Advanced oxidation processes for the removal of cyanobacterial toxins from drinking water

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Review

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Abstract

Drinking water production faces many different challenges with one of them being naturally produced cyanobacterial toxins. Since pollutants become more abundant and persistent today, conventional water treatment is often no longer sufficient to provide adequate removal. Amongst other emerging technologies, advanced oxidation processes (AOPs) have a great potential to appropriately tackle this issue. This review addresses the economic and health risks posed by cyanotoxins and discusses their removal from drinking water by AOPs. The current state of knowledge on AOPs and their application for cyanotoxin degradation is synthesized to provide an overview on available techniques and effects of water quality, toxin- and technique-specific parameters on their degradation efficacy. The different AOPs are compared based on their efficiency and applicability, considering economic, practical and environmental aspects and their potential to generate toxic disinfection byproducts. For future research, more relevant studies to include the degradation of less explored cyanotoxins, toxin mixtures in actual surface water, assessment of residual toxicity and scale-up are recommended. Since actual surface water most likely contains more than just cyanotoxins, a multi-barrier approach consisting of a series of different physical, biological and chemical – especially oxidative – treatment steps is inevitable to ensure safe and high quality drinking water.

Background

Cyanobacteria are the most diverse and widespread phototrophic prokaryotes inhabiting earth for several billions of years [1, 2]. Cyanobacteria can be found almost everywhere in terrestrial and aquatic environments, even in Antarctic lakes and hot springs [3]. Due to their dependence on nutrients and temperature, the increasing eutrophication of waterbodies and climate change promote more frequently and extensively occurring cyanobacterial blooms [2, 4–6]. Although not all blooms are poisonous, at least 40 cyanobacterial species are known to produce diverse secondary metabolites that are toxic to biota including plants [7], animals and humans. Consequently, cyanobacteria and their toxins pose a major risk to surface waters intended for drinking and recreational purposes, and adequate measures must be employed to prevent or eliminate cyanobacterial blooms and toxins.

The first approach should prevent the occurrence of cyanobacterial blooms in surface water by measures such as nutrient reduction, biomanipulation or the application of algaecides [4, 8]. Importantly, especially in the case of toxic cyanobacteria, the removal of intact cyanobacterial cells is essential to avoid the release of intracellular toxins, e.g. microcystins (MCs), anatoxin-a (ANTX) and saxitoxin (STX) [6, 9].

The second approach is the removal of cyanobacterial cells and metabolites in drinking water treatment facilities. Although most conventional drinking water treatment methods effectively remove cyanobacterial cells and intracellular metabolites, extracellular and dissolved cyanotoxins may bypass conventional methods such as rapid sand filtration and coagulation [2]. Hence, adequate and more advanced treatment measures must be implemented to ensure sufficient removal of cyanotoxins. While traditional treatment approaches such as physical retention, biodegradation or chemical oxidation can be effective, they all come with various practical, economic or environmental disadvantages.

Toxin removal by physical retention can be achieved by filter membranes with very low molecular weight cut-off pore sizes, i.e. nanofiltration and reverse osmosis, or adsorbents like activated carbon and bioadsorbents [10]. However, when dissolved cyanotoxins are only physically removed, appropriate measures for the disposal or further treatment of the toxin-enriched retentate is required. Additionally, filter beds and membranes may need to be backwashed regularly to prevent clogging, fouling and cyanobacterial growth on the filter medium [10, 11].

Although several cyanotoxins are biodegradable [12], their periodical occurrence may limit the microorganisms’ ability to degrade cyanotoxins, resulting in an initial lag-phase of up to a few days without pre-conditioning [10, 12]. Moreover, most enzymatic degradation mechanisms are still poorly understood which makes it difficult to predict the effectiveness of a biological treatment barrier [10, 12] and potential drawbacks such as the biotransformation of the less toxic gonyautoxin (GTX) into the more toxic STX [12].

Although commonly used oxidants such as chlorine and permanganate effectively degrade some cyanotoxins, others are not susceptible or require oxidant concentrations and reaction times that are substantially higher than those usually applied in drinking water treatment [2, 9, 13]. As a major disadvantage, chlorination can produce halogenated disinfection byproducts formed from the reaction of chlorine with organic matter or in the presence of bromide [14]. Furthermore, residual chlorine may impair the drinking water quality due its possibly perceptible taste and odor. Permanganate on the other hand does not promote the formation of toxic disinfection byproducts but may have negative effects on the water's taste and odor.
byproducts, nor does it produce taste or odor, but it tints the water pink at > 0.05 mg L⁻¹, which limits its application and residual concentration in drinking water [10].

As another form of oxidation, advanced oxidation processes (AOPs) have received a lot of attention for their application in drinking and wastewater treatment for the degradation of even recalcitrant organic compounds and disinfection of pathogens. In AOPs, reactive species, mainly \( \text{OH} \), and other mechanisms are formed in situ [10]. This review gives a detailed insight into AOPs which were investigated for cyanotoxin removal from drinking water to evaluate their feasibility and applicability. Therefore, we briefly outline current regulations for cyanotoxins in drinking water and basic principles of different AOPs. Following, we discuss the most relevant findings from the scientific literature on the degradation effectiveness, advantages and disadvantages of individual methods and the role of relevant water quality parameters. From there, information gaps are identified and recommendations for future research for the effective removal of cyanotoxins from drinking water are formulated.

**Cyanobacterial Toxins**

Cyanotoxins can cause a vast range of clinical signs, including acute hepatotoxicosis, peracute neurotoxicosis, gastrointestinal disturbances as well as respiratory and allergic reactions [6]. Many different cyanobacterial metabolites can be considered cyanotoxins [15]. Here, we will only focus on cyanotoxins for which information on their removal from drinking water was found.

**Microcystins**

MCs are the most commonly studied cyanotoxins produced by different cyanobacteria such as *Microcystis, Nostoc, Planktothrix* and many other species [16]. This group of water soluble cyclic heptapeptides consists of more than 100 congeners which exhibit similar toxicological properties due to their akin chemical structure, which mainly differs in two amino acids \( X \) and \( Z \) (Fig. 1) [6]. Hence, MCs are named according to these two variable amino acids, e.g. MC-LR with \( X \) and \( Z \) being leucine (L) and arginine (R), respectively. The hydrophobic Adda amino acid is often associated as the key structural element for MCs' biological activity [14]. Unless cyanobacterial cells lyse due to extrinsic stress or senescence, MCs are usually intracellular. In the presence of bacteria and photosynthetic pigments, dissolved MCs rapidly degrade in natural waters [6]. Depending on the degree of sunlight, content of natural organic matter (NOM) and presence of bacteria, MCs can have a half-life of 4 to 14 days in surface water [17].

**Nodularin**

Nodularin (NOD) and its seven analogues are cyclic pentapeptides produced by *Nodularia* and *Nostoc* strains. NOD's structure (Fig. 1) is similar to MC, leading to similar chemical and toxicological characteristics [6, 16]. Similar to MC, the hepatotoxic NOD is also intracellular until the bloom starts to decay [6].

**Cylindrospermopsin**

Cylindrospermopsin (CYN) was first isolated from *Cylindrospermopsis raciborskii* and later from other species including *Aphanizomenon* and *Oscillatoria*. So far, five analogues of this highly water soluble and planar-shaped alkaloid have been described (Fig. 1) [18, 19]. CYN is extracellular and is relatively stable to a wide range of heat, light and pH conditions. The alkaloid can persist in water for more than a month [6, 18]. However, when exposed to sunlight in the presence of cell pigments, CYN has a half-life of about 0.6 to 0.9 days [17].

**Anatoxins**

Anatoxin-a (Fig. 2) and its derivatives are produced by *Aphanizomenon, Dolichospermum* (formerly *Anabaena*), *Oscillatoria* and *Planktothrix*. The extremely potent alkaloid neurotoxin acts as a cholinergic nicotinic agonist causing nerve depolarization and neuromuscular blockage. ANTX is usually intracellular, but rapidly degrades once it is released from cells and is exposed to natural sunlight (half-life of approximately 100 min) and oxidants. However, in the absence of sunlight, ANTX can reach a half-life of several days to months. Main degradation products of ANTX and homoanatoxin-a are the notably less toxic dihydro- and epoxy analogues [9, 17, 20].

**Saxitoxins**

STX, also known as paralytic shellfish toxin, is produced by organisms from different taxonomic kingdoms – eukaryotic dinoflagellates and prokaryotic cyanobacteria. Cyanobacterial producers include *Aphanizomenon, Cylindrospermopsis, Dolichospermum* and *Lyngbya* [21]. STX can be substituted at various positions (Fig. 2), resulting in currently 57 known analogues, which can be grouped into non-
sulphated STXs, singly-sulfated GTXs and doubly-sulfated C-toxins. The toxicity of the STXs analogues inversely increases with the number of substituted sulfates [12, 21]. Because of its two cationic guanidine groups, the alkaloid is water soluble [9]. Unless cyanobacterial cells lyse, STX is usually intracellular [9].

**β-N-methy lamino-l-alanine**

β-N-methylamino-l-alanine (BMAA) is a non-proteinogenic amino acid (Fig. 2) reported to be present in terrestrial and marine, free-living and plant symbiotic cyanobacteria including *Aphanizomenon, Cylindrospermopsis, Microcystis* and *Nodularia* [22]. The possible association of BMAA with several neurotoxic outcomes is discussed in the literature, e.g. by Ploux et al. [22] and references cited therein.

### Exposure To Cyanobacterial Toxins And Current Regulations For Drinking Water

The presence of harmful cyanobacterial blooms and their toxins can evidently be traced back to the 19th century, where poisoning through ingestion of surface water led to sickness and death of livestock, pets and wildlife [23]. Ever since, cyanobacterial blooms and toxins have reportedly caused several, partly fatal incidents around the globe. In 1979, more than 100 people were poisoned and had to be hospitalized in Queensland, Australia due to the consumption of contaminated drinking water. Further investigations identified the water supply and later determined *Cylindrospermopsis raciborskii* as the source for the poisoning, which is now known as the Palm Island mystery disease [24]. Almost 20 years later, 76 hemodialysis patients died in Brazil due to the utilization of water contaminated with MCs and CYN for hemolysis treatment [25]. Besides posing a risk to human health, cyanotoxins can also have economic consequences [26]. Due to a massive *Planktothrix rubescens* bloom in the Serbian Vrutci reservoir with cell counts of about 10,000 cells L⁻¹ in the treated drinking water in December 2013, Serbian authorities prohibited the use of tap water in the city of Užice, Serbia (approximately 70,000 inhabitants). As a result of the incapability to remove cyanobacterial cells and toxins, an alternative, cyanobacteria-free water source – Suštčko vrelo reservoir – had to be used for several years until reconstruction of the Vrutci reservoir treatment facility was completed [27]. In a similar, but more far-reaching incident, the Ohio EPA put a temporary ban on tap water for the city of Toledo, Ohio, USA in August 2014. About 500,000 people were advised not to drink or otherwise use tap water after MC concentrations in the drinking water exceeded the regulatory threshold of 1 μg L⁻¹. After a few days, when MC concentrations decreased to below the limit, the ban was lifted [28, 29].

