Oxidation of microcystin-LR with chlorine and permanganate during drinking water treatment

Juan L. Acero, Eva Rodríguez, Maria E. Majado, Ana Sordo and Jussi Meriluoto

ABSTRACT

The oxidation of microcystin-LR (MC-LR) present in natural waters with chlorine and potassium permanganate under real drinking water treatment conditions has been investigated in the present work. The natural waters were spiked with MC-LR, using the typical concentration of $5\,\mu gL^{-1}$ found in natural waters. The influence of some operational parameters such as the initial oxidant concentration, pH and temperature and of some drinking water quality parameters such as the NOM and ammonia content has been studied. The initial chlorine concentration and the temperature have a positive effect on MC-LR elimination. However, the pH exerts a negative influence on the MC-LR elimination by chlorine, which indicates that HOCl is the main active oxidant species. High concentrations of NOM and ammonia, which consume chlorine, impede the elimination of MC-LR. During the oxidation with permanganate, the initial permanganate concentration and the temperature have a positive effect on MC-LR removal, while the pH and the ammonia content do not exert any influence on its oxidation. However, high concentrations of NOM reduce the extent of oxidation of MC-LR with permanganate.

Key words | chlorine, drinking water, microcystin-LR, oxidation kinetics, permanganate

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INTRODUCTION

The presence of toxic cyanobacteria in surface waters used for drinking water production is receiving increasing attention worldwide as a potential health concern. Not only are cyanobacteria responsible for many taste and odour issues, some cyanobacterial organisms produce toxic compounds called cyanotoxins. Release of cyanobacterial toxins may arise during the water management cycle, e.g., during an algicide treatment of the raw water, during pumping and conveyance of raw water and/or due to the effect of certain substances, such as oxidants, used during water treatment (Carmichael 1992). Microcystins, which are frequently occurring and widespread cyanotoxins, are hepatotoxins, i.e. they are known to cause liver damage (Chorus & Bartram 1999). Among microcystins, microcystin-LR (MC-LR) is the most common analogue in natural waters and is highly toxic with

an LD50 value of $50\,\mu gkg^{-1}$ (mouse, i.p.). The World Health Organization (WHO) has set a provisional guideline value of $1.0\,\mu gL^{-1}$ for MC-LR in drinking water (WHO 2004). This WHO guideline value is used as a basis in some countries such as Spain to set a drinking water standard for total MCs of $1.0\,\mu gL^{-1}$ (BOE 2003).

The application of conventional water treatment technologies (coagulation, flocculation/sedimentation, filtration) has been reported to be effective for the removal of cyanobacterial cells but ineffective for the removal of extracellular microcystins (Himberg et al. 1989; Chow et al. 1999; Hrudey et al. 1999). Chemical oxidation is a possible option as a safe barrier against cyanotoxins in order to reduce public health risk. Of the oxidants and disinfectants typically applied in waterworks, chlorine and permanganate

have been found to be effective for the removal of some of these toxins. MC-LR can be destroyed by chlorine as long as a sufficient dose is present, the oxidation process being pH dependent (Nicholson *et al.* 1994; Senogles-Derham *et al.* 2003). A chlorine residual of $0.5 \, mgL^{-1}$ after 30 min contact time was effective at pH < 8, whereas inadequate chlorine doses led to low or no toxin removal at higher pH. Tsuji *et al.* (1997) have identified dihydroxymicrocystin as the main degradation product, which is of lower toxicity. The oxidation of MC-LR by permanganate is effective for the removal of dissolved toxin in treated water (Rositano *et al.* 1998). Hall *et al.* (2000) reported that the addition of permanganate is a possible treatment for dissolved MC-LR in waters with low oxidant demand. Permanganate must be applied before sedimentation/filtration in order to control final manganese concentrations. However, the permanganate dose must be controlled since high doses might cause cell lysis and toxin release in raw water containing algal cells (Pietsch *et al.* 2002; Knappe *et al.* 2004). Therefore, the strategy for applying permanganate as a pre-oxidant in drinking water treatment is removing dissolved toxins without cell rupture (Drikas *et al.* 2001). Similar to chlorination, the oxidation of MC-LR with permanganate was proposed to lead to the formation of dihydroxymicrocystin (Rodriguez *et al.* 2007a).

We have determined the rate constants for the reactions of MC-LR with chlorine and potassium permanganate in previous studies. Apparent second-order rate constants for the chlorination of MC-LR at 20°C varied from $475 \, M^{-1}s^{-1}$ at pH 4.8 to $9.8 \, M^{-1}s^{-1}$ at pH 8.8 (Acero *et al.* 2005). Judging from these rate constant values, chlorination is a feasible option for microcystin degradation during oxidation and disinfection processes. The second-order rate constant for the reaction of MC-LR with permanganate at pH 7 and 20°C was determined to be $357.2 \, M^{-1}s^{-1}$, with a minimal influence of pH on the oxidation process (Rodriguez *et al.* 2007a).

