



ENGINEERING SCIENCES

Understanding the properties of activated carbon and biochar for the adsorption and removal of cyanotoxins: a systematic review

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Abstract: Cyanotoxins pose a health threat when present in the drinking water supply since conventional water treatment processes are not effective in removing extracellular metabolites hence, advanced treatment techniques are usually applied. Powdered activated carbon (PAC) is an effective adsorbent for removing toxins. However, since a high volume is necessary, alternative adsorbents have been investigated. Biochar, especially from renewable sources, is a potential adsorbent material that could replace PAC for removing toxins. This paper aimed to investigate which PAC properties play key roles in cyanotoxin adsorption by a systematic review addressing the adsorption of toxins such as microcystins-LR (MC-LR), cylindrospermopsin (CYL), and saxitoxins (STXs). As a result, the review showed that some commonly adopted indices (*i.e.* total surface area) are not relevant to cyanotoxin adsorption, especially if appraised alone. Along with a multi-barrier approach, PAC has to be applied taking into account the complexity of the water system, which includes a better understanding of the characteristics of the adsorbent, the target toxin, and the aqueous medium. The biochar systematic review showed that no studies have yet been designed specifically for the removal of toxins. Since biochar has not yet been applied to water treatment processes, the knowledge gap is even greater than for PAC.

Key words: Activated carbon, biochar, cyanotoxins, systematic review.

INTRODUCTION

Due to the increasing frequency and intensity of cyanobacterial blooms, researchers began investigating technologies for removing cyanotoxins from water supplies. Most cyanotoxins are water-soluble; thus, remediation measures involve chemical procedures which reduce or remove toxins entirely from water (Hitzfeld et al. 2000). Conventional treatment can eliminate intact cells and, therefore, the cell-bound cyanotoxin, but many studies have shown that conventional techniques such as coagulation, sedimentation, and filtration are inefficient in removing extracellular and soluble

toxins from water (Falconer et al. 1989, Himberg et al. 1989, Hoffmann 1976, Keijola et al. 1988, Albuquerque Junior et al. 2008, Campinas & Rosa 2006). In such cases, it may be necessary to employ advanced treatment methods, such as activated carbon (AC), membrane filtration, or oxidants, as a part of a multi-barrier approach (Pivokonsky et al. 2021). Such advanced methods add significantly to both the cost and complexity of the water treatment process (Velzeboer et al. 1995).

Activated carbon can be defined as a network of interconnected pores of varying sizes which are classified according to their diameter in micropores (<2.0 nm), mesopores

(2-50 nm), and macropores (>50 nm). The pores provide a large internal surface area to activated carbon, typically ranging from 800 to 1200 m².g⁻¹, enabling them to adsorb various contaminants from water (Donati et al. 1994). In drinking water treatment, activated carbon is employed in two forms: powdered (PAC) to perform adsorption simultaneously with clarification or granular (GAC) in columns or beds to perform adsorption in percolation units (Warhurst et al. 1997, Chen et al. 2023). While activated carbon does not have any impact on cyanobacteria and intracellular toxins, it can be successfully applied to remove extracellular cyanotoxins such as microcystins (MCs), cylindrospermopsin (CYL), and saxitoxins (STXs) (Merel et al. 2013). Several countries, including Canada, the USA, Australia, Great Britain, China, and Brazil, have reported that MC-LR contamination has negatively affected human and animal health. The World Health Organization (WHO) has set the recommended level of MC-LR-equivalent in drinking water to 1.0 µg.L⁻¹ (Drogui et al. 2012). Generally, PAC has induced the removal of toxins to concentrations below the WHO guidelines (Lambert et al. 1996).

Among the advanced water treatment methods, adsorption is advantageous methods because of its relative affordability and design simplicity for cyanotoxins removal (Abbas et al. 2020). For dealing with taste and odor problems, for example, PAC is commonly applied since it does not require significant plant adaptations or additional costs. Another advantage of PAC is that it can be used sporadically and at varying doses depending on the treatment requirements (Donati et al. 1994) since cyanobacterial problems are of an intermittent nature (Ho et al. 2011). Its application effectiveness depends on using the correct dose for each characteristic case. For example, a PAC overdose could achieve water devoid of toxicity, but the cost would be high. On the other hand, an under-dose could

compromise its effectiveness and result in potentially toxic water to consumers (Cook & Newcombe 2008).

In developing countries, where activated carbon is usually imported, the relative high cost can be a considerable disincentive against using it in water treatment. There is enormous potential for activated carbons to be produced from agricultural and industrial wastes within these countries (Warhurst et al. 1997). In Brazil, in 2004, the activated carbon import values reached approximately 3.2 thousand tons, translating to a cost of US\$ 6.5 million. In 2012, this value was close to US\$ 20 million (6.5 thousand tons). In 2013 it reached approximately 23.2 million dollars accounting for 7.5 thousand tons of activated carbon, thus leaving Brazil with a deficit in the trade balance for activated carbon (Nobre et al. 2015). In this context, the need to develop technologies for producing high-quality activated carbons, preferably from low-cost raw materials, is clear to substitute these importations (Albuquerque Junior et al. 2008).

Biochar is the solid product of pyrolysis, a material rich in carbon obtained when the biomass is heated in a closed vessel with little or no air available at relatively low temperatures (<700 °C) and which can be used for carbon sequestration, soil conditioning, and pollution remediation (Lehmann & Joseph 2009, Yin et al. 2017). Various carbonaceous materials such as agricultural residues, algal biomass, forest residues, manures, activated sludge, energy crops, digestate, etc., can be used to produce biochar (Oliveira et al. 2017). Biochar has been considered a potential substitute for activated carbon in environmental remediation and water treatment due to its low cost, relative abundance, and adsorption capacity (Inyang & Dickenson 2015). Since it is a porous-carbonaceous material and abundant in functional groups, biochar

has been widely studied as an adsorbent for the remediation of contaminants, including inorganic (heavy metals, ammonia, nitrate, phosphate, sulfide, etc) and organic pollutants (agrochemicals, antibiotics, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), volatile organic compounds (VOCs) and aromatic dyes) and gases (Li & Jiang 2017, Oliveira et al. 2017). Biochars have an excellent ability to remove various contaminants from aqueous solutions but are still an unexplored technology for the treatment of drinking water. Most of the recent literature has focused on applying biochar as a soil amendment, for carbon sequestration, and for reducing greenhouse gas emissions (Gwenzi et al. 2017). Therefore, knowledge about the practical application of biochar in water treatment operations, such as drinking water, is limited (Inyang & Dickenson 2015).

This paper aims to understand the properties of PACs produced from different feedstocks and clarify which physical and chemical properties play a major role in the adsorption of three most common types of cyanotoxins (microcystin-LR, saxitoxin, and cylindrospermopsin). Furthermore,

given the need for cheaper and more sustainable adsorption materials, we aim to understand the state-of-the-art research on biochar production and its application, specifically for cyanotoxins removal from drinking water. Covering this knowledge gap will help to understand the development of carbonaceous materials in water treatment, benefiting water industry, decision-makers, and water companies.

METHODOLOGY

To achieve these objectives, a systematic review was carried out following the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) protocol (Figures 1 and 2). A systematic review is a review of a well-formulated question that uses systematic and explicit methods to identify, select, and critically appraise relevant research (Moher et al. 2009). This type of study can provide researchers with an in-depth view of the past, enabling an overview of future research opportunities by identifying knowledge gaps.

