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Adsorption of microcystin onto activated carbon: A review

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Abstract. Microcystins (MCs) are toxins produced by cyanobacteria causing a major environmental threat to water resources worldwide. Although several MCs have been reported in previous studies, microcystin-LR (m-LR) has been extensively studied as it is highly toxic. Among the several techniques employed for the removal of this toxin, adsorption with AC has been extensively studied. AC has gained wide attention as an effective adsorbent of m-LR due to its ubiquity, high sorption capacity, cost effectiveness and renewability. In this review, the adsorption of m-LR onto AC was evaluated using the information available in existing scientific literature. The effects of the pore volume and surface chemistry of AC on the adsorption of m-LR considering the structural and chemical properties of ACs were also discussed. Furthermore, we identified the parameters that influence adsorption, including natural organic matter (NOM), pH, and ionic strength during the m-LR adsorption process. The effect of these parameters on MCs adsorption onto AC from previous studied is compiled and highlighted. This review may provide new insights into future activated carbon-m-LR adsorption research, and broaden its application prospects.

Keywords: algal bloom; adsorption; activated carbon; cyanobacteria; microcystins

1. Introduction

Cyanotoxins produced as secondary metabolites by cyanobacteria poses health hazards to human and animal health. (Campinas and Rosa 2010). Among the many types of cyanotoxins that have been discovered, microcystins (MCs, liver damaging toxins), are the most prevalent in water ecosystems and have, therefore, been widely studied (Brooks *et al.* 2016). The most common known congeners are m-LR, m-RR, and m-YR, which result from the presence of the L-forms of leucine (L), arginine (R), or tyrosine (Y) at positions 2 and 4 (Sivonen and Jones, 1999). As a result of MCs level of toxicity, the World Health Organisation (WHO), set a tolerable daily intake (TDI) value of m-LR for a 60 kg adult to be 0.04 μg/kg body weight/day, and the guideline value for its presence in drinking water as 1 μg/L (Chorus and Bartram, 1999). Owing to the high incidence of microcystins occurrence in water, coupled with the recognized potential health risk, methods/techniques for the detection and removal of cyanobacterial toxins has been increasing (Şengül *et al.* 2018, Taylor *et al.* 2011, Zamyadi *et al.* 2015). Although the conventional methods of coagulation/flocculation, sedimentation, and filtration can effectively remove cell-bonded MCs, these methods are ineffective for removing dissolved microcystins (Lawton and Robertson, 1999). Chow *et al.* (1999) stated that although conventional treatment (coagulation) removes cyanobacteria cells, sludge containing toxic cyanobacteria cells can break down rapidly and release dissolved toxin. This may be critical, as dissolved toxin is not removed by coagulation, flocculation and filtration. In general, micro- and ultra-filtration membranes could be expected to remove cyanobacterial cells effectively but there is also the risk of the cells releasing dissolved toxin in the absence of frequent back washing and proper isolation of the backwash water (Chow *et al.* 1997, Gijsbertsen-Abrahamse *et al.* 2006). There is existing literature on the efficacy of chlorination and ozonation for the removal of microcystins. A residual of at least 0.3 mg/L of ozone for 5 minutes will be sufficient for all of the most common microcystins. For chlorine, a dose of 3 mg/L applied to obtain a residual of 0.5 mg/L for at least 30 minutes will be effective (Acero *et al.* 2005, Ho *et al.* 2006a, Newcombe 2002, Nicholson *et al.* 1994, Rositano *et al.* 2001, Rositano *et al.* 1998). Microcystin LA may however require a higher residual, as it is slightly less susceptible to oxidation by chlorine (Ho *et al.* 2006). Yeo *et al.* (2018) also recently developed a numerical model to optimize the removal of m-LR with chlorine. Their model successfully estimated the removal rate of m-LR in a clear well.

