 5, 45141 Essen, Germany

[f]Xylem Services GmbH, Boschstraße 4-14, 32051 Herford; Germany

[g]Catalan Institute for Water Research (ICRA), 17003 Girona, Spain

[h]Catalan Institution for Research and Advanced Studies (ICREA), 08010 Barcelona, Spain.

[i]University of Bath, Department of Chemical Engineering and Water Innovation & Research Centre (WIRC@Bath),Bath BA2 7AY, United Kingdom

Keywords: Advanced oxidation processes, experimental design, probe compounds, trace organic chemicals, water treatment

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 (Comninellis et al., 2008) for the oxidative degradation of contaminants. The major radical formed in most AOPs is the hydroxyl radical ($^{\bullet}OH$) (Oturan, Aaron, 2014). Besides the $^{\bullet}OH$, 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 (Wang, Wang, 2020, 2021). Sulfate and chlorine radical-induced oxidations are often also referred to as AOP-like processes (Lee et al., 2020a). 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 (Ao et al., 2021, Ayoub et al., 2010, Chen et al., 2019, Gassie, Englehardt, 2017, Giannakis et al., 2021, Matilainen, Sillanpää, 2010, Oller et al., 2011, Oturan, Aaron, 2014, Pisarenko et al., 2012, Sillanpää et al., 2018). Radicals for AOPs in water, including $^{\bullet}OH$, 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 (El Kateb et al., 2019, Xu et al., 2021). Similarly, new advanced oxidation processes such as vacuum UV, plasma treatment as well as new oxidants and radical promoters have been proposed and investigated (Ansari et al., 2021, Lee et al., 2020b, Li et al., 2019, Tian et al., 2020). 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 (Scheideler et al., 2011, Wang et al., 2017, Xu et al., 2021). A large array of water contaminants, including so-called emerging contaminants, has been investigated to a great extent for their degradability by AOPs (Oturan, Aaron, 2014, Rodriguez-Narvaez et al., 2017).

Despite several recent reviews on AOPs (Cheng et al., 2016, Lee et al., 2020a, Miklos et al., 2018, Oturan, Aaron, 2014, Ribeiro et al., 2015), 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 (Gunten, 2018, Loeb et al., 2019). 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 (Bokare, Choi, 2014, Chaplin, 2014, Lee et al., 2016). 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 and, thus, energy demand (Lim et al., 2022, Zoumpouli et al., 2019) 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 (Gunten, 2018), these most widely applied AOPs typically also provide the highest energy efficiencies among AOPs (Miklos et al., 2018). However, less efficient AOPs might still provide suitable solutions for niche 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 (Loeb et al., 2019, Wang, Wang, 2018, Werschkun et al., 2014). 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.

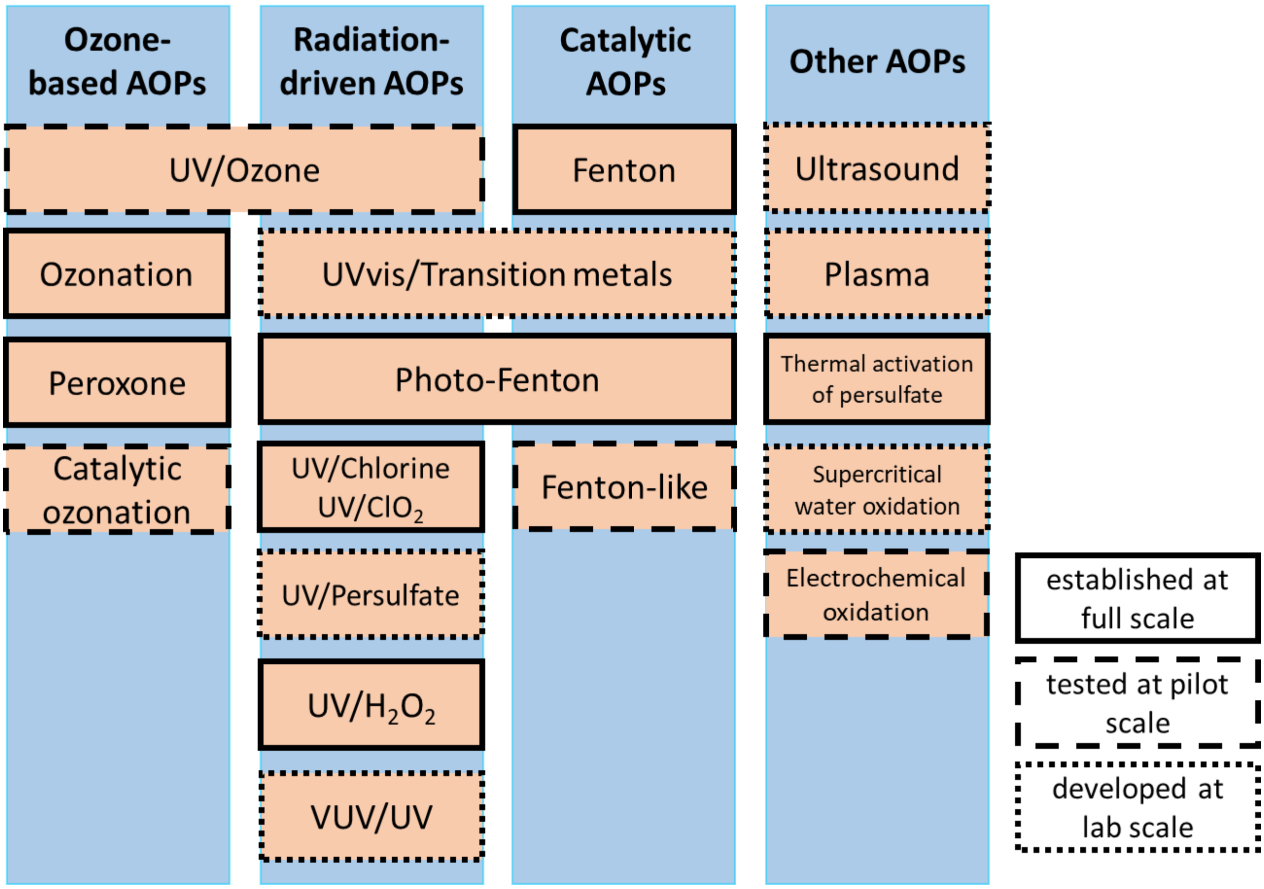

Figure 1. Broad overview and classification of different AOPs and AOP-like processes

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_2O_2), sodium percarbonate (Na_2CO_3 x 1.5 H_2O_2), peroxydisulfate ($S_2O_8^{2-}$), and monochloramine (NH_2Cl) or increase radical formation from oxidants such as ozone (Chen et al., 2022, Kasprzyk-Hordern et al., 2003, Liu et al., 2021, Wang et al., 2019b). This section focuses on dark catalytic processes, i.e., those without light as radical initiator, while light-induced AOPs are discussed in the section on radiation-driven AOPs. The most widely studied and applied homogeneous catalytic oxidation system is the Fenton reaction, in which H_2O_2 reacts with dissolved ferrous iron (Fe(II)) to generate $^{\bullet}OH$ (Bautista et al., 2008). 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 (Bautista et al., 2008, Bokare, Choi, 2014). 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_2O_2 at near-neutral pH conditions but only work under well-defined reaction conditions with careful consideration of catalyst toxicity (Bokare, Choi, 2014, Goldstein et al., 1993, Zhang, Zhou, 2019). A great deal of attention has been paid to both natural and synthetic solid catalysts such as iron-, manganese-, or cobalt-based materials (Hu, Long, 2016, Huang, Zhang, 2019, Luo et al., 2021), engineered nanomaterials (Hodges et al., 2018, Sun et al., 2018), metal-free polymers (Han et al., 2020, Yang et al., 2020), carbonaceous materials (Duan et al., 2018, Zhao et al., 2021), layered double hydroxides (Xie et al., 2021), metal-organic frameworks (Du, Zhou, 2021), and single-atom catalysts (Huang et al., 2021, Shang et al., 2021). 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 (Hodges et al., 2018). 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 (Hodges et al., 2018). 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 (Hodges et al., 2018). 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 (Hodges et al., 2018).

2.2 Recent progress in ozone-based advanced oxidation

In every ozonation process, $^{\bullet}OH$ are formed from the reaction of ozone with the water matrix, especially with organic matter (Pocostales et al., 2010, Sonntag, Gunten, 2012). However, since the formation of $^{\bullet}OH$ is "uncontrolled", ozonation is often not defined as an AOP. $^{\bullet}OH$ formation can be enhanced by the addition of H_2O_2 (either as solution or by electrochemical in situ production) in the peroxone process, pH elevation, catalytic ozonation, or ozone photolysis (Fischbacher et al., 2013, Lamsal et al., 2011, Lucas et al., 2010, Merényi et al., 2010a, Wang, Chen, 2020, Yao et al., 2018). UV/O_3 is discussed as a UV-based AOP in the next section.

In the peroxone process, ozone reacts fast with the H_2O_2 anion (HO_2^-) (k = 9.6×10^6 M^{-1} s^{-1}) with a yield of 0.5 mol $^{\bullet}OH$ per mol reacted ozone (Fischbacher et al., 2013, Merényi et al., 2010a). The peroxone process is often applied to mitigate formation of undesired bromate (Gunten, Oliveras, 1997, 1998) or to quench excess ozone with the advantage of further $^{\bullet}OH$ formation (Gunten, 2003b).

At elevated pH, ozone may react with hydroxide ions to form $^{\bullet}OH$. However, this reaction is rather slow (k = 70 M^{-1} s^{-1}) (Merényi et al., 2010b, Staehelin, Hoigne, 1982) 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 (Gunten, 2003a).

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 (Rekhate, Srivastava, 2020, Wang, Chen, 2020, Yan et al., 2019). 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 $^{\bullet}OH$, which is generated from ozone decomposition at the catalyst surface (Gottschalk, 2010, Rekhate, Srivastava, 2020). 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 $^{\bullet}OH$ 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_2, with some types leading to ozone decay without significant $^{\bullet}OH$ formation (Nawaz et al., 2017, Wang, Chen, 2020). Different mechanisms have been proposed for catalytic ozonation with activated carbon-based materials (Rekhate, Srivastava, 2020), 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" (Sánchez-Polo et al., 2005). 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 (Buxton et al., 1988, Neta et al., 1988). The applied wavelengths range from > 170 (VUV) to 700 nm (visible light) (Brezonik, Arnold, 2011). 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_2O_2, chlorine and chlorine dioxide, peroxydisulfate ($S_2O_8^{2-}$), ozone, and the photo-Fenton process. Photolysis and radical generation mechanisms in these processes are widely established and well-described in literature (Bulman et al., 2019, Chuang et al., 2017, Garoma, Gurol, 2004, Goldstein et al., 2007, Sonntag, 2008, Wacławek et al., 2017).

UV/H_2O_2 and UV/chlorine are the most widely applied processes (Kruithof et al., 2004, Kwon et al., 2020, Swaim et al., 2008, Wang et al., 2015, Wang et al., 2019a). The UV/H_2O_2 process is used in drinking water treatment and potable reuse schemes to remove trace contaminants that are difficult to remove otherwise (Collins, Bolton, 2016) and can be advantageous when ozone-based processes would result in undesired bromate formation from naturally occurring Br^- (Gunten, Oliveras, 1998). The energy demand of UV/H_2O_2 is higher compared to conventional ozonation and the peroxone process (Katsoyiannis et al., 2011).

In full-scale potable reuse schemes, UV/chlorine (HOCl) is increasingly used with and without the addition of chloramines (Kwon et al., 2020). Thereby, the photolysis of HOCl results in the formation of $^{\bullet}OH$ and chlorine atoms (Khajouei et al., 2022), the photolysis of chloramines gives rise to formation of aminyl radicals and chlorine atoms (Li et al., 2018). Reactions of these reactive species in water are discussed in more detail elsewhere (Lutze et al., 2015, McElroy, 1990). 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 (Guo et al., 2022a).

Sulfate radicals react more substrate specific than $^{\bullet}OH$ (Lee et al., 2020a). Therefore the UV/$S_2O_8^{2-}$ process benefits from reduced oxidant scavenging by the water matrix, but less reactive compounds are more difficult to eliminate compared to the UV/H_2O_2 process (Nihemaiti et al., 2018). The UV/$S_2O_8^{2-}$ process may provide tailored solutions towards individual substances or substance groups rather than broadband treatment envisioned in most AOP applications (Lee et al., 2020a). Compared to H_2O_2 [$\varepsilon_{H2O2,\lambda=254nm,}$ = 18.6 M^{-1} cm^{-1} (Stefan et al., 1996)] and $S_2O_8^{2-}$ [$\varepsilon_{S2O82-,\lambda=254nm}$ = 22 M^{-1} cm^{-1} (Heidt, 1942)], ozone has a high molar absorption coefficient of $\varepsilon_{O3,\lambda=254nm}$ = 3300 M^{-1} cm^{-1} (Sonntag, Gunten, 2012) resulting in an efficient photolysis into $^{\bullet}OH$ (Sonntag, 2008) that is 20 times more efficient than H_2O_2 photolysis at the same dissolved molar concentration. However, due to the combination of two energy-intensive processes, namely ozonation and UV irradiation, the UV/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-cComplexes (ε = (450 nm) ≈ 450 M^{-1} cm^{-1}) (Sonntag, 2008). Thereby, the complex cleaves into $HO_2^{\bullet}$ and Fe(II), and Fe(II) reacts with H_2O_2 to form $^{\bullet}OH$. 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 (Malato et al., 2009, Spasiano et al., 2015). Recent developments are related to using complexing agents to operate at pH 7 and using less costly reactor concepts (Cabrera-Reina et al., 2021, Clarizia et al., 2017).

Heterogeneous photocatalytic AOPs. Research on photocatalysis for degradation of refractory pollutants has been intense since the discovery of photocatalytic water splitting (Fujishima, Honda, 1972). Heterogeneous photocatalysis employs a range of semiconducting catalysts, of which TiO_2 and ZnO are the most widely researched materials (Chong et al., 2010, Lee et al., 2016). 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 (Malato et al., 2009), photocatalysis is rarely applied in water treatment beyond lab and pilot scale (Loeb et al., 2019). 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 (Malato et al., 2009). 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) (Cowie et al., 2020).

Lamp technology. New UV radiation sources in water treatment have been tested, primarily for disinfection and photocatalysis in the UV-A range (Hinds et al., 2019). 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 (Kneissl et al., 2019). 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 (Kneissl et al., 2019). The small size and control of individual LEDs enables an innovative reactor design and a larger range of applications (Autin et al., 2013, Song et al., 2016). 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 $^{\bullet}OH$ and solvated electrons (Legrini et al., 1993). 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 (Imoberdorf, Mohseni, 2011). 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 cm^{-1} ($\varepsilon_{H2O,\lambda=185nm,}$ = 0.032 M^{-1} cm^{-1}) (Weeks et al., 1963) 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 (Furatian, Mohseni, 2018). 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 (Lyon et al., 2014, Martijn et al., 2016). 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) (Miklos et al., 2018). 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)(Pinkard et al., 2021, Radjenovic et al., 2020, Topolovec et al., 2022, Vecitis et al., 2009). However, PFAS are highly persistent to ${}^{\bullet}$OH attack and breakdown is related to different mechanisms, e.g., pyrolysis during ultrasound treatment (Vecitis et al., 2008), or direct electron transfer at anode surface (Radjenovic et al., 2020).

