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Review

Scalability of advanced oxidation processes (AOPs) in industrial applications: A review

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ABSTRACT

Disinfection and decontamination of water by application of oxidisers is an essential treatment step across numerous industrial sectors including potable supply and industry waste management, however, could be greatly enhanced if operated as advanced oxidation processes (AOPs). AOPs destroy contaminants including pathogens by uniquely harnessing radical chemistry. Despite AOPs offer great practical opportunities, no reviews to date have highlighted the critical AOP virtues that facilitate AOPs' scale up under growing industrial demand. Hence, this review analyses the critical AOP parameters such as oxidant conversion efficiency, batch mode vs continuous-flow systems, location of radical production, radical delivery by advanced micro-/mesoporous structures and AOP process costs to assist the translation of progressing developments of AOPs into their large-scale applications. Additionally, the state of the art is analysed for various AOP inducing radical/oxidiser measurement techniques and their half-lives with a view to identify radicals/oxidisers that are suitable for *in-situ* production. It is concluded that radicals with short half-lives such as hydroxyl (10^{-4} μ sec) and sulfate (30–40 μ sec) need to be produced *in-situ* via continuous-flow reactors for their effective transport and dosing. Meanwhile, radicals/oxidisers with longer half-lives such as ozone (7–10 min), hydrogen peroxide (stable for several hours), and hypochlorous acid (10 min –17 h) need to be applied through batch reactor systems due to their relatively longer stability during transportation and dosing. Complex and costly synthesis as well as cytotoxicity of many micro-/mesoporous structures limit their use in scaling up AOPs, particularly to immobilising and delivering the short-lived hydroxyl and sulfate radicals to their point of applications. Overall, radical delivery using safe and advanced biocompatible micro-/mesoporous structures, radical conversion efficiency using advanced reactor design and portability of AOPs are priority areas of development for scaling up to industry.

1. Introduction

Advanced oxidation processes (AOPs) are techniques of disinfecting pathogens as well as breaking down harmful organic compounds predominantly in liquid media using the oxidising potential of radicals generated via chemical or physical pathways. AOPs include: ultraviolet radiation and ozone (UV + O₃) or UV and hydrogen peroxide (UV + H₂O₂) or (O₃ + H₂O₂), Fenton, photo-Fenton, electro-Fenton, Fluidized-Bed Fenton, nonthermal plasmas, sonolysis, photocatalysis, radiolysis, and supercritical water oxidation processes. Many AOPs are initiated

through radiolysis, sonolysis, or photolysis of water molecules without any chemical precursors. Wastewater, livestock, aquaculture, swimming pools as well as medical and clinical industries are the main industry sectors where AOPs are currently utilised. For example, UV, UV + H₂O₂, Fenton and photo-Fenton to treat industrial wastewater (Giannakis et al., 2017); Fenton-neutralisation-ultrafiltration in tandem for mature landfill leachate treatment (Primo et al., 2008); low dose O₃ + H₂O₂ for disinfection and microplutnant abatement (Epelle et al., 2023); H₂O₂ in commercial aquaculture (Wynne et al., 2020); photo-Fenton, electro-Fenton and UV + persulfate in winery and olive oil mill wastewater

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treatment as well as vacuum UV + H₂O₂ for slaughterhouse effluent treatment (Xin and Rehmann, 2020) can be noted.

There have been several reviews, perspectives and guest commentaries published on the various AOP technologies with in-depth discussions on fundamentals of AOPs and contaminant reaction pathways (Deng and Zhao, 2015; Comminellis et al., 2008; O'Shea and Dionysiou, 2012). Despite AOP fundamentals are well understood, industrial applications of AOP are yet to adopt scalable approaches that allow more efficient, portable, cost-effective, and environment-friendly AOP operations. Continuous growth in industrial business operations need technologies to adapt with evolving industrial demand. For example, Mahbub and Sharma (2019) reported the projected monthly freshwater (FW) demand beyond 2020 in a medium sized aquaculture industry of Tasmania for FW-based bathing treatment of Amoebic Gill Disease (AGD) will grow up to 120 ML per month. In another example scenario, Saravanane et al. (2014) estimated that around 120 GL of sewage will be generated in India during the projected year of 2051 with additional wastewater generation of around 50 GL. These challenges might be better addressed with AOP systems, however the principal challenges in adapting AOPs to cope with the widely varying demand of the industry are scalability of the AOPs (i.e., up and/or down-scaling techniques of predominantly hydroxyl (·OH) radical production), cost of reagent and energy usage, as well as difficulties in rapid and *in-situ* measurement of radical production efficiency via AOPs. Whilst both conventional batch and continuous-flow reactors are employed worldwide for industrial AOP operations to date, portable and low-cost continuous-flow reactors are slowly emerging in Europe and North America with a view to overcome difficulties in adapting AOPs in industrial scale (Hofman-Caris and Beerendonk, 2011).

Highly reactive radical species such as ·OH radicals are primary products that induces oxidation in almost all AOPs irrespective of their scale of applications (Kanakaraju et al., 2018; Tabrizi and Mehrvar, 2004), although other radicals and oxidisers such as persulfates (Ike et al., 2018), hydrogen peroxide (Wynne et al., 2020), chlorine and bromine are also employed to induce AOPs. While ·OH radicals have been widely discussed in all reviews on AOPs to date, other radicals and oxidisers did not receive similar attention in terms of their reactive/formative pathways during oxidation as well as their scalable production and measurement. Recently, Zahmatkesh et al. (2022) has illustrated effects of chlorination, ozonation and ·OH radical-based conventional AOPs on SARS-CoV-2 virus deactivation as well as on mineralisation of common wastewater contaminants. Research studies of effective micro-/mesoporous structures, e.g., yolk-shell Fe₃O₄-Cds nanoparticles (Shi et al., 2016), ultrasmall metal oxide frameworks (MOFs) (Shi et al., 2022) as well as yolk-shell Fe₃O₄-TiO₂ (Du et al., 2017) were investigated for their implementation in AOPs, although their cost effectiveness, rapid synthesis and biocompatibility are still a great challenge. However, the prospect of employing scalable AOPs in large industrial scale appears very promising as indicated in the research progresses achieved to date towards state-of-the-art batch and portable continuous-flow reactors, energy-efficient, low-cost and safe radiation sources (Mahbub and Nesterenko, 2016), accurate and field deployable radical measurement technologies as well as advances in micro- and mesoporous structures such as MOFs, zeolites, carbons, and amorphous glasses facilitating efficient delivery of radicals (Wright, 2007). Therefore, this review on these practical developments is timely, which aims to briefly discuss AOP basis and current trends, followed by discussions of AOP inducing reactive oxygen species, their measurement and parameters controlling the scalability of AOPs, radical production capacity/efficiency of various AOPs and prospect of AOPs in increased industrial demand, thereby facilitating scalability of AOPs for large industrial applications.

The scalability issues affecting various AOP operations under varied demand have been least discussed in the reviews published on AOPs to date. Comminellis et al. (2008) have provided a few examples of scaled-up AOP plants, but did not illustrate the parameters crucial for

achieving the scale-up. In this context, a thorough review of scalable AOPs will illustrate the continuously evolving innovations on various AOP parameters that are capable to cater for industrial needs during varied demand. Hence, we covered relevant literatures mainly from the last two decades (2000–2023) in this review study. Whilst this is not an exhaustive list of literatures on the topic, we also included few literatures from previous decades where relevant recent references are not available.

2. AOP basis and current trends

The definition of AOP was first proposed by (Glaze et al., 1987) as a process of generating ·OH radicals in sufficient quantity in aqueous phase for water treatment purposes. However, the scope of the definition of AOP has since been widened as gas-phase AOPs are also in use for purification and improvement of indoor air quality (Adnew et al., 2016). The production of ·OH radicals in aqueous or gas phase is initiated in the presence of chemical precursors such as O₃ or H₂O₂ with or without catalysts or promoters. Some physical processes such as radiolysis, sonolysis, photolysis or supercritical water oxidation can directly initiate the production of ·OH radicals in aqueous phase without the presence of any catalysts or promoters. As shown in Fig. 1, the produced ·OH radicals degrade organic molecules and pathogenic substances via hydrogen abstraction.

The degradation of contaminant illustrated in Fig. 1 only applies during homogeneous photolysis of H₂O₂ into ·OH radicals. In case of olefins and aromatic compounds, addition of the radical to the molecule is another pathway of degradation (Munter, 2001). Fig. 2 illustrates the sulfate radical addition to olefinic volatile organic compounds in secondary organic aerosol (SOA) producing a number of intermediate and tertiary degradation products along with molecular oxygen and water (Ren et al., 2021). The addition of ·OH radicals was identified as an efficient pathway of degradation of ciprofloxacin in wastewater (An et al., 2010).

We emphasize that the AOP induced degradation is also possible via other pathways, for example that includes ozone, peroxone (ozone + H₂O₂), Fenton, photo-Fenton and heterogeneous photocatalysis. The radical and non-radical pathways of different AOPs play an important role in their industrial scalability. In this regard, Wan et al. (2023) demonstrated the prospect of tuneable Cu-subnanometer particles (Cu-SNPs) to achieve the favourable non-radical degradation pathway of tetracycline via activation of peroxymonosulfate immobilised on Cu-SNP surface. Although the use of advanced functional materials in AOP such as, Cu-SNPs (Wan et al., 2023) or various eco-friendly absorbents (Sun et al., 2022) are still in laboratory stages to date, we envisage that further research on electron transfer behaviour, selectivity of advanced materials towards different chemicals as well as studies on their stability will enable the use of these materials in large scale AOPs.

Fig. 3 illustrates various AOP technologies that have been developed and implemented in the industries to date. The application of light sources is a differentiating factor in grouping AOPs into photolytic and non-photolytic categories (Munter, 2001; Quiroz et al., 2011). AOP technologies are implemented mainly through two modes of operation, namely, batch mode and continuous-flow mode. In conventional batch reactors, the AOP is undertaken in a single vessel for chemical oxidation of the target contaminants or pathogens. The batch reactors facilitating AOPs are then connected to a series of interconnected vessels, known as sequencing batch reactors or SBRs, that enhance the subsequent biological and/or physical treatment of liquid effluent (Christensen et al., 2009; Bernardes and Klapwijk, 1996; Singh and Srivastava, 2011).

To the contrary, the available technologies for scalable continuous-flow mode reactors are continuously evolving and research and development in continuous-flow reactors are ongoing in Europe and USA (Hofman-Caris and Beerendonk, 2011). Notable continuous-flow technologies employed for AOPs for treatment of wastewater are fixed-bed reactors, fluidized-bed reactors as well as membrane separation

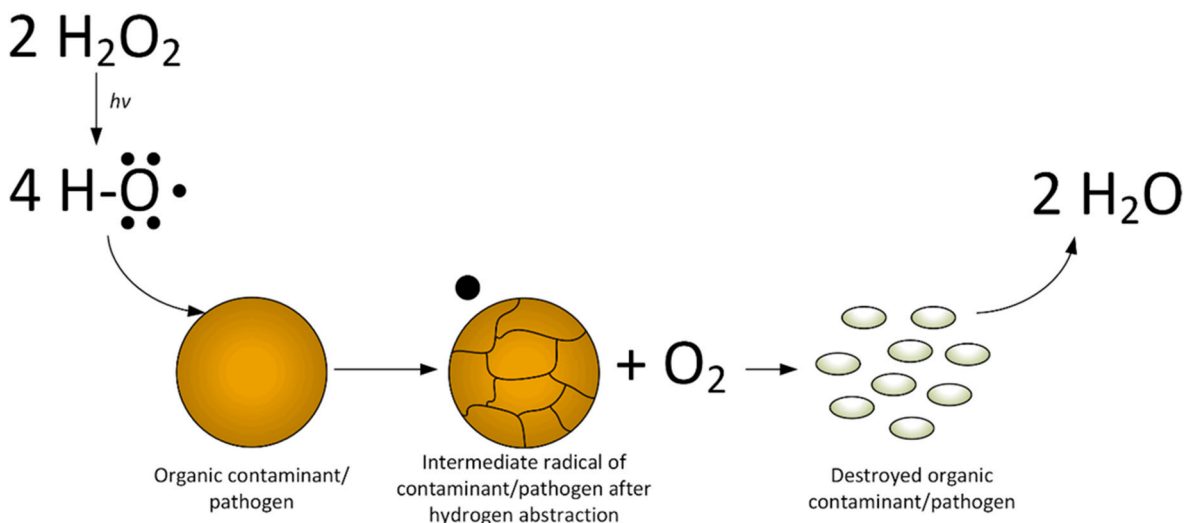


Fig. 1. Simplified example schematic of the functional role of hydroxyl radical formed by photolysis of hydrogen peroxide, to destroy a target organic contaminant or pathogen.