The molecular structure of the hepatotoxin is shown in Fig. 1. Prominent among the search for a more accurate, robust, and less expensive technique to remove MCs from water sources is adsorption by activated carbon (AC). AC adsorption is the most widely employed method for removing micropollutants, particularly hydrophobic compounds, in water treatment plants (Cook and Newcombe, 2002). Owing to the unique properties of activated carbon fibers in comparison to other carbonaceous materials, they are considered reliable for industrial applications (Dellero *et al.* 1999, Xie *et al.* 2004). Most studies relating to the adsorption of cyanotoxins by AC have focused on microcystins (Donati *et al* 1994, Keijola *et*

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Table 1 Review of literature analyzing microcystins in water streams

MCs identified	Technique	Focus of study	References	Location
m-RR, m-YR, m-LR, m-FR, m-WR	HPLC-DAD, LC-MS	Q, T	Douma *et al*. (2010)	Morocco
m-RR, m-LA, m-LR, m-YR	HPLC-MS/MS	Q	Amé *et al*. (2010)	Argentina
m-RR, m-LR, m-YR	HPLC-PDA, LC-MS/MS	Q	Triantis *et al*.(2010)	Greece
m-RR, m-YR, m-LR, m-LF, m-LA, m-LW, m-LY	LC-MS/MS	Q, C	Graham *et al*. (2010)	United States
m-LR, m-RR, m-YR, m-LA, m-LF, m-LW	LC-ESI-MS/MS	C, T	Krüger *et al*. (2010)	China
m-LR, m-RR	HPLC-UV	T	Peng *et al*. (2010)	China
m-LR, m-RR. m-YR	HPLC-MS/MS	D, Q	Li *et al*. (2010)	China
m-RR, m-YR, m-LR, m-FR, m-WR, Demethyl m-LR, Demethyl m-YR, Demethyl m-RR	MALDI-TOF	C, T	Fathalli *et al*. (2011)	Tunisia
m-LR, m-RR, m-YR, m-LY, m-LF, m-LW	LC-MS/MS	O, Q	Mooney *et al*. (2011)	Ireland
m-RR, m-YR, m-LR, m-LF, m-LA, m-LW	LC-ESI-MS	D, Q	Yen *et al*. (2011)	Taiwan
m-LR, m-RR, m-YR	HPLC-UV	D, Q	Liu *et al*. (2011)	China
m-RR, m-YR, m-LR, m-WR, m-YR	LC-ESI-MS	I, Q	Mbukwa *et al*. (2012)	South Africa
m-RR, m-YR, m-LR, m-LW	DGGE/qPCR/UPL	Q, C	Yen *et al*. (2012)	China
m-LR, m-RR, m-YR,	PCR/LC-MS	I, Q	Srivastava *et al*. (2012)	India
m-RR	HPLC-DAD, MALDI-TOF	I	Vasas *et al*. (2013)	Hungary
m-LR, m-RR, m-YR. m-LA, m-LF, m-RY, m-LY, m-LW, m-RL, m-RA	LC-HRMS, LC-MS/MS NMR	I, C	Miles *et al*. (2013)	Tanzania
m-LR, m-RR	HPLC-MS	Q	Duong *et al*. (2013)	Vietnam
m-LR, m-RR, m-YR	LC-ESI/Ion trap-MS/MS	D, T	Rodrigues *et al*. (2013)	Portugal
m-LR, m-RR, m-YR	HPLC-DAD	D, Q	Tian *et al*. (2013)	China
m-LR, m-RR, m-YR, m-LA	SPE/LC-ESI-MS/MS	D, Q	Kaloudis *et al*. (2013)	Greece
m-RR, desMe m-RR	MALDI-TOF-MS, LC/ESI-q/TOF-MS/MS	D, C	Ferranti *et al*. (2013)	Italy
m-LR, m-YR, m-RR, m-LF, m-LY, m-LW	LC-MS/MS	D, T	Faassen and Lürling (2013)	Netherlands
m-LR, m-RR	UPLC-MS/MS	I, Q, T	Rodriguez *et al*. (2014)	Germany
m-LA, m-RR	HPLC-DAD	O	Zastepa *et al*. (2014)	Canada
m-LR, m-RR	HPLC-DAD	Q	Yu *et al*. (2014)	China
m-LR, m-RR, m-YR	PCR/ LC-MS	C, Q, T	Srivastava *et al*. (2012)	India
m-LR, m-RR, m-YR	HPLC-DAD	I, Q, T	Pavlova *et al*. (2015)	Bulgaria
m-LR, m-RR, m-YR, m-LA, m-LF, m-LW	UPLC-MS/MS	D, Q	Zhang *et al*. (2015)	China
m-LR, m-RR, m-YR	LC-MS	C, Q, T	Singh *et al*. (2015)	India
m-LR, m-RR, m-YR	HPLC-MS/MS	D, T	Jia *et al*. (2016)	China
m-LR, m-RR, m-YR, m-LF, m-LW	UPLC-MS/MS	I, Q	Pekar *et al*. (2016)	Sweden
m-LR, m-RR, m-YR, m-FR, m-WR,	LC-MS/MS, PPIA	I, C	Bouhaddada *et al*. (2016)	Algeria
m-LR, m-RR	SPE/ LC-MS/MS	D, Q	Hu *et al*. (2017)	China
m-LR, m-RR, m-YR	UPLC-MS/MS	T	Zhong *et al*. (2017)	China
m-LR, m-RR	HPLC-UV	O	He *et al*. (2018)	China
m-LR, m-RR, m-YR, m-LA, m-LF, m-W*R*, m-LY, m-LW	LC-MS/MS	Q, T	Turner *et al*. (2018)	England
m-LR, m-RR, m-YR	HPLC-DAD	D, Q	Shang *et al*. (2018)	China