Application of ultrasound in water with frequencies of 20-1000 kHz generates oscillating gas bubbles. During the growth of these bubbles, expansion gas is drawn inside the bubble. Subsequent collapse of the bubbles leads to locally high temperatures (> 4000 K) at the microscale (Rae et al., 2005). The resulting pyrolysis of water vapour inside the bubbles yields ${}^{\bullet}$OH and H$^{\bullet}$ radicals, which do not readily recombine due to the high temperature (Sonntag, 2008). Hence, ${}^{\bullet}$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 (Miklos et al., 2018). 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 (Kumar et al., 2021). 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 (Lieberman, 2005). 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 $^{\bullet}OH$, 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 (Bruggeman et al., 2016). All these species can be involved in the degradation of a pollutant (Zeghioud et al., 2020) 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 (Bruggeman et al., 2016). Consequently, efficient reactor engineering is key to ensure adequate mass transfer and to develop practicable solutions (Malik, 2010). 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 (Wacławek et al., 2017). Due to the small bond dissociation energy of the peroxide bond (120 KJ mol^{-1}) (Sonntag, 2006), even moderate temperatures (> 40 °C) suffice to cleave persulfate into sulfate radicals (Liang, Bruell, 2008). 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 (Kim et al. 2022). A disadvantage of using persulfate is a strong drop in pH and strong radical scavenging effects in the concomitant presence of chloride and bicarbonate (Lutze et al., 2015).

Supercritical water oxidation (SCWO) has been shown to be applicable for the degradation of various wastes in laboratory scale and full scale (Brunner, 2009). 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 (Brunner, 2009). 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) (Brunner, 2009). In the super critical state, water becomes mixable with nonpolar compounds, while polar and ionic compounds may still remain soluble (Weingärtner, Franck, 2005). 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 (Sugiyama et al., 2005). 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_2O_2 can be used, which decomposes into oxygen upon its thermal decomposition (Brunner, 2009) .

In electrochemical advanced oxidation processes, $^{\bullet}OH$ are directly generated from water oxidation at the electrode surface (Chaplin, 2014). 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 (Shestakova, Sillanpää, 2017). 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 (Moreno-Andrés et al., 2018, Radjenovic, Sedlak, 2015). Due to the efficient conversion of electrical energy into $^{\bullet}OH$ and secondary oxidants (H_2O_2, O_3) and the chemical-free operation, electrical AOPs are often considered as environmentally-friendly treatment solutions (Tröster et al., 2004). 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 (Radjenovic, Sedlak, 2015). Current research is focused on new electrode design to optimize mass transfer and concepts to mitigate by-product formation (Shestakova, Sillanpää, 2017, Yang, 2020).

3 Comparison and benchmarking of AOPs

One of the first concepts for figures-of-merit for comparing AOPs was proposed in 1996 (Bolton et al. (1996)) and subsequently published as an IUPAC Technical Report (Bolton et al., 2001). 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 (Bolton et al., 2001). 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 (Bolton, Stefan, 2002, Stefan, Bolton, 2005). The EEO concept has been extensively applied on most AOPs, including ozonation and peroxone (Katsoyiannis et al., 2011, Pisarenko et al., 2012, Yao et al., 2018), electrochemical (Lanzarini-Lopes et al., 2017, Radjenovic, Sedlak, 2015), ultrasound-based (Mahamuni, Adewuyi, 2010), and both homogeneous and heterogeneous UV-based AOPs (Katsoyiannis et al., 2011, Saien et al., 2011, Zhang et al., 2020). 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_2O_2 requires reporting of probe compound concentration, molar absorption coefficients, second-order reaction rate constants with $^{\bullet}OH$ (k_{OH}), observed reaction rate constants (k_{obs}), and direct phototransformation rates. In addition, the water matrix pH, light absorbance, and $^{\bullet}$OH scavenging rates by non-target compounds, e.g., natural organic matter should be reported (Keen et al., 2018). 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 (Keen et al., 2018). The variance of literature data within individual AOPs indicates the difficulty to compare processes at different scale and in different water matrices (Miklos et al., 2018).

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” (Collins, Bolton, 2016). 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 (Collins, Bolton, 2016). 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 (Schmelling et al., 2006) (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.

4 Selection of suitable probe compounds, model compounds and scavengers

Chemical probe compounds, including scavengers and quenchers, have served a central role as diagnostic tools in AOP research (Wang, Wang, 2020). 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 (IUPAC, 2019). 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 (Lee et al., 2014, Wünsch et al., 2021). There is a wide range of probe compounds available for reactive species in water, as recently reviewed (Burns et al., 2012, Fennell et al., 2022, Nosaka, Nosaka, 2017, Rosario-Ortiz, Canonica, 2016, Scholes, 2022). Here, we briefly discuss 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 $^{\bullet}OH$ and $SO_4^{\bullet-}$, to milliseconds (ms) for less reactive species such as carbonate radicals and superoxide radicals (Burns et al., 2012, Zhou et al., 2017). Non-radical oxidants such as ozone and H_2O_2 are more stable with half-lives in the range of minutes to hours (Gardoni et al., 2012, Hoigné, Bader, 1994). In real water matrices, lifetimes for most reactive species may be much shorter due to the presence of reactants, including scavengers (see this section further 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 compiled reaction rate datasets for radicals in aqueous solutions (Buxton et al., 1988, Neta et al., 1988). However, these methods require expensive specialist non-portable 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 selective 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 on solids in heterogeneous processes or on electrodes in electrochemical AOPs. Ideally, probe compounds should only react 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_2O_2, and persulfate in UV-based AOPs), a suite of probe compounds or model compounds may be required that exhibit a wide-ranging selectivity toward the relevant individual oxidants present (Guo et al., 2021, Guo et al., 2022b, Zeng, Arnold, 2013). Similarly, the study of complex systems involving the formation of secondary and tertiary radicals may require a combination of probe compounds and selective scavengers (Guo et al., 2021, McElroy, 1990). 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 a scavenger 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 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 (Wang et al., 2020). Other, typically employed analytical techniques for probe compounds in AOP research include fluorescence spectroscopy, HPLC-UV/Vis or HPLC/MS, and to lesser extent ion chromatography.

The $^\bullet OH$ is the reactive species of highest interest for most AOPs. Treatment concepts based on $^\bullet OH$ can be adequately evaluated via 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_2O_2, including assessment of an external standard calibration method using methylene blue see Wang et al. (2020). Typical probe compounds for $^\bullet OH$ that can be readily measured via HPLC include *para*-chlorobenzoic acid (*p*CBA), *para*-nitrobenzoic (*p*NBA) acid, and atrazine (Huber et al., 2003, Katsoyiannis et al., 2011, Lutze et al., 2015, Wenk et al., 2011). 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 (Keen et al., 2014, Lado Ribeiro et al., 2019, Nöthe et al., 2009, Vione et al., 2006, Zhang, Parker, 2018), 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 rule of thumb, a scavenger should trap more than 95% of the reactive species, which can be determined by competition kinetics calculations as described by Willach et al. (2017). Typical scavengers for $^{\bullet}$OH are e.g., *tert*-butanol, and dimethyl sulfoxide (DMSO) (Flyunt et al., 2003). $^{\bullet}$OH reaction with *tert*-butanol and DMSO leads to the formation of formaldehyde (yield ≈ 25%) and methanesulfinic/methanesulfonic acid (yield of the sum of each ≈ 98%), respectively (Flyunt et al., 2003). Quantification of these transformation products allows to calculate the formed $^{\bullet}$OH (Flyunt et al., 2003). While a large variety of substances can be used to scavenge different reactive species (Wang et al., 2021), 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, provides additional challenges. Scavenger reactions may lead to formation of secondary reactive species or formation of unexpected products, which may interfere with reaction mechanisms, pathways, and kinetics (Zhou et al., 2015). The use of scavengers, thus, requires appropriate control experiments to assess reactivity of the scavenger with the oxidants, the target compounds, and the matrix. For heterogenous AOPs, reiteration of solubility and adsorption consideration 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 a selected probe compound 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 (Bolton, Linden, 2003), 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 causing an inner filter effect or consuming ozone (Sonntag, Gunten, 2012, Ulliman et al., 2018). In some cases, this can generate secondary reactive species (Hübner et al., 2015, Sonntag, Gunten, 2012). Second, matrix components can scavenge radicals terminating radical chain reactions in non-productive ways towards treatment targets (Ulliman et al., 2018). 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 (Wang, Wang, 2021). Depending on their respective reactivity with a target compound and their tendency to accumulate at higher concentrations due to their longevity compared to other radical species, such secondary reactive species can contribute significantly to the degradation of a target compound (Zhou et al., 2020). 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 (Canonica et al., 2008, Prasse et al., 2015b, Wenk et al., 2021). 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 (Canonica et al., 2005, Gottschalk, 2010, Maruthamuthu, Neta, 1978).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-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 H_2O_2. This is done by using set-ups that allow assessing photochemical reactions as function of the fluence rate (IUPAC, 2019) 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 (Katsoyiannis et al., 2011).

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 (Bolton et al., 2015). The same approach has been transferred also to AOPs (Velo-Gala et al., 2019).

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 (Kuhn et al., 2004), some of which have been revisited recently by Rabani et al. (2021). Among them we can distinguish opaque actinometers, e.g., the iodide/ iodate actinometer frequently used to determine 254 nm radiation (Rahn, 1997, Rahn et al., 2003) and non-opaque actinometers such as the uridine actinometer, also used to determine 254 nm radiation (Rabani et al., 2021). The first type essentially counts photons entering the solution yielding a value for irradiance, whereas with the second type an average fluence rate is directly estimated. 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 (Wols et al., 2012). 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 (Bolton, Linden, 2003).

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 (Rabani et al., 2021).

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 continuously stirred tank reactors (CSTR) and flow-through reactors. Among CSTRs, the most referred to and most standardized approach is the quasi-collimated beam apparatus (qCB) (Bolton, Linden, 2003). 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 (Bolton, Linden, 2003) and recently complemented with additional guidance on evaluation (Bolton et al., 2015). 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, 2022).

Other CSTR reactors 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 (Bolton, Linden, 2003). Radiation evaluation methods and processes for matching wavelength-dependent responses apply in analogy to action spectra for different pathogens and irradiation sources in disinfection (Bolton, Cotton, 2008).

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 (Malato et al., 2009).

5.3 Ozone-based processes

Ozone consumption and mass transfer. Transfer of results from lab-scale ozonation requires characterization of injected or reacted (consumed) ozone. 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 (Gottschalk, 2010). Standardized concepts to determine transfer efficiency of a reactor (e.g. k_La) do not provide a reliable characterization of ozonation because the high reactivity of ozone affects its transfer efficiency into water (Gottschalk, 2010). 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 (Hübner et al., 2013). 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^-, $k = 70\ M^{-1}s^{-1}$) giving rise to the formation of $^{\bullet}OH$ (Merényi et al., 2010b). In more complex matrices such as secondary effluents, elevated ozone decay through reactions with organic matter also leads to considerable $^{\bullet}$OH formation (Buffle, von Gunten, 2006). 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 single 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 $^{\bullet}$OH (Hübner et al., 2015). The $^{\bullet}$OH yield in the tested AOP should therefore always be assessed in comparison to single ozonation. In experiments with gaseous ozone, researchers also need to account for potential bias caused by effects on mass transfer (see previous discussion).

The R_{CT}-concept by Elovitz, von Gunten (1999), which defines the R_{CT} as the ratio between $^{\bullet}$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_{CT} values should be evaluated carefully because enhanced kinetics compared to single ozonation primarily reduce ozone exposure in the denominator (Wang, Yu, 2022). We therefore recommend 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).

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 basic 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 (Atkins, Paula, 2014, Zietzschmann et al., 2018), and easily measured prior to injection on a photometer or using the indigo method (Bader, Hoigné, 1981). 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 (Hübner et al., 2013).

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 (Gottschalk, 2010, Hübner et al., 2013). 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 O_3/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 (Zoumpouli et al., 2019). 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 (Ying et al., 2021). 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 $^{\bullet}$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 $^{\bullet}$OH can also be generated by finite reactions, e.g., from the reaction of ozone with activated carbon (Sánchez-Polo et al., 2005).

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 far less standardized (Bligaard et al., 2016), 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, 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. Besides, 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, solution pH can change the surface charge of heterogeneous catalysts and affect their reactivity (Gottschalk, 2010). Water quality measurements should include parameters listed in section 5.1.

Process evaluation. For an initial feasibility test with new catalyst materials, contaminant or probe compound degradation kinetics can be measured in direct comparison to an established catalyst using the same experimental set-up (see section 6.1). To generate scalable data for benchmarking of the process, the radical formation efficiency can be determined via an adequate system of probe compounds and radical scavengers as described in section 4. Given the complexity of a catalytic system, control experiments are required for the reactions of probe compounds with the oxidant and catalyst separately, including possible physical interactions with the catalyst. Catalytic activity can be normalized by combining observed kinetics with applied catalyst concentration to determine kinetics-related metrics such as turnover frequency (Kozuch, Martin, 2012), 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 (Kozuch, Martin, 2012). In addition to compound removal, the process evaluation should also include consumption, stability, life cycle, regeneration potential, and toxicity of the catalyst as well as (sacrificial) chemical and energy input demands.

Advantages and disadvantages of different lab set-ups. Since the evaluation of catalytic systems is inherently nontrivial, we recommend CSTR reactors for fundamental studies on evaluating catalytic activity. This is because CSTR reactors allow for straightforward control of the experimental environment and exclusion of mass transfer limitations for most catalytic systems. Flow-through or flow-by reactors can be appropriate in applications with inherent mass transfer limitations. For catalytic membranes, e.g., the applicable transmembrane flow velocity will be always a limiting factor. Similarly, using reactors with mass-transfer limited geometries can be important, when the innovation is a novel catalyst (support) geometry by itself (Tasso Guaraldo et al., 2021, Warren et al., 2022). However, in such cases mass transfer-related parameters 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

(Malik, 2010). Also results from sonolysis using slightly different reactor design at the same experimental conditions were not comparable (Hung, Hoffmann, 1999). 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 (Radjenovic, Sedlak, 2015), plasma (Malik, 2010), and cavitation processes (Gągol et al., 2018).

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 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 (Armstrong, 2015). However, the TRL concept is only partly applicable for AOPs, because other criteria such as energy efficiency are typically more decisive than the technical maturity or technology readiness of the process. Subsequent pilot- and full-scale implementation is briefly discussed in section 6.3 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. Typically, these studies do not impede the implementation of novel AOP concepts. 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.