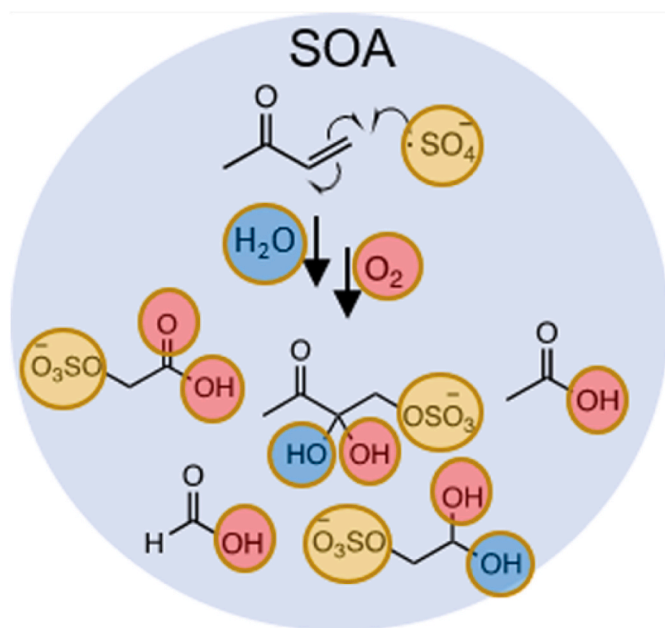


Fig. 2. Sulfate radical addition scheme to destroy olefinic volatile organic compounds adapted from Ren et al. (2021) with permission.

reactors. In the context of membrane separation, a relatively recent technology incorporating advanced photocatalysts with membranes in tandem that induces AOPs to treat persistent organic pollutants and foulants in natural and wastewater has been investigated in laboratory scales (Nyamutswa et al., 2021; Subramaniam et al., 2022). Fig. 4 demonstrates schematic diagram of continuous flow reactor in pilot scale.

Fig. 4 is an example of *in-situ* production of $\cdot\text{OH}$ radicals from H_2O_2 using UV reactor consisting of advanced light sources. In fact, both the photolytic and non-photolytic batch/continuous systems illustrated earlier in Fig. 3 can be implemented for *in-situ* production of various radicals from their parent materials. Later in section 3 we provide a list of these reactive oxygen species (ROS) and their formation pathways in Table 1. Recently, microwave (MW) assisted catalytic digestion of contaminant antibiotics found in wastewater such as, oxytetracycline (OTC) using sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and sodium hypochlorite (NaClO) in presence of laboratory synthesised Cu-biochar catalysts

showed around 100% and 73% total organic carbon (TOC) removal from the OTC structure, respectively (Zhang et al., 2023a). In this context, we emphasize the fact that although MW assisted catalytic digestion demonstrates prospect in AOP efficiencies, further investigation needs to be undertaken on isolation of thermal degradation from the catalytic degradation at high temperature of MW assisted digestion as well as industrial production of divalent transition metal cation loaded biochars for energy efficient MW-based contaminant degradation during AOPs.

3. AOP inducing reactive oxygen species (ROS)

The core function of an AOP is its ability to produce ROS. In Table 1, we observe that the reactive oxygen and sulfate species (all of them are termed as ROS that include free radicals and non-radicals herewith) are the principle reactive species utilised in AOP. From the reported half-lives of these ROS, it is interesting to note that only hydrogen peroxide, ozone, hypochlorous and hypobromous acids can be employed in portable manner from their point of production to the point of application. All other ROS must be produced *in-situ* at the location of their application due to their extremely short half-lives. While short half-lives are not problematic in AOPs (sometimes can be beneficial), this fact needs to be taken into consideration during engineering design of continuous-flow reactors for scalable production of radical species.

Table 1 also illustrates the equally important chemical/physical precursors of ROS as well as their predominant reactive/formative pathways. This information is important to ascertain the production efficiencies of ROS from their parent materials and the mineralisation efficiencies of AOP operations. ROS' accurate measurement techniques result the determination of such production or mineralisation efficiencies during AOP operations. Additionally, the capability of facile and rapid measurement of ROS produced/employed *in-situ* will ensure scalability of AOP operations when the up/downscaling of oxidation of target species become necessary. However, there is lack of reported capability of *in-situ*, rapid and inexpensive measurement of ROS used in AOP operations, which particularly hinders the scalable application of useful radicals for the purpose. We discuss the measurement techniques of the ROS in the following section with a view to identify the technological capacity gaps and measures taken to date to overcome these gaps.

3.1. Hydroxyl ($\cdot\text{OH}$) radical

There have been a number of electrochemical (EC), photometric

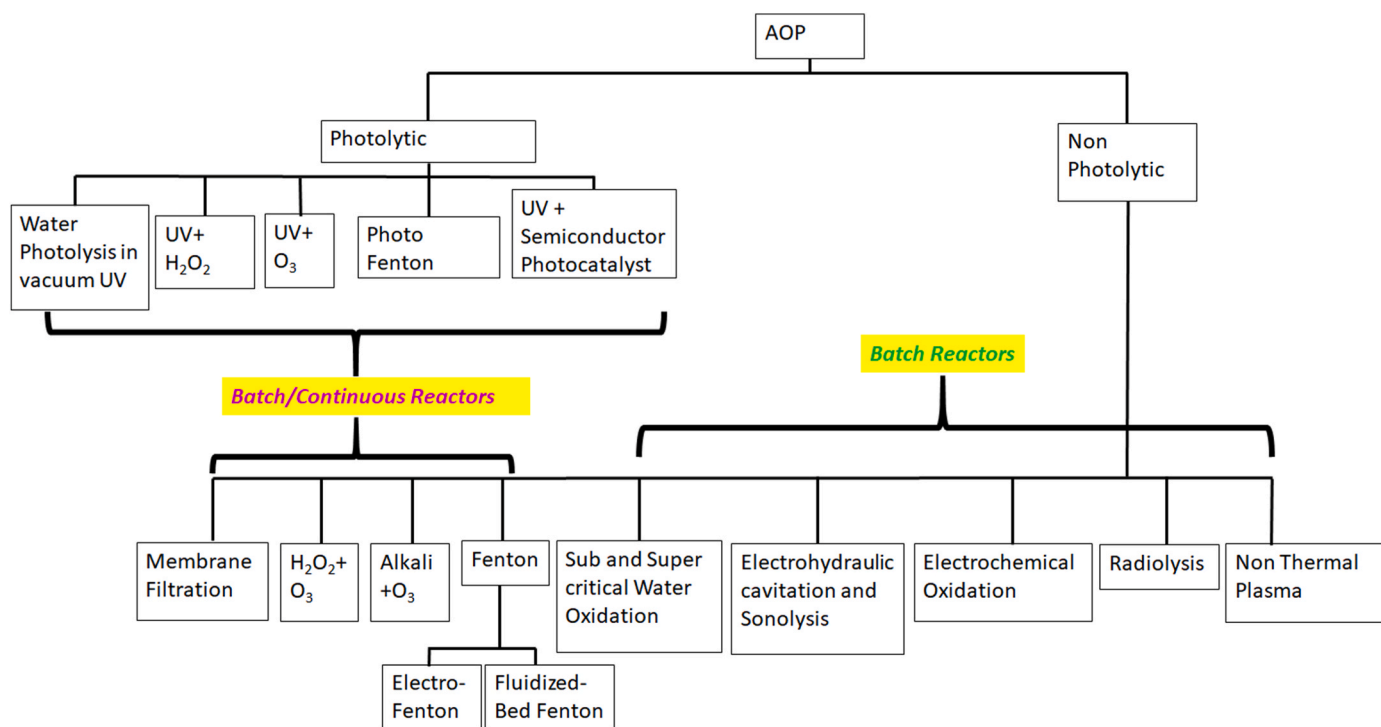


Fig. 3. Schematic showing the various AOP technologies that have been developed and implemented.

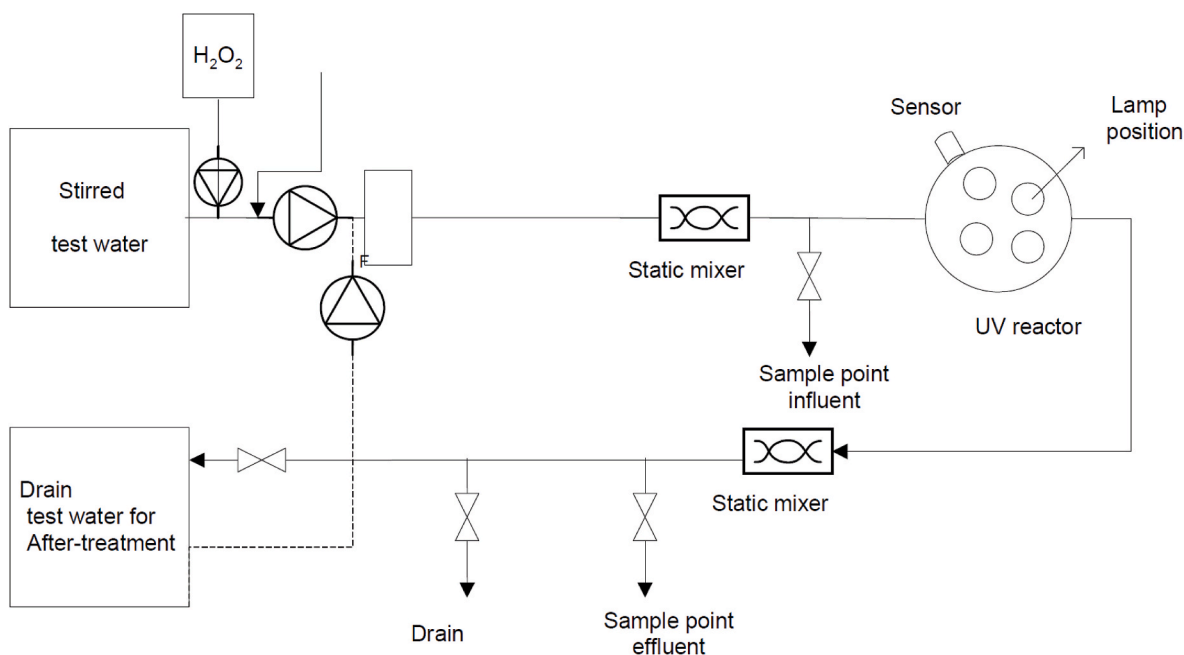


Fig. 4. Continuous-flow reactor scheme adapted from Hofman-Caris and Beerendonk (2011) with permission.