C: Characterization, D: Detection, I: Identification, O: Occurrence, Q: Quantification, T: Toxicity, HPLC-DAD/HPLC-PDA: High-performance liquid chromatography-photodiode array detector, LC-ESI-MS/MS: Liquid chromatography-electrospray ionization-tandem mass spectrometry, LC-HRMS: High-resolution LC-MS, MALDI-TOF: Matrix-assisted laser desorption ionization-time of flight spectrometry, NMR: Nuclear magnetic resonance, PPIA: Protein phosphatase inhibition assay, UPLC-MS/MS: Ultra-light liquid chromatography-electrospray ionization-tandem triple quadrupole/mass spectrometry.

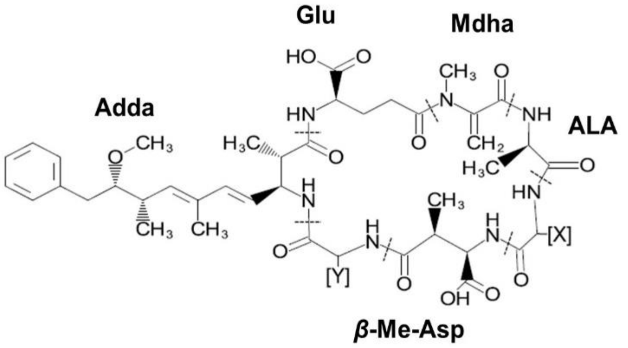

Fig.1 Structure of the peptide hepatotoxin, microcystin (Preece *et al.* 2017)

al. 1988, Lambert *et al.* 1996, Maatouk *et al.* 2002). Activated carbon has been found to be effective for MC removal due to the surface change and pore texture that activated carbon has (Ho *et al.*, 2011, Huang *et al.* 2007, Pavagadhi *et al.* 2013, Pendleton *et al.* 2001). The adsorption capacity depends on the accessibility of the organic molecules to the inner surface of the adsorbent, which depends on their size (Zhu *et al.* 2016). There are different types of carbon precursors that have been used for the preparation of activated carbon. These include coconut, coal, and wood among others, which have been activated by different methods such as chemical and physical activation leading to the creation of numerous mesopores (Mashile *et al.* 2018). Activated carbon is undoubtedly considered as a universal adsorbent for treatment and is commonly used for the removal of various pollutants from water because of convenience, ease of operation and simplicity of design (Faust and Aly, 1987). However, its widespread use in water treatment is sometimes restricted due to the high cost of commercial activated carbon. To address this shortcoming, several researchers have explored the use of a large variety of naturally occurring and agricultural waste materials (which are cheaper, renewable and occur abundantly) for the production of AC (Diao *et al.* 2002, Hena *et al.* 2014, Juang *et al.* 2000, Mashile *et al.* 2018, Warhurst *et al.* 1997).

