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TECHNICAL BULLETIN

Treatment of Cyanotoxins in Drinking Water with Activated Carbon

Recently, cyanobacteria and cyanotoxins have become a high profile drinking water quality concern in both the United States and abroad. The combination of weather conditions, agricultural phosphate runoff, and other factors has produced water conditions that have favored the formation of cyanobacteria in surface water supplies. When certain conditions are met, these micro-organisms are able to grow excessively in surface water sources, forming efflorescence and producing unwanted chemical substances, including cyanobacterial toxins. Large blooms of cyanobacteria have threatened drinking water supplies, forcing municipalities to restrict water usage and modify their water treatment practices.

The issue of cyanobacteria and cyanotoxins is not new; the World Health Organization (WHO) released a provisional drinking water guideline for microcystin-LR of 1 ppb in 1998, and the EPA's Office of Water has listed both cyanobacteria and cyanotoxins on the first three drinking water Contaminant Candidate Lists (CCL1 in 1998, CCL2 in 2005, CCL3 in 2009). However, the lack of standardized analytical methods has led to slow development of formal drinking water standards for these compounds. While EPA is considering adding cyanotoxins to the Unregulated Contaminant Monitoring Rule (UCMR), to date these compounds have not been included (although it should be noted that EPA may include microcystin-LR and cylindrospermopsin in UCMR4 in 2015).

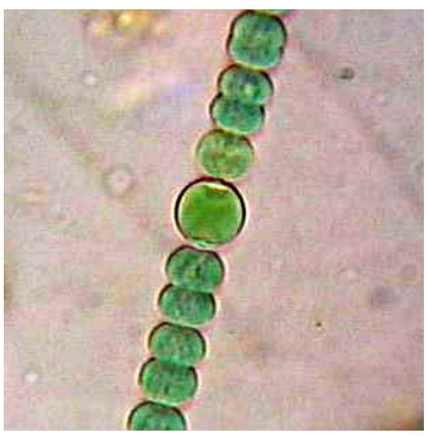
In the US, several states have implemented guidelines for cyanotoxins; three states (Minnesota, Ohio, and Oregon) have adopted guidance values for drinking water supplies for these compounds, and twenty states have adopted guidance values for recreational waterways. These guidance values, while not formal standards, at least provide some assistance to municipalities that have to periodically deal with harmful algal blooms (HABs).

What are Cyanobacteria?

Cyanobacteria are microscopic organisms of the eubacteria family or "real bacteria". Historically, these organisms were incorrectly referred to as "blue algae;" since the genetic material of cyanobacteria is not contained in a nucleus surrounded by a membrane, they are actually classified as bacteria and not as algae. While the designation of "blue algae" remains in use and comes from the color of the first identified species, it should be noted that not all cyanobacteria are blue: their colors range from green to purple.

Cyanobacteria have been present on Earth for at least 3 billion years. They have populated all areas, aquatic or terrestrial, and even in extreme conditions (Polar ice, ferruginous water sources, geysers, etc.). Certain cyanobacteria live in association with animal or plant organisms. In water, their existence may be planktonic (allowing themselves to be transported by water body movements) or benthic (bonded to immersed substrates). Due to their photosynthesizing system, cyanobacteria are able to synthesize sugars from CO_2, water, light and air.

Cyanobacteria are naturally found in surface waters, but are usually microscopic and invisible. Nevertheless, under certain conditions, they can proliferate and regroup in clumps visible to the naked eye to form blooms or efflorescences. These phenomena may lead to invasion of streams and even smothering of certain portions of bodies of water. Such proliferation is not predictable. Nonetheless, they require light, nutrients and oxygen.



Anabaena sperica

Green Efflorescence

What are Cyanotoxins?

