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D5.1 Compilation of state-of-the-art water treatment methods for toxins

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RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

1. Objective(s) of D5.1

The general aim of this deliverable is to discuss the state-of-the-art regarding water treatment methods for natural toxins. Reviewing the currently available scientific literature regarding the removal of natural toxins from drinking water is necessary to obtain an overview of the focus in research. It leads to a better understanding of the current state-of-the-art removal techniques used to treat contaminated water. Consequently, it helps to identify information gaps related to the topic. Since natural toxins are a large and chemically very diverse group of compounds produced by bacteria, fungi, insects, plants, and animals, this deliverable focuses on a selected class - cyanobacterial toxins. Cyanotoxins are in the central focus of the NaToxAq research activities and water treatment options have been explored with regard to major documented public health concerns. Other natural toxins represent a new research topic and information on their removal from water is limited and thus, insufficient for a detailed and critical review (see chapter 4.3 for examples).

2. Strategy for solving the task

The currently available literature reporting on the removal of cyanobacterial toxins from drinking water was thoroughly reviewed. As part of the review and as a basis for this deliverable, the currently available literature was analyzed to reveal the existing knowledge and preferences in research for i) certain cyanotoxins in regard to their removal from drinking water, and ii) treatment techniques employed to remove cyanotoxins from drinking water.

The assessment was done by comparing numbers of publications, i.e. counts, found for specific pre-selected and defined search terms. The search on which the review is based on was conducted before February 27, 2018, using Clarivate Analytics' Web of Science [1] advanced search service version v.5.27.2.

3. Delays and difficulties

There have been no delays.

4. Result

4.1. Cyanotoxins – introduction

Cyanotoxins are secondary metabolites produced by cyanobacteria, forming blooms more frequently nowadays due to the increased eutrophication of waterbodies, potentially leading to an increased global occurrence of cyanotoxins. Cyanobacteria can produce a range of intra- and extracellular hepato-, neuro-, derma- and endotoxic alkaloids with diverse chemical structures including e.g. polycyclic polypeptides, bicyclic amines and the currently only reported naturally occurring organophosphate. Some cyanotoxins, e.g. microcystins, nodularin, cylindrospermopsin, and lyngbyatoxins, have additionally been identified as carcinogens and/or potential endocrine disruptors. Cyanotoxins have been associated with numerous events of partly lethal animal, bird, and human poisonings and hence, pose a major threat to surface waters intended for drinking and recreational purposes. The following cyanotoxin groups, i.e. including derivates/congeners, are particularly addressed in this review: anatoxins (ANTX) including anatoxin-a(S), aplysiatoxins, β -N-methylamino-L-alanine (BMAA), cyanobacterial lipopolysaccharides (LPS), cylindrospermopsin (CYN), lyngbyatoxins, microcystins (MC), nodularin (NOD) and saxitoxins (STX) (see Figure 1 for representatives of each of the cyanotoxin classes).

As cyanotoxins have been identified as toxic contaminants impairing water quality and several of these compounds are not readily degraded in the environment, their technological removal from drinking water employing appropriate treatment is inevitable in order to enable the supply of safe drinking water. Diverse drinking (and waste-) water treatment techniques have been – and still are – developed to ensure high-quality drinking water.

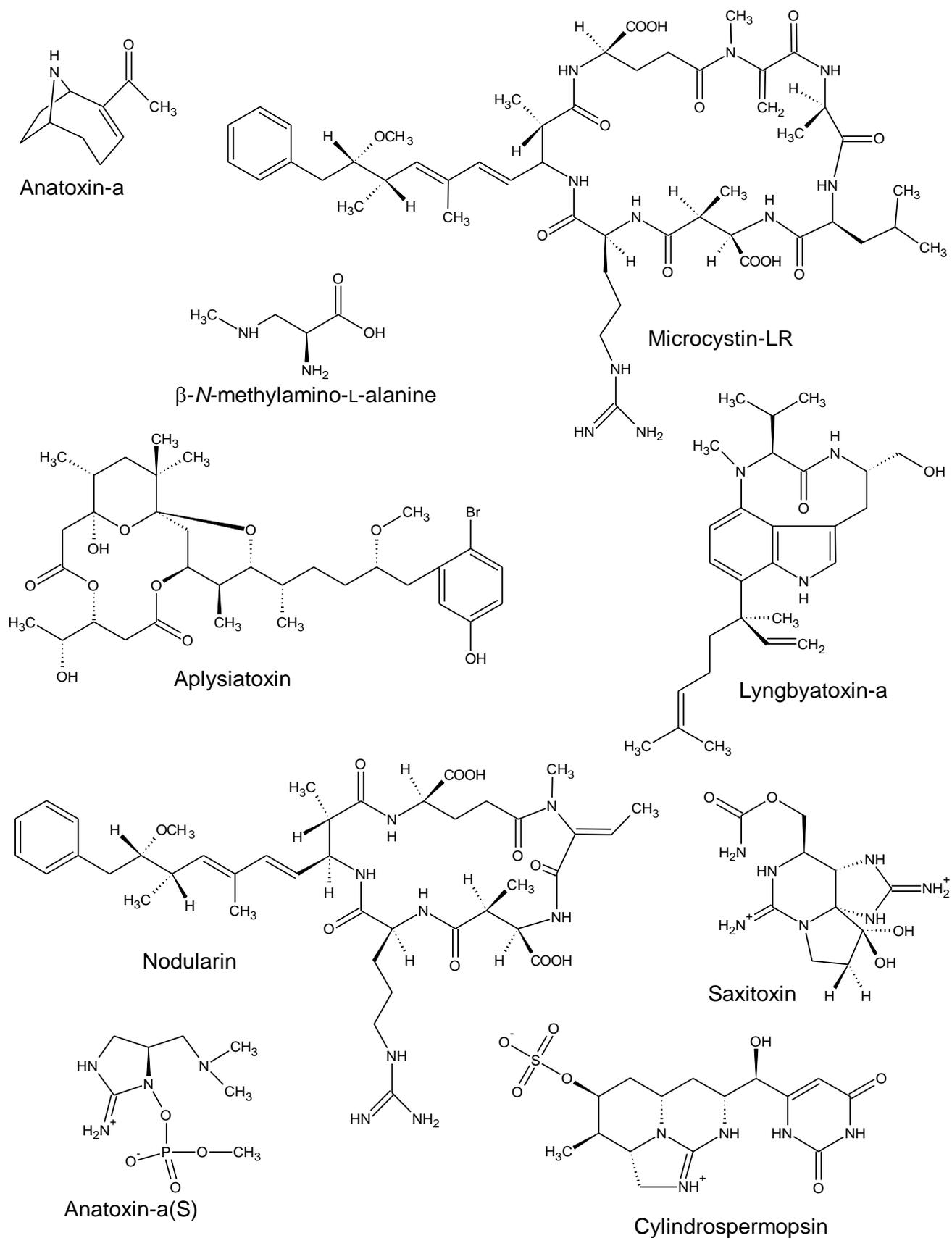


Figure 1: Examples of chemical structures of cyanotoxins: the hepatotoxins microcystin-LR [2], nodularin [3] and cylindrospermopsin [4], the neurotoxins anatoxin-a [5], anatoxin-a(S) [6], β -*N*-methylamino-L-alanine [7] and saxitoxin [8] as well as the dermatoxins aplysiatoxin [9] and lyngbyatoxin-a [10].

4.2. Cyanotoxin removal during water treatment – introduction

In this paper drinking water treatment approaches are grouped into i) Advanced Oxidation Processes (AOPs) and ii) conventional and other emerging treatment techniques.

AOPs are techniques that promote the *in situ* formation of highly reactive radicals and other chemical species and can include other mechanisms. The main reactive species generated in AOP-based techniques is the hydroxyl radical ($\bullet\text{OH}$), which non-selectively reacts with organic chemicals, primarily via addition to electron-rich moieties, e.g. unsaturated C=C bonds and aromatic systems, or abstraction of hydrogen from C-H groups [11,12]. Although ozonation is usually referred to as conventional oxidant, it is stated as AOP in this review, because of the *in situ* formation of $\bullet\text{OH}$ [12,13]. $\bullet\text{OH}$ is highly reactive with second-order rate constants usually ranging from 10^6 to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and having a higher redox potential compared to most of the other commonly used oxidants (see Table 1) [14,15]. AOPs have successfully been used for the treatment of water contaminated with a range of diverse chemical pollutants such as pharmaceuticals and personal care products, endocrine disrupting compounds and other persistent organic pollutants [12,15,16]. Furthermore, cyanobacterial blooms and their secondary metabolites, i.e. cyanotoxins, taste and odor compounds, have also been treated with AOPs [12,17].

Table 1: Redox potentials of several oxidants and reductants widely used for water treatment [12,18–21].

Oxidant/reductant	pH range	Redox potential E^0 (V/SHE)
Sulfate radical ($\text{SO}_4\bullet^-$)	acidic or neutral	2.5-3.1
Hydroxyl radical ($\bullet\text{OH}$)	acidic	2.7-2.8
	alkaline	1.8
Ferrate (FeO_4^{2-})	acidic	2.2
	alkaline	0.7
Ozone (O_3)	acidic	2.1
	alkaline	1.2
Persulfate ($\text{S}_2\text{O}_8^{2-}$)	acidic	2.0
Hydrogen peroxide (H_2O_2)	acidic	1.8
	alkaline	0.9
Peroxymonosulfate (HSO_5^-)	acidic	1.8
Perhydroxyl radical ($\text{HO}_2\bullet$)	-	1.7
Permanganate (MnO_4^-)	acidic	1.7
	alkaline	0.6
Hypochlorous acid (HOCl)	-	1.5
Chlorine (Cl_2)	-	1.4
Chlorine dioxide (ClO_2)	-	1.3
Peroxymonosulfate radical ($\text{SO}_5\bullet^-$)	neutral	1.1
Sulfite radical ($\text{SO}_3\bullet^-$)	neutral	0.6
Solvated electron (e^-_{aq})	-	-2.9

The category “conventional and other emerging treatment techniques” includes methods that have been traditionally used in the removal of diverse water pollutants and toxins, e.g. bank or sand filtration, coagulation and flocculation, adsorption to activated carbon, chemical oxidation and biodegradation, as well as emerging technologies that do not fall among AOPs, but should not be overlooked such as membrane filtration, reverse osmosis and adsorption to alternative adsorbents, e.g. iron- and carbon-based nanoparticles, bioadsorbents and graphene oxide. This category of treatment techniques includes physical separation of pollutants from water as well as chemical and enzymatic conversion of susceptible compounds (see Table 1 for examples of conventional oxidants and their redox potentials). Conventional and other emerging treatment techniques have been shown to successfully remove many different water pollutants such as endocrine disrupting compounds, other organic pollutants, microorganisms, and pathogens, while some methods are additionally used for the removal of particulates and sediments or for disinfection of the distribution system [22–24]. Cyanobacteria, cyanotoxins as well as taste and odor compounds have also been treated employing conventional and other emerging treatment methods [12–14,17].

4.3. Summary and conclusions

In the present paper, the currently available literature was reviewed to obtain an overview of the current state-of-the-art of the removal of cyanobacterial toxins from drinking water and to identify information gaps. Furthermore, the available literature was analyzed to reveal preferences for certain cyanotoxins and treatment methods in the context of the removal of cyanotoxins from drinking water, which also helps to formulate future research needs. The literature analysis was conducted using the Web of Science platform and pre-defined search terms and parameters to generate sets representing the individual toxins and treatment methods, which were then combined and compared. In the following paragraphs, the most important findings and general conclusions are summarized. For a detailed explanation of the methodology of the literature analysis and a more comprehensive review of the literature refer to the ANNEX.

Removal effectiveness

- Although many publications reporting on the use of AOPs for the removal of cyanotoxins introduce their work with the remark, that conventional treatment methods are less efficient than AOPs, approx. 62% of all publications focusing on the removal of cyanotoxins from drinking water report on the application of conventional and other emerging treatment techniques, based on the results of the present work (Figure 2), whereas about 38% report on the use of AOP-based approaches.
- The preference in treatments compared for all cyanotoxins, based on total counts for each treatment in relation to total counts of all treatments can be ranked as follows: adsorption > biodegradation > *photocatalysis* > *photolysis* = filtration > chemical oxidation > flocculation/coagulation > *ozonation* > *Fenton oxidation* > *EAOPs* > *sonolysis* > *NTP-based AOPs* > *SR-AOPs* > *radiolysis* (Figure 2, top left chart). Underlined and italicized treatments refer to conventional and other emerging as well as AOP-based treatments, respectively.

- Although H₂O₂ has a relatively high redox potential under acidic conditions (see Table 1), it was shown to be ineffective if utilized solely [2,25–27], but it is often used in combination with other AOPs to significantly enhance the cyanotoxin removal and is one of the essential ingredients to some of the techniques, i.e. Fenton-based methods.
- As another alternative and apparently more efficient treatment method than H₂O₂ oxidation, phytoremediation has shown to uptake MC-LR and thus, removing it from source water [28].

Specific technology-related issues

- As shown in the respective chapters (see ANNEX), each treatment method has its own technical and economic advantages and disadvantages, which have to be considered before implementing a treatment technique into the treatment chain.
- As not only cyanotoxins are of concern for drinking water safety, most research groups use rather non-toxic and environmentally friendly oxidants, catalysts and reagents.
- In comparison to conventional and other emerging treatment methods, most of the AOPs require substantial energy input, however, due to often higher removal efficiencies and current developments in the production of renewable energy these techniques are still considered to be of high potential for their application in drinking water treatment. Additionally, other disadvantages might be overcome if further research focusing on the optimization, scale-up, and implementation is performed.
- So far, the formation of toxic disinfection byproducts was only observed for ozonation in presence of bromide, and chlorination.
- In general, it is strongly recommended to apply multi-barrier treatment approaches to ensure high drinking water quality, as source waters might not only contain cyanotoxins, but also other quality impairing and regulated substances.

Water parameters and other conditions

- Generally, all treatment techniques are more or less strongly affected by technique-specific and water quality parameters such as pH and NOM content. The pH determines the structure of an oxidant or toxin, as indicated by their p*K_a* value(s) and NOM, as one of the most influential DOC representatives in natural waters, can act as a competitor to the toxin.
- In addition to what is mentioned in the respective chapters (see ANNEX), the removal efficiency of a treatment technique is generally affected by the initial oxidant/light/energy dose, the initial toxin concentration and the contact or reaction time. Obviously, the contact or reaction time needs to be sufficiently long to allow enough time for the interaction between the added or produced oxidative species or other degradation mechanism and the toxin. Similar, at higher initial toxin concentration, high enough doses must be applied to ensure efficient removal.
- Furthermore, at higher initial toxin concentration and depending on the extent and rate of mineralization, more transformation products can be formed which might compete for the reactive species, consequently inhibiting the removal of the parent cyanotoxin [29].

- Several research groups identified transformation products and proposed degradation pathways, which are usually similar if the degradation mechanism is similar, e.g. oxidation at certain sites of a cyanotoxin. Additionally, according to a few studies in which the treatment residuals were tested in different toxicological assays, the identified transformation products seem to be non-toxic [27,30–33]. The only exception so far is the biodegradation of one of the STX variants which was transformed into a more toxic variant [34].
- However, only a few studies actually reported results on the extent of mineralization, measured as either TOC reduction or CO₂ production.

Toxin-specific issues and gaps in knowledge

- Which treatment is most commonly applied for the removal of a certain cyanotoxin depends on the toxin itself. Hence, the orders of preference for a specific treatment for the individual cyanotoxins differ from each other and from the abovementioned ranking for all cyanotoxins. The overall ranking for all cyanotoxins is predominated by MCs, as the highest number of counts was found for this toxin category. However, this overall ranking can still be used for a general overview, as it is based on total counts, showing preferences in specific treatments, regardless of the type of cyanotoxin and as MCs receive the most attention, thus making this class the best representative for all cyanotoxins.
- Surprisingly, although photocatalysis is amongst the most commonly used AOP-based treatments for MCs, CYN, and NOD, and represents the most preferred AOP when searching for all toxins, no publications reporting on the application of photocatalysis for removing the other cyanotoxins, i.e. STXs, ANTXs, BMAA, lyngbyatoxins, aplysiatoxins and cyanobacterial LPS were found. Again, this might be due to the search parameters and terms rather than an actual scientific reason.
- Considering the cyanotoxins, the preference when comparing all treatments, as shown in Figure 9, can be ranked as follows: MCs >> CYN > ANTXs > STXs > NOD > BMAA > aplysiatoxin = lyngbyatoxin = cyanobacterial endotoxins = 0 counts. The significantly higher interest in the removal of MCs can be reasoned by the higher focus on MCs in all cyanotoxin-related research. For example, MC-LR is the only cyanotoxin for which the WHO proposed a provisional guideline value (GV) for drinking water of 1 µg/L, while toxicological and epidemiological data for other cyanotoxins is insufficient for derivation of GVs yet [35]. In addition, as MCs are more frequently studied in general and in terms of removal from drinking water, treatment approaches effectively removing MCs might be assumed to work for the removal of other cyanotoxins as well.
- Consequently, where efficiencies and optimal operational conditions for an individual treatment have been published in a large number of articles for MCs, the same information for the removal of other cyanotoxins might have been condensed in fewer publications, resulting in a larger number of publications for MCs. Furthermore, if the application of several treatments is conjunctly reported in one publication, the article's title might summarize the used methods in one term rather than naming all of them, which would lead to an exclusion from this search and a smaller number of counts for the respective toxin.