In the present study, the oxidation of MC-LR in surface water by chlorine and permanganate has been assessed. In addition to determining the oxidation kinetics, it is necessary to establish the required oxidant dose and the nature of the oxidation by-products (e.g., THM speciation) in order to understand the oxidation process. With this information, optimum operational conditions, optimum reactor design, effective process control and economical capital and operational costs can be achieved. Therefore, the main goals of this study were to evaluate the oxidant dose required for MC-LR oxidation, to establish the influence of the main operational parameters (pH, temperature and toxin concentration) and to investigate the effects of the main water quality parameters (NOM, ammonia, bromide) on the oxidation process. Finally, a kinetic model has been applied to predict the oxidation of other cyanotoxins such as cylindrospermopsin and ana-toxin-a in the surface water under study.

MATERIALS AND METHODS

Reagents

All reagents and solvents were of the purest available quality. Solutions of analytical reagents, chlorine, permanganate and phosphate buffers were prepared in ultra-pure water purified to $18.2 \, M\Omega \, cm$ by a MilliQ Academic (Millipore) water purification system. Stock solutions of chlorine were prepared by diluting a commercial solution of sodium hypochlorite (4% active chlorine, Aldrich) and standardized spectrophotometrically in the presence of excess of iodide to form triiodine (ε at $351 \, nm = 25,700 M^{-1} cm^{-1}$) (Bichsel & von Gunten 1999). A permanganate stock solution ($1.25 \, g \, L^{-1}$) was prepared by dissolving $KMnO_4$ in ultra-pure water and standardized spectrophotometrically (ε at $526 \, nm = 2,460 \, M^{-1}cm^{-1}$) (Stewart 1973). Sodium thiosulfate stock solution (10 mM) was prepared by dissolving $Na_2S_2O_3$ in ultra-pure water and used as a quenching reagent to stop the reaction of MC-LR with chlorine and permanganate. Phosphate buffers at different pH were prepared from disodium hydrogenphosphate and phosphoric acid. Similarly, borate buffer at pH 8 was prepared from sodium borate and boric acid. Humic acid, used as a DOC source, was purchased from Fluka.

Toxin materials

MC-LR used in the oxidation experiments was purified from *Anabaena* strain 90 (originally from the culture collection Prof. Kaarina Sivonen, University of Helsinki) according to the procedure detailed elsewhere (Acero *et al.* 2005; Spoof & Meriluoto 2005). In brief, the toxin was

extracted from freeze-thawed cyanobacterial cells by 50% aqueous methanol, concentrated by C_{18} solid-phase extraction and purified by low-pressure silica gel chromatography (90% aqueous methanol containing 0.1% trifluoroacetic acid as mobile phase) followed by high performance liquid chromatography (HPLC) on a C_{18} sorbent (27% acetonitrile and 73% 0.0135 M ammonium acetate in water as mobile phase). The purity of MC-LR was estimated as >98% based on reversed-phase analytical HPLC with UV absorbance detection at 238 nm according to Meriluoto & Spoof (2005*a*).

Analytical methods

Concentrations of MC-LR were determined by HPLC (Waters Alliance 2695 Separation Module and Waters 996 Photodiode Array Detector) by a method adapted from that proposed by Meriluoto & Spoof (2005*a*). The column was a C_{18} end-capped Merck Purospher STAR RP-18e, 3 μm particles, LiChroCART 55 × 4 mm I.D. and the injection volume 10 μl. Gradient elution (flow rate 1 ml min^{-1}) of acetonitrile/0.05% trifluoracetic acid (A) and water/0.05% trifluoracetic acid (B) was used by varying the volume percentage of A from 25% to 70% over 5 minutes. The photodiode array (PDA) detector was set in the range 200–300 nm, 238 nm being the wavelength selected for quantification. Due to the low toxin concentration in the experiments performed with natural waters, a solid phase extraction (SPE) was performed prior to HPLC analysis, by using Isolute C18 columns as described by Meriluoto & Spoof (2005*b*). The concentration factor was 1000:1 (200 ml samples were concentrated to 200 μl). The limit of quantification was 1.0 ng per 10 μl injection, which is equivalent to 0.1 mgL^{-1} or 0.1 μgL^{-1} for reaction samples analyzed by direct injection or after SPE respectively.

Total trihalomethanes (TTHM) were measured by gas chromatography, using head space injection and electron capture detection (HS-GC-ECD, Golfinopoulos *et al.* 2001). The permanganate concentration in natural water samples was analyzed with DPD (Clesceri *et al.* 1999) after filtering the sample through 0.22 μm nylon filters to remove manganese oxide. The chlorine concentration in surface water experiments was measured by the ABTS method (Pinkernell *et al.* 2000).