Cyanobacterial toxins (or cyanotoxins for short) are metabolites of cyanobacteria products and stored in their cells. Cyanotoxins are released in water during cell lysis, either by natural death and decay, by chemical oxidation or by friction. To date, nearly 100 species of cyanotoxins have been identified and classified in a few large families (Table 1), separated into different groups according to their effects on health:

- Hepatotoxins: Liver disease
- Neurotoxins: Nervous system disorders
- Dermatotoxins: Irritation of the skin and mucosa

NAME OF THE TOXIN	DISEASE/DISORDER	PRESENCE IN FRESHWATER
Saxitoxin	Neurotoxin	Infrequent
Neosaxitoxin	Neurotoxin	Infrequent
Anatoxin a	Neurotoxin	Infrequent
Microcystin	Hepatotoxin	Frequent
Nodularin	Hepatotoxin	Infrequent
Cylindrospermopsin	Hepatotoxin	Infrequent
Lyngbyatoxin	Dermatotoxin	Infrequent (marine environment only)
Aplysiatoxin	Dermatotoxin	Infrequent (marine environment only)
Lipopolysaccharides	Dermatotoxin (irritation of all tissues)	Infrequent

Table 1: The Large Families of Cyanotoxins

The mechanisms for production of toxins are relatively unknown, and the genetic and environmental factors responsible for toxin metabolism operation have not yet been identified. Thus, outbreaks remain unpredictable, according to current knowledge, and any cyanobacterial proliferation must be considered as potentially dangerous.

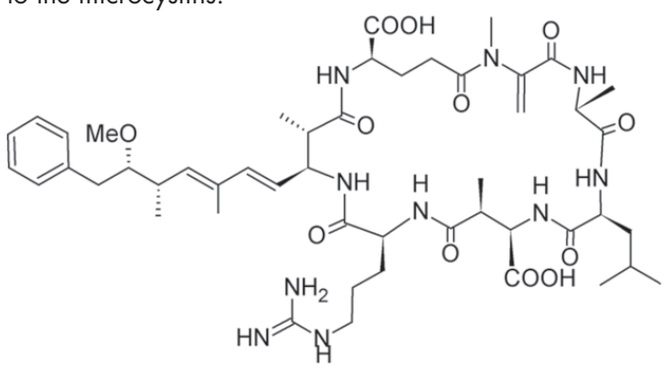
Some of the more common cyanotoxin compounds are as follows:

Microcystins

The most common cyanotoxins are microcystins, of which more than 65 different types have been identified.

Microcystin-LR, a recognized carcinogen, is especially studied and followed, and serves as an indicator of the presence of other toxins.

The chemical structure of microcystins includes 7 amino acids, of which 2 are variable (X and Z). The latter lend their name to the microcystins.



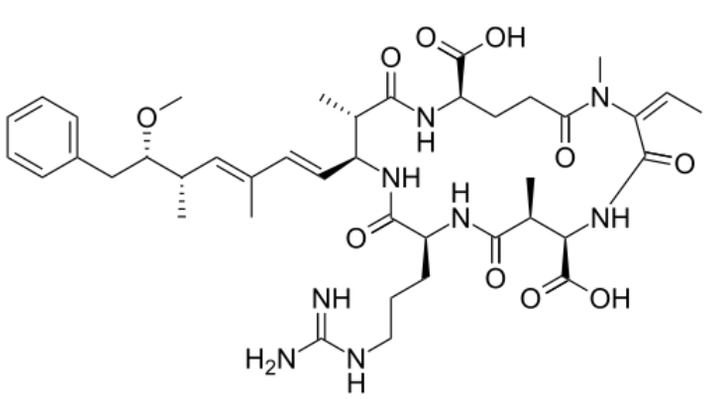
Microcystin-LR

TYPE OF MICROCYSTIN	VARIABLE AMINO ACID		TOXICITY (LD_{50} in µg/kg)
	X	Z	
Microcystin-RR	Arginine	Arginine	600
Microcystin-YR	Tyrosine	Arginine	70
Microcystin-LR	Leucine	Arginine	50
Microcystin-LA	Leucine	Alanine	50
Microcystin-LW	Leucine	Tryptophan	/
Microcystin-LF	Leucine	Phenylalanine	/

