Fact Sheet

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WCWC Walkerton Clean Water Centre
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CWAE Centre de Walkerton pour l'assainissement de l'eau
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Degradation of Microcystin-LR Using Chemical Oxidation Processes

Key Words: cyanotoxin, microcystins, drinking water, chlorine, ozone

Cyanotoxin Concerns

There has been increasing concern of environmental and human health impacts of cyanobacterial blooms in surface waters. In Ontario, reports of toxic cyanobacteria blooms in the Great Lakes and other watersheds have increased significantly since the 1990s (Winter et al., 2011). Cyanobacteria (blue-green algae) not only produce taste and odour compounds (e.g. geosmin and 2-Methylisoborneol), but can also produce cyanotoxins, which are considered as emerging contaminants in the water treatment industry. One of the most common cyanotoxins is microcystins. High levels of cyanotoxins in drinking water may cause adverse health effects on the nervous system and liver (US EPA, 2012).

Microcystins Standards in Ontario

Microcystins are the most widespread cyanotoxins that are present in natural waters. About 80 microcystin variants have been identified with microcystin-LR (MC-LR) being the most common variant (Sharma et al., 2012). Because of the toxicity of MC-LR, Ontario Drinking Water Quality Standard (O. Reg. 169/03) has established a maximum acceptable concentration of 1.5 µg/L for MC-LR.

Water Treatment Challenges

Microcystins are produced within several species of cyanobacteria and can be released into the water from stressed or unhealthy cells. The challenge of water treatment is to remove both intact cyanobacterial cells and released toxins. Oxidation before cell removal should be avoided during a cyanobacteria bloom event, since this can rupture cells and release toxins (Zamyadi et al., 2012). Additional treatment may be required to treat released toxins, however, any substantial adjustments should be reviewed by professionals. MC-LR can be oxidized from natural waters with certain oxidants and disinfectants typically applied in water treatment. For example, ozonation and advanced oxidation processes (AOPs) provide promising treatment options to destroy cyanotoxins (Sharma et al., 2012).

Chemical Oxidation Processes

Chlorine can oxidize MC-LR and reduce the concentration; however, an increase of pH reduces the MC-LR oxidation rate (Acero et al., 2005). It is best to keep pH<8 when chlorine is used. Chlorine-based weaker oxidants such as chloramine and chlorine dioxide have no significant effect on MC-LR degradation (Rodríguez et al., 2007). Permanganate is more reactive than chlorine in degrading MC-LR (Rodríguez et al., 2007). Ozone is more efficient in degrading MC-LR than chlorine and permanganate regardless of pH (Rodríguez et al., 2007). Alternative to conventional oxidative methods, AOPs generate highly oxidizing hydroxyl radicals to oxidize contaminants. It has been found that AOPs are the most effective oxidative method to degrade MC-LR (Sharma et al., 2012). Therefore, the efficiency order is AOP > ozone > permanganate > chlorine.

Comparing CT Values

The use of oxidants or disinfectants to inactivate microorganisms is commonly measured as CT value, which is the residual oxidant concentration (C) multiplied by the contact time (T). For example, CT values for the inactivation of *Giardia lamblia* cysts by various disinfectants at different pH are in the Procedure for Disinfection of Drinking Water in Ontario (Ontario MOE, 2006). Since there are no standardized CT values for the degradation of MC-LR, CT values for cyanotoxins inactivation can be compared with the standardized CT values required for inactivation of *Giardia lamblia* cysts.

The CT values for 0.5-, 1-, 2-log inactivation of *Giardia lamblia* cysts using free chlorine at 20^{0}C are shown in Figure 1 (dotted line), given a free chlorine residual of 1mg/L. According to the Procedure for Disinfection of Drinking Water in Ontario (Ontario MOE, 2006), at least 0.5-log (68%) inactivation of *Giardia lamblia* cysts must be provided by the disinfection portion of the overall treatment processes. When the CT for 2-log inactivation (99% inactivation) of *Giardia lamblia* cysts is used, 1-log removal of MC-LR can be achieved when pH is lower than 7.5. At pH higher than 7.5, the CT required for 1-log removal of MC-LR is higher than the CT for 2-log inactivation of *Giardia*.