In this review, previous studies on the detection, quantification, characterization, and toxicity of MCs and techniques used for their removal are summarized. The removal of m-LR, the most toxic microcystin, through adsorption using AC is then summarized. The importance of the structural and chemical properties of AC and the operational conditions affecting the adsorption process are also studied. The occurrence, quantification, and toxicity of MCs in water resources worldwide are presented in Table 1.

2. Adsorption of microcystin by activated carbon

Adsorption is a promising treatment technology for the removal of m-LR. The application of a granular activated carbon (GAC) contactor effectively reduced the m-LR concentrations below the guideline values (Chennette, 2017). Various studies have used activated carbon (granulated and powdered) to remove MCs and found that it performed well (Falconer *et al.* 1989b). For MC adsorption to occur, the MC must be able to penetrate activated carbon pores that are larger than or equal to its own size. MCs have been found to preferentially adsorb to mesopores than macro and micropores owing to its size (1.33 to 2.94 nm), which lies within the carbon mesopore size range of 2 to 50 nm (He *et al.* 2016b). An analysis of the different properties of GAC used by treatment plant showed that carbon with the largest volume of mesopores and macropores adsorbed the most m-LR (Huang *et al.* 2007).

A large amount of literature discussing AC sources (raw material) has identified the AC source as an important characteristic that dictates the AC's pore size and distribution, which then influences MC removal (Huang *et al.* 2007). Wood based activated carbon adsorbents have been found to have higher efficiencies in MC adsorption because of the presence of a number of mesopores in a small portion of the material. (Huang *et al.*, 2007, Lee and Walker, 2006, Pendleton *et al.*, 2001, Yan *et al.*, 2006). Donati *et al.* (1994) also found that wood-based PAC contains a higher volume of mesopores than coal, coconut, and peat-based PAC. Therefore, wood-based PAC exhibits the highest m-LR adsorption capacity. During the adsorption of m-LR, it is important to note that m-LR is a large molecule (MW= 994) that is a complex aggregate of amino acids. Therefore, it is hydrophobic in an aqueous solution (Huang *et al.* 2007). Thus, it is crucial to consider the physical and surface chemical properties of the adsorbent selected for m-LR removal (Huang *et al.* 2007). In their study on the effects of activated carbon properties on the capacity of m-LR adsorption, Huang *et al.* found that the carbon's properties influence the amount of m-LR adsorbed. Although AC can effectively remove MCs, there are some drawbacks. A high dose of PAC is required to meet the WHO guidelines (Falconer *et al.* 1989b, Song *et al.* 2005). Furthermore, the presence of natural organic matter reduces the MC adsorption capacity of PAC (Donati *et al.* 1994, Svrcek and Smith, 2004).

Other cyanobacterial toxins have been successfully removed by AC adsorption (Huang *et al.* 2007, Lambert *et al.* 1996, Wang *et al.* 2007, Yan *et al.* 2006). Other studies, (Chen *et al.* 1997, Dixon *et al.* 2011, Drikas *et al.* 2009, Ho *et al.* 2011, Lalezary-Craig *et al.* 1988, Ng *et al.* 2002, Orr *et al.* 2004, Persson *et al.* 2007) have also proved the efficient use of GAC and PAC to remove other cyanobacterial metabolites.

2.1 Significant characteristics of activated carbon

To understand the adsorption phenomena and the production and selection of an appropriate activated carbon for a target micropollutant, the chemical qualities of AC have been extensively explored (Greenwald *et al.* 2015, Watanabe *et al.* 2012). The properties that influence the efficiency of substance removal by activated carbon include the particle size, internal pore structure (pore size distribution), and pore surface chemistry (Watanabe *et al.* 2012). These are important factors that should be considered in the production and selection of an appropriate

Table 2 Studies on the characteristics of activated carbon and percentage removal rates of MCs