(PM), HPLC-UV as well as spectroscopic (SP) detection systems developed for detection of ·OH radical. The EC detection schemes employed 4-hydroxybenzoic acid (4-HBA) (Hu et al., 2008), and salicylic acid (SA) (Ai et al., 2005) as the ·OH radical trap. Hantzsch reaction of formaldehyde derived from ·OH radical and dimethyl sulfoxide, and subsequent addition of ammonia and 1,3-cyclohexanedione (CHD) at pH of 4.5 was employed by Tai et al. (2002) to determine ·OH radical via characteristic fluorescence with its excitation and emission wavelength at 400.4 and 452.3 nm, respectively. Indirect detection of par-chlorobenzoic acid (pCBA) via HPLC-UV during ozonation was proposed

as a mean for measuring ·OH radicals by Elovitz and Von Gunten (1999). The principle of SP detection schemes via nuclear magnetic resonance (NMR) involves trapping the ·OH radical to form stable adducts before their subsequent detection and quantification. For example, Argypopoulos et al. (2006) employed NMR spin trapping agent 5-diisopropoxy-phosphoryl-5-methyl-1-pyrroline-N-oxide (DIPPMPO) for ·OH radical quantitation via ³¹P NMR method. To the contrary, one of the SP detection schemes via resonance scattering (RS) method involves sodium iodide (NaI) and H₂O₂ in HCl-NaAc buffer (pH = 4.95) to allow resulting I₃⁻ reacting with rhodamine S (RhS) to form particles that

Table 1
List of reactive oxygen species utilised in AOPs.

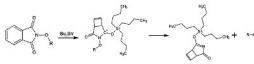
Reactive Oxygen Species	Chemical/physical precursors or catalysts	Main formative/reactive pathways	Half-lives, sec	Remark on application level	References
Hydroxyl radical	Hydrogen peroxide	$H_2O_2 \rightarrow HOO^\cdot + H^+$ $HOO^\cdot + H_2O_2 \rightarrow OH + H_2O_2 + O_2$	10^{-10}	Extremely reactive radical; not suitable for portability, used in disinfection of pathogens	Phaniendra et al., (2015); Mahbub et al., (2022); Liao and Gurol (1995)
Superoxide anion radical	Negative charge at conduction band of TiO ₂ semiconductor under UV radiation	$e_{cb}^- + O_2 \xrightarrow{h\nu} O_2^\cdot-$	10^{-6}	Extremely reactive radical; not suitable for portability, used in disinfection of pathogens	Phaniendra et al., (2015); Deng and Zhao (2015)
Alkoxy radical	Carbohydrate hypiodites and nitrates, phthalimides, nitrates, peroxides, hydroperoxides	$ROI \xrightarrow{h\nu/\Delta} RO + I$ $CH_3COONO_2 + ROH \rightarrow CH_3COOH + RONO_2$ $RONO_2 \xrightarrow{h\nu} RO + \cdot NO_2$	10^{-6}	Extremely reactive radical; not suitable for portability, used in biomedical applications	Phaniendra et al., (2015); Gray and Williams (1959); Lee et al. (2021)
Peroxy radical	Organic hydroperoxide	 $ROOH \rightarrow RO + \cdot OH$ $RO + ROOH \rightarrow ROH + ROO$ $2ROO \rightarrow ROOR + O_2$	17	Less reactive radical; not suitable for scalability, used in biomedical applications	Chamulitrat et al., (1989); Phaniendra et al., (2015)
Hydrogen peroxide	UV radiation and/or divalent transition metal cations	$H_2O_2 \xrightarrow{h\nu} 2OH$ $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$ $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO + H^+$ $2HOO \rightarrow H_2O_2 + O_2$	stable	Reactive non-radical suitable for portability, used in aquaculture, mining, dye and leather industry	Phaniendra et al., (2015); Deng and Zhao (2015)
Singlet oxygen	Hydrogen peroxide or dye sensitized photooxidation	$H_2O_2 + NaOCl \rightarrow NaCl + H_2O + ^1O_2$	10^{-6}	Extremely reactive non-radical; not suitable for portability	Phaniendra et al., (2015); Greer (2006)
Ozone	High voltage dielectric corona discharge, UV radiation	$Sens \xrightarrow{hv} ^1Sens \xrightarrow{\text{intersystem crossing}} ^3Sens \xrightarrow{^3O_2} Sens + ^1O_2$ $Air/O_2 \xrightarrow{\text{high voltage corona discharge}} O_2/O_3$ $3O_2 \xrightarrow{h\nu} 2O_3$	420–600	Reactive non-radical suitable for portability, used in wastewater treatment and pathogen disinfection	Weschler (2000); Rekhate and Srivastava (2020); Eliasson and Kogelschatz (1991)
Hypochlorous acid	Chlorine (Cl ₂) in aqueous solution	$Cl_2 + H_2O \rightleftharpoons HClO + H^+ + Cl^-$	$6 \times 10^{-2} - 6 \times 10^5$	Reactive non-radical suitable for portability, used in pathogen control in swimming pool and drinking water	Ishihara et al., (2017); Fair et al., (1948)
Hypobromous acid	Bromine (Br ₂) in aqueous solution, bromide (Br ⁻) ions, H ₂ O ₂ , HClO	$Br_2 + H_2O \rightleftharpoons HBrO + HBr$ $Br^- + H_2O_2 \rightleftharpoons HBrO + OH^-$ $Br^- + HClO \rightleftharpoons HBrO + Cl^-$	Few seconds to several hours	Reactive non-radical suitable for portability, used in pathogen control in swimming pool and drinking water	Von Gunten and Oliveras (1997); Liu et al., (2021)
persulfates	Peroxymonosulfates, peroxydisulfates	$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^\cdot-$ $H_2SO_5 \xrightarrow{h\nu} SO_4^\cdot + OH$ $S_2O_8^{2-} \xrightarrow{2e^-} SO_4^\cdot + SO_4^{2-}$ $H_2SO_5 \xrightarrow{2e^-} SO_4^\cdot + OH^-$	30×10^{-6} 40×10^{-6}	moderately reactive non-radical; not suitable for portability, used in wastewater treatment industry	Xia et al., (2020); Lee et al., (2020); Nawaz and Sengupta (2021); Ike et al., (2018)

exhibit strong RS spectra at $\lambda_{max} = 650$ nm (Liang et al., 2006).

Difficulties in portability and the non-linearity of the above-mentioned $\cdot OH$ radical detection schemes at very high concentrations (>0.5 mM) is a limiting factor in their deployment for *in-situ* measurement of $\cdot OH$ radical at large industrial scale. In this context, Mahbub et al. (2022) proposed a simple and portable approach for measuring up to 0.9 mM $\cdot OH$ radical *in-situ* using continuous-flow photoreactor and simple acid-base titration. As the half-lives of $\cdot OH$ radicals are extremely short (0.1 ns), the batch production and transport of $\cdot OH$ radicals from one place to another via tubes or containers is not an option for their large-scale industrial use. Therefore, further studies that include development of inexpensive, portable and scalable continuous-flow reactors facilitating *in-situ* industrial production and deployment of $\cdot OH$ radicals are extremely important.

3.2. Superoxide anion radical ($O_2^\cdot-$)

Hayyan et al. (2016) have classified four main detection mechanisms to detect $O_2^\cdot-$ radicals, namely, electrochemical (EC), absorbance-based UV/Vis spectroscopic, luminescence-based colorimetric and vibrational spectroscopic methods. These detection schemes mainly target $O_2^\cdot-$

radicals in chemical and biological systems with ultra-low detection limits. To date, there are no reports on investigations of the use of $O_2^\cdot-$ radicals in large scale industrial processes. This is mainly attributed to the extremely short half-lives of $O_2^\cdot-$ radicals and unlike $\cdot OH$ radicals, $O_2^\cdot-$ radicals are mainly generated as an intermediate during H_2O_2 decomposition. $O_2^\cdot-$ radicals can also act as precursors of hydroperoxy radicals (HOO^\cdot) via protonation of $O_2^\cdot-$ although further protonation leads towards H_2O_2 in aqueous media (Fernández-Castro et al., 2015). Electron spin resonance (ESR) spectroscopy were employed for measurement of HOO^\cdot in aqueous samples (Dimić et al., 2021). ESR is not a rapid and portable method and hence, it is not suitable during the large-scale use of radicals in AOP. In this context, we highlight the use of flow injection analysis-chemiluminescence (FIA-CL) based portable platform for laboratory scale trace measurement of HOO^\cdot by Zheng et al. (2003). Further investigations on FIA-CL based measurement of $O_2^\cdot-$ and HOO^\cdot in aqueous samples can be undertaken as this FIA-CL method is extremely suitable for field deployment.

3.3. Alkoxy radical (RO^\cdot)

Electron spin resonance (ESR) of several alcohols and spin trapping

method using 2-nitroso-2-methylpropane was proposed by Sargent and Gardy (1974) as an efficient detection mechanism of RO[•] radicals. The spin trapping of RO[•] radicals for ESR detection has application in medical industry as it was later employed by Tortolani et al. (1993) to detect alkoxy and carbon-centered free radicals in coronary sinus blood. However, there are no reports on investigations of the use of RO[•] radicals in large scale industrial processes to date. ESR detection of RO[•] radicals is not a rapid or portable method. Recently, RO[•] radical production from Ce(IV)-alkoxide complexes in CeCl₃/n-Bu₄NCl/ROH catalytic conditions under 400 nm photo absorption and the subsequent transient absorption (TA) spectroscopic characterisation of RO[•] radicals were reported by An et al. (2023). We emphasize that TA spectroscopy can be a suitable technique for *in-situ* measurement of RO[•] radicals in large-scale AOP operations.

3.4. Peroxyl radical (ROO[•])

Peroxyl radicals are mainly formed via lipid peroxidation inside living cells and several fluorescence probes have been developed for detection of ROO[•] radicals. For example, Gomes et al. (2005) reported parinaric acid (cis-PnA), 4,4-difluoro-5-(4-phenyl-1,3-butadienyl)-4-bora-3a,4a-diaza-s-indacene-3-undecanoic acid (C11-BODIPY5), dipyrromethole, diphenyl-1-pyrenylphosphine (DPP), β-phycoerythrin, and fluorescein/6-carboxyfluorescein with varying excitation and emission wavelengths. Peroxyl radicals can also form via iron catalysed decomposition of organic peroxides, namely *tert*-butyl hydroperoxide (t-BuOOH), methyl ethyl ketone peroxide (MEKP), and cumene hydroperoxide (Akaike et al., 1992). They demonstrated that ROO[•] radicals generated in heme iron-organic peroxide system remained high in concentrations for up to 30 min and displayed strong bactericidal action against gram-positive bacteria. Considering these findings, we emphasize that such heme iron-organic peroxide system can be further investigated for continuous production of ROO[•] radicals in industrial scale using continuous-flow reactors. As the above-mentioned fluorescence probes generally detect ROO[•] radicals in micro to nano-molar ranges, for detection of ROO[•] radicals in high millimolar concentrations, electron spin resonance (ESR) spin trapping with 5,6-dimethyl-1-pyrroline-N-oxide (DMPO) would be more suitable than fluorescence probes.