Experiments with natural water

The oxidation of MC-LR by chlorine and permanganate was investigated in experiments performed with surface water from Lake "Villar del Rey" (located in the south-west of Spain), which is used as a drinking water source. Natural water samples were taken in summer (LS) and winter–spring (LW). The main water quality parameters are detailed in Table 1. MC-LR or other cyanotoxins did not occur naturally in this Lake water. Experiments were run with different initial oxidant doses, pH (by buffering the water sample with phosphate (pH 6–7) or borate (pH 8) buffers (10 mM)) and temperature, covering well the conditions found in full-scale drinking water treatment. The initial MC-LR spiked in most of the experiments was 5 μgL^{-1}, a typical concentration found in natural waters (Spoof *et al.* 2003). The oxidant concentration was 2–4 mgL^{-1} for chlorine and 0.5–1.5 mgL^{-1} for permanganate, typical of an oxidation step in drinking water treatment. Experiments were performed by adding an aliquot of the stock oxidant solution to the buffered natural water containing MC-LR. For each desired reaction time, several samples were withdrawn from the reactor, one to analyze the concentrations of chlorine or permanganate, and one or two to measure MC-LR and THMs (in the case of chlorination) after quenching the reaction with sodium thiosulfate. MC-LR concentrations were measured by HPLC after SPE enrichment.

RESULTS AND DISCUSSION

Toxin removal in natural water by chlorine

Several experiments of MC-LR oxidation by chlorine were performed with lake water LW (selected because it represents the minimum reactivity with oxidants), modifying the chlorine dose, pH and temperature. The initial MC-LR concentration in these experiments was

Table 1 | Natural water quality parameters

Water	PH	DOC(mgL^{-1})	Bicarbonate (mM)	Ammonia (μgL^{-1})	Bromide (μgL^{-1})
LW	7.3	5.4	0.47	49	17
LS	7.4	6.7	0.52	85	22

around $5\,\mu gL^{-1}$. Figure 1 shows the results obtained in a chlorination experiment performed with $3\,mgL^{-1}$ of chlorine (pH = 7.3 and T = 20°C). An initial fast decrease of the oxidant concentration can be observed in the figure, due to fast reactions of chlorine with highly reactive organic and inorganic matter present in the natural water. Then, the oxidant decay became slower until complete depletion, which was reached after 24 hours. MC-LR elimination was fast, being almost complete after one hour in this experiment with an initial chlorine concentration of $3\,mgL^{-1}$. Concentrations of MC-LR below the guideline value of $1\,\mu gL^{-1}$ were reached after 30 minutes and with an oxidant exposure (CT-value, defined as the integral of oxidant concentration over the reaction time) of $35\,mgL^{-1}min$, comparable to the chlorine exposure required for disinfection purposes (USEPA 2003; Acero *et al.* 2005). These results confirm that chlorine is a suitable oxidant for MC-LR removal during drinking water treatment.

The initial dose of chlorine was investigated in the range 2–$4\,mgL^{-1}$ (LW water, pH = 7.3 and T = 20°C). It can be observed in Figure 2 that there is a clear positive influence of the initial chlorine concentration on the elimination of MC-LR. Higher chlorine dose leads to higher chlorine CT and therefore greater toxin removal. In this surface water, MC-LR is easily reduced to below $1\,\mu gL^{-1}$ when the initial concentration of chlorine was higher than $2\,mgL^{-1}$. Note that in Figure 2 only the concentration profiles during the first hour have been plotted. However MC-LR removal continued until complete chlorine depletion, around 24 hours.

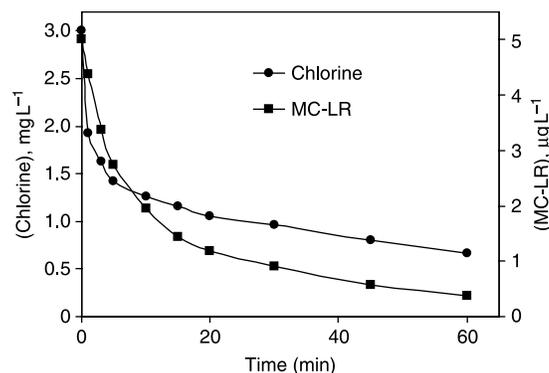The influence of the initial chlorine dose was also investigated in the surface water LS, with higher organic

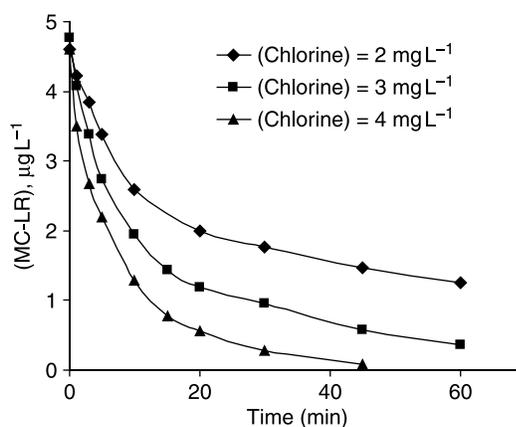**Figure 2** | Influence of the chlorine dose on the oxidation of MC-LR in LW water at pH 7.3 and 20°C.

