Microcystin-LR removal from drinking water supplies by chemical oxidation and activated carbon adsorption

S. Sorlini and C. Collivignarelli

ABSTRACT

Microcystin-LR (MC-L) is among the most toxic and frequent cyanotoxins found in surface water and a provisional value of 0.001 mg/L is indicated by World Health Organization guidelines for water for human consumption. Among the conventional processes used for surface water treatment, the most effective in microcystin removal are chemical oxidation and adsorption. This study investigated two processes for the treatment of raw water of lake of Garda, drawn from the drinking water treatment plant of Desenzano d/G (Brescia, Italy), spiked with pure MC-LR. The experimental tests on adsorption with activated carbon were performed using carbon from both a mineral (M21) and a plant source (C25). Determination of the adsorption isotherm show that the activated carbon M21 is more effective than C25 in MC-LR removal. During the continuous flow column test with the carbon M21, the limit concentration for MC-LR was reached after about 4,000 bed volumes. Finally, chemical oxidation with sodium hypoclorite, which is more effective than chlorine dioxide for MC-LR removal, shows a yield of 80% with a concentration of 3 mgCl_2/L with a consequent reduction of MC-LR concentration from 10 to 1.5–2 μg/L.

Key words | activated carbon, chemical oxidation, chlorine, cyanobacteria, cyanotoxins, microcystin-LR

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INTRODUCTION

Cyanobacterial toxins are toxins produced by cyanobacteria (blue-green algae). They include neurotoxins (e.g. microcystins), hepatotoxins (e.g. microcystins), skin irritants and other toxins. Both hepatotoxins and neurotoxins are produced by cyanobacteria commonly found in surface water supplies; however, the neurotoxins are relatively unstable and, as such, are not considered to be as widespread as hepatotoxins in the water supply. Most of the hepatotoxins are collectively referred to as microcystin, because the first hepatotoxin was isolated from *Microcystis aeruginosa*. Among the more than 80 microcystins identified to date, only a few occur frequently and in high concentrations. Microcystin-LR is among the most frequent and most toxic microcystin congeners. Frequently occurring cyanobacterial genera that contain these toxins are *Microcystis, Planktothrix* and *Anabaena*. Microcystins usually occur within the cells; substantial amounts are released to the surrounding water only in situations of cell rupture (i.e. lysis). Microcystin-LR is a potent inhibitor of eukaryotic protein serine/threonine phosphatases 1 and 2A. The primary target for microcystin toxicity is the liver, as microcystins cross cell membranes chiefly through the bile acid transporter. A health-based guideline value for total microcystin-LR (free plus cell-bound) of 1 μg/L was derived, assuming significant exposure from drinking-water. The guideline value is considered as provisional, as there is evidence of hazard, but the available information on health effects is limited (WHO 2006). Relevant concentrations of cyanotoxins in surface waters have been registered in many countries: China, Portugal, Australia, Finland and USA (WHO 1999). To date, the most lethal outbreak attributed to exposure to cyanobacterial toxins in drinking water have occurred in different places such as Brazil, Zimbabwe,

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Cameroon, China, Austria and Australia (GCDWQ 2002). In Italy many regions are affected by cyanobacteria blooms, and the main common genera are *Microcystis* (*M. aeruginosa* and *M. flos-aquae*), *Aphanizomenon* (*Ap. flos-aquae*) and *Anabaena* (*A. flos-aquae* and *A. planctonica*) and, with less widespread diffusion, *Planktothrix rubescens* (Mattei *et al.* 2005; Funari *et al.* 2006). The most frequent toxins generated by these cyanobacteria in Italian waters are microcystins, cylindrospermopsin and Anatoxin-a (Mattei *et al.* 2005). The factors affecting toxins production by cyanobacteria are not well known, but some environmental factors (light, temperature, pH, carbon, nitrogen and phosphate concentration) seem to be important. Cyanobacteria toxins tend to be associated with cyanobacterial cells and may be membrane bound or occur free within the cells. Most of the toxin release occurs as cells age and die and can passively leak their contents. Therefore, toxins release can increase in the drinking water treatment plants, after the application of some processes that can produce cyanobacteria cells lysis.

