

Review

Recent Advancements in the Removal of Cyanotoxins from Water Using Conventional and Modified Adsorbents—A Contemporary Review

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Abstract: The prevalence of cyanobacteria is increasing in freshwaters due to climate change, eutrophication, and their ability to adapt and thrive in changing environmental conditions. In response to various environmental pressures, they produce toxins known as cyanotoxins, which impair water quality significantly. Prolonged human exposure to cyanotoxins, such as microcystins, cylindrospermopsin, saxitoxins, and anatoxin through drinking water can cause severe health effects. Conventional water treatment processes are not effective in removing these cyanotoxins in water and advanced water treatment processes are often used instead. Among the advanced water treatment methods, adsorption is advantageous compared to other methods because of its affordability and design simplicity for cyanotoxins removal. This article provides a current review of recent developments in cyanotoxin removal using both conventional and modified adsorbents. Given the different cyanotoxins removal capacities and cost of conventional and modified adsorbents, a future outlook, as well as suggestions are provided to achieve optimal cyanotoxin removal through adsorption.

Keywords: cyanotoxin removal; biochar; activated carbon; molecularly imprinted polymers; nanotubes; chitosan; adsorption materials

1. Introduction

Algae are one of the most primitive and pervasive life forms on the planet. For millennia harmful algal blooms (HABs) have occurred naturally, arising from a multitude of both marine and freshwater microalgae species, whereby the algae produce toxins in response to various environmental pressures. There are some indications that HABs are increasing in frequency due to global warming, eutrophication, deposition of nitrogen and phosphorus from anthropogenic activities, interspecies chemical warfare, as well as from negative impacts upon the landscape (i.e., loss of vegetation, loss of riparian habitat) [1–10]. Cyanobacteria are capable of adapting to extreme climates and can thrive under nutrient limiting conditions [11,12].

The release of HAB toxins can have a variety of negative consequences. For example, some negative ecological impacts include fish kills, shellfish poisonings, cattle, and other domestic animal poisonings from surface waters that are afflicted with HAB toxins [13–16]. Additionally, instances of negative economic impacts may stem from income reduction due to the loss of recreational use, and commercial and subsistence fishing resources [14]. Finally, negative human health impacts are illustrated by

chronic and acute exposures to algal toxins via drinking water, exposure to aerosols carrying algal toxins, shellfish poisoning, bathing, and other routes of exposure, such as from bioaccumulation in crops [13,15,17–19]. In 2017 the United States Geological Survey (USGS) agency conducted a survey of cyanotoxins in 11 major coastal and inland rivers of the United States (US), as shown in Figure 1 [20]. The surveyed rivers represent major sources of recreational and drinking water for millions of people and animals in the US. The presence of cyanotoxins or cyanotoxin genes were detected in all of the rivers, except the Connecticut River [20].

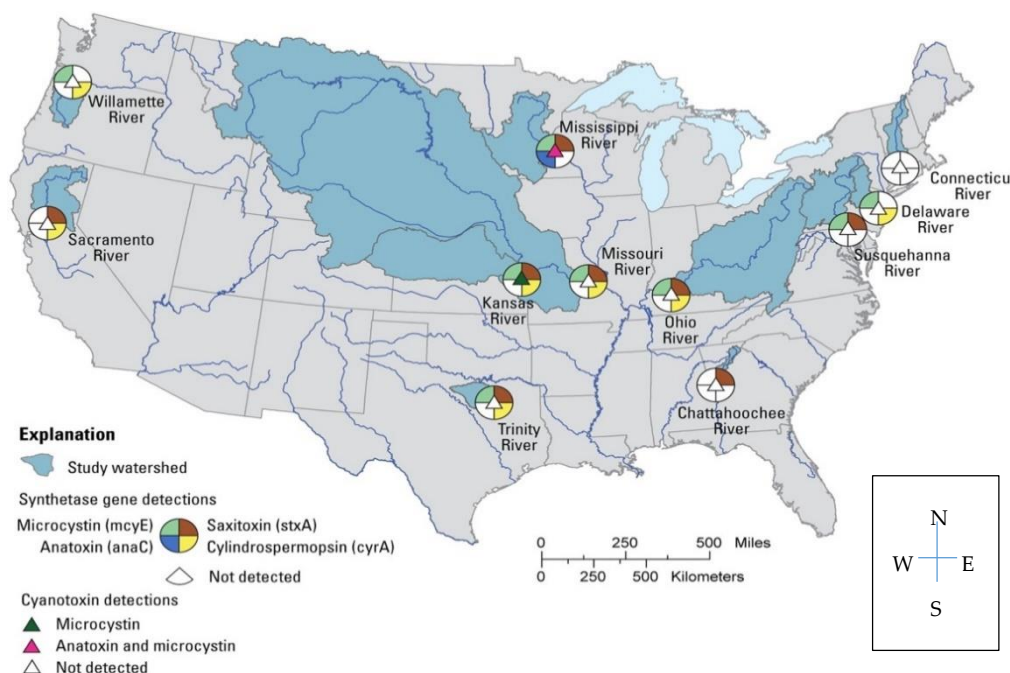


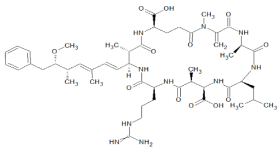
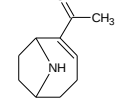
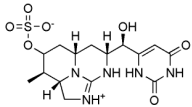
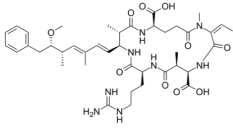
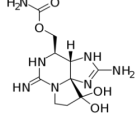
Figure 1. United States Geological 2017 Survey (USGS) of 11 major coastal and inland rivers of the US for the detection of four cyanotoxins and their genes: mcyE (microcystins), anaC (anatoxins), stxA (saxitoxins), and cyrA (cylindrospermopsin) [20].

However, currently in the US there are no regulatory limits on the concentrations of HAB toxins in drinking water, only health advisory limits. For example, the US Environmental Protection Agency (USEPA) sets a 10-day drinking water health advisory limit for microcystin-LR (the main toxin produced by *Microcystis*) at 1.6 $\mu\text{g/L}$ for school-age children and adults, and 0.3 $\mu\text{g/L}$ for bottle-fed infants. The USEPA 10-day drinking water health advisory limit for cylindrospermopsin (a toxin produced by *Aphanizomenon flos-aquae*) is 3.0 $\mu\text{g/L}$ for school-age children and adults, and 0.7 $\mu\text{g/L}$ for bottle-fed infants [21]. Many countries have set their health advisories according to the World Health Organization's provisional guidance, which was set at 1.0 $\mu\text{g/L}$ for microcystin-LR in 1998 [22].

One approach to mitigate HAB toxins is to evaluate algal stressors from a holistic viewpoint. Using an integrated approach to risk assessment (e.g., humans, biota, and natural resources) and applying the data generated can offer better-informed risk management of HABs [3,23–26]. If the stressors and potential growth of HABs can be prevented or mitigated through the implementation of subtle, yet important, ecological changes (i.e., reduction of nitrogen and phosphorus through increased use of riparian habitats, wetlands mitigation, reduction of farm soil runoff, reduction in rising temperatures due to climate change), then costs associated with removal of the toxins can be reduced. However, when risk management approaches do not work effectively, or when they completely fail, HAB toxins will occur in drinking water sources and potentially find their way into finished drinking water. Engineering controls are needed to ensure safe drinking water sources and finished drinking water supplies that are free of HAB toxins.

Research on the removal of algal toxins has primarily focused on *Microcystis*, although other species associated with HABs continue to rise in the US [4,27] and globally [28]. For example, the filamentous cyanobacteria *Dolichospermum* (formerly known as *Anabaena*) cells can produce various algal toxins: microcystins, anatoxins, and saxitoxins; and *Aphanizomenon flos-aquae* can produce cylindrospermopsin [7]. Table 1 provides a brief list of algal toxins and their physico/chemical properties.

Table 1. Physico/chemical properties of several algal toxins.

Algal Toxin	Chemical Structure	MW	Molecular Formula	Log D _{ow}
Microcystin-LR		994.55 Da	C ₄₉ H ₇₄ N ₁₀ O ₁₂	pH 5.5 = −4.68 pH 7.4 = −4.70
Anatoxin-a		165.12 Da	C ₁₀ H ₁₅ NO	pH 5.5 = −1.72 pH 7.4 = −0.72
Cylindrospermopsin		415.42 Da	C ₁₅ H ₂₁ N ₅ O ₇ S	pH 5.5 = −4.23 pH 7.4 = −4.30
Nodularin *		824.44Da	C ₄₁ H ₆₀ N ₈ O ₁₀	pH 5.5 = −3.88 pH 7.4 = −3.94
Saxitoxin *		299.13 Da	C ₁₀ H ₁₇ N ₇ O ₄	pH 5.5 = 1.0 pH 7.4 = −5.49

* Chemical structures are drawn by Ed (Edgar181)—own work, public domain, <https://commons.wikimedia.org/w/index.php?curid=16209132>.