6.1 Phase 1 – Feasibility study

In phase 1, the general feasibility of the developed 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 might already provide direct comparison to established materials or concepts.

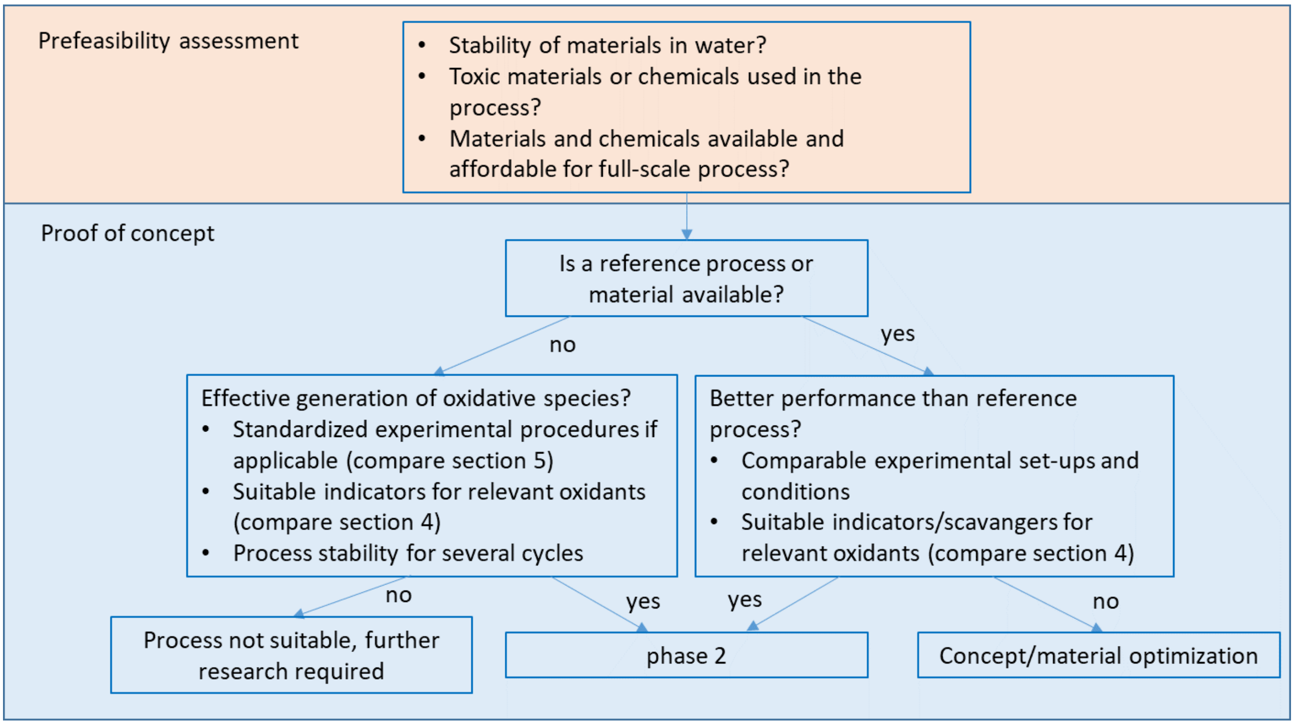

Figure 2. Systematic approach to assess the feasibility of new developments in advanced oxidation

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 process (e.g., municipal and industrial wastewater, seawater or drinking water). The new process or material has to be durable or self-renewing under these conditions. For example, in case of metal-based electrodes corrosion may occur in waters with high salinity. New materials may be prone to cause toxicity e.g., by leaching of heavy metals, which may require precautionary measures. For instance, cobalt is a powerful catalyst to initiate sulfate radical formation. However, cobalt is also a toxic heavy metal, which should only be used after immobilization on a surface (Anipsitakis et al., 2005). In general, researchers should verify that the applied materials are approved by regulations 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 (Kim et al., 2018, Yang et al., 2022). Another example is ultrasound treatment, which is often tested in an artificial argon atmosphere, which would incur high costs in full-scale applications (Sidnell et al., 2022). Robust materials with no toxicity and high abundance of resources can be used at large scale (e.g., for municipal wastewater treatment). More sophisticated catalysts that require, e.g., rare earth metals, may be tailored to special 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, which 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.

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 system can be identified, the proof-of-concept study should demonstrate superior performance of the new process (i.e., more efficient pollutant degradation or less by-product formation) in comparison to the reference process or material. An ideal reference system would closely mimic the set-up and reaction conditions of the proposed new water treatment process.

A direct comparison to a reference system 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. Ideal reference materials might not be available in all cases. A recent study proposed a new material for catalytic activation of H_2O_2 at neutral pH (Xu et al., 2021). Since heterogeneous Fenton processes with established materials are operated at acidic pH, a direct comparison at pH 7 is not possible.

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 principally 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). Details for the feasibility tests are determined by knowledge already available for a given process at study. In some cases (e.g., the combination of UV-LEDs with H_2O_2), a general feasibility study might not be needed because the reaction mechanism and major oxidants are already well-known. In such cases, evaluation of the process would directly start 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 a benchmark AOP to account for matrix-specific efficiencies. 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).

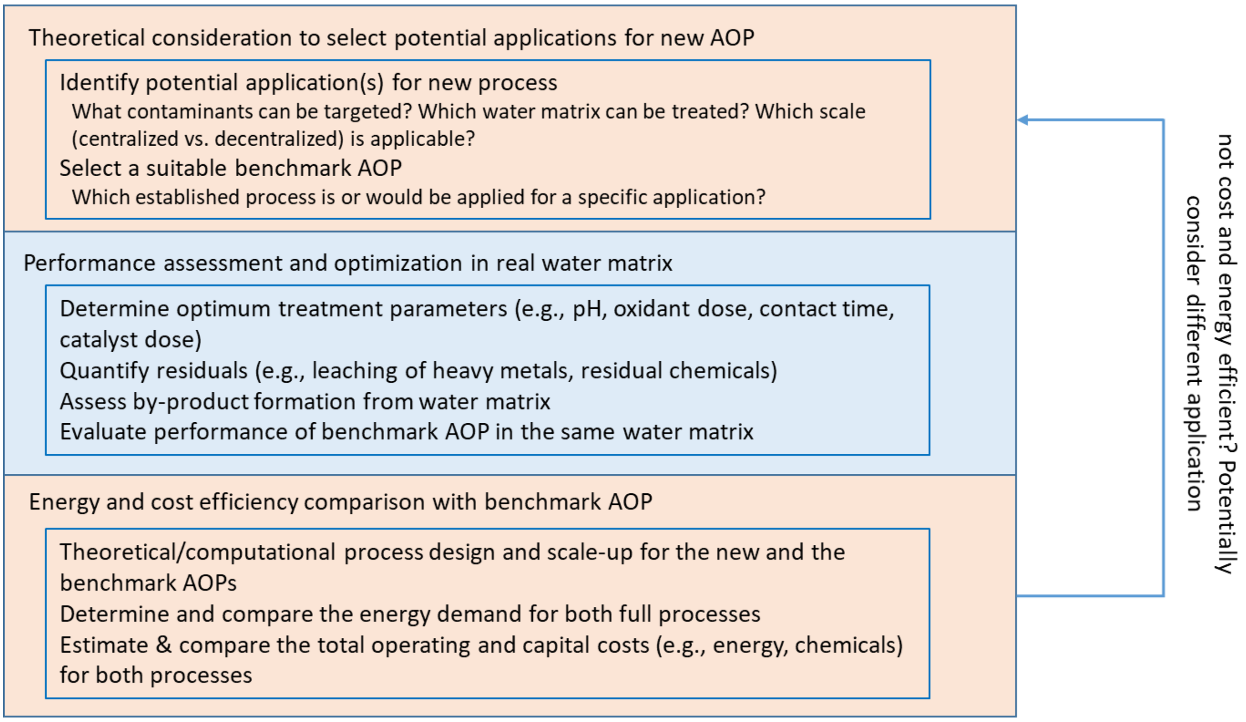

Figure 3. Systematic approach for benchmarking new concepts for advanced oxidation

Theoretical consideration to select potential applications for new AOP. Before conducting actual 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 a high energy demand (e.g., ultrasound, see section 2), potential by-product formation (e.g., electrochemical oxidation, UV/chlorine), required pH range (Fenton reaction), or the selectivity of oxidants (e.g., $^{\bullet}$OH vs. sulfate radicals). Unique features of these oxidative processes can still make them attractive for applications in different water matrices (industrial wastewater, mine waters, 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 (Xu et al., 2021). 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 (Loeb et al., 2019), ballast water treatment (Werschkun et al., 2014), and activation of persulfates (Lee et al., 2020a).

In addition, a specific treatment goal needs to be defined for the selected application. This goal may include % elimination of a chemical, or a 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. 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. 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, $^{\bullet}$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 (e.g., oxidant dose). 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 are not scalable, we recommend to theoretically upscale both experimentally tested AOPs to a representative full-scale operation. For standard processes such as ozonation or UV/H_2O_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). For new AOPs, upscaling of lab-scale results might not be straightforward because pilot- and full-scale applications are not established. In such cases, researchers need to first think of the design of the final process at full scale. Some processes might be upscaled by implementation of individual modules (e.g., additional electrodes). Other AOPs might need a full new design because processes applicable at pilot scale or full scale are not available (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. At scale, efficacy and efficiency of each process is compared or used for a Life Cycle Assessment (LCA) inventory (Mery et al., 2013). Traditionally, scale-up is done after a process is validated at lab scale followed by constructing a pilot-scale plant based on which the full-scale process is anticipated by performing a dimensional analysis. Although effective, the traditional scale-up route is inert, expensive and must advance significantly before data is acquired. Thus, when looking for preliminary insight into the environmental impact of a novel process that is being tested, this is not a sensible approach, and we ought to resort to predictive models based on laboratory data. Equipment used at lab scale is not comparable to commercial equipment. In addition, multiple steps of a treatment train are looked at individually. For this reason, it is recommended to approach the scale-up of a process by scaling up each individual component of the complete process separately. While auxiliary equipment (e.g., pumps) can be scaled up by selecting appropriate commercial equipment available on the market, process scale-up itself depends on the nature of the examined process. In an attempt to standardize this approach, a scale-up methodology was proposed by (Piccinno et al., 2016).

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 tested at pilot scale. Even though laboratory experiments are conducted in real water matrices, some aspects such as the longevity of materials, the influence of changes in the water matrix, the effects of hyphenation with other treatment and unforeseen effects can only be revealed in pilot tests. The latter are ideally carried out directly at the planned site of operation. Pilot testing can proof or disproof the applicability of a new material and may show, e.g., that a photocatalyst loses its photocatalytic activity too quickly or deteriorates mechanically. In such cases, the concept of the new process must be revised. Considering the undesired effects revealed in the pilot tests, solutions may be developed through revisiting and revising the investigations in-depths in phase 2.

Successful pilot-testing is paving the way for full-scale applications of the new AOPs. The latter ideally complement the spectrum of well-characterized and ready for use AOPs to provide treatment solutions for a wide spectrum of pollutants and scales. This treatment portfolio is then available for selecting the most appropriate AOP for a specific treatment target.

Selection of suitable oxidation processes for specific treatment targets. Specific treatment targets are defined according to a particular problem such as degradation of highly recalcitrant pollutants. Developing treatment solutions for emerging persistent contaminants may also include treatment solutions for specific water matrices. New treatment targets can be triggered by revised regulatory requirements for specific chemicals and chemical classes, e.g., the recent regulations for poly- and perfluoroalkyl substances in drinking water (EU, 2020). In addition, the detection of emerging contaminants such as persistent mobile organic chemicals may trigger the need to evaluate the efficiency of existing and novel processes for their mitigation (Schulze et al., 2019). The final selection of a suitable oxidation process depends on the reactivity of the target contaminant(s) but is also always based on other parameters including water quality (OBP precursors, scavengers, turbidity), treatment scale, and potential other treatment objectives (disinfection, removal of other target contaminants). Based on these considerations, we propose a three-step approach to systematically identify a suitable AOP for the defined application (Figure 4).

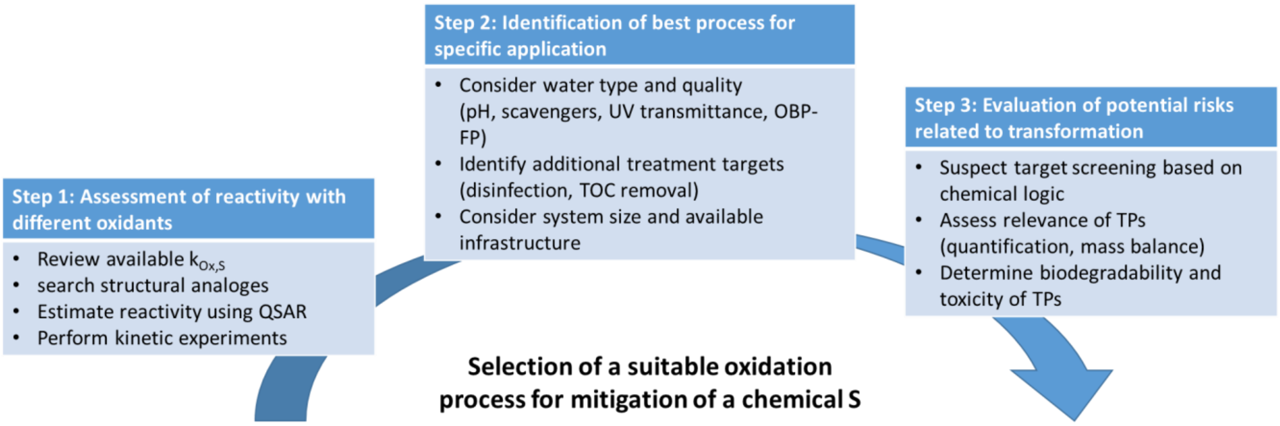

Figure 4. Systematic concept for the identification of optimum oxidation processes

In a first step, reactivity of target contaminants with different oxidants (e.g. ozone, $^{\bullet}$OH and sulfate radicals) should be systematically evaluated including also gathering UV/Vis absorption spectra information in water as solvent and direct photo-transformation quantum yields, when photochemical AOPs are considered. This can be initiated by searching the literature for reaction rate constants with oxidants and additional information available on target compound fate in oxidative and photochemical processes. For compounds with unknown reactivity, reactivity could be estimated based on structural analogues (Lee, Gunten, 2012) or using in-silico tools based on quantitative structure-activity relationships (Lee et al., 2017). Simple lab-scale experiments can be conducted to complement existing knowledge on compound reactivity with different oxidants or in specific treatment processes. This stage should also consider alternative solutions to oxidation, as some chemicals are not effectively removed by oxidation (e.g., flame retardants, perfluorinated alkyl substances) or more cost-efficient processes can be applied for their removal (e.g., adsorption or biodegradation).