3.5. Singlet oxygen (¹O₂)

Singlet molecular oxygen (¹O₂) is an important intermediate in photooxidation of ground state triplet oxygen (³O₂). Greer (2006) elucidated two distinct routes of production of ¹O₂: 1. Dye-sensitized photooxidation of ground state oxygen, and 2. A chemical reaction between NaOCl and H₂O₂. Earlier, Thomas (2000) proposed a polymeric coating for large scale production of ¹O₂ under low intensity visible light targeting mineralisation of range of organic compounds in drinking water. An alternative method of ¹O₂ generation from storable calcium peroxide diperoxyhydrate (CaO₂·2H₂O₂) was proposed by Pierlot et al. (2002). Molecular phosphorescence at 1270 nm has been employed as a direct detection method of ¹O₂, whilst indirect methods using spectrophotometric, fluorescent or chemiluminescent probes were also reported by Wu et al. (2011). The quantum yield of formation of ¹O₂ from its ground state is reported extremely low (10⁻⁵ to 10⁻⁷), and hence the direct detection of ¹O₂ suffers from low sensitivity (Jiménez-Banzo et al., 2008). To the contrary, fluorescence probes have been employed commercially for selective and sensitive detection of ¹O₂. For example, 9-[2-(3-carboxy-9,10-diphenyl)anthryl]-6-hydroxy-3H-xanthen-3-one (DPAX) and 9-[2-(3-carboxy-9,10-dimethyl) anthryl]-6-hydroxy-3H-xanthen-3-one (DMAX) were employed by Tanaka et al. (2001) and Thermo Fisher has introduced Singlet Oxygen Sensor Green (SOSG) fluorescence probe which, according to the vendor, does not show any appreciable response to [•]OH or O₂^{•-}. Although not reported yet, we envisage that SOSG fluorescence probe can be investigated in measuring production efficiency of ¹O₂ during its generation in large scale.

3.6. Hydrogen peroxide (H₂O₂)

H₂O₂ is a versatile oxidiser/reducer used in the disinfection of pathogens as well as breaking down both organic and inorganic compounds achieved through their oxidation or reduction in aqueous solutions. Due to the reportedly long stability of H₂O₂ in aqueous solutions, significant initiatives have already been undertaken to facilitate its large-scale industrial production. For measuring the high concentrations (up to 30% H₂O₂), SOLVAY has reported a ceric sulfate-based titration using Ferriox indicator (phenanthroline monohydrate added to the ferrous sulfate solution). To the contrary, permanganate-based titration of H₂O₂ is a direct titration method for highly concentrated samples without the need for any indicator. Even though interference of chloride anions and stability of permanganate over time have been reported as some drawbacks in permanganate titration of H₂O₂ (Cox, 1985), Huckaba and Keyes (1948) reported periodic standardisation of permanganate by sodium oxalate resulted high accuracy in measuring up to 90% H₂O₂ concentrations.

Many reports have been published on trace detection of H₂O₂ in aqueous (e.g., freshwater) and biological samples (e.g., blood serum) via electrochemical (EC) detection on various novel metal organic and doped carbon frameworks (Sherino et al., 2018; Tujunen et al., 2015; Neal et al., 2017). Additionally, spectroscopic (SP) methods using azo dyes (Wang et al., 2019) and colorimetric (CL) methods using silver nanoparticles (Nitinaivinij et al., 2014) were developed for indirect determination of trace H₂O₂ in water. Simultaneously, horseradish peroxidase (HRP)-based enzymatic methods hyphenated with EC platform (HRP-EC) for trace detection of H₂O₂ in biological systems (Xin et al., 2013) are also proposed. Considering the reported range of detection by these SP (0.3–175 μM), CL (1.6–80 μM) and HRP-EC methods (0.02–2.5 mM), we emphasize that only the enzymatic degradation-based EC methods can be employed as a portable alternative of the titrimetric method during quality control steps of large-scale industrial production of highly concentrated H₂O₂. Investigations of improved nanostructures to immobilise HRP on various electrodes can be undertaken with a view to facilitate *in-situ* high molar detection ranges for commercially produced H₂O₂.

3.7. Ozone (O₃)

Dissolved O₃ in water has found its widespread implications as an effective disinfection agent in aquaculture. Buchan et al. (2005) have compared amongst iodometric, colorimetric and oxidation/reduction potential (ORP) measurements to detect dissolved O₃ in water, and found that N, N-diethyl-p-phenylenediamine (DPD)-based colorimetric method resulted most accurate detection of O₃ in non-laboratory conditions. Bader and Hoigné (1981) reported O₃ detection via spectrophotometric determination of decolorization of indigo trisulfonate with a range of 0.005–30 ppm in aqueous solutions. Dow et al. (2015) also employed indigo method for measuring O₃ around ceramic membranes in a pilot plant for real secondary wastewater treatment. Currently, commercial instruments for measuring O₃ in gas phase are available. Zahn et al. (2012) have characterised a sensitive and fast atmospheric O₃ measuring equipment that employed coumarin-47 dye-based dry chemiluminescence (CL). To the contrary, Jiménez et al. (1997) reported luminescent agent such as, ethylene and nitrogen monoxide-based dry CL for measuring gas phase O₃. However, requirement of high accuracy in gas flowrates as well as difficulty in *in-situ* gas handling during the gas phase CL detection of O₃ warrant investments in research and investigation of liquid phase O₃ measurement using dye-based colorimetric and/or luminescent agent-based CL techniques. Flow injection analysis (FIA) is a versatile technique for CL detection of numerous species including dissolved O₃ in aqueous phase (Fletcher et al., 2001). In this context, we envisage FIA-CL poses the prospect of developing fast, selective, inexpensive, and portable platform capable of accurate quantitation of high molar concentrations of

dissolved O₃.

3.8. Hypochlorous acid (HClO)

HClO is formed via hydrolysis of molecular chlorine in aqueous solution and at the typical pH of most types of water (i.e., from pH 3–9), HClO and hypochlorite ions (ClO⁻) predominantly remain in the solution (Kodera et al., 2005). Using Ag/AgCl electrode in NaClO₄ as background electrolyte via cyclic voltammetry (CV), Kodera et al. (2005) reported a portable method for detection of low free-chlorine as HClO concentrations between 0.2 and 5 mg/dm³. Earlier, Sournia-Saquet et al. (1999) employed CV and chronoamperometry and established a linear range of 1–50 ppm detection of HClO in 3 gm/L NaCl background electrolyte. Both of these EC methods of HClO measurement are applicable to monitor the chlorine levels in swimming pool and drinking water industry whose limit must be lower than 5 ppm. Although these electrochemical methods of measuring HClO facilitated precision in trace level, these methods would not be suitable for measuring high concentrations that might be required in large industrial scale. Lengthy and laborious potassium permanganate (KMnO₄) titration of excess H₂O₂ during its reaction with (ClO⁻) in acidic pH resulted indirect detection of HClO at higher concentration range (1.9 mM–19 mM) (Jonnalagadda and Gengan, 2010). They also replaced the titrimetric method with photometric method employing absorbance measurement of residual H₂O₂ with fixed amount of excess KMnO₄, resulting a four-stage calibration procedure with varying linear range for each step. With the advances in portable and miniature spectrophotometers, the photometric method poses the prospect of rapid, inexpensive and *in-situ* measurement of HClO with single-step linear concentration range. Investigations of lengthening optical path length in microfluidic scale (e.g., substrate integrated hollow waveguide reported by Ribessi et al. (2016)) targeting an increased linear absorbance range of photometric methods can be undertaken.

3.9. Hypobromous acid (HBrO)

Hydrolysis of molecular bromine (Br₂) is a major source of HBrO in aqueous solutions. HBrO may also form when ubiquitous bromide (Br⁻) ions present in water react with HClO during chlorination (Liu et al., 2021). Although HBrO is a highly reactive agent that oxidizes wide varieties of organic matters and pathogens, undesirable and carcinogenic disinfection-by-products (DBPs) such as bromate and brominated organic compounds form via nucleophilic addition or oxidation of HBrO in presence of H₂O₂ (Von Gunten and Oliveras, 1997). At alkaline pH of 8, high rate of reduction of HBrO into Br⁻ avoids production of bromate or brominated organic compounds. However, at low to moderate pH of 5, half-life of HBrO increases to several hours, thereby increasing the chance of formation of hazardous bromine compounds in aqueous solutions. Although Pinkernell and Von Gunten (1999) reported addition of ammonia as one of the possible control options for mitigating bromate formation during water disinfection, we envisage that utilisation of HBrO as a water disinfectant poses increased cost and high risks to human health and environment.

Pinkernell et al. (2000) have demonstrated trace level detection (1–20 μM) of total reactive bromine as sum of HBrO and three bromo-amine species (NH₂Br, NHBBr₂, NBr₃) using photometric method where bromine species reacted with ABTS (2,2-azino-bis(3-ethyl-benzothiazoline)-6-sulfonic acid-diammonium salt) to form a green coloured product that was measured at 405 or 728 nm. However, chlorine species also reacted with ABTS, thus interfered with reactive bromine detection in their studies. To date, there are no reports on selective detection of HBrO in aqueous solutions. In blood plasma, selective fluorescence probes for HBrO were developed by Huo et al. (2020) by stirring a coumarin derivative in hydroxyl amine and methanol for 8 h. We envisage that FIA-CL would be a much faster and *in-situ* method for selective measurement of HBrO during large-scale AOP operations

that employ aqueous Br₂ solutions. In this regard, we highlight the fact that Takahashi et al. (2008) proposed electrogeneration of HBrO in pH 5–7 in aqueous solution of Br₂ and the simultaneous detection of ammonium ion via CL reaction between HBrO and NH₄Cl in a micro FIA-CL system. Therefore, this same CL reaction scheme can also be implemented for *in-situ* measurement of HBrO for a known concentration of ammonium ion in the cases of HBrO based AOP systems.

3.10. Persulfates

Peroxymonosulfates (PMS) and peroxydisulfates (PDS) are the precursors of sulfate (SO₄⁻) radicals and both PMS and PDS have been utilised as viable alternatives of ·OH radical based advanced oxidation processes in aqueous solutions (Lee et al., 2020). Due to the relatively longer half-lives (30–40 μs) of SO₄⁻ radicals compared to that of ·OH radical (0.1 ns) (Xia et al., 2020), a number of analytical methods have been developed for selective and sensitive detection of SO₄⁻ radicals in aqueous samples. These include electron paramagnetic resonance (EPR) detection of SO₄⁻ radicals in UV-PMS and UV-PDS systems (Chen et al., 2022), benzoic acid (BA)-PMS-Co²⁺ system for fluorescence detection of resulting salicylic acid as indirect detection of SO₄⁻ radicals (Huang et al., 2018), UV or visible spectroscopic detection e.g., oxidative decolorization of methyl orange (MO) with SO₄⁻ radicals at 507 nm (Zhang et al., 2016) as well as UV absorption of cerium(III) sulfate at 325 nm (Wang et al., 2018) or that of barium chloranilate at 332 millimicrons or nm (Bertolacini and Barney, 1958). A radiometric determination of SO₄⁻ radicals was proposed by Bogen and Welford (1978), where SO₄⁻ radicals were quantitatively measured by gamma counting of excess ¹³³Ba that precipitates with SO₄⁻ radicals. The radioactive method is not suitable for *in-situ* and rapid measurement of SO₄⁻ radicals as it required overnight sample preparation as well as tedious yield correction calculation using ³⁵S tracers. The abovementioned visible spectroscopic method using MO at 507 nm (Zhang et al., 2016) is a fast and simple method with linear range 0.5–100 μM and we emphasize that both spectroscopic and fluorometric methods pose the prospect of rapid, *in-situ* and accurate detection of SO₄⁻ radicals in aqueous solutions.

In summary, fast and facile *in-situ* methods for reliable measurement of AOP inducing ROS is a prerequisite for developing scalable AOP technology. Capacity gaps exist in current initiatives for *in-situ* measurement of ·OH and SO₄⁻ radicals during implementation of such 'short-lived' radicals via continuous flow-based reactors. Amongst the other 'long-lived' oxidisers such as H₂O₂, O₃, HBrO and HClO, facile *in-situ* methods for reliable measurement of H₂O₂ currently exists for its scalable implementation via both batch and continuous flow-based reactor systems.