Various engineering controls have engendered a range of success in the removal of HAB toxins. Some commonly used engineering controls at drinking water treatment plants (DWTPs) are filtration, ozonation, coagulation, chlorination, reverse osmosis, photocatalysis, potassium permanganate, and powdered activated carbon [15,29–37]. However, newer techniques are being explored, such as inactivation by ultrasound, biological approaches for neutralizing toxins, starch-based flocculation, silica-quaternary ammonium nanofilm-coated fiberglass mesh, and engineered polysaccharide lyases [33,38–41].

This review article will focus on newly developed adsorbent materials. For example, carbon- and silica-based adsorption materials, iron-modified adsorbents, and a few novel adsorption technologies, such as nanotubes and chitosan-cellulose, to remove or mitigate algal toxins from natural waters. We will compare the performance of coal-based adsorbents, coconut-based activated carbon, biochar, as well as examine the adsorption kinetics and isotherm parameters of various granulated activated carbons and powdered activated carbon materials. As such, we expect that this contemporary review will be useful for scientists and engineers as a guide for selecting a cost-effective adsorbent for the treatment of HAB toxins in water sources.

2. Adsorption by Activated Carbon

2.1. Non-Agricultural Based Activated Carbon

Activated carbon (AC) is an effective adsorbent in the removal of contaminants from water. AC is either used in the form of granular activated carbon (GAC) or powdered activated carbon (PAC). Mineral coal is among one of the raw materials for AC [42]. AC, based on wood and agricultural

waste, offers a cost-effective way of replenishing coal-based adsorbents. Regardless of its form, AC is an excellent adsorbent that can remove several contaminants from solutions. Table 2 summarizes the performance of AC adsorbents during the treatment of cyanotoxins. The adsorption capacity is driven by the micropore (primary micropore, diameter (d) ≤ 0.8 nm, and secondary micropore, $0.8 < d \leq 2$ nm), mesopore ($2 < d \leq 50$ nm), and macropore ($d > 50$ nm) spaces, in addition to functional groups. When in solution, AC forms aggregates with diverse pore size, which boosts the internal surface area on the hydrophobic interior [43], promoting the adsorption of organic matter like cyanotoxins. However, the presence of large molecules, like natural organic matter (NOM), hinders the adsorption; they occupy the macropores, blocking access to mesopore and micropores by smaller molecules, like cyanotoxins.

Nodularin, a toxin is produced by the cyanobacterium *Nodularia spumigena*, can compromise the quality of treated effluent wastewater. Nodularin is a potent hepatotoxin and can cause liver hemorrhage in mice at 50 $\mu\text{g/kg}$; nodularin accelerates and supports liver cell division, thus acting as a carcinogenic agent [44]. Mashile et al. [45] evaluated the removal of nodularin in wastewater from a treatment facility, and its receiving river water, in South Africa, using waste-tire PAC. During the study, no nodularin was detected in the influent wastewater. However, after treatment, 16.6 ± 0.5 ng/L nodularin was detected in the effluent, and 14.2 ± 0.8 ng/L was found in the river water. The presence of nodularin in wastewater effluent was attributed to the rupture of cyanobacteria during the mechanical treatment of wastewater, thus releasing the toxin from the cells. The optimum adsorption capacity of PAC occurred at pH 5.0, achieving $99.8 \pm 1.5\%$ nodularin abatement from river and lake water samples.

The carboxylic group of nodularin remains relatively stable at pH < 4.0 ; above this pH, the molecule becomes negatively charged [46]. The point of zero charge (pH_{ZPC}) of tire-PAC is at pH 5.37, which means that it is positively charged at pH < 5.4 . The presence of negatively charged nodularin and positively charged adsorbent facilitated the electrostatic attraction increasing the adsorption of nodularin. The heat of adsorption, using the Temkin model, was greater than a unit, indicating that the electrostatic mechanism is a major force driving the adsorption process [45]. The adsorption of saxitoxin with bituminous PAC elicited similar results [47]. Bituminous PAC has a pH_{ZPC} of 6.1; thus, at pH > 7.0 , it can easily attract the positively charged saxitoxin.

The source from which PAC is made can greatly influence the adsorption capacity of cyanotoxins. Cook and Newcombe [48] explored the performance of wood PAC and coal-based PAC in the adsorption of four microcystins: microcystin-RR, -LR, -YR, and -LA. Water containing microcystin-LA (MC-LA) and microcystin-LR (MC-LR) was spiked with microcystin-YR (MC-YR) and microcystin-RR (MC-RR). The water was treated with both coal and wood PAC for 3.0 days at pH 6.0–8.5. After the treatment, coal-based PAC outperformed wood-based PAC. In both cases, the removal of microcystin followed: MC-RR $>$ MC-YR $>$ MC-LR $>$ MC-LA. This is because the adsorption of microcystin is governed by the net charge on the molecule, which was controlled by the number of negatively charged carboxyl, D-glutamate, and β -methylaspartate groups, and positively charged base amino groups. At pH 6.0–8.5, MC-RR, MC-YR, MC-LR, and MC-LA have a net charge of 0, -1 , -1 , and -2 , respectively. The difference in MC-YR and MC-LR adsorption is attributed to the hydrophilic nature of MC-LR, although the adsorption of these microcystins did not correlate with the octanol-water partition coefficient of the compounds [49].

Like PAC, the performance of GAC in the treatment of cyanotoxins depends on the GAC properties which facilitate the electrostatic attraction. The application of GAC in the removal of decarbamoylsaxitoxin (dc-STX) exhibited a repulsive force between positively charged GAC and cationic saxitoxins [50]. Silva Buarque et al. [50] further studied the effect of pore size on the adsorption of saxitoxin, and it was found that mesopores played an essential role in promoting adsorption capacity and adsorption kinetics of coconut GAC. GAC with an elevated amount of mesopores exhibited higher adsorption capacity and a higher pseudo-second-order rate constant. Small pore diameters facilitated large surface areas [51], which improved the adsorption of contaminants. GAC surface charge also influenced its adsorption capacity.

Table 2. Performance of different coal-based adsorbents during the treatment of cyanotoxins.

Toxin	Adsorbent/Process	Conditions	Adsorption Characteristics/ Mechanisms	Performance Removal	Ref.
Microcystin-RR	AC fibers-sodium alginate- <i>Sphingopyxis</i> sp.	temp: 32.5 °C, pH = 6.9		0.77 µg/mL/h	[52]
Nodularin	Tire PAC	C ₀ = 50–5000 µg/L, dose: 8.0 g/L, pH = 5.0, Temp: 25 °C	Electrostatic, Langmuir isotherm, PSO, film diffusion	345 µg/g	[45]
Microcystin-RR, -LR, -YR and -LA	Wood PAC	C ₀ = 2–10 µg/L, dose: 23–50 g/L, contact time: 3 day, pH 6.0–8.5		MC-RR ≈ 85%, MC-YR ≈ 51%, MC-LR ≈ 37%, MC-LA ≈ 5%	[48]
	Coal PAC	C ₀ = 2–10 µg/L, dose: 23–50 g/L, contact time: 3 day, pH 6.0–8.5		MC-RR ≈ 98%, MC-YR ≈ 79%, MC-LR ≈ 70%, MC-LA ≈ 30%	[48]
Saxitoxin	Coal PAC	C ₀ = 25 µg/L, dose: 1.0–80.0 mg/L, contact time: 0.5–24 h, pH: 8.2–10.7	Electrostatic	85.0–100%	[47]
Cylindrospermopsin	Tire PAC	C ₀ : 25 µg/L, dose: 50.0 mg/L, contact time: 60 min, pH: 3.0	Langmuir isotherm, PSO, electrostatic	107 µg/g	[53]
Microcystin-LR, -LA	Biological GAC	C ₀ : 5.0 µg/L, Time: 6 months, EBCT: 15 min		100%	[54]
Saxitoxin (STX) dc-STX	GAC	C ₀ : 10.5 µg/L dc-STX & STX: 60.4 µg/L, dose: 300 mg/L, temp: 28 °C, pH: 7.0, contact time 24 h	PSO, chemisorption	17.412 µg/mg dc-STX 3.034 µg/mg STX	[50]
Anatoxin-a	F400 GAC	C ₀ : 100 µg/L, Time: 90 day, dose: 50 mg/L	Freundlich isotherm	7.1 µg/mg	[55]
Microcystin-LR	Bituminous coal GAC	C ₀ : 50 µg/L, Time: 72 h, dose: 0–11 mg/L	Langmuir isotherm	6–10 µg/mg	[56]

PSO = pseudo-second-order; Ref. = Reference.