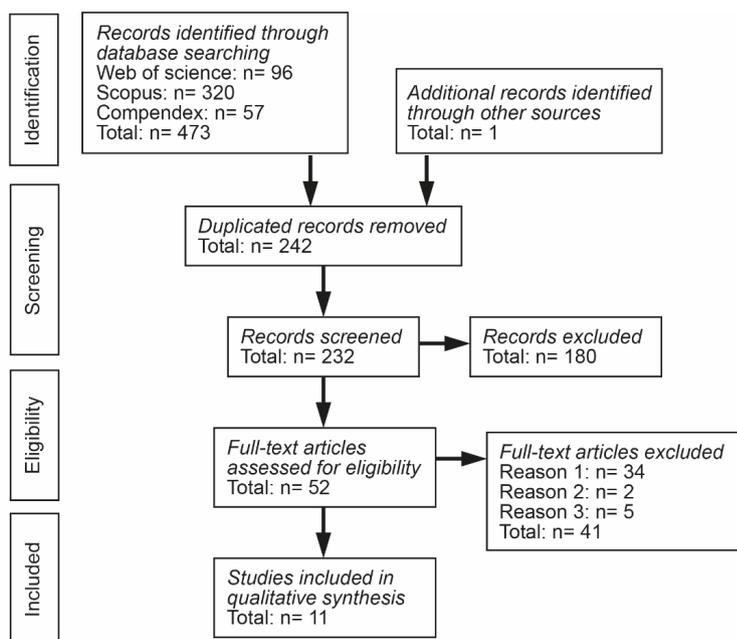


Figure 1. PRISMA flow of information through the different phases for the systematic review of PAC.

Different databases (Scopus, Web of Science, and Compendex) were searched using the combination of 8 keywords (cyanotoxin, algal toxin, MC-LR, saxitoxin, cylindrospermopsin, adsorption, activated carbon, and biochar) using the Boolean expressions AND and OR so that the publications collected were on the specific topic of this research. The data were collected from peer-reviewed journal papers written in English. In the study eligibility phase, different criteria were considered: if the paper does not focus on the characteristics and properties of PAC and/or toxins (Reason 1), the paper is not available online (Reason 2), and it is a book chapter or review paper (Reason 3).

The PAC search retrieved a total of 473 studies, which were narrowed down to 13, as shown in the PRISMA flow diagram (Figure 1). As a systematic review is an iterative process, based on the references of the included studies, other papers not found in the search mechanisms mentioned above were added to this review under “Additional records identified through

other sources”. For the biochar search, a total of 20 papers was obtained. These were then narrowed down to 7, as shown in the PRISMA flow diagram (Figure 2).

The quality assessment of all the papers found in this search was carried out using EndNote X9. Firstly, the duplicated papers were excluded from the retrieved results. Then, the title and abstract of the remaining papers were examined. After this, the papers that did not satisfy the inclusion criteria and/or were utterly unrelated studies were excluded (screening phase). In the final phase, the remaining studies were fully assessed for eligibility. The data was analyzed, extracted, summarized, and discussed in the following sections.

ACTIVATED CARBONS

Starting material and PAC type

The internal structure of activated carbons and their pore size distribution depend on the starting material and the activation method. For

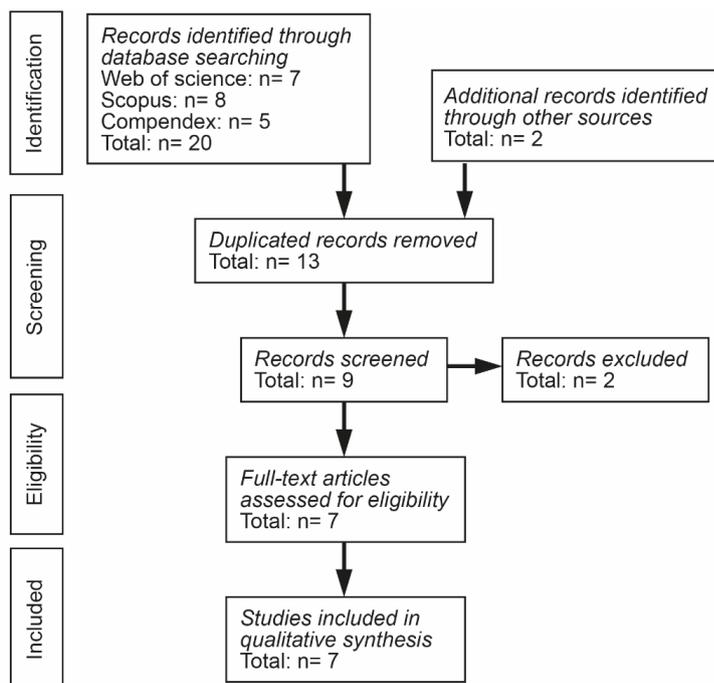


Figure 2. PRISMA flow of information through the different phases for the systematic review of biochar.

example, wood-based carbon shows a regular system of pores, whereas coal-based carbon shows a random network of pores (Donati et al. 1994). While studying the adsorption of microcystins onto activated carbon fibers (ACF), Albuquerque Junior et al. (2008) found that the structures of activated carbon from macadamia nutshell, dried coconut shell endocarp, and unripe coconut mesocarp were more suitable for the production of microporous carbons, while sugar cane bagasse and pinewood residues were better suited to the production of mesoporous carbons (Supplementary Material - Table SI). Some authors have demonstrated in their studies that the type of PAC was shown to be an important factor for the efficient removal of geosmin and saxitoxins with a coal-based carbon shown to be superior to a wood-based carbon using water from two different reservoirs (Capelo-Neto & Buarque 2016, Coelho et al. 2020, Ho et al. 2009).

Many studies relating to the adsorption of cyanotoxins onto activated carbon have been carried out on microcystins, specially MC-LR (Albuquerque Junior et al. 2008, Bajracharya et al. 2019, Cook & Newcombe 2008, Donati et al. 1994, Huang et al. 2007, Lee & Walker 2006, Şengül et al. 2018). Some suggest that coal and wood-based carbons are the best options for microcystin adsorption due to their large mesopore volume (Ho et al. 2011). Bajracharya et al. (2019), comparing the uptake of MC-LR onto PAC versus time at pH of 8.5 in the presence of NOM, demonstrated that the wood and coal-based PAC showed significant differences in MC-LR adsorption. The adsorption rate onto the wood-based carbon was faster than that of other PAC types. Their finding was consistent with previous studies (Donati et al. 1994, Huang et al. 2007), in which wood-based carbons reached equilibrium more rapidly than coal-based carbons due to

the higher amount of mesopores in wood-based PACs compared to other PACs.

Albuquerque Junior et al. (2008), comparing pore volume distribution results for coconut- and wood-based PAC (Table SI) to those obtained by Donati et al. (1994) and Pendleton et al. (2001), found that the pinewood PAC had a volume of secondary micropores of $0.35 \text{ cm}^3 \cdot \text{g}^{-1}$ and a volume of mesopores of $1.06 \text{ cm}^3 \cdot \text{g}^{-1}$, which improved the available pores for the adsorption of complex molecules, like MCs, in about 93.15 %. As for the PAC obtained from coconut shell endocarp, the material had a volume of secondary micropores of $0.28 \text{ cm}^3 \cdot \text{g}^{-1}$ and a volume of mesopores of $0.21 \text{ cm}^3 \cdot \text{g}^{-1}$, representing an increase in 172.22 % in the number of available pores compared to the studies aforementioned, showing a correlation between the activated carbon porosity and the starting material.