Conventional surface water treatment processes are only partially successful in removing or destroying cyanobacterial toxins. Among the conventional processes, chemical oxidation and adsorption with activated carbon can represent efficient solutions for removal of algal toxins.

With regard to oxidation, both microcystin-LR and -RR can be easily decomposed by chlorination with sodium hypochlorite. Tsuji *et al.* (1997) observed that microcystin-LR removal after 60 min contact time was about 36% with a chlorine dose of 0.7 mg/L and 100% at a dose of 2.8 mg/L. At this concentration, chlorine increased its efficiency up to 99% after 30 min. Although these results seem to encourage the use of chlorine for toxin removal, pre-oxidation of the cell itself must be avoided, because it frequently causes toxin release from algae and produces trihalomethanes during water treatment. The kinetics of reactions between chlorine and the microcystins were determined by Acero *et al.* (2005) that found that the increase of pH has a negative effect on the microcystin degradation rate (similar results were observed for MC-LR, MC-RR and MC-YR) and concluded that chlorination can be applied in pre-oxidation and disinfection processes for cyanobacterial toxins control if the pH is kept below 8. Merel *et al.* (2010) presents a state of the art on cyanotoxins in water and their behaviour towards chlorination; they found that chlorination is very effective on microcystins and its efficiency depends on pH, chlorine dose and oxidant nature. Kull *et al.* (2004) found that the overall rate constant k for the reaction between MC-LR and ClO_2 was modest, suggesting that ClO_2 is not a suitable oxidant for the degradation of microcystins in drinking water treatment processes. Kull *et al.* (2006) have also shown that ClO_2 is rapidly consumed by fulvic and humic acids, leaving less ClO_2 residual to oxidise MC-LR and the generated oxidation products are be non toxic. A kinetic database has been compiled by Rodrìguez *et al.* (2007a) for different oxidants and the results showed that permanganate can effectively oxidize Anatoxin-a and MC-LR, while chlorine can oxidize Cylindrospermopsin and MC-LR and ozone is capable of oxidizing all three toxins at the highest rate. The formation of trihalomethanes in the treated water may be a restriction to the application of sufficiently high chlorine doses: a concentration of chlorine lower than 3 mg/L should be applied to avoid a trihalomethane concentration in the treated water above the standard value of 100 μg/L.

Alternative systems for MC-LR oxidation of MC-LR are based on the use of ozone (Rositano *et al.* 2001; Maatouk *et al.* 2002; Miao *et al.* 2010), potassium permanganate (Rodrìguez *et al.* 2007b), hydrogen peroxide and advanced oxidation with H_2O_2/UV (Rositano & Nicholson 1994).

Among the conventional processes, activated carbon adsorption, which is commonly adopted in drinking water treatment plants, appears to be one of the most effective options. Different sources of activated carbon have been investigated for their ability to adsorb microcystin-LR. Wood-based products were found to be most effective because of their high mesopore volume. It was found that treatment with 25 mg/L of wood-based powder activated carbon (PAC), with a contact time of 30 min, could reduce the concentration of microcystin-LR from 50 to <1 μg/L (Drikas 1994). Adsorption of MC-LR was improved with activated carbon with higher mesopore and macropore volume while natural organic matter caused a reduction in the capacity of carbon for MC-LR (Huang *et al.* 2007). The adsorption of microcystin toxins using granular activated carbon was described by Ho & Newcombe (2007) using experimentally-derived Freundlich and kinetic parameters. They also observed that biological