2.2. Agricultural Based Activated Carbon Adsorbents

Activated carbon can be very expensive to make due to its regeneration and reactivation processes [57]. However, to make activated carbon more affordable, the costs incurred during the synthesis of activated carbon can be reduced by using agricultural residues. For example, low-cost agricultural residues such as coconut shells, bamboo, and olive pits can be used as alternative raw materials for producing activated carbon [58–63]. These agricultural residues are inexpensive, locally accessible, more abundantly available, and can contribute to resource sustainability. The downside to using agricultural residues can be a higher economic and environmental cost, as associated with both the creation and regeneration of those materials. In Ani, et al., they review various biomass materials used as adsorbents [63]. The review article points out that in the production of biomass adsorbents either pyrolysis or physical/chemical activation is necessary to produce the adsorbents from the biomass [63]. These can both be intensive processes that use a lot of natural energy to pyrolyze the biomass adsorbents or produce ultra-pure water to rinse and clean the final products.

2.2.1. Coconut Shell

Coconut shell-based activated carbon has proven to be effective for the removal of heavy metals, dyes, and organic matter [57,64–66]. The characteristics of the different coconut shell-based activated carbons were studied for the removal of cyanotoxins are summarized in Table 3. Coconut shell-based activated carbon is predominated by primary (<0.8 nm) and secondary (0.8–2 nm) micropores, while coal-based activated carbon has a higher percentage of macropores and micropores, and wood-based carbon is predominated by mesopores. Pore size affects the surface area of the adsorption process; a smaller pore size will exclude larger size contaminants, which adversely affect the adsorption of cyanobacteria [61].

Table 3. Characteristics of coconut-based activated carbon adsorbents.

Adsorbent	Process	Surface Area m ² /g	Pore Size Volumes cm ³ /g	Zeta Potential mV	Ref.
Coconut shell-based GAC, commercially obtained from Norit	Pulverized and sieved through 60 × 80 mesh size	950	Meso = 0.089 Micro = 0.812	NA	[66]
Coconut-based PAC	NA	1216.22	Meso = 0.11 Micro = 0.45	−35.37	[67]
Coconut-based carbon, Aqua Carb CX 1230	Enhanced activation	1568	Meso = 0.08 Micro = 0.64	NA	[68]
Coconut shell-based PAC, GX 203	NA	752.8	NA	3.02	[69]
Coconut palm-based AC, Brazil	Particles ground to size < 100 µm	715.5	NA	NA	[70]
Coconut shell, GAC	Steam activation	1001	Meso = 0.114 Micro = 0.374	NA	[71]

NA = information not available; Ref. = Reference.

PAC is more effective than GAC for adsorption of microcystins [67]. In 1993, Donati et al. [60] compared the removal of MC-LR using two coconut shell-based PACs, three coal-based PACs, two wood-based, and one peat moss-based PACs. The raw material of the PAC determined the amount of pore volume. It was observed that wood-based PAC had the greatest volume of micropores and mesopores, followed by coal-, coconut shell- and peat moss-based. The most effective adsorption was achieved by wood-based PAC with maximum adsorption of 280 µg of MC-LR per mg carbon in Milli-Q water samples. The coal-based PACs were next best, with adsorptions of 116, 75, and 70 µg of MC-LR per mg of carbon. The lowest maximum adsorption capacities were given by coconut shell-based PACs at 40 and 20 µg of MC-LR per mg of carbon, followed by peat moss-based PACs at 20 µg of MC-LR per mg of carbon. Similar results were observed in a study where micropores were dominant for coconut shell-based ACs, thereby reducing the adsorption capacity of MC-LR [68]. Therefore, the carbon pore size, mostly mesopores, dominates MC-LR adsorption rather than micropores, and the raw material of the adsorbent determines the percentage of the availability of the mesopores.

In a study conducted by Pendleton et al. [62], a comparison of MC-LR adsorption by wood-based and coconut-based AC was investigated. It was observed that wood-based AC has more oxygen content than that of coconut-based AC. The pH_{ZPC} of wood-based AC and coconut-based AC was approximately 3.4 and 6.2, respectively. Depending on the pH, the net surface charge of wood-based AC is stronger than that of coconut shell-based AC. At pH 6.5, wood-based AC consists of a net negative charge, whereas coconut shell-based AC has approximately a neutral charge. The Langmuir isotherm was suitable for describing adsorption of MC-LR for both wood-based AC and coconut shell-based AC. Wood-based AC outperformed coconut shell-based AC, showing a greater affinity for adsorption. It was found that pH greatly affects the adsorption process of MC-LR. Lower pH leads to increased adsorption, due to the free carboxyl group in the D-glutamic acid, and the β-methyl aspartic acid residues of the MC-LR, all leading to a decrease in microcystin water solubility and increasing the affinity for adsorption onto carbon surfaces. At low pH, there is an increased amount of MC-LR adsorbed by the coconut shell-based AC, highlighting strengthened intramolecular forces within the molecule, which lowers the overall molecular dimensions. Therefore, increased adsorption using larger amounts of micropores from coconut shell-based AC is possible. In general, adsorption is an exothermic process. Similarly, adsorption of microcystin is an entropy-driven process for all carbon, except for one wood-based AC. It was suggested that secondary micropores also play an important role along with mesopores. Therefore, secondary micropore volume, along with mesopores, should be considered for effective adsorption of MC-LR onto any carbon surface.

In contrast with other studies, the presence of macropores should also be considered for increased adsorption capacity of MC-LR along with the mesopores [69]. In the study conducted by Huang et al. [69], adsorption of MC-LR onto three different carbons was considered. Similar pore volumes were observed, with wood AC having a higher number of mesopores compared to coconut and bituminous coal ACs. The pH_{ZPC} for coconut shell, bituminous, and wood-based AC is 5.2, 5.8, and 4.1, respectively. The initial spiking concentration of MC-LR was 15–250 $\mu\text{g/L}$, and adsorption performance varied with each AC type, from 37% to 100% removal. It was observed that macropores also contributed to the adsorption of MC-LR onto all carbons, due to an increase in the intraparticle diffusion rate. MC-LR adsorption using coconut shell- and bituminous-based carbons showed similar patterns to that of non-porous carbon black. Even at higher dosing of 500 mg/L of coconut shell- and bituminous-based AC, no significant improvement of adsorption capacity for MC-LR was shown. Therefore, it was concluded that micropores do not play an important role in the adsorption of MC-LR onto activated carbon. However, the adsorption of MC-LR was strongly affected by the functional group on the surface of the AC. The adsorption was higher with carbons having a greater number of basic surface groups (hydroxyl or phenolic groups), along with higher pH_{ZPC} values. Any interaction of AC with chlorine was shown to decrease MC-LR adsorption onto carbon, as carbon becomes more hydrophilic due to the Cl and O groups on its surface, significantly reducing available adsorbent sites for MC-LR to sorb onto its surface.

The adsorption behavior of dc-STX and STX onto commercial coconut shell-based GAC was studied by Capelo-Neto et al. [70]. Their kinetic study was conducted with an initial concentration of 7 and 60 $\mu\text{g/L}$ for dc-STX and STX, respectively. The GAC used in their study had a pH_{ZPC} of 10; thus, it has a net negative charge at pH 7, whereas the STX has a mixture of mono-cationic and di-cationic species. Cationic speciation of the STX dominates over the anionic nature of the GAC; therefore, electrostatic repulsion plays an important role in the adsorption of STX by GAC [47]. Adsorption of dc-STX and STX was best fitted by the Langmuir isotherm, with K_L values of 5.974 and 0.464 $\text{L}/\mu\text{g}$ for dc-STX and STX, respectively. In comparison, adsorption of dc-STX was less than that of STX, due to its lower initial concentration. In a similar study, conducted by Capelo-Neta and Silva Buarque [70], four different coconut shell-based GACs, with the same surface charge but different BET surface areas and pore sizes, were tested. Those GACs with a greater percentage of mesopores showed the highest STX removal. The adsorption of dc-STX and STX followed a pseudo-second-order model, indicating chemisorption [50]. For the removal of STX, GACs with a net negative charge, at pH 6–8 in synthetic treated water samples, performed better.

There has been limited research on the adsorption of anatoxins and cylindrospermopsin using coconut shell-based adsorbents. Yanting Liu [61] demonstrated the removal of microcystin, cylindrospermopsin, and anatoxin using coal-, wood-, and coconut shell-based GAC from drinking water. The initial concentrations of each of the toxins were 100 $\mu\text{g/L}$, and batch adsorption experiments were conducted at a rotation speed of 150 rpm and pH 7. Among all adsorbents, wood-based GAC had a higher BET surface area, along with more volume of mesopores and micropores. Coconut-based GAC had higher amounts of micropores, but very little mesopores. For cylindrospermopsin adsorption, coconut shell- and wood-based GAC attained equilibrium after 2 h, whereas coal-based GAC achieved equilibrium after 6 h of contact time. For cylindrospermopsin removal, wood performed better than coconut-based GACs. Anatoxin-a (ANTA) adsorption had the least removal with equilibrium times of 72 h, 72 h, and 168 h for wood-, coconut shell-, and coal-based GACs, respectively [61]. Slower adsorption was seen for ANTA compared to the other two cyanotoxins, irrespective of the adsorbent material.