Ho et al. (2009) found that coal-based PAC was shown to be more effective carbon for removing saxitoxins. Again, this can be attributed to the different characteristics of the PACs, particularly the greater surface area and more microporous nature of coal-based PACs. Differences were observed in the adsorption of the individual saxitoxin variants, where the amount of adsorption of the variants by both PACs followed the trend: STX > GTX2 > GTX3 > C1 \approx C2. Fortunately, the adsorption trend followed the toxicity; the most toxic variant (STX) was also the most easily removed by PAC, while the C-toxins are the most difficult to be removed. The authors also presented that a previous study reported similar adsorption trends using different PACs and attributed this to the variants' size, with greater removal for smaller molecular sizes. The authors also dismissed the notion that the charge of the variants may have influenced adsorption, but with greater adsorption happening by using carbon with a high positive surface charge.

Particle size

In a study investigating the adsorption of cylindrospermopsin and microcystins from drinking water supplies, Ho et al. (2011) obtained results that suggested that the PACs used had a wide range of pores which could balance the influence of natural organic matter (NOM) also present. The most contrasting characteristic between the coal-based PACs was the effective particle size, ranging from 20-25 μm to 10 μm (Table SI). The authors also argued that, even though previous studies had shown that the adsorption equilibrium of a microcontaminant is not affected by particle size, the particle size can influence the adsorption kinetics, with faster adsorption in smaller PAC sizes.

Elemental composition

From the data obtained from eight PACs, Donati et al. (1994) suggested that no significant relationship existed between the starting material and the surface composition. In contrast, the starting material appeared to be related to the type of impurity on the carbons. The X-ray photoelectron spectroscopy (XPS) data showed that while carbon-to-oxygen ratios varied, there was no apparent relationship to the level of MC-LR adsorption, assuming that trace levels of impurities did not influence MC-LR adsorption.

Studying the properties of activated carbon, Pendleton et al. (1997) found that the surfaces of coconut-based are less hydrophilic than wood-based carbons. That means, for more hydrophilic surfaces, there is a stronger interaction between the water molecules and the surface, making it difficult the displacement of the water molecules by the target contaminant. Adsorption of the relatively hydrophobic molecule shows that water is more readily displaced from low oxygen-content activated carbons than those with high oxygen content (Pendleton et al. 2001).

Therefore, wood-based carbons show lower adsorption energies and, consequently, lower adsorption capacity for the target contaminants, such as MIB (2-methylisoborneol). The authors suggested that selecting an appropriate carbon depends on its surface hydrophilicity, which can be determined by elemental analysis.

Table SI includes the bulk oxygen content for each carbon. The wood-based carbons contained more oxygen than coconut-based ones. In the different PACs used by Shi et al. (2012) for STX adsorption, the oxygen content increased in the following order: bituminous coal < wood < lignite coal. In their study, the PAC carbon-oxygen content did not relate to the STX removal trend. The authors concluded that different factors, such as pH, PAC type, dosage, contact time, and NOM concentration, play different roles in adsorption efficiency for STX removal using PAC.

Surface functional groups and surface charge

Donati et al. (1994) argued that while it is suggested that charge and functional groups on the carbon surface and functional groups of the toxin molecule do not affect the adsorption of MC-LR. However, they do affect the adsorption of natural organic matter (NOM) which may also contribute to competitive adsorption. A study by Pendleton et al. (2001) showed that both the adsorbent surface chemistry and the primary micropore volume have virtually no influence on the amount of MC-LR adsorbed from ultrapure water. On the other hand, Huang et al. (2007) demonstrated that the functional groups on the carbon surface were an essential factor in its ability to adsorb MC-LR.

The most common oxygenated groups on activated carbons surface are carboxylic acids, carbonyls, quinones, phenolic hydroxyls, anhydrides, ethers, lactones, and lactols (Toles et al. 1999). To investigate the effects of surface

chemistry on MC-LR adsorption, Huang et al. (2007) modified the surface chemistry of wood carbon by thermal reduction at 550 °C and 950 °C. The reduced activated carbons had 6.9% and 4.2% oxygen content, respectively, whereas virgin wood carbon had a higher oxygen content of 11.5% (Table S1). While the oxygen content was reduced, the micro and mesopores showed almost no change. Therefore, the toxin was exposed to activated carbons with increased hydrophobic character but with the same volume available for adsorption. It was also found that an increased amount of carboxylic groups on the surface leads to increased water cluster formation, which could result in weaker dispersion interactions with organic adsorbates. The authors assumed that the influence of surface chemistry (i.e., oxygen content) applies at low adsorptive concentrations; thus, the amount adsorbed in virgin carbon was considerably lower than the two treated carbons. Another chemical characteristic the authors highlighted regarded the surface chemical groups according to their acid-base character. At a fixed pH of 7.5, the authors found a good correlation between these groups and MC-LR adsorption. The virgin carbon possessed more basic groups and was more effective than acid-washed carbons. Data from these carbons indicated that the raw carbons contained more hydroxyl groups than the acid-washed carbons.

Shi et al. (2012) suggest that activated carbon pore structure and surface chemistry, including the type and number of functional groups, play an important role in removing organic compounds in drinking water treatment. Their experimental results showed that STX sorption capacity followed the trend: lignite-coal based < bituminous-coal based < wood-ash based. While this order of sorption capacity corresponds to the order of BET surface areas (Table S1), normalization of the removal data to

BET surface area showed that BET surface area accounted only for a part of the trend observed. Another significant factor was hypothesized to be related to the surface charge. The pH_{PZC} for wood-ash and bituminous-coal-based ACs (4.9 and 6.1, respectively) are less than the solution pH; hence, both PACs would have a net negative charge at pH 8.2. The pH_{PZC} for lignite-coal based was 10.9, greater than solution pH so the surface of lignite-coal based would have a net positive charge at pH 8.2. Because STX is approximately 75% cationic and 25% neutral at a pH of 8.2, STX would be expected to be repulsed by the lignite-coal-based surface and attracted to the bituminous-coal and wood-ash-based surfaces, consistent with the observed trend of lignite-coal based providing the least STX removal.

Activated carbon surface can exhibit either acidic or basic character. The former may be due to the presence of functional groups (i.e. carboxyls, phenols, lactones, and acid anhydrides), which dissociate to produce a negative surface charge, and the latter can be attributed to delocalized π -electrons of the basal planes, nitrogen functionalities, and surface oxygen-containing groups (i.e. pyrones, chromenes, diketones, and quinones), which accept protons from the solution and are responsible for the positive surface charge (Pivokonsky et al. 2021). Most activated carbons show a negative surface charge at high pH values (alkaline solutions) due to the presence of negatively charged carboxylate and anhydride anionic surface functional groups on their surface (Huang et al. 2007). Non-electrostatic adsorption mechanisms most often control the removal of neutral organics from water via carbon adsorption in water treatment. However, when an organic compound has a cationic or anion character, it becomes more polar and may be poorly adsorbed by activated carbon via non-specific physisorption, while electrostatic

mechanisms could be enhanced. Infrared spectroscopy data obtained for the wood-based carbons showed that the oxygen content was present in the adsorbent as hydroxyl, phenol, or lactol groups as well as ethers, carbonyls, quinones, and lactones. Since these activated carbons were chemically activated with phosphoric acid (Table SI), a proportion of the oxygen content was also attributed to surface phosphate groups. The coconut-based activated carbons, however, contained only ethers, carbonyls, quinones, and lactones functional groups, and no surface OH groups (Pendleton et al. 2001). Albuquerque Junior et al. (2008) verified that carbons obtained from different raw materials also presented the acid groups mentioned above on their surfaces. They can become ionized in water solution, producing H⁺ ions; and consequently, the pore surface of the activated carbon obtains negative charges.

