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Impact of PAC Type and Water pH on Removal of Microcystin-LR and Saxitoxin

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Abstract

The projection focused on the removal of microcystin-LR (MC-LR) and saxitoxin (STX) with different powdered activated carbon (PAC) sources in distilled and raw source water. Wood-lignite-based (WL) PAC adsorbed more MC-LR and STX than the bituminous coal-based (BC). For 0.3 μg/LSTX in distilled water, WL adsorbed more STX than with BC. Across all pH and concentration combinations, WL adsorbed more MC-LR in distilled water and raw surface water than BC. For instance, when 0.3 μg/L STX was present with 1.6 μg/L MC-LR at pH 6, removal was 31% and 62%, and increased to 49% and 65%, respectively at pH 8. The increased removal was attributed to competition with natural organic matter, which was depicted as a 19% removal at pH 6 versus 4% removal at pH 8. When both toxins were present at 1.6 mg/m^3, removal when water pH of 8 was 61% for STX and 72% for MC-LR.

Keywords

Cyanotoxin, Pore Size, Charge, pH, Drinking Water Treatment

1. Introduction

Cyanobacteria, also called blue-green algae, grow in waters with high nutrient levels, sunlight and at temperatures of 25˚C or above. Blooms of cyanobacteria, or harmful algal blooms (HABs), can simultaneously contain toxic and non-toxic strains of the same species [1]. HABs can lead to deterioration of the ecosystem and threaten drinking water safety [2]. The occurrence and intensity of HABs are increasing and the unpredictability of whether a bloom will produce toxins makes reservoir management difficult [3] [4]. In some areas of the United States, if the water source exceeds 100,000 cells/mL of cyanobacteria, the treatment plant may be rendered ineffective, and a "do not use order" is issued until cell counts are lowered [5].

The most common freshwater cyanotoxins are microcystin (MC), cylindrospermopsin, anatoxin-a, (ATX-a), saxitoxin (STX), nodularin, and lyngbyatoxins [5] [6]. The U.S. Environmental Protection Agency (USEPA) has "do not use" drinking water advisories for school-age children and adults for microcystins (1.6 μg/L), and cylindrospermopsin (3.0 μg/L). The Ohio EPA (OEPA) has expanded the 1.6 mg/m^{3}advisory to also include saxitoxin and anatoxin-a [5]. Cyanotoxins are categorized based on mode of action: i) hepatotoxins like MC, nodularin, and cylindrospermopsin, which cause liver injuries; ii) neurotoxins like ATX-a and STX that damage the nervous system; and iii) dermatoxins like lyngbyatoxin-a, aplysiatoxin, and lipopolysaccharides which are skin irritants [7].

Microcystin-LR (MC-LR) is the most abundant variant of MC [8]. It is a complex molecule with a diameter of around 1.1 - 2.94 nm and a molecular weight of 995 [9]. MC-LR is neutral at pH 2.09 - 2.19. Below pH of 2, MC-LR has positive charge whereas, above the neutral pH, MC-LR has negative charge [10]-[12]. STX has a molecular weight of 299 and a molecular formula of $C_{10}H_{17}N_7O_4$ [7]. It is water-soluble and heat-stable. The several amine groups on STX may lose or gain protons based on the pH of the water which may impact adsorption.

Conventional drinking water plants processes of coagulation, flocculation, sedimentation, and filtration are effective at removing intact cells, but ineffective at treating extracellular toxins [13] [14]. Although new technologies such as membrane filtration and advanced oxidation can effectively remove cyanotoxins, their capital cost and maintenance make them too expensive for many public water systems. Several studies on powdered activated carbon (PAC) have proved it to be effective at cyanotoxin removal and easy to operate with no significant capital cost or space requirement [15]. PAC is chemically stable, has a high surface area and pore volume, and has high efficiency for removing contaminants at low concentrations [16] [17]. For raw surface water with seasonal or short-term high risk, the ability to optimize PAC dosage and contact time with the targeted contaminant can be an advantage [18].

The water's pH and ionic strength, the presence of organic matter, and the PAC material source, pore size, and charge will influence the extent of adsorption and subsequent treatment efficiency [19]. Pore-size distribution of PAC is classified as macropores > 50 nm, 2 nm < mesopores < 50 nm, and micropores < 2 nm [20]. The size of MC-LR prevents its access to most micropores and is readily adsorbed on mesopores [21]. Ho *et al.* [22] showed that STX removal was more effective with PAC containing micropores. The highest to lowest volumes of mesopores are wood > bituminous coal > coconut, and micropores are coconut > coal > wood [23]. In general, PAC is more effective for hydrophobic contaminants such as MC-LR than hydrophilic ones [20].