Anatoxin adsorption was highest with coconut shell-based PAC, followed by coal- and wood-based PACs. It was observed that cylindrospermopsin adsorption favored PACs with a greater amount of mesopores along with a certain amount of secondary micropores (0.8–2 nm), with wood-based PACs having the highest capacity [61]. For ANTA, coconut shell-based PACs performed best due to a greater volume of micropores, and wood-based PACs performed the worst,

because of a larger amount of mesopores. Similar results were observed in a study conducted on ANTA [71]. However, the lower adsorption rate of ANTA is not fully understood, as ANTA's molecular dimensions (0.97×0.633 nm) fit the secondary micropores and all larger pores, which should increase its adsorption rate. The pseudo-second-order model and the Freundlich isotherm were suitable for describing the adsorption of the three cyanotoxins onto the different types of PACs. The kinetics and isotherm parameters are summarized in Table 4.

Table 4. The adsorption kinetics and isotherm parameters for different coconut-based granular activated carbon (GACs) and powdered activated carbon (PACs).

Toxin	C_0 , $\mu\text{g/L}$	Conditions	Isotherm Parameters	Comments	Ref.
Microcystin-LR	250	Milli Q water 25 ± 1 °C, pH = 7.5, 24 h	Langmuir, $q_m = 16.1$ mg/g $K_L = 2$ L/mg	Intraparticle diffusion $K_p = 0.118$ mg/g $\text{h}^{0.5}$ $q_e = 14.5$ mg/g	[66]
Microcystin-LR	2000	Deionized water: 22 ± 18 °C, pH = 8.5, 16 rpm, 7 day	Freundlich, $K_f = 1259$, $1/n = 1$	NA	[72]
Decarbamoylsaxitoxin (dc-STX)	60	Ultrapure water, 28 °C, 15 rpm pH = 7	Langmuir, $q_m = 0.253$ mg/g $K_L = 5974$ L/mg	NA	[49,71]
Carbamate saxitoxin (STX)	7	Ultrapure water, 28 °C, 15 rpm, pH = 7	Langmuir, $q_m = 2.129$ mg/g $K_L = 0.464$ L/mg	NA	[49,71]
Microcystin-LR	100	Ultrapure water, 150 rpm pH = 7	Freundlich, $K_f = 3.67$ (mg/g) ($\mu\text{g/L}$)- $1/n$, $1/n = 0.22$	Pseudo second order kinetics $q_e = 2.01$ $\mu\text{g/g}$, $k_2 = 5.8$ mg/ $\mu\text{g/h}$	[60,68]
Anatoxin-a (ANTA)	100	Ultrapure water, 150 rpm, pH = 7	Freundlich, $K_f = 3.18$ (mg/g) ($\mu\text{g/L}$)- $1/n$, $1/n = 1.76$	Pseudo second order kinetics $q_e = 1.94$ $\mu\text{g/g}$, $k_2 = 0.067$ mg/ $\mu\text{g/h}$	[60,68]
Cylindrospermopsin	100	Ultrapure water, 150 rpm pH = 7	Freundlich, $K_f = 3.88$ (mg/g) ($\mu\text{g/L}$)- $1/n$, $1/n = 0.32$	Pseudo second order kinetics $q_e = 2.15$ $\mu\text{g/g}$, $k_2 = 14.58$ mg/ $\mu\text{g/h}$	[18]

NA = not available; Ref = Reference.

In general, the adsorption capacity of adsorbent materials and the chemical behaviors of cyanotoxins vary greatly. Therefore, adsorbent materials should be selected based not only on the pore size but other factors as well, such as surface charges of the adsorbents and the cyanotoxins. Figure 2 illustrates various mechanisms of adsorption between cyanotoxins and adsorbent materials.

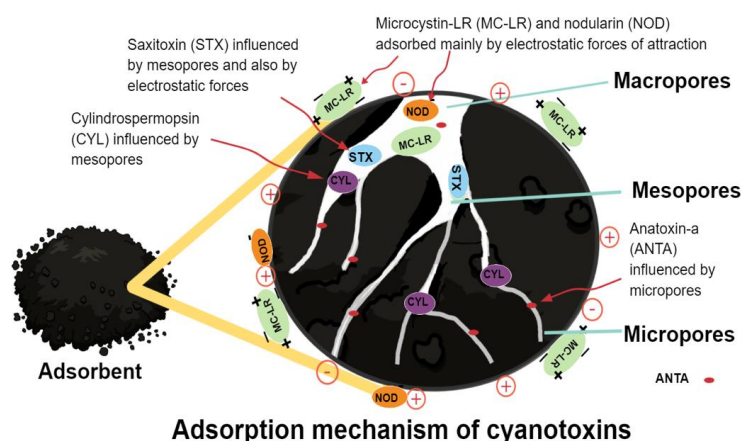


Figure 2. Adsorption mechanisms between cyanotoxins and adsorbent materials.

2.2.2. Lignin

Lignin-based ACs can be prepared from lignocellulosic materials present in natural sources [72]. The sources of lignocellulosic materials include plant-based biomass like wood, agricultural waste, grasses, etc. [73]. Cavalcanti et al. [74] studied MC-LR adsorption using five different natural AC fibers of lignocellulosic materials: pine wood residues, macadamia nutshells, dried coconut shell endocarp, unripe coconut mesocarp, and sugar cane bagasse. These natural fibers were used to produce activated carbon fibers (ACF) by carbonization, followed by steam activation at 900 °C. However, there were differences in the volume of primary and secondary micropores and mesopores. It was observed that pine wood- and sugar cane bagasse-based ACFs produced larger mesopore volumes, 1.06 and 0.39 cm³/g, respectively. The secondary micropore volumes formed in the ACFs in the following order: unripe coconut mesocarp > pinewood > macadamia nutshell > coconut shell endocarp > sugar cane bagasse.

The pine wood-, sugarcane bagasse-, and coconut shell-based ACFs removed MC-LR at 99.27, 98.73, and 62.31%, respectively, within a 40 min equilibrium time [74]. A comparison of commercial ACFs produced from the same raw materials was also included in the study. The commercial ACFs showed lower removal kinetics than the natural fibers. The adsorption followed pseudo-second-order kinetics with a higher value rate constant for pine wood-based ACFs than the rest ($q_2 = 55.55$ µg/mg, $k_2 = 0.162$ mg/µg/min, $R^2 = 1$). The adsorption of MC-LR onto pinewood- and sugarcane bagasse-based AC fibers fit better with the Langmuir's model than the Freundlich model. The parameters for Langmuir isotherm of pinewood and sugarcane bagasse-based AC fibers are k_L 2.23 and 1.33 (L/mg), and q_m 200 and 161.3 (µg/mg), respectively. The adsorption of the microcystins was due to electrostatic interactions; as carboxyl surface groups on the ACFs dissociate to form negatively charged species, they attract the positively charged microcystin-LR.

2.2.3. Biochar

Biochar, a carbon-rich and low-cost adsorbent, has recently been used for removing organic and inorganic pollutants from water and wastewater. In oxygen-limiting conditions and under different pyrolysis temperatures (300–1000 °C) [75], biochar can be generated from a variety of materials such as municipal [76,77] and agricultural waste [76,78,79], and animal manure [76,80,81]. Several articles addressing the adsorption potential of biochar illustrate that adsorption is influenced by surface area, porosity, and surface functional groups [75,82,83]. However, limited studies have focused on the cyanotoxin adsorption capacity of biochar for contaminant removal in water and wastewater. Among numerous structural variants of microcystin, only MC-LR has been considered for biochar adsorption studies. The adsorption capacity is a function of biochar characteristics, pH, and dissolved organic matter of the aqueous solution.

At higher pyrolysis temperatures, biochar showed greater carbonization, specific area, and aromaticity [84], thereby possessing better adsorption capacity as a result of π - π electron donor-acceptor interaction. The size of MC-LR (1.4–2.9 nm) is another major factor for adsorption via the pore filling effect [85]. Biochar produced at 600 °C showed better adsorption capacity because of higher mesopore volume [86]. In contrast, MC-LR adsorption by biochar produced at 300 °C had larger enthalpy values (44.25 kJ/mol), indicating that chemisorption was the main MC-LR removal mechanism [87]. Manure-based biochar exhibited more ash content than comparable biochar derived from agricultural waste, possibly due to the presence of minerals [81]. At the same pyrolysis temperature, manure-based biochar showed enhanced sorption capacity of MC-LR compared to wood-based biochar, as ash contributes to the polar groups and organic matter available for adsorption [86]. In a different study, acid treatment on chicken manure biochar resulted in increased porosity and surface area by removing pore-blocking elements such as acid-soluble ash minerals and organic matters [88].

MC-LR adsorption onto biochar is highly pH-dependent. At acidic pH, (pK_{a1} , 2.09; pK_{a2} , 2.19; and pK_{a3} , 12.48), MC-LR exists as a singly dissociated anion (MC-LR[−]) [87,89]. Biochar exhibits positive charges if the solution pH is below the pH_{PZC} . As a result, the adsorption is facilitated by

coulombic attraction between MC-LR[−] and a positively charged biochar surface [86,87]. Removal of surface acidic groups at higher pyrolysis temperature resulted in an increase in pH_{PZC} which further enhanced the MC-LR adsorption capacity of biochar [86]. The adsorption isotherm of MC-LR was well explained by both the Langmuir ($R^2 = 0.96\text{--}0.99$) [87] and Freundlich models ($R^2 = 0.90\text{--}0.99$) [86].