AC type	Surface area m^2/g	Carbon pore volume		Removal rate %	References
		Mesoporous	**Microporous**		
PAC/UF	1112	379^a	733^a	70-98	Campinas and Rosa (2010)
(G_1), (G_2), (G_3)	950, 950, 1050	0.089^b, 0.175^b, 0.760^b	0.812^b, 0.689^b, 0.242^b	37-100	Huang *et al*. (2007)
UF/PAC	1400	80^c	20^c	84	Şengül *et al*. (2018)
MNS-based ACF	1,079.5	0.20^b	0.30^b	-	Albuquerque Júnior *et al*. (2008)
CS-based ACF	1,090.0	0.21^b	0.27^b	99.27	Albuquerque Júnior *et al*. (2008)
SCB-based ACF	1,174.3	0.39^b	0.23^b	98.73	Albuquerque Júnior *et al*. (2008)
UCM-based ACF	1,269.6	0.12^b	0.50^b	-	Albuquerque Júnior *et al*. (2008)
PWR-based ACF	1,550.1	1.06^b	0.35^b	62.31	Albuquerque Júnior *et al*. (2008)
CALGON AC B	871.2	0.03^b	0.32^b	3.7	Albuquerque Júnior *et al*. (2008)
Carboleste AC F	789.5	0.04^b	0.30^b	43	Albuquerque Júnior *et al*. (2008)
NORIT GAC	956.0	0.17^b	0.41^b	-	Albuquerque Júnior *et al*. (2008)
B1 (G3)	-	0.40^f	0.52^f	189^g	Pendleton *et al*. (2001)
F (G3)	-	0.38^f	0.46^f	200^g	Pendleton *et al*. (2001)
N (G3)	-	0.26^f	0.42^f	161^g	Pendleton *et al*. (2001)
A1 G1)	-	0.05^f	0.68^f	2^g	Pendleton *et al*. (2001)
P (G1)		0.07^f	0.29^f	7^g	Pendleton *et al*. (2001)
Cecarbon PAC 200	863	0.39^b	0.10^b	70^g	Donati *et al*. (1994)
Picatif PCO normal	991	0.42^b	0.02^b	40^g	Donati *et al*. (1994)
Picazine	1197	0.60^b	0.49^b	280^g	Donati *et al*. (1994)
Calgon-type WPL	1000	0.44^b	0.05^b	75^g	Donati *et al*. (1994)
PHO ASTM M32	1067	0.45^b	0.03^b	20^g	Donati *et al*. (1994)
Norit W20	863	0.23^b	0.06^b	20^g	Donati *et al*. (1994)
Nuchar SA	1366	0.72^b	0.27^b	220^g	Donati *et al*. (1994)
Prototype PAC	1329	0.66^b	0.19^b	116^g	Donati *et al*. (1994)
Calgon Filtasorb 300	1057	0.14^b	0.23^b	99	Chennette (2017)
Norit 0.8 GAC (1)	1035	301.7^a	0.35^b	> 90	Julio (2011)
Norit 0.8 GAC (2)	1083	346.4^a	0.36^b	> 90	Julio (2011)
PAC Norit SA-UF	1112	0.357^b	0.343^b	93-98	Campinas (2009)

ACFs: Activated carbon fibers, (a) m^2/g, (b) cm^3/g, (c) %, (d) m-LR, (e) m-RR, (f) mL(liq)/g, (g) µg/mg, GAC: Granular activated carbon, (G_1): Coconut shell, (G_2): Bituminous coal, (G_3): Wood-based, CS: Coconut Shell endocarp, MNS: Macadamia nut shell, PWR: Pine wood residues, PAC: Powdered activated carbon, PAC A & B: Coal-based, SCB: Sugar cane bagasse, UCM: Unripe coconut mesocarp, UF: Ultrafiltration

type of AC for a target micropollutant and for understanding the adsorption process (Greenwald *et al.* 2015, Watanabe *et al.* 2012). The porous structure of activated carbon provides it with a large surface area, typically between 400 and 1500 m^2/g, which significantly increases the number of adsorption sites (He *et al*. 2016b). Powdered and granular activated carbons typically exhibit a heterogeneous pore structure of micropores, mesopores, and macropores (Kasaoka *et al.* 1989). Therefore, during the adsorption of biological contaminants on ACs, the presence of these heterogeneous volumes of pores contributes to its importance as a useful adsorbent (Kasaoka *et al*. 1989).

Some recent works have reported the successful production of AC from different materials and use in wastewater treatment for the adsorption of different substances (Khaleel *et al.* 2015, Alighardashi *et al.* 2017, Wijetunga and Gunasekara 2017, Ingole *et al*. 2016).