In order to protect humans from exposure to cyanotoxins through consumption of contaminated drinking water, adequate treatment measures must be employed. However, even if effective removal techniques are in place, a comprehensive drinking water guideline, containing a thorough monitoring and actions program, is indispensable. A set of threshold values can thus help to take actions in case they are exceeded. So far, the WHO suggested a provisional guideline value (GV) for MC-LR of 1 μg L⁻¹ based on a total daily intake (TDI) of 0.04 μg kg⁻¹ d⁻¹ derived from acute toxicity data [30]. However, GVs for others cyanotoxins have not been proposed yet due to the lack of toxicological and epidemiological data. The upcoming update on the WHO Guidelines for Drinking-water Quality, to be published in 2020-2021, is expected to include recommendations for ANTX, CYN and STX as well as a revision of the GV for MC. Updates can be found on the homepage [31]. The currently proposed GV for MC-LR was accepted or adapted by many countries across the globe [32]. The lack of toxicological and epidemiological data on effects of exposure to other cyanotoxins also raises the question on effects from cyanotoxin mixtures and chronic exposure. The US EPA was the first to propose a chronic TDI (0.003 μg kg⁻¹ d⁻¹) for MC-LR and lowered their acute TDI (0.006 μg kg⁻¹ d⁻¹) based on updated data [16].

**AOPs for cyanotoxin removal from drinking water**

Although many different reactive chemical species can be produced, short-lived •OH is often considered to be the most important species generated in AOPs in water, most likely due to its comparably high reactivity as indicated by its redox potential (Table 1). This non-selectively and randomly attacking oxidant primarily reacts with organic compounds in two distinctive mechanisms: i) via an electrophilic attack at electron-rich moieties such as C=C double bonds, aromatic systems and neutral amines, and ii) via hydrogen abstraction from C-H groups [33]. At neutral pH, •OH can also react in an often kinetically disfavored one-electron transfer mechanism [34].

The following sections address the existing knowledge on the removal of different cyanotoxins by AOPs in detail. We were able to identify studies that investigated the use of hydrogen peroxide, ozone, photolysis (including the combination with oxidants and catalysts), Fenton oxidation, non-thermal plasmas, sulfate radicals, electrochemical oxidation, sonolysis and radiolysis.

**Hydrogen peroxide**
Although $\text{H}_2\text{O}_2$ has a higher redox potential than e.g. chlorine under acidic conditions (Table 1) and is often used as a precursor for $\cdot\text{OH}$ as well as to improve the effectiveness of AOPs, it is relatively ineffective for the degradation of cyanotoxins if employed solely. Removal of MC-LR, CYN, ANTX and BMAA by $\text{H}_2\text{O}_2$ was reported to be $< 10\%$ [37–41]. Even at $30\,\text{°C}$ for 3.5 h, only about 3 % MC-LR was removed by $\text{H}_2\text{O}_2$ [36].

### Ozone-based AOPs

Ozonation is widely employed in drinking water treatment for disinfection of microorganisms and oxidation of various organic pollutants [42]. Even though ozonation itself technically is not an AOP as $\text{O}_3$ is usually produced in the gaseous phase, we discuss it in this review, because $\text{O}_3$ can be used as an AOP precursor and it decomposes to $\cdot\text{OH}$ in situ under alkaline conditions (eqs. (1) and (2)) [2, 43]. Ozone itself has a relatively high redox potential at acidic pH (Table 1) and reacts with organic compounds in a similar but more selective manner compared to $\cdot\text{OH}$. It attacks electron-rich groups such as unsaturated $\text{C}=$-$\text{C}$, aromatic systems and neutral amines [9]. Numerous studies showed the high effectiveness of $\text{O}_3$ for the degradation of MCs, NOD, CYN, ANTX and BMAA [14, 19, 37, 44–46]). On the other hand, ozonation is not recommended for STXs degradation, as the toxicity to mice of a STX extract treated with $\text{O}_3$ and $\text{O}_3$/H$_2$O$_2$ was reduced by $< 10\%$ only [47].

### Photolysis

Photolysis occurs in the environment by exposure to sunlight and is commonly employed for disinfection in water treatment utilizing UV light. Upon absorption of light, energy is released from a molecule through physical and chemical processes which include the

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**See formula 1 - 8 in the supplementary files section.**

Ozone can be used as an AOP precursor in combination with other oxidants, UV light (see the chapter on photolysis in combination with oxidants), catalysts and adsorbents, which increase $\cdot\text{OH}$ formation. One of the most commonly used and comparatively cheap $\text{O}_3$-based AOPs is the peroxone process, in which $\text{O}_3$ reacts with deprotonated $\text{H}_2\text{O}_2$ to produce $\cdot\text{OH}$ (eq. (2)). This process has been shown to further increase the degradation of MCs and ANTX compared to $\text{O}_3$ alone [44, 45]. Similarly, degradation of both toxins also increased when Fe$^{2+}$ was combined with $\text{O}_3$ (eqs. (3) and (4)) [44, 45]. However, the combination of $\text{O}_3$ with the Fenton's reagent (see the chapter on Fenton oxidation) only improved MC-LR degradation at low $\text{O}_3$ concentrations due to the oxidation of Fe$^{2+}$ at higher levels [48]. Instead of Fe$^{2+}$, the commonly used photocatalyst TiO$_2$ can also be used. CYN degradation improved by almost 30 % when $\text{O}_3$ was combined with TiO$_2$ due to increased $\text{O}_3$ decomposition to $\cdot\text{OH}$ and CYN adsorption to the catalyst [49].

With regard to water quality parameters, pH plays an important role because it can affect both the toxin speciation and the oxidant, influencing thus the treatment effectiveness. Although $\text{O}_3$ reactivity with the conjugated diene in MCs’ Adda amino acid was shown to be pH-independent, reactions with the amine and uracil moiety in ANTX and CYN, respectively, depend on the pH in consistence with the toxins’ pK$_a$ value [14, 19]. In contrast, Al Momani et al. [45] observed a substantially reduced MC-LR degradation when increasing the pH from 2 to 11. This indicates, that not only toxin speciation, but also reactivity and availability of dissolved ozone are pH-dependent. Under alkaline conditions, $\text{O}_3$ redox potential decreases by almost 50 % (Table 1) and ozone decomposition to $\cdot\text{OH}$ increases (eqs. (1), (2) and (5)). Additionally, if $\cdot\text{OH}$ quenching by NOM and alkalinity (as carbonate/bicarbonate, eqs. (6) and (7)) is reduced due to low availability, ozone consumption is further promoted by $\cdot\text{OH}$ (eq. (8)) [43]. BMAA degradation with $\text{O}_3$ was also observed to be pH-dependent but direct $\text{O}_3$ attack was less important, while secondary oxidants such as HO$_2^-$ formed from $\text{O}_3$ under alkaline conditions (eq. (1)) played a substantial role [37]. Moreover, the selectivity of $\text{O}_3$ toward specific electron-rich moieties was shown to be pH-dependent, as the $\text{C}=$-$\text{C}$ double bonds in CYN and ATNX are primarily attacked at pH $< 7$-$8$, whereas oxidation of the amine groups dominates at higher pH [14, 19, 46]. Overall, reaction rates for the ozonation at pH 8 was in the order of MC-LR > CYN > ANTX [19].

Besides $\cdot\text{OH}$ quenching, NOM may also quench $\text{O}_3$. In the presence of 2 mg L$^{-1}$ humic acid, MC-LR and −RR degradation by $\text{O}_3$ reduced by approximately 25 % [45]. In fact, NOM concentration was shown to be more influential on the degradation than its composition and alkalinity [19, 49]. In addition to water quality parameters discussed above such as pH, alkalinity and NOM, the actual concentration of cyanotoxins and other pollutants, dictate the $\text{O}_3$ demand of water. However, the effects of water quality on the pollutant removal are neglable once a residual $\text{O}_3$ concentration is present in the treated water. Hence, an ozone residual of $> 0.3$ mg L$^{-1}$ for $\geq 5$ min, which is typically applied in water treatment plants, is recommended for cyanotoxin removal [2].
breakdown of a compound [50]. Although ANTX readily degrades under sunlight in absence of photosensitizers \( (t_{1/2} = 1\text{-}2\text{ h at alkaline pH}) [51]\), other cyanotoxins such as MCs and CYN are less susceptible to direct photodegradation by sunlight [52]. Efficacy of photolytic treatment strongly depends on the wavelength, i.e. energy of the used light. For instance, ANTX has an absorption maximum in the range of 230-240 nm, which determines the toxin’s resistance to UV-A irradiation (315-400 nm), while it degrades by 70 % under UV-C irradiation at 254 nm [39]. Similarly, NOD degradation also improved when UV light of a shorter wavelength, i.e. higher energy, was used [53]. With vacuum-UV at 172 nm, water is directly photolyzed to form \( \cdot OH \) (eq. (9)), which further increased ANTX degradation and substantially reduced the UV dose required for complete removal. However, direct water photolysis is strongly limited to a light penetration depth in water of < 100 μm, which makes \( \cdot OH \) formation by vacuum-UV less attractive to drinking water treatment compared to other AOPs [54].

See formula 9 in the supplementary files.

Besides wavelength, light intensity is a crucial parameter as well. MC-LR degradation increased by about 30-40 % when light intensity was tripled [55]. Moreover, at 254 nm and a dose of 564 mJ cm\(^{-2}\), approximately 66 % MC-LR degradation was achieved, while at 312 nm, a much higher dose of 11,304 mJ cm\(^{-2}\) was required to yield similar results [55, 56]. In addition to irradiation, degradation also depends on the toxin structure as shown in a study on UV-photolytic treatment of four MCs, where degradation increased from MC-LR < -RR < -YR < -LA owing to the different amino acid structures (A = alanine, L = leucine, R = arginine, Y = tyrosine) [41].

UV-based treatments are so far the only methods for which MC-LR detoxification due isomerization of the 4(E),6(E)-Adda chain (Fig. 1) to 4(Z)- or 6(Z)-Adda was observed. Furthermore, degradation mechanisms include decarboxylation, which has only been reported for UV-based methods and sulfate radical-based AOPs (SR-AOPs; see the chapter on sulfate radical-based AOPs) [56, 57].