Second, the best-suited oxidative treatment for case-specific conditions should be selected including information on water quality, process dimensions, and potential benefits from synergistic effects. Synergies could include the activity of individual oxidants as disinfectant and the formation of biodegradable products in treatment scenarios when oxidation is combined with biological processes. Although different processes are often based on the same reactive species (e.g., $^{\bullet}$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 (Lado Ribeiro et al., 2019). The most promising approaches can then be tested using lab-scale systems with model solutions (to identify reaction kinetics) as well as with real water matrices.

Risks related to the transformation of target pollutants may become relevant for applications with elevated pollutant concentrations such as industrial wastewater treatment or remediation of contaminations in groundwater. Also the identification of most relevant transformation products should follow a systematic approach, which includes available knowledge on the chemical reactions of different oxidants (Lee, Gunten, 2016). To facilitate the study of transformation product formation, experiments with the known parent pollutants can be done in pure water under controlled conditions. Suspected transformation products can be identified based on the structure of the parent compounds, knowledge from literature, and in-silico chemistry (Tentscher et al., 2019). Ideally, product screenings should be accompanied by mass-balances to quantify the fractions of both known and unknown transformation products formed from a specific 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 (Brack et al., 2016). 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 (Völker et al., 2019). In fact, several transformation products formed during oxidation processes such as NDMA and carbonylic compounds display a strong toxicity, but can be readily removed by biological post-treatment steps (Marron et al., 2020, Schmidt, Brauch, 2008, Zoumpouli et al., 2021). Since oxidation processes are typically coupled with biological treatment, the biodegradability of relevant transformation products should be evaluated to assess the entire treatment train.

6.4 Scientific approaches for mechanistic investigation and extended risk assessment

Lab- and pilot-scale 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_2O_2) based on fundamental investigations on the formation mechanisms (Gunten, 2003a, Heeb et al., 2014). Other examples in advanced oxidation include the characterization of nitrite as a scavenger or the identification of NDMA precursors and formation pathways (Spahr et al., 2017a).

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. (2010a). Potential risks related to the formation of unknown by-products may be addressed through bioanalytical tools (Völker et al., 2019) or non-target screening methods for previously unknown and unregulated by-products (Lavonen et al., 2013).

High-resolution mass spectrometry (HRMS) can be a powerful method-of-choice to identify transformation products when it is combined with mechanistic considerations to corroborate reaction pathways. The analysis of known transformation products can help to identify relevant reactive species and formation pathways (Spahr et al., 2017b), and corroborate or falsify results from identification of reactive species. In addition, screening for unknown products can assist to elucidate relevant transformation pathways (Bletsou et al., 2015, Prasse et al., 2015a). 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 $^{\bullet}OH$ 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 high resolution mass spectrometry (HRMS) (Tentscher et al., 2019). Further insights on the potential of these in-silico tools for mechanistic evaluation of oxidative processes and example applications are provided in literature (Merényi et al., 2010a, 2010b, Tentscher et al., 2019, Zhang et al., 2022). Bioassays with suitable endpoints can be applied for indicating mixture toxicity effects after water treatment (Prasse et al., 2015a), identifying unknown toxic chemicals through effect-directed analysis (Brack et al., 2016), and monitoring certain classes of chemicals (Escher et al., 2011). For instance, the estrogen receptor alpha (ER-α) is activated in the presence of endocrine disruptors (Könemann et al., 2018), which can be expressed as estradiol equivalent concentrations. However, similar targeted approaches to monitor induced effects from oxidative processes are not available. Völker et al. (2019) 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.

7 Acknowledgment

This study was initiated from the Technical Committee “Oxidative Processes” within the German Water Chemistry Society. We gratefully thank Emil Bein and Nebojša Ilić for their feedback and input in different subsections.

8 References

Amano, H.; Collazo, R.; Santi, C. de; Einfeldt, S.; Funato, M.; Glaab, J.; Hagedorn, S.; Hirano, A.; Hirayama, H.; Ishii, R.; Kashima, Y.; Kawakami, Y.; Kirste, R.; Kneissl, M.; Martin, R.; Mehnke, F.; Meneghini, M.; Ougazzaden, A.; Parbrook, P. J.; Rajan, S.; Reddy, P.; Römer, F.; Ruschel, J.; Sarkar, B.; Scholz, F.; Schowalter, L. J.; Shields, P.; Sitar, Z.; Sulmoni, L.; Wang, T.; Wernicke, T.; Weyers, M.; Witzigmann, B.; Wu, Y.-R.; Wunderer, T.; Zhang, Y. The 2020 UV emitter roadmap. *J. Phys. D: Appl. Phys.* **2020,** *53* (50), 503001. DOI: 10.1088/1361-6463/aba64c.

Anipsitakis, G. P.; Stathatos, E.; Dionysiou, D. D. Heterogeneous activation of oxone using Co3O4. *J. Phys. Chem. B* **2005,** *109* (27), 13052–13055. DOI: 10.1021/jp052166y.

Ansari, M.; Sharifian, M.; Ehrampoush, M. H.; Mahvi, A. H.; Salmani, M. H.; Fallahzadeh, H. Dielectric barrier discharge plasma with photocatalysts as a hybrid emerging technology for degradation of synthetic organic compounds in aqueous environments: A critical review. *Chemosphere* **2021,** *263*, 128065. DOI: 10.1016/j.chemosphere.2020.128065.

Ao, X.-W.; Eloranta, J.; Huang, C.-H.; Santoro, D.; Sun, W.-J.; Lu, Z.-D.; Li, C. Peracetic acid-based advanced oxidation processes for decontamination and disinfection of water: A review. *Water Res.* **2021,** *188*, 116479. DOI: 10.1016/j.watres.2020.116479.

APRIA Systems. Collimated beam reactor. https://photochemistry.apriasystems.es/products-collimated-beam/ (accessed September 7, 2022).

Armstrong, K. Emerging Industrial Applications. *Carbon Dioxide Utilisation*; Elsevier, 2015; pp 237–251. DOI: 10.1016/B978-0-444-62746-9.00013-X.

Atkins, P. W.; Paula, J. de. *Atkins' physical chemistry*, Tenth edition; Oxford University Press: Oxford, 2014.

Autin, O.; Romelot, C.; Rust, L.; Hart, J.; Jarvis, P.; MacAdam, J.; Parsons, S. A.; Jefferson, B. Evaluation of a UV-light emitting diodes unit for the removal of micropollutants in water for low energy advanced oxidation processes. *Chemosphere* **2013,** *92* (6), 745–751. DOI: 10.1016/j.chemosphere.2013.04.028.

Ayoub, K.; van Hullebusch, E. D.; Cassir, M.; Bermond, A. Application of advanced oxidation processes for TNT removal: A review. *Journal of Hazardous Materials* **2010,** *178* (1-3), 10–28. DOI: 10.1016/j.jhazmat.2010.02.042.

Bader, H.; Hoigné, J. Determination of ozone in water by the indigo method. *Water Res.* **1981,** *15* (4), 449–456. DOI: 10.1016/0043-1354(81)90054-3.

Bautista, P.; Mohedano, A. F.; Casas, J. A.; Zazo, J. A.; Rodriguez, J. J. An overview of the application of Fenton oxidation to industrial wastewaters treatment. *J. Chem. Technol. Biotechnol.* **2008,** *83* (10), 1323–1338. DOI: 10.1002/jctb.1988.

Bletsou, A. A.; Jeon, J.; Hollender, J.; Archontaki, E.; Thomaidis, N. S. Targeted and non-targeted liquid chromatography-mass spectrometric workflows for identification of transformation products of emerging pollutants in the aquatic environment. *TrAC Trends in Analytical Chemistry* **2015,** *66*, 32–44. DOI: 10.1016/j.trac.2014.11.009.

Bligaard, T.; Bullock, R. M.; Campbell, C. T.; Chen, J. G.; Gates, B. C.; Gorte, R. J.; Jones, C. W.; Jones, W. D.; Kitchin, J. R.; Scott, S. L. Toward Benchmarking in Catalysis Science: Best Practices, Challenges, and Opportunities. *ACS Catal.* **2016,** *6* (4), 2590–2602. DOI: 10.1021/acscatal.6b00183.

Bokare, A. D.; Choi, W. Review of iron-free Fenton-like systems for activating H2O2 in advanced oxidation processes. *Journal of Hazardous Materials* **2014,** *275*, 121–135. DOI: 10.1016/j.jhazmat.2014.04.054.

Bolton, J. R.; Bircher, K. G.; Tumas, W.; Tolman, C. A. Figures-of merit for the technical development and application of advanced oxidation processes. *Journal of Advanced Oxidation Technologies* **1996,** *1*, 13–17. DOI: 10.1515/jaots-1996-0104.

Bolton, J. R.; Bircher, K. G.; Tumas, W.; Tolman, C. A. Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems (IUPAC Technical Report). *Pure and Applied Chemistry* **2001,** *73* (4), 627–637. DOI: 10.1351/pac200173040627.

Bolton, J. R.; Cotton, C. E. *The ultraviolet disinfection handbook*, 1st ed.; American Water Works Association: Denver, Colo, 2008.

Bolton, J. R.; Linden, K. G. Standardization of Methods for Fluence (UV Dose) Determination in Bench-Scale UV Experiments. *Journal of Environmental Engineering* **2003,** *129* (3), 209–215. DOI: 10.1061/(ASCE)0733-9372(2003)129:3(209).

Bolton, J. R.; Mayor-Smith, I.; Linden, K. G. Rethinking the Concepts of Fluence (UV Dose) and Fluence Rate: The Importance of Photon-based Units - A Systemic Review. *Photochemistry and photobiology* **2015,** *91* (6), 1252–1262. DOI: 10.1111/php.12512.

Bolton, J. R.; Stefan, M. I. Fundamental photochemical approach to the concepts of fluence (UV dose) and electrical energy efficiency in photochemical degradation reactions. *Res. Chem. Intermed.* **2002,** *28* (7-9), 857–870. DOI: 10.1163/15685670260469474.

Brack, W.; Ait-Aissa, S.; Burgess, R. M.; Busch, W.; Creusot, N.; Di Paolo, C.; Escher, B. I.; Mark Hewitt, L.; Hilscherova, K.; Hollender, J.; Hollert, H.; Jonker, W.; Kool, J.; Lamoree, M.; Muschket, M.; Neumann, S.; Rostkowski, P.; Ruttkies, C.; Schollee, J.; Schymanski, E. L.; Schulze, T.; Seiler, T.-B.; Tindall, A. J.; Aragão Umbuzeiro, G. de; Vrana, B.; Krauss, M. Effect-directed analysis supporting monitoring of aquatic environments--An in-depth overview. *The Science of the total environment* **2016,** *544*, 1073–1118. DOI: 10.1016/j.scitotenv.2015.11.102.

Brezonik, P. L.; Arnold, W. A. *Water chemistry*. *An introduction to the chemistry of natural and engineered aquatic systems;* Oxford University Press: Oxford, 2011.

Bruggeman, P. J.; Kushner, M. J.; Locke, B. R.; Gardeniers, J. G. E.; Graham, W. G.; Graves, D. B.; Hofman-Caris, R. C. H. M.; Maric, D.; Reid, J. P.; Ceriani, E.; Fernandez Rivas, D.; Foster, J. E.; Garrick, S. C.; Gorbanev, Y.; Hamaguchi, S.; Iza, F.; Jablonowski, H.; Klimova, E.; Kolb, J.; Krcma, F.; Lukes, P.; Machala, Z.; Marinov, I.; Mariotti, D.; Mededovic Thagard, S.; Minakata, D.; Neyts, E. C.; Pawlat, J.; Petrovic, Z. L.; Pflieger, R.; Reuter, S.; Schram, D. C.; Schröter, S.; Shiraiwa, M.; Tarabová, B.; Tsai, P. A.; Verlet, J. R. R.; Woedtke, T. von; Wilson, K. R.; Yasui, K.; Zvereva, G. Plasma–liquid interactions: a review and roadmap. *Plasma Sources Sci. Technol.* **2016,** *25* (5), 53002. DOI: 10.1088/0963-0252/25/5/053002.

Brunner, G. Near and supercritical water. Part II: Oxidative processes. *The Journal of Supercritical Fluids* **2009,** *47* (3), 382–390. DOI: 10.1016/j.supflu.2008.09.001.

Buffle, M.-O.; von Gunten, U. Phenols and Amine Induced HO • Generation During the Initial Phase of Natural Water Ozonation. *Environ. Sci. Technol.* **2006,** *40* (9), 3057–3063. DOI: 10.1021/es052020c.

Bulman, D. M.; Mezyk, S. P.; Remucal, C. K. The Impact of pH and Irradiation Wavelength on the Production of Reactive Oxidants during Chlorine Photolysis. *Environmental science & technology* **2019,** *53* (8), 4450–4459. DOI: 10.1021/acs.est.8b07225.

Burns, J. M.; Cooper, W. J.; Ferry, J. L.; King, D. W.; DiMento, B. P.; McNeill, K.; Miller, C. J.; Miller, W. L.; Peake, B. M.; Rusak, S. A.; Rose, A. L.; Waite, T. D. Methods for reactive oxygen species (ROS) detection in aqueous environments. *Aquat Sci* **2012,** *74* (4), 683–734. DOI: 10.1007/s00027-012-0251-x.

Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O − in Aqueous Solution. *Journal of Physical and Chemical Reference Data* **1988,** *17* (2), 513–886. DOI: 10.1063/1.555805.

Cabrera-Reina, A.; Miralles-Cuevas, S.; Sánchez Pérez, J. A.; Salazar, R. Application of solar photo-Fenton in raceway pond reactors: A review. *The Science of the total environment* **2021,** *800*, 149653. DOI: 10.1016/j.scitotenv.2021.149653.

Canonica, S.; Kohn, T.; Mac, M.; Real, F. J.; Wirz, J.; Gunten, U. von. Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds. *Environ. Sci. Technol.* **2005,** *39* (23), 9182–9188. DOI: 10.1021/es051236b.

Canonica, S.; Meunier, L.; Gunten, U. von. Phototransformation of selected pharmaceuticals during UV treatment of drinking water. *Water Res.* **2008,** *42* (1-2), 121–128. DOI: 10.1016/j.watres.2007.07.026.

Chaplin, B. P. Critical review of electrochemical advanced oxidation processes for water treatment applications. *Environmental Science. Processes & Impacts* **2014,** *16* (6), 1182–1203. DOI: 10.1039/c3em00679d.

Chen, N.; Lee, D.; Kang, H.; Cha, D.; Lee, J.; Lee, C. Catalytic persulfate activation for oxidation of organic pollutants: A critical review on mechanisms and controversies. *Journal of Environmental Chemical Engineering* **2022,** *10* (3), 107654. DOI: 10.1016/j.jece.2022.107654.

Chen, W.; Gu, Z.; Wen, P.; Li, Q. Degradation of refractory organic contaminants in membrane concentrates from landfill leachate by a combined coagulation-ozonation process. *Chemosphere* **2019,** *217*, 411–422. DOI: 10.1016/j.chemosphere.2018.11.002.