2.1.1 Effect of carbon pore volume

An important property that influences the adsorption process is the pore size distribution (PSD) of the adsorbent, which determines the fraction of the total pore volume that an adsorbate of a given size can utilize (Pelekani and Snoeyink, 1999). Previous research has established a link between an adsorbent's pore size and its consequent influence on the adsorption process. First, Newcombe *et al.* (1997) stated that the adsorption strength increases as the pore size decreases due to the increased number of contact points between the adsorbate and the adsorbent's surface. Second, when the micropore width becomes less than approximately twice the adsorbate's diameter, the adsorption potentials between opposing pore walls begin to overlap (Dubinin, 1960). In addition, Li *et al.* (2002) stated that size exclusion limits the adsorption of contaminants with a given size and shape if the pores are too small. Owing to the presence of a greater number of contact points between the molecule and the adsorbent, adsorbate particles will preferentially access pores that exhibit a similar size (Pelekani and Snoeyink, 1999). A study using three GACs based on coconut shells, bituminous coal, and wood noted the importance of surface properties in the adsorption of MCs (Huang *et al.* 2007). Various studies that have been conducted on AC pore sizes and the percentage removal rates of MCs are summarized in Table 2.

2.1.2 Effect of carbon surface chemistry

The discovery of atoms other than carbon as building blocks of AC surfaces has necessitated study on the effects of the presence of these atoms as they define the chemical characteristics of the activated carbon's surface. Oxygen is an important heteroatom found on the surface of AC occurring as carboxylic acid, phenolic hydroxyl, and quinone carbonyl groups (Boehm, 1994, Caly and Radovic, 1994). The nature and number of these oxygen complexes, which largely depend on the treatment temperature and activation method (Snoeyink and Weber, 1967), have been reported to have a positive correlation with the density of hydrophilic sites (De Ridder *et al.* 2013). These heteroatoms are equally crucial in determining the acidity/basicity of the AC surfaces in an aqueous solution. Upon exposure to oxygen at 473-973 K or to oxidants, such as air, water vapor, hydrogen peroxide, and some acids (nitric and sulfuric), AC can develop acidic characteristics, and develop basic characteristics upon high-temperature treatment (> 973 K) (Campinas, 2009). Considine *et al.* (2001) also asserted that the MC adsorption capacities of AC can be largely determined by the hydrophilicity of the carbon, as indexed by its oxygen content. The electrostatic interactions between the carbon's surface and the adsorbate molecules play an important role in the adsorption process. Therefore, a positive surface will attract a negatively charged molecule, while a negatively charged surface will repel a negatively charged molecule (Newcombe *et al.* 1997). Huang *et al.* (2007) studied the effect of surface chemistry on MC adsorption by AC and observed a connection between the surface oxygen groups and adsorption in the aqueous phase. Specifically, a higher number of carboxylic groups on the carbon's surface results in an increase in MC adsorption. Julio (2011) also demonstrated that, although the structure and surface chemistry are two crucial properties to consider when selecting a form of AC, surface chemistry had a greater impact on the amount of MC adsorbed. He asserted that modifying the carbon (making it more basic and/or more porous) is a quick, cheap, and efficient method of improving the m-LR adsorption rate of the AC. By carefully modifying the surface chemistry of the AC, the author concluded that surface chemistry an extremely important property to consider for m-LR adsorption. However, Donati *et al.* (1994) and Pendleton *et al.* (2001) reported no significant effect of carbon surface chemistry on MC adsorption.