Surface area and pore size distribution

Differences in pore structure and size distribution result in different adsorption properties. As reported by Donati et al. (1994), previous researchers studied the effect of pore size distribution on the adsorption of small taste and odor (T&O) compounds, such as 2-methylisoborneol (MIB). They reported that competitive adsorption between these small molecules and naturally occurring humic material depended on pore size distribution and concluded that there is no correlation between the tendency of activated carbons to adsorb a particular compound and the commonly used adsorption capacity indexes such as molasses number, iodine number, phenol number, and surface area. The results found by Donati et al. (1994) showed that pore volume was strongly dependent on the starting material. The wood-based carbons had a larger micropore and mesopore volume than other carbons. The

coconut and peat moss-based carbons had low mesopore volume, and the coal-based carbons lay somewhere in between (Table SI). Nonetheless, one of the coal-based PACs, which possessed a relatively high micropore and mesopore volume compared to other coal-based PACs, did not follow this pattern, possibly because of a different activation mode, as suggested by the authors. Donati et al. (1994) also showed that the wide-ranging MC-LR adsorption maxima for the PACs are directly related to the mesoporous volume. The wood-based PAC, the most effective MC-LR adsorbent, had the greater mesoporous volume (Table SI) compared with the other PACs. Furthermore, here was little correlation between micropore volume and MC-LR adsorption.

Lee & Walker (2006) findings are in agreement with the previous study, confirming that pore size distribution plays a vital role in MC-LR adsorption because this toxin, with an estimated diameter of 3 nm, is too large to enter micropores (< 2.0 nm) but adsorbs in mesopores (2-50 nm). The wood-based PAC used in this study had significant mesopore volume, while micropores dominated the coconut-based PAC. The total available surface area was unimportant, given that the wood-based carbon had a slightly lower specific surface area than the coconut-based carbon (Table SI). Therefore, wood-based PAC was more effective at removing MC-LR than coconut-based carbon primarily due to greater mesopore volume. Similarly, Huang et al. (2007) analyzed different activated carbons used at a water treatment plant, showing that PACs with the largest volume of mesopores and macropores adsorbed MC-LR to the most considerable extent. Pivokonsky et al. (2021) include that the adsorption efficiency of algal metabolites is given by the combination of the pore size distribution of the activated carbon rather than by the absolute surface area value.

Algal metabolites preferentially become trapped in the pores corresponding to their size because plenty of contact points are available between the contaminants' molecules and the PAC surface.

Ho et al. (2011) found that the removal of a wide range of molecular weight compounds increased with PAC dose, which was attributed to the pore structure of the PACs. Therefore, due to this observation, they implied that the type of NOM might not significantly influence the cyanotoxins' adsorption when using the tested PACs (Table SI), as their adsorbents contained a broad pore size distribution. It is also important to highlight that there is a consensus amongst most suppliers that a high specific surface area is important for removing a particular contaminant. Still, this assumption must be made with caution. Although an adsorbent may possess a high specific surface area (usually measured by nitrogen adsorption), the surface area available for the adsorption of a particular toxin may be pretty small due to molecular sieve effects (Pendleton et al. 2001).

Molecular size of cyanotoxins

The adsorption characteristics of an adsorbent-adsorbate system also depend on the size of the adsorbate compounds. As previously discussed, when an activated carbon has less volume in the mesopore region, it cannot adsorb as much MC-LR as a highly mesoporous carbon because of the larger size of this cyanotoxin, which prevents it from entering smaller micropores (Donati et al. 1994). Huang et al. (2007) argue that by reducing the pH, the electrostatic repulsion between neighboring negatively charged sites is also decreased and is responsible for stretching out the MC-LR molecules, thus, reducing MC-LR size due to its tendency to coil, reducing its overall molecular dimensions. The authors also suggested that besides the change in molecular

dimensions, the formation of hydrogen bonds is also one of the main reasons for increasing adsorption at lower pH.

In a study by Ho et al. (2009) using two types of PAC (micro and mesoporous), it was observed that coal-based carbons contained a greater volume of micropores than wood-based, which are favorable for the adsorption of smaller molecular weight compounds. Smaller toxin molecules, such as STXs, can utilize surface areas within micropores and larger pores; thus, using microporous instead of mesoporous carbon is recommended for STX removal (Newcombe & Nicholson 2004). However, larger molecules, including much of the natural organic matter (NOM) and MC-LR (Huang et al. 2007), are generally too large to utilize the micropores. Usually, NOM can interfere with the sorption of smaller adsorbates via two mechanisms: direct competition for sorption sites and pore blockage (Shi et al. 2012). Although it is believed that the most significant adsorption competition would exist between compounds of similar size and shape, competitive adsorption is not only dependent upon the size of the competing compound but also highly dependent upon the pore volume distribution of the adsorbent (Ho et al. 2011).

Effect of pH

As already discussed in previous sections, factors such as the charge and nature of functional groups on both the carbon surface and the adsorbate are also known to influence adsorption processes, turning parameters such as the pH and ionic strength of a system critical to consider and understand (Donati et al. 1994). The solution pH affects PAC adsorption due to adsorbent surface chemical group preferential polarization (Pendleton et al. 2001). Huang et al. (2007) reported that previous authors examined the effect of pH in the range of 5-7

on humic acid adsorption by activated carbon and demonstrated that the adsorption affinity for humic acid is indirectly proportional to pH increase. Full-scale drinking water treatment processes involve competitive adsorption between the target contaminant and many other dissolved species classified as humic substances or dissolved organic matter (DOM). Such mixtures make a complex system challenging to analyze and interpret, as commented by the authors.

A study conducted by Shi et al. (2012) demonstrated that pH significantly impacts the adsorptive efficiency of PAC for STX removal. At an intermediate pH of 8.2 for water treatment, the relative performances of three PACs (Table SI) were (from lowest to highest capacity): lignite-coal-based < bituminous-coal-based < wood-based. In their study, the adsorption efficiency of STX increased with increasing pH because of the electrostatic interactions between functional groups of STX (speciation) and PAC surface due to the ionization of surface groups present in the PAC, causing a reduction in the repulsive electrostatic interactions between the positively charged STX and the adsorbent. In contrast, MC adsorption was enhanced with decreasing pH because MC is predominantly negatively charged at a pH range of 3-12 (Pivokonsky et al. 2021). These results suggest that the choice of PAC should be closely matched to the objectives of the PAC treatment. Furthermore, they also reinforced that water quality conditions play a critical role in PAC sorption performance and must be well understood or studied in laboratory or field experiments to optimize water treatment performance.