Adsorption efficiency will also depend on the cyanotoxin concentration. As the concentration increases, the gradient increases of contaminants in water and the surface of PAC with the same dosage. This leads to faster adsorption to obtain equilibrium [10]. The low solubility of contaminants increases adsorption on PAC. An

increase in temperature can increase the solubility of contaminants in water and adversely affects adsorption [24].

Previous studies have typically focused on one cyanotoxin. However, the cyanotoxin typically present in surface water can change during the cyanobacteria growth cycle and more than one cyanotoxin can contaminate surface water at a time. The objective of this project was to assess the removal of STX and MC-LR with PAC treatment when these toxins were present alone and simultaneously. It was hypothesized that i) the PAC source, ii) water pH, and iii) the presence of a second cyanotoxin will impact removal efficiency. Identifying PAC sources that can effectively remove more than one cyanotoxin over different pH and cyanotoxin can provide drinking water treatment managers the ability to optimize their operating conditions.

2. Materials and Methods

2.1. Water Sources

Distilled water was produced using a Barnstead/Thermolyne still (model no. A1013B). Surface water was obtained from Lake Rockwell, the primary drinking water reservoir of the City of Akron, Ohio. It was collected from a spigot at the inlet pipe of the plant and used within 24 hours of collection.

2.2. MC-LR, STX, and Humic Acid Sources

One mg of MC-LR was purchased from Cayman Chemical. Upon arrival, MC-LR was dissolved in 500 µL of 75% methanol and 25% distilled water solution [25]. The vial was sealed and gently shaken to mix the toxin with methanol and distilled water. STX standard solution (saxitoxin dihydrochloride) of 500 µL vials was purchased from Eurofins Abraxis (CRM-00-STX). STX standard arrived as a solution of 20.5 µg/g in aqueous HCl at a pH of 2.63. Each toxin was transferred from original vials using a micropipette and placed in separate screw-on cap vials for storage at −20˚C (freezer) until use.

Pahokee peat humic acid was purchased from the International Humic Substances Society (St. Paul MN, USA). The International Humic Substances Society determined there was 56.37% carbon with a carbon distribution of 5% carbonyl, 20% carboxyl, 47% aromatic, and 4%.

2.3. PAC Sources and Determination of Point of Zero Charge

WL PAC is a blend of wood and lignite while BC PAC was a bituminous coal. Based on the source, the PAC contained primary micropores (d < 0.8 nm), secondary micropores (0.8 - 2 nm), mesopores (2 - 50 nm) or macropores (d > 50 nm) [20].

The pH_{PZC} (*i.e.*, pH where the surface charge of the PAC is zero) was determined for each PAC using the drift method [26]. Jars were filled with 0.01 M NaCl and adjusted to a particular pH between 5 to 12. After adjusting the pH to the required initial value (initial), each jar was dosed with 3 grams of PAC sample and mixed for three days. The pH measured at the end of three days was called pH (final).

The graph of pH (initial) vs. pH (final) was plotted to determine the pH constant value (pH initial = pH final). The pore size and pH_{PZC} for each carbon used in the study are given in Table 1.

Table 1. PAC source material, pore size, and pH_{ZPC}.

	WL	BC
Source material	Blend of wood and lignite	Bituminous coal
Pores	Micro, Meso, and macropores	Micro and macropores
Size	90% < 44 μm	90% < 44 μm
pH_{PZC}	9.65	9.44
Iodine number (mg/g)	800	500

2.4. Experimental Approach

A six-chambered Phipps and Bird (model 7790-900B) gang mixer was used to evaluate cyanotoxin removal with PAC. The mixing speed for rapid mix (coagulation) and flocculation were scaled to that used in the City of Akron's drinking water treatment plant (DWTP). The lab-scale velocity gradient was 134 revolutions/min for 20 sec and 17 revolutions/min for 45 min for rapid mix and flocculation, respectively [27].

The experiments were conducted using distilled water and raw surface water with MC-LR at the initial concentration of 0.3, 1.6, and 20 μg/L and STX at 0.3 and 1.6 μg/L. Cyanotoxin concentrations were based on the 2019 Ohio Environmental Protection Agency thresholds [5]. The experimental pH of distilled water was 6 and 9 and of raw water was 6, 8, and 9. The experiments were also conducted on the simultaneous presence of MC-LR and STX. Each PAC type tested used a dose of 15 mg/L, which was the same as that used by the City of Akron DWTP.