Although the application of biochar for cyanotoxins adsorption is not yet common, its excellent adsorption capacity of other water pollutants (e.g., heavy metals, pharmaceuticals) makes it a good candidate as a potential adsorbent for cyanotoxins removal from wastewater. As discussed above, the electrostatic attraction between the positively charged biochar surface and negatively charged MCLR[−] anions played a major role in enhanced adsorption.

2.3. Effect of Organic Matter

The presence of organic matter can diminish the removal of cyanotoxins from water. For example, the large structure of humic acid can block the adsorption pores and sites on the adsorbent. Humic acids contain functional groups like carboxylic acids, and alcohols, making them negatively charged at typical pH (5–7) for cyanotoxin adsorption (Table 2). The presence of multiple charges on humic acid makes it a strong competitor for adsorption sites. Mashile et al. [45] observed a decrease in adsorption of nodularin as the concentration of humic acid increased. At 1000 mg/L humic acid, the removal efficiency of nodularin decreased by 15% compared to no humic acid present. Similarly, the adsorption of saxitoxin onto bituminous PAC depended on pH and the presence of natural organic matter (NOM) [47]. In water containing NOM at 28 ± 2 mg-dissolved organic carbon/L, saxitoxin removal decreased at pH 5.7 and 7.05, but there were very little changes in the removal at pH 8.2 and 10.2. At 80 mg/L PAC and pH ≥ 8.2 , bituminous PAC removed over 85% of saxitoxin in 30 min whether or not NOM was present. In a basic pH environment, bituminous PAC has an overall negative charge, while saxitoxin is cationic; this condition facilitates electrostatic attraction. On the other hand, the presence of anionic NOM at neutral and acidic pH may interfere through interactions between NOM and the cationic saxitoxin [47].

The presence of organic matter in a GAC column affects the adsorption of cyanotoxins. Kelley [90] studied the effect of organic matter on MC-LR adsorption by preloading GAC columns at 0%, 55%, and 100% NOM capacity, as determined in initial trials, and conducting rapid small-scale column tests using river water supplemented with MC-LR. Increasing the organic matter loading reduced the bed volumes until breakthrough; at 0%, 55%, and 100% NOM the bed volumes achieved before the MC-LR exceeded Ohio EPA's action level of 0.3 µg/L, were 3900, 2400, and 200, respectively. Loading the column with high organic content reduced the mass transfer zone. As noted in the study, NOM-saturated GAC would not be effective for MC-LR removal during an algal bloom.

2.4. Biological Enhancement of Activated Carbon

Ren et al. [52], modified ACFs biologically to boost MC-RR removal. AC fibers were modified with sodium alginate (SA) and *Sphingopyxis* sp. The Box-Behnken design was applied to study the effect of pH, temperature, and inoculum. The adsorbent was prepared by suspending *Sphingopyxis* sp. and ACFs in SA for 2 h. SEM analysis of the modified adsorbent exhibited successful attachment of *Sphingopyxis* sp. onto ACFs with SA acting as an adhesive. Temperature and pH strongly influence microbial activity; thus, temperature (20–40 °C) and pH (3–11) were investigated in the ranges indicated. Increasing the temperature and pH elicited a positive correlation with microcystin removal from aqueous solution. However, temperatures > 32.0 °C and pH > 6.8 lowered the performance of the biologically modified ACF. Inoculation of bacteria at 15.0% (*m/v*) favored MC-RR destruction rate, achieving 0.77 µg/mL/h removal. The authors observed a high reusability rate of the biologically modified ACFs; the adsorbent achieved over 70% microcystin removal after the 7th cycle of reuse.

In a biological environment, toxin reduction is accomplished through adsorption and/or biodegradation. During the initial stage, the removal of cyanotoxins is entirely attributed to adsorption. When the AC is exhausted, biodegradation is initiated. Combining a biological

system with AC offers a long-term treatment of toxins like cyanotoxins. Wang et al. [54] studied the reduction of microcystins using a GAC column inoculated with bacteria sourced from a biofilm of a conventional GAC column. Water was spiked with 5.0 µg/L microcystins (MC-LR and MC-LA) and pumped into a GAC column inoculated with approximately 8×10^7 bacteria/mL. Effluent samples were collected at regular intervals for over six months to assess microcystin removal. The system maintained almost 100% microcystin reduction for the entire test period. Parallel experiments with sterile GAC were run concurrently with the biological AC (BAC) system. For a sterile GAC column, a continuous drop in treatment capacity was observed; after six months, the performance decreased to 70% and 40% for MC-LR and MC-LA, respectively. Thus, after six months, biodegradation accounts for approximately 30% of MC-LR and 60% of MC-LA reduction. Designing a BAC system requires attention to biofilm formation conditions; bacteria can form a biofilm around the AC, reducing the adsorbate penetration into the micro/mesopores of AC. The main advantage of biologically modified adsorbents is that they can simultaneously reduce nutrients like phosphorus and nitrogen. ACFs, modified with *Sphingopyxis* sp., concurrently removed 32.45%, 94.57%, and 64.07%, and 0.76 µg/mL/h of nitrogen, phosphorus, chemical oxygen demand, and microcystins, respectively [52].

3. Modified and Non-Traditional Carbon-Based Adsorbents, and Other Adsorbents

Carbon-based adsorbents have been used to treat cyanotoxins in water; however, their adsorption capacity greatly varies depending upon the nature of toxins, the contamination level, water quality, and characteristics of the adsorbent including pore size and its distribution. For instance, microcystin removal is limited using AC because of its smaller micropores, which are not very effective for the adsorption of the large microcystin molecules [91]. Generally, higher doses of carbon-based adsorbents are required to meet the product water criteria, resulting in large volumes of exhausted carbon. The value of the global activated carbon market was \$6.587 billion (US\$) in 2019 and is expected to reach \$11.376 billion (US\$) by the end of 2025 [92]. Once the carbon-based adsorbents are saturated/exhausted, they are generally disposed of with or without treatment depending upon the nature of the adsorbate.

Disposal of exhausted adsorbent without any treatment can result in leaching of adsorbate into the environment. Carbon-based adsorbents such as GAC can be regenerated by heating at high temperatures; however, the associated energy cost makes this option less attractive, especially when the adsorption capacity of regenerated adsorbent is less than that of the virgin adsorbent. The regeneration of adsorbent can only be beneficial when its adsorption capacity is comparable to virgin adsorbents, and the regeneration procedure is eco-friendly and with low energy demands, thereby minimizing the frequent need for virgin adsorbent. Given the above issues associated with AC and the frequency and extent of water contamination with cyanotoxins, there has been an intensive search for the development of cost-effective, new, and/or surface-modified adsorbents for their treatment [93].

3.1. Graphene

Graphene oxide (GO), an atomic sheet of graphite laced with oxygen-containing groups, was investigated for the removal of MC-LR and MC-RR in water [94]. The adsorption of both MC-LR and MC-RR on GO was quick with an equilibrium time of 5 min [94]. The adsorption capacity of GO for both microcystins was higher than that of commercially available AC. The adsorption capacities for MC-LR and MC-RR were 1878 and 1700 µg/g, whereas the adsorption capacity associated with commercially AC was 1482 and 1034 µg/g, respectively. At pH 5, GO and both microcystins carried different charges (cationic for GO and anionic form for both microcystins), resulting in maximum removal. Pavagadhi et al. [94] reported that the removal efficiencies of MC-RR and MC-LR in water were not significantly different ($p > 0.05$) in the presence of anions and cations. The adsorption of MC-LR on GO was significantly reduced (28.4%–63.8%) in the presence of nitrate, chloride, and nitrite, whereas fluoride, sulfate, and phosphate decreased MC-RR adsorption noticeably (1.9%–16.9%). In the

case of cations, MC-LR adsorption significantly reduced (8.6%–49.5%) in the presence of magnesium, sodium, potassium, and calcium. Only MC-RR adsorption on GO was negatively affected (13.1%) by sodium. Also reported in the study, MC-RR was more favorably adsorbed on GO when both MC-LR and MC-RR were present in aqueous solutions containing different ions. This could be due to the different types of amino acids present in their chemical composition. The differences in negative and positive groups among various microcystins may result in their different adsorption characteristics [49]. The exhausted GO adsorbent was regenerated with 1 N NaOH, and the removal efficiencies of both microcystins only decreased about 10% after the 8th cycle of reuse [94].