and inorganic content (Table 1). Figure 3 depicts the values of the residual MC-LR concentration (after total chlorine consumption) in experiments performed with different chlorine dose ([chlorine]$_0$ = 0–$3\,mgL^{-1}$, pH = 7.3 and T = 20°C). There was a higher instantaneous consumption of chlorine in this water with higher organic and inorganic content, since the oxidation of MC-LR was not observed until the initial chlorine dose was above $1.2\,mgL^{-1}$. Then, once the initial chlorine demand was satisfied, removal of toxin was observed. It can be seen that a chlorine dose above $2.5\,mgL^{-1}$ is needed to remove MC-LR to below the guideline value of $1\,\mu gL^{-1}$. Therefore the water quality parameters, especially the NOM present, influence the elimination of MC-LR. Both the concentration and characteristics of the NOM are known to strongly influence the reaction with chlorine as NOM containing a higher proportion of conjugated and substituted aromatic moieties
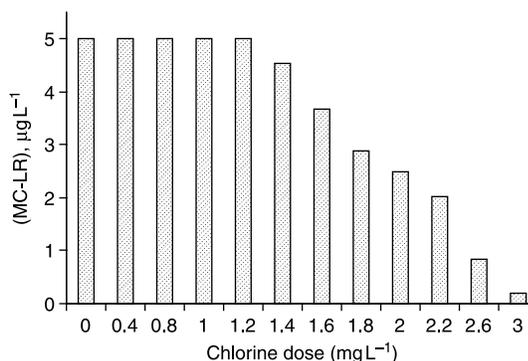

Figure 1 | Elimination of MC-LR in LW water with $3\,mgL^{-1}$ of chlorine at pH 7.3 and 20°C.

Figure 3 | Residual concentration of MC-LR (after total chlorine depletion) during chlorination of LS water at pH 7.3 and 20°C.

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is more susceptible to chlorine attack (Korshin et al. 1997; Ho et al. 2006). As a consequence, it is necessary to calibrate each water with respect to the rate of chlorine depletion in order to determine the initial dose that leads to the required CT value or toxin removal.

The efficiency of microcystin elimination during a chlorination process depends on the chlorine stability in the drinking water being treated and on the reactivity of chlorine towards the toxin. The chlorine stability varies with the natural water quality parameters such as NOM, ammonia and bromide concentrations and also with the treatment conditions (pH and temperature). Therefore, to predict microcystin removal, in addition to the knowledge of microcystin chlorination rate constants, chlorine decay kinetics have to be characterized in each particular water, for both an oxidation pretreatment or final disinfection. In any case, the chlorination treatment is efficient if the microcystin concentration is reduced to below the guideline value of $1\,\mu gL^{-1}$. For these reasons, the influence of the water quality parameters and operational conditions on the efficiency of MC-LR elimination were established in the present work.

With respect to influence of some operational conditions, the temperature has a slight positive effect on MC-LR elimination. The time required to decrease MC-LR concentration to below $1\,\mu gL^{-1}$ was reduced from 40 to 20 min when the temperature was increased from 10 to 25°C ([chlorine]$_0$ = 3 mgL^{-1}, pH = 7.3). On one hand, chlorine decay is faster and, therefore, the CT value is lower (data not shown). On the other hand, the apparent rate constants are higher at higher temperature, according to an activation energy of $58.5\,kJmol^{-1}$ (Acero et al. 2005).

The final outcome of both effects is a slight positive influence of temperature on the elimination of MC-LR.