Raw water was filtered through 0.45 μm filter paper made of mixed cellulose ester (Nitrate and Acetate) purchased from Fisher Scientific. Raw water had an average of 1.7 meq/L alkalinity, 2.48 mg/L total organic carbon and pH of 7.4. Both distilled and raw water were stored at room temperature between 19˚C - 22˚C before experiments. Potassium diphosphate dibasic and potassium phosphate monobasic (Fischer Scientific) were added to water at 0.02 M and were used as a buffer for pH adjustment. Once the pH was adjusted, each jar was filled with 1 L of the adjusted distilled or raw water.

Fifteen mg of PAC dose was added to a beaker, then made into a slurry using 10 mL from the gang mixer jar. Prior to adding the PAC back to the gang mixer jar, the required cyanotoxin(s) was added and mixed at 200 revolutions/min for approximately one minute to properly mix toxins. A set of distilled water experiments was amended with 13 mg/L Pahokee peat humic acid (HA) to assess the impact of organic matter on treatment efficiency. After mixing of toxins in mixer, PAC slurry from small beakers was added to each of the corresponding non-control jars, and no PAC was added to the controls. Once the coagulation and flocculation mixing were over, the PAC was allowed for five minutes.

A composite sample was collected from three locations in the jar using a sterile pipette. For STX, a 9 mL sample was mixed with 1 mL of 10× diluent for preservation. As MC-LR does not need a preservative, 10 cm^3 of sample was collected from each jar and transferred to separate sample vials. Samples with expected concentrations above the analytical method's detection limit were diluted with distilled water to yield a concentration within the detection interval of the equipment. Once sample collection was done, each sample bottle was gently shaken and placed in the refrigerator until analysis. The pH of all jars was checked after experiments to ensure the pH did not change during the experiment. Cyanotoxins were analyzed at an EPA certified using ELISA (Enzyme-linked immunosorbent assay). The upper detection limit of ELISA is 5 µg/L for MC-LR and 0.4 µg/L for STX.

2.5. Statistical Analysis

Control vs treatments for all conditions were compared using a 1-sample t-test. ANOVA, Tukey, and 2-sample t-test comparisons were run to compare treatment efficiencies based on pH, concentration, toxin type, and type of water (natural and distilled). Any two conditions were compared using a 2-sample t-test. Multiple analyses of variance (ANOVA) and Tukey were used to compare three or more conditions. An equal variance was assumed. The mass of toxin removed (Δ = Control – Treatment) was used for comparing conditions. Statistical analysis was done using Minitab. Statistically significant and/or different data was represented in $p < 0.05$ and insignificant and/or similar in $p > 0.05$.

3. Results and Discussion

3.1. STX Removal When Present as the Sole Toxin

Control (no PAC) vs treatment (PAC) runs were performed with WL, and BC when 0.3 µg/L STX was the sole toxin in distilled and raw water at pH 6, 8, and 9 (**Figure 1**). The removal was significant for all varying PAC types and water pH with STX ($p < 0.05$), except with WL at pH 6 ($p > 0.05$). For 0.3 µg/L STX in distilled water (**Figure 1(a)**) at pH 6, average removal was 15% and 21% with WL and BC, respectively ($p > 0.05$). At pH 9 distilled water (**Figure 1(a)**), 0.3 µg/L STX removed was 77%, and 49% with WL, and BC, respectively and the PAC performance trend was WL > BC ($p < 0.05$). For both PAC types, more 0.3 µg/L STX was removed when the water was at pH 9 than pH 6 ($p < 0.05$). STX has a neutral charge at pH 9 and its positive charge increases (+1 to +2) from pH 6 to 8 [28]. As the same charges repel each other, the adsorption efficiency of positively charged STX to positively charged PAC will decrease as pH lowers.

When 0.3 µg/L STX was added to raw water (**Figure 1(b)**) at pH 6, 8, and 9, WL removed 65%, 62%, and 29%, respectively ($p < 0.05$). Removal at pH 9 was lower ($p < 0.05$) than when pH was 6 and 8 ($p > 0.05$). Rorar *et al.* [27] reported similar removal of 31%, 30%, and 13% for pH 6, 7, and 9, respectively with a PAC made of a proprietary blend (PB) of wood, coconut, and coal for Akron source water. At lower pH, more of the NOM present in surface water adsorbed to PAC surface,

thereby blocking the adsorption sites. This was more pronounced when STX was present at low concentration. At pH 8, WL removed 60% of STX compared to 46% with BC ($p < 0.05$). Although all PAC types may have the same effect on STX based on the pH_{PZC} and surface charge, WL performed better given the contribution of micropores from multiple sources. Shi *et al.* [28] reported the highest to lowest micropores for PAC sources as lignite coal > wood-based > bituminous coal and concluded removal efficiency was wood > bituminous coal > lignite coal. As lignite coal was the only PAC with the same charge as STX at experimental pH levels, it had the lowest efficiency showing the effect of charges on adsorption. Hence, pore size and charge are equally important in STX adsorption.