Cheng, M.; Zeng, G.; Huang, D.; Lai, C.; Xu, P.; Zhang, C.; Liu, Y. Hydroxyl radicals based advanced oxidation processes (AOPs) for remediation of soils contaminated with organic compounds: A review. *Chemical Engineering Journal* **2016,** *284*, 582–598. DOI: 10.1016/j.cej.2015.09.001.

Chong, M. N.; Jin, B.; Chow, C. W. K.; Saint, C. Recent developments in photocatalytic water treatment technology: a review. *Water Res.* **2010,** *44* (10), 2997–3027. DOI: 10.1016/j.watres.2010.02.039.

Chuang, Y.-H.; Chen, S.; Chinn, C. J.; Mitch, W. A. Comparing the UV/Monochloramine and UV/Free Chlorine Advanced Oxidation Processes (AOPs) to the UV/Hydrogen Peroxide AOP Under Scenarios Relevant to Potable Reuse. *Environmental science & technology* **2017,** *51* (23), 13859–13868. DOI: 10.1021/acs.est.7b03570.

Clarizia, L.; Russo, D.; Di Somma, I.; Marotta, R.; Andreozzi, R. Homogeneous photo-Fenton processes at near neutral pH: A review. *Applied Catalysis B: Environmental* **2017,** *209*, 358–371. DOI: 10.1016/j.apcatb.2017.03.011.

Collins, J.; Bolton, J. R. *Advanced oxidation handbook*, First edition; American Water Works Association: Denver, CO, 2016.

Comninellis, C.; Kapalka, A.; Malato, S.; Parsons, S. A.; Poulios, I.; Mantzavinos, D. Advanced oxidation processes for water treatment: Advances and trends for R&D. *Journal of Chemical Technology & Biotechnology* **2008,** *83* (6), 769–776. DOI: 10.1002/jctb.1873.

Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast). *DWD*, 2020.

Du, X.; Zhou, M. Strategies to enhance catalytic performance of metal–organic frameworks in sulfate radical-based advanced oxidation processes for organic pollutants removal. *Chemical Engineering Journal* **2021,** *403*, 126346. DOI: 10.1016/j.cej.2020.126346.

Duan, X.; Sun, H.; Wang, S. Metal-Free Carbocatalysis in Advanced Oxidation Reactions. *Accounts of chemical research* **2018,** *51* (3), 678–687. DOI: 10.1021/acs.accounts.7b00535.

El Kateb, M.; Trellu, C.; Darwich, A.; Rivallin, M.; Bechelany, M.; Nagarajan, S.; Lacour, S.; Bellakhal, N.; Lesage, G.; Héran, M.; Cretin, M. Electrochemical advanced oxidation processes using novel electrode materials for mineralization and biodegradability enhancement of nanofiltration concentrate of landfill leachates. *Water Res.* **2019,** *162*, 446–455. DOI: 10.1016/j.watres.2019.07.005.

Elovitz, M. S.; von Gunten, U. Hydroxyl Radical/Ozone Ratios During Ozonation Processes. I. The R ct Concept. *Ozone: Science & Engineering* **1999,** *21* (3), 239–260. DOI: 10.1080/01919519908547239.

Escher, B. I.; Lawrence, M.; Macova, M.; Mueller, J. F.; Poussade, Y.; Robillot, C.; Roux, A.; Gernjak, W. Evaluation of contaminant removal of reverse osmosis and advanced oxidation in full-scale operation by combining passive sampling with chemical analysis and bioanalytical tools. *Environmental science & technology* **2011,** *45* (12), 5387–5394. DOI: 10.1021/es201153k.

Fennell, B. D.; Mezyk, S. P.; McKay, G. Critical Review of UV-Advanced Reduction Processes for the Treatment of Chemical Contaminants in Water. *ACS Environ. Au* **2022,** *2* (3), 178–205. DOI: 10.1021/acsenvironau.1c00042.

Fischbacher, A.; Sonntag, J. von; Sonntag, C. von; Schmidt, T. C. The (•)OH radical yield in the H2O2 + O3 (peroxone) reaction. *Environmental science & technology* **2013,** *47* (17), 9959–9964. DOI: 10.1021/es402305r.

Flyunt, R.; Leitzke, A.; Mark, G.; Mvula, E.; Reisz, E.; Schick, R.; Sonntag, C. von. Determination of • OH, O 2•- , and Hydroperoxide Yields in Ozone Reactions in Aqueous Solution. *J. Phys. Chem. B* **2003,** *107* (30), 7242–7253. DOI: 10.1021/jp022455b.

Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972,** *238* (5358), 37–38. DOI: 10.1038/238037a0.

Furatian, L.; Mohseni, M. Influence of major anions on the 185 nm advanced oxidation process - Sulphate, bicarbonate, and chloride. *Chemosphere* **2018,** *201*, 503–510. DOI: 10.1016/j.chemosphere.2018.02.160.

Gardoni, D.; Vailati, A.; Canziani, R. Decay of Ozone in Water: A Review. *Ozone: Science & Engineering* **2012,** *34* (4), 233–242. DOI: 10.1080/01919512.2012.686354.

Garoma, T.; Gurol, M. D. Degradation of tert-butyl alcohol in dilute aqueous solution by an O3/UV process. *Environ. Sci. Technol.* **2004,** *38* (19), 5246–5252. DOI: 10.1021/es0353210.

Gassie, L. W.; Englehardt, J. D. Advanced oxidation and disinfection processes for onsite net-zero greywater reuse: A review. *Water Res.* **2017,** *125*, 384–399. DOI: 10.1016/j.watres.2017.08.062.

Giannakis, S.; Lin, K.-Y. A.; Ghanbari, F. A review of the recent advances on the treatment of industrial wastewaters by Sulfate Radical-based Advanced Oxidation Processes (SR-AOPs). *Chemical Engineering Journal* **2021,** *406*, 127083. DOI: 10.1016/j.cej.2020.127083.

Goldstein, S.; Aschengrau, D.; Diamant, Y.; Rabani, J. Photolysis of aqueous H2O2: quantum yield and applications for polychromatic UV actinometry in photoreactors. *Environ. Sci. Technol.* **2007,** *41* (21), 7486–7490. DOI: 10.1021/es071379t.

Goldstein, S.; Meyerstein, D.; Czapski, G. The Fenton reagents. *Free Radical Biology and Medicine* **1993,** *15* (4), 435–445. DOI: 10.1016/0891-5849(93)90043-T.

Gottschalk, C. *Ozonation of Water and Waste Water*. *A Practical Guide to Understanding Ozone and Its Applications*, 2nd ed.; John Wiley & Sons Incorporated: Hoboken, 2010.

Gunten, U. von. Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Res.* **2003a,** *37* (7), 1469–1487. DOI: 10.1016/S0043-1354(02)00458-X.

Gunten, U. von. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Res.* **2003b,** *37* (7), 1443–1467. DOI: 10.1016/S0043-1354(02)00457-8.

Gunten, U. von. Oxidation Processes in Water Treatment: Are We on Track? *Environmental science & technology* **2018,** *52* (9), 5062–5075. DOI: 10.1021/acs.est.8b00586.

Gunten, U. von; Oliveras, Y. Kinetics of the reaction between hydrogen peroxide and hypobromous acid: Implication on water treatment and natural systems. *Water Res.* **1997,** *31* (4), 900–906. DOI: 10.1016/S0043-1354(96)00368-5.

Gunten, U. von; Oliveras, Y. Advanced Oxidation of Bromide-Containing Waters: Bromate Formation Mechanisms. *Environmental science & technology* **1998,** *32* (1), 63–70. DOI: 10.1021/es970477j.

Guo, K.; Wu, Z.; Chen, C.; Fang, J. UV/Chlorine Process: An Efficient Advanced Oxidation Process with Multiple Radicals and Functions in Water Treatment. *Accounts of chemical research* **2022a,** *55* (3), 286–297. DOI: 10.1021/acs.accounts.1c00269.

Guo, Y.; Long, J.; Huang, J.; Yu, G.; Wang, Y. Can the commonly used quenching method really evaluate the role of reactive oxygen species in pollutant abatement during catalytic ozonation? *Water Res.* **2022b,** *215*, 118275. DOI: 10.1016/j.watres.2022.118275.

Guo, Y.; Zhang, Y.; Yu, G.; Wang, Y. Revisiting the role of reactive oxygen species for pollutant abatement during catalytic ozonation: The probe approach versus the scavenger approach. *Applied Catalysis B: Environmental* **2021,** *280*, 119418. DOI: 10.1016/j.apcatb.2020.119418.

Han, M.; Duan, X.; Cao, G.; Zhu, S.; Ho, S.-H. Graphitic nitride-catalyzed advanced oxidation processes (AOPs) for landfill leachate treatment: A mini review. *Process safety and environmental protection : transactions of the Institution of Chemical Engineers, Part B* **2020,** *139*, 230–240. DOI: 10.1016/j.psep.2020.04.046.

Heeb, M. B.; Criquet, J.; Zimmermann-Steffens, S. G.; Gunten, U. von. Oxidative treatment of bromide-containing waters: formation of bromine and its reactions with inorganic and organic compounds--a critical review. *Water Res.* **2014,** *48*, 15–42. DOI: 10.1016/j.watres.2013.08.030.

Heidt, L. J. The Photolysis of Persulfate. *The Journal of Chemical Physics* **1942,** *10* (5), 297–302. DOI: 10.1063/1.1723724.

Hinds, L. M.; O'Donnell, C. P.; Akhter, M.; Tiwari, B. K. Principles and mechanisms of ultraviolet light emitting diode technology for food industry applications. *Innovative Food Science & Emerging Technologies* **2019,** *56*, 102153. DOI: 10.1016/j.ifset.2019.04.006.

Hodges, B. C.; Cates, E. L.; Kim, J.-H. Challenges and prospects of advanced oxidation water treatment processes using catalytic nanomaterials. *Nature nanotechnology* **2018,** *13* (8), 642–650. DOI: 10.1038/s41565-018-0216-x.

Hoigné, J.; Bader, H. Characterization Of Water Quality Criteria for Ozonation Processes. Part II: Lifetime of Added Ozone. *Ozone: Science & Engineering* **1994,** *16* (2), 121–134. DOI: 10.1080/01919519408552417.

Hu, P.; Long, M. Cobalt-catalyzed sulfate radical-based advanced oxidation: A review on heterogeneous catalysts and applications. *Applied Catalysis B: Environmental* **2016,** *181*, 103–117. DOI: 10.1016/j.apcatb.2015.07.024.

Huang, B.; Wu, Z.; Zhou, H.; Li, J.; Zhou, C.; Xiong, Z.; Pan, Z.; Yao, G.; Lai, B. Recent advances in single-atom catalysts for advanced oxidation processes in water purification. *Journal of Hazardous Materials* **2021,** *412*, 125253. DOI: 10.1016/j.jhazmat.2021.125253.

Huang, J.; Zhang, H. Mn-based catalysts for sulfate radical-based advanced oxidation processes: A review. *Environment international* **2019,** *133* (Pt A), 105141. DOI: 10.1016/j.envint.2019.105141.

Huber, M. M.; Canonica, S.; Park, G.-Y.; Gunten, U. von. Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environ. Sci. Technol.* **2003,** *37* (5), 1016–1024. DOI: 10.1021/es025896h.

Hübner, U.; Keller, S.; Jekel, M. Evaluation of the prediction of trace organic compound removal during ozonation of secondary effluents using tracer substances and second order rate kinetics. *Water Res.* **2013,** *47* (17), 6467–6474. DOI: 10.1016/j.watres.2013.08.025.

Hübner, U.; Zucker, I.; Jekel, M. Options and limitations of hydrogen peroxide addition to enhance radical formation during ozonation of secondary effluents. *Journal of Water Reuse and Desalination* **2015,** *5* (1), 8. DOI: 10.2166/wrd.2014.036.

Hung, H.-M.; Hoffmann, M. R. Kinetics and Mechanism of the Sonolytic Degradation of Chlorinated Hydrocarbons: Frequency Effects. *J. Phys. Chem. A* **1999,** *103* (15), 2734–2739. DOI: 10.1021/jp9845930.

Imoberdorf, G.; Mohseni, M. Modeling and experimental evaluation of vacuum-UV photoreactors for water treatment. *Chemical Engineering Science* **2011,** *66* (6), 1159–1167. DOI: 10.1016/j.ces.2010.12.020.

IUPAC. *The IUPAC Compendium of Chemical Terminology;* International Union of Pure and Applied Chemistry (IUPAC): Research Triangle Park, NC, 2019.

Kasprzyk-Hordern, B.; Ziółek, M.; Nawrocki, J. Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment. *Applied Catalysis B: Environmental* **2003,** *46* (4), 639–669. DOI: 10.1016/S0926-3373(03)00326-6.

Katsoyiannis, I. A.; Canonica, S.; Gunten, U. von. Efficiency and energy requirements for the transformation of organic micropollutants by ozone, O3/H2O2 and UV/H2O2. *Water Res.* **2011,** *45* (13), 3811–3822. DOI: 10.1016/j.watres.2011.04.038.

Keen, O.; Bolton, J.; Litter, M.; Bircher, K.; Oppenländer, T. Standard reporting of Electrical Energy per Order (EEO) for UV/H 2 O 2 reactors (IUPAC Technical Report). *Pure and Applied Chemistry* **2018,** *90* (9), 1487–1499. DOI: 10.1515/pac-2017-0603.

Keen, O. S.; McKay, G.; Mezyk, S. P.; Linden, K. G.; Rosario-Ortiz, F. L. Identifying the factors that influence the reactivity of effluent organic matter with hydroxyl radicals. *Water Res.* **2014,** *50*, 408–419. DOI: 10.1016/j.watres.2013.10.049.

Khajouei, G.; Finklea, H. O.; Lin, L.-S. UV/chlorine advanced oxidation processes for degradation of contaminants in water and wastewater: A comprehensive review. *Journal of Environmental Chemical Engineering* **2022,** *10* (3), 107508. DOI: 10.1016/j.jece.2022.107508.

Kim, C.; Ahn, J.-Y.; Kim, T. Y.; Shin, W. S.; Hwang, I. Activation of Persulfate by Nanosized Zero-Valent Iron (NZVI): Mechanisms and Transformation Products of NZVI. *Environmental science & technology* **2018,** *52* (6), 3625–3633. DOI: 10.1021/acs.est.7b05847.

Kneissl, M.; Seong, T.-Y.; Han, J.; Amano, H. The emergence and prospects of deep-ultraviolet light-emitting diode technologies. *Nat. Photonics* **2019,** *13* (4), 233–244. DOI: 10.1038/s41566-019-0359-9.