However, the pH exerts a negative influence on the MC-LR elimination by chlorine as can be observed in Figure 4. The pH influence on chlorine decay rate is depicted in Figure 4(a), where a slight positive influence of pH can be observed. However, MC-LR elimination was faster at lower pH values as can be observed in Figure 4(b). These results corroborate the pH profile of the apparent second-order rate constant for the chlorination of MC-LR, a pH increase leading to lower apparent rate constants (Acero et al. 2005). Lowering pH could influence the reactivity of chlorine since the acid base equilibrium favours the presence of hypochlorous acid (HOCl), a stronger oxidant than the hypochlorite ion (ClO$^-$) which is the major species of chlorine at alkaline pH (pK$_a$ = 7.5). HOCl is the chlorine species responsible for the oxidation of MC-LR (Acero et al. 2005). However, the reactivity of phenolic structures present in NOM with HOCl is greater at higher pH values, when phenolic compounds are present in their anionic form, thus accelerating chlorine consumption at slightly basic pH (Gallard & von Gunten 2002). As a consequence, pH is a key variable in the chlorination process, having an optimum value for the oxidation of each kind of compound. Specifically, for the oxidation of MC-LR, pH should be kept at around neutral or slightly acidic. Therefore, when calcium or sodium hypochlorite are used in high doses, then the pH will need to be adjusted to below 8 to guarantee the efficiency of the process. Moreover, the pH might be corrected in waters with basic pH in order to ensure toxin removal during chlorination.
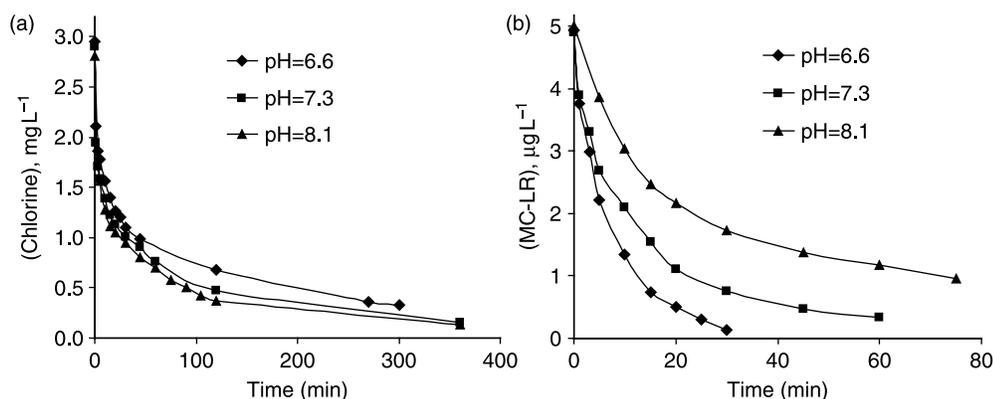

Figure 4 | Influence of pH on the chlorine decay (a) and MC-LR oxidation (b) in LW water at 20°C with an initial chlorine dose of 3 mgL^{-1}.

Similar experiments were performed with LW water ($3 \, mgL^{-1}$ chlorine, pH 7.3 and 20°C) by spiking different initial concentrations of MC-LR in the range $5-25 \, \mu gL^{-1}$, as typically found in natural waters (Spoof *et al.* 2003). This chlorine dose ($3 \, mgL^{-1}$) was enough to completely oxidize MC-LR, even at the relatively high toxin concentration of $25 \, \mu gL^{-1}$. The reaction time needed to reduce the MC-LR concentration to below $1 \, \mu gL^{-1}$ was 30, 50 and 90 min for the initial toxin concentrations of 5, 15 and $25 \, \mu gL^{-1}$, respectively. The chlorine dose of $3 \, mgL^{-1}$ is therefore well capable of oxidizing typical concentrations of MC-LR in the studied water.

The influence of some other drinking water quality parameters such as the DOC, bromide and ammonia content has also been investigated. These experiments were performed by adding a certain amount of humic acids (DOC source), bromide or ammonia to the surface water LW. Most of these experiments were performed at pH 7.3 and 20°C with an initial chlorine dose of $3 \, mgL^{-1}$. The removal of MC-LR observed in the experiments after the complete depletion of chlorine is detailed in Table 2. Thus, an increase in the DOC from 5.4 to $10 \, mgL^{-1}$ leads to a reduction in the MC-LR removal from 100% to 57%, which is due to the high chlorine consumption in reactions with the higher amount of NOM present. A similar tendency was obtained with the addition of ammonia which decreased the MC-LR removal from 100 to 85% when the ammonia content was increased from 49 to $133 \, \mu gL^{-1}$. Chlorine reacts with ammonia to form monochloramine, which is a weaker oxidant than HOCl (Vikesland *et al.* 2001). In addition, previous investigations have demonstrated that monochloramine is ineffective at oxidizing microcystin in natural water, with rate constants of less than $1 \, M^{-1} \, s^{-1}$ (Hart *et al.* 1998; Rodriguez *et al.* 2007b).

However, a different trend was observed when the bromide concentration was increased from 17 (natural water) to $100 \, \mu gL^{-1}$, the MC-LR elimination being similar in both experiments. These results can be explained if HOBr (which is formed in the reaction of HOCl with bromide) also reacts with MC-LR. HOBr is a more powerful oxidant than HOCl and its reactions with some groups of unsaturated aromatic compounds such as phenols have rate constants several orders of magnitude higher than those of HOCl (Gallard & von Gunten 2002). Therefore, the decrease in the toxin removal expected from the lower chlorine CT, is compensated by the more ready oxidation of MC-LR with HOBr. Since HOBr would also react rapidly with NOM and ammonia present in the natural water, the oxidation of microcystins might become important only in those waters with high bromide content (Rodriguez *et al.* 2007b).