While considering MC-LR adsorption, when the pH is lowered from 6.5 to 2.5, a decrease in the MC-LR water solubility is expected. Therefore, an increase in MC-LR affinity for the carbon surface is predicted. At low pH, the toxin molecule may behave as a filament, while at high pH, the

structure may become an open “net”, offering larger dimensions or cross-sectional area. Thus, pH changes can modify MC-LR molecular shape (Pendleton et al. 2001).

Huang et al. (2007) found that for all the different activated carbons tested (coconut shell, bituminous coal, and wood-based ACs), the adsorption of MC-LR increased as pH was lowered from 8 to 3. At pH 3, all the carbons shifted from a positively charged surface to a neutral charge (pH_{pzc}) at 5.2 for coconut shell, 5.8 for bituminous coal, and 4.1 for wood-based PAC (Table SI), indicating an increase in the negative charges. The pH at the point of zero charge (pH_{pzc}) is the pH value at which the surface ionic groups are neutralized, providing the adsorbent with an uncharged surface (Pendleton et al. 2001). Conversely, in high pH solutions, MC-LR is negatively charged, and as most activated carbons show negative charges at alkaline pH, repulsion forces between the surface of carbon and MC-LR occur. Another factor regarding MC-LR is that at low pH, the weak acidic functional groups are undissociated, presenting a hydrophobic nature, and therefore are better adsorbed to the carbon surface than dissociated acidic functional groups at high pH, as already discussed in the surface functional groups section.

Similarly, Bajracharya et al. (2019) reported that, in the absence of NOM and at a pH of 5.2, the adsorption of MC-LR to PAC increased with decreasing pH, with all four PAC types exhibiting their most extensive amounts of adsorbed MC-LR. On the other hand, in the presence of NOM, the quantity of MC-LR adsorbed by PAC tended to decrease with decreasing pH, except for the coconut-based PAC. In wood-based and coal blend-based PACs this trend was more significant, where the amount of adsorbed toxin decreased by 28 and 40%, respectively, as the pH decreased from 9.5 to 5.2. Therefore, the

reduction in MC-LR adsorption with decreasing pH likely reflects an increase in the adsorption of NOM with decreasing pH.

Effects of NOM

Water quality strongly influences the removal of cyanotoxins by activated carbon since NOM can compete and limit their adsorption (Donati et al. 1994, Huang et al. 2007). Donati et al. (1994) found that the UV_{254} absorbance of river water decreased significantly over time, indicating adsorption of both NOM and MC-LR. Competition for adsorption sites results in a decrease in MC-LR adsorption in raw water compared to ultrapure water. This can be expected as MC-LR is of a similar size to a large proportion of NOM in natural waters. In the same study, the effect of competitive adsorption between MC-LR and NOM was inferior in the wood-based PAC compared to other carbons. Wood-based PACs are highly mesoporous, so they can more readily accommodate both MC-LR and NOM substances of similar size. However, in less mesoporous adsorbents, such as coal, coconut, and peat moss-based PAC, there is greater competition for the fewer mesoporous sites available, which results in a more significant decrease in MC-LR adsorption. Blockage of transport pores by large organic molecules can also contribute to this since wood-based carbons possess a regularly ordered structure, enabling easier passage to the adsorption pores than the random network of pores in coal, coconut, and peat moss-based carbons. The authors suggest that this could explain why MC-LR adsorption for coal-based was reduced by 46% in river water, despite having relatively high mesopore volume compared with the other non-wood-based carbons (Campinas et al. 2013, Donati et al. 1994).

The competitive effects of NOM and organic matter pre-loading on activated carbon were evaluated by Lambert et al. (1996), which showed

that both decreased the ability of activated carbon to remove MC-LR. Although activated carbon can efficiently adsorb MC-LR, reaching a lower concentration of toxin would require a high and unusual amount of PAC to compensate for the presence of NOM in both water and the adsorbent (Merel et al. 2013). Bajracharya et al. (2019) found that the type of NOM also seemed to impact PAC performance, with NOM associated with algal bloom conditions exhibiting more of an impact on MC-LR adsorption than did NOM associated with terrestrial sources. The magnitude of the impact of NOM on MC-LR adsorption varied with PAC type, and it followed, from highest to lowest, this order: wood, coal blend, bituminous coal, and coconut shell (Bajracharya et al. 2019).

Huang et al. (2007) evaluated the competitive effect of NOM on MC-LR adsorption using wood-based activated carbon by conducting adsorption isotherm experiments with both natural waters containing NOM and ultrapure water. The maximum adsorbed capacity (Q_{max}) was observed to be much lower in the competitive isotherm compared with the ultrapure water. MC-LR removal decreased from 12% to 65%. Due to its characteristics (high in hydrophilic organics and more polar than MC-LR), NOM in the natural water competed with MC-LR for sorption sites.

Ho et al. (2009) found that the effect of water quality on the adsorption of STXs was minor, with a negligible difference observed between the removals in reservoir waters. These results suggest that lower competitive effects were evident and may be due to the wide range of pores of the carbons. Contradictorily, Shi et al. (2012) evaluated the impact of competition with NOM using natural water collected from a local pond in which the dissolved organic carbon (DOC) concentration was very high ($28 \pm 2 \text{ mg.L}^{-1}$). The results showed that the most significant

effects of NOM on STX adsorption occurred at pH 7.05, with much smaller amounts of STX removed when NOM was present, compared to DI water. The authors hypothesized that the STX–NOM solution-phase interactions might have been enhanced at this pH due to the increasingly cationic nature of the STX in the presence of the negatively charged NOM. These interactions may have inhibited the adsorption of STX on the carbon surface.

NOM competes with target contaminants for adsorption sites on the surface of PAC, and thus, in high concentration, NOM would result in greater competition and, consequently, reduce the adsorption of the target contaminant. Furthermore, NOM can also block pores, reducing the target contaminant's adsorption (Ho et al. 2008). For these mechanisms, NOM molecular weight is critical as the small molecular weight fraction (<1000 Da) is more important in competitive adsorption because, once adsorbed, they reduce the capacity of PAC for the target compound. On the other hand, the large molecular weight fraction causes pore blockage/constriction, thus, reducing the rate of the adsorption of the target compound (Bajracharya et al. 2019).

The relative impact of the two mechanisms varies to some extent on the type of PAC. Bajracharya et al. (2019) analyzed the presence of NOM and its impact on the rate and the amount of MC-LR adsorption in different types of PACs. For the wood-based PAC, the rate of MC-LR adsorption decreased to a greater quantity in the presence of NOM than the extent of adsorption, suggesting pore blockage was more important than direct competition for this type of PAC. The bituminous coal-based PAC demonstrated a higher reduction in adsorption capacity than the adsorption rate. Therefore, site competition was the most important mechanism for this PAC. On the other hand, the coal blend-based PAC

showed similar decreases in both the extent and rate, indicating neither mechanism dominated. The authors assumed these differences likely reflect the presence of different forms of porosity on the PAC types and the ability of the NOM molecules to access sites within these pores. Similarly, when testing PAC adsorption, results showed that the adsorption of MC-LR was reduced by 11.3% in the presence of NOM as both MC-LR and NOM compete for similar mesoporous sites due to the similar molecular size of the two compounds (Lee & Walker 2006).