Table 2: Primary microcystins

Nodularins

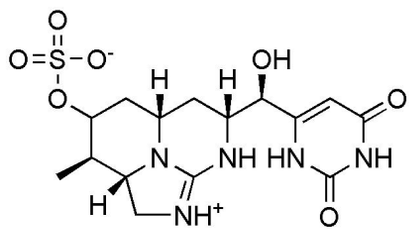
Nodularins are hepatotoxins including 5 amino acids.
The most frequent Nodularin has groups R1 and R2 of CH3 and for variable amino acid Z, Z-arginine.
The efflorescences of the Nodularia spumegina species, producing this nodularin, have been located in Australia and New Zealand.



Nodularin-R

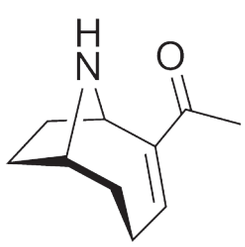
Cylindrospermopsin

Cylindrospermopsin is regarded as a hepatotoxin alkaloid. It presents a different mode of action from that of other hepatotoxins. It has long been reported in tropical areas. Nevertheless, now, episodes of appearance of this toxin are reported in many countries around the World.



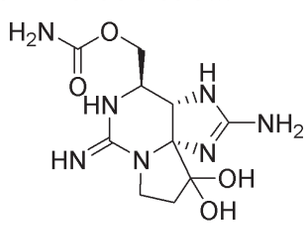
Anatoxin-a

Anatoxin-a is a neurotoxin. It is primarily produced by Anabaena, Oscillatoria and Planktothrix types of cyanobacteria. Because it is relatively unstable in neutral pH or basic aqueous solution, the probability of Anatoxin-a reaching high enough concentrations to produce a public health problem is low. Anatoxin-a has been detected in different countries, including Canada and northern European countries.



Saxitoxins

Saxitoxins are of neurotoxins that act by blocking nerve transmission, which can lead to paralysis.
Saxitoxins have primarily been recorded in Australia, Portugal, the United States and Brazil.
Concentrations are often expressed as STX-equivalent, since it is the most toxic variant. The conversion factors are recorded in the table below.



TYPE OF SAXITOXIN	VARIABLE CHEMICAL GROUPS					RELATIVE TOXICITY
	R1	R2	R3	R4	R5	
STX	H	H	H	$CONH^2$	OH	1
GTX2	H	H	OSO^{3-}	$CONH^2$	OH	0.359
GTX3	H	OSO^{3-}	H	$CONH^2$	OH	0.638
GTX4	OH	OSO^{3-}	H	$CONH^2$	OH	0.726
C1	H	H	OSO^{3-}	$CONHSO^{3-}$	OH	0.006
C2	H	OSO^{3-}	H	$CONHSO^{3-}$	OH	0.096