Cyclodextrin-functionalized magnetic composite of graphene and porous silica (G-Fe₂O₃-γ-CD) was studied for the selective removal of MC-LR from water in the presence of different types of NOM and metal ions [91]. The removal capacity of G-Fe₂O₃-γ-CD for MC-LR removal was 160 mg/g. The high removal capacity of G-Fe₂O₃-γ-CD was attributed to the high loading capacity of graphene for cyclodextrin on its flat surface, which contributed towards MC-LR removal. G-Fe₂O₃-γ-CD provided several advantages for MC-LR removal including the following: (1) G-Fe₂O₃-γ-CD was dispersible in water, which led to a better interaction between MC-LR and cyclodextrin; (2) the presence of Fe₂O₃ provided a magnetic separation of adsorbed MC-LR from the adsorbent, and (3) the removal capacity of G-Fe₂O₃-γ-CD for MC-LR removal was minimally affected in the presence of various metal ions and NOM. However, there was a 20% decrease in its removal capacity after the 3rd cycle of reuse, which could be due to loss of cyclodextrin from the graphene surface, aggregation of the adsorbent material, or inefficient removal of MC-LR during the regeneration procedure (magnetic + ethanol washing) [91]. GO, reduced graphene oxide (rGO), iron oxide (Fe), and iron oxide + GO (FeGO) were also used as coating materials to enhance the surface properties of sand for MC-LR removal in water [95]. MC-LR removal performance of Fe, rGO, FeGO, and rGO coated sand varied significantly (<5%–79%) and different chemical interactions were responsible for MC-LR removal as shown in Figure 3.

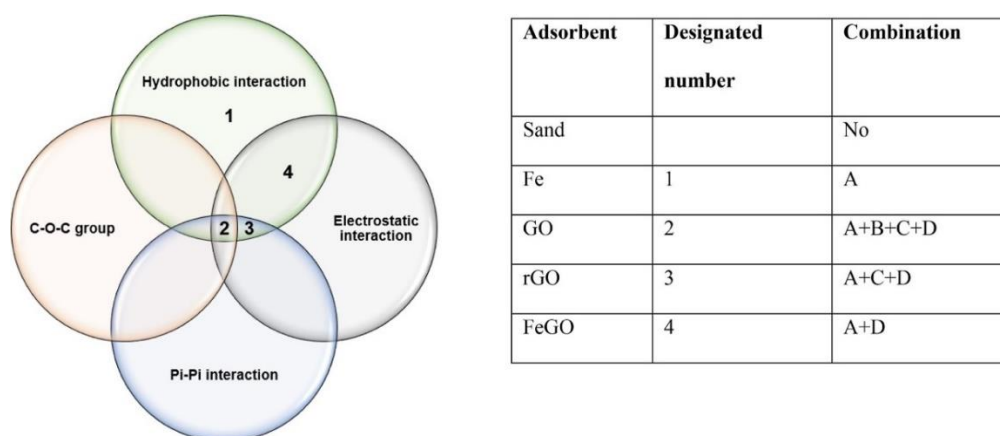


Figure 3. Venn-diagram showing common microcystin-LR (MC-LR) interaction factors for different coated sand adsorbents. A: hydrophobic interaction, B: epoxy/ether group (C-O-C), C: pi-pi interaction, D: electrostatic interaction, reproduced from ref. [95] with permission from Elsevier.

3.2. Iron Modified Sorbents

Iron oxide nanoparticles were tested for the removal of cyanotoxins in water [96–98]. Gao et al. [96] studied the influence of water pH, inorganic cations, and organic compounds on the removal of MC-LR in water using iron oxide nanoparticles. The MC-LR (initial concentration = 2.5 g/L) removal capacity was higher (100%) at acidic conditions (pH = 2–4) compared to neutral conditions (approximately 50%), whereas its removal drastically decreased (<10%) at basic conditions (pH = 9–11) using 0.1 mg/L of iron oxide nanoparticles. This could be due to electrostatic attraction between iron oxide and MC-LR, because MC-LR had a negative charge in water, while the iron oxide surface showed

a net positive charge at $\text{pH} < 9$. The inorganic cations such as sodium (100 mmol) had minimal effect on MC-LR removal, whereas its removal increased by 29% in the presence of calcium (100 mmol). MC-LR removal decreased in the presence of organic compounds containing more carboxyl groups. The MC-LR removal was significantly lower (20%) in the presence of citric acid compared to the presence of benzoic acid in water (36%). The removal efficiency of MC-LR was higher (45%) using iron oxide nanoparticles in the absence of organic compounds. This is because a carboxyl group has a strong affinity towards iron oxide and competes with MC-LR for its active sites. The maximum adsorption capacity of iron oxide nanoparticles was 0.15 mg/g for MC-LR, which was significantly lower than AC (83.3 mg/g) [69]; thus, its potential application for treatment of water contaminated with MC-LR is limited.

Multifunctional magnetic bentonite material ($\text{Fe}_3\text{O}_4\text{@AIB}$) showed higher adsorption capacity (161.3 mg/g), than iron oxide nanoparticles (0.15 mg/g), for MC-LR removal [98]. Like iron oxide nanoparticles, $\text{Fe}_3\text{O}_4\text{@AIB}$ worked better for MC-LR removal under highly acidic conditions ($\text{pH} = 2$) compared to a basic environment ($\text{pH} = 10$) because of the existence of opposite surface charges between the iron surface and MC-LR, as well as similar hydrophobicities of MC-LR and the adsorbent at acidic conditions. The removal efficiencies of MC-LR was lower (88%) in river water compared to Milli-Q water (94.4%). The regeneration of saturated $\text{Fe}_3\text{O}_4\text{@AIB}$ and its reusability were not explored [98].

Hena et al. [99] investigated the use of polypyrrole as a coating material on Fe_3O_4 nanoparticles for the removal of MC-YR, -LA, -RR, -LR, and cylindrospermopsin in water. pH played a significant role in the removal of these cyanotoxins; the favorable pH for MC-LA, -YR, and -LR was 7, whereas MC-RR and Cylindrospermopsin were better removed at pH 9. The adsorption capacities of polypyrrole Fe_3O_4 nanoparticles for MC-LA, -LR, -YR, -RR, and cylindrospermopsin were 259.02, 301.11, 336.08, 238.91, and 272.86 $\mu\text{g}/\text{mg}$, respectively. The exhausted adsorbent was regenerated by treating with 2 M NaOH or HCl at different pH conditions ($\text{pH} = 2\text{--}10$) for 20 min. Desorption of 99% of adsorbed cyanotoxins was achieved at pH 2. The adsorption capacity of the regenerated adsorbent was minimally affected after reusing it for three times. However, a 30%–40% decrease in the removal capacity of the adsorbent for all cyanotoxins was observed after eight cycles of adsorbent regeneration [99].

3.3. Modified/Functionalized Carbon and Silica-Based Adsorbents

Traditional adsorbents, including AC, have lower removal capacity for MC-LR and MC-RR because of their special cyclic and stable structures and larger molecular sizes [100]. AC mainly contains micropores in its structure that cannot host the larger molecules of MC-LR and MC-RR efficiently [101]. The volume, area, and molecular length of MC-LR molecules in water are 2.63 nm^3 , 1.8 nm^2 , and 1.9 nm [102], and MC-RR also has similar molecular dimensions [101]. Given the molecular sizes of both MC-LR and MC-RR, Teng et al. [101] synthesized different types of ordered mesoporous silica and evaluated the role of their mesostructure and surface chemistry toward microcystins removal. Among the studied adsorbents, mesoporous silica templated from Pluronic P123 (SBA-15, BET surface area: 800 m^2/g , mesopores surface area: 510 m^2/g , pore volume: 1.12 cm^3/g , and pore size: 8.7 nm) had maximum adsorption capacity for both MC-LR (5.99 mg/g) and MC-RR (13 mg/g) at a significantly faster removal rate (equilibrium time: 1–2 min). Further improvement in the adsorption capacity of SBA-15 for hydrophobic MC-LR was made by grafting carboxyl, amino, and quaternary ammonium organic groups onto the porous surface of SBA-15. The grafting of quaternary ammonium on SBA-15 increased the removal of MC-LR from 50% to 95% at pH 4. The increase in MC-LR removal could be due to ion-pairing or the existence of electrostatic attraction between adsorbent and adsorbate [103] because quaternary ammonium compounds contain both a hydrophobic methyl group and a positively charged N that are beneficial for the removal of negatively charged MC-LR [101].