Cyanotoxins usually co-occur with NOM which can act as photosensitizer and improve the degradation. For instance, MC-RR photodegradation by sunlight substantially increased in presence of the cyanobacterial pigment phycocyanin [58]. However, photosensitizer concentration is essential as it was shown for MC-LR degradation. At lower concentrations, pigment availability was the limiting factor, while at higher concentrations, light attenuation was significant [59]. In a similar manner, ANTX photodegradation was more effective in the presence of NOM but the degradation decreased with increasing NOM concentration. Experiments with quenchers showed that besides excited NOM, \( ^1 \)O\(_2\) and \( \cdot \)OH also contributed to the toxin degradation and that \( ^1 \)O\(_2\) was more important than \( \cdot \)OH [60]. In contrast, photosensitized CYN degradation was observed to be mainly driven by \( \cdot \)OH (about 65-70 %), with \( ^1 \)O\(_2\) and excited NOM only playing minor roles [61]. This disagreement may not only be related to the different toxins, but also to experimental conditions and using fulvic acid and solar light vs humic acid and UV-C light, respectively. Although phycocyanin did not improve CYN photodegradation, other cyanobacterial compounds were observed to accelerate NOD and CYN degradation [53, 62, 63]. In fact, the presence of different pigment types was shown to affect MC-LR photodegradation effectivity in the following order: without pigment < chlorophyll a < β-carotene < water-extractable pigments < solvent-extractable pigments [58]. Furthermore, higher light intensities led to pigment bleaching and degradation which adversely affected MC-LR degradation [59].

Turbidity is one of the most important water quality parameters for photodegradation. Light absorption by non-target water constituents not acting as photosensitizer attenuates light and reduces penetration depth. Therefore, photodegradation is usually efficient in relatively clear water, after most turbidity has been removed [10]. Other water quality parameters may also affect the degradation as shown for ANTX degradation by UV-C radiation, where toxin removal was more effective at acidic pH with an optimum at pH = 6.4, most likely due to ANTX speciation under acidic conditions (\( pK_a = 9.4 \)) and possible inter- and intramolecular hydrogen bonding under alkaline pH. Also, higher temperatures led to increased ANTX degradation, but the changes became insignificant at T > 24 °C. Lastly, as for most AOPs, alkalinity was observed to decrease ANTX degradation due to quenching of reactive species [60].

In order to achieve high degradation yields, UV doses substantially higher than those commonly used for disinfection in water treatment (10-40 mJ cm\(^{-2}\) [9]) are required. Consequently, to reduce energy demand and operating costs for large-scale water treatment, the combination of UV with oxidants or photocatalysts – as discussed in the following paragraphs – is inevitable.

**Photolysis in combination with oxidants**

The combination of UV radiation with \( \text{H}_2\text{O}_2 \) or \( \text{O}_3 \) improves pollutant degradation due to the photolytic production of \( \cdot \)OH (eqs. (10) and (11)) [56]. Moreover, \( \cdot \)OH and \( \text{SO}_4^{\cdot} \) are produced from peroxymonosulfate (PMS) or peroxydisulfate (also persulfate, PS) upon UV
activation (see the chapter on sulfate radical-based AOPs). In a UV/chlorine system, \( \cdot \text{OH}, \text{Cl}_2, \text{OCl}^- \) and other reactive species are formed following eqs. (12) to (16) [64].

**See formulas 10-17 in the supplementary files.**

UV in combination with oxidants has been studied for the removal of MCs, CYN, ANTX and BMAA. For all for toxins, UV-based treatment was substantially more effective when \( \text{H}_2\text{O}_2 \) was added [37, 39, 40, 54, 55, 60]. Increasing \( \text{H}_2\text{O}_2 \) concentration improved cyanotoxin degradation only up to a certain oxidant concentration. Once the optimal \( \text{H}_2\text{O}_2 \) level was exceeded, \( \cdot \text{OH} \) quenching by \( \text{H}_2\text{O}_2 \) (eq. (17)) outbalanced radical formation [54, 55, 60]. Different studies reported that MCs were degraded at higher rates compared to CYN, ANTX and BMAA because of their higher reactivity with \( \cdot \text{OH} \). This is caused by MCs’ size and higher number of functional moieties that are partly more susceptible to radical attack [37, 41, 65]. The importance of the structure for the reactivity with \( \cdot \text{OH} \) is further affirmed when looking at different MCs. The major part of their structures is similar with the main difference being two amino acids (see Fig. 1). However, these minor differences suffice to yield different degradation rate constants: MC-YR (1.63 \( \times \) 10\(^{10}\) M\(^{-1}\) s\(^{-1}\)) > MC-RR (1.45 \( \times \) 10\(^{10}\) M\(^{-1}\) s\(^{-1}\)) > MC-LR (1.13 \( \times \) 10\(^{10}\) M\(^{-1}\) s\(^{-1}\)) > MC-LA (1.10 \( \times \) 10\(^{10}\) M\(^{-1}\) s\(^{-1}\)) [41]. When \( \text{O}_3 \) was added to UV instead of \( \text{H}_2\text{O}_2 \), MC-LR degradation also became more effective compared to UV- and \( \text{O}_3 \)-only treatment. \( \text{O}_3 \) decomposition to \( \cdot \text{OH} \) is accelerated under UV irradiation and as a consequence, both \( \text{O}_3 \) and \( \cdot \text{OH} \) oxidize pollutants [56, 66]. Although \( \text{O}_3 \), i.e. its production, may be more expensive compared to \( \text{H}_2\text{O}_2 \) and TiO\(_2\) (for UV/TiO\(_2\) see the chapter on photocatalysis), to achieve similar results, shorter reaction times and lower oxidant doses were required compared to UV/\( \text{H}_2\text{O}_2 \) treatment [56]. Due to the UV irradiation, decarboxylation and isomerization of MC-LR was observed, which did not occur in \( \text{O}_3 \)-only treatment. Furthermore, compared to UV- and \( \text{O}_3 \)-only treatment, UV/\( \text{O}_3 \) had a higher potential to degrade MC-LR and its degradation intermediates simultaneously under the same conditions [56].

As another, cheaper alternative to \( \text{H}_2\text{O}_2 \), the addition of chlorine has been studied in UV-based AOPs [67]. UV/chlorine was shown to be more effective compared to UV/\( \text{H}_2\text{O}_2 \), UV- and chlorine-only MC-LR treatment. Besides producing a variety of reactive oxygen and chlorine species (eqs. (12) to (16)), \( \text{Cl}_2 \) is more selective than \( \cdot \text{OH} \) and preferably reacts with electron-rich moieties [64]. Similar to UV/\( \text{H}_2\text{O}_2 \), increasing the chlorine dose led to a more effective MC-LR degradation due to an increase in reactive chlorine species production and higher contribution to toxin degradation [64, 67]. However, the use of chlorine may lead to the formation of halogenated degradation products such as chloroform and dichloroacetic acid produced from MC-LR following a series of oxidation steps Duan et al. [67]. Even though yields of these chlorinated byproducts increased with prolonged treatment time, residual cytotoxicity after UV/chlorine treatment was lower compared to untreated MC-LR [67].

Besides oxidant type and dose, the UV radiation itself is an important factor, as the peroxide bond in \( \text{H}_2\text{O}_2 \) is cleaved only upon irradiation with light of \( \lambda \times 300 \text{ nm} \) [39]. Hence, MC-LR and ANTX degradation by UV-A/\( \text{H}_2\text{O}_2 \) (\( \lambda_{\text{UV-A}} \approx 400-315 \text{ nm} \)) has been reported to be substantially less effective compared to UV-B/\( \text{H}_2\text{O}_2 \) and UV-C/\( \text{H}_2\text{O}_2 \) (\( \lambda_{\text{UV-B}} \approx 315-280 \text{ nm}, \lambda_{\text{UV-C}} \approx 280-100 \text{ nm} \)), respectively [39, 55, 68].

Similar to other AOPs, water quality parameters can influence UV/oxidant degradation efficacy. In the UV/oxidant setup NOM rather acts as oxidant and radical quencher than as photosensitizer, thus decreasing removal efficacy, which is in contrast with NOM action during photolysis without the addition of oxidants. NOM may compete with the oxidant for UV photons which consequently reduces reactive species formation [60, 65, 69]. The UV/\( \text{O}_3 \) system was also affected by NOM but to lesser extent than \( \text{O}_3 \)-only treatment of MC-LR [56]. In case of UV/chlorine degradation of MC-LR, NOM did not only decrease the degradation, but also resulted in a higher yield of chlorinated byproducts. This yield was observed to be dependent on NOM as well as chlorine dosage [67]. In the presence of bromide, MC-LR degradation increased due to the formation of HOBr which is more reactive than HOCl toward phenolic and amine moieties. Furthermore, UV activation of HOBr formed reactive bromine species which may have contributed to MC-LR degradation [64]. Alkalinity decreased UV/\( \text{H}_2\text{O}_2 \) and UV/chlorine degradation efficacy similar to NOM due to \( \text{H}_2\text{O}_2 \) and radical quenching [64, 69].

UV/oxidant removal efficacy is also affected by water pH. For ANTX removal by UV/\( \text{H}_2\text{O}_2 \), the highest efficacy was achieved at pH 6.7, while at lower pH the \( \cdot \text{OH} \) yield decreased due to reactions with \( \text{H}^+ \) and at alkaline pH \( \text{ANTX} \) is deprotonated and exists as neutral amine (\( \text{PK}_a = 9.4 \)). In this form, inter- and intramolecular hydrogen bonds can form which affect ANTX reactivity with \( \cdot \text{OH} \) [39]. In contrast, for BMAA removal, alkaline pH appeared to increase the degradation rate constant due to BMAA speciation at higher pH [37]. In UV/\( \text{O}_3 \) systems, the pH does not only determine toxin speciation, but also \( \text{O}_3 \) stability, which decreases at alkaline pH and may affect toxin
degradation. However, this effect seemed to be less influential for MC-LR degradation by UV/O₃ compared to O₃-only treatment [56]. In UV/chlorine-based treatment, the oxidant itself is also strongly affected by the pH, when HOCl dissociates to OCl⁻ at alkaline pH (pKₐ = 7.5). OCl⁻ has a lower molar absorption and thus a lower radical yield. Furthermore, OCl⁻ reacts at a higher rate with ·OH and Cl⁻ compared to HOCl. The optimum pH for MC-LR degradation by UV/chlorine was determined to be pH 7.4 [67]. In contrast, in another study MC-LR degradation by UV/chlorine was shown to be most effective at pH 6 and decreased at pH 7 [64]. Most of the experimental conditions seemed to be very similar, i.e. oxidant type and concentration, UV wavelength, MC-LR concentration and pH-buffer composition but notable differences were the UV intensity and pH-buffer concentration, which could have affected the outcomes. Both studies also examined the contribution of different reactive species to MC-LR degradation and reported different findings. In the first study, at neutral pH, MC-LR degradation by UV/chlorine was dominated by ·OH (42.5 %), while Cl₂ (25.4 %), ClO⁻/OCl⁻ (13.3 %), Cl⁻ (11.1 %) and UV (8.5 %) contributions were lower [67]. In the second study, at neutral pH, MC-LR degradation was driven by HOCl/OCl⁻ (47.3 %), while reactive chlorine species (21.3 %), UV (21.1 %) and ·OH (10.3 %) were only partially responsible for MC-LR degradation. Also in the second study, the UV intensity was about twice as high compared to the first study, which may explain the difference in the higher UV contribution [64].