Könemann, S.; Kase, R.; Simon, E.; Swart, K.; Buchinger, S.; Schlüsener, M.; Hollert, H.; Escher, B. I.; Werner, I.; Aït-Aïssa, S.; Vermeirssen, E.; Dulio, V.; Valsecchi, S.; Polesello, S.; Behnisch, P.; Javurkova, B.; Perceval, O.; Di Paolo, C.; Olbrich, D.; Sychrova, E.; Schlichting, R.; Leborgne, L.; Clara, M.; Scheffknecht, C.; Marneffe, Y.; Chalon, C.; Tušil, P.; Soldàn, P.;

Danwitz, B. von; Schwaiger, J.; San Martín Becares, M. I.; Bersani, F.; Hilscherová, K.; Reifferscheid, G.; Ternes, T.; Carere, M. Effect-based and chemical analytical methods to monitor estrogens under the European Water Framework Directive. *TrAC Trends in Analytical Chemistry* **2018,** *102*, 225–235. DOI: 10.1016/j.trac.2018.02.008.

Kozuch, S.; Martin, J. M. L. “Turning Over” Definitions in Catalytic Cycles. *ACS Catal.* **2012,** *2* (12), 2787–2794. DOI: 10.1021/cs3005264.

Kruithof, J. C.; Kamp, P. C.; Belosevic, M.; Stefan, M. UV/H2O2 retrofit of PWN's water treatment plant Andijk for primary disinfection and organic contaminant control. *2nd IWA Leading-Edge Conference on Water and Wastewater Treatment Technologies*; Water and environmental management series; IWA Publ: London, 2004; pp 53–65.

Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. Chemical actinometry (IUPAC Technical Report). *Pure and Applied Chemistry* **2004,** *76* (12), 2105–2146. DOI: 10.1351/pac200476122105.

Kumar, A.; Škoro, N.; Gernjak, W.; Puač, N. Cold atmospheric plasma technology for removal of organic micropollutants from wastewater—a review. *Eur. Phys. J. D* **2021,** *75* (11). DOI: 10.1140/epjd/s10053-021-00283-5.

Kwon, M.; Royce, A.; Gong, Y.; Ishida, K. P.; Stefan, M. I. UV/chlorine vs. UV/H 2 O 2 for water reuse at Orange County Water District, CA: a pilot study. *Environ. Sci.: Water Res. Technol.* **2020,** *6* (9), 2416–2431. DOI: 10.1039/D0EW00316F.

Lado Ribeiro, A. R.; Moreira, N. F.; Li Puma, G.; Silva, A. M. Impact of water matrix on the removal of micropollutants by advanced oxidation technologies. *Chemical Engineering Journal* **2019,** *363*, 155–173. DOI: 10.1016/j.cej.2019.01.080.

Lamsal, R.; Walsh, M. E.; Gagnon, G. A. Comparison of advanced oxidation processes for the removal of natural organic matter. *Water Res.* **2011,** *45* (10), 3263–3269. DOI: 10.1016/j.watres.2011.03.038.

Lanzarini-Lopes, M.; Garcia-Segura, S.; Hristovski, K.; Westerhoff, P. Electrical energy per order and current efficiency for electrochemical oxidation of p-chlorobenzoic acid with boron-doped diamond anode. *Chemosphere* **2017,** *188*, 304–311. DOI: 10.1016/j.chemosphere.2017.08.145.

Lavonen, E. E.; Gonsior, M.; Tranvik, L. J.; Schmitt-Kopplin, P.; Köhler, S. J. Selective chlorination of natural organic matter: identification of previously unknown disinfection byproducts. *Environmental science & technology* **2013,** *47* (5), 2264–2271. DOI: 10.1021/es304669p.

Lee, J.; Gunten, U. von; Kim, J.-H. Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks. *Environmental science & technology* **2020a,** *54* (6), 3064–3081. DOI: 10.1021/acs.est.9b07082.

Lee, K. M.; Lai, C. W.; Ngai, K. S.; Juan, J. C. Recent developments of zinc oxide based photocatalyst in water treatment technology: A review. *Water Res.* **2016,** *88*, 428–448. DOI: 10.1016/j.watres.2015.09.045.

Lee, M.; Blum, L. C.; Schmid, E.; Fenner, K.; Gunten, U. von. A computer-based prediction platform for the reaction of ozone with organic compounds in aqueous solution: kinetics and mechanisms. *Environ. Sci. Process. Impacts* **2017,** *19* (3), 465–476. DOI: 10.1039/C6EM00584E.

Lee, M.-Y.; Wang, W.-L.; Du, Y.; Hu, H.-Y.; Huang, N.; Xu, Z.-B.; Wu, Q.-Y.; Ye, B. Enhancement effect among a UV, persulfate, and copper (UV/PS/Cu2+) system on the degradation of nonoxidizing biocide: The kinetics, radical species, and degradation pathway. *Chemical Engineering Journal* **2020b,** *382*, 122312. DOI: 10.1016/j.cej.2019.122312.

Lee, Y.; Gunten, U. von. Quantitative structure-activity relationships (QSARs) for the transformation of organic micropollutants during oxidative water treatment. *Water Res.* **2012,** *46* (19), 6177–6195. DOI: 10.1016/j.watres.2012.06.006.

Lee, Y.; Gunten, U. von. Advances in predicting organic contaminant abatement during ozonation of municipal wastewater effluent: reaction kinetics, transformation products, and changes of biological effects. *Environ. Sci.: Water Res. Technol.* **2016,** *2* (3), 421–442. DOI: 10.1039/c6ew00025h.

Lee, Y.; Kovalova, L.; McArdell, C. S.; Gunten, U. von. Prediction of micropollutant elimination during ozonation of a hospital wastewater effluent. *Water Res.* **2014,** *64*, 134–148. DOI: 10.1016/j.watres.2014.06.027.

Legrini, O.; Oliveros, E.; Braun, A. M. Photochemical processes for water treatment. *Chem. Rev.* **1993,** *93* (2), 671–698. DOI: 10.1021/cr00018a003.

Li, M.; Li, W.; Wen, D.; Bolton, J. R.; Blatchley, E. R.; Qiang, Z. Micropollutant Degradation by the UV/H2O2 Process: Kinetic Comparison among Various Radiation Sources. *Environmental science & technology* **2019,** *53* (9), 5241–5248. DOI: 10.1021/acs.est.8b06557.

Li, W.; Patton, S.; Gleason, J. M.; Mezyk, S. P.; Ishida, K. P.; Liu, H. UV Photolysis of Chloramine and Persulfate for 1,4-Dioxane Removal in Reverse-Osmosis Permeate for Potable Water Reuse. *Environmental science & technology* **2018,** *52* (11), 6417–6425. DOI: 10.1021/acs.est.7b06042.

Liang, C.; Bruell, C. J. Thermally Activated Persulfate Oxidation of Trichloroethylene: Experimental Investigation of Reaction Orders. *Ind. Eng. Chem. Res.* **2008,** *47* (9), 2912–2918. DOI: 10.1021/ie070820l.

Lieberman, M. A. *Principles of plasma discharges and materials processing*, 2nd ed.; Wiley-Interscience: Hoboken, N.J, 2005.

Lim, S.; Shi, J. L.; Gunten, U. von; McCurry, D. L. Ozonation of organic compounds in water and wastewater: A critical review. *Water Res.* **2022,** *213*, 118053. DOI: 10.1016/j.watres.2022.118053.

Liu, X.; He, S.; Yang, Y.; Yao, B.; Tang, Y.; Luo, L.; Zhi, D.; Wan, Z.; Wang, L.; Zhou, Y. A review on percarbonate-based advanced oxidation processes for remediation of organic compounds in water. *Environmental research* **2021,** *200*, 111371. DOI: 10.1016/j.envres.2021.111371.

Loeb, S. K.; Alvarez, P. J. J.; Brame, J. A.; Cates, E. L.; Choi, W.; Crittenden, J.; Dionysiou, D. D.; Li, Q.; Li-Puma, G.; Quan, X.; Sedlak, D. L.; David Waite, T.; Westerhoff, P.; Kim, J.-H. The Technology Horizon for Photocatalytic Water Treatment: Sunrise or Sunset? *Environmental science & technology* **2019,** *53* (6), 2937–2947. DOI: 10.1021/acs.est.8b05041.

Lucas, M. S.; Peres, J. A.; Li Puma, G. Treatment of winery wastewater by ozone-based advanced oxidation processes (O3, O3/UV and O3/UV/H2O2) in a pilot-scale bubble column reactor and process economics. *Separation and Purification Technology* **2010,** *72* (3), 235–241. DOI: 10.1016/j.seppur.2010.01.016.

Luo, H.; Zeng, Y.; He, D.; Pan, X. Application of iron-based materials in heterogeneous advanced oxidation processes for wastewater treatment: A review. *Chemical Engineering Journal* **2021,** *407*, 127191. DOI: 10.1016/j.cej.2020.127191.

Lutze, H. V.; Kerlin, N.; Schmidt, T. C. Sulfate radical-based water treatment in presence of chloride: formation of chlorate, inter-conversion of sulfate radicals into hydroxyl radicals and influence of bicarbonate. *Water Research* **2015,** *72*, 349–360. DOI: 10.1016/j.watres.2014.10.006.

Lyon, B. A.; Milsk, R. Y.; DeAngelo, A. B.; Simmons, J. E.; Moyer, M. P.; Weinberg, H. S. Integrated chemical and toxicological investigation of UV-chlorine/chloramine drinking water treatment. *Environmental science & technology* **2014,** *48* (12), 6743–6753. DOI: 10.1021/es501412n.

Mahamuni, N. N.; Adewuyi, Y. G. Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation. *Ultrasonics sonochemistry* **2010,** *17* (6), 990–1003. DOI: 10.1016/j.ultsonch.2009.09.005.

Malato, S.; Fernández-Ibáñez, P.; Maldonado, M. I.; Blanco, J.; Gernjak, W. Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. *Catalysis Today* **2009,** *147* (1), 1–59. DOI: 10.1016/j.cattod.2009.06.018.

Malik, M. A. Water Purification by Plasmas: Which Reactors are Most Energy Efficient? *Plasma Chem Plasma Process* **2010,** *30* (1), 21–31. DOI: 10.1007/s11090-009-9202-2.

Marron, E. L.; Prasse, C.; van Buren, J.; Sedlak, D. L. Formation and Fate of Carbonyls in Potable Water Reuse Systems. *Environmental science & technology* **2020,** *54* (17), 10895–10903. DOI: 10.1021/acs.est.0c02793.

Martijn, B. J.; van Rompay, A. R.; Penders, E. J. M.; Alharbi, Y.; Baggelaar, P. K.; Kruithof, J. C.; Rietjens, I. M. C. M. Development of a 4-NQO toxic equivalency factor (TEF) approach to enable a preliminary risk assessment of unknown genotoxic compounds detected by the Ames II test in UV/H_2O_2 water treatment samples. *Chemosphere* **2016,** *144*, 338–345. DOI: 10.1016/j.chemosphere.2015.08.070.

Maruthamuthu, P.; Neta, P. Phosphate radicals. Spectra, acid-base equilibriums, and reactions with inorganic compounds. *J. Phys. Chem.* **1978,** *82* (6), 710–713. DOI: 10.1021/j100495a019.

Matilainen, A.; Sillanpää, M. Removal of natural organic matter from drinking water by advanced oxidation processes. *Chemosphere* **2010,** *80* (4), 351–365. DOI: 10.1016/j.chemosphere.2010.04.067.

McElroy, W. J. A laser photolysis study of the reaction of sulfate(1-) with chloride and the subsequent decay of chlorine(1-) in aqueous solution. *J. Phys. Chem.* **1990,** *94* (6), 2435–2441. DOI: 10.1021/j100369a044.

Merényi, G.; Lind, J.; Naumov, S.; Sonntag, C. von. Reaction of ozone with hydrogen peroxide (peroxone process): a revision of current mechanistic concepts based on thermokinetic and quantum-chemical considerations. *Environ. Sci. Technol.* **2010a,** *44* (9), 3505–3507. DOI: 10.1021/es100277d.

Merényi, G.; Lind, J.; Naumov, S.; Sonntag, C. von. The reaction of ozone with the hydroxide ion: Mechanistic considerations based on thermokinetic and quantum chemical calculations and the role of HO4- in superoxide dismutation. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2010b,** *16* (4), 1372–1377. DOI: 10.1002/chem.200802539.

Mery, Y.; Tiruta-Barna, L.; Benetto, E.; Baudin, I. An integrated “process modelling-life cycle assessment” tool for the assessment and design of water treatment processes. *Int J Life Cycle Assess* **2013,** *18* (5), 1062–1070. DOI: 10.1007/s11367-012-0541-5.

Miklos, D. B.; Remy, C.; Jekel, M.; Linden, K. G.; Drewes, J. E.; Hübner, U. Evaluation of advanced oxidation processes for water and wastewater treatment - A critical review. *Water Res.* **2018,** *139*, 118–131. DOI: 10.1016/j.watres.2018.03.042.

Moreno-Andrés, J.; Ambauen, N.; Vadstein, O.; Hallé, C.; Acevedo-Merino, A.; Nebot, E.; Meyn, T. Inactivation of marine heterotrophic bacteria in ballast water by an Electrochemical Advanced Oxidation Process. *Water Res.* **2018,** *140*, 377–386. DOI: 10.1016/j.watres.2018.04.061.

Nawaz, F.; Cao, H.; Xie, Y.; Xiao, J.; Chen, Y.; Ghazi, Z. A. Selection of active phase of MnO2 for catalytic ozonation of 4-nitrophenol. *Chemosphere* **2017,** *168*, 1457–1466. DOI: 10.1016/j.chemosphere.2016.11.138.

Neta, P.; Huie, R. E.; Ross, A. B. Rate Constants for Reactions of Inorganic Radicals in Aqueous Solution. *Journal of Physical and Chemical Reference Data* **1988,** *17* (3), 1027–1284. DOI: 10.1063/1.555808.

Nihemaiti, M.; Miklos, D. B.; Hübner, U.; Linden, K. G.; Drewes, J. E.; Croué, J.-P. Removal of trace organic chemicals in wastewater effluent by UV/H2O2 and UV/PDS. *Water Res.* **2018,** *145*, 487–497. DOI: 10.1016/j.watres.2018.08.052.

Nosaka, Y.; Nosaka, A. Y. Generation and Detection of Reactive Oxygen Species in Photocatalysis. *Chem. Rev.* **2017,** *117* (17), 11302–11336. DOI: 10.1021/acs.chemrev.7b00161.

Nöthe, T.; Fahlenkamp, H.; Sonntag, C. von. Ozonation of wastewater: rate of ozone consumption and hydroxyl radical yield. *Environ. Sci. Technol.* **2009,** *43* (15), 5990–5995. DOI: 10.1021/es900825f.

Oller, I.; Malato, S.; Sánchez-Pérez, J. A. Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination--a review. *The Science of the total environment* **2011,** *409* (20), 4141–4166. DOI: 10.1016/j.scitotenv.2010.08.061.