When STX concentration was increased to 1.6 µg/L in distilled water at pH 6 (**Figure 2(a)**), WL removed 40% ($p < 0.05$) and BC removed 26% ($p < 0.05$). Both treatment efficiencies were higher for 1.6 µg/L than 0.3 µg/L ($p < 0.01$). Pavagadhi *et al.* [10] also found that removal increased with an initial concentration of toxin. For 1.6 µg/L STX added to distilled water at pH 9, most of the data was above the detection limit of ELISA (samples could not be reanalyzed). For WL the control was >0.4 µg/L and treatments were 0.216 µg/L, 0.3 µg/L, and >0.4 µg/L while BC had both control and treatments concentrations above 0.4 µg/L. Though the analysis does not provide accurate results, it could still be concluded from the overall data that WL removed more STX than BC. This result also agrees with 0.3 µg/L STX at pH 9 and 1.6 µg/L at pH 6 in distilled water. However, the best-performing pH for 1.6 µg/L STX cannot be concluded due to insufficient data.

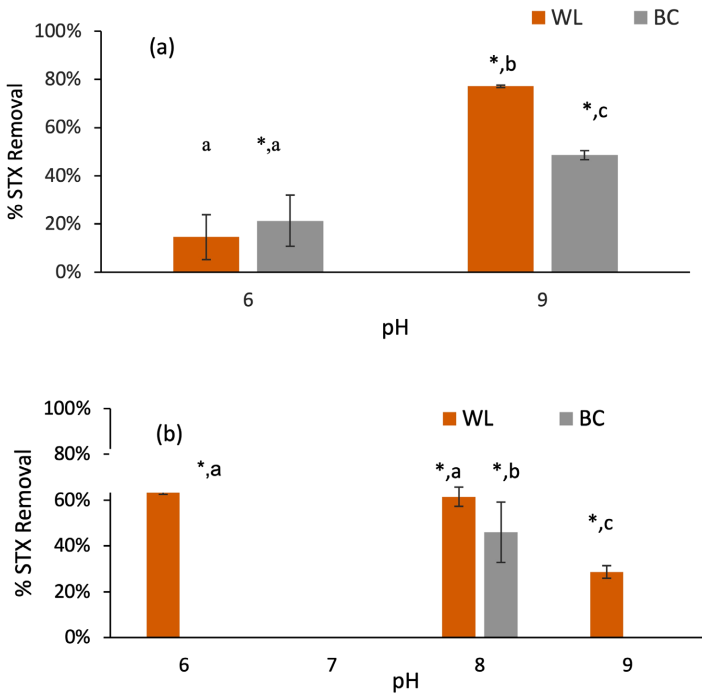

Figure 1. 0.3 µg/L STX removal when present as sole toxin with PAC WL and BC in (a) distilled water at pH 6 and 9 and (b) Raw surface water at pH 6, 8 and 9. Data marked with * are signficantly different than controls. Bars that share the same letter are not statistically different from each other.