Removal capacity and limitations

Donati et al. (1994) found that the initial rate of MC-LR uptake from river water for both wood and coal-based PACs was slower than that observed in ultrapure water. The adsorbents showed a decrease in initial uptake of MC-LR of 36 and 42% for wood and coal-based PACs, respectively. The wood-based carbons were the most effective adsorbents, adsorbing 280 and 220 $\mu\text{g MC-LR.mg}^{-1}$ carbon, respectively. The least effective adsorbents were the coconut-based, adsorbing 40 and 20 $\mu\text{g MC-LR.mg}^{-1}$ carbon, and the peat moss-based, which adsorbed 20 $\mu\text{g MC-LR.mg}^{-1}$ carbon (Table SI).

Sugarcane bagasse and pinewood-activated carbon fibers showed adsorption of 161.3 and 200.0 $\mu\text{g MC-LR.mg}^{-1}$ carbon, respectively. When compared to other results available in the literature, these results give an idea of the profile of the carbon that should be used in water treatment plants to remove toxins like MCs, requiring a volume of secondary micropore above $0.35 \text{ cm}^3.\text{g}^{-1}$ and a volume of mesopore greater than $0.40 \text{ cm}^3.\text{g}^{-1}$ (Albuquerque Junior et al. 2008). The adsorption of MC-LR onto activated carbon fibers from pinewood and sugarcane bagasse showed the same tendency described in previous studies (Donati et al. 1994, Pendleton et al. 2001). The greater the volumes of secondary

micropores and mesopores of the carbons, the greater their capacity to adsorb MC-LR. The authors also attribute the greater adsorption affinity for the cyanotoxin in the pinewood-based PAC compared to the sugarcane bagasse PAC due to the higher volumes of secondary micropores and mesopores in the former (Table SI).

Wood-based PAC achieved 84% of total microcystin removal with a 20 mg.L⁻¹ PAC dose when the initial concentration of microcystin was 30 µg.L⁻¹. The adsorption efficiency of microcystin did not show significant changes at higher doses. The pore size distribution was PAC's most important physical property for considering adsorption performance. It is also apparent that the kinetic rate of adsorbed microcystin increases by increasing the adsorbent dose, but the maximum amount adsorbed was at a dose of 20 mg.L⁻¹ of PAC (Şengül et al. 2018).

In another study, wood, coal blend, bituminous coal, and coconut shell-based PACs removed about 93, 46, 20, and 10%, respectively, of the initial 50 µg.L⁻¹ MC-LR concentration. The authors suggested that using PAC alone at a dose equal to or less than 5 mg.L⁻¹, regardless of source material, likely would not remove MC-LR below the WHO guidelines (Bajracharya et al. 2019). Therefore, while activated carbon can efficiently adsorb cyanotoxins, their complete adsorption would require a high amount of different adsorbent types. Consequently, activated carbon should not be considered as an individual remediation measure but as a part of a multi-barrier approach (Merel et al. 2013).

BIOCHAR

Role of Feedstocks

Due to their low surface area, some non-activated biochars can be inferior to commercially activated carbons in their sorption capacity

for organic contaminants (Inyang & Dickenson 2015, Lu et al. 2022). Although biochars share some similarities with activated carbon, there is a consensus that they exhibit high physical-chemical and structural heterogeneities, depending on the feedstock and pyrolysis conditions. There is still a reluctance to use biochar as a low-cost, renewable alternative to activated carbon, a trend also reported for other adsorbents (Gwenzi et al. 2017).

Li et al. (2018) found that biochar produced at higher temperatures (600°C) had higher ash content compared to those produced at a lower temperature (300°), following this trend: chicken manure biochar > maize straw biochar > pine sawdust biochar (Table SIII). Therefore, this suggests that biochars derived from animal wastes tend to contain higher mineral ash content than those from plant residues. The interaction of higher ash content with organic matter in biochars could influence the sorption characteristics of organic pollutants. Moreover, mineral ash content may provide additional cation and/or anion binding sites for ionizable organic compounds (IOCs) adsorption, such as MC-LR (Li et al. 2018). These authors also found that, depending on the feedstock type and temperature, the biochars varied significantly in their structural properties and capacity to adsorb MC-LR from water. They suggested that chicken manure-derived biochars have great potential as low-cost sustainable sorbents to diminish MC-LR risks. In another study for the MC-LR adsorption, different feedstocks were tested, and the capacity of biochar for MC-LR removal was in the following order: Kentucky bluegrass biochar > coffee residue biochar > grape pomace biochar > rice husk biochar > microalgae biochar. MC-LR adsorption tended to improve with the increase in pyrolysis temperature (Song et al. 2021).

Li et al. (2018) found that for plant residue-derived biochars, the organic carbon contents

increased as temperatures rise, implying a greater carbonization degree when pyrolysis is carried out at higher temperatures. Oppositely, the organic carbon content of biochars containing high ash mineral content varied inversely with increasing temperature. The authors believe this is primarily due to the higher ash content of animal waste-derived than plant residue-derived biochars. The authors also found that the bulk functionalities differed between the tested biochars (pine sawdust, maize straw, and chicken manure), which they attribute to being feedstock and pyrolysis temperature dependent. The study also suggested that the ash mineral naturally present in the biochar could enhance the sorption of MC-LR through mechanisms such as electrostatic interaction, pore-filling, and H-bonding effect, which are linked to the point of zero charges, mesoporosity, and total surface functionality, respectively.

Elemental Composition and surface chemistry

Wei & Lu (2021) obtained biochar from rice straw pyrolyzed at different temperatures, and each biochar showed different elemental compositions (Table SIII). As the pyrolysis temperatures increased from 300 to 700 °C, the carbon (C) contents improved, whereas the hydrogen (H) and oxygen (O) contents declined. Meanwhile, the nitrogen (N) contents remained generally unchanged during the process. The H/C atomic ratio (aromaticity index) decreased with the temperature rising from 300 °C to 700 °C, indicating that the aliphatic carbon was pyrolyzed into aromatic carbon. With the increasing pyrolysis temperature, the molar O/C ratio (polarity index) significantly decreased, making the surface of rice straw biochar more hydrophobic. Meanwhile, the decrease of the [(O + N)/C] ratio (polarity index) indicated a reduction of the surface polar functional groups. The temperature had a significant correlation

with the indexes mentioned above. The authors found that for rice straw biochar pyrolyzed at 300 °C, the surface functional groups had almost no changes, whereas for other biochars, the intensity of the adsorption peaks decreased, and the O-H bond stretching vibrations in the region of 3,683 cm^{-1} disappeared. On the other hand, for the biochars pyrolyzed at higher temperatures (500-700 °C), the $-\text{NO}_2$ adsorption peak in the region of 1,591 cm^{-1} shifted to a higher wavelength after MC-LR adsorption. Therefore, the authors attribute these functional groups presented on the surface of rice straw biochars as the adsorption sites for MC-LR.

Song et al. (2021) produced biochar using Kentucky bluegrass as feedstock at different pyrolysis temperatures (Table SIII). In their results, the C content increased during pyrolysis due to the loss of volatile substances while H and O contents decreased, consequently reducing the O/C (polarity) and H/C (aromaticity) indexes. In contrast, ash contents increased with the increase in pyrolysis temperature. The pH_{pzc} of the biochar slightly increased from 6.35 to 7.07 as the temperature increased. Moreover, the minerals, including P, K, Ca, Mg, and Fe, slightly increased with a rise in the pyrolysis temperature.