2.2 Influencing water parameters in MCs adsorption

2.2.1 Effect of natural organic matter

Some studies on the effect of natural organic matter (NOM) on the adsorption of MCs onto AC are presented below in Table 3. The effect of the presence of NOM on the m-LR removal efficiency by PAC has been reported in many studies (Campinas *et al.* 2013, Cook and Newcombe, 2008, Pendleton *et al.* 2001). The micro contaminant removal efficiency of PAC is largely affected by competitive adsorption with NOM, and pore blockage and direct site competition are the most likely modes of competition (Campinas, 2009). Competing NOM may sometimes not access the same sites as the target molecules due to pore size exclusion, but it can constrict or block pores and obstruct the transportation of the target molecule to the final adsorption sites, causing a reduction in the adsorption rate (Pelekani and Snoeyink, 1999). Several authors confirmed that widening the PAC pore size distribution could reduce or even prevent pore blockage by NOM (Donati *et al.* 1994, Li *et al.* 2002, 2003, Newcombe *et al.* 1997, Pelekani & Snoeyink, 1999, Quinlivan *et al.* 2005). Studies have demonstrated that low-molecular-weight NOM compounds exert a higher competitive effect on micropollutants, which is due to direct site competition (Campinas, 2009). However, other studies have found that smaller NOM compounds may also cause pore constriction/blockage (Li *et al.* 2002, 2003, Newcombe *et al.* 2002, Pelekani & Snoeyink, 1999). The presence of NOM may affect the capacity of AC to adsorb MC and attenuate its rate of adsorption, thereby reducing its efficacy.

Table 3 Effect of natural organic matter (NOM) on adsorption of MCs

Targeted MCs	Nature of NOM	NOM concentration (mg/L)	Effect on adsorption capacity	References
m-LR	Tannic + humic acids	5	Reduction in removal from 98% to 67%	Campinas and Rosa (2010)
m-LR	-	-	Decrease in removal from 65% to 12%	Huang *et al.* (2007)
m-LR	-	25	Decreased in removal of 15% with 25 mg/L of NOM	Zhang *et al.* (2011)
m-LR	SRFA	5	Reduction in m-LR removal of 11.3%	Lee and Walker (2006)
m-LR	Natural organics	-	Decrease in Picazine removal of MC of 11%	Donati *et al.* (1994)
m-LR	Natural organics	-	Decrease in Nuchar SA removal of MC of 23%	Donati *et al.* (1994)
m-LR	Natural organics	-	Decrease in PAC removal of MC of 46%	Donati *et al.* (1994)
m-LR	SRFA	5	Decrease in removal from 97.3% to 86%	Lee *et al.* (2009)
m-LR	Tannic acid		Decrease in m-LR removal from 98% to 48%	Julio (2011)
m-LR	Tannic + humic acids	1.5-2.7	Decrease in m-LR removal of 30%	Campinas (2009)

MCs: microcystins, SRFA: Suwannee River Fulvic Acid

2.2.2 Effect of pH

Many authors have discussed the effect of pH on the adsorption of MC by activated carbons as the ionizable functional groups on the carbon's surface may respond to

Table 4 Effect of pH on adsorption of MCs

Targeted MC	pH range	Trend of effect	Reference
m-LR	8.0 -3.0	MC adsorption increases at a low pH	Huang *et al.* (2007)
m-LR	9.0 - 3.0	MC adsorption increases with a decrease in pH	Mashile *et al.* (2018)
m-LR	6.5-2.5	Increase in m-LR removal	Pendleton *et al.* (2001)
m-LR, m-RR	-	Adsorption capacity for MCs decreased with an increase in pH	Zhu *et al.* (2016)
m-LR	9.0 - 3.0	16 % increase in MC removal with a decrease in pH	Zhang *et al.* (2011)

changes in pH (Pendleton *et al.* 2001). Studies on the effects of pH on m-LR adsorption by activated carbon revealed that adsorption increases with decreasing pH (from 8 to 2.5) (Huang *et al.* 2007, Pendleton *et al.* 2001). Zhu *et al.* (2016) observed that at high pH values and the electrostatic repulsion between negatively charged MCs molecules and AC were responsible for the low PAC adsorption capacity. However, at low pH levels, electrostatic repulsion disappeared and the MC molecules became electrically neutral, which then enhanced its adsorption by PAC. For most ACs, the surface charge is negative at a high pH due to the increase in hydroxyl groups and anions. Moreover, MCs are also negatively charged under basic conditions, which results in repulsion between PAC and MCs. Thus, a high pH is unfavorable for the adsorption of MCs by AC. Under acidic conditions, the weak acid functional groups in MCs become more conducive to adsorption by AC (Huang *et al.* 2007). Furthermore, at a low pH, the MC molecules begin to cluster and the molecular size decreases, which increases the surface area available for adsorption by activated carbon. Moreover, AC contains more acidic functional groups under acidic conditions. The formation of hydrogen bonds between MC molecules and the surface of activated carbon enhances the adsorption capacity of AC (Lanaras *et al.* 1991). Some studies that have discussed the influence of pH on MC adsorption by AC are presented in Table 4.