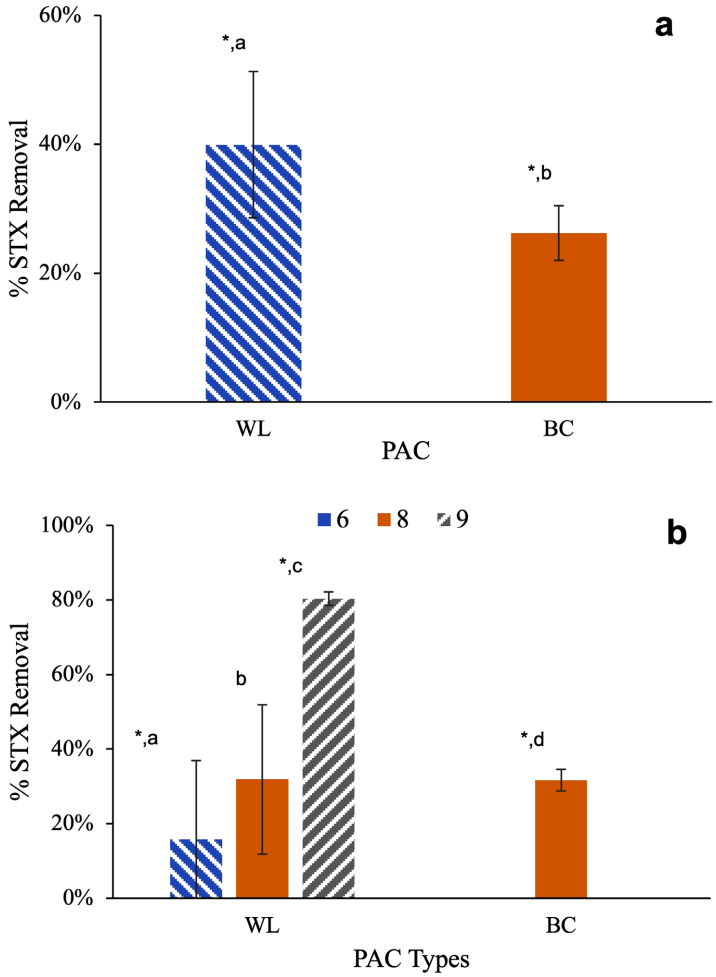

Figure 2. 1.6 µg/L STX removal as a sole toxin with PAC WL and BC used in (a) distilled water at pH 6 and (b) Raw water at pH 6, 8, and 9. Data marked with * are significantly different from controls. Bars that do not share a letter are significantly different.

WL removed 16%, 32%, and 80% of 1.6 µg/L STX in raw water (**Figure 2(b)**) at pH 6 ($p < 0.05$), 8, ($p > 0.05$) and 9 ($p < 0.05$), respectively. When raw water was at pH 8, WL removed a slightly STX than 32% of 1.6 µg/L STX with BC ($p < 0.05$). STX removal was higher at pH 9 than at pH 6 ($p < 0.05$). Shi *et al.* [28] and Rorar *et al.* [27] concluded STX removal increased with an increase in pH. This could be due to the decrease in similar charges of STX and PAC at higher pH.

WL removed more of 1.6 µg/L STX than 0.3 µg/L STX ($p < 0.05$) when the raw water pH was raised to 9. In contrast, the removal was similar for both concentrations when water was at pH 6 and 8 ($p > 0.05$). STX removal with BC at pH 8 was more effective when concentration was higher ($p < 0.05$), which aligns with the results of Pavagadhi *et al.* [10]. Removal of 1.6 µg/L STX was similar for distilled and raw water at pH 6. NOM can block adsorption sites reducing the removal of targeted contaminants [12] [15] [29] [30]. This could be a combination of competition of pore size and attraction of opposite charges. STX removal exhibited a mixed response to the presence of NOM.

3.2. MC-LR Removal When Present as the Sole Toxin

MC-LR removal at 0.3 µg/L, 1.6 µg/L, and 20 µg/L was statistically significant for treatments using WL and BC regardless of pH levels ($p < 0.05$). At pH 6 (Figure 3(a)), 59% of the 0.3 µg/L MC-LR was removed with WL which was higher than 42% with BC ($p < 0.05$). However, for 1.6 µg/L MC-LR, WL and BC yielded similar treatment efficiencies ($p > 0.05$). At pH 9 (Figure 3(b)), 72% of the 0.3 µg/L MC-LR was removed with WL and 21% with BC; whereas for 1.6 µg/L MC-LR, WL removed 86% and BC removed 33%. At pH 9 (Figure 3(b)), both 0.3 and 1.6 µg/L had higher MC-LR reduction with WL than BC ($p < 0.05$). Villars *et al.* [31] and Koshigoe *et al.* [32] also reported that a PAC wood-coal blend with higher mesopores would remove more MC-LR than bituminous coal PAC.

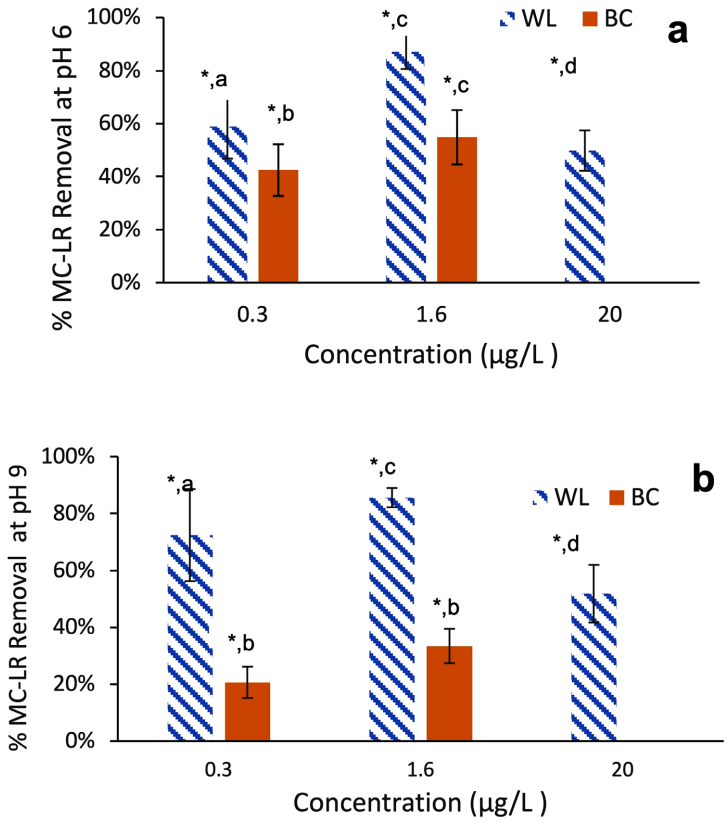

Figure 3. Percent removal of MC-LR with WL and BC when present as the sole contaminant in distilled water at (a) pH of 6 and (b) pH of 9. Data marked with * are significantly different from controls. Bars that do not share a letter are significantly different.