Zeng & Kan (2021) used bermudagrass as feedstock for biochar production. Their study compared raw biochar (non-activated) with iron-activated biochar for MC-LR removal (Table SIII). The C content of activated biochar decreased due to the high iron content from the FeCl_3 activation. In addition, the O and H contents of the activated biochar were much lower than those of non-activated biochar, which indicates that the FeCl_3 activation favored the elimination of O and H. Moreover, the lower H/C, O/C, and [(O+N)/C] in the activated biochar suggested that the aromaticity and hydrophobicity increased while the polarity decreased after the FeCl_3 activation.

As for the spent mushroom substrate, as the pyrolysis temperature rose from 300 to 600 °C, the C contents of the biochars increased, but the O and H contents declined. Consequently, the atomic ratios of [(O+N)/C], O/C, and H/C decreased significantly. The authors also found that the adsorption bands were weakened as the pyrolysis temperature was increased, which is in agreement with the decrease of O content at higher pyrolysis temperatures. This confirms a loss of O- containing functional groups (e.g. hydroxyl, carboxyl, and carbonyl) due to dehydration and decarboxylation (Liu et al. 2021). Interestingly, these authors also showed that biochar produced under the N₂ atmosphere showed slightly higher degrees of peak intensity than biochar produced under the CO₂ atmosphere. A higher pyrolysis temperature and CO₂ better developed the physical structure of biochars, while lower pyrolysis temperatures and N₂ generated more surface functional groups in biochars.

Based on recent literature, Li et al. (2018) suggested that polar surface groups might affect adsorption more than bulk polarity. In that sense, a more significant presence of surface O- and H-containing polar groups can form more hydrogen bonds with the MC-LR molecule's H, N, and O atoms and readily facilitate MC-LR sorption.

Surface charge

Wei & Lu (2021) showed that, as pyrolysis temperature increased from 300 to 700 °C, the pH_{pzc} of all rice straw biochars increased, ranging from 3.5 to 5.5, and the alkalinity increased as well. The authors attributed this due to two reasons: the oxygen-containing functional groups on the surface of the biochar (such as hydroxy) decreased with the increasing pyrolysis temperature (Zhang et al. 2015), and, secondly, at 400 °C carbonates would be formed (Yuan

et al. 2011). Regarding FeCl₃ activation, the pH_{pzc} of bermudagrass biochars increased from 4.19 to 7.36 after activation, implying that acidic functional groups were reduced under the activation conditions (Zeng & Kan 2021).

Morphology and Microstructures

In Wei & Lu's (2021) study, all rice straw biochars presented a porous structure and a large surface. The pore canals were narrow and sparse at lower temperatures with a smooth surface. However, the pores gradually became larger and denser with an increase in the pyrolysis temperature. Small and dense micropores existed in each pore canal, with an increasing quantity. Song et al. (2021) demonstrated that biochar generated at higher pyrolysis temperatures developed a crystallization structure due to concentrated minerals such as Ca, Si, Mg, P, K, etc.

Effect of pH

For the adsorption of MC-LR in rice straw biochar, all adsorbents demonstrated better adsorption capacity at a lower pH of 3, while there was no significant difference in MC-LR removal rates at pH 7 and 9. The pH_{pzc} of all the biochars was in the range of 3.5–5.5; their zeta potentials were positive at pH 3 while negative at pH 7 and 9. On the other hand, MC-LR has a negative charge when pH > 2.19; therefore, the electrostatic attraction explains why the rice straw biochar showed better adsorption capacity at a lower pH. Moreover, as previously discussed, MC-LR molecules become smaller at lower pH, reducing overall molecular dimensions. As a result, hydrogen bonds could be formed between the coiled molecules and the biochar surface charges, promoting the improvement of the adsorption capacity (Huang et al. 2007, Wei & Lu 2021). Comparably, Li et al. (2014) also found that adsorption significantly decreased as pH increased. The authors supposed that

electrostatic attraction may occur between the positively charged biochar surface and the negatively charged MC-LR. Moreover, higher adsorption of MC-LR at lower pHs may be attributed to the positive charges on the carbon surface with decreasing pH, whereas at higher pHs, the similar electronegative nature results in the repulsion of MC-LR from the biochar surface.

Liu et al. (2021), using spent mushroom substrate as a starting material, found that the adsorption efficacy of MC-LR to biochar produced at a higher temperature (600 °C) was inversely correlated to the solution pH. Similarly, increasing the pH led to an increase in the negative charges of the biochar surfaces. Hence, electrostatic repulsion between the toxin and the adsorbent was expected, weakening the adsorption efficacy. As the pH of natural water usually stands between 6 and 8, at which the adsorption efficacy of the higher pyrolytic biochar reached 79.1–83.2%, the authors suggested that it could be a promising adsorbent for MCs removal from natural water. In line with the mentioned studies, at lower pH, higher adsorption was observed with the maximum MC-LR adsorption capacity at pH 3 (5,034 $\mu\text{g}\cdot\text{g}^{-1}$) and pH 4 (3,676 $\mu\text{g}\cdot\text{g}^{-1}$) for Kentucky bluegrass-biochar (750 °C). However, lower MC-LR adsorption capacities (2714–2964 $\mu\text{g}\cdot\text{g}^{-1}$) were observed at higher pH (5–9) (Song et al. 2021).

Zeng & Kan (2021) also found optimal pH values at pH 3 and 4, while the adsorption capacity decreased with higher pH. However, adsorption capacity values at pH 7–8 (8.36–9.03 $\text{mg}\cdot\text{g}^{-1}$) were not significantly different from those at pH 3–4 (9.64–9.69 $\text{mg}\cdot\text{g}^{-1}$), suggesting that iron-activated biochar has excellent potential for the treatment of MC-LR from natural water and wastewater with various pH values.

Surface area and pore distribution

Li et al. (2018) found in their study that all tested chicken manure biochars and

maize straw biochar produced at higher pyrolysis temperature – both possessing high mesoporosity – demonstrated to be better sorbents compared to the other biochars tested, which contained a lower mesoporosity, even though some of these had greater total pore volume and/or microporosity (Table SII). The authors also suggested that the pore-filling effect could be one central mechanism that dominates MC-LR sorption and outweighs the aromaticity or surface functionality roles for the biochars produced from specific feedstocks and pyrolysis temperatures.

Wei & Lu (2021) found that the average pore size of all rice straw adsorbents was within the mesopore range (2–50 nm). Thus, microcystins are easier and preferential to be adsorbed onto the biochars. With the increase of pyrolysis temperatures from 300 °C to 700 °C, the total pore volume and the micropore volume increased (Table SII). In addition, the specific surface area of the biochars improved significantly from 3.87 $\text{m}^2\cdot\text{g}^{-1}$ to 360.9 $\text{m}^2\cdot\text{g}^{-1}$. At the highest temperature, the surface area of the adsorbent was nearly 100 times higher than that of biochar produced at the lowest temperature, which the authors attributed to the carbonization process of biomass.

Generally, the specific surface area of Kentucky bluegrass biochars improved with the increase in pyrolysis temperature, but this trend was the inverse at 550 °C and 750 °C. The porosity revealed a similar trend with the specific surface area, which the authors attributed to the destruction of the porous structure of biochar and the blocking of pores by tar (Song et al. 2021). For biochar produced from bermudagrass, compared to non-activated biochar (85.82 $\text{m}^2\cdot\text{g}^{-1}$), the iron-activated material showed a nearly ten times higher surface area (835.10 $\text{m}^2\cdot\text{g}^{-1}$), suggesting the FeCl_3 activation

can provide significant improvement in terms of surface area (Zeng & Kan 2021).