- According to the results, CYN is the only toxin category for which a higher number of publications reports on the utilization of AOP-based approaches (approx. 70% of all treatments) compared to conventional and other emerging treatments (approx. 30% of all treatments). Besides the reason for that being of scientific nature, i.e. due to different physico-chemical properties compared to e.g. MCs (see chapter 5.4.2 in the paragraph on CYN), it also might just be because of the used search terms and publication titles, which is expected to be very likely.

It has to be noted, that the present work represents an overview of the current state-of-the-art and focus in research in the removal of cyanotoxins from drinking water applying different treatment techniques showing trends in research interest. The results are expected to change if the search is repeated later for mainly two reasons. First of all, as time goes by, publications might be added which have not been available at the time of this analysis, possibly altering the outcome. And second, if the search terms, Booleans or parameters are altered, the results will most likely change as well. Due to the limitation of this literature analysis to only include counts which mention the respective search terms in the title, it does not reveal the true number of publications focusing on this topic, thus the true research preferences might be different from the results discussed here. However, based on the author's previous knowledge and experience, this difference is expected to be of minor consequence and after all, this work is still presenting a valid overview on the current state-of-the-art.

In conclusion, the author wants to emphasize again, that further research on the less studied cyanotoxins is needed, not only to provide more information on how to remove these compounds but also to help to formulate appropriate threshold values for drinking water. Furthermore, some of the less studied treatment methods, i.e. some of the AOPs provide a huge potential for the removal of cyanotoxins, cyanobacterial cells, and other organic pollutants. This is especially important as adsorption, filtration, and coagulation and flocculation usually only physically remove pollutants. If these are not combined with e.g. biodegradation or other oxidation methods, either proper storage or further treatment of the resulting material is required. Besides that, in most studies, pure toxin standards or extracts were diluted in either MilliQ water or buffered solutions, whereas only a few simulated real matrices using e.g. humic acid as NOM representative and even less used actual surface water as sample matrix. Hence, there is another aspect that needs to receive more attention, e.g. in form of scale-up studies, to reveal how matrix effects in natural waters affect the removal of cyanotoxins from a more complex matrix, if they are accompanied by more than just NOM and cyanobacterial cell residues.

An additional screening of the literature was performed while working on this deliverable. It focused on the removal of other natural toxins from different groups such as alkaloids (e.g. lupinine and others), glycosides (e.g. solanine, ptaquiloside and others), phytoestrogens (formononetin, genistein, daidzein and equol), terpenes (thujone, grayanotoxins and artemisin), proteinogenic (ricin, shiga and shiga-like toxins and others) and other compounds (cicutoxin, glucosinolates, pterodin and others). This literature survey revealed that no or only very limited information on the removal of these compounds from water is currently available. Hence, the lack of information on and apparently interest in the removal of these naturally produced compounds from water might indicate that their relevance to drinking water and water resources is still insufficiently investigated.

5. ANNEX – Detailed methodology and results

The ANNEX provides a detailed description of how the literature search was conducted as well as the results of the literature analysis and review.

5.1. Methodology of the literature search and analysis

The literature search was performed using all databases the Web of Science service offers. Based on pre-selected search terms, 27 sets representing the different toxin and treatment categories were generated and subsequently used for the analysis. During the search, the parameters “timespan”, “auto-suggest publication names” and “search language” were set to “all years”, “on” and “auto”, respectively. The results were not filtered for specific document types to include all available publications.

5.2. Generation of the sets

23 basic sets were generated using specific search terms for the respective treatment and cyanotoxin categories, from which four combined sets (see Table 2) were compiled. Pre-selection of these categories was based on the author’s research focus and prior knowledge on the removal of cyanotoxins from drinking water and treatment techniques. As aforementioned, each cyanotoxin category includes all respective compounds, derivatives, and congeners.

Treatment techniques were grouped as conventional and other emerging treatments and advanced oxidation processes (AOPs) (see Table 2 for the groups). The search was conducted using the title (TI=()) instead of the topic tag (TS=()), to minimize the number of publications whose content is not related to the respective search term, but might be accounted for in the results because the term is mentioned in the article. For example, if searched for topic instead of title using “TS=(**microcystin**) AND TS=(ozon* OR O₃/H₂O₂)” one of the shown articles reports on the degradation of oxcarbazepine by UV/persulfate. It occurs in the results because MCs are mentioned in the introduction to state, that UV/persulfate has shown to be efficient in degrading MC-LR and because the terms “microcystin” and “ozonation” appear in the list of references [36]. Thus, using title instead of topic for the search excludes those non-related publications from the analysis. On the other hand, since only publications with respective search terms included in the title were accounted for, a significant number of publications might be missing if their title does not include any of the used search terms. For example, Al Momani et al.’s article “Degradation of cyanobacteria toxin by advanced oxidation processes” [2] reports results on the degradation of MC-LR and -RR by O₃, H₂O₂, O₃/H₂O₂, O₃/Fe(II) and Fenton oxidation, but since the title does not contain any of the used search terms, it was not accounted for in the analysis.

An asterisk “*” was used to include related terms, e.g. TI=(**fenton** OR Fe(II)/H₂O₂) to find publications related to “Fenton”, “Fenton’s” and “photo-Fenton” or to find congeners and derivatives of cyanotoxins, e.g. TI=(**anatoxin**) to find “Anatoxin”, “Anatoxin-a”, “Homoanatoxin-a” and other variations. The four combined sets (#24 to #27) were generated

by combining respective basic sets via an “OR” Boolean. A list of pre-selected treatment and cyanotoxin categories, generated sets and related search terms is compiled in Table 2.

Table 2: List of basic and combined sets and related search terms.

Set description	Set	Category	Search term/Boolean
Basic sets – cyanotoxins	#1	MC	TI=(<i>*microcystin*</i>)
	#2	CYN	TI=(<i>*cylindrospermopsin*</i>)
	#3	NOD	TI=(<i>*nodularin*</i>)
	#4	STX (incl. gonyautoxins)	TI=(<i>*saxitoxin* OR *gonyautoxin*</i>)
	#5	ANTX (incl. anatoxin-a(S) ¹)	TI=(<i>*anatoxin*</i>)
	#6	BMAA	TI=(<i>*BMAA* OR *methylamino-L-alanine*</i>)
	#7	Aplysiatoxin	TI=(<i>*aplysiatoxin*</i>)
	#8	Lyngbyatoxin	TI=(<i>*lyngbyatoxin*</i>)
	#9	cyanobacterial LPS	TI=(cyanobacterial endotoxin* OR cyanobacterial lipopolysaccharide* OR cyanobacterial LPS)
Basic sets – AOPs	#10	Ozonation	TI=(ozon* OR O3/H2O2)
	#11	Photolysis	TI=(photoly* OR photochemic* OR photodegrad* OR UV OR UV/H2O2 OR UV/persulfate OR UV/ozon* OR UV/O3 OR photo-ozon*)
	#12	Photocatalysis	TI=(photocataly* OR UV/TiO2)
	#13	Fenton oxidation (incl. photo-Fenton)	TI=(<i>*fenton* OR Fe(II)/H2O2</i>)
	#14	Sonolysis (incl. hydrodynamic cavitation)	TI=(cavitation* OR sonoly* OR ultraso*)
	#15	Electrochemical AOPs	TI=(electrochemic* oxidat* OR electrochemic* advanced oxidation OR EAOP* OR *electro-fenton* OR anodic oxidat* OR electrogenerated oxidant* OR electrochemic* inactivat* OR electrochemic* degrad*)
	#16	Non-thermal plasma	TI=(nonthermal plasma OR non-thermal plasma OR cold plasma OR atmospheric pressure plasma OR electric* discharge OR dielectric barrier discharge OR gliding arc discharge OR corona discharge OR discharge plasma)
	#17	Radiolysis	TI=(<i>*radioly* or electron beam or gamma *radiat*</i>)
	#18	Sulfate radical-AOP	TI=(<i>*sulf* radical* or PMS</i>)

¹ The set anatoxin includes both anatoxin-a (and related congeners/derivates) and anatoxin-a(S), which are distinct cyanotoxins but difficult to clearly separate from each other in the search due to their similar names.

Table 2: List of basic and combined sets and related search terms. (continued)

Set description	Set	Category	Search term/Boolean
Basic sets – conventional and other emerging treatments	#19	Biodegradation	TI=(biodegrad* OR biological* degrad* OR biological* treat* OR biological remov* OR microbial degrad* OR microbial treat* OR microbial remov* OR bacterial degrad* OR bacterial* treat* OR bacterial remov*)
	#20	Adsorption	TI=(activated carbon OR activated charcoal OR *sorp* OR sorbent OR PAC OR GAC)
	#21	Filtration	TI=(*filtrati* OR filter OR reverse osmosis)
	#22	Flocculation/coagulation (incl. sedimentation and clarification)	TI=(floccula* OR coagula* OR sedimenta* OR clarificat*)
	#23	Chemical oxidation	TI=(*chlorin* OR permanganate OR ferrat*)
Combined sets	#24	All toxins	#9 OR #8 OR #7 OR #6 OR #5 OR #4 OR #3 OR #2 OR #1
	#25	All treatments	#23 OR #22 OR #21 OR #20 OR #19 OR #18 OR #17 OR #16 OR #15 OR #14 OR #13 OR #12 OR #11 OR #10
	#26	All AOPs	#18 OR #17 OR #16 OR #15 OR #14 OR #13 OR #12 OR #11 OR #10
	#27	All conventional and other emerging treatments	#23 OR #22 OR #21 OR #20 OR #19

5.3. Description of the analysis

For the analysis, respective sets were combined by an “AND” Boolean in order to evaluate the preferences in research and possibly related industry for specific treatment techniques and cyanotoxins. The employed measure is the number of counts, which represents the number of scientific publications related to the searched set or combination of sets. Research preferences in treatment techniques used to remove cyanotoxins were analyzed by combining sets for all and individual toxins with selected treatment methods and comparing total counts for all, AOP-based, conventional and other emerging and individual treatments. Combining sets of all, individual treatments with all and individual toxins and comparing total counts revealed information on preferences on cyanotoxins related to their removal from drinking water. Following the AND-combination of sets, results were analyzed by setting counts of a category, i.e. basic sets, in relation to total counts of all categories belonging to its respective topic, i.e. all, AOP-based or conventional and other emerging treatments or all toxins. Note, that the total counts of a topic, e.g. “all treatments vs. all toxins” does not refer to the combined sets #24 to #27, but to the sum of the counts of all respective basic sets within each of the topics.

Besides not counting publications that do not contain the respective search term within the title as mentioned in chapter 5.2, some articles occur in more than one toxin or treatment category if their title contains search terms of more than one category. For example, Edwards et al.’s article “Biodegradation of microcystins and nodularin in freshwaters” [37] which occurs when searching for the biodegradation of MCs (#1 AND #19) and NOD (#3 AND #19). In terms of treatments, an article might occur in more than one category if either more than one different treatment technique was studied or if different treatments were combined. Counts that occur in more than one toxin or treatment category were not excluded from the results, instead, the number of replicates was determined.

It is important to note, that when repeating the literature search at a later time, results might be different as new publications will be added to the databases as time passes. Similar will happen if search terms or parameters are altered.

5.4. Results and discussion

5.4.1. Evaluation of preferences in scientific literature for certain treatment techniques for all cyanotoxins

In order to evaluate the most commonly reported treatment techniques for all cyanotoxins, set #24 (all toxins) was combined with sets #10 to #23 (individual treatments) and #25 to #27 (all, AOP-based and conventional and other emerging treatments) via an AND Boolean. Results are displayed in Figure 2, with the top left, top right and bottom left charts showing the distribution of counts for all, AOP-based and conventional and other emerging treatment techniques, respectively.

5.4.1.1. Comparison of all treatments techniques

When comparing all treatments, 71 of a total of 589 counts occurred in more than one treatment category. Conventional and other emerging treatments account for approx. 62% of all publications, whereas AOPs only account for 38%. Besides ozonation, photolysis, and photocatalysis, AOP-based treatments are rather new compared to conventional treatments such as filtration and biodegradation and thus, are less commonly applied in drinking water treatment. Industry and related authorities in general, as stakeholders and providers of research funding, represent two of the driving factors having a determining influence on which subjects, problems or challenges are addressed in scientific research. Hence, research might have been focusing on industrially and economically relevant techniques, i.e. conventional and other emerging treatments rather than on exploring novel AOPs such as electrochemical AOPs (EAOPs) or non-thermal plasmas (NTPs). Additionally, scientists and authorities were paying more attention to cyanobacteria and their removal in the beginning, as many of the cyanotoxins had not even been identified back then [38], which might also be a reason for the preference towards conventional and other emerging treatments. More than 1/3 of all publications report on the application of adsorption (19.52%) and biodegradation (18.17%) for the removal of cyanotoxins. Photocatalysis is the most studied AOP and the third most studied of all techniques with 14.43% of all counts, followed by photolysis and filtration (11.21% each) and chemical oxidation (9.17%). Although flocculation/coagulation and ozonation are commonly employed water treatment techniques, they only account for 3.57% and 3.23% of all counts in terms of cyanotoxin removal, respectively. All remaining techniques, i.e. Fenton oxidation, EAOPs, sonolysis, NTP-based methods, sulfate radical (SR) AOPs and radiolysis account for 9.52% altogether. The remaining treatments are all AOP-based methods, ranging from 2.38% (Fenton oxidation) to 0.85% (radiolysis).

5.4.1.2. Comparison of AOP-based treatment techniques

If only AOP-based treatments are considered, 23 of a total of 226 counts appeared in more than one treatment category. As mentioned in chapter 5.4.1.1, photocatalysis (37.61%) is the most commonly reported AOP used for treating cyanotoxins, followed by photolysis (29.20%), which together account for approx. 2/3 of AOP-related counts. The fact, that photocatalysis receives more attention than photolysis is slightly surprising because the main difference is the addition of a photocatalyst. This could be due to higher degradation efficiencies of

photocatalysis and potential reduction of costs [13,18], but it also might be due to the search itself, i.e. used search terms and parameters, rather than an actual scientific reason. Direct and indirect photodegradation are already widely employed for the investigation of the stability and fate of substances in the environment. Although technical or procedural requirements and setups of the photo- and photocatalytic methods applied in drinking water treatment may differ from those used in fate studies, the general mechanistic understanding is already existent and probably much broader than for other techniques that have only been adapted, but were not originally meant for treatment purposes, e.g. NTPs, especially since photolysis is already intentionally used in drinking water treatment. The reported utilization of ozonation, Fenton oxidation, EAOPs and sonolysis ranges from 8.41% to 4.87% in decreasing order. For NTP-based treatments (3.10%), sulfate radical-based AOPs (2.65%) and radiolysis (2.21%) less than ten publications for each category were found within this search. The big gap between e.g. ozonation and photolysis or photocatalysis could be due to the latter one's diversity in terms of experimental parameters and conditions, such as the source and type of light (visible, UV-A, -B or -C, natural or artificial) or type of catalyst. Additionally, techniques such as radiolysis are probably less studied for treatment purposes as the required technical expertise and appliances, operational costs, related safety, and precautionary measures are rather high and intense compared to e.g. Fenton oxidation, which requires a Fe^{2+} salt and H_2O_2 , preferably at acidic pH, as main ingredients [27].