2.2.3 Effect of ionic strength

Another important factor that affects electrostatic interactions between MCs and AC is the ionic strength. The carbon-adsorbate interactions are mainly hydrophobic or electrostatic. The ionic matrix of water plays a crucial role in the electrostatic interactions. The ionic strength may enhance or reduce MC adsorption by AC (Campinas and Rosa, 2006). When attractive electrostatic interactions occur between the carbon's surface and the adsorbate and the concentration of the adsorbate on the carbon's surface is low (surface concentration), an increase in ionic strength will hinder adsorption (Newcombe and Drikas, 1997). However, if electrostatic interactions are repulsive or the concentration of the adsorbate is high (leading to lateral repulsion between the adsorbed molecules), non-electrostatic forces govern adsorption and an increase in ionic strength will enhance adsorption (Campinas and Rosa, 2006, Newcombe and Drikas, 1997) as it induces a shielding effect. Such effects of ionic strength on MCs may be attributed to the prevailing type of adsorbate-adsorbent interactions, which depend on the net charges and hydrophobicity of the carbon and adsorbent, the cation charge (mono or divalent), and the adsorbate's surface concentration and molecular size (Campinas and Rosa, 2006). When explaining the relationship between ionic strength and the molecular size of the adsorbate, Randtke and Snoeyink (1983) reported that the adsorptive capacity of GAC for organic anions (particularly those with a high molecular weight) increases significantly as the concentrations of salts increase. However, recent studies indicate that the effect of ionic strength depends on two adsorbate variables, i.e., the surface concentration (Bjelopavlic *et al.* 1999, Newcombe and Drikas, 1997) and molecular size (Kilduff *et al.* 1996, Li *et al.* 2002). Some studies that have reported the effect of ions on MC adsorption are presented in table 5.

Table 5 Effect of ions on adsorption of MCs

Targeted MCs	Ions	Ionic strength (mM)	Trend of effect	Reference
m-LR	Ca^{2+}	2-100	Increase in the rate of m-LR adsorption	Campinas and Rosa (2006)
m-LY, m-LW, m-LF	K+, Ca^{2+}	2-100	Enhanced adsorption rate	Campinas and Rosa (2006)
m-LR	KCl + $CaCl_2$	2.5-10	Enhanced m-LR adsorption	Campinas and Rosa (2006)
m-LR,	Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}	-	Increases in m-LR adsorption of 16, 18, 24, and 16%, respectively	Zhu *et al.* (2016)
m-RR	Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}	-	Increases in m-RR adsorption of 16, 15, 19, and 16%, respectively	Zhu *et al.* (2016)
m-LR	Ca^{2+}	2-100	Increase in the m-LR adsorption capacity with increases in the calcium concentration	Campinas (2009)

3. Conclusions

AC has been used extensively in the adsorption/removal of MC since its discovery as a strong and reliable adsorbent. The superior adsorption capacity of AC compared to other adsorbents is mainly attributed to its high performance relative to its cost, non-toxicity, provision of a large external surface area that can be easily accessed by biological contaminants, and presence of well-developed meso and micropores. The adsorption capacity of AC is versatile and can be utilized in the removal of a diverse range of biological contaminants, including cyanobacterial toxins from aquatic systems, particularly microcystin. Several factors have been found significantly influence MC adsorption onto AC, including the carbon particle size, carbon surface chemistry, presence of organic matter, pH value of the liquid, and the presence of ions. The amount of available literature for the application of AC for microcystin treatment is increasing at a tremendous pace, with several enhancement of biosorption capacity through modification of biosorbent, assessment of biosorbents under multicomponent pollutants, mechanistic modelling to fully grasp the sorption mechanisms, and regeneration studies. Overall, AC offers an efficient, cheap, non-toxic and biocompatible adsorbent for MC removal.

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