**Photocatalysis**

Instead of oxidants, photoactive semiconductors can be used to improve UV-based cyanotoxin degradation. Upon exposure to light with energy exceeding the band gap between occupied valence band and unoccupied conductance band, an electron migrates from the valence to the conductance band. The formed valence band hole yields an oxidative site, while the now occupied conductance band provides a reducing site. As a result, three reaction mechanisms are possible: i) direct oxidation at the valence band, ii) ·OH formation from H₂O or OH⁻ at the valence band, and iii) O₂⁻ and subsequent H₂O₂ formation from O₂ at the conductance band [70].

Photocatalysis was shown to be effective for the removal of MCs, NOD and CYN [71–74]. Besides toxin degradation, adsorption onto the catalyst is often reported as a fourth removal mechanism. In a study with different MCs, degradation was faster, when adsorption to the catalyst was the highest [75], while in another study, no correlation of MC and NOD degradation with dark adsorption was observed [74]. In the first study, TiO₂ powder was used as received [75], while in the second study, the catalyst was coated onto glass spheres [74], which may have caused these contradicting findings. Effectivity of dark adsorption depends on toxin composition and hydrophobicity in particular. Adsorption to TiO₂ increased with increasing pollutant hydrophobicity and was thus pH-dependent caused by compound speciation and change of hydrophobicity at certain pH. Hence, for MCs, adsorption increases at acidic pH [75, 76].

Because of its high oxidizing power, chemical stability and low cost, TiO₂ is a commonly used photocatalyst [70]. Toxin degradation is accelerated with increasing TiO₂ concentration, but levelled off once a certain catalyst concentration was reached [72–74]. However, TiO₂ is only photoactive at UV light, which limits its applicability. Therefore, TiO₂ has been doped with mostly non-metal elements to reduce the band gap and consequently decrease the energy required for its activation [77]. Although N-doped TiO₂ was less effective than pure TiO₂ under UV and solar light, MC-LR could only be removed under visible light with N-TiO₂ [73]. Further, N-F-co-doped TiO₂ achieved higher removal compared to N- or F-TiO₂ under visible light [77]. For the removal of 6-hydromethyl uracil, a CYN model compound, under UV light, degradation efficacy for different co-doped TiO₂ was in order: N-F-TiO₂ > P-F-TiO₂ > S-TiO₂, while N-F-TiO₂ was the only catalyst which removed the uracil derivate under visible light [78]. MC-LR could be removed by Vis/S-TiO₂ due to the different toxin structure, allowing MC-LR adsorption to the photocatalyst and consequently allowing for degradation [79]. Similarly, C-doped TiO₂ showed lower removal rates under UV light compared to pure TiO₂, but in contrast, achieved MC-LR and CYN degradation under visible light. Differences in the reaction products and reactive species involved revealed distinct reaction mechanisms under UV and visible light [71]. Under UV light, ·OH was the primary reactive species, while under visible light, O₂⁻ became more important [71, 78, 80]. Besides doped TiO₂, other photocatalysts, e.g. WO₃ and Fe₂O₃ showed high response to solar light and were used for MC-LR degradation [81, 82]. Similar to TiO₂, doping of WO₃ improved MC-LR degradation and dopants can be ordered according to the removal rate: WO₃ < CuO-WO₃ < Pd-WO₃ < Pt-WO₃ [81]. When BiOBr was used as photocatalyst, MC-LR and CYN degradation was achieved by direct reaction with the catalyst instead of radicals, which followed a different reaction mechanism, involving decarboxylation [83, 84].

A major limitation of photocatalysis is the need to remove the catalyst in a subsequent treatment step, which becomes even more difficult if nano-scale powder is used. Hence, employing heterogeneous or immobilized photocatalysts improves or avoids removal and makes photocatalysis more attractive for large-scale water treatment. Besides substrates like glass or PVC, cellulose acetate and PET monoliths were found to be the best supporting materials for TiO₂ photocatalytic treatment of MC-LR and CYN [85]. When coated onto
granular activated carbon, TiO₂ photocatalysis of MC-LR improved compared to pure TiO₂ powder due to increased adsorption to TiO₂ or to activated carbon sites in vicinity to the catalyst [86]. In case of Fe-based photocatalysts, immobilization to a substrate is evitable because they can be separated magnetically [82].

Similar to photolysis, photocatalysis efficacy depends on the light characteristics, i.e. wavelength and intensity in particular. Although doped TiO₂ is also activated under visible light, degradation rates are reduced by two to three orders of magnitude compared to UV or solar light [71, 73]. With higher light intensities, more electron-hole pairs are formed regardless of the employed photocatalyst, which results in higher toxin removal [72, 81].

When UV/TiO₂ was combined with H₂O₂, higher MC-LR degradation was achieved compared to UV/TiO₂ or UV/H₂O₂ alone [87]. Although dark adsorption to the catalyst decreased in the presence of the oxidant, H₂O₂ decomposition to ·OH increased when TiO₂ was present. However, H₂O₂ concentration was shown to be a crucial factor, as the MC-LR degradation rate was highest at 0.005 % H₂O₂ in solution and decreased at higher concentrations [87]. Besides adding oxidants, photocatalysis can also be enhanced when used in photoelectrocatalysis. Similar to elemental doping of a photocatalyst, photoelectrocatalysis improves the photocatalytic activity by removing electrons from the catalyst to reduce the recombination of electron-hole pairs to instead utilize the holes in the conductance band for oxidant production and pollutant reduction [88]. Under given experimental conditions, MC-LR degradation was substantially more effective by photoelectrocatalysis using Ag/AgCl/TiO₂ nanotube electrodes compared to photocatalysis and electrochemical degradation alone [89]. Because this approach is based on an electrolytic cell, parameters such as electrolyte composition affect the degradation and need to be optimized (see the chapter on electrochemical oxidation).

Also for photocatalytic toxin removal, water quality parameters such as pH and NOM have major an impact. For instance, regardless of type and doping of the photocatalyst, higher MC and CYN removal was achieved under acidic conditions [72, 76, 82]. However, when different scavengers were used during MC-LR degradation by Vis/NF-TiO₂, the solution pH did not only affect dark adsorption, but also played a crucial role in the formation and reactivity of reactive oxygen species [80]. Although NOM can act as photosensitizer in photolysis, it may adsorb to the catalyst surface and quench reactive species produced by photocatalysis which reduces toxin removal. Similarly, high alkalinity quenches and thus limits ·OH availability [76]. Another crucial water quality parameter is dissolved O₂ which functions as precursor for O₃⁻ and H₂O₂ formation at the conductance band. Under O₂-free atmosphere, cyanotoxin degradation substantially decreased or was completely inhibited [72, 78]. In the presence of Fe⁺³ and Cu²⁺, toxin degradation increased due to ·OH production in a Fenton-like reaction [78, 81] (see the chapter on Fenton oxidation). At lower concentrations, Cl⁻ can function as precursor for Cl₂ which was shown to increase MC-LR degradation. However, when exceeding an optimal Cl⁻ concentration, ·OH quenching and Cl₂ formation became more efficient and suppressed toxin degradation [81].

Fenton Oxidation

In a Fenton reaction ·OH is produced via the reaction shown in eq. (18). The Fenton's reagent thereby refers to Fe²⁺/H₂O₂, but other transition metals, e.g. chromium, copper, manganese as well as other oxidants, e.g. HClO, S₂O₈²⁻ or HSO₅⁻ can also produce ·OH or SO₄⁻ in Fenton-like reactions (see the chapter on sulfate radical-based AOPs for SO₄⁻ production) [36, 90]. Fenton oxidation of several cyanotoxins was studied, and the removal effectiveness was found to be in order of MC-RR > CYN > MC-LR >> ANTX > STX [36, 38, 44, 45, 91, 92].

See formulas 18-21 in the supplementary files.

The Fe²⁺ to H₂O₂ ratio is amongst the most crucial parameter that must be optimized to prevent parasitic reactions which inhibit ·OH formation. In case of H₂O₂ excess, Fe³⁺ is reduced to Fe²⁺ at a slower rate as the Fenton reaction, consuming H₂O₂ to yield HO₂⁻ (eqs. (19) and (20)). The formation of the less reactive HO₂⁻ is competing with the formation of more reactive ·OH (Table 1). An excess in H₂O₂ also leads to the formation of HO₂⁻ by ·OH depletion (eq. (17)). Additionally, ·OH can be quenched by an excess of Fe²⁺ (eq. (21)) [90]. Several studies reported different optimal Fe²⁺ to H₂O₂ ratios, even for the same toxins, which emphasizes that experimental conditions like toxin concentration and solution pH must be considered [38, 44, 45, 93].

Fenton oxidation is often reported to be most effective at pH ≈ 3 [90]. At alkaline pH, Fe²⁺ forms hydroxides which tend to precipitate, thus reducing Fe²⁺ availability to produce ·OH [38]. Furthermore, H₂O₂ stability decreases at alkaline pH which further limits ·OH.
formation [94]. On the other hand, under too strong acidic conditions, H+ inhibits Fe3+ reduction which also decreases Fe2+ availability [93]. For practical applications, treatment closer to neutral pH may be beneficial as it would reduce resources and costs required for pH adjustments before and after Fenton treatment while keeping a sufficient effectiveness, e.g. 77 % MC-LR removal at pH 3 and 68 % removal at pH 5, [38]. In order to extend the pH range, heterogeneous or immobilized catalysts can be used which additionally improves its removability from water. For instance, across a pH range of 5-8 in a photo-Fenton process, heterogeneous FeY was shown to yield a higher catalytic activity than Fe2+ [95]. Although alkaline pH is often reported to decrease Fenton effectiveness due to lower ·OH-yields, the formation of alternative oxidants at neutral and alkaline pH was proposed in a study with Reactive Black 5 and As3+ [96]. Oxidation increased again under alkaline pH which was associated with high-valent iron species, i.e. Fe4+, in form of hydroxo-complexes [96].