degradation appeared to be the predominant removal mechanism in pilot-scale conditions. Wang *et al.* (2009) observed that granular activated carbon (GAC) filtration has shown to be promising as it is not only an efficient adsorbent, but also can support biodegradation of microcystins, extending the lifetime of this application. Up to 70% removal of microcystin-LR was still observed after 6 months of operation of the sterile GAC column, indicating that adsorption still played a vital role in the removal of this toxin. The adsorption efficiency of the PAC for both MC-LR and MC-LA was affected by the amount of dissolved organic carbon (DOC) in the water, with lower adsorption for both compounds with higher DOC concentration (Cook & Newcombe 2008). Pendleton *et al.* (2001) observed that both the adsorbent surface chemistry and the primary micropores volume have virtually no influence on the amount of MC-LR adsorbed, and an adjustment of the solution pH conditions to low pH results in an enhanced adsorption of MC-LR. Craig & Bailey (1995) showed a significant breakthrough of MC after 5 months of operation of a GAC filter using an empty bed contact time (EBCT) of 15 min. In addition, they showed that an EBCT of 6 min resulted in a significant microcystin breakthrough after 1 month of operation. Pilot-scale tests (Bernezeau 1994) treating microcystins at 30–50 μg/L showed greater than 90% toxin removal for water treatment volumes up to 7,000–10,000 activated carbon bed volumes (BV) before efficiency dropped to less than 63% (probably because of saturation of the GAC with DOC). Studies by Hart & Stott (1993), using rapid column tests to simulate the performance of GAC, showed that for EBCTs typically used in water treatment of 10–15 min, the best performing carbon had a bed life of only 30–45 days. The removal of MC-LR in a real treatment plant was evaluated by Lambert *et al.* (1996) that found that the conventional treatment processes combined with activated carbon generally removed more than 80% of MCs from raw water, with a residual concentration of 0.1–0.5 mg/L for both GAC and PAC treatment facilities.

The aim of this study was to evaluate the oxidation of MC-LR with chlorine and the removal by means of adsorption with activated carbon. The tests were performed on raw water, spiked with pure MC-LR, drawn from Lake Garda in the drinking water treatment plant of Desenzano (Brescia).

METHODS

Water matrix

The water used for the experimental test was obtained by spiking the natural water of Lake Garda with standard microcystin-LR. The natural water was taken from the lake at 65 m depth and 1,100 m distance from the coast and its chemical and biological characteristics are shown in Table 1. During the experimental period MC-LR concentration in raw water was lower than the detection limit (0.05 μg/L). Pure MC-LR (($C_{49}H_{74}N_{10}O_{12}$, purity >95% (HPLC), isolated from *Microcystis aeruginosa*)), was added to the natural water in order to reach different initial MC-LR concentrations: 25 μg/L for the sorption isotherm determination, 1.5 μg/L for column test filtration with activated carbon and 10 μg/L for the oxidation tests.

Activated carbon

The experimental tests were performed on two different activated carbons, whose characteristics are described in

Table 1 | Raw lake water quality during the experimental period

Parameter	Value (range)
pH	7.8–8.3
Temperature (°C)	11.3–12.7
Alkalinity (mg $CaCO_3$/L)	80–110
Turbidity (NTU)	<1
Color	<1
TOC (mg/L)	2.7–3.4
DOC (mg/L)	1.9–2.4
UV absorbance 254 nm (1/cm)	0.018–0.124
Permanganate oxidability (mg/L)	1.0–1.7
Total bacterial count at 22 °C (CFU/1 mL)	>300
Total bacterial count at 36 °C (CFU/1 mL)	>300
Coliforms 37 °C (CFU/100 mL)	8–40
Escherichia coli (CFU/100 mL)	2–40
Enterococci (CFU/100 mL)	3–9
Clostridium perfrigens (CFU/100 mL)	3–7
Algae (total algal content) (N/100 mL)	230–1,800
Microcystin-LR (μg/L)	0.05

NTU: nephelometric turbidity units; TOC: total organic carbon; DOC: dissolved organic carbon; CFU: colony forming units.

Table 2 | Characteristics of the activated carbons

Activated carbon	Origin	Granulometry (mm)	Bulk density (kg/m^3)	Iodine number (mg/g)	Methylene blue index (mg/g)	B.E.T. specific surface (m^2/g)[a]	Porosity
M21	Mineral	0.06–2.36	470	>1,000	>22	1,070	Mesoporous
C25	Plant	0.06–2.36	470	850	23.4	1,250	Microporous

[a]B.E.T.: Brunauer Emmett Teller.

Table 2. The mineral carbon (Poractiv M21, named M21) is produced from anthracite, and the plant carbon (Poractiv C25, named C25) is produced from coconut. Column tests were conducted on the carbon that had displayed the best properties based on the results of previous tests, namely mineral carbon M21.