For 0.3 µg/L MC-LR, WL showed similar removal at both pH values ($p > 0.05$), whereas BC showed a higher reduction at pH 6 than at pH 9 ($p < 0.05$). Comparing pH values for 1.6 µg/LMC-LR, more MC-LR was removed with WL when in water with pH 6 than pH 9 ($p < 0.05$). BC yielded similar MC-LR removal at both pH levels ($p > 0.05$). WL showed a similar removal of 50% and 52% at pH 6 and 9 ($p > 0.05$), respectively, for 20 µg/L MC-LR (Figure 3). This was attributed to the charge of MC-LR at pH 6 and 9 which may have a similar affinity towards PAC

without any influence from organic matter and ions. The increase in MC-LR adsorption with decreasing pH was consistent with the results of Huang *et al.* (2007). For the removal of 20 µg/L MC-LR with BC, at pH 6 and 9, the concentration of control was above the detection limit of ELISA.

For all concentrations of MC-LR added to City of Akron source water (**Figure 4**), removal was significant regardless of pH and PAC source ($p < 0.05$). 0.3 µg/L MC-LR removal was 78%, 64%, and 84% (**Figure 4(a)**) with WL at pH 6, 8, and 9, respectively ($p < 0.05$). MC-LR removal was higher at pH 9 than at pH 6 ($p < 0.05$). Liu *et al.* [33] found that more Suwanee River fulvic acid adsorbed onto clays at a pH of 5 than 7. If NOM adsorbed to a higher extent at the lower pH it could interfere with the subsequent adsorption of MC-LR. This was the opposite of what was observed in distilled water. The trend exhibited in distilled water was similar to Bajracharya *et al.* [34] reported that MC-LR removal increased with pH with wood-coal blend PAC and that NOM reduced adsorption. NOM can also compete for adsorption sites and block pores based on its size [12], thus, reducing MC-LR adsorption at pH 6 than at pH 9. For 1.6 µg/L MC-LR, WL removed 75%, 62%, and 84% of MC-LR for pH 6, 8, and 9, respectively. WL showed no difference in removal based on pH ($p > 0.05$). This could be due to the concentration gradient effect for higher concentrations regardless of pH [10]. The removal of 60% of 20 µg/L MC-LR with WL at pH 8 (**Figure 4**), which was substantially higher than 12% obtained by BC ($p < 0.05$). The same trend was observed regardless of concentration, where MC-LR removal was higher with WL than 21% of BC ($p < 0.05$) for both 0.3 and 1.6 µg/L concentration at pH 8 (**Figure 4(b)**). Villars *et al.* [31] and Liu *et al.* [33] also found that more PAC with higher mesopore content results in higher MC-LR adsorption. For both distilled and raw water, the mass of MC-LR adsorbed with WL increased with an increase in concentration ($p < 0.05$). However, BC showed similar removal at all concentrations ($p > 0.05$), except at pH 6 of 0.3 and 1.6 µg/L in distilled water ($p < 0.05$). This was attributed to the limited mesopores of BC.