In Fenton-like reactions, transition metals and oxidants other than Fe2+ and H2O2 produce ·OH. For instance, Fe3+ can be used instead of Fe2+. However, MC-LR degradation was shown to be significantly slower, because Fe3+ first is reduced to Fe2+ by H2O2 (eqs. (19) and (20)) before it eventually produces ·OH [97]. Besides MC-LR, CYN and ANTX were also shown to be degraded by a Fenton-like system, namely Fe3+, which was bond to a macrocyclic ligand system, in combination with H2O2 [91]. In another study, Cu2+ in combination with ascorbic acid was used to degrade MC-LR. Ascorbic acid reduced Cu2+ to Cu+ which then activated O2 via O2·−. Cu+/H2O2 produced ·OH at a rate of approximately 100 M⁻¹ s⁻¹ which is in a similar range as the Fe2+/H2O2 system (76 M⁻¹ s⁻¹) [98].

Fenton oxidation can be improved when combined with UV/Vis light which leads to photoreduction of Fe3+ to Fe2+ as well as photolytic ·OH generation from H2O2 [68]. Photo-Fenton was shown to be more effective compared to dark Fenton MC-LR degradation due to combined effects of photolytic and Fenton mechanisms [99]. Due to the continuous photoreduction of Fe3+ and photocatalytic ·OH generation from Fe3+ in form of Fe(OH)2+, UV-C/Fe3+/H2O2 was more effective than UV-C/Fe2+/H2O2 for the degradation of MC-LR [68]. Furthermore, the spectrum of the irradiation light was also shown to affect MC-LR degradation, as UV-C and solar light were more effective than UV-A [68, 100]. Other hybrid Fenton techniques use ultrasound or electrolysis (for electro-Fenton see the chapter on electrochemical oxidation) to improve pollutant removal. In sono-Fenton, ·OH formation is further accelerated by combining sonochemical (see the chapter on sonolysis) and Fenton mechanisms [101].

As for most AOPs, NOM quenches produced ·OH and may thus reduce the effectiveness of Fenton oxidation [38]. Although CYN degradation by Fenton oxidation decreased in the presence of NOM, the effect appeared to be less extensive compared to e.g. ozonation and UV/TiO2 [92]. Photo-Fenton may be more affected by NOM due to light attenuation [68]. However, the effect of NOM on the degradation strongly depends on its type and composition. The removal rate of MC-LR by solar photo-Fenton in presence of different NOM types was in the order of fulvic acid > NOM-free > humic acid > a mixture of fulvic and humic acids plus bicarbonate as alkalinity. Humic acid usually has a larger molecular weight and contains more aromatic moieties than fulvic acid which, in turn, may act as a chelating agent, stabilizing Fe2+ [102]. Similarly, when zero-valent iron nanoparticles were used in a heterogeneous Fenton-like reaction, humic acid seemed to form Fe2+-cleaving iron complexes which resulted in higher MC-LR degradation [103].

Non-thermal plasma

Low or atmospheric pressure plasmas in which most of the energy is transmitted to free electrons (temperatures of ≥ 10⁴ K), while the remaining heavy species only receive minor amounts of energy (temperatures of ≤ 10³ K) are called non-thermal plasmas (NTPs). A broad spectrum of reactive species is generated by NTPs, including hot electrons, photons, and heavy species such as radicals, excited atoms, molecules and ions, reactive oxygen and nitrogen species. Additionally, some discharges may generate shock waves [104, 105]. NTPs are generated by electric discharges in the gaseous or liquid phase, or at their interface and due to the overall low plasma temperature can be employed in many different fields including water treatment [104, 106]. In fact, because of higher efficiencies compared to other means of O₃ production, O₃ generators are often based on electric discharges in air or oxygen [106].

For an electric discharge in gas, the gas type and composition dictate which reactive species are produced. For a discharge in air or oxygen, one of the most important processes is O₃ formation. However, in the presence of N₂, i.e. in discharges in air, NOx are also produced, which lead to acidification and nitrification of the solution if the gas is bubbled through water afterwards [107]. O₃ produced in gas can directly react with pollutants or dissolve into the liquid when the gas is bubbled through the solution after the discharge, where it can also decompose to ·OH [108]. If oxygen-free gases such as Ar are used, no reactive oxygen species are produced in the gas-phase, but when the gas passes through water, ·OH can be formed upon reaction with ionized or excited species in the gas [109]. In electric discharges in water, low energy electrons excite water molecules, whereas high energy electrons dissociate water. Both reactions lead to
the formation of •OH (eqs. (22) and (23)), which is one of the main reactive species produced by a discharge in water. H2O2 is formed as a recombination product of •OH [107]. With a discharge in liquid, reactive species can directly react with pollutants in the plasma channels or close to the plasma-liquid boundary without the need to diffuse from the gaseous into the liquid phase [110]. For an electric discharge at the gas-liquid interface, plasma channels usually form on top of the liquid surface as the liquid acts as counter electrode. Here, reactive species are formed in the gaseous and liquid phase and can easily diffuse into the other phase [111, 112].

See formulas 22 and 23 in the supplementary files.

So far, NTPs were studied for the removal of MCs, ANTX and BMAA [108, 109, 111–115]. Besides the type of reactive species produced in an electric discharge, other parameters also affect the treatment efficacy. Studies on MC-LR removal in a gas-liquid surface discharge showed, that a higher operating voltage increased the degradation due to a higher energy input [111, 115], and similar results were shown for the degradation of ANTX in a dielectric barrier discharge in O2 and subsequently bubbling the gas through the sample solution [108]. Here, an increased operating voltage led to higher O3 concentrations, which in turn also resulted in higher •OH levels in water due to decomposition of dissolved O3 [108]. However, for discharges in air, maximal O3 concentration may not be achieved with the highest voltage, because of increasing O2 consumption in NOx reactions and O3 depletion in reactions with N and NO at higher voltages [116]. Besides operating voltage, pH was also shown to affect the MC-LR degradation effectiveness in an Ar-water surface discharge, in which an acidic pH was beneficial for the removal [109]. Since MC-LR was expected to be unaffected in the studied pH range, the •OH concentration was assumed to be reduced under alkaline pH due to reaction with OH• [109]. The concentrations of the formed reactive species can also be increased by higher gas flow rates [115].

The electrode distance also impacts the plasma chemistry, when decreasing distance between high voltage electrode and the water surface, the energy increases and intensifies the reactions induced by the plasma. For a shorter electrode distance, the transfer time into the solution is reduced especially for short-lived reactive species [111, 112, 115], where long transfer times can reduce the degradation effectiveness. This is why catalysts have been studied as additives in NTPs to transform long-lived species like O3 and H2O2 into the more reactive •OH. For example, Mn-doped carbon xerogels not only increase the •OH concentration, but also adsorb e.g. MC-LR, thus immobilizing the toxin to enhance reactions with oxidants [112, 114]. Because electric discharges also generate UV light, photocatalysts like TiO2 have also been studied as additives to increase the formation of •OH (see the chapter on photocatalysis) [114]. Due to the formation of H2O2 in water, another alternative is the addition of Fe2+ to yield the Fenton's reagent (see the chapter on Fenton oxidation) [115]. Plasma generation, intensive heat and direct electro-physical and –chemical processes at the electrode can lead to corrosion, resulting in the release of metal ions from the electrodes. Correspondingly, electrodes made from catalytic active materials may release e.g. Fe2+ from stainless steel, which, in combination with H2O2 produced by the discharge, increases thus •OH formation [107].

Besides pollutant degradation during the actual treatment, plasma treated water has been shown to yield residual – post-treatment – oxidative and microbicidal effects. Up to a few days after exposure to an electric discharge, plasma treated water still effectively degraded for example BMAA [113]. Although this phenomenon is still not fully elucidated, long-lived reactive species such as O3, H2O2 and peroxynitrous acid (HNO2) may be responsible for this residual effect [104].

When simulating a real water matrix by adding, for example, K2HPO4, NaNO3 or humic acid, degradation of MC-LR was reduced due to competition for •OH [109]. For ANTX degradation by a dielectric barrier discharge in O2, KNO3, KH2PO4 and glucose were shown to affect the degradation similarly [108].

Sulfate Radical-based Aops

In SR-AOPs, SO4• is the major reactive species generated from PMS or PS. It is more selective than •OH and has a higher redox potential at neutral pH (Table 1), which may make it more suitable for water treatment across a broader pH range [35, 36, 117]. Furthermore, PS and PMS are more stable than H2O2, increasing precursor transportability across longer distances within water [117]. Moreover, the peroxide bond in PS has a lower bond dissociation energy which requires less energy for radical production compared to H2O2 [118].

SO4• can be generated by cleaving the peroxide bond in PMS and PS using energy-based activations through heat, UV irradiation, ultrasound and plasma (eqs. (24) and (25)) [35, 117, 119]. Activation of PMS and PS in redox reactions can be achieved using transition metals in a Fenton-like mechanism (see the chapter on Fenton oxidation), O-functionalized activated carbon, electrochemical processes, radiolysis (e− formation in water, eq. (46)) and ozone (eqs. (26)-(33)) [35, 117, 120, 121]. Unexpectedly, phosphate-buffered saline (PBS),
a commonly used pH-buffer, was also shown to activate PMS, and the PBS/PMS system effectively degraded model water pollutants Acid Orange 7, rhodamine b and 2,4,6-trichlorophenol [122].

See formulas 24 - 39 in the supplementary files.

SR-AOPs are a worthy alternative to ⋅OH-based AOPs due to the simultaneous generation of ⋅OH as secondary radical when PMS is used as precursor (eqs. (24) and (26)), in the presence of water (eq. (35)), under alkaline conditions (eq. (36)) or when PMS is activated using O₃ (eqs. (31) to (34)). Consequently, ⋅OH is the primary reactive species at alkaline pH, whereas SO₄⁻ is the dominant radical at acidic pH. At neutral pH, both radicals equally contribute to pollutant oxidation [117, 121]. The reaction of both radicals forms PMS (eq. (37)), which in turn can again be activated to generate SO₄⁻ and ⋅OH [117]. Additionally, the reaction of ⋅OH with HSO₄⁻ or H₂SO₄ can also produce SO₄⁻ (eqs. (38) and (39)) [120].

SO₄⁻ generally reacts with organic pollutants in three distinctive routes: i) via hydrogen abstraction from C-H bonds, ii) via addition to unsaturated bonds and iii) via electron transfer reactions from carboxylates, amines and aromatic compounds [35]. The third mechanism promotes decarboxylation, which, besides for SR-AOPs, has only been reported for UV-based degradation of cyanotoxins [56, 83, 84, 121, 123]. PMS and PS also function as oxidants, but SO₄⁻ is usually more effective and faster given its substantially higher redox potential (Table 1). PS is usually preferred over PMS due to its higher stability, water solubility, photosensitivity and is more frequently used in standard methods and commercial instruments [35].