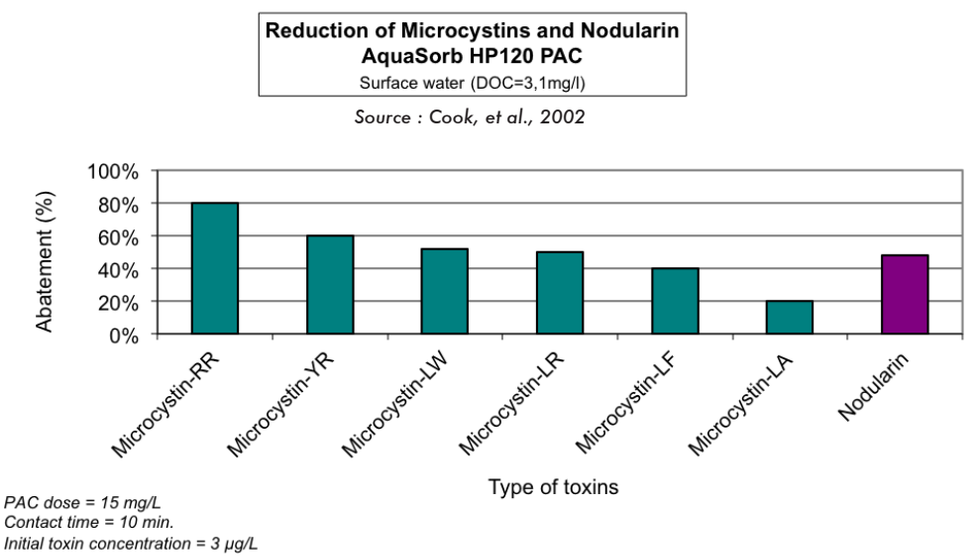
Table 3: Primary Saxitoxins

Treatment of Cyanotoxins: Powdered Activated Carbon (PAC)

A common technology for removing cyanotoxin compounds is Powdered Activated Carbon (PAC). Through its ease of application, PAC is well suited toward accidental, sudden or seasonal water issues, such as the appearances of cyanobacterial toxins. Also, PAC has the ability to taper back pollution peaks, and thus ensures a longer life expectancy of granular activated carbon (GAC) placed downstream in the same treatment chain.

PAC Treatment of Microcystins and Nodularin

Due to its frequency of detection and use as an indicator of other potential toxins, Microcystin-LR is of particular interest for water treatment. The elimination of microcystins, because of the quasi-global distribution of episodes of appearance, is a major concern in the treatment of drinking water.



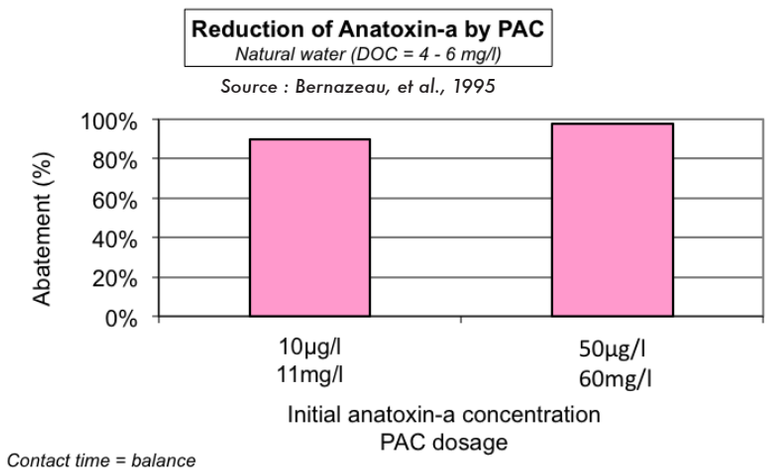
The large molecular size of these compounds tends to favor a more macroporous PAC for treatment. The above data is for AquaSorb™ HP120, a chemically activated wood based carbon. Other favorable results would be seen with other carbons with a significant pore volume in the target range, such as AquaSorb™ CB1-MW.

As noted in the data, Nodularin presents adsorption efficiency close to that of microcystin-LR.

PAC Treatment of Cylindrospermopsin

Cylindrospermopsin is also relatively well eliminated from water through dosing of PAC. It's molecular size also favors carbons with high mesopore and macropore volume. Applicable grades would include AquaSorb™ CB1-MW, AquaSorb CB3-MW, or AquaSorb HP120. Carbon dosages of 15 mg/l and contact times of 30 minutes resulted in cylindrospermospin reductions of 60% to 100%, depending on carbon type. In this testing, the water analyzed with a DOC of 3.5 mg/L and initial concentration of cylindrospermopsin of 3.25 µg/L.