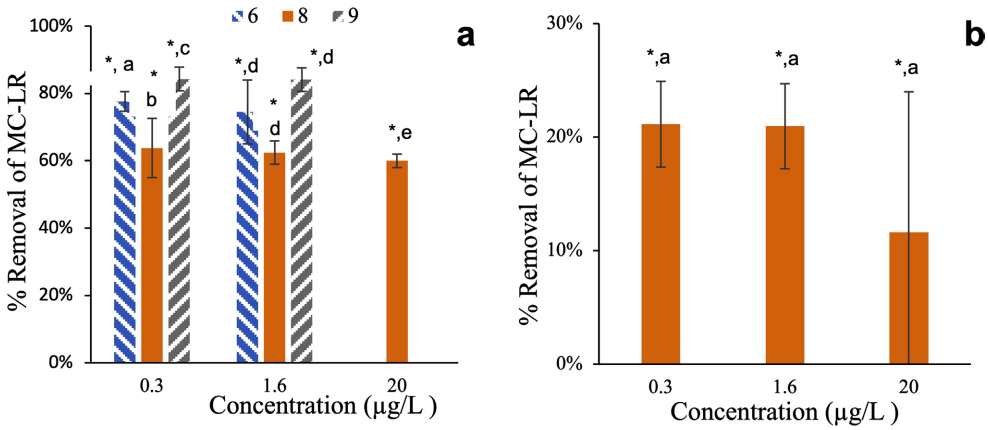

Figure 4. Percent removal of MC-LR when present as the sole contaminant in raw surface water at (a) WL at pH of 6, 8 and 9 and (b) BC at pH of 8. Data marked with * are significantly different from controls. Bars that do not share a letter are significantly different.

3.3 MC-LR and STX Removal When Simultaneously Present

WL performed better than BC for most experiments of individual toxins; therefore, it was the PAC source used when both MC-LR and STX were present. **Figure 5(a)** shows the removal of 1.6 μg/L MC-LR and 0.3 μg/L STX in the presence of NOM with WL in raw water (pH 6 and 8) and distilled water at pH 8. Both toxins had significant removal for all conditions tested ($p < 0.05$). At pH 8, distilled water removed a higher amount of MC-LR (0.82 μg) than STX (0.25 μg), ($p < 0.05$). This was the same trend for raw water, which removed higher MC-LR at 65% than STX at 49% ($p < 0.05$). For the same condition at pH 8 (**Figure 5(a)**), distilled water and raw water removed 16% ($p < 0.05$) and 4% ($p > 0.05$) NOM, respectively. MC-LR depicting a lower percent removal than STX in distilled water could be due to i) direct competition from NOM [35], ii) pore blockage by NOM, iii) repulsion due to the same charges of MC-LR and NOM [12] [30], and iv) positively charged STX in the absence of competition may show affinity towards negatively charged NOM and MC-LR, thus increasing the its overall removal when distilled water. In raw water at pH 6, MC-LR removal was higher (62%) than STX (31%, $p < 0.05$). Raw water with a pH 8 exhibited a similar treatment trend of more MC-LR removed than STX ($p < 0.05$). Shi *et al.* [28] and Bajracharya *et al.* [34] obtained the same trend of increased MC-LR and STX removal with an increase in pH. For toxin concentrations (MC-LR > STX), Rorar *et al.* [27] reported that with an increase in pH, MC-LR removal increased for treatment with PB, in contrast to STX which had a similar or increased reduction in raw water. NOM removal (**Figure 5(a)**) was higher in raw water at pH 6 (19%) than at pH 8 ($p < 0.05$). Increased opposite charges of NOM and PAC at pH 6 can increase the adsorption of NOM. This can either reduce the removal of toxins by competition with sites or enhance adsorption by increasing surface hydrophobicity [33]. When STX and MC-LR were present simultaneously, they both showed a reduced removal in raw water compared to distilled water spiked with HA. However, this was opposite to the results when the toxins were present alone. In the absence of other components from raw water, STX may partially neutralize the effect of repulsion of MC-LR to NOM, which may increase NOM's adsorption resulting in the blocking of more pores for toxins.

Figure 5(b) illustrates the removal of cyanotoxins when present simultaneously at different concentrations. The removal of both toxins was significant under all conditions ($p < 0.05$). Forty-eight percent of 0.3 μg/L MC-LR and 66% of 0.3 μg/LSTX were removed with WL for raw water at pH 8. Statistically, the mass of MC-LR and STX removed were similar ($p > 0.05$). The presence of the same concentration gave an equal opportunity for both toxins to adsorb. A low concentration of MC-LR would potentially block fewer pores, leaving adsorption sites for STX. For this condition (**Figure 5(b)**), the NOM (26%) removed was highest among other concentrations of simultaneous toxins at pH 8 ($p < 0.05$). Lower concentrations of both toxins may have left some pores available where NOM could readily be adsorbed [9]. The other reason could be the low concentration of MC-LR, which may have shown less repulsion towards NOM, thus increasing its re-

moval. STX may have shown an affinity towards NOM and MC-LR due to the opposite charge. Thus, NOM can both help and hinder toxin adsorption [33] [36].