Oturan, M. A.; Aaron, J.-J. Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review. *Critical Reviews in Environmental Science and Technology* **2014,** *44* (23), 2577–2641. DOI: 10.1080/10643389.2013.829765.

Piccinno, F.; Hischier, R.; Seeger, S.; Som, C. From laboratory to industrial scale: a scale-up framework for chemical processes in life cycle assessment studies. *Journal of Cleaner Production* **2016,** *135*, 1085–1097. DOI: 10.1016/j.jclepro.2016.06.164.

Pinkard, B. R.; Shetty, S.; Stritzinger, D.; Bellona, C.; Novosselov, I. V. Destruction of perfluorooctanesulfonate (PFOS) in a batch supercritical water oxidation reactor. *Chemosphere* **2021,** *279*, 130834. DOI: 10.1016/j.chemosphere.2021.130834.

Pisarenko, A. N.; Stanford, B. D.; Yan, D.; Gerrity, D.; Snyder, S. A. Effects of ozone and ozone/peroxide on trace organic contaminants and NDMA in drinking water and water reuse applications. *Water Res.* **2012,** *46* (2), 316–326. DOI: 10.1016/j.watres.2011.10.021.

Pocostales, J. P.; Sein, M. M.; Knolle, W.; Sonntag, C. von; Schmidt, T. C. Degradation of ozone-refractory organic phosphates in wastewater by ozone and ozone/hydrogen peroxide (peroxone): the role of ozone consumption by dissolved organic matter. *Environmental science & technology* **2010,** *44* (21), 8248–8253. DOI: 10.1021/es1018288.

Prasse, C.; Stalter, D.; Schulte-Oehlmann, U.; Oehlmann, J.; Ternes, T. A. Spoilt for choice: A critical review on the chemical and biological assessment of current wastewater treatment technologies. *Water Res.* **2015a,** *87*, 237–270. DOI: 10.1016/j.watres.2015.09.023.

Prasse, C.; Wenk, J.; Jasper, J. T.; Ternes, T. A.; Sedlak, D. L. Co-occurrence of Photochemical and Microbiological Transformation Processes in Open-Water Unit Process Wetlands. *Environmental science & technology* **2015b,** *49* (24), 14136–14145. DOI: 10.1021/acs.est.5b03783.

Rabani, J.; Mamane, H.; Pousty, D.; Bolton, J. R. Practical Chemical Actinometry-A Review. *Photochemistry and photobiology* **2021,** *97* (5), 873–902. DOI: 10.1111/php.13429.

Radjenovic, J.; Duinslaeger, N.; Avval, S. S.; Chaplin, B. P. Facing the Challenge of Poly- and Perfluoroalkyl Substances in Water: Is Electrochemical Oxidation the Answer? *Environmental science & technology* **2020,** *54* (23), 14815–14829. DOI: 10.1021/acs.est.0c06212.

Radjenovic, J.; Sedlak, D. L. Challenges and Opportunities for Electrochemical Processes as Next-Generation Technologies for the Treatment of Contaminated Water. *Environmental science & technology* **2015,** *49* (19), 11292–11302. DOI: 10.1021/acs.est.5b02414.

Rae, J.; Ashokkumar, M.; Eulaerts, O.; Sonntag, C. von; Reisse, J.; Grieser, F. Estimation of ultrasound induced cavitation bubble temperatures in aqueous solutions. *Ultrasonics sonochemistry* **2005,** *12* (5), 325–329. DOI: 10.1016/j.ultsonch.2004.06.007.

Rahn, R. O. Potassium Iodide as a Chemical Actinometer for 254 nm Radiation: Use of Iodate as an Electron Scavenger. *Photochemistry and photobiology* **1997,** *66* (4), 450–455. DOI: 10.1111/j.1751-1097.1997.tb03172.x.

Rahn, R. O.; Stefan, M. I.; Bolton, J. R.; Goren, E.; Shaw, P.-S.; Lykke, K. R. Quantum Yield of the Iodide–Iodate Chemical Actinometer: Dependence on Wavelength and Concentration¶. *Photochemistry and photobiology* **2003,** *78* (2), 146. DOI: 10.1562/0031-8655(2003)078%3C0146:qyotic%3E2.0.co;2.

Rekhate, C. V.; Srivastava, J. K. Recent advances in ozone-based advanced oxidation processes for treatment of wastewater- A review. *Chemical Engineering Journal Advances* **2020,** *3*, 100031. DOI: 10.1016/j.ceja.2020.100031.

Ribeiro, A. R.; Nunes, O. C.; Pereira, M. F. R.; Silva, A. M. T. An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. *Environment international* **2015,** *75*, 33–51. DOI: 10.1016/j.envint.2014.10.027.

Rodriguez-Narvaez, O. M.; Peralta-Hernandez, J. M.; Goonetilleke, A.; Bandala, E. R. Treatment technologies for emerging contaminants in water: A review. *Chemical Engineering Journal* **2017,** *323*, 361–380. DOI: 10.1016/j.cej.2017.04.106.

Rosario-Ortiz, F. L.; Canonica, S. Probe Compounds to Assess the Photochemical Activity of Dissolved Organic Matter. *Environmental science & technology* **2016,** *50* (23), 12532–12547. DOI: 10.1021/acs.est.6b02776.

Saien, J.; Ojaghloo, Z.; Soleymani, A. R.; Rasoulifard, M. H. Homogeneous and heterogeneous AOPs for rapid degradation of Triton X-100 in aqueous media via UV light, nano titania hydrogen peroxide and potassium persulfate. *Chemical Engineering Journal* **2011,** *167* (1), 172–182. DOI: 10.1016/j.cej.2010.12.017.

Sánchez-Polo, M.; Gunten, U. von; Rivera-Utrilla, J. Efficiency of activated carbon to transform ozone into *OH radicals: influence of operational parameters. *Water Res.* **2005,** *39* (14), 3189–3198. DOI: 10.1016/j.watres.2005.05.026.

Scheideler, J.; Lekkerkerker-Teunissen, K.; Knol, T.; Ried, A.; Verberk, J.; van Dijk, H. Combination of O3/H2O2 and UV for multiple barrier micropollutant treatment and bromate formation control - an economic attractive option. *Water Practice and Technology* **2011,** *6* (4). DOI: 10.2166/wpt.2011.0063.

Schmelling, D., Cotton, C., Owen, D., Mackey, E., Wright, H., Linden, K. G., Malley, J. P. *Ultraviolet disinfection guidance manual for the final long term 2 enhanced surface water treatment rule*, 2006.

Schmidt, C. K.; Brauch, H.-J. N,N-dimethylsulfamide as precursor for N-nitrosodimethylamine (NDMA) formation upon ozonation and its fate during drinking water treatment. *Environ. Sci. Technol.* **2008,** *42* (17), 6340–6346. DOI: 10.1021/es7030467.

Scholes, R. C. Emerging investigator series: contributions of reactive nitrogen species to transformations of organic compounds in water: a critical review. *Environmental Science. Processes & Impacts* **2022,** *24* (6), 851–869. DOI: 10.1039/D2EM00102K.

Schulze, S.; Zahn, D.; Montes, R.; Rodil, R.; Quintana, J. B.; Knepper, T. P.; Reemtsma, T.; Berger, U. Occurrence of emerging persistent and mobile organic contaminants in European water samples. *Water Res.* **2019,** *153*, 80–90. DOI: 10.1016/j.watres.2019.01.008.

Shang, Y.; Xu, X.; Gao, B.; Wang, S.; Duan, X. Single-atom catalysis in advanced oxidation processes for environmental remediation. *Chemical Society reviews* **2021,** *50* (8), 5281–5322. DOI: 10.1039/d0cs01032d.

Shestakova, M.; Sillanpää, M. Electrode materials used for electrochemical oxidation of organic compounds in wastewater. *Rev Environ Sci Biotechnol* **2017,** *16* (2), 223–238. DOI: 10.1007/s11157-017-9426-1.

Sidnell, T.; Wood, R. J.; Hurst, J.; Lee, J.; Bussemaker, M. J. Sonolysis of per- and poly fluoroalkyl substances (PFAS): A meta-analysis. *Ultrasonics sonochemistry* **2022,** *87*, 105944. DOI: 10.1016/j.ultsonch.2022.105944.

Sillanpää, M.; Ncibi, M. C.; Matilainen, A. Advanced oxidation processes for the removal of natural organic matter from drinking water sources: A comprehensive review. *Journal of environmental management* **2018,** *208*, 56–76. DOI: 10.1016/j.jenvman.2017.12.009.

Song, K.; Mohseni, M.; Taghipour, F. Application of ultraviolet light-emitting diodes (UV-LEDs) for water disinfection: A review. *Water Res.* **2016,** *94*, 341–349. DOI: 10.1016/j.watres.2016.03.003.

Sonntag, C. von. *Free-Radical-Induced DNA Damage and Its Repair*. *A Chemical Perspective*; SpringerLink Bücher; Springer Berlin Heidelberg: Berlin, Heidelberg, 2006.

Sonntag, C. von. Advanced oxidation processes: Mechanistic aspects. *Water Science and Technology* **2008,** *58* (5), 1015–1021. DOI: 10.2166/wst.2008.467.

Sonntag, C. von; Gunten, U. von. *Chemistry of ozone in water and wastewater treatment*. *From basic principles to applications;* IWA Publishing: London, 2012.

Spahr, S.; Cirpka, O. A.; Gunten, U. von; Hofstetter, T. B. Formation of N-Nitrosodimethylamine during Chloramination of Secondary and Tertiary Amines: Role of Molecular Oxygen and Radical Intermediates. *Environmental science & technology* **2017a,** *51* (1), 280–290. DOI: 10.1021/acs.est.6b04780.

Spahr, S.; Gunten, U. von; Hofstetter, T. B. Carbon, Hydrogen, and Nitrogen Isotope Fractionation Trends in N-Nitrosodimethylamine Reflect the Formation Pathway during Chloramination of Tertiary Amines. *Environmental science & technology* **2017b,** *51* (22), 13170–13179. DOI: 10.1021/acs.est.7b03919.

Spasiano, D.; Marotta, R.; Malato, S.; Fernandez-Ibañez, P.; Di Somma, I. Solar photocatalysis: Materials, reactors, some commercial, and pre-industrialized applications. A comprehensive approach. *Applied Catalysis B: Environmental* **2015,** *170-171*, 90–123. DOI: 10.1016/j.apcatb.2014.12.050.

Staehelin, J.; Hoigne, J. Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide. *Environmental science & technology* **1982,** *16* (10), 676–681. DOI: 10.1021/es00104a009.

Stefan, M. I.; Bolton, J. R. Fundamental approach to the fluence-based kinetic and electrical energy efficiency parameters in photochemical degradation reactions: polychromatic light. *Journal of Environmental Engineering and Science* **2005,** *4* (Supplement 1), S13-S18. DOI: 10.1139/s04-026.

Stefan, M. I.; Hoy, A. R.; Bolton, J. R. Kinetics and Mechanism of the Degradation and Mineralization of Acetone in Dilute Aqueous Solution Sensitized by the UV Photolysis of Hydrogen Peroxide. *Environmental science & technology* **1996,** *30* (7), 2382–2390. DOI: 10.1021/es950866i.

Sugiyama, W.; Yamamura, T.; Park, K. C.; Tomiyasu, H.; Satoh, I.; Shiokawa, Y.; Okada, H.; Sugita, Y. Recovery of radioactivity as solids from nonflammable organic low-level radioactive wastes using supercritical water mixed with RuO2. *The Journal of Supercritical Fluids* **2005,** *35* (3), 240–246. DOI: 10.1016/j.supflu.2005.02.003.

Sun, M.; Chu, C.; Geng, F.; Lu, X.; Qu, J.; Crittenden, J.; Elimelech, M.; Kim, J.-H. Reinventing Fenton Chemistry: Iron Oxychloride Nanosheet for pH-Insensitive H 2 O 2 Activation. *Environ. Sci. Technol. Lett.* **2018,** *5* (3), 186–191. DOI: 10.1021/acs.estlett.8b00065.

Swaim, P.; Royce, A.; Smith, T.; Maloney, T.; Ehlen, D.; Carter, B. Effectiveness of UV Advanced Oxidation for Destruction of Micro-Pollutants. *Ozone: Science & Engineering* **2008,** *30* (1), 34–42. DOI: 10.1080/01919510701753390.

Tasso Guaraldo, T.; Wenk, J.; Mattia, D. Photocatalytic ZnO Foams for Micropollutant Degradation. *Adv. Sustainable Syst.* **2021,** *5* (5), 2000208. DOI: 10.1002/adsu.202000208.

Tentscher, P. R.; Lee, M.; Gunten, U. von. Micropollutant Oxidation Studied by Quantum Chemical Computations: Methodology and Applications to Thermodynamics, Kinetics, and Reaction Mechanisms. *Accounts of chemical research* **2019,** *52* (3), 605–614. DOI: 10.1021/acs.accounts.8b00610.

Tian, F.-X.; Ye, W.-K.; Xu, B.; Hu, X.-J.; Ma, S.-X.; Lai, F.; Gao, Y.-Q.; Xing, H.-B.; Xia, W.-H.; Wang, B. Comparison of UV-induced AOPs (UV/Cl2, UV/NH2Cl, UV/ClO2 and UV/H2O2) in the degradation of iopamidol: Kinetics, energy requirements and DBPs-related toxicity in sequential disinfection processes. *Chemical Engineering Journal* **2020,** *398*, 125570. DOI: 10.1016/j.cej.2020.125570.

Topolovec, B.; Škoro, N.; Puač, N.; Petrovic, M. Pathways of organic micropollutants degradation in atmospheric pressure plasma processing - A review. *Chemosphere* **2022,** *294*, 133606. DOI: 10.1016/j.chemosphere.2022.133606.

Tröster, I.; Schäfer, L.; Fryda, M.; Matthée, T. Electrochemical advanced oxidation process using DiaChem®electrodes. *Water Science and Technology* **2004,** *49* (4), 207–212. DOI: 10.2166/wst.2004.0264.

Ulliman, S. L.; Miklos, D. B.; Hübner, U.; Drewes, J. E.; Linden, K. G. Improving UV/H 2 O 2 performance following tertiary treatment of municipal wastewater. *Environ. Sci.: Water Res. Technol.* **2018,** *4* (9), 1321–1330. DOI: 10.1039/C8EW00233A.

Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R. Kinetics and mechanism of the sonolytic conversion of the aqueous perfluorinated surfactants, perfluorooctanoate (PFOA), and perfluorooctane sulfonate (PFOS) into inorganic products. *The journal of physical chemistry. A* **2008,** *112* (18), 4261–4270. DOI: 10.1021/jp801081y.

Vecitis, C. D.; Park, H.; Cheng, J.; Mader, B. T.; Hoffmann, M. R. Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA). *Front. Environ. Sci. Eng. China* **2009,** *3* (2), 129–151. DOI: 10.1007/s11783-009-0022-7.