SR-AOPs have been studied for the removal of MCs, CYN and ANTX, mainly focusing on UV and catalyst activation [36, 40, 41, 124]. Even without activation, high removal (≥ 90 %) of MC-LR and CYN was achieved after > 500 min of treatment for PS and > 100 min of treatment for PMS, while ANTX was almost unaffected by PMS without activation. However, when UV radiation was added, degradation of these three toxins became more effective [40, 41, 124]. MC-LR and CYN degradation efficacy was in order of UV/PS > UV/PMS > UV/H₂O₂ [40, 41]. Due to its structure, MC-LR was faster degraded than CYN because it provides more moieties prone to radical attack [40, 41]. Studies with different MC variants showed that under UV-only, degradation increased following MC-LR < -RR < -YR < -LA, while the differences were only small in the presence of PMS, PS or H₂O₂ [41]. Similar to MC-LR and CYN, degradation efficiencies for MC-LA, -RR and -YR followed UV/PS > UV/PMS > UV/H₂O₂ > UV-only [41]. Similar to other photolytic AOPs, the wavelength influenced the degradation efficacy in UV-activated SR-AOPs. For example, ANTX removal increased when the wavelength was decreased from 290 to 260 nm [124]. A follow-up experiment with radical quenchers revealed, that under the experimental conditions used, ANTX degradation was dominated by SO₄⁻ [124].

In contrast to UV activation, MC-LR degradation efficacy was in a different order: Co²⁺/PMS (pH = 5.8) > Fe²⁺/H₂O₂ (pH = 3) >> Ag⁺/PS (pH = 5.8) because PMS accepts e⁻ more easily than H₂O₂ and PS [36]. Moreover, activation of PS requires substantially higher transition metal concentrations [36, 125].

MC-LR degradation was further improved by addition of TiO₂ to the UV/PMS or UV/PS system due to photolytic and photocatalytic (see the chapter on photocatalysis) production of SO₄⁻ and ⋅OH [126], and addition of transition metals can promote (photo-) Fenton-like mechanisms. For instance, Cu²⁺ and Fe²⁺ improved CYN degradation by UV/PMS, even in the presence of NOM [40]. Similar results were observed for ANTX, and – again – UV/PMS/Cu²⁺ yielded better results compared to UV/PMS/Fe²⁺ [124]. Besides type and properties of the activation mechanism, an increase in the oxidant concentration seems to generally increase the degradation rate due to the formation of more reactive species [36, 40, 124].

As for other AOPs, water quality parameters may considerably influence cyanotoxin degradation by SR-AOPs. Reaction rate constants of SO₄⁻ with NOM were shown to be two orders of magnitude lower compared to rate constants of ⋅OH with NOM but quenching effects can still occur and particularly depend on NOM composition and concentration [40, 125]. For ANTX degradation by UV/PMS, ≤ 2 mg L⁻¹ of NOM were shown to improve toxin removal due to photosensitization. But at higher NOM concentrations, radical scavenging outbalanced this photosensitizing effect, and inhibited ANTX degradation [124]. Interestingly, humic acid and quinones, which are active functional humic acid moieties, were shown to activate PS and effectively degraded for example PCB28 [127]. Hence, NOM may not only act as photosensitizer, but certain moieties may eventually react with PS to produce SO₄⁻.

Besides NOM, alkalinity can also act as radical scavenger, especially since carbonate and bicarbonate concentrations (mg L⁻¹) highly exceed toxin concentrations (μg L⁻¹) in surface water [40, 124]. The pH of the treated water is another important factor which determines
the speciation of toxins, catalysts as well as oxidants. In UV/SR-AOPs at acidic conditions around pH 3, MC-LR degradation rate constants substantial increased compared to buffered solutions with pH 4.8 and pH 6.4 for PMS and PS, respectively [36]. ANTX removal by UV/PMS on the other hand, was most effective at pH 6.4 and decreased under more acidic (pH 3.0) and alkaline conditions (pH 8.0) [124]. However, when the Co²⁺/PMS system was acidified, MC-LR removal decreased from 100 % after 5 min at pH = 5.8 to 27 % after 60 min at pH = 3 and became substantially less effective compared to the Fenton reagent at pH = 3 [36]. This decrease in MC-LR degradation is rather caused by inhibition of PMS decomposition than reduced reactivity of SO₄⁻ at acidic pH.

**Electrochemical oxidation**

In an electrolytic process, pollutant oxidation can occur directly, via electron transfer to the anode surface and indirectly, via electrochemically formed reactive species including •OH, H₂O₂, O₂ (eqs. (40)-(42)) and others depending on electrolyte composition, which is why it is also referred to as electrochemical AOP (EAOP). Based on the setup of the treatment cell, EAOPs can be grouped into four different classes. The simplest is direct and indirect anodic oxidation (AO) of a pollutant. At neutral or acidic pH and in the presence of air or O₂, H₂O₂ can additionally be generated by cathodic reduction (eq. (43), AO-H₂O₂). To further increase the treatment, Fe²⁺ can be added to yield •OH (electro-Fenton, EF). In EF, continuous cathodic electrogeneration of H₂O₂ and cathodic Fe³⁺ regeneration to Fe²⁺ (eq. (44)) perpetually produce the Fenton's reagent if an undivided cell is used (see the chapter on Fenton oxidation). If EF is exposed to light (photoelectro-Fenton, PEF), the Fenton reaction itself can be improved by photolytic H₂O₂ cleavage to •OH (see the chapters on photolysis and Fenton oxidation). In EAOPs, non-active anodes with high O₂-overpotential (potential for O₂ development) such as boron-doped diamond anodes (BDD) are usually employed. The higher the O₂-overpotential, the weaker is the physisorption of •OH to the anode surface, which, in turn, leads to higher •OH availability in the solution [90].

*See formulas 40 - 44 in the supplementary files section.*

Where $M(/\cdot \cdot \cdot \cdot )$ means •OH is physisorbed to the anode surface $M$. Electrochemical oxidation of MC, NOD and CYN has been investigated with different electrodes and treatment parameters [120, 128–131]. One of the most influential factors in terms of degradation effectiveness and operating costs are the electrodes used in EAOPs. BDDs are often used due to their high O₂-overpotential, and regardless of the used electrolytes, achieved higher MC-LR degradation compared to mixed metal oxide electrodes such as IrO₂-Ta₂O₅/Ti [130]. Even when coated onto Ti as carrier material, MC-LR removal was in order of Ti/BDD > Ti/IrO₂ > Ti/Pt > Ti/SnO₂ under otherwise same conditions [129]. However, BDD electrodes are costly and cheaper alternatives such as electrodes synthesized from nanosized TiO₂ coated onto a graphite carrier were efficient for MC-LR degradation [128].

Besides electrode material, the applied current affects the degradation efficacy with higher current densities resulting in higher toxin removal [120, 129]. The efficacy of an EAOP also depends on the electrolyte composition and its electric conductivity. For instance, MC-LR degradation in filtered lake and tap water improved after increasing the conductivity by adding Na₂CO₃ [128, 132]. The electrolyte composition also dictates which reactive species are produced and thus, EAOPs can be tailored towards specific requirements and pollutants. Although the order of cyanotoxin removal for electrolyte salts is usually Cl⁻ > SO₄²⁻ > NO₃⁻ > CO₃²⁻ [129, 133, 134], SO₄²⁻ is often suggested as best choice because of lower production of toxic disinfection byproducts from halogen-based electrolytes and avoidance of eutrophication from N- and P-based electrolytes [129, 134]. The risk of halogenated byproducts can be reduced at low salt concentrations and higher current densities but this would, in turn, increase electric energy demand [133].

Influence of water parameters on degradation of cyanotoxins by EAOPs have only scarcely been investigated but studies showed NOM scavenging of produced reactive species [130]. For the effect of pH on MC-LR degradation by EAOPs, contradicting observations were reported. While Zhang et al. [135] found no significant effect on MC-LR degradation rate constants across a range of pH from 5 to 9, Zhou et al. [130] observed higher MC-LR degradation at lower pH. Both studies used different electrolytes (NaNO₃ and Na₂SO₄, respectively), which may explain the different results. In a photoelectrocatalytic treatment of MC-LR using Ag/AgCl/TiO₂ nanotubes electrodes, the degradation appeared to be pH-dependent due to more effective adsorption to TiO₂ under acidic pH and a lower potential level of the valence band of the photoelectrode at alkaline pH which decreased MC-LR oxidation [89].

**Sonolysis**

In sonolysis, ultrasound is used to form liquid-free cavities, i.e. bubbles, in a liquid medium due to rapid changes in pressure created by an oscillating ultrasonic wave. When these bubbles collapse, high energy is released in form of average bubble temperatures of 4200 K
and pressures of 500 atm [10]. Volatile and nonpolar pollutants can be degraded in the cavitation by direct pyrolysis, thermolysis, hydrolysis or hydroxylation with H·OH formed from the gas-phase thermolysis of water (eq. (45)) [10]. Besides acoustically, i.e. due to ultrasound, cavities can also be formed hydrodynamically, where cavities are generated when a liquid is forced to flow under reduced pressure which leads to a local drop of the static pressure to below the critical value. This can be achieved e.g. by a local increase of the flow rate, flow line curvature or channel constrictions [136].

See formula 45 in the supplementary files section.

Non-volatiles and compounds with an amphiphilic or less polar character are degraded in the interfacial boundary layer between the bubble and bulk where temperatures of up to 2000 K and high H·OH concentrations are present. Non-volatile and polar compounds are degraded in the bulk aqueous phase by H·OH migrating away from the cavitation or H2O2 formed in the system [10]. The degradation effectiveness thus depends on the pollutant’s physico-chemical properties and preferred chemical environment, i.e. polar/nonpolar or volatile/non-volatile [137]. Besides pyrolysis, thermolysis and chemical reactions, shockwaves and high shear forces are released, which can be utilized e.g. to destruct and lyse cyanobacterial cells [10]. Depending on the pollutant and desired processes, the ultrasonic wave frequency can be adjusted to favor formation and reactions of H·OH (200-600 Hz) or higher temperatures and pressures (< 200 Hz) [10].

So far, studies focused solely on the sonolytic treatment of MCs [137–140], and the highest degradation was observed in the approximate frequency range of 150-410 kHz. Both lower and higher frequencies resulted in less effective degradation due to lower H·OH concentrations [139, 140]. An increase in the applied power yielded higher MC degradation but the degradation rate was substantially faster only in the first few minutes of the treatment and later became indistinguishable when comparing 30, 60 and 90 W [140]. In addition to the power (in W) or intensity (in W cm⁻²), the distribution of the ultrasound within the treated area affects the treatment efficiency [10]. A study with different radical scavengers showed, that about 39 % of the degradation was achieved by H·OH in the bulk solution and about 35 % degradation was achieved by H·OH at the bubble interface [138]. Due to its non-volatile and polar character, MC-LR is not expected to reside inside the cavity but the nonpolar Adda side chain most likely resides in the bubble interfacial region [138]. MC-LR degradation can be improved under acidic conditions that increase the hydrophobicity of the Adda moiety [138]. Some MC degradation can also be attributed to hydrolysis and pyrolysis in the interfacial region, while shear forces are unlikely to cause mechanical destruction of the toxin [138]. Also H2O2 is produced in sonolytic processes and can act as a quencher reducing the MC-LR degradation, it can simply be overcome by adding Fe²⁺, which eliminates H2O2 and further increases H·OH formation (for the chapter on Fenton oxidation) [137]. Interestingly, NOM, e.g. from cyanobacterial cells, appeared to only have a small effect on the treatment effectiveness [138].