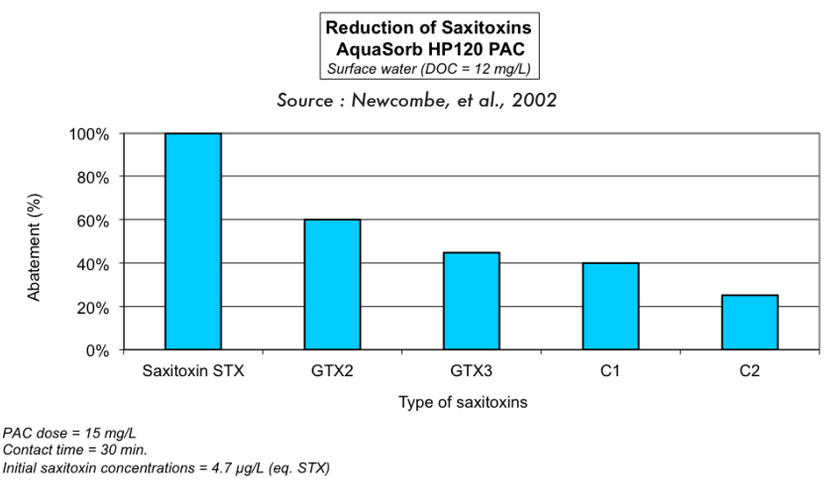
PAC Treatment of Anatoxin-a



PAC is an effective method for the elimination of Anatoxin-a. In comparison, effectiveness is close to that observed for microcystin-LR. For example, under the same operating conditions as those used in the Microcystin study, in order to reach 90% reduction from an initial toxin concentration of 10µg/L, a dosage of 7-9 mg/L of PAC was required for microcystin-LR, while a dosage of 11 mg/L was required for anatoxin-a (results obtained upon equilibrium).

PAC Treatment of saxitoxins

As with other algal toxins, PAC has proven to be effective on saxitoxins, for which the most toxic is the STX.



Powdered Activated Carbon is effective for the treatment of saxitoxins, even if the reduction level varies according to the types of saxitoxins. Because the adsorption order observed follows the order of the toxicity of these compounds, the conclusion is that the PAC is effective for the elimination of the toxicity associated with the presence of saxitoxins.

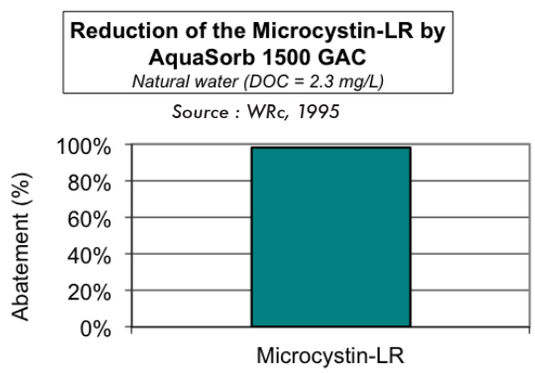
The results presented were obtained for a contact time of 30 minutes. In this study, a longer contact time of 60 minutes was also used. At this higher contact time, identical % reductions were seen for STX, GTX2, GTX3 and C2. Only the elimination of C1 was slightly improved.

Treatment of Cyanotoxins: Granular Activated Carbon (GAC)

Granular activated carbon is also an effective method for the elimination of cyanobacterial toxins. As with powdered activated carbon, the effectiveness of granular activated carbon depends on various parameters, such as the type of toxin, organic matter and other pollutant content in the water (by GAC competition or pre-saturation effects), the type of carbon, etc.

GAC Treatment of Microcystin-LR

For the elimination of microcystin-LR, a mesoporous GAC such as AquaSorb™ 1500 type activated carbon has proven to be effective, again due to the larger molecular size of the microcystin compounds.