Determination of the adsorption isotherm

The efficiency of MC-LR removal with the two activated carbons was evaluated by carrying out various adsorption tests, in batch conditions, according to the ASTM D 3860-79 (1980) method. The carbon sample was pulverized by grinding (95% with a mass of less than 50 mm) and then oven dried at 105 °C for 24 h. Each test was conducted by splitting the lake water sample (previously spiked with 25 μg/L of MC-LR) into equal parts of 500 mL and administering increasing amounts of carbon to each volume (1, 2.5, 5, 7.5, 10, 25, 50 mg). The contact time was 2 h, i.e. the time needed to reach equilibrium. At the end of the required contact time, carbon filtration was carried out on each of the 8 volumes with a 0.45 μm filter and a the final equilibrium concentration of MC-LR (C_f) was determined. The experimental data were processed in order to determine the Freundlich adsorption isotherm, using the adsorption equation $q = k \times C_f^{1/n}$ (q = equilibrium mass of adsorbate (MC-LR) removed/mass of carbon (μg of adsorbate/g of carbon); C_f = equilibrium concentration of residual adsorbate in the solution (μg of MC-LR/L of solution)). The adsorption equation in the log form ($\mathrm{Log}(q) = \mathrm{Log}(k) + 1/n\ \mathrm{Log}(C_f)$) represents the equation of a line. The coefficient k and n can be determined by a linear interpolation of the experimental points. Coefficient k ((mg/g)(L/mg)$^{1/n}$) is an empirical constant providing an indication of the adsorptive capacity of the carbon and $1/n$ (unitless) is an empirical constant providing an indication of the intensity of adsorption.

Chemical oxidation tests

The test for water chemical oxidation were conducted with sodium hypochlorite and chlorine dioxide with the concentrations and contact time indicated in Table 3. Raw water was spiked with an initial MC-LR concentration of 10 μg/L. The chemical oxidation with sodium hypochlorite was applied by addition of a commercial solution (40% concentration of free active chlorine) into 500 mL water samples. For each experimental dosage of oxidant, the test was repeated on three different samples of raw water. After the chemical addition, the water sample was rapidly mixed (250 rpm) with the jar test device for the required contact time (Figure 1(a)). Chemical oxidation with chlorine dioxide, for each dose, was repeated on three equal volumes of water (500 mL each) in dark closed glass bottles (Figure 1(b)) in order to minimize the degradation and the air dispersion of the reagent. Reagent-water was mixed by a magnetic stirrer. At the end of each test, the oxidation process was stopped by adding sodium thyosulphate (volume of 0.5 mL with a 0.1 M concentration).

Column test with granular activated carbon

The column test was conducted using two glass columns (inner diameter 3 cm, height 60 cm), each filled with

Table 3 | Conditions applied in the chemical oxidation tests

Reagent	Concentration (mgCl/L)	Contact time (minutes)
NaClO	0.5, 1.0, 1.5, 3.0, 4.5	60
ClO_2	0.5, 1.0, 1.5	60

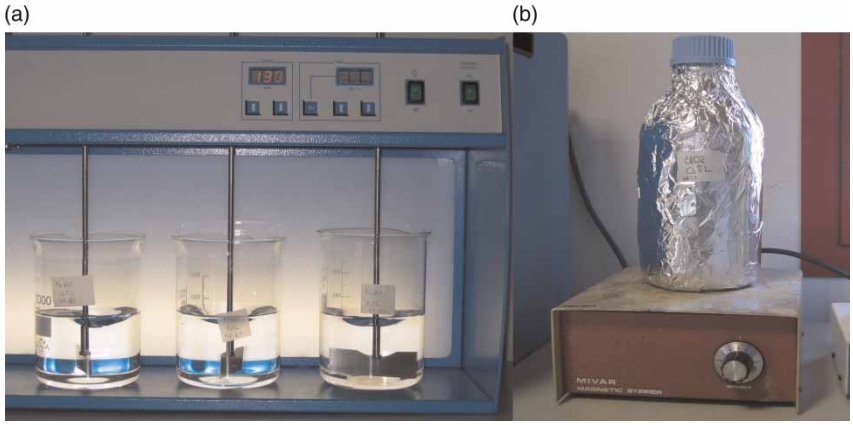

Figure 1 | Oxidation test of MC-LR with sodium hypochlorite (a) and chlorine dioxide (b).

150 mL GAC. The height of the material in the column was 41 cm and, starting from the bottom, was composed of: 5 cm of glass beads with a diameter of 6 mm; 5 cm of glass beads with a diameter of 3 mm; a 21 cm layer of GAC; two layers of glass beads over the GAC, the same as the two lower layers.