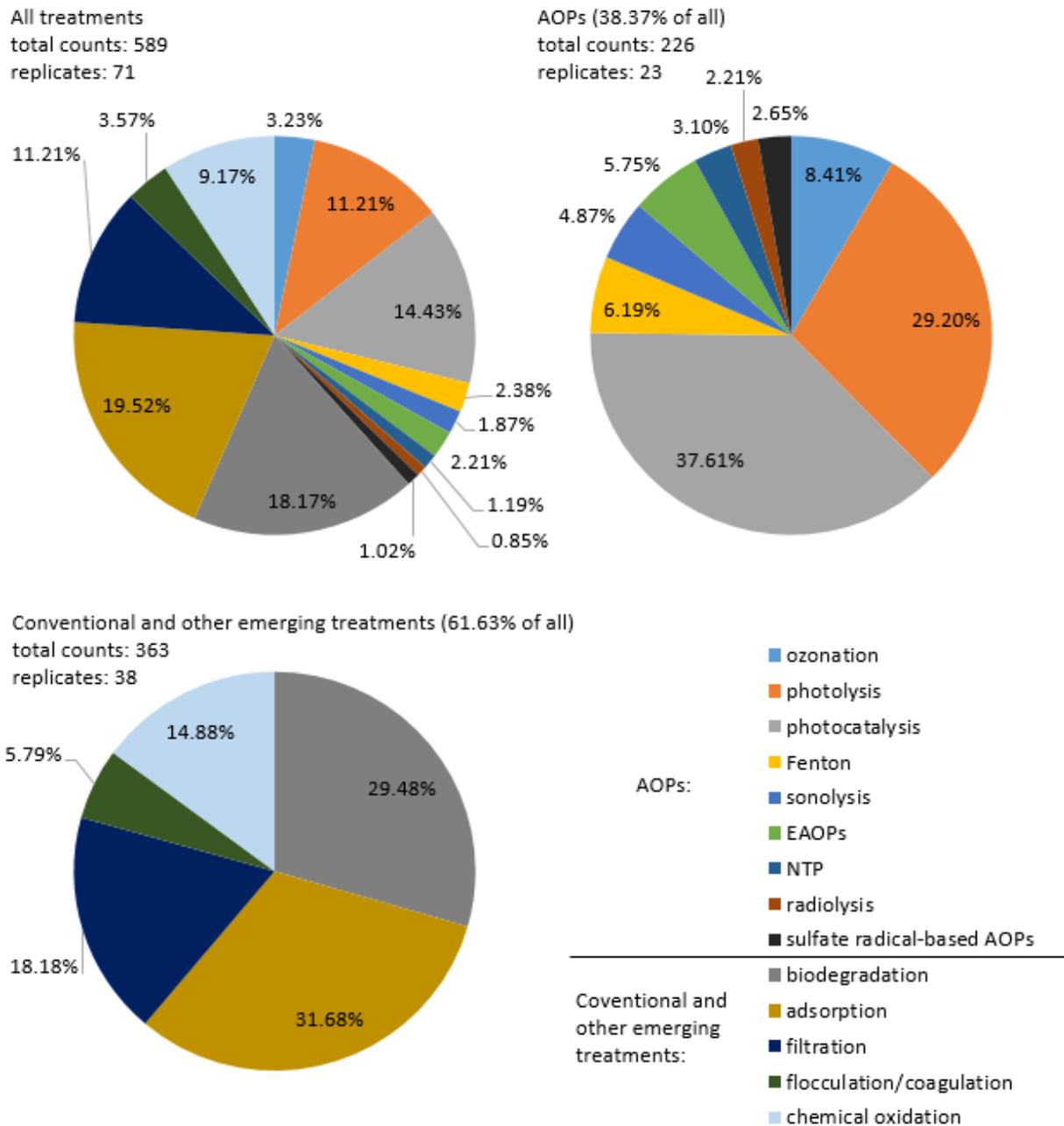


Figure 2: Analysis of the currently available scientific literature for preferences for certain treatment techniques for all cyanotoxins by comparing all (top left), AOP-based (top right) and conventional and other emerging (bottom left) treatments.

5.4.1.3. Comparison of conventional and other emerging treatment techniques

When only conventional and other emerging treatments are compared, 38 of a total of 363 counts occurred in more than one treatment category. Adsorption (31.68%) and biodegradation (29.48%) are the two most applied treatments according to the literature, which together, account for almost 2/3 of all counts. Filtration (18.18%), chemical oxidation (14.88%) and flocculation/coagulation (5.79%) represent the remaining part. Although the flocculation/coagulation approach is widely used in water treatment and is more intensely studied for the removal of cyanobacteria, information on its application for cyanotoxin removal is limited so far. The main goal when treating cyanobacteria is to remove intact cells, in order

to prevent lysis of intracellular substances, such as certain cyanotoxins [39]. As flocculation and coagulation processes are relevant for cyanobacterial cell removal, cyanotoxins might receive less attention, as the intact cells are removed before or without excreting cyanotoxins. Despite that, the true number of counts for flocculation/coagulation related treatment of cyanotoxins might actually be smaller, as some publications report the application of this approach to remove cyanobacterial cells and related effects on cell lysis and release of cyanotoxins rather than the removal of cyanotoxins, but include the respective toxin in the title, e.g. Hou et al.'s article "Changes in *Microcystis aeruginosa* cell integrity and variation in microcystin-LR and proteins during Tanfloc flocculation and floc storage" [39].

One main difference between AOPs and conventional and other emerging treatments is, that all AOPs are able to degrade or even (partially) mineralize the cyanotoxins, whereas only biodegradation and chemical oxidation can degrade and (partially) mineralize the contaminants. In other words, only about 44% of the publications for conventional and other emerging treatments include not only physical removal but the actual degradation of the cyanotoxins. If the cyanotoxins are only physically removed from drinking water, they have to be appropriately handled afterward, by e.g. adequate storage or subsequent degradation. However, several publications report the use combinations of e.g. adsorption or filtration with biodegradation or adding chemical oxidants within the drinking water treatment process employing non-degrading methods.

5.4.2. Evaluation of preferences in scientific literature for certain treatment techniques for individual cyanotoxins

The most commonly applied treatment techniques were also compared for each of the pre-selected cyanotoxins by AND-combining the sets #1 to #9 (individual toxins) with sets #10 to #23 (individual treatments) and #25 to #27 (all, AOP-based and conventional and other emerging treatments). Results are displayed in Figure 3 to Figure 8 for MCs, CYN, NOD, STXs, ANTXs, and BMAA, with the top left, top right and bottom left charts showing the distribution of counts for all, AOP-based and conventional and other emerging treatment techniques, respectively, except for BMAA, which only shows conventional and other emerging treatments.

Microcystins

The distribution of the counts for MCs combined with the individual treatments is similar to what can be seen when comparing the treatment techniques for all toxins (see Figure 2 and Figure 3). For all treatments, 477 publications were found including 57 replicated counts, with 61% of all counts being conventional and other emerging treatments and 39% being AOP-based techniques. The most reported treatments are biodegradation (19.92%), adsorption (18.24%), photocatalysis (15.30%), photolysis (9.85%), filtration (9.64%) and chemical oxidation (9.43%). The remaining techniques flocculation/coagulation, ozonation, Fenton oxidation, EAOPs, sonolysis, NTP-based methods, radiolysis and SR-AOPs range from 3.56% to 0.42% in decreasing order.

From a total of 187 counts, including 33 replications, almost 2/3 of AOP-based treatments reported for the removal of MCs are photocatalysis (39.04%) and photolysis (25.13%). Ozonation, Fenton oxidation, EAOPs, sonolysis, NTP-based methods, radiolysis and SR-based treatments range from 8.56% to 1.07% in decreasing order.

For conventional and other emerging treatments, 33 replicates of a total of 290 counts occurred in more than one treatment category. Biodegradation (32.76%) has the highest share, followed by adsorption (30.00%), filtration (15.86%), chemical oxidation (15.52%) and flocculation/coagulation (5.86%).

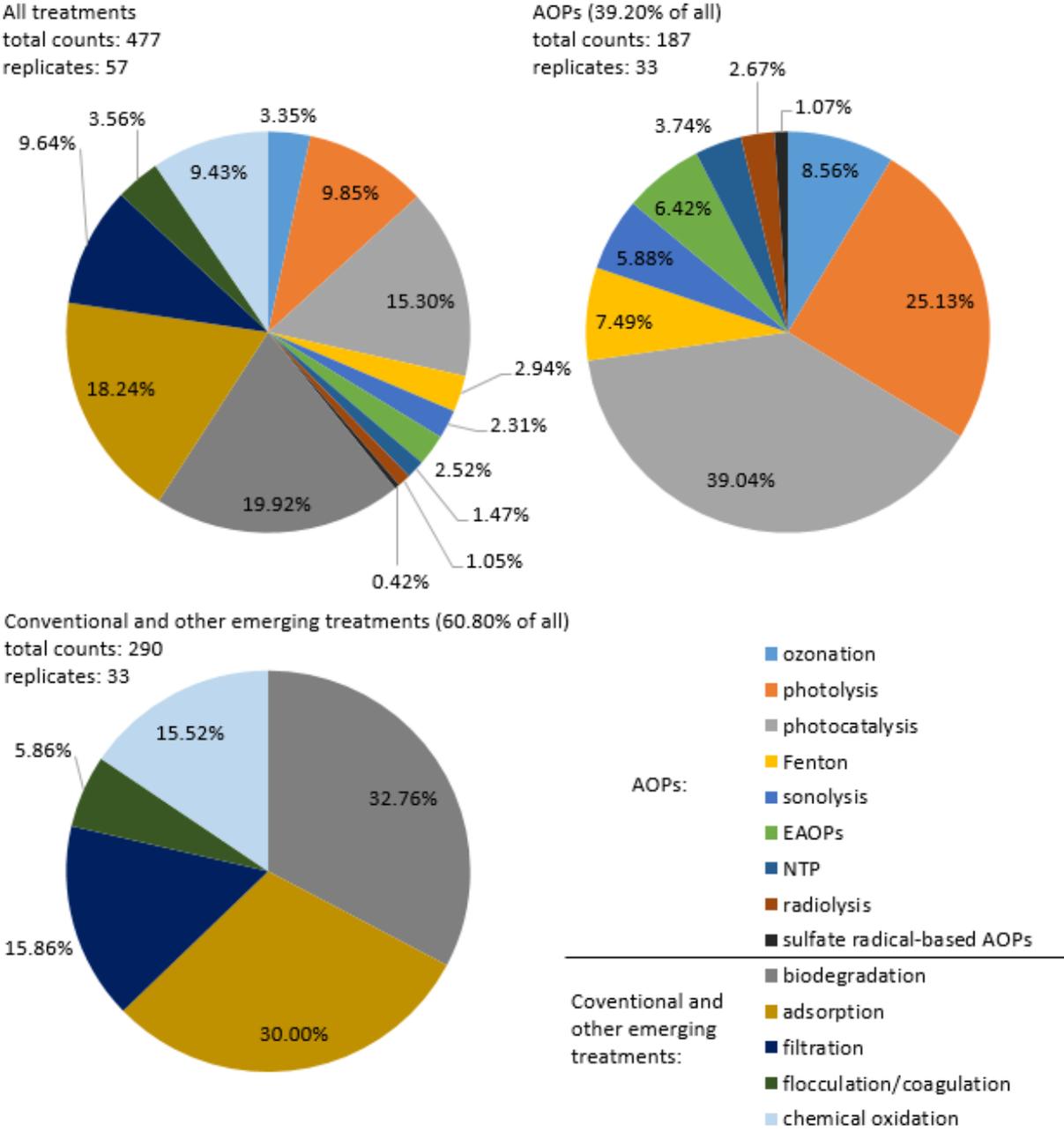


Figure 3: Analysis of the currently available scientific literature for preferences for certain treatment techniques for microcystins by comparing all (top left), AOP-based (top right) and conventional and other emerging (bottom left) treatments.

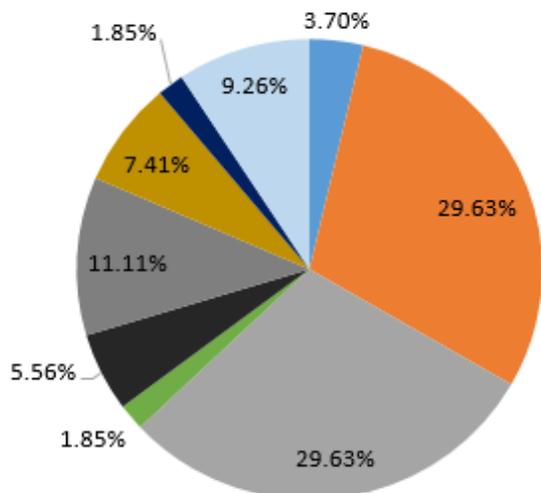
Cylindrospermopsin

When comparing all treatments, nine of a total of 54 counts occurred in more than one treatment category. For CYN, conventional and other emerging treatments only account for approx. 30% of all publications, whereas AOPs account for about 70%, which is obviously different from before. The fact, that not all of the pre-selected treatments were reportedly applied for CYN removal also stands out compared to MCs. Photolysis and photocatalysis each have a share of 29.63% and thus represent more than 1/2 of all publications, followed by biodegradation (11.11%) and chemical oxidation (9.26%), adsorption (7.41%), SR-AOPs (5.56%), ozonation (3.70%), EAOPs and filtration (1.85% each). The shift in interest towards AOPs could be due to the different physico-chemical properties such as size and polarity compared to MCs, affecting the toxin's susceptibility to certain treatments, which might require adjusting treatment parameters to less beneficial conditions for conventional treatment techniques.

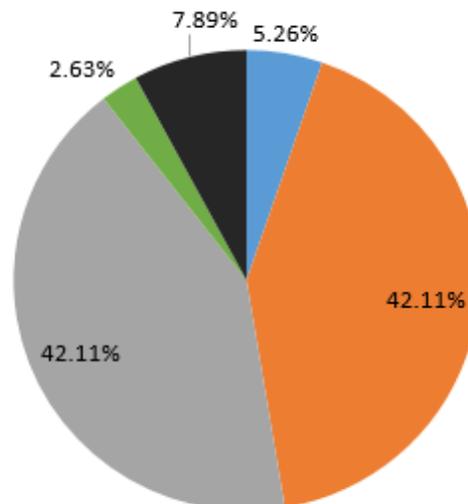
If only AOPs are considered, eight of a total of 38 counts occurred in more than one treatment category. As aforementioned, photolysis and photocatalysis are the treatment techniques receiving the most attention, accounting for 42.11% of all AOP-based methods each, followed by SR-AOPs (7.89%), ozonation (5.26%) and EAOPs (2.63%). Publications reporting on Fenton oxidation, sonolysis, NTP-based AOPs, and radiolysis were not found at all for the treatment of CYN. Contradictory, the author is aware of at least one article reporting on the utilization of Fenton for the removal of CYN [40].

One replicate of a total of 16 counts occurred for the treatment of CYN applying conventional and other emerging treatment techniques. Compared to MCs, chemical oxidation of CYN receives relatively high attention in relation to the other treatments, which again could be due to differences in the physico-chemical properties and thus its susceptibility to degradation using chemical oxidants. Biodegradation accounts for 37.50%, followed by chemical oxidation (31.25%), adsorption (25.00%) and filtration (6.25%), whereas flocculation/coagulation is not reported.

All treatments
total counts: 54
replicates: 9



AOPs (70.37% of all)
total counts: 38
replicates: 8



Conventional and other emerging treatments (29.63% of all)
total counts: 16
replicates: 1

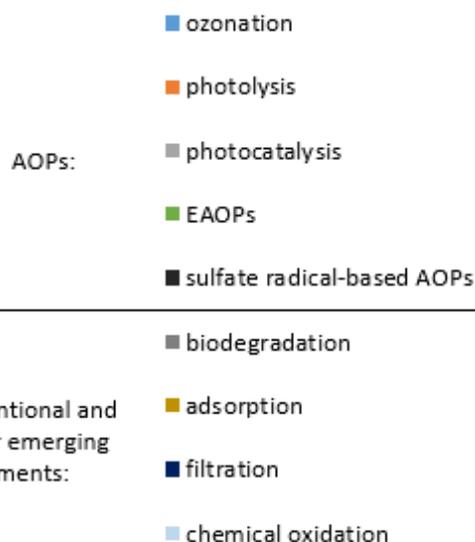
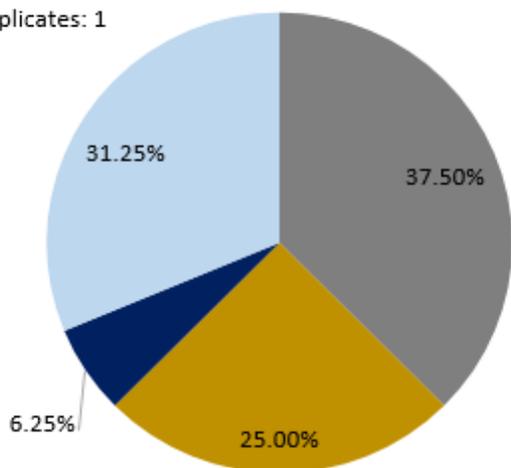


Figure 4: Analysis of the currently available scientific literature for preferences for certain treatment techniques for cylindrospermopsin by comparing all (top left), AOP-based (top right) and conventional and other emerging (bottom left) treatments.

Nodularin

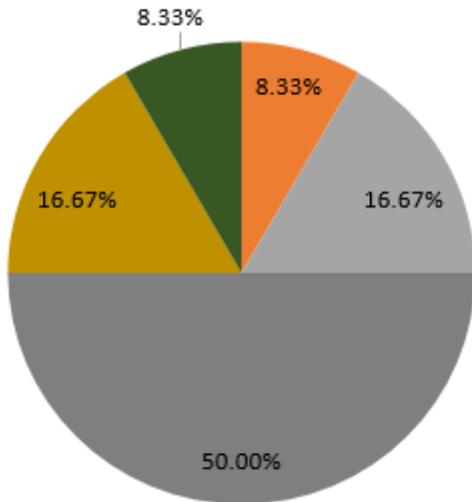
For treatment of NOD, only twelve publications were found for all treatments, including one replication, with conventional and other emerging treatments accounting for 75% and AOPs accounting for 25% of all counts. Biodegradation has a share of 50.00%, thus being the most used treatment, followed by photocatalysis and adsorption (16.67% each) as well as photolysis and flocculation/coagulation (8.33% each). Although both cyanotoxins are structurally related, there is a wide discrepancy between NOD and MCs in terms of total numbers of publications. Although it has been found to be a stronger tumor promoter than MCs, NOD seems to be of less interest, probably due to its less frequent occurrence [41]. However, studies investigating

the removal of both toxins observed the efficient removal of NOD under similar conditions used to remove MCs [25,37,42]. Hence, research might not show much interest in NOD, because conditions used for MC removal might be expected to also be suitable for NOD degradation.