Velo-Gala, I.; Farré, M. J.; Radjenovic, J.; Gernjak, W. N -Nitrosodimethylamine (NDMA) Degradation by the Ultraviolet/Peroxodisulfate Process. *Environ. Sci. Technol. Lett.* **2019,** *6* (2), 106–111. DOI: 10.1021/acs.estlett.8b00667.

Vione, D.; Falletti, G.; Maurino, V.; Minero, C.; Pelizzetti, E.; Malandrino, M.; Ajassa, R.; Olariu, R.-I.; Arsene, C. Sources and sinks of hydroxyl radicals upon irradiation of natural water samples. *Environ. Sci. Technol.* **2006,** *40* (12), 3775–3781. DOI: 10.1021/es052206b.

Völker, J.; Stapf, M.; Miehe, U.; Wagner, M. Systematic Review of Toxicity Removal by Advanced Wastewater Treatment Technologies via Ozonation and Activated Carbon. *Environmental science & technology* **2019,** *53* (13), 7215–7233. DOI: 10.1021/acs.est.9b00570.

Wacławek, S.; Lutze, H. V.; Grübel, K.; Padil, V. V.; Černík, M.; Dionysiou, D. Chemistry of persulfates in water and wastewater treatment: A review. *Chemical Engineering Journal* **2017,** *330*, 44–62. DOI: 10.1016/j.cej.2017.07.132.

Wang, C.; Moore, N.; Bircher, K.; Andrews, S.; Hofmann, R. Full-scale comparison of UV/H2O2 and UV/Cl2 advanced oxidation: The degradation of micropollutant surrogates and the formation of disinfection byproducts. *Water Res.* **2019a,** *161*, 448–458. DOI: 10.1016/j.watres.2019.06.033.

Wang, C.; Rosenfeldt, E.; Li, Y.; Hofmann, R. External Standard Calibration Method To Measure the Hydroxyl Radical Scavenging Capacity of Water Samples. *Environmental science & technology* **2020,** *54* (3), 1929–1937. DOI: 10.1021/acs.est.9b06273.

Wang, D.; Bolton, J. R.; Andrews, S. A.; Hofmann, R. UV/chlorine control of drinking water taste and odour at pilot and full-scale. *Chemosphere* **2015,** *136*, 239–244. DOI: 10.1016/j.chemosphere.2015.05.049.

Wang, J.; Chen, H. Catalytic ozonation for water and wastewater treatment: Recent advances and perspective. *The Science of the total environment* **2020,** *704*, 135249. DOI: 10.1016/j.scitotenv.2019.135249.

Wang, J.; Wang, S. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chemical Engineering Journal* **2018,** *334*, 1502–1517. DOI: 10.1016/j.cej.2017.11.059.

Wang, J.; Wang, S. Reactive species in advanced oxidation processes: Formation, identification and reaction mechanism. *Chemical Engineering Journal* **2020,** *401*, 126158. DOI: 10.1016/j.cej.2020.126158.

Wang, J.; Wang, S. Effect of inorganic anions on the performance of advanced oxidation processes for degradation of organic contaminants. *Chemical Engineering Journal* **2021,** *411*, 128392. DOI: 10.1016/j.cej.2020.128392.

Wang, L.; Lan, X.; Peng, W.; Wang, Z. Uncertainty and misinterpretation over identification, quantification and transformation of reactive species generated in catalytic oxidation processes: A review. *Journal of Hazardous Materials* **2021,** *408*, 124436. DOI: 10.1016/j.jhazmat.2020.124436.

Wang, W.-L.; Wu, Q.-Y.; Li, Z.-M.; Lu, Y.; Du, Y.; Wang, T.; Huang, N.; Hu, H.-Y. Light-emitting diodes as an emerging UV source for UV/chlorine oxidation: Carbamazepine degradation and toxicity changes. *Chemical Engineering Journal* **2017,** *310*, 148–156. DOI: 10.1016/j.cej.2016.10.097.

Wang, Y.; Yu, G. Challenges and pitfalls in the investigation of the catalytic ozonation mechanism: A critical review. *Journal of Hazardous Materials* **2022,** *436*, 129157. DOI: 10.1016/j.jhazmat.2022.129157.

Wang, Z.; Sun, P.; Li, Y.; Meng, T.; Li, Z.; Zhang, X.; Zhang, R.; Jia, H.; Yao, H. Reactive Nitrogen Species Mediated Degradation of Estrogenic Disrupting Chemicals by Biochar/Monochloramine in Buffered Water and Synthetic Hydrolyzed Urine. *Environmental science & technology* **2019b,** *53* (21), 12688–12696. DOI: 10.1021/acs.est.9b04704.

Warren, Z.; Guaraldo, T. T.; Wenk, J.; Mattia, D. Synthesis of photocatalytic pore size-tuned ZnO molecular foams. *J. Mater. Chem. A* **2022,** *10* (21), 11542–11552. DOI: 10.1039/D2TA02038F.

Weeks, J. L.; Meaburn, G. M. A. C.; Gordon, S. Absorption Coefficients of Liquid Water and Aqueous Solutions in the Far Ultraviolet. *Radiation Research* **1963,** *19* (3), 559. DOI: 10.2307/3571475.

Weingärtner, H.; Franck, E. U. Supercritical water as a solvent. *Angewandte Chemie (International ed. in English)* **2005,** *44* (18), 2672–2692. DOI: 10.1002/anie.200462468.

Wenk, J.; Graf, C.; Aeschbacher, M.; Sander, M.; Canonica, S. Effect of Solution pH on the Dual Role of Dissolved Organic Matter in Sensitized Pollutant Photooxidation. *Environmental science & technology* **2021,** *55* (22), 15110–15122. DOI: 10.1021/acs.est.1c03301.

Wenk, J.; Gunten, U. von; Canonica, S. Effect of dissolved organic matter on the transformation of contaminants induced by excited triplet states and the hydroxyl radical. *Environmental science & technology* **2011,** *45* (4), 1334–1340. DOI: 10.1021/es102212t.

Werschkun, B.; Banerji, S.; Basurko, O. C.; David, M.; Fuhr, F.; Gollasch, S.; Grummt, T.; Haarich, M.; Jha, A. N.; Kacan, S.; Kehrer, A.; Linders, J.; Mesbahi, E.; Pughiuc, D.; Richardson, S. D.; Schwarz-Schulz, B.; Shah, A.; Theobald, N.; Gunten, U. von; Wieck, S.; Höfer, T. Emerging risks from ballast water treatment: the run-up to the International Ballast Water Management Convention. *Chemosphere* **2014,** *112*, 256–266. DOI: 10.1016/j.chemosphere.2014.03.135.

Willach, S.; Lutze, H. V.; Eckey, K.; Löppenberg, K.; Lüling, M.; Terhalle, J.; Wolbert, J.-B.; Jochmann, M. A.; Karst, U.; Schmidt, T. C. Degradation of sulfamethoxazole using ozone and chlorine dioxide - Compound-specific stable isotope analysis, transformation product analysis and mechanistic aspects. *Water Res.* **2017,** *122*, 280–289. DOI: 10.1016/j.watres.2017.06.001.

Wols, B. A.; Hofman-Caris, C.; Harmsen, D. J.; Beerendonk, E. F.; van Dijk, J. C.; Chan, P.-S.; Blatchley, E. R. Comparison of CFD, Biodosimetry and Lagrangian Actinometry to Assess UV Reactor Performance. *Ozone: Science & Engineering* **2012,** *34* (2), 81–91. DOI: 10.1080/01919512.2012.651398.

Wünsch, R.; Mayer, C.; Plattner, J.; Eugster, F.; Wülser, R.; Gebhardt, J.; Hübner, U.; Canonica, S.; Wintgens, T.; Gunten, U. von. Micropollutants as internal probe compounds to assess UV fluence and hydroxyl radical exposure in UV/H2O2 treatment. *Water Res.* **2021,** *195*, 116940. DOI: 10.1016/j.watres.2021.116940.

Xie, Z.-H.; Zhou, H.-Y.; He, C.-S.; Pan, Z.-C.; Yao, G.; Lai, B. Synthesis, application and catalytic performance of layered double hydroxide based catalysts in advanced oxidation processes for wastewater decontamination: A review. *Chemical Engineering Journal* **2021,** *414*, 128713. DOI: 10.1016/j.cej.2021.128713.

Xu, J.; Zheng, X.; Feng, Z.; Lu, Z.; Zhang, Z.; Huang, W.; Li, Y.; Vuckovic, D.; Li, Y.; Dai, S.; Chen, G.; Wang, K.; Wang, H.; Chen, J. K.; Mitch, W.; Cui, Y. Organic wastewater treatment by a single-atom catalyst and electrolytically produced H2O2. *Nat Sustain* **2021,** *4*, 233–241. DOI: 10.1038/s41893-020-00635-w.

Yan, L.; Bing, J.; Wu, H. The behavior of ozone on different iron oxides surface sites in water. *Scientific reports* **2019,** *9* (1), 14752. DOI: 10.1038/s41598-019-50910-w.

Yang, Q.; Niu, X.; Zhu, Y.; Cui, Y.; Chao, Y.; Liang, P.; Zhang, C.; Wang, S. Modulating anion defect in La0.6Sr0.4Co0.8Fe0.2O3-δ for enhanced catalytic performance on peroxymonosulfate activation: Importance of hydrated electrons and metal-oxygen covalency. *Journal of Hazardous Materials* **2022,** *432*, 128686. DOI: 10.1016/j.jhazmat.2022.128686.

Yang, Y. Recent advances in the electrochemical oxidation water treatment: Spotlight on byproduct control. *Front. Environ. Sci. Eng.* **2020,** *14* (5). DOI: 10.1007/s11783-020-1264-7.

Yang, Y.; Li, X.; Zhou, C.; Xiong, W.; Zeng, G.; Huang, D.; Zhang, C.; Wang, W.; Song, B.; Tang, X.; Li, X.; Guo, H. Recent advances in application of graphitic carbon nitride-based catalysts for degrading organic contaminants in water through advanced oxidation processes beyond photocatalysis: A critical review. *Water Res.* **2020,** *184*, 116200. DOI: 10.1016/j.watres.2020.116200.

Yao, W.; Ur Rehman, S. W.; Wang, H.; Yang, H.; Yu, G.; Wang, Y. Pilot-scale evaluation of micropollutant abatements by conventional ozonation, UV/O3, and an electro-peroxone process. *Water Res.* **2018,** *138*, 106–117. DOI: 10.1016/j.watres.2018.03.044.

Ying, Z.; Yecheskel, Y.; Huo, M.; Hübner, U.; Zucker, I. Ozone Consumption by Soils: A Critical Factor in In Situ Ozonation Processes. *ACS EST Water* **2021,** *1* (11), 2403–2411. DOI: 10.1021/acsestwater.1c00236.

Zeghioud, H.; Nguyen-Tri, P.; Khezami, L.; Amrane, A.; Assadi, A. A. Review on discharge Plasma for water treatment: mechanism, reactor geometries, active species and combined processes. *Journal of Water Process Engineering* **2020,** *38*, 101664. DOI: 10.1016/j.jwpe.2020.101664.

Zeng, T.; Arnold, W. A. Pesticide photolysis in prairie potholes: probing photosensitized processes. *Environmental science & technology* **2013,** *47* (13), 6735–6745. DOI: 10.1021/es3030808.

Zhang, K.; Parker, K. M. Halogen Radical Oxidants in Natural and Engineered Aquatic Systems. *Environmental science & technology* **2018,** *52* (17), 9579–9594. DOI: 10.1021/acs.est.8b02219.

Zhang, Y.; Wang, H.; Li, Y.; Wang, B.; Huang, J.; Deng, S.; Yu, G.; Wang, Y. Removal of micropollutants by an electrochemically driven UV/chlorine process for decentralized water treatment. *Water Res.* **2020,** *183*, 116115. DOI: 10.1016/j.watres.2020.116115.

Zhang, Y.; Zhou, M. A critical review of the application of chelating agents to enable Fenton and Fenton-like reactions at high pH values. *Journal of Hazardous Materials* **2019,** *362*, 436–450. DOI: 10.1016/j.jhazmat.2018.09.035.

Zhang, Y.-J.; Huang, G.-X.; Winter, L. R.; Chen, J.-J.; Tian, L.; Mei, S.-C.; Zhang, Z.; Chen, F.; Guo, Z.-Y.; Ji, R.; You, Y.-Z.; Li, W.-W.; Liu, X.-W.; Yu, H.-Q.; Elimelech, M. Simultaneous nanocatalytic surface activation of pollutants and oxidants for highly efficient water decontamination. *Nature communications* **2022,** *13* (1), 3005. DOI: 10.1038/s41467-022-30560-9.

Zhao, Y.; Yuan, X.; Li, X.; Jiang, L.; Wang, H. Burgeoning prospects of biochar and its composite in persulfate-advanced oxidation process. *Journal of Hazardous Materials* **2021,** *409*, 124893. DOI: 10.1016/j.jhazmat.2020.124893.

Zhou, L.; Sleiman, M.; Ferronato, C.; Chovelon, J.-M.; Richard, C. Reactivity of sulfate radicals with natural organic matters. *Environ Chem Lett* **2017,** *15* (4), 733–737. DOI: 10.1007/s10311-017-0646-y.

Zhou, Y.; Chen, C.; Guo, K.; Wu, Z.; Wang, L.; Hua, Z.; Fang, J. Kinetics and pathways of the degradation of PPCPs by carbonate radicals in advanced oxidation processes. *Water Res.* **2020,** *185*, 116231. DOI: 10.1016/j.watres.2020.116231.

Zhou, Y.; Jiang, J.; Gao, Y.; Ma, J.; Pang, S.-Y.; Li, J.; Lu, X.-T.; Yuan, L.-P. Activation of Peroxymonosulfate by Benzoquinone: A Novel Nonradical Oxidation Process. *Environmental science & technology* **2015,** *49* (21), 12941–12950. DOI: 10.1021/acs.est.5b03595.

Zietzschmann, F.; Stapf, M.; Sperlich, A.; Ruhl, A. S.; Miehe, U.; Gnirß, R.; Jekel, M. *TestTools – Entwicklung und Validierung von schnellen Testmethoden zum Spurenstoffverhalten in technischen und natürlichen Barrieren des urbanen Wasserkreislaufs;* Universitätsverlag der TU Berlin, 2018.

Zoumpouli, G. A.; Scheurer, M.; Brauch, H.-J.; Kasprzyk-Hordern, B.; Wenk, J.; Happel, O. COMBI, continuous ozonation merged with biofiltration to study oxidative and microbial transformation of trace organic contaminants. *Environ. Sci.: Water Res. Technol.* **2019,** *5* (3), 552–563. DOI: 10.1039/C8EW00855H.

Zoumpouli, G. A.; Zhang, Z.; Wenk, J.; Prasse, C. Aqueous ozonation of furans: Kinetics and transformation mechanisms leading to the formation of α,β-unsaturated dicarbonyl compounds. *Water Res.* **2021,** *203*, 117487. DOI: 10.1016/j.watres.2021.117487.