Radiolysis

Radiolysis uses ionizing radiation with energies of approximately 100 eV, which is substantially higher than energies usually required for ionization of organic compounds (< 15 eV) and cleavage of chemical bonds (1-5 eV) [141]. Commonly used radiation sources are radionuclides and electrostatic accelerators emitting γ-radiation and electron beams, respectively [141, 142]. Radiolysis requires specialized instrumentation and expertise which is rare in water treatment facilities. However, because it produces a range of reactive chemical species in water and no precursors or other additives are needed, it can be useful for in-depth studies of oxidation mechanisms. The radiolytic decomposition of water is shown in the following equation (radiation yields G (in µmol J⁻¹) are given in parentheses) [142, 143]:

See formula 46 in the supplementary files section.

So far, only studies with MCs, CYN and ANTX used radiolysis [19, 143–145]. The rate constants for H·OH attacking specific functional moieties of MC-LR were determined in the following order: benzene ring in Adda moiety (10¹⁰ M⁻¹ s⁻¹) ≥ diene in Adda moiety (10¹⁰ to 10⁹ M⁻¹ s⁻¹) > aliphatic hydrogens (10⁸ M⁻¹ s⁻¹) [143]. Although hydrogen abstraction is the slowest reaction pathway, it is still assumed to be significant due the large number of > 50 potential reaction sites [143]. The overall calculated rate constant for the reaction of H·OH with MC-LR (using literature values for appropriate surrogates, mainly amino acids) 2.1 x 10¹⁰ M⁻¹ s⁻¹ [143], is very close to the experimentally derived rate constant 2.3 x 10¹⁰ M⁻¹ s⁻¹, for which the H·OH attack at the Adda group accounted for almost 70 % in the model [143]. For CYN, the overall rate constant of 5.1 x 10⁹ M⁻¹ s⁻¹ was measured with the uracil side chain being the main susceptible moiety for H·OH attacks (84 %), whereas the attack at the guanidine group is less important [61]. In another study, the rate constants for the reaction of H·OH with MC-LR and CYN using radiolysis were determined to be within the same order of magnitude, 1.1 x 10¹⁰ M⁻¹ s⁻¹ and 5.5 x 10⁹ M⁻¹ s⁻¹, respectively [19]. The negligibly different factors are most likely caused by differences in the experimental
conditions and methodologies used in the different studies. The order of rate constants was found to be MC-LR > CYN > ANTX, which corresponds to the toxins’ molecular size and number of H-atoms that can be abstracted by \( \cdot \text{OH} \) [19].

The efficiency of radiolytic treatment of MCs is dose-dependent and can be improved by adding \( \text{Na}_2\text{CO}_3 \) or \( \text{H}_2\text{O}_2 \) which leads to the formation of \( \text{HO}_2 \) and \( \cdot \text{OH} \), respectively [144]. In contrast, nitrite and nitrate were shown to decrease the removal due to scavenging of \( \cdot \text{OH} \) [144]. Furthermore, since \( \cdot \text{OH} \) is a non-selective oxidant, radiolytic treatment can obviously be impacted by water quality parameters such as NOM [19, 145].

**Comparison Of AOPs**

**Degradation efficiency of AOPs**

When comparing different AOPs, especially considering their application in large-scale water treatment, degradation efficiency is amongst the most crucial parameters. It relates the required energy, oxidant or catalyst dose to the efficacy of the treatment. For energy efficiency of AOPs, electrical energy per order (\( \text{E}_{\text{EO}} \)) is often chosen as a figure of merit. \( \text{E}_{\text{EO}} \) is defined as electrical energy in kWh required to remove a pollutant by one order of magnitude, i.e. 90 \%, in 1 m³ of water [146]. In case of oxidants or catalysts, the “stored electric energy” of a compound can be calculated based on prices for electric energy (price per kWh) and the respective compound (price per kg) [147].

Based on a comprehensive review on AOPs for water treatment and data on their energy efficiency reported in peer-reviewed literature, Miklos et al. [146] grouped established and emerging AOPs according to their \( \text{E}_{\text{EO}} \) values (Fig. 3). According to this review, most reported \( \text{E}_{\text{EO}} \) values did not include auxiliary oxidants or catalysts in the calculations. The first group comprises AOPs with median \( \text{E}_{\text{EO}} \) values of < 1 kWh m⁻³ which represents a realistic range for full-scale application. The second group includes AOPs with median \( \text{E}_{\text{EO}} \) values of 1-100 kWh m⁻³ which energy extensive but in case of specific problems, these AOPs may provide an attractive solution, also for eventual large-scale applications. The last group contains AOPs with median \( \text{E}_{\text{EO}} \) values of > 100 kWh m⁻³ which are currently not considered to be energy efficient [146]. Nevertheless, future developments may lead to optimization and reduction of energy demands and related costs.

\( \text{E}_{\text{EO}} \) values for cyanotoxin removal by AOPs have only rarely been reported. For UV/H₂O₂ treatment of MC-LR and CYN, \( \text{E}_{\text{EO}} \) values were 4.5 × 10⁻³-6.1 × 10⁻³ and 1.6 × 10⁻³ kWh m⁻³, respectively [40, 148]. For UV/PMS and UV/PS treatment, \( \text{E}_{\text{EO}} \) values were estimated to range from 10⁻⁴ to 10⁻⁵ kWh m⁻³, respectively, for CYN, and 0.7 and 0.2 kWh m⁻³, respectively, for MC-LR [40, 126]. For electrochemical oxidation of MC-LR, the \( \text{E}_{\text{EO}} \) ranged from 48 to 67 kWh m⁻³ depending on electrode material [129]. These \( \text{E}_{\text{EO}} \) values seem to agree with the results by Miklos et al. [146]. However, for UV/TiO₂ treatment, low \( \text{E}_{\text{EO}} \) values, approximately 0.08 to 0.14 kWh m⁻³, were reported for MC-LR and 0.03 to 0.015 kWh m⁻³ for MC-LR-LA and -RR in two independent studies [126, 149] which are at least two to three orders of magnitude lower compared to the results by Miklos et al. [146]. Although energy efficient UV-LEDs were used in the second study [149], the light source itself seems not to have a substantial effect since demanding UV xenon lamps were used in the study of Antoniou et al. [126].

Interestingly, process capacity, i.e. laboratory-, pilot and full-scale application, was inversely correlated with \( \text{E}_{\text{EO}} \) values which decreased with increasing process capacity. This indicates that up-scaling apparently improves energy efficiency and the demands derived from laboratory-scale experiments may not be correctly translated to full-scale processes. Furthermore, water quality (pure, drinking, ground- and wastewater) did not affect \( \text{E}_{\text{EO}} \) values significantly, even when relevant parameters such as NOM, UV transmittance and turbidity were considered [146].

**Potential of disinfection byproduct formation**

An important aspect is the formation of toxic disinfection byproducts (DBPs) during AOP treatment, where halogenated organic and inorganic compounds such as trihalomethans, haloacetic acids, haloacetonitrils, chlorates, bromates and others are of special concern [146]. Because of their toxicity, the WHO recommended guideline values for several DBPs like chloroform (300 μg L⁻¹), bromoform (100 μg L⁻¹), perchlorate (70 μg L⁻¹) and bromate (10 μg L⁻¹) [150–152]. DBP formation depends on the employed AOP as well as the water matrix, i.e. presence of nitrogen, organic matter and halogens [146].
Formation of bromate is relevant for O₃ and O₃-based AOPs, where up to 50 % of bromide (at concentrations > 100 μg L⁻¹) can be converted to bromate [146], and •OH may promote bromate formation by about 30-70 % [153]. Attenuation is possible by decreasing pH, O₃ or bromide concentration and in the presence of H₂O₂ [153, 154]. Chlorate formation by O₃ and O₃-based AOPs may only be relevant if the treatment contains a pre-chlorination step [146].

In most •OH-dominated AOPs, bromate formation can usually be neglected in the abundance of organic matter or H₂O₂ due to radical quenching [146, 154]. Chlorate and perchlorate are only produced under specific conditions when reactive chlorine species are abundant, which may further react with organic matter to form halogenated DBPs. Generally, DBP formation by •OH is considered to be noncritical with the exception for some approaches like high density •OH generation at electrode surfaces in EAOPs [146].

For SR-AOPs, bromate formation is effectively inhibited by small concentrations of organic matter [146, 154] but reactions of SO₄²⁻ with chloride may produce Cl⁻ and subsequently chlorate at pH < 5 [154].

UV irradiation does not produce inorganic DBPs but can form nitrite due to photolysis of nitrate which may subsequently lead to the formation of nitrated aromatic compounds. In UV/chlorine processes, organic halides can be formed at alkaline pH and chloride concentrations of > 1 g L⁻¹ [146].

Practical, environmental and economic considerations

Besides treatment efficiency, other relevant factors may impact the choice of AOP for a specific situation. Table 2 summarizes advantages, disadvantages and potential ways to overcome certain drawbacks of discussed AOPs considering mainly practical, environmental and economic aspects.

Conclusion

Cyanobacterial blooms and toxins evidently pose a serious risk to drinking water and human health. Although cells and intracellular toxins can effectively be removed by conventional treatment, dissolved cyanotoxins require more advanced treatment such as AOPs based on reactive species including •OH, SO₄²⁻ and other mechanisms.

However, treatment efficacy is strongly impacted by water quality parameters, where, for example, NOM, alkalinity and pH can impact reactive species stability and abundance, while pH also determines toxin speciation and susceptibility to degradation. Furthermore, NOM, chloride and bromide may function as precursors for toxic DBPs. Hence, AOPs, especially their process parameters, need to be optimized for individual situations also considering economic aspects such as operational and maintenance costs.

So far, most studies focused on single toxin removal in either pure or “simulated surface water”. More research is thus needed on the degradation of environmentally relevant cyanotoxin mixtures, which are likely to co-occur in the environment, in actual surface water or water withdrawn from a drinking water treatment process prior to the oxidation step. Further, various degradation products have been tentatively identified in different studies but eventual residual toxicity of the treated cyanotoxin solution is rarely examined. Adequate toxicological assays can be recommended to ensure that toxins are not only degraded but actually detoxified, especially if degradation products are not analyzed or if DBPs are likely to be produced during the treatment process.