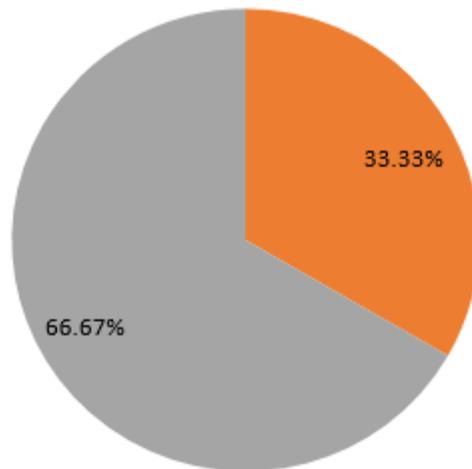
When AOPs are considered, only three counts occurred in total, with photocatalysis and photolysis accounting for 66.67% and 33.33%, respectively. Other AOP-based methods for the removal of NOD have not been found in this search. The author is aware of at least one article reporting on the EAOP-based treatment of NOD [43].

For conventional and other emerging treatments, one of a total of nine counts occurred in more than one treatment category. Again, biodegradation has the highest share accounting for 66.67% of all counts, followed by adsorption (22.22%) and flocculation/coagulation (11.11%). Chemical oxidation has not been found using the abovementioned search terms.

All treatments
total counts: 12
replicates: 1



AOPs (25.00% of all)
total counts: 3
replicates: 0



Conventional and other emerging treatments (75.00% of all)
total counts: 9
replicates: 1

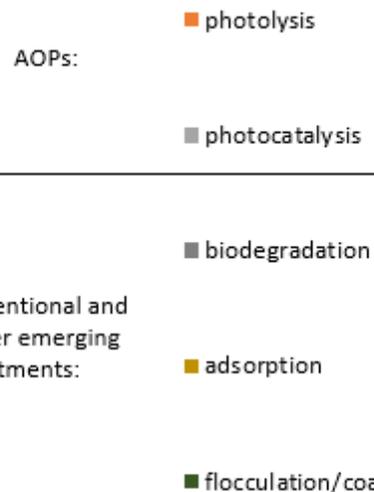
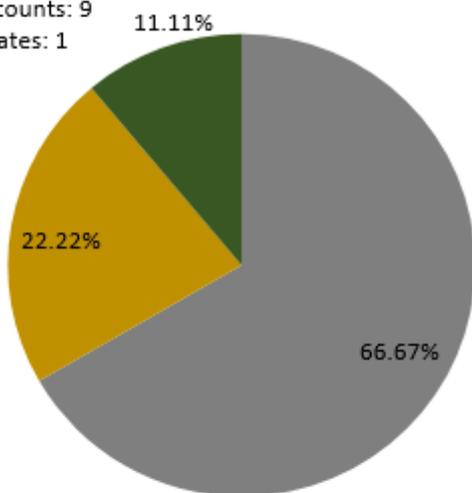


Figure 5: Analysis of the currently available scientific literature for preferences for certain treatment techniques for nodularin by comparing all (top left), AOP-based (top right) and conventional and other emerging (bottom left) treatments.

Saxitoxins

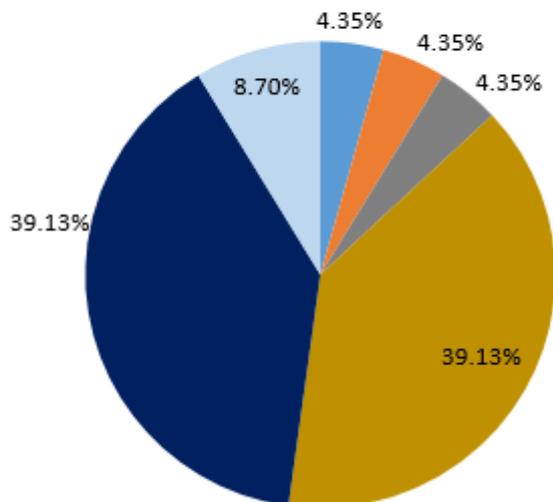
For all treatments, three of a total of 23 counts occurred in more than one treatment category, with approx. 91% of all publications being related to conventional and other emerging treatments, whereas AOPs account for only about 9%. For STXs filtration and adsorption (39.13% each) represent more than 3/4 of all publications, followed by chemical oxidation (8.70%) as well as ozonation, photolysis, and biodegradation (4.35% each).

When only AOPs are considered, one of a total of two counts refers to photolysis and ozonation each. Photocatalysis, Fenton oxidation, sonolysis, EAOPs, NTP-based methods, radiolysis, and SR-AOPs have not been studied for the treatment of STXs according to the results of this search.

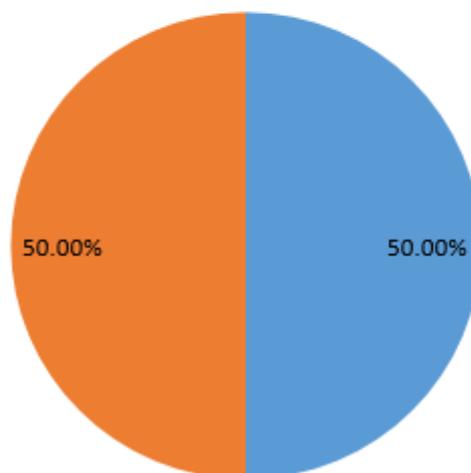
For conventional and other emerging treatments, two of a total of 21 counts occurred in more than one treatment category. As aforementioned, filtration and adsorption (42.86%) represent the highest shares, which might be related to the fact, that filtration and adsorption are expected to be efficient, as STXs are easily accumulated in marine organisms via filtration from water and consumption of smaller organisms from a lower trophic level within the food chain and deposition in the organisms' cell tissue [8]. The remaining part includes chemical oxidation (9.52%) and biodegradation (4.76%), whereas no publication on flocculation/coagulation was found using the pre-defined search terms.

STXs are an extraordinary group of natural neurotoxins, as they can be produced by marine eukaryotic dinoflagellates and marine and freshwater prokaryotic cyanobacteria. STX and its analogs seem to be stronger associated with saltwater rather than freshwater environments in terms of human intoxication [8]. However, fresh- and groundwater is often used for the production of drinking water, which could explain the relatively low number of total counts and low interest in the removal of STXs from drinking water.

All treatments
total counts: 23
replicates: 3



AOPs (8.70% of all)
total counts: 2
replicates: 0



Conventional and other emerging treatments (91.30% of all)
total counts: 21
replicates: 2

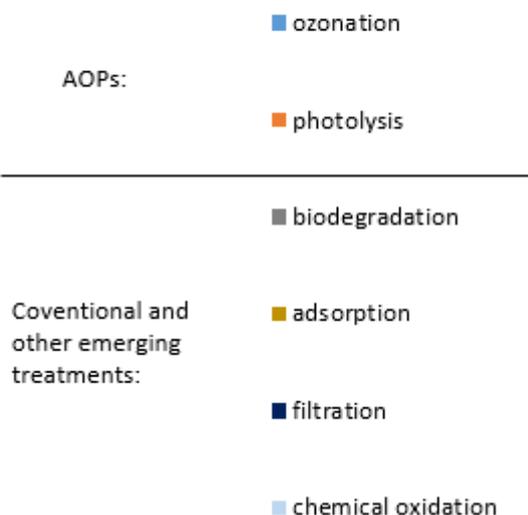
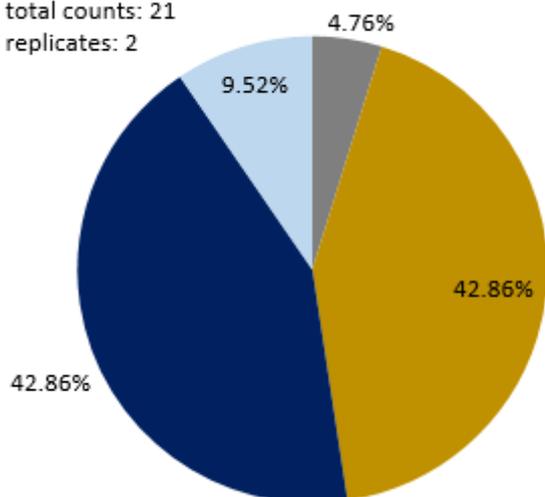


Figure 6: Analysis of the currently available scientific literature for preferences for certain treatment techniques for saxitoxins by comparing all (top left), AOP-based (top right) and conventional and other emerging (bottom left) treatments.

Anatoxins and anatoxin-a(S)

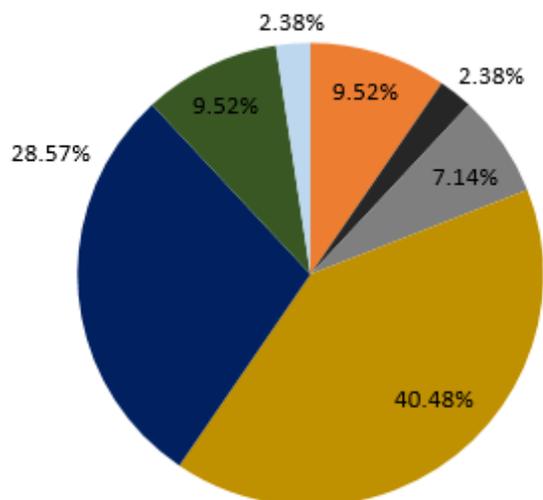
In total, 42 counts including three replications, were found for all treatments, with approx. 88% accounting for conventional and other emerging treatments and only about 12% accounting for AOP-based techniques. Similar to STXs, adsorption (40.48%) and filtration (28.57%) techniques received the most attention regarding the removal of ANTXs, accounting for more than 2/3 of all publications. Photolysis and flocculation/coagulation each have a share of 9.52%, followed by biodegradation (7.14%), SR-AOPs and chemical oxidation (2.38% each).

Although anatoxin-a and anatoxin-a(S) have similar names, none of the publications reported on the treatment of the organophosphate anatoxin-a(S).

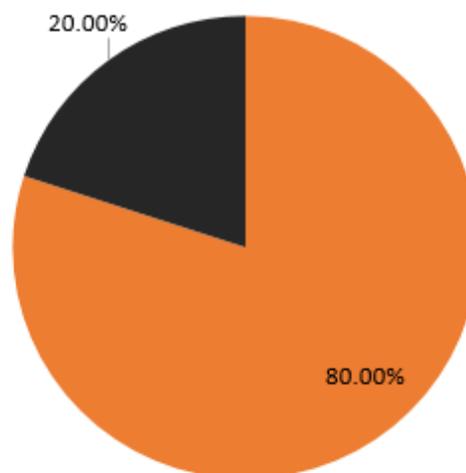
Regarding AOP-based treatments, five publications, including one replication, report on the use of photolysis (80.00%) and SR-based techniques (20.00%). According to the results and the low number of publications found, the neurotoxins could be assumed to be less susceptible to oxidation due to their chemical structures. However, even if only a few publications were found, in these studies removal efficiencies of > 95% were shown when employing UV-C/H₂O₂ or UV/PMS for example [44,45]. Furthermore, the author is aware of additional publications reporting on NTP-based treatment, ozonation and Fenton oxidation of ANTXs [26,46].

When considering conventional and other emerging treatments, two of a total of 37 counts occurred in more than one treatment category. Adsorption (45.95%) and filtration (32.43%) have the highest shares, followed by flocculation/coagulation (10.81%), biodegradation (8.11%) and chemical oxidation (2.70%).

All treatments
total counts: 42
replicates: 3



AOPs (11.90% of all)
total counts: 5
replicates: 1



Conventional and other emerging treatments (88.10% of all)
total counts: 37
replicates: 2

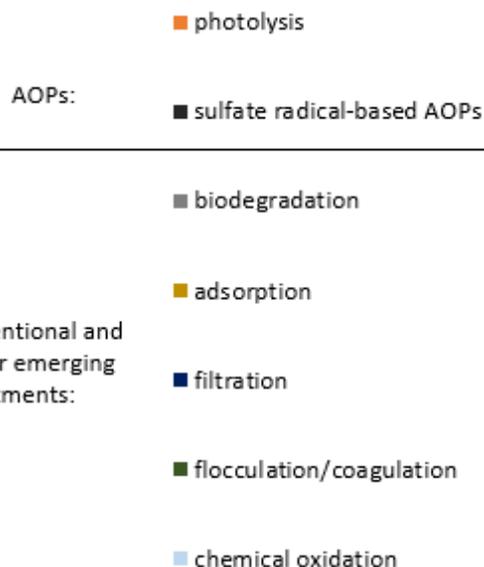
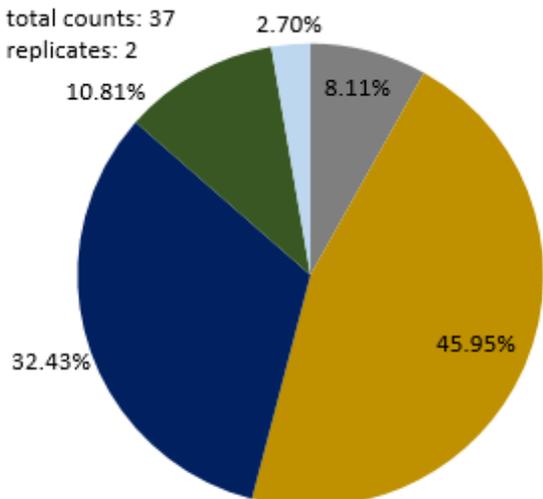


Figure 7: Analysis of the currently available scientific literature for preferences for certain treatment techniques for anatoxins by comparing all (top left), AOP-based (top right) and conventional and other emerging (bottom left) treatments.

β -N-methylamino-L-alanine

For BMAA, only four publications were found within this search, with all of them reporting on the application of conventional and other emerging treatments. From these counts, chemical oxidation accounts for 50.00%, whereas adsorption and filtration have a share of 25.00% each. In general, BMAA is of less interest to drinking water treatment-related research so far, which might be the main reason for not having found any publications on AOP-based treatments.

Conventional and other emerging treatments
(100.00% of all)
total counts: 4
replicates: 0

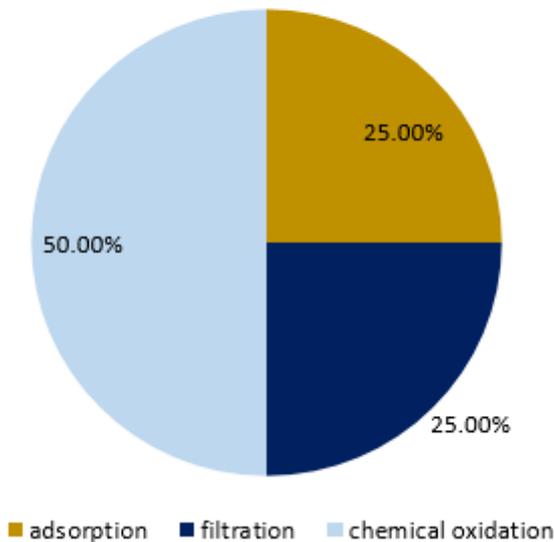


Figure 8: Analysis of the currently available scientific literature for preferences for certain conventional and other emerging treatment techniques for β -*N*-methylamino-L-alanine.

Aplysiatoxin, lyngbyatoxin and cyanobacterial endotoxins

For aplysiatoxin, lyngbyatoxin and cyanobacterial endotoxins, no publications related to their treatment were found within this search.

5.4.3. Evaluation of preferences in scientific literature for certain cyanotoxins for all and individual treatment techniques

In this chapter, the currently available literature is analyzed for preferences in certain cyanotoxins in regard to their removal from drinking water. Therefore, the cyanotoxin sets (#1 to #9 and #24) were combined with the treatment sets (#10 to #23 as well as #25 to #27) via an AND Boolean. The chapter is grouped into all, AOP-based and conventional and other emerging treatments, and individual treatments with results being displayed in Figure 9 to Figure 25.

Furthermore, in this chapter, the reader will find an overview of the different treatment techniques, including a brief summary of the underlying technical principles, information about the removal of cyanotoxins and practical advantages and disadvantages of the respective techniques.

5.4.3.1. Comparison of all treatment techniques

When comparing the cyanotoxins for all treatments, 21 of a total of 539 counts occurred in more than one toxin category. More than 3/4 of all publications focus on the removal of MCs (77.92%), followed by CYN (8.35%), ANTXs (7.24%), STXs (3.71%), NOD (2.04%) and BMAA (0.74%). As aforementioned, publications reporting on the treatment of aplysiatoxins, lyngbyatoxins, and cyanobacterial endotoxins have not been found. Similar to what can be seen above, MCs receive the most attention in terms of drinking water treatment, but also in general, in all cyanotoxin-related research, which is mainly because *Microcystis* are the most commonly bloom-forming cyanobacteria in freshwaters and also involved in many cases of animal and human intoxication [38], which places MCs amongst the most frequently occurring cyanotoxins. Despite their related chemical structures, the significant difference in NOD and MCs agrees with what was discussed for NOD in chapter 5.4.2. In accordance to what was discussed for STXs in chapter 5.4.2, these cyanotoxins receive relatively low attention in terms of their treatment, because they seem to be more relevant to saltwater and related organisms rather than for fresh- and drinking water.

total counts: 539
replicates: 21

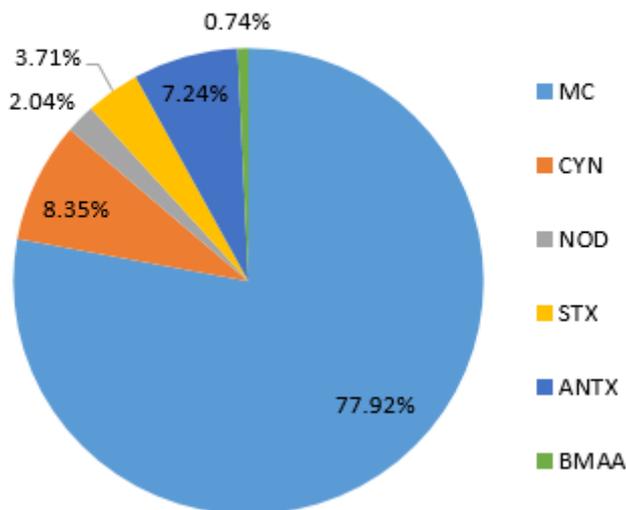


Figure 9: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for all treatment techniques by comparing all cyanotoxins.