4. Parameters controlling the scalability of AOP

4.1. Conversion efficiency from parent materials

Irrespective of ease and/or accuracy of measuring high concentrations of radical products (e.g., ·OH, SO₄⁻, O₃ etc.) inducing AOP, the percentage conversion (either in terms of product formed or contaminant mineralised/initial concentration of parent materials, or conversion efficiency) plays a very crucial role in scalability of the corresponding AOPs. Comparisons amongst conversion efficiency of various AOPs will require standardised investigations of radicals/oxidisers produced via similar platforms, e.g., continuous-flow or batch reactors. Although the chemistry of the kinetics of conversion of radicals are very different from each other, using the similar conversion platform will facilitate practical comparison amongst suitable radicals for large-scale use in the industry. Currently, such standardised comparisons are not available. Table 2 illustrates % conversion of various radicals and oxidisers achieved through different conversion platforms.

From Table 2, we observe that except for the Zhang et al. (2013) study, the radical conversion efficiencies in either batch or continuous

modes were within comparable ranges between 5 and 20%. Zhang et al. (2013) employed magnetically separable CuFe_2O_4 spinel in water that apparently enhanced the % conversion of PMS into SO_4^- radicals. The synthesis of CuFe_2O_4 spinel was tedious process and the method was evaluated in laboratory scale of 200 mL only. Other metal-oxide framework (MOFs) such as, siderite, magnetite and Fe^{2+} were employed by Feng et al. (2018) in batch reactors for activating persulfates (PS). Ike et al. (2018) explored the role of silver, iron and copper based activation of PS, as well as metal-free activation using nanocarbon materials. They reported that PS can also be activated by UV or waste heat, with waste heat being proposed as the most sustainable option for pollutant degradation. Electrogeneration of SO_4^- radicals from PMS and/or PDS in batch electrolysis at current densities $\geq 10 \text{ mA cm}^{-2}$ and energy consumption ranging $41\text{--}190 \text{ kW h m}^{-3}$ has been discussed in detail by Divyapriya and Nidheesh (2021). In this context, we highlight that the prospect of continuous-flow reactors in increasing the % conversion of PMS/PDS into SO_4^- radicals hasn't been reported yet.

We envisage that there is scope for scalability studies of converting PMS and/or PDS to SO_4^- by incorporating reactor coils and mixing chambers via continuous-flow systems to enhance mixing of PMS and/or PDS with MOFs with a view to increase % conversion. Physical or chemical mechanisms of activating the PMS/PDS such as, UV, ultrasound, heating, MOFs or carbon-based materials resulting various degrees of PMS/PDS activation should be investigated via continuous-flow modes to enhance scalability of the systems. Various energy and electron transfer mechanisms for activating PMS/PDS systems are listed in Xia et al. (2020) and Lee et al. (2020) studies. The conversion principles of H_2O_2 into $\cdot\text{OH}$ radicals using multilayer continuous-flow UV reactor was thoroughly investigated by Mahbub et al. (2022), where they demonstrated that the initial concentration of H_2O_2 , pH of the solution as well as non-linear regime of Beer-Lambert law of photo-absorption of molecules played important roles in conversion of H_2O_2 into $\cdot\text{OH}$ radicals. Fig. 5 demonstrates the non-linear trend of photoconversion of H_2O_2 .

Here in Fig. 5, we observe that the homogeneous photoconversion of H_2O_2 into $\cdot\text{OH}$ radical is a non-linear function of initial concentration of H_2O_2 as the parent material in a continuous flow-based photoreactor. This information has economic implications in scalable production of $\cdot\text{OH}$ radical, as there seems to be an optimised reactor condition in Fig. 5 that produces maximum concentration of radicals from minimum concentration of parent materials. Such relationships may also exist in the conversion of other ROS shown in Table 2, e.g., O_3 from O_2 , SO_4^- from PMS/PDS and HOCl from NaOCl/NaCl via continuous flow reactors. Therefore, further research focussed on optimising the conversion efficiency of the reactors is required in order to achieve scalable AOP operations.

4.2. Location of radical production

The capability of transporting radicals from point of production to point of delivery as well as the capability of their efficient dosing will have an impact on the scalable application of different radicals for

industrial purposes. The half-lives of radicals will directly affect their transport and efficient dosing. For example, radicals with short half-lives such as $\cdot\text{OH}$ radicals ($10^{-4} \mu\text{sec}$), SO_4^- radicals ($30\text{--}40 \mu\text{sec}$) need to be produced *in-situ* for effective transport and dosing, whereas radicals/oxidisers with longer half-lives such as O_3 ($7\text{--}10 \text{ min}$), H_2O_2 (stable for several hours), HClO ($10 \text{ min} - 17 \text{ h}$) can be transported after production at locations different from dosing. Therefore, batch reactor system can be easily implemented for O_3 , H_2O_2 and HClO , whilst it is imperative to employ continuous-flow reactor for *in-situ* production and dosing of $\cdot\text{OH}$ and SO_4^- radicals. An example of industrial scale electrochemical production of HClO via batch reactors for agricultural and food industries is reported by Al-Haq et al. (2005) and their reactor system is illustrated in Fig. 6.

The transport of radicals and/or oxidisers is extremely important for efficient aquaculture processes, particularly disease control of fisheries and environmental sustainability of aquaculture effluents worldwide. Mahbub et al. (2022) proposed use of $\cdot\text{OH}$ radicals produced via continuous-flow photoreactor for treatment of amoebic gill disease (AGD) in Atlantic Salmons. Researchers also investigated other oxidisers, such as H_2O_2 (Wynne et al., 2020), peracetic acid (Lazado et al., 2019) and sodium percarbonate (Taylor et al., 2021) in batch reactor mode to treat AGD. 60% concentrated H_2O_2 is commercially used to treat and control skin and gill flukes of Yellowtail Kingfish. Except for $\cdot\text{OH}$ radicals, all other oxidisers were transported from their point of production to point of application. This allowed their large-scale industrial use in very large volume ranging from 2000 L to 10,000 L per day. AOPs involving radicals with short half-lives and not suitable for transportation (e.g., $\cdot\text{OH}$ and SO_4^- radicals), must demonstrate innovations in terms of *in-situ* production of highly concentrated radicals from low cost and portable oxidisers to achieve scalability in large-scale industry applications. In this context, Mahbub et al. (2022) have demonstrated production of concentrated $\cdot\text{OH}$ radicals ($40\text{--}83 \text{ mM}$) from relatively low concentrations of H_2O_2 ($0.1\text{--}5 \text{ M}$) using scalable photoreactors consisting of serially connected mercury (Hg) UV radiation. To date, there are no report on scalable production of SO_4^- radicals from PMS/PDS as mentioned in previous section. Hence, the prospect of continuous-flow reactor technology incorporating advanced microfluidics, radiometrically characterised light/radiation sources, metal oxide frameworks (MOFs) to immobilise radicals and their subsequent release to enhance portability, physical measures such as microwave/ultrasound as well as serial/parallel reactor set-up need to be investigated to produce highly concentrated $\cdot\text{OH}$ and SO_4^- radicals from relatively low concentrations of H_2O_2 and PMS/PDS, respectively.

4.3. Advanced micro- and mesoporous structures for efficient delivery of radicals in AOP

Maintaining the effective concentration of radicals until reaching the target is a major obstacle in the development of highly efficient AOPs particularly since the concentration of radicals/oxidisers attenuates with time as well as during transport from their point of production to

Table 2
Suitable platforms for AOP inducing radicals/oxidisers.

AOP inducing substance/ radicals	Parent materials	Percentage conversion of parent materials into radicals/ oxidisers (%)	Platform used	References
$\cdot\text{OH}$	H_2O_2	18	Continuous-flow Hg-UV (254 nm) reactor	Mahbub et al., (2022)
	H_2O_2	14.8	Batch reactor- <i>anatase</i> TiO_2 -UV (365 nm)	Hiroyuki et al., (1994)
	H_2O	4.6	Batch reactor- <i>anatase</i> TiO_2 -UV (365 nm)	
O_3	O_2	10–20	Continuous-flow	Gibalov and Peitsch (2006)
HOCl	NaCl , NaOCl	5–20	(batch)	Block and Rowan (2020)
SO_4^-	PMS	100	(batch)	Zhang et al., (2013)
	PMS and PDS	12.9–16.4	(batch)	Feng et al., (2018)

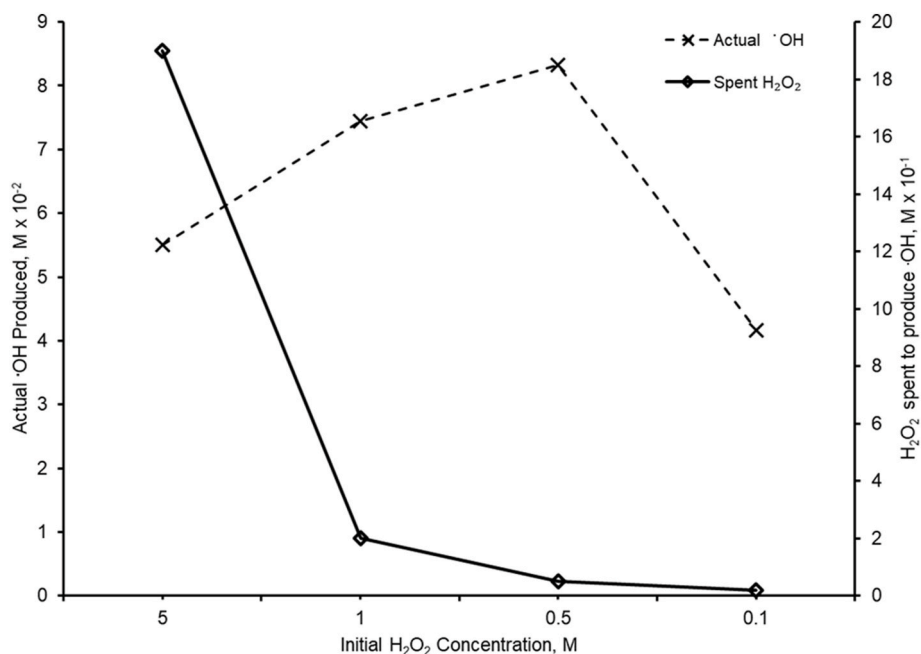


Fig. 5. Non-linear relation between spent H₂O₂ and ·OH radical produced by a serially connected multilayer UV photoreactor (adapted from Mahbub et al. (2022) with permission).