It was also found that efficiency as well as estimated operational and maintenance costs of an AOP at laboratory-scale do not easily translate to full-scale treatment. Hence, there is a need for more research of pilot- and full-scale applications to promote AOPs and provide essential information to drinking water treatment plant operators. For instance, photocatalysis for water treatment has been studied for decades but there are still not many, if any at all, full-scale drinking water treatment applications.

Finally, since cyanotoxins will most likely not be the only challenge to a drinking water treatment facility, a combination of different treatment methods, including different AOPs, in a multi-barrier approach needs to be considered to produce harmless, high quality drinking water.

Declarations

Ethics approval and consent to participate

Not applicable.
Consent for publication

Not applicable.

Availability of data and material

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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Author's contribution

MS performed the literature research and drafted the manuscript, LB revised the text. Both authors read and approved the final version of the manuscript.

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Abbreviations

A: Alanine; AC: Activated carbon; ANTX: Anatoxin-a; AO: Anodic oxidation; AOP: Advanced oxidation process; BDD: Boron-doped diamond; BMAA: β-N-methylamino-l-alanine; CYN: Cylindrospermopsin; DBP: Disinfection byproduct; EAOP: Electrochemical advanced oxidation process; EEO: Electrical energy per order; EF: Electro-Fenton; GTX: Gonyautoxin; GV: Guideline value; L: Leucine; LED: Light-emitting diode; MC: Microcystin; NOD: Nodularin; NOM: Natural organic matter; NTP: Non-thermal plasma; PBS: Phosphate-buffered saline; PCB28: 2,4,4'-Trichlorobiphenyl; PEF: Photoelectro-Fenton; PET: Polyethylene terephthalate; pKₐ: Negative decadic logarithm of the acid dissociation constant; PVC: Polyvinyl chloride; PMS: Peroxymonosulfate; PS: Peroxydisulfate, persulfate; R: Arginine; SHE: Standard hydrogen electrode; SR: Sulfate radical; STX: Saxitoxin; t₁/₂: Half-life; TDI: Total daily intake; US EPA: United States Environmental Protection Agency; UV: Ultraviolet; Vis: Visible; WHO: World Health Organization; Y: Tyrosine

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### Tables

**Table 1** Redox potentials of commonly used oxidants indicating their reactivity.
| Oxidant                              | pH range          | Redox potential in V/SHE \(^a\) |
|--------------------------------------|-------------------|----------------------------------|
| Sulfate radical (SO\(_4^{\text{-}}\)) | Acidic to neutral | 2.5-3.1 \(^b\)                  |
| Hydroxyl radical (\(\text{HO}^{\cdot}\)) | Acidic            | 2.7 \(^b\)                      |
|                                      | Neutral to alkaline | 1.8 \(^b\)                      |
| Ferrate ([FeO\(_4^{2-}\)]\(^2\))    | Acidic            | 2.2 \(^c\)                      |
|                                      | Alkaline          | 0.7 \(^c\)                      |
| Ozone (O\(_3\))                     | Acidic            | 2.1 \(^b\)                      |
|                                      | Alkaline          | 1.2 \(^b\)                      |
| Peroxydisulfate (S\(_2\text{O}_8^{2-}\)) | Acidic            | 2.0 \(^b\)                      |
| Hydrogen peroxide (H\(_2\text{O}_2\)) | Acidic            | 1.8 \(^b\)                      |
|                                      | Alkaline          | 0.9 \(^b\)                      |
| Peroxymonosulfate radical (SO\(_{5}^{\cdot}\)) | Acidic            | 1.8 \(^b\)                      |
| Peroxymonosulfate (HSO\(_5^{\cdot}\) or SO\(_3^{2-}\)), \(\text{pK}_{a} = 9.4\) | Acidic            | 1.8 \(^b\)                      |
| Hydroperoxy radical (HO\(_2^{\cdot}\)) | -                 | 1.7 \(^e\)                      |
| Permanganate (MnO\(_4^{\cdot}\))    | Acidic            | 1.7 \(^b\)                      |
|                                      | Alkaline          | 0.6 \(^b\)                      |
| Hypochlorous acid (HOCl)             | -                 | 1.5 \(^d\)                      |
| Chlorine (Cl\(_2\))                 | -                 | 1.4 \(^e\)                      |
| Chlorine dioxide (ClO\(_2\))        | -                 | 1.3 \(^e\)                      |
| Peroxymonosulfate radical (SO\(_5^{\cdot}\)) | Neutral          | 1.1 \(^d\)                      |
| Sulfite radical (SO\(_3^{\cdot}\))  | Neutral           | 0.6 \(^d\)                      |

\(^a\) SHE = Standard Hydrogen Electrode; \(^b\) [35]; \(^c\) [10]; \(^d\) [36]; \(^e\) [13].

**Table 2** Advantages, disadvantages and measures to overcome drawbacks [in brackets] of different AOPs considering practical, environmental and economic aspects.
| AOPs                        | Advantages                                                                 | Disadvantages                                                                 |
|-----------------------------|----------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Ozonation and O₃-based AOPs | • Ozonation widely employed in water treatment                            | • Toxicity of gaseous O₃ [Needs O₃-destructor and sufficient ventilation for  |
|                             | • O₃ is more selective than ·OH and less affected by NOM                   | safe working environment a]                                                   |
|                             | • O₃ decomposes to ·OH in water                                            | • O₃ production is expensive b                                                |
| Photolysis                  | • UV often used for disinfection                                          | • Dissolved O₃ stability is affected by pH and alkalinity                     |
|                             | • Pollutant degradation requires high UV doses [UV-LEDs are mercury-free,  | • Turbidity reduces penetration depth and attenuates light [Requires removal  |
|                             |   have longer lifetime, low energy demand and operational costs c, d]     | of turbidity prior to treatment; NOM can act as photosensitizer and improve    |
|                             | • Gas discharge-based UV lamps have relatively short lifetime and high    | degradation]                                                                   |
|                             |   energy demand [UV-LEDs are mercury-free, have longer lifetime, low      | • Chlorine may yield toxic halogenated byproducts                             |
|                             |   energy demand and operational costs]                                     |                                                                               |
| Photolysis in combination   | • UV often used for disinfection                                          |                                                                               |
|   with oxidants             | • UV/H₂O₂ forms two ·OH due to homolytic cleavage                        | • Turbidity reduces penetration depth and attenuates light [Requires removal  |
|                             | • H₂O₂ is easy to handle and environmentally sound                        | of turbidity prior to treatment]                                              |
|                             | • Chlorine more readily activated by UV cheaper compared to H₂O₂          | • Gas discharge-based UV lamps have relatively short lifetime and high energy  |
|                             | • Chlorine may yield toxic halogenated byproducts                         |   demand [UV-LEDs are mercury-free, have longer lifetime, low energy demand   |
|                             |                                                                               |   and operational costs]                                                     |
| Photocatalysis              | • UV often used for disinfection                                          | • TiO₂ requires UV activation [Doping with other elements allows use of visible |
|                             | • Most often used catalyst TiO₂ is non-toxic and cheap e                   |   and solar light; UV-LEDs are mercury-free, have longer lifetime, low energy  |
|                             | • Pollutant degradation directly by catalyst and indirectly by reactive    |   demand and operational costs]                                              |
|                             |   species                                                                  | • Turbidity reduces penetration depth and attenuates light [Requires removal  |
|                             |                                                                               |   of turbidity prior to treatment]                                           |
| Fenton oxidation            | • Iron is highly abundant and non-toxic, H₂O₂ is easy to handle and      | • Requires acidic conditions with optimum pH ≈ 3 reported [Heterogeneous or   |
|                             |   environmentally sound                                                    |   immobilized catalysts may extend pH range]                                |
|                             | • Relatively inexpensive reagents and no energy demand                    | • Release of iron (or other transition metals) into water or deposition into   |
|                             | • Can use also e.g. ferric iron or other transition metals                |   sludge [Requires sludge removal and its treatment; use of heterogeneous or   |
|                             | • Potential incorporation of Fenton into iron-based coagulation by addition|   immobilized catalyst reduces environmental release]                          |
|                             |   of H₂O₂  f, g                                                           |                                                                               |
|                             | • Photo- and sono-Fenton increase efficacy and reduce costs, especially   |                                                                               |
|                             |   for solar photo-Fenton                                                   |                                                                               |

Non-thermal plasma
• Reagent-free treatment
• Continuous production of reactive species, electrons and photons
• Degrades pollutants persistent to other AOPs
• Residual oxidative and disinfective effect of plasma treated water, which may reduce energy demands and costs; alternative to post-chlorination avoiding chlorine taste and odor

Sulfate radical-based AOPs

• Various ways of PMS and PS activation, where activation by redox reactions reduces costs
• Continuous production of reactive species in electric discharges and electrochemical processes
• High reactivity across broad pH spectrum
• \(SO_4^{2-}\) can degrade pollutants resistant to \(\cdot OH\)
• Lower energy for cleavage of peroxide bond in PS
• \(SO_4^{2-}\) less affected by NOM and alkalinity than \(\cdot OH\)

Electrochemical oxidation

• Large number of commercial electrolytes and electrodes
• Pollutant degradation directly at electrodes and indirectly by reactive species
• Continuous production of reactive species

• Catalytic electrodes (Ti, Ir, Pt, BDD) have high efficiency, but are more expensive than metallic (Cu, Fe, Zn) which can produce secondary contamination
• Cheap and environmentally sound alternatives proposed – e.g. Ti-coated C-electrode made from pencils or carbon sticks from recycled batteries
• Cl-based electrolytes may lead to formation of halogenated byproducts
• N- and P-based electrolytes increase N and P in water (eutrophication)

Sonolysis

• Reagent-free and clean technology
• Pollutant removal by chemical reactions, thermo- and pyrolysis, and shockwaves and shear forces
• Easy scale-up of hydrodynamic cavitation processes
• Higher energy inputs increasing the treatment costs [Optimization towards lower frequencies may reduce energy demand; combination with other AOPs reduces costs; hydrodynamic cavitation avoids noise, energy demand and costs]
• Treatment of large volumes requires greater number of ultrasound transducers
• Cavitation is a violent process destructive to materials and requires periodical maintenance

Radiolysis

• Homogeneous system
• Use of scavengers produce specific or single reactive species valuable for studying degradation mechanisms
• High capital costs and safety measures
• Rather unsuitable for large-scale drinking water treatment
Figures

Figure 1

Structures of cyanobacterial hepatotoxins.
Figure 2

Structures of cyanobacterial neurotoxins.
Grouping of established and emerging AOPs according to their median EEO values (based on the review by Miklos et al. [146]).

**Supplementary Files**

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