Compared to functionalized SBA-15, bimodal amine-functionalized mesoporous carbon (MsC-NH_2) featuring higher surface area (1063 m^2/g), lower pore volume (0.7 cm^3/g), and pore size (2.3–4.8 nm) showed better MC-LR removal [100]. The adsorption capacities of MsC-NH_2 for

MC-LR in batch and column experiments were 580 and 334 mg/g, respectively. Although mesoporous carbon functionalized with a carboxyl group (MsC-COOH) had a higher surface area (1290 m²/g) and a similar pore size (2.4–4.9 nm), it had less adsorption capacity (69 mg/g) in batch experiments. The difference in adsorption capacity was most likely due to surface charges of MsC-NH₂ and MsC-COOH. MsC-NH₂ had a positive surface charge compared to MsC-COOH (negatively charged) at pH 7, which favored the interaction with negatively charged MC-LR. Park et al. [104] investigated the MC-LR adsorption mechanism on protonated mesoporous carbon (MC-H), protonated mesoporous silica (MS-H), and their amino-functionalized forms (amino-functionalized mesoporous carbon (MC-NH₂) and amino-functionalized silica (MS-NH₂)). Figure 4 shows the governing factors of MC-LR adsorption on MC-H, MS-H, MC-NH₂, and MS-NH₂. In the case of MC-H, pore diffusion was found to be the dominant factor for MC-LR adsorption. The presence of a hydrophobic aromatic ring in the Adda chain and leucine unit in the carbon framework provided additional binding sites for MC-LR resulting in better adsorption capacity than silica. In the case of MC-NH₂, the grafting of the amino group only increased the initial MC-LR adsorption rate due to electrostatic interactions. However, the presence of amino groups on mesoporous carbon could lower the total adsorption capacity because of damage to the mesopores structure during the grafting procedure and through electrostatic interaction with MC-LR near the mesopores, which could obstruct the other MC-LR molecules from accessing the internal sorption sites. Mesoporous carbon had better MC-LR removal capacity than silica due to pi-pi electron donor-acceptor interactions. In the case of MS-H, its highly negatively charged surface and tube-like pores which allowed the MC-LR to leach through the pores were likely responsible for poor adsorption capacity [104].

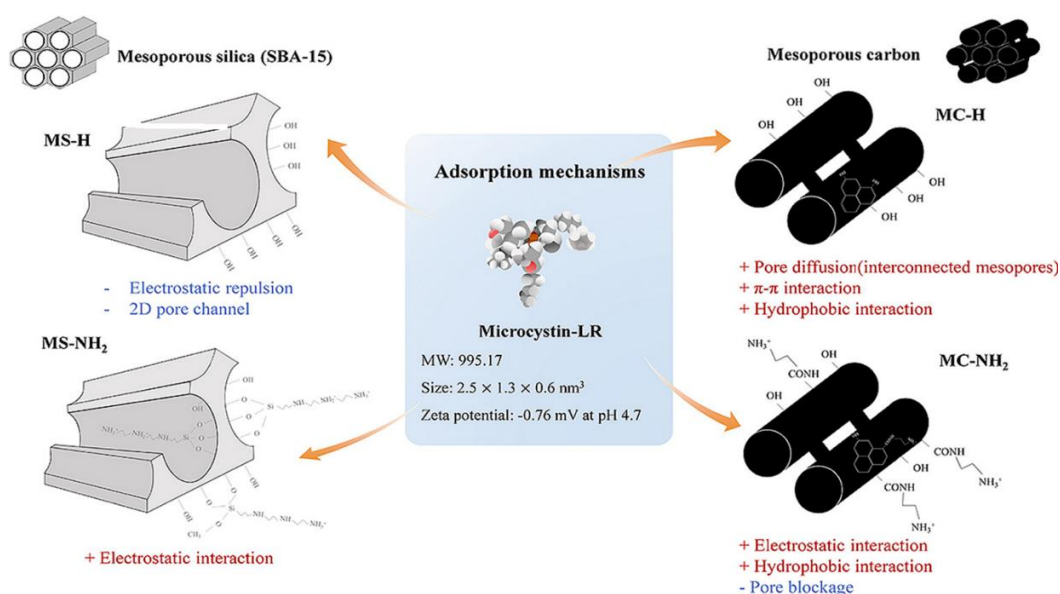


Figure 4. Governing factors for MC-LR adsorption on mesoporous silica (MS-H), mesoporous carbon (MC-H), amino-functionalized silica (MS-NH₂), and amino-functionalized mesoporous carbon (MC-NH₂). Reproduced from ref. [104] with permission from Elsevier.

Ethanol-water washing was effective in eluting the adsorbed MC-LR, as well as for the regeneration of MsC-NH₂ [100]. To investigate the effect of surface area and structure of bimodal mesoporous carbon (non-functionalized MsC), its removal capacity was compared with MsC-NH₂ and MsC-COOH. Similar to MsC-COOH, the MsC surface had a negative charge but showed higher MC-LR removal (132 mg/g) in batch experiments, because of its higher surface area (1680 m²/g vs. 1290 m²/g) [100]. This indicates that the structural properties of the adsorbent are still an important factor for the removal of MC-LR using mesoporous adsorbents. The effect of competing ions such as NOM on the adsorption capacity of mesoporous adsorbent was not evaluated.

Beside functionalized mesoporous silica and carbon, mesoporous graphitic carbon nitride (mpg-C₃N₄) was protonated to investigate its removal capacity for MC-LR and MC-RR in water [105]. After the treatment of mpg-C₃N₄ with concentrated HCl (for protonation), the BET surface area, total pore volume, and average pore width slightly increased (<10%). The removal efficiencies of both MC-LR and MC-RR were 96% in 15 min using the protonated adsorbent (mpg-C₃N₄-H⁺). Removal of both MC-LR and MC-RR followed pseudo-second-order kinetics, and their rate constants increased with an increasing initial concentration of microcystins. Langmuir isotherms showed that the maximum adsorption capacities of mpg-C₃N₄-H⁺ for MC-LR and MC-RR were 2360.96 and 2868.78 µg/g, respectively. Although the adsorption capacity of mpg-C₃N₄-H⁺ was significantly lower than MC-NH₂, its microcystin removal efficiencies remained stable and high (>90%) after two cycles of regeneration. As a practical application point, all of these surface-functionalized mesoporous carbons should be further studied for the removal of microcystins in the presence of competing compounds such as NOM and metal ions.

4. Critical Evaluation of Adsorption Technologies

Adsorption of cyanotoxins has gained much attention due to its greater removal efficiency and a less complicated operational process compared to the conventional treatment techniques. Various adsorbents including AC [106], biochar [87], mesoporous carbon [107], composites of carbon and TiO₂ nanotubes [108], mesoporous silica [101], polymers [109], waste biomass [110], chitosan-cellulose composite [111], graphene oxide [94], and iron oxide nanoparticles [96] were studied to effectively adsorb different classes of cyanotoxins from aqueous phase either alone or coupled with coagulation, filtration, or flocculation.

AC, the most commonly used adsorbent, failed to adsorb large-sized MC-LR due to the presence of micropores that are <2 nm [107]. Several researchers have focused on combining PAC/GAC with another treatment technology to improve removal efficiency. The combination of coagulation, PAC, and ultrafiltration effectively improved drinking water quality by removing large-sized MC-LR and small-sized saxitoxins. Specific components were targeted by each removal process: intercellular toxins via coagulation, extracellular toxins via PAC adsorption, and residual cyanobacteria or toxins via ultrafiltration. Cell lysis, a major drawback of this multi-step process, releases intracellular toxins during treatment. The problem can be resolved by a higher PAC dose; however, this makes the process more expensive [112]. In another study, mesoporous carbon showed a 30-fold higher adsorption capacity of MC-LR than microporous PAC which can hold the same adsorption capacity even after three regeneration cycles [107].

The use of photocatalysts such as TiO₂ is not energy efficient and can produce toxic byproducts [38]. Also, the presence of natural organic substances in water can adversely impact cyanotoxin adsorption by PAC. However, the composite of carbon and TiO₂ nanotubes effectively addressed both issues and adsorbed hydrophobic MC-LR more than 95%. Also, the adsorption efficiency was further improved upon with the addition of carbon nanotube content, indicating the effectiveness of adsorption over photodegradation [108].

Although the efficiency of carbon-based adsorption mostly depends on the dosage and type of carbon used, the removal rate is always higher than iron-based adsorbents [93]. Carbon nanotubes can adsorb four times more microcystins than AC or clay materials as the pore size of nanotubes is an excellent match for microcystins [113]; however, production and modification of carbon nanotubes as adsorbents are prohibitively expensive [114]. Table 5 summarizes the adsorption capacity of several adsorbents used for cyanotoxins.

Energy consumption during regeneration and high operational costs of AC encourage the use of environmentally friendly waste biomass-based sorbents [103] and cost-effective molecularly imprinted polymers [109]. For example, peat—a natural and early stage of coal—showed a moderate adsorption capacity of MC-LR [103], but it has the advantage of being available throughout the world [115]. Molecularly imprinted polymers can be effectively regenerated after seven cycles of use without

hampering removal efficiency and with reduced concern regarding adsorbent disposal. However, large-scale production is still a challenge for its application in the water treatment process [109].

Table 5. Comparative analysis of cyanotoxin adsorption on several adsorbents.