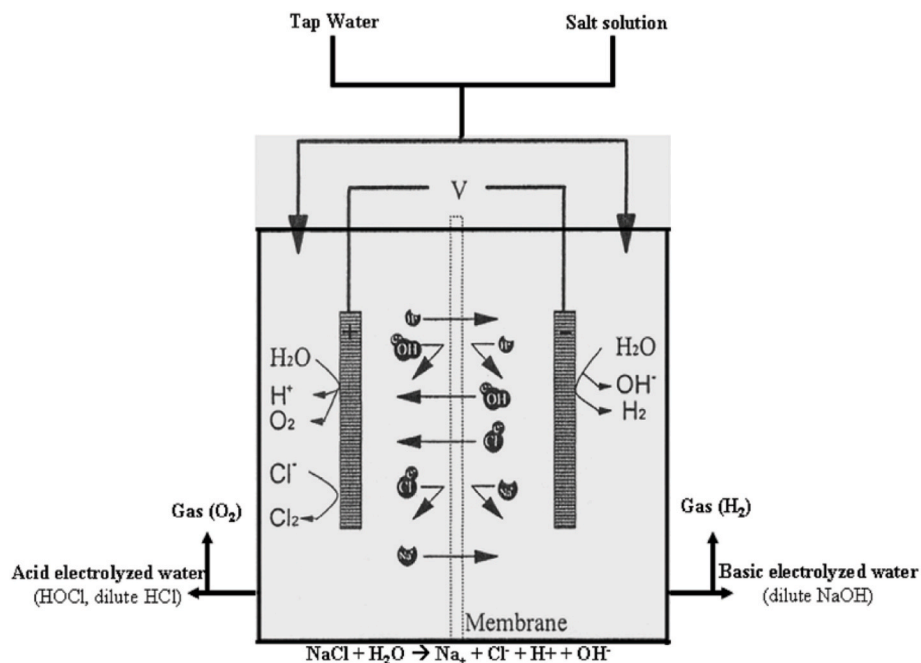


Fig. 6. Electrochemical batch reactor for large-scale production of HClO (adapted from Al-Haq et al. (2005) with permission) termed as “acid electrolysed water” from tap water and NaCl.

point of application. Yaghi et al. (1995) reported selective binding and removal of functional groups by microporous materials, such as metal organic frameworks (MOFs), zeolites, carbons, and amorphous glasses due to their extremely narrow pore size distributions ranging 0.5–2 nm. Selective binding of hydroxyl ·OH radical is also reported via in-house synthesis of Cu-SBA-15 mesoporous materials showing favourable catalytic activity in oxidative degradation of organic dye (Miao et al., 2019). Indirectly, the potential of 0–2% wt graphene entrapping FeOOH particles (alternately known as iron sludge) during Fenton-based wastewater treatment resulting more than 90% degradation of organic

contaminants was reported by Guo et al. (2017). Although mesoporous structures facilitate favourable outcome in terms of degrading organic compounds in laboratory scale, the capacity of micro/mesoporous structures for efficient delivery of radicals during AOPs in the context of their industrial applications hasn’t been reported yet. The capabilities of delivering drugs using mesoporous materials such as, MCM-41, SBA-15, MCM-48 as well as some MOFs as systemic-delivery and implantable local-delivery systems for humans have been discussed by Vallet-Regí et al. (2007). Due to their inertness, these mesoporous materials are excellent candidates for carrying ·OH and SO₄^{·-} radicals for disease and

pest control in aquaculture as well as in wastewater disinfection industries.

The use of oxidisers for disease control in aquaculture industry is ever evolving and researchers are working on finding new and improved methods of applying various oxidisers and radicals such as, H_2O_2 (Wynne et al., 2020), peracetic acid (Lazado et al., 2019), sodium percarbonate (Taylor et al., 2021) as well as $\cdot\text{OH}$ radicals (Mahbub and Yeager, 2023) in *in-vitro*, laboratory, pilot and industry scale containers used for fish bathing. Achieving reproducible outcomes in terms of disease control and fish health were the main obstacle in these reports to date, which we attribute to the dose efficacy of radicals/oxidisers and degree of deactivation of the pathogens. The efficacy of radical dose and pathogen deactivation in aquaculture industry can be greatly benefited from the potential of micro- and mesoporous inert materials to bind and deliver radicals and oxidisers to the point of application. Zhang et al. (2023b) have listed the micro- and mesoporous structures (e.g., MCM-41, SBA-15, Ce-MOFs, Fe_3O_4 , CuO to name a few) employed by researchers to date to overcome the inefficiencies of AOPs that suffer from the low availability due to the ultrashort lifetime of radicals. In our opinion, their complex and costly synthesis as well as cytotoxicity pose the major obstacles in employing these advanced structures for enhancing performances of AOPs in industrial scale. In this context, the biocompatibility and safety of silica-based materials such as, SBA-15 and MCM-48 have facilitated their use as drug carriers and controlled release systems in human body (Vallet-Regí et al., 2007). Therefore, we envisage that future investigations should focus on radical immobilisation and their subsequent release mechanisms using the biocompatible and non-toxic silica-based mesoporous structures namely, SBA-15 and MCM-48 with a view to utilise these materials in industry scale and efficient AOP operations.

4.4. Cost

Mousset et al. (2021) introduced laboratory scale cost comparison of five AOPs using accumulated oxygen-equivalent chemical-oxidation dose (AOCD) as a standardisation parameter amongst the AOPs. Using the AOCD criteria, the total cost of chemicals used, power employed and sludge managed for 50%, 75% and 99% mineralisation of a model contaminant (in this case phenol) was compared and Mousset et al. (2021) found that electro-Fenton incurred the lowest cost. Cañizares et al. (2009) coined a similar standardisation parameter termed as oxygen-equivalent chemical-oxidation capacity (OCC) whilst comparing conductive-diamond electrochemical oxidation, ozonation and Fenton oxidation. However, these abovementioned cost-comparisons did not include the operation and maintenance cost of equipment over the design period of the AOP plant. Therefore, we emphasize that the laboratory-based AOCD/OCC cost of different AOPs are unable to predict the industry scale cost of corresponding AOPs correctly. Additionally, the social, environmental, economic and greenhouse gas emission impact of large-scale AOP plants need to be assessed as part of their feasibility studies which cannot be estimated from laboratory scale cost investigations.

Life cycle costing (LCC) (Mahbub and Sharma, 2019) and assessment (LCA) (Sharma et al., 2009) of capital infrastructure required for AOP plants that includes their social, environmental and economic impact can be a suitable approach to estimate the long-term industry scale cost to help business owners to take their investment decisions. In this context, Mahbub and Sharma (2019) have demonstrated use of well-established LCC approach to predict the cost of civil and water infrastructures as well as the equivalent CO_2 (eCO_2) emission (as fraction of total emissions from energy embodied in the process) for sourcing freshwater from various sources for fish bathing in a large aquaculture industry of Australia for a 10-year life cycle. We emphasize the fact that contaminant types and load, sludge load, initial reagent used such as H_2O_2 , Cl_2 , Br_2 , peroxy mono- and disulfates, catalyst used such FeSO_4 , radiation source characteristics, input voltage for corona discharge as

well as electrode surface employed will incur continuous operational cost over the design life of AOP plants during scaling-up. The total energy embodied in producing the AOP operational infrastructure will also incur costs during AOP operations. Hence, any LCC or LCA-based large-scale study investigating long term operational cost of industrial AOP operation should consider the abovementioned parameters.

In Summary, existing conversion efficiencies of various AOP operations range between 5% and 20%. Technologies are still evolving for the production of highly concentrated $\cdot\text{OH}$ and $\text{SO}_4\cdot^-$ radicals from relatively low concentrations of H_2O_2 and PMS/PDS, respectively. It will be interesting to observe the potential of silica based biocompatible micro/mesoporous structures in improving the conversion efficiency and portability of both short and long-lived radicals during scalable AOP operations. Additionally, scalable AOP operations must consider the associated costs in industry scale as existing technological advances for radical production and conversion are confined within laboratory scales. Herein, we highlight the fact that innovations in scalable production of radical via advanced reactor technology (Mahbub et al., 2022), as well as radical binding and transport using micro- and/or mesoporous materials will have a positive impact via reducing the scale-up cost of AOP plants in future.

4.5. Further challenges in AOP scale-up

In-situ production of ROS from parent materials in both economically and environmentally sustainable manner is a big challenge in AOP scale up. Various batch/continuous processes mentioned earlier in Fig. 3 e.g., water photolysis in vacuum UV, UV + H_2O_2 , UV + O_3 , $\text{H}_2\text{O}_2 + \text{O}_3$, Fenton, elctro/photo Fenton as well as fluidized bed Fenton can enable such *in-situ* production of ROS. Further research on continuous flow-based reactor design with a view to achieve efficient radical conversion from parent materials as well as research on advanced functional micro/mesoporous biocompatible silica-based materials to achieve effective radical dosing and portability will eventually result towards sustainable and scaled-up AOP operations. The graphical abstract illustrates the summary of these future challenges in achieving scalable AOPs.

5. Conclusions

The conversion efficiency of AOPs and portability of radicals/oxidisers in terms of their delivery to the points of applications are the two primary parameters for upscaling AOP technologies from laboratory scale to industry scale. Innovative designs in batch or continuous-flow reactors will certainly facilitate efficient conversion of parent materials into useful radicals inducing AOPs. The application of micro- and/or mesoporous structures for selective binding and delivering radicals from their place of production to place to application will become a game changer in AOP upscaling, as such initiative would result huge cost reduction during AOP scale-up. Hence, we envisage that modern AOP-based research targeting large scale industrial applications will incorporate the conversion efficiency of AOPs via innovative continuous-flow reactors as well as portability of radicals/oxidisers via advanced micro/mesoporous structures to overcome the existing scalability challenges.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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References