The raw water was stored in a plastic container (55 L volume) and fed into the column by a flow from bottom to top (up flow) through the use of a pump with a capacity of 0.5–1 L/h. The mineral activated carbon (M21) was used in the column test. During the test, the initial concentration of MC-LR spiked in lake raw water was 1.5 μg/L, the water flow was 0.6 L/h and the EBCT between water and carbon was 15 min.

Analytical methods

The analysis of MC-LR was carried out to determine the amount dissolved in water and the endocellular fraction. One litre of water was filtered through a GF/F Whatman filter (0.7 mm); the filtrate (designated phase 1) used to measure the dissolved amount, and the matter trapped on the filter (phase 2) was used for the endocellular amount. The filtrate (phase 1) was acidified with acetic acid (at 10%) and concentrated by filtration with a 10 mL/min flow on filter cartridge Envi C18 previously prepared with 10 mL of methanol. The cartridge was successively washed with 10 mL of distilled water, dried for 10 min in a flow of nitrogen and then eluted with 5 mL of methanol with a flow of 1 mL/min. The volume of 5 mL of methanol was evaporated in an oven at 45 °C under a flow of nitrogen, and the dry residuum was diluted in 1 mL of distilled water in order to obtain the final sample of dissolved toxin. Analysis of the endocellular toxin required extraction of the toxins from the algal cells on the filter (phase 2) by means of an ultrasound bath. The filter was placed in a beaker with 10 mL of methanol and the cells disrupted with four consecutive 1-min bursts of ultrasound. At the end of this procedure the filter was removed and the liquid was evaporated in an oven at 45 °C in a flow of nitrogen. The dry residuum was liquefied with 1 mL of distilled water, centrifuged for 3 min at 4,500 rpm, and the supernatant was recovered for analysis of the endotoxins.

The MC-LR was analyzed by means of an ESI-LC/MS/MS system made up of two Varian Prostar 210 gradient pumps coupled to a triple quadruple Varian 1200L spectrometer and automatic sampler Varian Prostar 410. The analysis was carried out with an analytic column Pursuit C18 (150 mm × 2 mm packed with a stationary phase C18 – 5 μm dimension at 35 °C) with water/methanol diluted in 0.1% formic with a flow of 200 μL/min. Ionization of the molecules leaving the chromatographic column was carried out by means of an ESI interface with positive polarity and the transitions used for the analysis were 996 → 213 (for quantification) and 996 → 135 (as qualifier ion). Quantification was performed by means of a calibration line in the range 5–80 ppb. The recovery during the solid phase extraction (SPE) showed good repeatability (CV < 20%) and good yield (>80%).

RESULTS AND DISCUSSION

Chemical oxidation tests

The results of the tests of chemical oxidation (Figure 2) show that sodium hypochlorite is very efficient in oxidation of MC-LR; with only 3 mg/L of oxidant 80% removal of the molecule occurs, thus reducing the concentration of MC-LR from 10 μg/L of raw water to 1.5–2 μg/L of the treated water. Achieving a reduction in the value for MC-LR below the World Health Organization (WHO) guideline value is possible only with high dosages of chlorine (greater than 3 mg/L). In contrast, chlorine dioxide offers very limited rates of removal of MC-LR which amount to 20% in the case of the maximum dosage tested (4.5 mgCl/L).

The concentration of residual chlorine in the water at the end of 60 min contact time in the oxidation tests is shown in Figure 3. The data show that the concentration of residual chlorine clearly increases with increasing dosage of chlorine used in the test; in addition, in the case of equal dosages of chlorine, residual chlorine is always greater (approximately twice as great) in the case of oxidation with chlorine dioxide compared with hypochlorite. This suggests a lesser reactivity of chloride dioxide with the matrix of the water used in the test.

Adsorption with activated carbon

Some preliminary tests were carried out with pulverized activated carbons in order to determine the time required to reach the equilibrium state in the process of adsorption of MC-LR. The results relating to carbon M21, shown in Figure 4, and also valid for the carbon C25, show that the removal of MC-LR by carbon is a rather rapid process which takes places during a variable period of time that ranges from 1 to 2 h, with a respective dosage of 100 and of 8 mg/L of activated carbon. The time of two hours has thus been adopted as the reference time for reaching the condition of equilibrium in adsorption of MC-LR on activated carbon.