5.4.3.2. Comparison for AOP-based treatment techniques

Considering only AOP-based treatments, eight of a total of 211 counts occurred in more than one toxin category. Again, MCs have the highest share (81.52%) and the other toxins follow a pattern similar to the comparison for all treatments, except for a shift in order between NOD (1.42%) and STXs (0.95%). In addition to the three cyanotoxins mentioned above, publications for treating BMAA with AOPs were not found as well. BMAA, in general, is less explored and scientists rather focus on studying its occurrence, toxicity, and mode of action. Furthermore, BMAA is quite distinct compared to the other cyanotoxins, as it is the smallest molecule and the only one neither consisting of a cyclic structure nor an unsaturated C=C bond, which might make it less susceptible to oxidation.

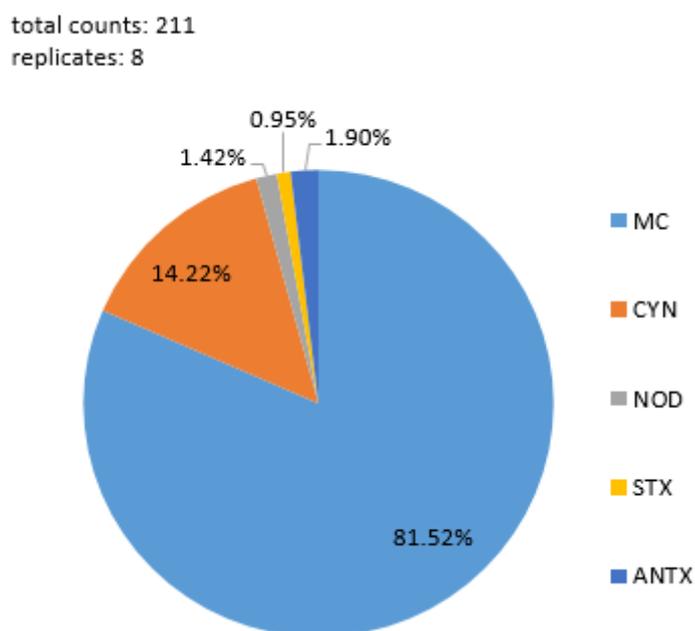


Figure 10: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for AOP-based treatment techniques by comparing all cyanotoxins.

Ozonation

For the ozonation of cyanotoxins, 19 publications have been found. Again, MCs have the largest share (84.21%), followed by CYN (10.53%) and STXs (5.26%). Ozone is widely used in drinking water treatment due to its relatively high redox potential at acidic pH (see Table 1) and as it promotes the *in situ* formation of $\bullet\text{OH}$ under alkaline conditions [12]. Ozonation exhibits two reaction mechanisms: i) direct ozone attack at unsaturated C=C bonds and e^- -rich moieties such as activated aromatic and neutral amine groups, and ii) non-selective attack through $\bullet\text{OH}$ at C-H bonds, unsaturated C=C bonds and e^- -rich groups [14,47]. So despite the fact that the structural features of the MC molecule targeted by ozone or $\bullet\text{OH}$, e.g. conjugated double bonds (C4-C5 and C6-C7) in the Adda chain, are known [48] and although these features are also present in the NOD molecule, no publication was found for the ozonation of NOD. Furthermore, no counts occurred for the treatment of ANTXs with ozone, however, the author is aware of articles studying the ozonation of ANTXs [25,26,49,50] and NOD [25].

total counts: 19
replicates: 0

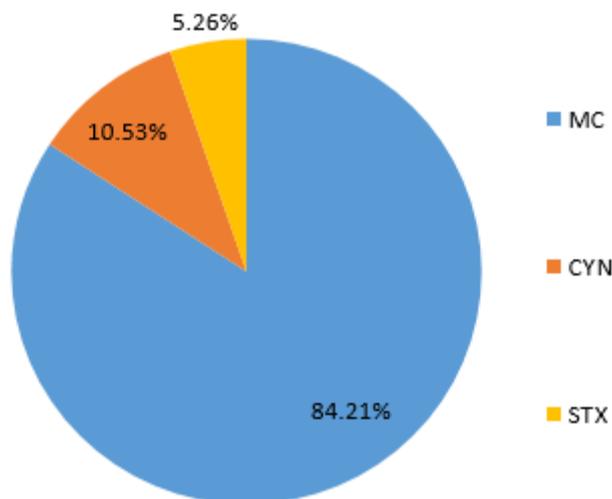


Figure 11: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for ozonation by comparing all cyanotoxins.

MCs, in most studies MC-LR is used as representative, CYN, NOD and ANTX are readily degraded by ozone with efficiencies ranging from 90 – 100%, depending on the initial ozone to toxin ratio [25,48]. However, STX is less susceptible to oxidation with ozone with removal efficiencies of $\leq 20\%$ [13]. Even if combined with H_2O_2 , the toxicity of a cell-free *A. circinalis* extract was only reduced by less than 10% [51]. For the other cyanotoxins, combining ozone with H_2O_2 showed an increase in the removal efficiency. Furthermore, the ozonation process can be enhanced in combination with e.g. UV light, Fenton's reagent, catalysts or sorbents by increasing the $\bullet OH$ formation [2,25,26,32,52–55]. As STXs can be degraded applying other treatment techniques, ozone is not recommended according to the currently available data.

The reactivity of ozone, represented by its redox potential, is pH-dependent and $\bullet OH$ is preferably formed at alkaline pH. Consequently, the cyanotoxin removal can be influenced by the solution pH [25,50]. Other water quality parameters can also affect the removal efficiency. An increased alkalinity (in form of carbonate) scavenges the $\bullet OH$ formation and thus, increases the ozone residual [56], whereas natural organic matter (NOM) can act as a competitor to the cyanotoxin and reduce the removal efficiency [13,57]. Onstad et al. [50] compared the removal of MC-LR, CYN, and ANTX from two different lake waters with dissolved organic carbon (DOC) contents of 1.6 mg/L and 13.1 mg/L. In order to remove 95% of the three toxins, with an approx. 8.2-fold increase in DOC, the ozone doses had to be increased by a factor of ≥ 10 for MC-LR, ≥ 5 for CYN and ≥ 2.5 for ANTX to > 2 mg O_3/L [50]. However, the competitive effect of NOM is smaller for ozone than for $\bullet OH$ due to the higher selectivity towards e^- -rich moieties [47,50].

As gaseous ozone can adversely affect human health, sufficient ventilation and/or an ozone destructor unit need to be installed if required, to maintain a safe working environment [58]. Another major disadvantage over other AOPs is the possible formation of bromate disinfection byproducts in the presence of Br^- , which can be reduced if ozone is combined with H_2O_2 [59].

Photolysis

For photolysis, three of a total of 69 counts occurred in more than one toxin category. MCs receive the most attention with a share of 68.12% of all photolysis-related counts, followed by CYN (23.19%), ANTXs (5.80%), NOD and STX (1.45% each). Both articles reporting on STX do not describe the photolytic degradation, but the alteration of the binding activity of STX through UV irradiation and thus, no information for the photolysis of STX is available to the author's knowledge. Photolysis is widely applied in drinking water treatment plants for disinfection. However, light can also directly degrade organic compounds and produce reactive species, e.g. $\bullet\text{OH}$, which in turn can oxidize contaminants.

total counts: 69
replicates: 3

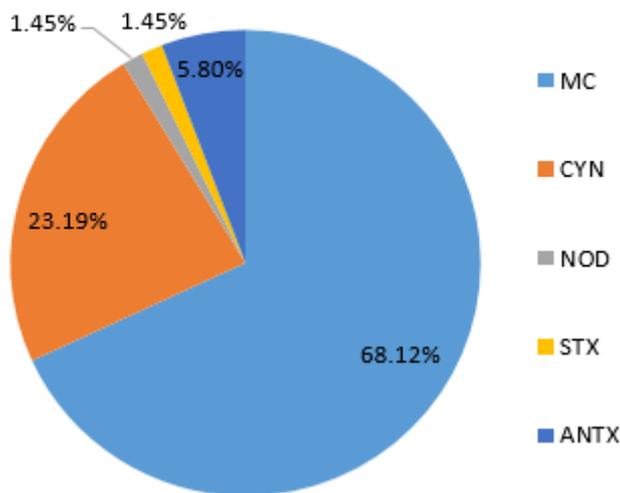


Figure 12: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for photolysis by comparing all cyanotoxins.

ANTX rapidly degrades under sunlight and naturally occurring conditions with a half-life in the range of 1 – 2 h [60]. Other cyanotoxins are less susceptible to sunlight. Wörmer et al. [61] observed about 79% removal of MC extracts diluted in autoclaved reservoir water with an initial DOC content of approx. 15.3 mg/L after 22 days of exposure to sunlight and about 27% removal of CYN under the same experimental conditions. In another study, a MC extract was degraded by about 14% after 26 days of exposure to sunlight without photosensitizers being present. However, when cyanobacterial pigments such as chlorophyll a or phycocyanins were added to the diluted MC extract, the degradation was accelerated and increased with increasing concentration of the pigments [62], indicating the key role of photosensitizers for the photolytic degradation. When solely utilizing UV light, removal efficiencies of up to 100% can be achieved in minutes or hours rather than days as Tsuji et al. [63] observed when using UV light at 254 nm and a UV dose of 1530 mJ/cm². The degradation of ANTX can also be accelerated compared to degradation under sunlight when using UV-C light; $\geq 95\%$ removal was achieved using UV light at 172 nm and a UV dose of 96 mJ/cm² within 150 s with decreasing efficiency at higher UV dose if natural water was used as a matrix [64]. The applied UV dose is still significantly lower as the dose required for MC degradation (mentioned above), aqueous CYN

and NOD solutions, which have been degraded with $\geq 95\%$ efficiency at a UV-C dose of 1287 mJ/cm² and $< 25\%$ efficiency at UV-B dose of 104 mJ/cm², respectively [65,66]. Again, higher removal efficiency was observed when a NOD extract was treated, most likely due to photosensitized cyanobacterial cell residues [66]. Mineralization, measured as TOC removal, could not be observed for MC-LR across a range of different UV doses and prevalent experimental conditions [54].

During photolysis, isomerization was observed in several studies, which was not observed for most of the other AOPs. It appeared to happen e.g. under weaker UV light and the produced isomers could subsequently be photolyzed or oxidized [54,63]. For a cost-effective and efficient treatment, the used light intensity and λ need to be optimized as both substantially affect the removal of the cyanotoxins [67]. The photolysis of MC-LR appeared to be less pH-dependent and the efficiency was significantly less decreased by the increase of humic acid from 1.4 to 5.3 mg/L, about 4%, compared to ozonation [54]. In fact, 4.7 mg/L DOC, with the greatest fraction being fulvic acid, even led to an increase in the removal of MC-LR by UV light in another study [56], which agrees with the results shown for the photodegradation using sunlight and photosensitizers (mentioned above). pH might play a role when adding oxidants such as H₂O₂ or O₃, and consequently •OH, as they are affected by pH or when the transformation of the cyanotoxin is caused by any other reactive species formed during photolysis [65].

Photolysis can be enhanced by adding oxidants such as H₂O₂ or O₃, photosensitizers or photo-active catalysts, which is discussed in the following chapter. Combining photolysis with e.g. oxidants might have a beneficial effect on the energy consumption and operational costs, as UV-B/H₂O₂ was shown to be more efficient than UV-C for the degradation of MC-LR [67]. A major limiting factor for photolysis is the solution's turbidity, which is why it is normally employed after e. g. physical separation of cyanobacterial cells [12]. Furthermore, UV doses in the range of 10 – 40 mJ/cm² are normally used for the disinfection of drinking water [14], whereas doses applied for the removal of cyanotoxins are usually higher, which is why photolysis is often stated to be ineffective under normal water treatment conditions [13,65].

Photocatalysis

Considering photocatalysis, six of a total of 91 counts occurred in more than one toxin category. MCs have the largest share (80.22%), followed by CYN (17.58%) and NOD (2.20%). Even though publications reporting the photolytic degradation of ANTXs have been found, there are no counts for photocatalysis, which is surprising, as the major difference is the application of a catalyst to enhance the photolytic degradability and as photocatalysis is widely applied [18]. The most commonly used photocatalyst is titanium dioxide (TiO₂), which is a semiconductor. Photocatalysis can progress in three reaction mechanisms: i) direct oxidation at the valence band (e⁻-hole), ii) formation of •OH at the valence band, and iii) e⁻ donation from the conductance band.

total counts: 91
replicates: 6

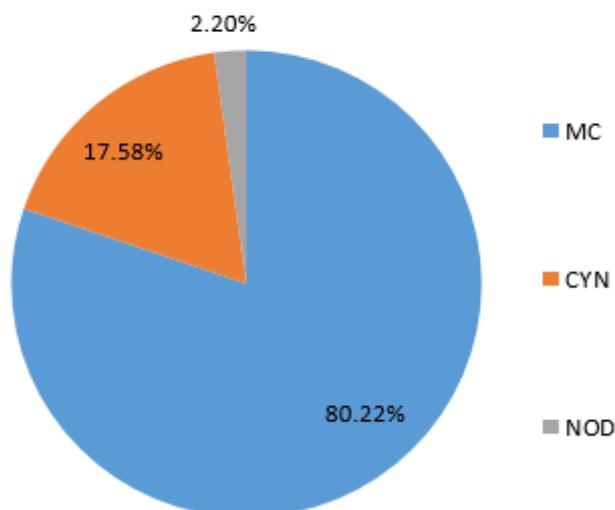


Figure 13: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for photocatalysis by comparing all cyanotoxins.

MCs, CYN, and NOD were readily decomposed by photocatalysis within several min to < 1 h using UV-A and Vis light in combination with either TiO₂ powder or immobilized TiO₂ [30,68,69]. Doses can range from 64 mJ/cm² for UV-A light to 10701 mJ/cm² for UV/Vis light [68,69]. Fotiou et al. [68] reported a > 2-fold faster degradation of CYN utilizing UV-A light instead of solar light for the same type and dose of TiO₂ catalyst and the same initial toxin concentration, indicating the λ -dependency of the irradiation. Although TiO₂ is the most commonly used photocatalyst, other substances have also been used for the degradation of cyanotoxins, e.g. Fe₂O₃ or BiOBr [40,70,71]. 86% removal of MC-LR was achieved using Vis light at a dose of 7182 mJ/cm² and Fe₂O₃ nanopowder [70].

In order to address one major issue, i.e. the separation of the catalysts from the treated water, several groups utilized immobilized catalysts. The used substrates, e.g. granular activated carbon (GAC), glass microspheres, PVC tubes or cellulose acetate monoliths can increase the removal through adsorption to their own surface and assist the oxidation, and/or simplify the separation of the catalysts from the water after the treatment [69,72,73]. Lee et al. [72] observed a significant increase in the removal of MC-LR when using TiO₂-coated GAC instead of TiO₂ powder due to oxidation of MC-LR directly to the TiO₂ particles and MC-LR adsorption to GAC in vicinity of the TiO₂ from where it migrated to the TiO₂. Doping the pristine TiO₂ particles with e.g. Bi decreased the bandgap, allowing them to increase the Vis light absorption, consequently improving the degradation of MC-LR [74]. Lawton et al. [30] also observed > 50% removal of MC-LR without UV irradiation due to adsorption to the TiO₂ surface, which was also observed to some extent when other photocatalysts were utilized [70].

Mineralization, measured as CO₂, of MC-LR of about 49% was achieved using UV-A/TiO₂-GAC [72], whereas in another study only about 10% of MC-LR were mineralized after treatment with UV-A/TiO₂ [30]. Using Bi-doped TiO₂ and Vis light, about 85% of the initial MC-LR was mineralized to CO₂, measured as TOC, after 20 h of irradiation [74].

Photocatalysis mainly depends on the light intensity and λ , utilized type and dose of catalyst, water quality parameters such as pH and NOM content, and presence of gaseous O_2 , i.e. as pure O_2 or air, as the removal efficiency under e.g. Ar or N atmosphere was significantly reduced [18,75,76]. Similar to photolysis, photocatalysis can also be enhanced by e.g. adding H_2O_2 into the solution [73]. As mentioned above, photolysis usually results in efficient removal of cyanotoxins at impractically high UV doses, which can be reduced if photocatalysts are employed to enhance the degradation [13]. Photocatalysts such as TiO_2 are usually not of toxicological concern for the aquatic environment [18,30].