- Adnew, G.A., Meusinger, C., Bork, N., et al., 2016. Gas-phase advanced oxidation as an integrated air pollution control technique. *AIMS Environ. Sci.* 3 (1), 141–158.
- Ai, S., Wang, Q., Li, H., et al., 2005. Study on production of free hydroxyl radical and its reaction with salicylic acid at lead dioxide electrode. *J. Electroanal. Chem.* 578, 223–229.
- Akaike, T., Sato, K., Ijiri, S., et al., 1992. Bactericidal activity of alkyl peroxy radicals generated by heme-iron-catalyzed decomposition of organic peroxides. *Arch. Biochem. Biophys.* 294 (1), 55–63.
- Al-Haq, M.I., Sugiyama, J., Isobe, S., 2005. Applications of electrolyzed water in agriculture & food industries. *Food Sci. Technol. Res.* 11 (2), 135–150.
- An, Q., Xing, Y.-Y., Pu, R., et al., 2023. Identification of Alkoxy radicals as hydrogen atom transfer agents in Ce-catalyzed C–H functionalization. *J. Am. Chem. Soc.* 145, 359–376.
- An, T., Yang, H., Li, G., et al., 2010. Kinetics and mechanism of advanced oxidation processes (AOPs) in degradation of ciprofloxacin in water. *Appl. Catal. B Environ.* 94, 288–294.
- Argyropoulos, D.S., Li, H., Gaspar, A.R., et al., 2006. Quantitative ³¹P NMR detection of oxygen-centered and carbon-centered radical species. *Bioorg. Med. Chem.* 14, 4017–4028.
- Bader, H., Hoigné, J., 1981. Determination of ozone in water by the indigo method. *Water Res.* 15 (4), 449–456.
- Bernardes, R.S., Klapwijk, A., 1996. Biological nutrient removal in a sequencing batch reactor treating domestic wastewater. *Water Sci. Technol.* 33 (3), 29–38.
- Bertolacini, R.J., Barney, J.E., 1958. Ultraviolet spectrophotometric determination of sulfate, chloride, and fluoride with chloranilic acid. *Anal. Chem.* 30 (2), 202–205.
- Block, M.S., Rowan, B.G., 2020. Hypochlorous acid: a review. *Dentoalveolar Surgery* 78 (9), P1461–P1466.
- Bogen, D.C., Welford, G.A., 1978. Radiometric determination of sulfate. *J. Radioanal. Chem.* 42, 307–312.
- Buchan, K.A.H., Martin-Robichaud, D.J., Benfey, T.J., 2005. Measurement of dissolved ozone in sea water: a comparison of methods. *Aquacult. Eng.* 33, 225–231.
- Cañizares, P., Paz, R., Sáez, C., et al., 2009. Costs of the electrochemical oxidation of wastewaters: a comparison with ozonation and Fenton oxidation processes. *J. Environ. Manag.* 90, 410–420.
- Chamulitrat, W., Takahashi, N., Mason, R.P., 1989. Peroxyl, alkoxy, and carbon-centered radical formation from organic hydroperoxides by chloroperoxidase. *J. Biol. Chem.* 264 (14), 7889–7899.
- Chen, L., Duan, J., Du, P., et al., 2022. Accurate identification of radicals by in-situ electron paramagnetic resonance in ultraviolet-based homogenous advanced oxidation processes. *Water Res.* 221, 118747 <https://doi.org/10.1016/j.watres.2022.118747>.
- Christensen, A., Guro, M.D., Garoma, T., 2009. Treatment of persistent organic compounds by integrated advanced oxidation processes and sequential batch reactor. *Water Res.* 43, 3910–3921.
- Cominellis, C., Kapalka, A., Malato, S., et al., 2008. Advanced oxidation processes for water treatment: advances and trends for R&D. *J. Chem. Technol. Biotechnol.* 83, 769–776.
- Cox, W.G., 1985. A volumetric method for titrimetric analysis of hydrogen peroxide, Report number NSWC-TR-85-210. Naval Surface Weapons Center, Maryland, USA. Retrieved from: <https://apps.dtic.mil/sti/tr/pdf/ADA163582.pdf>.
- Deng, Y., Zhao, R., 2015. Advanced oxidation processes (AOPs) in wastewater treatment. *Curr. Pollution. Rep.* 1, 167–176.
- Dimić, D.S., Milenković, D.A., Avdović, E.H., et al., 2021. Advanced oxidation processes of coumarins by hydroperoxyl radical: an experimental and theoretical study, and ecotoxicology assessment. *Chem. Eng. J.* 424, 130331.
- Divyapriya, G., Nidheesh, P.V., 2021. Electrochemically generated sulfate radicals by boron doped diamond and its environmental applications. *Curr. Opin. Solid State Mater. Sci.* 25, 100921.
- Dow, N., Roehr, J., Murphy, D., et al., 2015. Fouling mechanisms and reduced chemical potential of ceramic membranes combined with ozone. *Water Pract. Technol.* 10 (4), 806–813. <https://doi.org/10.2166/wpt.2015.100>.
- Du, D., Shi, W., Wang, L., et al., 2017. Yolk-shell structured Fe₃O₄@void@TiO₂ as a photo-Fenton-like catalyst for the extremely efficient elimination of tetracycline. *Appl. Catal. B Environ.* 200, 484–492.
- Eliasson, B., Kogelschatz, U., 1991. Modeling and applications of silent discharge plasmas. *IEEE Trans. Plasma Sci.* 19 (2), 309–323.
- Elovitz, M.S., Von Gunten, U., 1999. Hydroxyl radical/ozone ratios during ozonation processes. I. The r_{ct} concept. *Ozone Sci. Eng.* 21 (3), 239–260. <https://doi.org/10.1080/01919519908547239>.
- Epelle, E.I., Macfarlane, A., Cusack, M., et al., 2023. Ozone application in different industries: a review of recent developments. *Chem. Eng. J.* 454, 140188.
- Fair, G.M., Morris, J.C., Chang, S.L., et al., 1948. The behavior of chlorine as a water disinfectant. *J. (Am. Water Works Assoc.)* 40 (10), 1051–1061.
- Feng, Y., Wu, D., Li, H., et al., 2018. Activation of persulfates using siderite as a source of ferrous ions: sulfate radical production, stoichiometric efficiency, and implications. *ACS Sustain. Chem. Eng.* 6, 3624–3631.
- Fernández-Castro, P., Vallejo, M., San Román, M., et al., 2015. Insight on the fundamentals of advanced oxidation processes. Role and review of the determination methods of reactive oxygen species. *J. Chem. Technol. Biotechnol.* 90, 796–820.
- Fletcher, P., Andrew, K.N., Calokerinos, A.C., et al., 2001. Analytical applications of OH^\bullet injection with chemiluminescence detection: a review. *Luminescence* 16, 1–23.
- Giannakis, S., Rtimi, S., Pulgarin, C., 2017. Light-assisted advanced oxidation processes for the elimination of chemical and microbiological pollution of wastewaters in developed and developing countries. *Molecules* 22 (7), 1070. <https://doi.org/10.3390/molecules22071070>.
- Gibalov, V.I., Pietsch, G.J., 2006. On the performance of ozone generators working with dielectric barrier discharges. *Ozone Sci. Eng.* 28, 119–124.
- Glaze, W.H., Kang, J.-W., Chapin, D.H., 1987. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. *Ozone Sci. Eng.* 9, 335–352.
- Gomes, A., Fernandes, E., Lima, J.L.F.C., 2005. Fluorescence probes used for detection of reactive oxygen species. *J. Biochem. Biophys. Methods* 65, 45–80.
- Gray, P., Williams, A., 1959. The thermochemistry and reactivity of alkoxy radicals. *Chem. Rev.* 59 (2), 239–328.
- Greer, A., 2006. Christopher Foote's discovery of the role of singlet oxygen [¹O₂ (1Δ_g)] in photosensitized oxidation reactions. *Accounts Chem. Res.* 39 (11), 797–804.
- Guo, S., Yuan, N., Zhang, G., et al., 2017. Graphene modified iron sludge derived from homogeneous Fenton process as an efficient heterogeneous Fenton catalyst for degradation of organic pollutants. *Microporous Mesoporous Mater.* 238, 62–68.
- Hayyan, M., Hashim, M.A., AlNashef, I.M., 2016. Superoxide ion: generation and chemical implications. *Chem. Rev.* 116, 3029–3085.
- Hiroyuki, N., Kazuo, O., Hiroaki, O.-N., et al., 1994. Efficient hydroxyl radical production and their reactivity with ethanol in the presence of photoexcited semiconductors. *Bull. Chem. Soc. Jpn.* 67 (8), 2031–2037.
- Hofman-Caris, C.H.M., Beerendonk, E.F., 2011. New concepts of UV/H₂O₂ oxidation, Report number BTO 2011.046. Water Research Foundation, KWR, The Netherlands. Retrieved from: <https://www.scribd.com/document/348566117/New-Concepts-of-UV-H2O2#>.
- Hu, Y.-L., Lu, Y., Zhou, G.-J., et al., 2008. A simple electrochemical method for the determination of hydroxyl free radicals without separation process. *Talanta* 74, 760–765.
- Huang, G.-X., Si, J.-Y., Qian, C., et al., 2018. Ultrasensitive fluorescence detection of peroxymonosulfate based on a sulfate radical-mediated aromatic hydroxylation. *Anal. Chem.* 90, 14439–14446.
- Huckaba, C.E., Keyes, F.G., 1948. The accuracy of estimation of hydrogen peroxide by potassium permanganate titration. *J. Am. Chem. Soc.* 70 (4), 1640–1644.
- Huo, X., Wang, X., Yang, R., et al., 2020. A novel fluorescent probe for highly selective and sensitive detection of hypobromous acid in arthritis model mice. *Sensor. Actuator. B Chem.* 315, 128125.
- Ike, I.A., Linden, K.G., Orbell, J.D., Duke, M., 2018. Critical review of the science and sustainability of persulfate advanced oxidation processes. *Chem. Eng. J.* 338, 651–669.
- Ishihara, M., Murakami, K., Fukuda, K., et al., 2017. Stability of weakly acidic hypochlorous acid solution with microbicidal activity. *Biocontrol Sci.* 22 (4), 223–227.
- Jiménez-Banzo, A., Ragàs, X., Kapusta, P., et al., 2008. Time-resolved methods in biophysics. 7. Photon counting vs. analog time-resolved singlet oxygen phosphorescence detection. *Photochem. Photobiol. Sci.* 7, 1003–1010.
- Jiménez, A.M., Navas, M.J., Galán, G., 1997. Air analysis: determination of ozone by chemiluminescence. *Appl. Spectrosc. Rev.* 32 (1 & 2), 141–149.
- Jonnalagadda, S.B., Gengan, P., 2010. Titrimetric and photometric methods for determination of hypochlorite in commercial bleaches. *J. Environ. Sci. Health, Part A* 45 (8), 917–922.
- Kanakaraju, D., Glass, B.D., Oelgemöller, M., 2018. Advanced oxidation process-mediated removal of pharmaceuticals from water: a review. *J. Environ. Manag.* 219, 189–207.
- Kodera, F., Umeda, M., Yamada, A., 2005. Detection of hypochlorous acid using reduction wave during anodic cyclic voltammetry. *Jpn. J. Appl. Phys.* 44 (22), L 718–L 719.
- Lazado, C.C., Timmerhaus, G., Pedersen, L.-F., et al., 2019. Peracetic acid as a potential treatment for amoebic gill disease (AGD) in Atlantic salmon - Stage 1, Report number 21/2019. The Norwegian Seafood Research Fund, Norway. ISBN 978-82-8296-600-9 (pdf), ISSN 1890-579X.
- Lee, J., Von Gunten, Kim, U., H. J., 2020. Persulfate-based advanced oxidation: critical assessment of opportunities and roadblocks. *Environ. Sci. Technol.* 54, 3064–3081.
- Lee, K.-W., Wan, Y., Li, X., et al., 2021. Recent progress of alkyl radicals generation -based agents for biomedical applications. *Adv. Healthcare Mater.* 10 (10), 2100055.
- Liang, A.-H., Zhou, S.-M., Jiang, Z.-L., 2006. A simple and sensitive resonance scattering spectral method for determination of hydroxyl radical in Fenton system using rhodamine S and its application to screening the antioxidant. *Talanta* 70, 444–448.
- Liao, C.-H., Guro, M.D., 1995. Chemical oxidation by photolytic decomposition of hydrogen peroxide. *Environ. Sci. Technol.* 29, 3007–3014.
- Liu, Q., Xu, X., Fu, J., et al., 2021. Role of hypobromous acid in the transformation of polycyclic aromatic hydrocarbons during chlorination. *Water Res.* 207, 117787.
- Mahbub, P., Nesterenko, P.N., 2016. Application of photo degradation for remediation of cyclic nitramine and nitroaromatic explosives. *RSC Adv.* 6, 77603–77621.
- Mahbub, P., Sharma, A., 2019. Investigation of alternative water sources for fish farming using life cycle costing approach: a case study in North West Tasmania. *J. Hydrol.* 579, 124215.
- Mahbub, P., Smallridge, A., Irtassam, A., et al., 2022. Scalable production of hydroxyl radicals (OH^\bullet) via homogeneous photolysis of hydrogen peroxide using a continuous-flow photoreactor. *Chem. Eng. J.* 427, 131762.