From the obtained results, it can be concluded that toxin elimination is proportional to the chlorine CT. The chlorine dose needed to reach a certain CT value in the reactor depends on the water quality parameters, due to their influence on the chlorine stability. This is especially important in surface water from rivers or eutrophic lakes where chemical/physical parameters (e.g. temperature, pH, DOM, ammonia, bromide) can change frequently. In general, any compound which reacts with chlorine (DOM, ammonia) decreases the chlorine exposure, and therefore, impedes toxin elimination. As a consequence, higher chlorine doses must be used in waters with high organic and inorganic content in order to reach the chlorine CT required to reduce MC-LR concentration to below the guideline value.

A negative consequence of the chlorination process is the formation of disinfection byproducts, especially trihalomethanes (THMs) from the reaction of chlorine with the NOM present in the natural water. The formation of THMs has also been measured. With the applied chlorine concentration of $3 \, mgL^{-1}$ (pH 7.3, 20°C), sufficient for complete toxin removal (contact time of 24 hours), the concentration of total THMs was $110 \, \mu gL^{-1}$, slightly above the standard value of $100 \, \mu gL^{-1}$ according to EU legislation (EU 1998). The pH dependence of THMs formation is positive (which is undesirable), since the final values of THMs formation in experiments performed with $3 \, mgL^{-1}$ chlorine at pH 6.6 and 8.1 were 87 and $131 \, \mu gL^{-1}$, respectively. In general, the dominant THM was chloroform, followed by bromodichloromethane. The presence of

Table 2 | Influence of the water quality parameters on MC-LR chlorination (LW water, $[\text{chlorine}]_0 = 3 \, mgL^{-1}$, pH = 7.3, T = 20°C)

DOC (mgL^{-1})	Ammonia (μgL^{-1})	Bromide (μgL^{-1})	MC-LR removal (%)
5.4	49	17	100
10	49	17	57
5.4	133	17	85
5.4	49	100	100

chlorodibromomethane and bromoform was not significant. Formation of THMs would be different in other waters, depending on the natural organic matter present and on its reactivity towards chlorine. Therefore, the chlorination process has to be optimized in each particular water in order to reach the desired toxin removal without forming THMs above standard values.

Toxin removal by permanganate in natural water

Similar experiments were performed with Lake "Villar del Rey" waters (LS and LW) by using permanganate as oxidant and modifying the operational variables (permanganate dose, pH and temperature) and the water quality parameters (NOM, ammonia and bromide). Figure 5 shows the results obtained in an experiment performed with LW water at pH 7.2 and 20°C with an initial permanganate concentration of $1.1\,mgL^{-1}$. The initial fast decrease of permanganate can be due to fast reactions with highly reactive organic and inorganic matter present in natural water. However this decrease is less pronounced than that of chlorine because permanganate does not react with ammonia. Then, the oxidant decay became slower until complete depletion, which was reached after 2.5 hours. MC-LR elimination was also fast, being almost completely removed after one hour. Concentrations of MC-LR below the guideline value of $1\,\mu gL^{-1}$ were reached after 25 minutes when the oxidant exposure (CT-value) was calculated to be $12\,mgL^{-1}min$. This high degree of oxidation of MC-LR b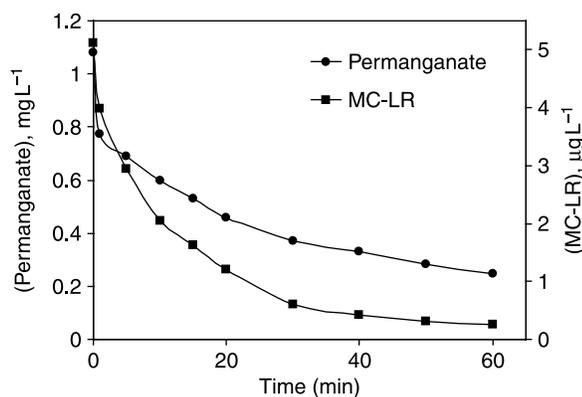y permanganate can be explained by the relatively high second-order rate constant of their reaction, which has been reported to be $357.2\,M^{-1}s^{-1}$ (Rodriguez *et al.* 2007*a*).

Similar to the chlorination process, the influence of the permanganate dose ($0.3–1.5\,mgL^{-1}$) on MC-LR elimination was investigated (LW water, pH = 7.2, 20°C). It can be observed in Figure 6 the positive effect of the initial oxidant dose on the toxin removal, due to the higher permanganate CT when the initial concentration is higher. From these results, it can be observed that a permanganate concentration above $1\,mgL^{-1}$ was required in order to reduce MC-LR concentration to below the guideline value of $1\,\mu gL^{-1}$.