Fenton oxidation

For the treatment with Fenton oxidation, 14 counts have been found, with all of them being related to the removal of MCs. However, the author is aware of at least one article reporting on the Fenton oxidation of CYN [40] and one on ANTXs [26]. Although Fenton oxidation is used and studied for the removal of other organic pollutants such as pharmaceuticals [77], it has not drawn much attention for its application for the treatment of cyanotoxin-laden drinking water. Fenton oxidation generally describes the production of $\bullet OH$ by the reaction of Fe^{2+} with H_2O_2 , whereas other transition metals and oxidants can also be used, which is then named Fenton-like oxidation [15].

total counts: 14
replicates: 0

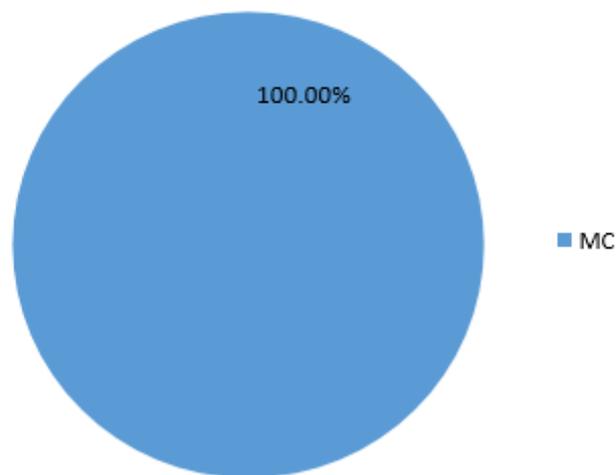


Figure 14: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for Fenton oxidation by comparing all cyanotoxins.

MC-LR, CYN, and ANTX were completely removed within ≤ 30 min using Fe^{2+} to H_2O_2 ratios of 1.5, 0.04 and 3, respectively. For the degradation of CYN, the H_2O_2 was significantly higher compared to the studies on MC-LR and ANTX, which were both completely degraded in ≤ 3 min [2,26,40]. Hence, the Fe^{2+} to H_2O_2 ratio is shown to play an important role. Fenton oxidation can be improved significantly when exposed to UV or visible light as Bandala et al. [78] showed for the degradation of MC-LR, which could potentially result in the reduction of amounts of Fenton reagents used in the treatment process. Additionally, as light with wavelengths from the UV and Vis spectra can be utilized, natural sunlight might be a suitable light source, reducing energy and maintenance costs [78,79].

Fenton oxidation can be significantly cheaper than other AOPs, as it usually only requires low-cost, non-toxic chemicals instead of expensive instruments [80]. Furthermore, Fenton oxidation can be added to an already existing drinking water treatment process using iron salts as coagulant by simply adding H_2O_2 [27]. However, limiting factors are the high acidity, i.e. $\text{pH} \approx 3$, which is required for the Fenton reaction to occur and the high amounts of iron, which both can be reduced depending on the type of Fenton(-like) reagent or system used [15,27,77,79]. Another very important aspect is the need to optimize the transition metal to oxidant ratio, otherwise competing reactions can deplete the formed $\bullet\text{OH}$ [15]. Other water quality parameters, such as NOM as a competitor for $\bullet\text{OH}$ and temperature can affect the efficiency [2,26,27]. Although iron is highly abundant in the environment, homogeneous Fenton systems can lead to an unfavorable increase of iron in water, which can be prevented by applying heterogeneous Fenton systems in which the iron can be retrieved from the treated water [15,27,79,81].

Sonolysis

For sonolysis, a similar pattern to Fenton oxidation can be seen, as all of the eleven counts account for the removal of MCs. According to the results, sonolysis is not studied very often for the treatment of cyanotoxins, but ultrasonication is frequently used for the extraction of compounds, e.g. cyanotoxins, from a sample matrix or producing organisms, e.g. cyanobacteria (see e.g. [61,82] for examples of sonication being used for the extraction of cyanotoxins). Assumingly, since many scientists sonicate their compounds of interest during extraction and homogenization, sonolysis might simply not be expected to significantly degrade the target compound, which could be the reason for the lack of interest in and information regarding sonolytic degradation of cyanotoxins. During sonolysis of a liquid medium, e.g. water, cavities are generated, which form localized hotspots of very high temperatures of $\geq 10^3$ K and pressures of approx. 500 atm upon collapse. Hence, $\bullet\text{OH}$ are produced through thermolysis of water, which can consequently migrate into the bulk solution and oxidize water pollutants. Besides oxidation, these pollutants can also be thermolyzed or hydrolyzed if they migrate into the cavitation bubble or to the bubble-bulk interfacial region surrounding the cavitation bubble [12,29]. In addition, sonolytic treatment can also affect a physical surface, e.g. cyanobacterial cells, due to shockwaves, high shear forces, microstreams and -jets [12].

total counts: 11
replicates: 0

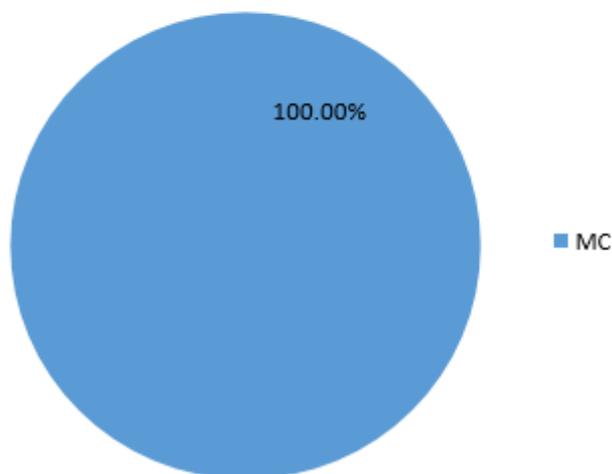


Figure 15: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for sonolysis by comparing all cyanotoxins.

After 6 min of ultrasonication at 640 kHz, $\geq 85\%$ MC-LR was removed from a pure solution [29]. When increasing the initial MC-LR concentration by a factor of approx. 370 to 1 mM, 105 min of ultrasonication were required to achieve $> 80\%$ removal [83]. Similarly, the degradation rate was slightly decreased if a MC-LR extract was used, due to the presence of cyanobacterial cell exudates [29]. Since cyanotoxins are usually non-volatile compounds, they are not expected to significantly migrate into the cavitation bubble. However, nonpolar moieties such as the Adda amino acid found in MCs and NOD can be attracted to the bubble-bulk interfacial region, whereas the polar part of the cyanotoxin stays in the bulk solution [29].

The applied frequency is substantial to the cavitation process as it influences the size and lifetime of the cavitation bubble, which in turn determines whether $\bullet\text{OH}$ reactions or higher temperatures and pressures are favored. Oxidation is favored at frequencies ranging from approx. 200 – 600 kHz, whereas thermolysis occurs more often at lower frequencies. Besides the frequency, the intensity and distribution of the sound waves and solution pH are also influencing the treatment efficiency [12,83]. The major advantage of sonolysis over many other AOPs is, that it does not require the addition of reagents and is applicable for the treatment of turbid solutions and slurries, making it a highly potential technique for drinking water treatment [29,83]. However, related energy costs are considered a major drawback, which can be reduced when operating under specific conditions or combining sonolysis with other treatment methods such as chlorination, ozonation, Fenton oxidation, coagulation or photolysis [83–85]. Furthermore, peroxides such as H_2O_2 can be formed during sonolytic treatment, which can reduce the degradation efficiency due to depletion of $\bullet\text{OH}$. However, by adding Fe^{2+} to the solution, H_2O_2 is reduced to $\bullet\text{OH}$, i.e. Fenton reaction, which further accelerates the degradation [83].

Electrochemical oxidation

For EAOPs, 13 counts have been found, with MCs accounting for 92.31% and CYN accounting for 7.69%, whereas treating the other cyanotoxins with electrochemical oxidation has not been reported according to the search results. However, the authors are aware of at least one article reporting the treatment of NOD with EAOPs [43]. In general, EAOPs have received quite some attention for the removal of organic pollutants such as pesticides or pharmaceuticals [15] and cyanobacteria [86], which shows its potential. Furthermore, electrochemical oxidation has been used for the HPLC-based determination of STXs. The toxins are electrochemically oxidized after column separation to selectively produce a fluorescent derivate which enables the instrumental determination of these neurotoxins without derivatization or application of mass spectrometry [87]. Even though the context is different, the successful utilization of EAOPs for the oxidation of STXs has been shown. Degradation using EAOPs include direct oxidation at the anode surface and indirect oxidation via oxidants, e.g. $\bullet\text{OH}$, H_2O_2 , O_3 and other reactive species, which can be electrochemically produced depending on the constituents of the electrolyte [15].

total counts: 13
replicates: 0

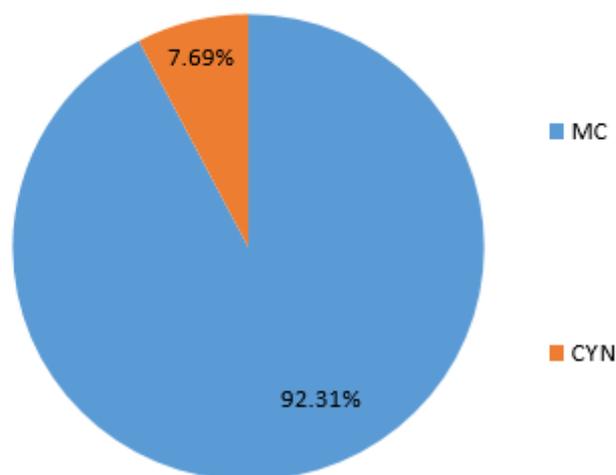


Figure 16: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for EAOPs by comparing all cyanotoxins.

More than 95% of MC-LR and CYN were degraded within 15 and 30 min, respectively employing electrochemical oxidation with current densities of $< 60 \text{ mA/cm}^2$ and Na_2SO_4 as electrolyte [86,88]. As mentioned above, one publication reported the electrochemical oxidation of NOD [43], however, no removal efficiency is given, as this article focuses on the examination of the underlying degradation mechanisms.

The removal efficiency of EAOPs generally can be affected by the employed setup, i.e. electrode material, interelectrode gap and type of cell, electrolyte, i.e. constituents, pH and conductivity, applied voltage/current and temperature [15,86,89–91]. For example, Lobón et al. [92] observed an increase in removal of MC-LR when increasing the conductivity of the

electrolyte as this enhanced the current flow. Furthermore, Zhou et al. [90] observed a decrease in the degradation rate of MC-LR after addition of humic acid as NOM model compound and algal organic matter, extracted from a *M. aeruginosa* culture, to the reaction vessel. NOM showed a stronger reduction in the degradation rate, due to a larger fraction of unsaturated moieties which act as oxidant scavenger [90]. As H₂O₂ can be produced during electrochemical oxidation, the addition of Fe²⁺ or exposure to light can enhance the removal efficiency through the production of •OH by Fenton oxidation or photolytic cleavage of H₂O₂, respectively. Since H₂O₂ is continuously electrogenerated at the cathode from oxygen or air at neutral or acidic pH and Fe²⁺ is cathodically regenerated from Fe³⁺, the Fenton reagent is perpetually produced in the so called electro-Fenton process if an undivided cell is used [15]. As a positive side effect, Jeon et al. [93] observed cathodic deposition of inorganic phosphorus while removing *M. ichthyoblabe* cells and MC-LR.

EAOPs are usually easy to operate and can be considered environmentally friendly, depending on the electrode material and chemicals used as or added to the electrolyte [89,92]. If e.g. halogenated chemicals are added to the electrolyte, toxic byproducts can be formed during electrochemical oxidation [91]. However, one of the main cost-determining features are the electrodes used for the electrochemical treatment which can be expensive depending on the material, but studies have been conducted developing cheaper, e.g. carbon-based alternatives. In addition, operational costs can be reduced when improving the current flow by increasing the conductivity of the electrolyte, resulting in a reduction of energy consumption used for the treatment [92].

NTP-based AOPs

For NTP-based treatments, only seven publications have been found in this search, all relating to the removal of MCs. The author is aware of at least one article on the NTP-based treatment of ANTXs [46]. Unfortunately, this article is in Korean except for an English abstract. Although NTP has not been meant for water treatment initially, this technique has already been adapted for this purpose and applied as an AOP for the degradation of organic water pollutants such as pharmaceuticals and pesticides [94]. It has also been shown to successfully inactivate cyanobacterial cells [95,96], which, in addition to the few counts found for the degradation of MCs, points toward a high potential for its application in the treatment of cyanotoxin-laden drinking water. NTPs can generate a diverse range of reactive agents including hot electrons, photons, radical oxygen or nitrogen species such as •OH or NO•. In NTPs, most of the energy is transmitted to the electrons, resulting in a comparatively low overall temperature of the plasma, which enables NTPs being applicable for a wide range of potential applications, e.g. as a surgical scalpel, in ozone generators or for disinfection of thermolabile food packing materials [97–99].

total counts: 7
replicates: 0

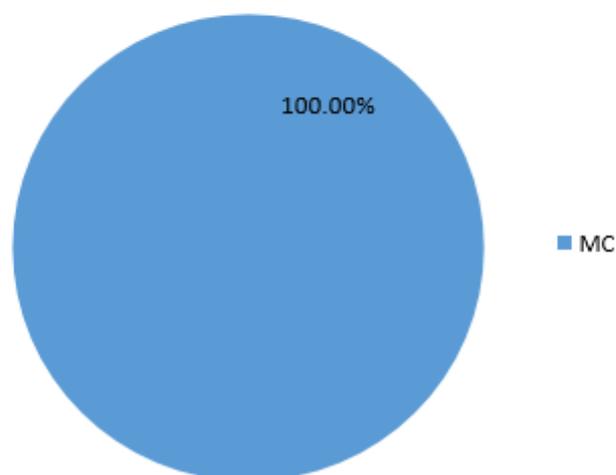


Figure 17: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for NTP-based treatment techniques by comparing all cyanotoxins.

MC-LR and ANTX were rapidly degraded in ≤ 10 min using a glow discharge with 1.3 kV DC and a dielectric barrier discharge with 15.2 kV AC, respectively [31,46]. The removal efficiency depends on the type of plasma, input voltage, interelectrode gap², gas type and flow rate, and water quality parameters such as NOM, TN, TP and pH [31,46,100]. Zhang et al. [31] observed a significant decrease in the removal efficiency from 96.2% to 30.1% after 0.5 min of treatment with 1.3 kV when increasing the pH from 2.09 to 9.02. Furthermore, an increase in the input voltage and a decrease in the gap between anode and cathode (or water surface) resulted in an improvement of the removal of MC-LR, as both parameters affect the electric field strength and consequently the energy of the plasma used to generate the reactive species [100,101].

The use of NTPs for drinking water treatment is advantageous over other treatment techniques, as no chemical additives other than gas are required, it can be employed for the treatment of turbid solutions or slurries, only requires simple equipment and is easy to operate, has a high energy efficiency, is environmental compatible and plasma treated water can exhibit a prolonged microbicidal effect, comparable to the prolonged disinfection effect due to a chlorine residue [31,96,99,102]. This might be beneficial for the removal of e.g. cyanotoxins from drinking water, as it could lead to a reduction in required voltage input, i.e. energy costs if a sufficient removal of a pollutant can be achieved over time without further exposure to an electric field. One major limiting factor is the diffusion of the formed $\bullet\text{OH}$ which, due to their very short lifetime might not migrate over long distances within a liquid. However, there have been attempts to solve this issue by adding catalysts to the solution which transform more stable oxidants such as O_3 and H_2O_2 into the more reactive $\bullet\text{OH}$ [103]. So far several transition metals have been tested, including Mn-, Ti- and Mn/Ti-doped xerogels as well as TiO_2 and Fe^{2+} powders [101,103,104]. TiO_2 can utilize the generated UV light to produce $\bullet\text{OH}$, whereas the

² In gas-liquid interfacial discharges, the water surface can function as electrode.

addition of Fe^{2+} to the solution in presence of H_2O_2 results in the formation of $\bullet\text{OH}$ via the Fenton reaction [101].

Radiolysis

For radiolysis, only five publications were found, all referring to the removal of MCs from drinking water. Additionally, the author is aware of at least one article in which the use of γ – radiation is described for the determination of rate constants for the reaction of $\bullet\text{OH}$ with MC-LR, CYN and ANTX [50]. However, radiolysis has successfully been used for the treatment of organic pollutants and cyanobacteria [105–107]. In aqueous solutions with a solute concentration < 0.1 M, the majority of the energy provided by ionizing radiation is absorbed by water leading to the formation of a range of chemical species, including solvated e^- and $\bullet\text{OH}$. Hence, chemical changes of a pollutant molecule resulting from the reaction with the reactive species. At a higher solute concentration, solute molecules can be directly radiolyzed [20].

total counts: 5
replicates: 0

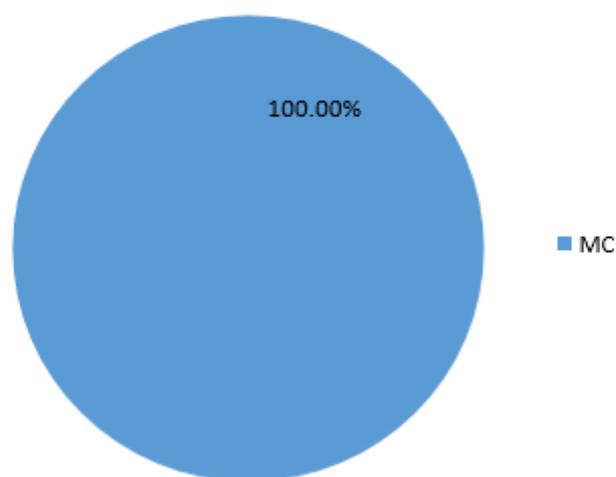


Figure 18: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for radiolysis by comparing all cyanotoxins.