The Freundlich adsorption isotherms were determined for adsorption of MC-LR with activated carbon. The results show a good correlation between the experimental data obtained with carbon M21 compared with a greater dispersion in the case of the carbon C25 (Figure 5). In most concentrations of active carbons tested (which show different values for final concentration (C_f)), one can see a greater capacity for adsorption in the case of the carbon

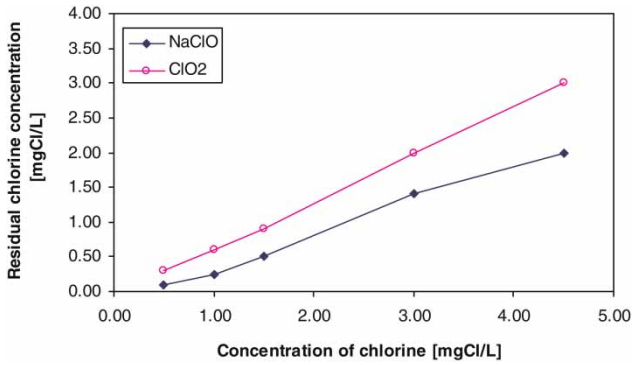

Figure 3 | Residual chlorine after MC-LR oxidation with sodium hypochlorite and chlorine dioxide.

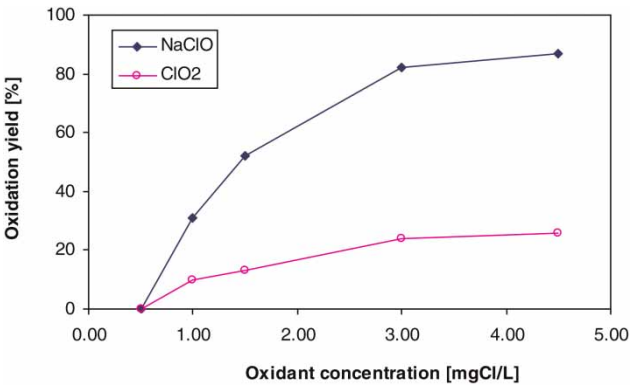

Figure 2 | Oxidation yield of MC-LR at different sodium hypochlorite and chorine dioxide concentration.

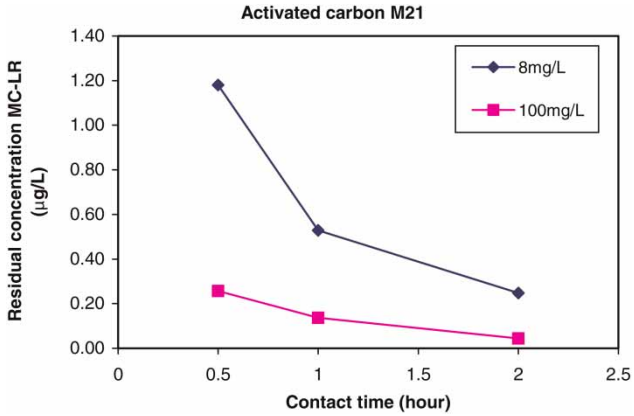

Figure 4 | Residual concentration of MC-LR versus different contact times with activated carbon M21.

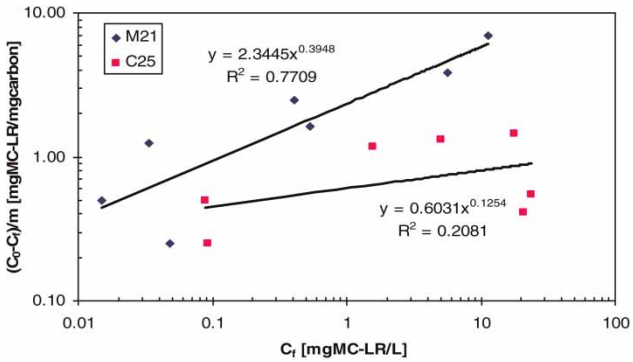

Figure 5 | Activated carbon sorption isotherm for MC-LR.