The permanganate dose needed to reach a certain CT value in the reactor also depends on the water quality parameters, due to their influence on the permanganate stability. Figure 7 shows the elimination of MC-LR in an experiment performed in LS water (high DOC content) by varying the initial permanganate dose (pH = 7.2, 20°C). Even a low permanganate concentration is able to partially eliminate MC-LR, contrary to what occurred in the chlorination process, as seen in Figure 3. Therefore, the initial permanganate demand in reactions with the natural water matrix is much lower than the chlorine demand. In this LS water, a dose of $1.2\,mgL^{-1}$ was required to reduce MC-LR concentration to below the guideline value of $1\,\mu gL^{-1}$.

The effects of other operational conditions were investigated during the oxidation of MC-LR in natural water with permanganate as well. The temperature exerts a slightly positive effect on MC-LR removal, similar to chlorine. Therefore, the increase of the second-order rate constant at higher temperature (activation energy of
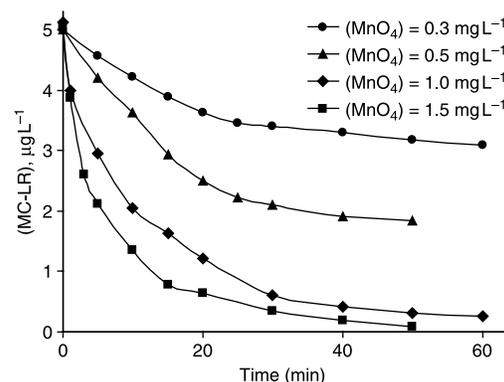

Figure 5 │ Elimination of MC-LR in LW water with $1.1\,mgL^{-1}$ of permanganate at pH 7.2 and 20°C.

Figure 6 │ Influence of the permanganate dose on the oxidation of MC-LR in LW water at pH 7.2 and 20°C.
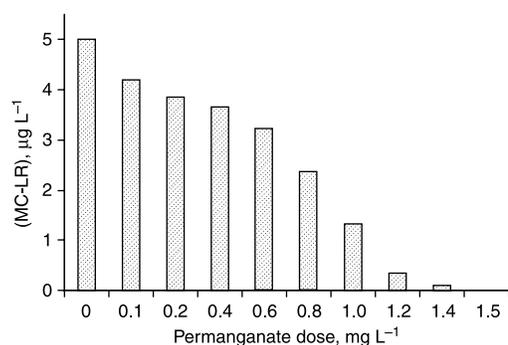
Figure 7 | Residual concentration of MC-LR (after total permanganate depletion) during the oxidation of LS water with permanganate at pH 7.2 and 20°C.

$28.8\,kJmol^{-1}$, Rodriguez *et al.* 2007*a*) compensates for the decrease of the oxidant exposure due to the slightly faster permanganate depletion. However, the pH effect on the MC-LR elimination by permanganate is not appreciable, as can be observed in Figure 8. Moreover, permanganate decays were very similar at different pH values (data not shown). These results can be explained by the independence on pH of the second-order rate constant for the reaction between permanganate and MC-LR. As a consequence, pH is not a key variable in the oxidation of natural waters with permanganate, at least for MC-LR removal.

The influence of some other drinking water quality parameters such as the DOC, bromide and ammonia content has been studied in experiments performed in LW water at pH 7.2 and 20°C, with an initial permanganate dose of $1.0\,mgL^{-1}$. In the case of an increase in the DOC content from $6\,mgL^{-1}$ to $10\,mgL^{-1}$, the elimination of MC-LR was appreciably reduced from 100% to 40%, due to the fast reaction of permanganate with humic acids, which decrease the permanganate exposure. However no influence of the bromide and ammonia content
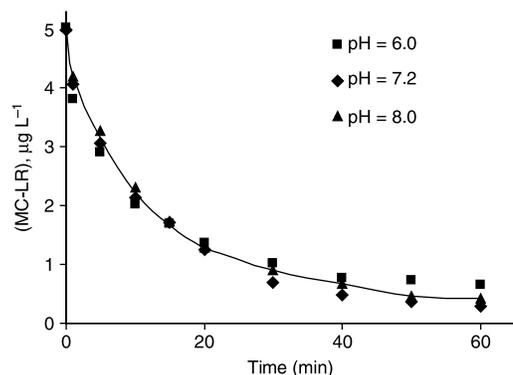

Figure 8 | Influence of pH on the MC-LR oxidation in LW water at 20°C with an initial permanganate dose of $1\,mgL^{-1}$.

was observed on MC-LR elimination, which can be explained by the negligible reactivity of bromide and ammonia with permanganate. As a consequence, the organic matter present in the natural water is the main quality parameter to be considered to establish the permanganate dose and the optimum operational conditions in order to reach the desired dissolved toxin oxidation without causing cell lysis and to improve the efficiency of the subsequent coagulation-sedimentation steps where the manganese oxide formed is removed.