- Mahbub, P., Yeager, T., 2023. Prospect of hydroxyl radical exposure during seawater bathing to treat Amoebic Gill Disease in Atlantic salmon. *Aquacult. Res.* 12 <https://doi.org/10.1155/2023/5074580>.
- Miao, K.-K., Luo, X.-L., Wang, W., et al., 2019. One-step synthesis of Cu-SBA-15 under neutral condition and its oxidation catalytic performance. *Microporous Mesoporous Mater.* 289, 109640.
- Mouset, E., Loh, W.H., Lim, W.S., et al., 2021. Cost comparison of advanced oxidation processes for wastewater treatment using accumulated oxygen-equivalent criteria. *Water Res.* 200, 117234.
- Munter, R., 2001. Advanced oxidation processes – current status and prospects. *Proc. Est. Acad. Sci., Chem.* 50 (2), 59–80.
- Nawaz, T., Sengupta, S., 2021. Wastewater: novel treatment technologies and source for epidemiological studies. In: Ahuja, S. (Ed.), *Handbook of Water Purity and Quality*, second ed. Academic Press, pp. 293–337.
- Neal, C.J., Gupta, A., Barkam, S., et al., 2017. Picomolar detection of hydrogen peroxide using enzyme-free inorganic nanoparticle-based sensor. *Sci. Rep.* 7, 1–10.
- Nitinavinij, K., Parnklang, T., Thammachareon, C., et al., 2014. Colorimetric determination of hydrogen peroxide by morphological decomposition of silver nanoparticles coupled with chromatography analysis. *Anal. Methods* 6, 9816–9824.
- Nyamutswa, L.T., Blair, H., Dimuth, N., et al., 2021. Sunlight-transmitting photocatalytic membrane for reduced maintenance water treatment. *ACS ES&T Water* 1, 2001–2011.
- O'Shea, K.E., Dionysiou, D.D., 2012. Advanced oxidation processes for water treatment. *J. Phys. Chem. Lett.* 3, 2112–2113.
- Phaniendra, A., Jestadi, D.B., Periyasamy, L., 2015. Free radicals: properties, sources, targets, and their implication in various diseases. *Indian J. Clin. Biochem.* 30 (1), 11–26.
- Pierlot, C., Nardello, V., Schrive, J., et al., 2002. Calcium peroxide diperoxohydrate as a storable chemical generator of singlet oxygen for organic synthesis. *J. Org. Chem.* 67, 2418–2423.
- 1 Pinkernell, U., Nowack, B., Gallard, H., Von Gunten, U., 2000. Methods for the photometric determination of reactive bromine and chlorine species with ABTS. *Water Res.* 34 (18), 4343–4350.
- Pinkernell, U., Von Gunten, U., 1999. Control options for bromate minimization during ozonation processes: kinetically based approach. In: proceedings of the 14th Ozone World Congress, International Ozone Association., Dearborn, MI, pp.441-450.
- Primo, O., Rueda, A., Rivero, M.J., et al., 2008. An integrated process, Fenton reaction-ultrafiltration, for the treatment of landfill leachate: pilot plant operation and analysis. *Ind. Eng. Chem. Res.* 47, 946–952.
- Quiroz, M.A., Bandala, E.R., Martínez-Huitle, C.A., 2011. Advanced oxidation processes (AOPs) for removal of pesticides from aqueous media. In: Stoytcheva, M. (Ed.), *Pesticides - Formulations, Effects, Fate*. IntechOpen, pp. 685–730.
- Rekhate, C.V., Srivastava, J.K., 2020. Recent advances in ozone-based advanced oxidation processes for treatment of wastewater- A review. *Chem. Eng. J. Adv.* 3, 100031.
- Ren, H., Sedlak, J.A., Elrod, M.J., 2021. General mechanism of sulfate radical addition to olefinic volatile organic compounds in secondary organic aerosol. *Environ. Sci. Technol.* 55, 1456–1465.
- Ribessi, R.L., Neves, T.A., Rohwedder, J.J.R., et al., 2016. iHEART: a miniaturized near-infrared in-line gas sensor using heart-shaped substrate-integrated hollow waveguides, 141, 5298–5303.
- Saravanane, R., Ranade, V.V., Bhandari, V.M., Rao, A.S., 2014. Urban wastewater treatment for recycling and reuse in industrial applications: Indian scenario. In: Ranade, V.V., Bhandari, V.M. (Eds.), *Industrial Wastewater Treatment, Recycling and Reuse*. Elsevier, pp. 283–322.
- Sargent, F.P., Gardy, E.M., 1974. The detection of alkoxy and other radicals in the gamma radiolysis of alcohols by an electron spin resonance and spin trapping method. *Can. J. Chem.* 52, 3645–3650.
- Sharma, A.K., Grant, A.L., Grant, T., et al., 2009. Environmental and economic assessment of urban water services for a greenfield development. *Environ. Eng. Sci.* 26 (5), 921–934.
- Sherino, B., Mohamad, S., Halim, S.N.A., et al., 2018. Electrochemical detection of hydrogen peroxide on a new microporous Ni-metal organic framework material-carbon paste electrode. *Sensor. Actuator. B Chem.* 254, 1148–1156.
- Shi, H., He, Y., Li, Y., et al., 2022. Confined ultrasmall MOF nanoparticles anchored on a 3D-graphene network as efficient and broad pH-adaptive photo-Fenton-like catalysts. *Environ. Sci.: Nano* 9, 1091–1105.
- Shi, W., Du, D., Shen, B., et al., 2016. Synthesis of yolk-shell structured Fe₃O₄@void@CdS nanoparticles: a general and effective structure design for photo-fenton reaction. *ACS Appl. Mater. Interfaces* 8 (32), 20831–20838.
- Singh, M., Srivastava, R.K., 2011. Sequencing batch reactor technology for biological wastewater treatment: a review. *Asia Pac. J. Chem. Eng.* 6, 3–13.
- Sournia-Saquet, A., Lafage, B., Savall, A., 1999. Determination of hypochlorous acid by amperometric measurement with a microelectrode. *C. R. Acad. Sci.* 2, 497–505.
- Subramaniam, M.N., Goh, P.S., Kanakaraju, D., et al., 2022. Photocatalytic membranes: a new perspective for persistent organic pollutants removal. *Environ. Sci. Pollut. Control Ser.* 29, 12506–12530.
- Sun, Y., Zhang, Q., Clark, J.H., et al., 2022. Tailoring wood waste biochar as a reusable microwave absorbent for pollutant removal: structure-property-performance relationship and iron-carbon interaction. *Bioresour. Technol.* 362, 127838.
- Tabrizi, G.B., Mehrvar, M., 2004. Integration of advanced oxidation technologies and biological processes: recent developments, trends, and advances. *J. Environ. Sci. Health, Part A* 39 (11–12), 3029–3081.
- Tai, C., Gu, X., Zou, H., et al., 2002. A new simple and sensitive fluorometric method for the determination of hydroxyl radical and its application. *Talanta* 58, 661–667.
- Takahashi, M., Nakamura, K., Jin, J., 2008. Study on the indirect electrochemical detection of ammonium ion with in situ electrogenerated hypobromous acid. *Electroanalysis* 20 (20), 2205–2211.
- Tanaka, K., Miura, T., Umezawa, N., et al., 2001. Rational design of fluorescein-based fluorescence probes. Mechanism-based design of a maximum fluorescence probe for singlet oxygen. *J. Am. Chem. Soc.* 123 (11), 2530–2536.
- Taylor, R.S., Slinger, J., Lima, P.C., et al., 2021. Evaluation of sodium percarbonate as a bath treatment for amoebic gill disease in Atlantic salmon. *Aquacult. Res.* 52 (1), 117–129.
- Thomas, R.N., 2000. Final Report: Singlet Oxygen Disinfection of Drinking Water. Retrieved from.
- Tortolani, A.J., Powell, S.R., Mišić, V., et al., 1993. Detection of alkoxy and carbon-centered free radicals in coronary sinus blood from patients undergoing elective cardioplegia. *Free Radical Biol. Med.* 14, 421–426.
- Tujunen, N., Kaivosoja, E., Protopopova, V., et al., 2015. Electrochemical detection of hydrogen peroxide on platinum-containing tetrahedral amorphous carbon sensors and evaluation of their biofouling properties. *Mater. Sci. Eng. C* 55, 70–78.
- Vallet-Regí, M., Balas, F., Arcos, D., 2007. Mesoporous materials for drug delivery. *Angew. Chem. Int. Ed.* 46, 7548–7558.
- Von Gunten, U., Oliveras, Y., 1997. Kinetics of the reaction between hydrogen peroxide and hypobromous acid: implication on water treatment and natural systems. *Water Res.* 31 (4), 900–906.
- Wan, Z., Cao, W., Xu, Z., et al., 2023. Revealing intrinsic relations between Cu scales and radical/nonradical oxidations to regulate nucleophilic/electrophilic catalysis. *Adv. Funct. Mater.* 33, 2212227.
- Wang, C., Chen, R., Zhang, R., et al., 2018. Simple spectrophotometric determination of sulfate free radicals. *Anal. Methods* 10 (28), 3470–3474.
- Wang, D., Qiu, S., Wang, M., et al., 2019. Spectrophotometric determination of hydrogen peroxide in water by oxidative decolorization of azo dyes using Fenton system. *Spectrochim. Acta Mol. Biomol. Spectrosc.* 221, 117138.
- Weschler, C.J., 2000. Ozone in indoor environments: concentration and chemistry. *Indoor Air* 10, 269–288.
- Wright, P.A., 2007. *Microporous Framework Solids*. Royal Society of Chemistry.
- Wu, H., Song, Q., Ran, G., et al., 2011. Recent developments in the detection of singlet oxygen with molecular spectroscopic methods. *Trends Anal. Chem.* 30 (1), 133–141.
- Wynne, J.W., Stratford, C., Slinger, J., et al., 2020. The interaction between temperature and dose on the efficacy and biochemical response of Atlantic salmon to hydrogen peroxide treatment for amoebic gill disease. *J. Fish. Dis.* 43, 39–48.
- Xia, X., Zhu, F., Li, J., et al., 2020. A review study on sulfate-radical-based advanced oxidation processes for domestic/industrial wastewater treatment: degradation, efficiency, and mechanism. *Front. Chem.* 8, 592056.
- Xin, Y., Fu-bing, X., Hong-wei, L., et al., 2013. A novel H₂O₂ biosensor based on Fe₃O₄-Au magnetic nanoparticles coated horseradish peroxidase and graphene sheets-Nafion film modified screen-printed carbon electrode. *Electrochim. Acta* 109, 750–755.
- Xin, Z., Rehmann, L., 2020. Application of advanced oxidation process in the food industry. In: Bustillo-Lecompte, C. (Ed.), *Advanced Oxidation Processes - Applications, Trends, and Prospects*. IntechOpen.
- Yaghi, O.M., Li, G., Li, H., 1995. Selective binding and removal of guests in a microporous metal-organic framework. *Nature* 378, 703–706.
- Zahmatkesh, S., Amesho, K.T.T., Sillanpää, M., 2022. A critical review on diverse technologies for advanced wastewater treatment during SARS-CoV-2 pandemic: what do we know? *J. Hazard. Mater. Adv.* 7, 100121.
- Zahn, A., Weppner, J., Widmann, H., et al., 2012. A fast and precise chemiluminescence ozone detector for eddy flux and airborne application. *Atmos. Meas. Tech.* 5, 363–375.
- Zhang, J., Ma, J., Zou, J., et al., 2016. Spectrophotometric determination of persulfate anion via oxidative depolarization of methyl orange induced by ferrous ions. *Desalination Water Treat.* 57 (52), 25235–25241.
- Zhang, T., Zhu, H., Croué, J.-P., 2013. Production of sulfate radical from peroxymonosulfate induced by a magnetically separable CuFe₂O₄ spinel in water: efficiency, stability, and mechanism. *Environ. Sci. Technol.* 47, 2784–2791.
- Zhang, Q., Sun, Y., Xu, W., et al., 2023a. Efficient microwave-assisted mineralization of oxytetracycline driven by persulfate and hypochlorite over Cu-biochar catalyst. *Bioresour. Technol.* 372, 128698.
- Zhang, B.-T., Yan, Z., Liu, Y., et al., 2023b. Nanoconfinement in advanced oxidation processes. *Crit. Rev. Environ. Sci. Technol.* 53 (12), 1197–1228. <https://doi.org/10.1080/10643389.2022.2146981>.
- Zheng, J., Springston, S.R., Wienstein-Lloyd, J., 2003. Quantitative analysis of hydroperoxyl radical using flow injection analysis with chemiluminescence detection. *Anal. Chem.* 75, 4696–4700.