M21, mesoporous of a mineral type compared to carbon C25, microporous of a vegetable type. This result, which is consistent with what has been reported by other authors (Huang *et al.* 2007), is explicable on the basis of the greater affinity of MC-LR for mesoporous carbons compared with micro and macroporous types.

The test of adsorption of MC-LR in column was carried out only for the mineral activated carbon M21, since this had shown the best results in terms of adsorption. The values for concentration of MC-LR in water leaving the column as a function of time (Figure 6) show that given a concentration of MC-LR in the water to be treated of 1.5 μg/L, the toxin in the treated water is undetectable for 10–15 days, at which time the curve of elimination reaches the breakthrough point. The breakdown of the carbon occurs after 40 days of functioning, when the filtered water shows a concentration higher than the 1 μg/L indicated guideline value of the WHO. In this situation, the

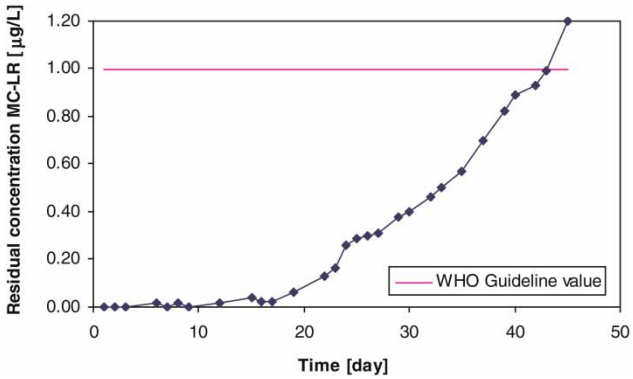

Figure 6 | Residual concentration of MC-LR in treated water during column test filtration with activated carbon M21.

activated carbon worked until 4,170 BV, a value less than that of 7,000–10,000 BV reported by Bernezeau (1994) and in line with the duration of 30–45 days observed by Hart & Stott (1993). This rapid breakdown can be attributed in part to the rapid contamination of the activated carbon by suspended material (algae, colloids, etc.) in the raw water used in these tests and the absence of any filter backwashing operation during the column filtration.

A common way to quantify the performance of a GAC adsorber is in terms of carbon usage rate (CUR), calculated as $CUR = M_{GAC}/(Qt_{bk})$, where M_{GAC} is the mass of GAC in the column (kg), Q is the flowrate to the adsorber (m^3/h) and t_{bk} is the time to breakthrough (d). A CUR value of 0.112 gGAC per liter of treated water was calculated with the data of the column filtration test while the specific throughput was calculated as 1/CUR and a value of 9 L/gGAC was obtained.

CONCLUSIONS

The experimental tests were carried out using water taken from Lake Garda at the point of the input for the water treatment plant for Desenzano to which was added pure commercial MC-LR.

The tests carried out with activated carbon in powder form showed that both the carbons tested (mesoporous mineral active carbon (M21) and microporous (C25)) generate a rapid breakdown of MC-LR and the processes stabilizes in about 2 h. According to tests relating to the determination of isotherms of adsorption (Freundlich's isotherm) one sees a greater specific capacity of adsorption by activated carbon M21 than carbon C25.

In the test of adsorption in columns with continuous flow, the breakdown of activated carbon M21 is reached after 40 days of functioning, when in treated water a concentration of MC-LR higher than 1 μg/L is reached. This condition corresponds to a specific throughput of 9 L/gGAC and a CUR of 0.112 gGAC/L.

During the oxidation test, an oxidation yield of MC-LR of 80% was obtained with a NaClO dose of 3 mgCl/L. Final concentration of MC-LR lower than WHO guideline value (1 μg/L) can be obtained only for chlorine doses higher than 3 mg/L. In contrast, chlorine dioxide offers

very limited removal of MC-LR which amounts to 20% in the case of the maximum dosage tested (4.5 mgCl/L).

Activated carbon can be alternatively used as PAC, generally added before the filtration step, or in GAC filters depending on raw water quality and plant configuration. As concerns chemical oxidation, chlorine, that is more effective than chlorine dioxide for MC-LR oxidation, can be applied as a final step, in addition or substitution to GAC filtration (depending on water quality), in order to minimize THM formation and to eliminate the risk of toxin release from cyanobacteria cells, that have been previously separated from water.

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