Oxidation of cylindrospermopsin and anatoxin-a

The determination of the oxidant exposure (CT) from the experimental oxidant decay in the natural water allows the prediction of the oxidation of other micropollutants, such as cyanotoxins, if the rate constant for the reaction between the oxidant and the micropollutant is known. Effectively, the behaviour of the toxin concentration can be calculated from Equation (1), where k is the second-order rate constant for the reaction of the oxidant with the toxin under consideration at the pH of the water and the CT value can be determined by Equation (2) (Rodriguez *et al.* 2007*b*).

$$[\text{toxin}] = [\text{toxin}]_0 \exp(-k \cdot \text{CT}) \tag{1}$$

$$\text{CT} = \int_0^t [\text{oxidant}] \cdot dt \tag{2}$$

Following this procedure, the oxidation of other important cyanotoxins, such as cylindrospermopsin (CYN) and anatoxin-a (ANTX), can be predicted when present in the natural water under study. A kinetic database has been compiled for the oxidation of these toxins with ozone, chlorine, chlorine dioxide and permanganate (Rodriguez *et al.* 2007*b*). Therefore, the rate constants for the reactions of chlorine and permanganate with MC-LR, CYN and ANTX required to perform such prediction at any pH are available. Thus, chlorination rate constants at pH 7.3 are 75, 1085 and $0.7\,M^{-1}s^{-1}$ for MC-LR, CYN and ANTX, respectively, while rate constants for reactions of permanganate with MC-LR, CYN and ANTX are 357, 0.3 and $2.3 \times 10^4\,M^{-1}s^{-1}$, respectively. Accordingly, the oxidation of the mentioned toxins has been calculated (using Equation (1)) in some experiments performed with LW water by using these rate constants and the CT values determined by Equation (2). The
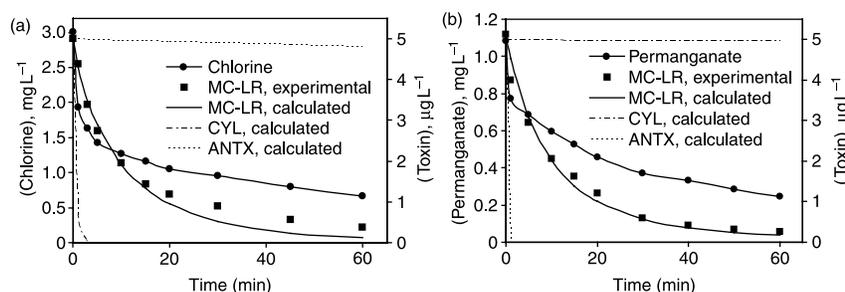
Figure 9 | Toxin oxidation during LW water treatment with (a) chlorine ($3.0\,mgL^{-1}$, pH 7.3, 20°C) and (b) permanganate ($1.1\,mgL^{-1}$, pH 7.2, 20°C). Symbols represent measured data for MC-LR and lines represent model calculations.

results are shown in Figure 9, where the lines represent the model calculations and the symbols the experimental results (only for MC-LR). The good coincidence between experimental and predicted values for MC-LR indicates that this kinetic approach can be successfully applied to predict the oxidation of micropollutants in natural waters.

The natural water from Lake "Villar del Rey" is the drinking water source for the city of Badajoz. This surface water is oxidized with permanganate and chlorine under similar conditions to those applied in this study. From the results depicted in Figure 9, it can be assumed that chlorine is an excellent oxidant for the removal of dissolved CYN and also a feasible option for the oxidation of MC-LR if the pH is kept below 8, and the total THM formation is under the drinking water standard value. However, chlorine is not able to oxidize ANTX. Similarly, permanganate is a feasible oxidant for the elimination of MC-LR and specially ANTX. However, permanganate is not able to oxidize CYN.

CONCLUSION

Chlorine and potassium permanganate are feasible oxidants for the elimination of MC-LR in natural waters if adequately applied. The oxidant doses required to reduce typical MC-LR concentrations found in natural water to below the WHO guideline value in drinking water of $1\,\mu gL^{-1}$ are 3 and $1\,mgL^{-1}$ for chlorine and permanganate respectively. These oxidant doses are within the range typically applied in waterworks. The temperature effect on the oxidation of MC-LR with both chlorine and permanganate in the range 10–25°C is slightly positive. However, while the pH effect is not significant for the oxidation with permanganate, the chlorination of MC-LR is favoured at neutral or slightly acidic pHs.

The water quality parameters play an important role on the efficiency of toxin elimination during the oxidation of natural waters for drinking water production. While high concentrations of NOM and ammonia hinder the elimination of toxins in the chlorination process, high bromide concentration can accelerate the oxidation process through the formation of HOBr. These results demonstrate that any water has to be calibrated with respect to the initial chlorine or permanganate dose needed to reach the oxidant CT required to remove the toxins. In addition, these findings are very valuable for choosing the applied oxidant dose and the operational conditions which result in an optimized oxidation process. These results can be used to design drinking water treatment systems which will efficiently remove the toxins from natural water sources, thus protecting public health.

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