Zhang et al. [108] observed a dose-dependent removal of MC-LR and –RR with an efficiency of $> 96\%$ employing ≥ 5 kGy γ – radiation. Parameters that affect the removal efficiency are the radiation dose, additives in the solution and water quality parameters such as NOM [105,108]. H_2O_2 and Na_2CO_3 have been shown to increase the formation of $\bullet\text{OH}$ and $\text{HO}_2\bullet$, respectively, whereas nitrate, nitrite and Triton X-100, a nonionic tenside, led to a decrease in removal due to scavenging of e^-_{aq} and $\bullet\text{OH}$ [108].

Although radiolysis is unlikely to be used in large-scale drinking water treatment, it can be used to study the mechanism of $\bullet\text{OH}$ -driven oxidation. Song et al. [109] determined rate constants for the reaction of $\bullet\text{OH}$ with specific sites of the MC-LR molecule in the following order $\bullet\text{OH}$ attack at the benzene ring in the Adda moiety ($10^{10} \text{ M}^{-1} \text{ s}^{-1}$) \geq $\bullet\text{OH}$ attack at diene in the Adda moiety (10^{10} to $10^9 \text{ M}^{-1} \text{ s}^{-1}$) $>$ $\bullet\text{OH}$ attack at aliphatic hydrogens ($10^8 \text{ M}^{-1} \text{ s}^{-1}$). Based on their results, they concluded, that the $\bullet\text{OH}$ attack at the Adda moiety accounts for almost 70% of the

overall rate constant for MC-LR ($2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [109]. As mentioned above, radiolytic treatment of CYN and ANTX has also been studied, but with a focus on determining the rate constants of their reaction with $\bullet\text{OH}$, so no removal efficiencies were reported [50].

As mentioned in chapter 5.4.1.2, one major drawback of radiolysis is the applied radiation itself. The use of ionizing radiation has higher operational requirements, i.e. for normal drinking water treatment and related research facilities atypical technical expertise and specialized equipment is necessary to perform radiolytic treatments. Commonly used radiation sources are radionuclides and electrostatic accelerators producing γ – radiation and electron beams, respectively [110]. As ionizing radiation can be harmful to biological systems, precautionary and protective measures have to be defined and fulfilled.

Sulfate radical-based AOPs

When comparing the cyanotoxins for SR-AOPs-based treatment, six counts occurred in total. CYN has the highest share, accounting for 50.00% of all related publications, followed by MCs (33.33%) and ANTXs (16.67%). No publications for NOD and STXs have been found in this search. When comparing this treatment technique with other AOPs, it is the only one for which MCs are not the most studied cyanotoxins in terms of their removal from drinking water. The main difference between this and other AOPs is the production of $\text{SO}_4^{\bullet-}$ as main reactive species besides $\bullet\text{OH}$. However, $\text{SO}_4^{\bullet-}$ can be generated in a similar manner as $\bullet\text{OH}$, via activation by energy, catalysts/transition metals or reaction with oxidants and other reagents using $\text{S}_2\text{O}_8^{2-}$ or HSO_5^- as precursors. So far UV radiation, plasma, ultrasound, transition metals (Fenton(-like) reactions), activated carbon, electrochemical oxidation, radiolysis, ozone, PBS buffer, low levels of NOM, and combinations such as UV/ TiO_2 or light/transition metals have been shown to successfully activate PMS or PS [19,21,111–115]. $\text{SO}_4^{\bullet-}$ can react with water pollutants via i) hydrogen abstraction, ii) addition to double bonds, and iii) e^- -transfer from e^- -rich moieties [21].

total counts: 6
replicates: 0

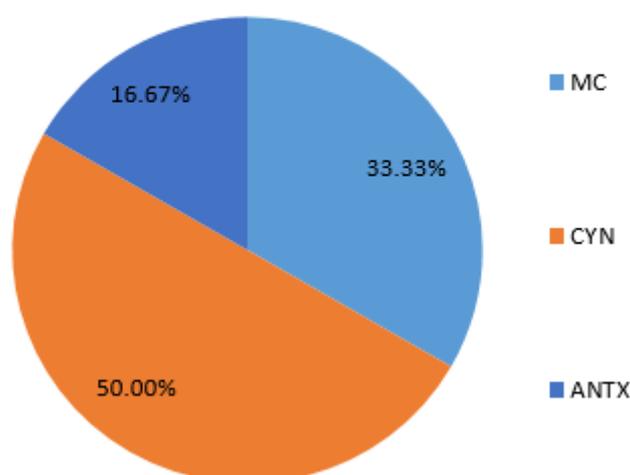


Figure 19: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for sulfate radical-based AOP techniques by comparing all cyanotoxins.

MC-LR, CYN, and ANTX have successfully been removed by SR-AOPs activating PMS and PS with different activation methods with efficiencies of up to 100%. He et al. [116] observed UV/PS to be more efficient than UV/PMS followed by UV/H₂O₂ for the removal of CYN under prevalent conditions, which agrees with results reported by Antoniou et al. [19] for the removal of MC-LR. On the other hand, Co²⁺/PMS was more efficient than the conventional Fenton, i.e. Fe²⁺/H₂O₂, followed by Ag⁺/PS when treating MC-LR-laden solutions at respective optimum pH. The Co²⁺/PMS system was more efficient than Fenton at pH5.8 but was partially inhibited under acidic conditions at pH3. Furthermore, when using heat as an activator, temperatures of 30 and 37 °C resulted in only approx. 4% removal applying H₂O₂ as oxidant, whereas PMS and PS at 30 °C were able to remove approx. 77% and 52% MC-LR, respectively [19]. A rather unexpected PMS activator is PBS, which is probably one of the most widely used buffers for neutral pH. The PBS/PMS system efficiently degraded and even (partially) mineralized Acid Orange 7, rhodamine B and 2,4,6-trichlorophenol. PBS can be very beneficial over other activation methods, as it does not require energy input, is comparably cheap and non-toxic, and phosphate can be present in natural waters at relatively high levels [114].

The removal efficiency can be affected by type, properties, and parameters of the activator, type and initial concentration of precursor, and water quality parameters such as pH, NOM, nitrate, transition metals and alkalinity [19,21,45,111]. Alkalinity, in form of CO₃²⁻ and HCO₃⁻ are known •OH-scavengers and were also shown to reduce the removal efficiency of ANTX using a UV/PMS system [45]. However, in the same study, transition metals commonly present in water and low levels of NOM were observed to increase the removal efficiency [45]. Fang et al. [111] conducted a more comprehensive study, showing that NOM constituents were able to enhance the degradation of 2,4,4'-trichlorobiphenyl at low levels even without UV irradiation, but led to a decrease in removal efficiency once a certain concentration was exceeded due to scavenging of SO₄^{-•}.

SO₄^{-•} exhibit a similar redox potential as •OH under acidic conditions and a higher redox potential at neutral pH (see Table 1). In addition, a very advantageous feature of SR-AOPs is the simultaneous generation of •OH as secondary radical in the presence of water, under alkaline conditions or when ozone is used to activate PMS. SO₄^{-•} is the predominant species at acidic pH, whereas •OH is the primary reactive species at higher pH. At neutral pH both radical species equally participate in the oxidation of pollutants [19,21,112,113]. Due to the consistency in reactivity across a broader pH range and the simultaneous generation of SO₄^{-•} and •OH, SR-AOPs might be more suitable for field applications than •OH-based AOPs. Furthermore, SR-AOPs are generally cost-effective and environmentally friendly. Depending on the activation method, operational costs can be reduced, e.g. when using catalysts or PBS rather than energy [21,114]. However, some transition metals can be toxic to the aquatic environment [114], which is why it would be favorable to either use non-toxic alternatives or heterogeneous system to prevent their release to the treated water. As for electro-Fenton, the activation via electrochemical oxidation can also lead to a quasi-constant supply of SO₄^{-•} due to the anodic regeneration of the precursor which could reduce its required initial concentration [112].

5.4.3.3. Comparison for conventional and other emerging treatment techniques

When evaluating preferences for certain cyanotoxins applying conventional and other emerging treatments, 13 of a total of 338 counts occurred in more than one toxin category. As expected, MCs have the highest share, accounting for 76.04% of all related counts. The remaining part is shared by ANTXs (10.36%), STXs (5.62%), CYN (4.44%), NOD (2.37%) and BMAA (1.18%). The most obvious differences compared to AOPs are the shift in the order of preference and the interest in the removal of BMAA. STXs is the least studied of the five cyanotoxins for AOPs, but it is the third most frequently reported of the six toxins for conventional and other emerging treatments, which might be due to the expected efficiency of adsorption and filtration techniques, as explained in chapter 5.4.2 in the paragraph on STXs. The interest in CYN decreases from second for AOPs to the fourth for conventional and other emerging treatments in the order of research interest according to the results of this search. In general, there is much more interest in studying conventional and other emerging treatments (62% of all counts) rather than AOPs (38% of all counts) for the removal of cyanotoxins, as it is shown in chapter 5.4.1.1 for the preferences for specific treatments. When comparing Figure 10 and Figure 20, the difference in the share of MCs should be highlighted, showing that, although there is a higher interest in conventional and other emerging treatments as seen from the total counts, the interest in MCs is decreased by approx. 5.5%.

total counts: 338
 replicates: 13

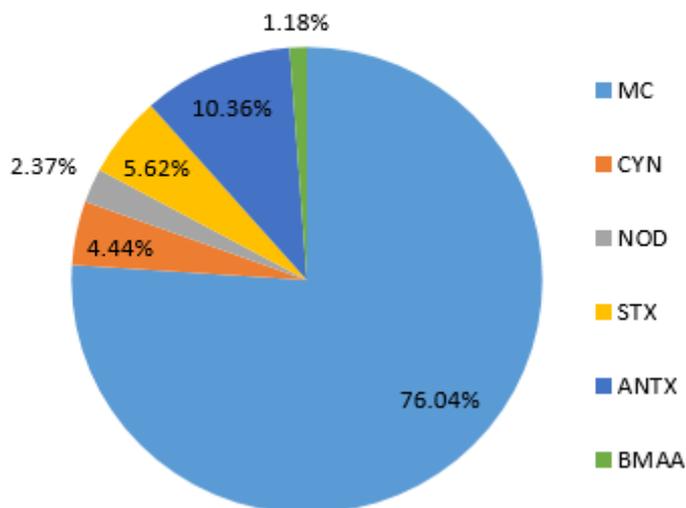


Figure 20: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for conventional and other emerging treatment techniques by comparing all cyanotoxins.

Biodegradation

For biodegradation, four of a total of 111 counts occurred in more than one toxin category, with MCs accounting for 85.59%, followed by CYN and NOD (5.41% each), ANTXs (2.70%) and STXs (0.90%). No publications were found for the biodegradation of BMAA. Again, there is a shift in interest compared to all conventional and other emerging treatments. The increase of interest in biodegradation of NOD compared to ANTXs and STXs could be explained by the similar chemical structure to MCs (see chapter 5.4.2 in the paragraph on NOD). Furthermore, STXs and ANTX might be of less interest, as studies have shown that STXs were

biotransformed into more toxic variants and ANTX is expected to be readily biodegraded in natural waters [13,14,34,42].

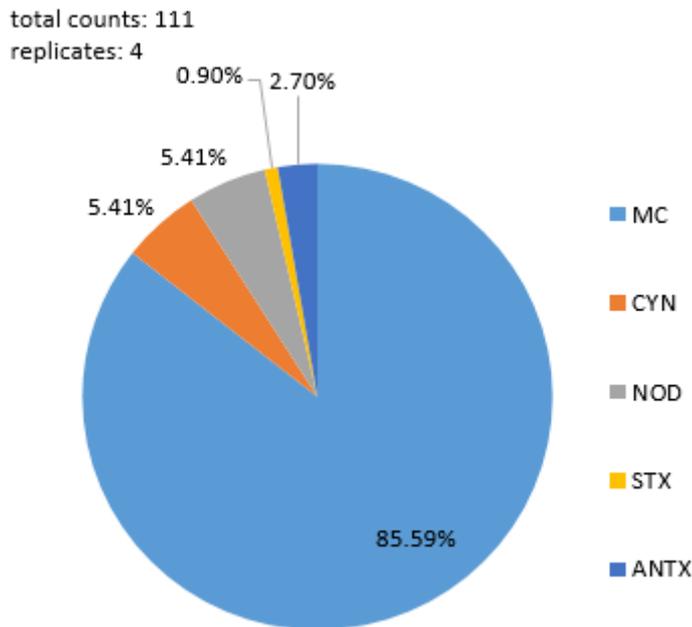


Figure 21: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for biodegradation by comparing all cyanotoxins.

Biodegradation of cyanotoxins can already happen as naturally occurring fate process before the contaminated water even reaches a drinking water treatment plant. Besides, biodegradation of water pollutants has intentionally been used for centuries in drinking and wastewater treatment [117]. Biodegradation is usually applied in combination with adsorption or filtration, where biofilms can form on the surface of the adsorbent or filter, respectively, and can be enhanced by pre-treatment using ozone [12,13]. Several studies showed the effective removal of MCs, NOD, CYN, ANTX and STXs after sufficiently long contact time and high biological activity [13,37,51,117,118]. Ho et al. [42] compiled a detailed list of microorganisms capable of degrading MCs and NOD with *Arthrobacter*, *Brevibacterium*, *Rhodococcus* and *Sphingomonas* to mention just a few examples. *Aeromonas* and *Bacillus* strains were identified as CYN-degraders, whereas marine bacteria, i.e. *Pseudomonas* and *Vibrio* have been observed to degrade STX [42,119,120]. Some microbial strains are capable of degrading different cyanotoxins and for MC- and NOD-degrading organisms, responsible gene clusters have been identified [42,120].

Factors obviously affecting the removal efficiency of biodegradation processes are the presence of specific microorganisms capable of degrading the respective cyanotoxin and the specificity of their excreted microbial enzymes reacting with the susceptible cyanotoxin sites, but also the composition, size, and surface of the medium on which the biofilm attaches to [12,42]. For instance, GAC has been suggested to be a better medium for the attachment of biofilms than sand due to its rougher surface. Furthermore, the initial toxin concentration, water quality parameters such as pH, temperature, character and amount of NOM and other constituents, e.g. metals, can also affect the degradation [42,119]. For instance, the MC removal efficiency was

observed to decrease from > 95% in summer to < 65% in autumn, which was attributed to the decreasing temperature [14].

The major advantages of biodegradation are its low technical, maintenance and cost requirements, simplicity, and environmentally benign character, as usually, no further chemicals need to be added, making it a “natural” treatment technique [42,117]. Furthermore, it enhances the removal efficiency of adsorption and filtration processes, as the pollutants are not only physically removed, but degraded [13,42]. Moreover, if applied after ozonation, biodegradation can remove biodegradable disinfection byproducts [13]. Another way of further enhancing biodegradation might be the application of a bioelectrochemical reactor in which microbial reactions are stimulated and promoted by inducing stress to the microorganisms [121].

Nevertheless, limitations are an initial lag-phase between toxin introduction into the biological treatment unit and actual degradation as the biofilm needs to acclimate to newly introduced substances, the maintenance of physiological conditions preferred by the present microorganisms and extensive biomass growth on the adsorbent or filter, increasing the need for backwashing [12–14,42,117]. Additionally, cyanotoxins usually only occur periodically and a biofilm might lose its degradation ability in the absence of the respective cyanotoxins [13]. However, the lag-phase can be reduced and the degradation ability regained by pre-inoculating the biofilm with the respective cyanotoxin(s) [13,42,117]. If chlorination and biologically active adsorption or filtration are sequentially used, the biological activity is unlikely to be maintained due to sustained disinfection effects [13,42]. As it is of high importance to drinking water quality and safety, it is worth mentioning again, that under certain conditions, some STXs were biotransformed to even more toxic variants.