The biochars produced at a higher temperature from peeled wood chips presented a significant amount of meso and macropores for MC-LR adsorption, as their micropore volume was almost half its total volume (Table SII). On the other hand, peeled wood chips biochars produced at a lower temperature presented no micropores. They possessed a much larger average pore diameter (Table SII), which indicated that their total surface area would be more suitable and available for MC-LR adsorption (Li et al. 2014). After coexisting with DOM, the adsorption capacity of MC-LR decreased, which means that DOM, such as tannic acid (TA), acted as a strong competitor by occupying the effective adsorption sites for MC-LR in the mesopore and macropore regions due to the larger molecule size of TA than MC-LR (Li et al. 2014).

To improve porosity in biochars, acid-soaking is an effective method, primarily due to mineral removal and the exposition of hidden and blocked pores. Another advantage of deashing could be the release of dissolved organic residues and removing carbon fragments from biochars, enabling a more porous structure. In their study, (Liu et al. 2018) observed that deashing slightly increased the surface area and pore volume of low-temperature biochars (≤ 400 °C) while significantly increasing the surface area in high-temperature biochars (≥ 500 °C). Therefore, deashing might influence the physicochemical properties of biochars, consequently affecting MC-LR sorption behavior.

Pyrolysis temperature and other pyrolytic conditions

At the same pyrolysis temperature, compared to other feedstocks, chicken manure biochar exhibited the strongest sorption for

MC-LR, contributed mainly by electrostatic attraction, pore-filling, and H-bonding effects, corresponding to their higher pH_{PZC} , mesoporous volume, and total surface functionality (Li et al. 2018). The studied rice straw biochars showed a significantly positive association of temperature to the specific surface area, total pore volume, and mesoporous volume, while temperature and average pore diameter distribution were negatively correlated. The higher the pyrolysis temperature, the better its adsorption capacity on MC-LR (Table SII), thus, indicating that the adsorption efficiency of rice straw biochars was positively related to the pyrolysis temperature. The biochar produced at 700 °C exhibited the best adsorption capacity for MC-LR. The highest pyrolytic temperature provided the largest specific surface area ($360.9 \text{ m}^2 \text{ g}^{-1}$), which can offer more effective binding sites for target contaminants. Moreover, the high pyrolysis temperature also provided better-developed structures than those at lower temperatures, meeting the size of MC-LR (Wei & Lu 2021).

The spent mushroom substrate biochars showed the greatest ash content when pyrolyzed at 600 °C, decreasing as the pyrolysis temperature was lowered to 300 °C. Both the S_{BET} and porosity of biochars were significantly improved as the temperature was raised from 300 to 600 °C (Table SIII). At the lowest temperature, the pore structures were less developed, while the porosity was better developed at 600 °C due to more water loss in the dehydration process, volatilization of organic matter, and fracture/collapse (Liu et al. 2021). In their study, Song et al. (2021) found that the relationship between the adsorption capacities of different biochars and H/C ratio associated with the pyrolytic temperature as an indicator of hydrophobic value had a high correlation in all tested biochars. The result indicated that the highest pyrolytic temperature

was observed as the optimal condition (Table SIII), and hydrophobic interaction revealed one of the possible MC-LR adsorption mechanisms. Generally, these phenomena deduced that the biochar produced at higher pyrolysis temperature could influence the adsorption of contaminants due to an increase in the surface area, higher hydrophobicity, and concentration of specific elements (i.e., P, K, Ca, Mg, and Fe, etc.). In another study, high-temperature (700 °C) peeled wood chips biochar showed a high carbon content, low H/C ratio (Table SIII), and high specific surface area (Table SII), which implies the formation of a highly carbonized aromatic structure. By contrast, low-temperature biochar (300 °C) exhibited low carbon content, high H/C ratio, and low specific surface area, indicating that some organic residues from the feedstock remain on its structure after incomplete carbonization (Li et al. 2014).

Influence of ions on MC-LR adsorption

Evaluating the adsorption capacity in water from a river and a lake, Song et al. (2021) observed a considerable decrease in MC-LR adsorption compared to DI water results. The adsorption capacities from the river and lake water were 1,000 $\mu\text{g}\cdot\text{g}^{-1}$ and 1,421 $\mu\text{g}\cdot\text{g}^{-1}$, respectively, while in DI water, it was 2,769 $\mu\text{g}\cdot\text{g}^{-1}$. The authors suggested that the decrease in the adsorption capacity could be due to the cationic and anionic metal ions, as they found a higher amount of metal ions such as Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-} in the natural waters. This phenomenon is likely due to the rapid absorption of ions Mg^{2+} , Ca^{2+} , and NO_3^- onto the biochar surface, resulting in the removal of the metal ions, rather than MC-LR.

Zeng & Kan (2021) also investigated the use of biochar in natural water. The iron-activated biochar was tested with the MC-LR spiked with environmentally relevant concentrations (5, 25, and 50 $\mu\text{g}\cdot\text{L}^{-1}$) in DI water and lake water. For

both experiments, the final MC-LR concentration was lower than 1 $\mu\text{g}\cdot\text{L}^{-1}$, which can meet the World Health Organization (WHO) guideline. The authors also suggested that because the adsorbent could be magnetically removed, iron-activated biochars appear applicable to the treatment of lake waters containing MC-LR due to their effective adsorption, magnetic separation, and regeneration.

Activated biochar

Zeng & Kan (2021) found that, compared with the control (no activation), the FeCl_3 activation led to a significant increase in MC-LR adsorption capacity. Depending on the impregnation rate, the adsorption capacity was affected. In their study, MC-LR adsorption capacity was greatly improved (from 0.76 to 9.00 $\text{mg}\cdot\text{g}^{-1}$) when the iron impregnation ratio rose from 0 to 2; but at a ratio of 3, the adsorption capacity was decreased. The authors argue that a high dose of ferric activator could cause hyperactivation while deteriorating pore structure, causing blockage of pores with aggregated iron and lowering surface area.

CONCLUSIONS

The current work provided an understanding that the general indexes adopted by water companies and decision-makers appear to lack a deeper knowledge of carbon absorbents for toxin removal. One such factor is the specific surface area which, by itself, is a poor indicator of adsorption capacity. Thus, water companies should appreciate a combination of detailed data of the adsorbate, adsorbent, and aqueous solution properties for the correct selection of PAC or biochar. Overall, this systematic review has shown that, although activated carbon has been widely used for cyanotoxin removal, not enough data is available and fewer studies have been carried out for different toxins other than MC-LR,

leaving many gaps for toxins such as saxitoxins and cylindrospermopsins. As for biochar, the knowledge gaps are even greater when it comes to cyanotoxins adsorption. In addition, no studies have been found on producing a biochar specifically for cyanotoxins removal and on the impact it could cause on drinking water quality. Therefore, without further studies, biochar is not yet a reliable option for water treatment, especially on full-scale operations, due to the great diversity in feedstock options, manufacturing procedures, and properties.

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SUPPLEMENTARY MATERIAL

Tables SI, SII, SIII.

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