Adsorbent	Cyanotoxin	Adsorption Capacity (%)	mg Adsorbed/ g Adsorbent	References
Tire-based AC	Nodularin	99	0.4	[44]
GAC	MC-LR	~100	83.3	[66]
PAC	MC-LR	86	NA	[113]
Activated carbon fibers	MC-LR	99.5	17	[114]
Biochar	MC-LR	64	3.5	[87]
Carbon nanotubes	MC-LR	NA	14.8	[111]
Bamboo charcoal	MC-LR	80	1.2	[85]
Mesoporous carbon	MC-LR	97	0.5	[105]
Waste biomass	MC-LR	90	0.3	[102]
Natural clay particles	MC-LR	81	4.6	[115]
Graphene oxide	MC-LR	>90	1.7	[94]
	MC-RR	>90	1.8	
Iron oxide	MC-LR	100	0.2	[95]
Suspended particulate matter	MC-LR	95	NA	[89]
Molecularly imprinted polymers	MC-LR	100	3.6	[107]
Carbon and TiO ₂ nanotubes composite	MC-LR	96	NA	[106]
	CYL *	70	NA	
Chitosan-cellulose composite	MC-LR	91	96	[109]
Coagulation-PAC-ultrafiltration	Saxitoxins	90	NA	[110]
	MC-LR	92	NA	
Magnetic bentonite	MC-LR	94.4	161.3	[97]
Amino-functionalized mesoporous carbon	MC-LR	NA	580	[99]
			334	

* CYL = cylindrospermopsin; NA = not available.

Adsorption is considered to be a relatively low-cost advanced treatment method requiring 50–150 US\$ per million liters of water [116] depending on the type of adsorbent used. The high cost for large-scale AC usage has fostered the development of alternatives such as biochar (0.35–1.2 US\$/kg; 2.9–10 g MC-LR adsorbed/US\$) [117] or waste-based biomass [118]. It is clear from Table 5 that the chitosan-cellulose composite material showed the highest adsorption per g of adsorbent. Chitosan, a sea material-based adsorbent, can remove more than 5 times as much MC-LR compared to AC at a lower cost (2–4 US\$/kg; 24–48 g MC-LR adsorbed/US\$) [111]. While PAC offers a comparatively cheaper process than GAC, the removal efficiency is higher for GAC [119]. A study on molecularly imprinted polymers showed that the cost to treat MC-LR-contaminated water was 412 US\$ per million liters; however, the process is 40% more efficient than commercially used PAC [109]. Natural clay particles are an inexpensive (0.04 US\$/kg) adsorbent; however, the removal capacity is lower than AC and biochar [120]. Given that more than 80% adsorption of cyanotoxins is achievable using all the adsorbents studied, an exceptionally higher adsorption capacity of >500 mg/g for MC-LR was achieved with mesoporous carbon (modified or pristine). The exhausted carbon can be easily regenerated using only methanol [100,107] which makes it a stable and efficient adsorbent for future use. In summary, low-cost adsorbents can achieve 100% removal under optimal conditions, but regeneration and proper management of exhausted adsorbents are still a matter of concern.

5. Future Outlook

As indicated, climate change and other environmental factors might lead to more frequent and higher concentrations of cyanotoxins in drinking water supplies, though much remains uncertain [4,7,8]. Both droughts and flooding may contribute to cyanobacteria growth through increased salinity, shifts in biologically available nitrogen, and nutrient loading in first flush storm events [121,122]. With changing environmental conditions, some critical issues to consider are who is most likely to be affected by cyanotoxins, how can treatment efficacy be assessed quickly, and what are the current research gaps.

While existing data show cyanotoxins present in water sources in the US and worldwide [20,123–125], treatment plants and private water sources may not be affected uniformly. Surface water accounts for nearly three-quarters of annual water withdrawals in the US but about 50% of the public water supply that reaches about 141 million people or 43.5% of the US population [126]. Drinking water for rural areas in the US is almost extensively provided by groundwater (99%) [126], which means urban areas are more affected by cyanotoxins as they are primarily found in surface waters. Groundwater may be impacted, especially in the case of wells that are close to surface water [127] or desert wells [18,128]; however, it is not common to find cyanotoxins in groundwater unless it is under the direct influence of surface water. Consequently, engineered management of cyanotoxins in drinking water is mainly an issue faced by urban water treatment plants.

Whether large or small systems in the US are affected similarly could be answered in the future through data from the fourth unregulated contaminant monitoring rule (UCMR 4) assessment monitoring that will conclude in late 2020. Microcystins, nodularin, anatoxin-a, and cylindrospermopsin are all included for national monitoring [129]. UCMR 4 data should provide insight into who is more affected by cyanotoxins at a national level, which could prompt a more targeted monitoring campaign in the future.

Assessing treatment efficacy quickly is vital for ensuring safe drinking water supplies. With adsorption columns, breakthrough times are highly dependent on the natural organic matter [90]; therefore, systems should be monitored regularly to confirm performance. Standard approaches for quantifying cyanobacteria and cyanotoxins are microscopy, mass spectrometry, polymerase chain reaction (PCR), biochemical assays, bioassays, and immunoassays [124,130]. Most methods require days before the result is available, whereas water treatment utilities need quick answers. Smaller utilities also might not have access to expensive instrumentation (e.g., mass spectrometry). Surrogate testing using pigments (chlorophyll-a, phycocyanin) and cell counts has been used for direct analysis of water [131] and remote sensing [132,133], but these indicators have not estimated concentration and toxicity well [134,135]. A few online or rapid monitoring options exist, including optical biosensing [136], fluorescence [137], and quantitative real-time PCR [138]; nevertheless, there is a considerable need for more development in rapid and online monitoring of cyanotoxins.

Lastly, we highlight a few research gaps for cyanotoxin removal, specifically regarding adsorption. While the combination of ozone and BAC (O₃-BAC) has been investigated for trace organic removal for well over a decade [139,140], it was only recently explored for cyanotoxins [141]. Ozone is both beneficial and problematic; the dose must be carefully selected as it effectively breaks down most extracellular cyanotoxins [142], but it can also lyse cyanobacteria [143] to release intracellular material that could increase total cyanotoxins. Ozone also breaks down organic matter, which would reduce AC pore blockage from large NOM molecules, and facilitates biodegradation by increasing oxygen concentrations and assimilable organic carbon. Either ozone or BAC could be successfully used to reduce cyanotoxins, except for saxitoxin by ozone alone [144], but together they form a multi-barrier treatment process. Considering that water supplies may have unpredictable water quality in the future, incorporating multi-barrier treatments will increase the resilience of water treatment plants.

Pilot-scale and full-scale systems offer a greater understanding of contaminant removal under practical operating conditions. While full- or pilot-scale studies exist for GAC and PAC [145,146], most of the carbon adsorbents featured in this paper have only been tested at a laboratory-scale. Further studies are needed to assess removal under realistic operation conditions and to evaluate the effects of environmental cyanotoxins, which occur in several forms: dissolved extracellular, extracellular adsorbed to particulate matter, and intracellular [147]. Laboratory-scale studies typically focus on dissolved extracellular cyanotoxins through spiked-water experiments, which is only part of the picture. Actual cyanotoxin removal during full-scale treatment could be under or over reported depending on particulate adsorption or cell lysing.

Another area of low attention is point-of-use (POU) treatment. Recent work looked at household reverse osmosis systems [148] and household carbon filters [149] for only MC-LR removal.

POU treatment is especially beneficial to small communities, those who have private water systems, or when large-scale treatment applications are not feasible or when premise plumbing decreases water quality. Upadhyayula et al. [150] detailed cost and operation considerations for carbon nanotubes, which are highly effective for POU microcystin removal, but not practical for full-scale treatment. In the case of larger urban treatment plants, POU is another way to provide multi-barrier treatment, though the cost is typically placed on the user. Considering that cyanotoxins are typically seasonal, POU treatment for a few months could be more cost-effective than an all-year, full-scale GAC or BAC system at the water treatment plant.

6. Conclusions

Adsorption is a commonly employed treatment method for removing cyanotoxins in water. Hydrophobic and electrostatic interactions between the adsorbent surface and cyanotoxins are mainly responsible for cyanotoxins removal. The adsorption of cyanotoxins depends on the surface area of adsorbent, porosity, surface chemistry, water quality and pH, and type of toxins. Micropores and mesopores of AC promote cyanotoxin adsorption more than macropores. Mesopores can easily be accessed by small and large cyanotoxins; thus, AC with more mesopores will have a higher adsorption capacity. Natural organic matter in water competes for active sites of AC resulting in lower cyanotoxins removal. pH strongly influences the removal of cyanotoxins; maximum adsorption is achieved between pH 5–6 using AC. Biologically modified adsorbents can simultaneously reduce nutrients (phosphorus and nitrogen) and cyanotoxins; however, this may not be a feasible option where cyanobacterial blooms are a seasonal problem. Difficulties in regeneration and disposal of spent AC are reasons to shift toward the use of environmentally friendly waste biomass-based sorbents (e.g., biochar) and modified sorbents (e.g., graphene oxide, functionalized mesoporous carbon, silica, and surface coated magnetic nanoparticles).

Most of the modified sorbents have higher sorption capacity than AC and can easily be regenerated without affecting their adsorption capacity. However, the synthesis cost of modified sorbents is higher than AC and most of the research so far is limited to laboratory scale. For optimal removal of cyanotoxins in water, both economic and environmental issues associated with the treatment technology should be considered. This review article may be of help to the water industry and small communities for choosing the suitable adsorbent in single and/or multi-barrier approaches for removing cyanotoxin in water effectively.

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