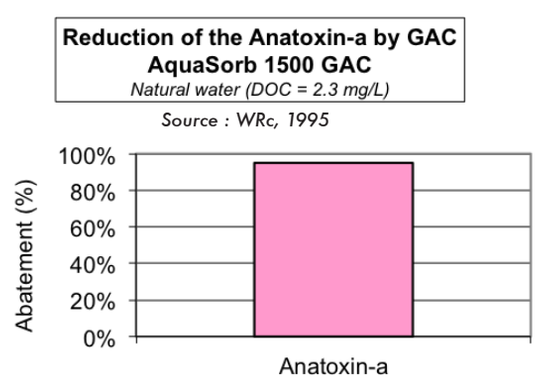


Contact time = 7.5 min
Doping = 17 days
Initial Microcystin-LR concentrations = 9.6 µg/L

In addition to physical adsorption, microcystins are biodegradable compounds, and biodegradation of microcystin-LR on GAC can occur under the correct conditions. Jacobi's AquaSorb™ PICABIOL2 type biological activated carbon is an option in these cases. For biodegradation to occur, it is important that the presence of toxins be regular, thus allowing the biomass formed on the GAC to be maintained. Contact times of 15 minutes minimum are required for proper operation of a biological GAC bed.

GAC Treatment of Anatoxin-a

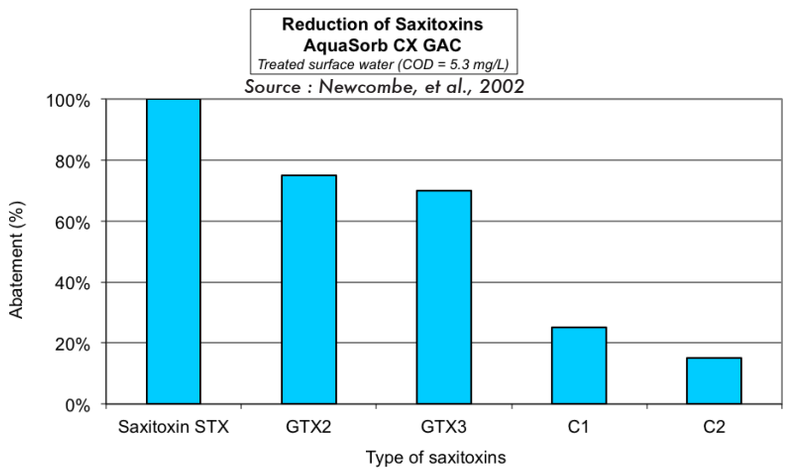
Similar to Microcystin-LR, Anatoxin-a can be effectively removed with a mesoporous carbon such as AquaSorb™ 1500. Also, biodegradation also remains an option, for which a carbon designed for biological operation (AquaSorb™ PICABIOL2) can be employed.



Contact time = 7.5 min.
Doping = 14 weeks
Initial Anatoxin-a concentrations = 9.2 µg/L

GAC Treatment of Saxitoxins

In contrast to the other types of cyanotoxins described in this paper, Saxitoxins are better suited to a microporous activated carbon, such as coconut shell-based carbons. Past studies have utilized Jacobi AquaSorb™ CX:



After 5 months of filter operation
Intermittent doping during 24 hours at 0, 1 and 5 months (simulation of seasonal appearance)
Contact time = 15 min.
Initial concentrations *STX=1-10µg/l* *GTX2=3-15µg/l* *GTX3=2-6µg/l* *C1=12-40µg/l* *C2=2-5µg/l*

The above study was designed to simulate a seasonal appearance of toxins. The study simulated five months of operation, with doping of toxins carried out episodically (at the beginning of the experiment, after 1 month and after 5 months). The goal was to simulate sudden, seasonal episodes of cyanobacterial efflorescences.

The adsorption of saxitoxins on GAC presents the same trend as the reduction observed with PAC. The efficiencies relative to the elimination follow the same order: The STX and GTX are well eliminated, while C1 and C2 are less well eliminated by this treatment. Thus, as previously, because the toxicity of toxins also follows this classification, we can say that the activated carbon allows for good elimination of the total toxicity.

Conclusion:

Cyanotoxins have continued to grow in importance as a drinking water treatment challenge for municipal water systems. Fortunately, activated carbon, both in powdered and granular forms, has proven to be an effective treatment method for various commonly encountered cyanotoxin compounds. Depending on the type of cyanotoxin compound present, various types of carbon products can be effectively utilized.

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Image and Chemical Structure Acknowledgements

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