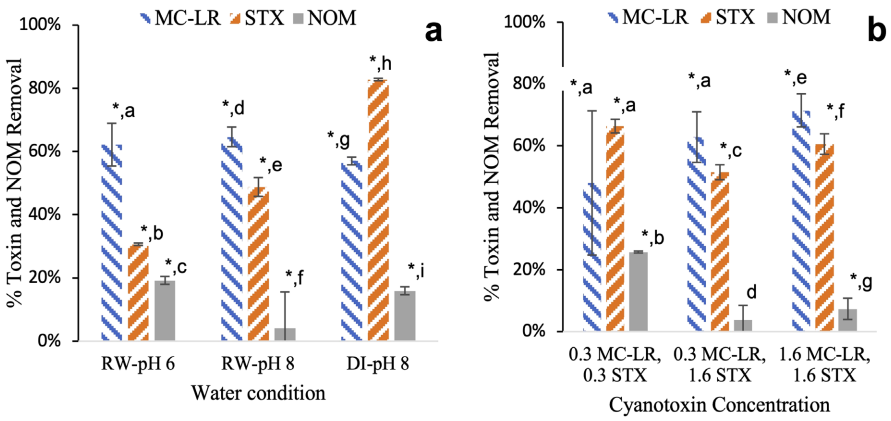

Figure 5. Simultaneous removal of MC-LR and STX with WL in raw surface water (a) 1.6 μg/L MC-LR and 0.3 μg/L STX and (b) other concentrations of MC-LR and STX simultaneously present at pH of 8. Data marked with * are significantly different from controls. Bars that do not share a letter are significantly different.

Removal was efficient for both toxins (61% STX and 72% MC-LR) and had a concentration of 1.6 μg/L in pH 8 raw water ($p < 0.05$). WL simultaneously removed 7% ($p < 0.05$) of NOM for this condition. A higher negative charge on MC-LR and its larger size may have led to more adsorption than STX. When less MC-LR was present, more STX was removed. The removal of 0.3 μg/L MC-LR and 1.6 μg/L STX with WL at pH 8 was 63% ($p < 0.05$) and 52% ($p < 0.05$), respectively. Although the treatment percentage appears less for STX, more mass was removed (0.83 μg STX vs. 0.19 μg MC-LR, $p < 0.05$). NOM removal was 4% for the same sample ($p > 0.05$).

Higher concentrations of toxin having higher removal even in the presence of another toxin was attributed to the concentration gradient effect. Among all the combinations of MC-LR and STX concentration, removal of 0.3 μg/L STX was higher when present alone or with a lower concentration of MC-LR ($p < 0.05$). However, for 1.6 μg/L STX, an increase in MC-LR concentration promoted the removal of STX ($p < 0.05$), which was also true for 0.3 μg/L STX in distilled water. For all cases, STX removal was effective in the presence of MC-LR. This was consistent with Rorar *et al.* [27], which revealed that MC-LR did not inhibit the removal of STX. Similarly, MC-LR removal was effective in the presence of STX.

The extent of MC and STX removal that can be achieved will depend on the sorption mechanism(s) associated with PAC removal which include, but are not limited to, electrostatic interactions, surface complexation, π-π interactions, pore-filling, and diffusion [37]-[40]. The dominant mechanism will depend on the specific cyanotoxin present, water chemistry, and PAC source used. Some studies have stated that PAC made from coal and wood-based materials are the most effective for MC removal due to higher mesopore volumes [41]. For instance, Jaszczyszyn *et*

al. [42] reported that the coal-based PAC used in their study had only half the mesopores as the wood-based PAC. Changes in electrostatic interactions have also been found to increase cyanotoxin removal [40]. Huang and Lenhart [43] reported that the electrostatic interactions between MC-LR's functional groups and wood-based PAC increased MC removal. Park *et al.* [44] studied the adsorption of MC-LR with different sorbents and reported a two-stage process: fast surface adsorption and gradual adsorption as MC diffused into mesopores. Regardless of the adsorption mechanism, as mentioned earlier the presence of NOM can both hinder and help adsorption. Liu *et al.* [33] found that if fulvic acid-based NOM adsorbed to PAC surface, it decreased the sorption and removal of MC-LR while Bajracharya *et al.* [34] found algal-derived NOM to be more inhibitive than fulvic acid-NOM.

4. Conclusion

This research studied the effect of PAC source material, pH, concentration, and NOM on the removal of MC-LR and STX when present alone and combined. The PAC types showed effective toxin removal for 95.8% of the cases studied. In general, WL (wood and lignite coal) performed better than BC (bituminous coal) for both toxins at the same pH conditions when only one toxin was present. Thus, the PAC source influenced adsorption. Higher treatment efficiencies were achieved when PAC had high pH_{PZC} and higher content of specific pore sizes to adsorb MC-LR and STX. In raw water, MC-LR was higher at pH 9. For STX, removal was in general higher at pH 9 than at pH 6 or 8. NOM adsorption was highest when cyanotoxin was low, such as when MC-LR and STX were present simultaneously at 0.3 μg/L. It is important to note that the high detection limit for the ELISA STX assay restricted analysis at some concentrations, which limited the full assessment of removal efficiency due to concentration.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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