Adsorption

For adsorption, five of a total of 120 counts occurred in this search, with 72.50% representing MCs related studies, followed by ANTXs (14.17%), STXs (7.50%), CYN (3.33%), NOD (1.67%) and BMAA (0.83%). For adsorption, ANTX and STXs receive more attention than CYN and NOD, which at least for STXs could be due to its known potential to bioaccumulate in marine organisms as discussed in chapter 5.4.2 in the paragraph on STXs. ANTX on the other hand is one of the smallest cyanotoxins, which might result in an easier adsorption even onto smaller pores. Adsorption is the adhesion of a substance to an adsorbent due to physical and/or chemical interactions between the adsorbent’s surface and the compound, usually only resulting in the physical removal, unless the adsorbent itself can produce reactive species (e.g. zero-valent iron nanoparticles (nZVI), see below) or is covered with a biofilm (see the paragraph on biodegradation in chapter 5.4.3.3). Adsorption is based on electrostatic interactions (ionic or charged functional groups) and hydrophobic interactions (van-der-Waals forces due to the polarity of a substance and the adsorbent’s surface) and is widely used in drinking water treatment, most commonly applying granular or powdered activated carbon (GAC and PAC, respectively) [12,13].

total counts: 120
replicates: 5

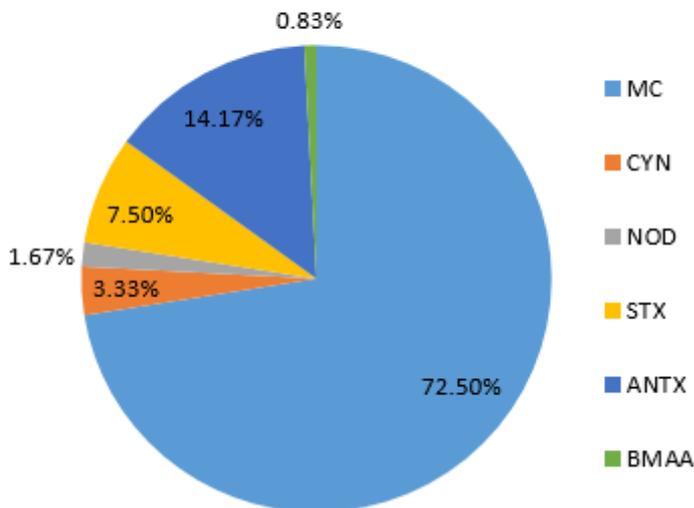


Figure 22: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for adsorption by comparing all cyanotoxins.

Cyanotoxins can be readily removed via adsorption, strongly depending on the adsorbent's characteristics, which need to be considered prior to its utilization. Activated carbon, the most commonly used carbon-based adsorbent, with pore sizes of $> 1 - 2$ nm and $< 1 - 2$ nm were shown to effectively remove MCs and STXs, respectively. For CYN, studies suggested pore sizes of the same range as used for the removal of MCs, as the hydrodynamic diameter is larger than expected from its molecular weight [12–14]. Up to 4 $\mu\text{g/L}$ MCs and CYN, and 10 $\mu\text{g/L}$ STX were effectively removed using up to 50 mg/L PAC after 1 h and ≤ 5 mg/L DOC. When using GAC, breakthrough of MCs, CYN, and STX is usually expected to occur after three to twelve months, depending on other water quality parameters as well as how often and to what extent the adsorbent is exposed to these cyanotoxins [12,13]. Alternative adsorbents have also been studied. Pavagadhi et al. [122] used graphene oxide which appeared to provide a higher adsorption capacity for MCs than GAC, removing 1700 $\mu\text{g/g}$ of MC-LR and 1878 $\mu\text{g/g}$ of MC-RR, whereas the used GAC adsorbed 1481.7 $\mu\text{g/g}$ and 1034.1 $\mu\text{g/g}$, respectively. Carbon nanotubes, synthetic carbon-based polymers and bioadsorbents such as chitin and oyster shell powder also showed higher removal efficiencies for MCs and STXs than activated carbon [12,123]. nZVI was used as a non-carbon, environmentally friendly alternative, forming flocs after removing cyanobacterial cells and MCs which can easily be removed via sedimentation. Additionally, besides adsorption processes, $\bullet\text{OH}$ can be formed which oxidize the pollutant [124].

The adsorption efficiency can be affected by the toxin itself, i.e. by its physico-chemical properties and molecular size, by the adsorbent's properties, including pore size and type, adsorption capacity and other surface characteristics, by water quality parameters such as pH, temperature and NOM content, and the adsorbent dosage (PAC) or freely available adsorption sites (GAC) [12–14,57,122,123,125]. Adsorption is most commonly integrated within the treatment chain and/or combined with other techniques to further enhance the efficiency and/or remove the adsorbent afterward.

One major advantage of adsorption-based treatment processes is the diverse range of types and properties of adsorbents that can be utilized. For instance, GAC is usually applied in fixed bed reactors as an additional treatment step or as replacement for primary filter media and hence, is used for long-term applications providing a constant barrier and habitat for biofilms which can remove biodegradable contaminations, whereas PAC is normally added as suspension providing a short-term barrier only when required, e.g. periodically occurring cyanotoxins are present, making it a more flexible and adjustable alternative to GAC [12–14]. On the other hand, nZVI showed a higher selectivity toward cyanobacteria compared to algae, daphnia, fishes, and plants, which could be used if cyanobacteria are the main problem, while activated carbon is non-selective and thus, can simultaneously remove a broader range of contaminants [13,124]. In contrast, each of the adsorbents also has some disadvantages. PAC is generally more expensive than GAC, needs to be removed after the adsorption treatment and cannot be regenerated, resulting in the need for proper disposal or further treatment – GAC and graphene oxide, for example, are reusable after sufficient regeneration [12–14,122]. As activated carbon is non-selective, potentially being suitable as an adsorbent for the simultaneous removal of different substances, this feature can also have a negative side effect, as competing reactions with e.g. NOM can occur, which is usually present in much higher concentrations [13].

Filtration

For filtration, three of a total of 69 counts occurred in more than one toxin category. 66.67% of all related counts referred to the removal of MCs, followed by ANTXs (17.39%), STXs (13.04%), CYN and BMAA (1.45% each). No publications for the removal of NOD using filtration was found in this search. However, the author is aware of at least one publication reporting on the removal of NOD using filtration [126]. The removal mechanisms of filtration and adsorption can be similar, i.e. separation due to size exclusion and sorption due to physico-chemical interactions with the used filter medium/membrane or sorbent, depending on the applied methods and materials, which might be why the order of preference in adsorption (Figure 22) is similar to what can be seen for filtration (Figure 23). During filtration, particulate or dissolved substances are physically rejected from passing a filter medium (conventional filtration) or semi-permeable layer (membrane filtration). Rejection occurs due to different interactions of the filter medium or membrane with the cyanotoxins, including size exclusion, electrostatic and hydrophobic interactions, steric hindrance and adsorption [12,14].

total counts: 69
replicates: 3

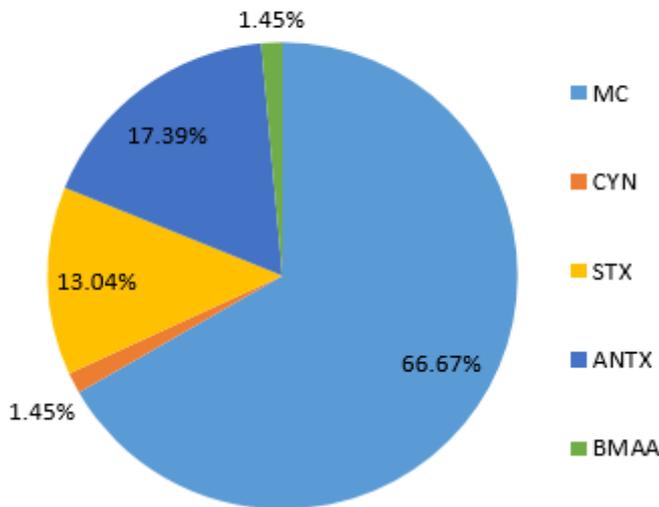


Figure 23: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for filtration by comparing all cyanotoxins.

Conventional (bank and sand filtration) and membrane (micro-, ultra-, nanofiltration and reverse osmosis (MF, UF, NF, and RO, respectively)) filtration are commonly applied in drinking water treatment [14]. NF and RO have been shown to be effective for the removal of MCs, NOD, CYN, ANTX, and STXs, whereas MF and UF are considered to be unreliable for the removal of dissolved cyanotoxins due to their larger pore size [13,14,57,127,128]. Larger molecules such as MCs might be removed by UF due to e.g. adsorption to the filter membrane or due to adsorption to PAC and subsequent removal via size exclusion [12]. Bank and sand filtration usually remove dissolved cyanotoxins via adsorption and/or biodegradation [125].

The removal efficiency depends on the present form, e.g. ionic functional groups, as well as size or hydrodynamic diameter of the cyanotoxin compared to the molecular weight cut-off pore size of the membrane, electrostatic interactions, membrane fouling which may alter the permeability, and water quality parameters such as pH [13,14]. As filtration is generally widely applied, no or only slight adjustments might be required to adapt an existing treatment setup to remove dissolved cyanotoxins. On the other hand, membrane filtration usually only provides physical removal, resulting in cyanotoxin enriched concentrates, which need to be properly disposed or further treated, e.g. with AOPs or electro-dialytic processes [18,129]. However, conventional filtration is often combined with biodegradation, as biofilms can form on the surface of the filter medium, which can reduce the need for further treatment [18].

Flocculation and coagulation

When considering flocculation and coagulation processes, one of a total of 22 counts occurred in more than on toxin category. MCs have the highest share of 77.27%, followed by ANTXs (18.18%) and NOD (4.55%). No publications for the application of flocculation/coagulation have been found for CYN, STXs, and BMAA. As mentioned in chapter 5.4.1.3, the flocculation/coagulation approach is of relevance for cyanobacterial cell removal, but is of less interest for the removal of cyanotoxins, as it is ineffective for the removal of dissolved

cyanotoxins. The reason why there were still 22 publications found in this search is most likely because these publications study the removal of cyanobacterial cells and intracellular toxins, the release of toxins from cells during the treatment through lysis and/or the fate of toxins during floc storage. Coagulation and flocculation has been used for at least one century for the removal of particulates and suspended matter and is still a very important method for water treatment in many countries. The traditional coagulation and flocculation process consists of adding of coagulants/flocculants and rapidly mixing. In coagulation, often applying metal salts, charged compounds are neutralized leading to precipitation. These precipitates and other suspended substances are then agglomerated during flocculation, forming larger flocs, which are then removed by e.g. sedimentation and/or filtration [12].

total counts: 22
 replicates: 1

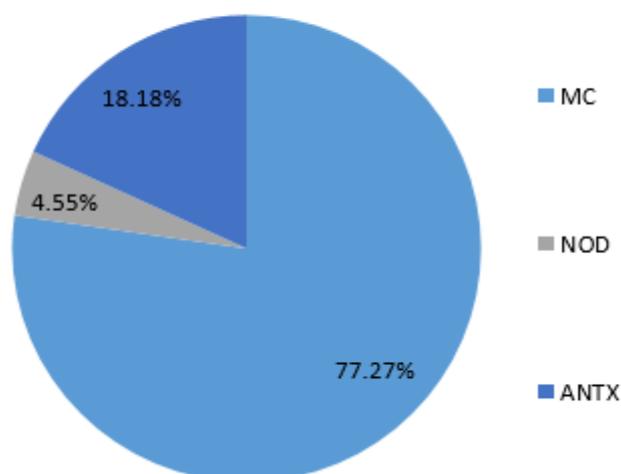


Figure 24: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for flocculation/coagulation by comparing all cyanotoxins.

Coagulation/flocculation using commonly employed coagulants/flocculants has been shown to be ineffective for the removal of dissolved/extracellular cyanotoxins [12,13,57,130,131]. However, intracellular cyanotoxins are removed, as cyanobacterial cells are efficiently separated from surface water without disruption of the cells and consequential release of intracellular metabolites [12,14]. Nevertheless, the effective removal of extracellular cyanotoxins can be achieved when treating the source water with a multi-barrier treatment chain including a coagulation/flocculation step. For example, when PAC is used to adsorb the cyanotoxins, the adsorbent can be removed from water by the formation of flocs and subsequent removal through sedimentation [12]. Besides PAC, chitosan has been studied, acting as an adsorbent for MCs and coagulant [132,133]. When using ferrate or ferric chloride as a coagulant, simultaneous oxidation of MC-LR by ferrate and coagulation of organic compounds by ferric ions occurred (for further information on ferrate and ferric chloride oxidation see the following paragraph on chemical oxidation) [82,134].

Chemical oxidation

For chemical oxidation, one of a total of 55 counts occurred in more than one toxin category. MCs account for 81.82% of all related publications, followed by CYN (9.09%), STXs and BMAA (3.64% each) as well as ANTXs (1.82%). Chemical oxidation is widely used for disinfection and degradation of microbial contamination and organic pollutants in drinking and wastewater treatment. Consequently, more studies regarding its efficiency on the removal of cyanotoxins were expected to be found. MCs have a relatively big chemical structure with several functional groups potentially being susceptible to oxidation, which might explain the larger share compared to other, smaller toxins. Surprisingly, no publications reporting on the chemical oxidation of NOD has been found in this search, despite its similar chemical structure compared to MCs. However, the authors are aware of at least one publication mentioning the effective chlorination of NOD [135]. The low number of counts found for ANTXs removal is most likely attributed to the inefficiency of chlorination to remove the neurotoxin [49].

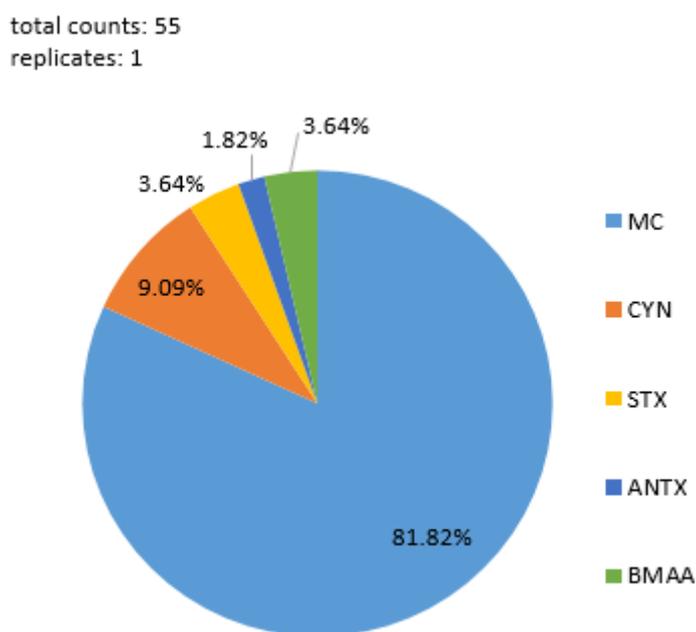


Figure 25: Analysis of the currently available scientific literature for preferences for certain cyanotoxins for chemical oxidation by comparing all cyanotoxins.

Chemical oxidation is widely used for the removal of pollutants and for disinfection of the distribution system using a variety of reagents including permanganate, chlorine- and iron-based chemicals (see Table 1 for the redox potentials of several commonly used oxidants) [16,18]. Chlorination effectively removes MCs, NOD, CYN, and STX, but was shown to be ineffective for the removal of ANTX [13,25,49,135]. As one of the only treatment methods that have been studied for the removal of BMAA, chlorination effectively degraded the neurotoxin via formation of chlorinated intermediates which could then slowly autodecompose. However, the chlorinated BMAA-intermediates could be converted back to BMAA under reductive conditions, for example, if the chlorine residual in the distribution system is depleted, which may pose a serious risk to consumers [136]. It is important to note, that not all chlorine-based reagents show the same oxidation capability. Nicholson et al. [135] found the removal efficiency for MCs and NOD to be in the order aqueous chlorine > hypochlorite >>

monochloramine \approx no significant effect. The latter one was also shown to be inefficient for the removal of CYN and STX [14]. Moreover, chlorine dioxide was shown to require impractically long contact time and/or high doses to sufficiently remove susceptible cyanotoxins [49,50].

Permanganate, usually applied as potassium salt, effectively removes MCs and ANTXs but was ineffective for the degradation of CYN and STX [13,25,49,57]. Permanganate showed faster removal than chlorine and no formation of halogenated disinfection byproducts was observed, which is known to potentially happen when employing certain chlorine-based oxidants [25,49]. The degradation pathway of MCs when using permanganate and chlorine-based compounds was reported to be similar to the pathways proposed for the oxidation by O_3 and $\bullet OH$, mainly attacking unsaturated double bonds, but at a slower reaction rate [18,49]. Iron-based oxidants, i.e. ferrate and ferric chloride were shown to effectively oxidize MCs and ferric iron is known to act as coagulant, possibly reducing the need of adding several different reagents to induce both processes, oxidation, and coagulation [12,82,134]. However, the results published by Takenaka and Tanaka [134] using ferric chloride could not be reproduced by Gajdek et al. [137] using the same conditions. In addition to these contradictory results, iron-based oxidants have only been studied for the removal of MCs so far.

The removal efficiency using chemical oxidants mainly depends on the type of oxidant and water quality parameters such as NOM content and pH, which also affect the oxidant demand of the water itself [14,49,135]. For example, an alkaline pH results in a decreased removal efficiency when aqueous chlorine or hypochlorite are used, as the formed hypochlorous acid dissociates to the less reactive hypochlorite under elevated pH [18,49].

The probably most obvious advantage of conventional chemical oxidation is the already frequent and wide application in drinking water treatment. However, one major disadvantage is the possible formation of toxic disinfection byproducts, which so far, was only observed for ozonation and chlorination. Furthermore, chlorine residual used for the disinfection of the distribution system can adversely impact taste and odor of drinking water [14,49].

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