The CT for ozone to achieve 2-log removal of cyanotoxins for a range of pH 6-9 is shown in Figure 2. Ozone is very effective at inactivating MC-LR. Even if the CT for 0.5-log inactivation of *Giardia lamblia* cysts is used, a 2-log removal of MC-LR can be easily achieved.

Although MC-LR concentration in treated water can be reduced by chlorine and ozone, the level of reduction needed to meet the regulation is dependent on the concentration in the raw water. For example, if MC-LR concentration in raw water is 100 μg/L and only chlorine is used to treat the water, 2-log removal of MC-LR is needed to reduce the level to 1 μg/L, which is lower than the regulated value (1.5 μg/L). In this situation, applying chlorine CT to achieve 1-log removal of MC-LR would be insufficient as the final concentration of MC-LR would be 10 μg/L.

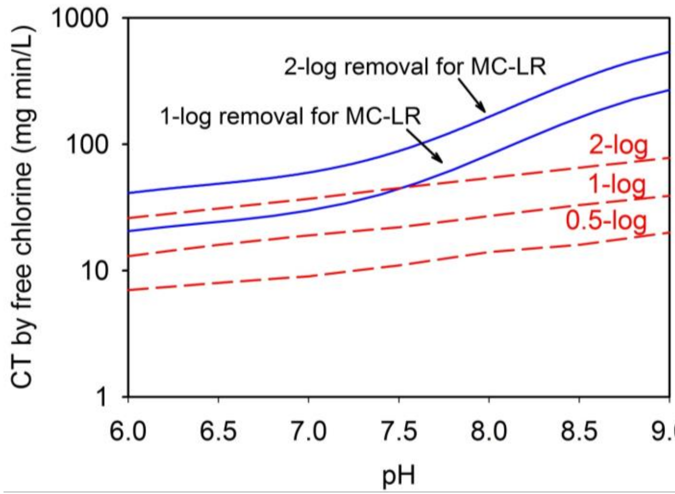

Figure 1. CT (mg·min/L) values of free chlorine for microcystin-LR. Dotted lines represent CT values for 0.5-, 1-, 2-log inactivation of *Giardia lamblia* cysts by free chlorine at 20^{0}C.

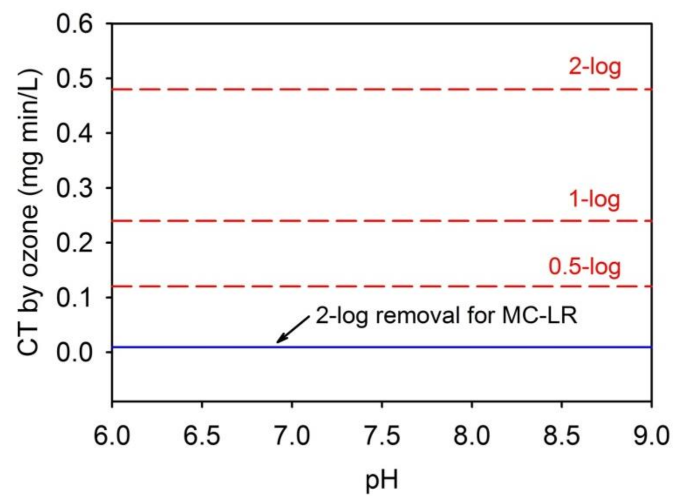

Figure 2. CT (mg·min/L) values of ozone for microcystin-LR. Dotted lines represent CT values for 0.5-, 1-, 2-log inactivation of *Giardia lamblia* cysts by ozone at 20^{0}C.

Influencing Factors

A number of factors influence the chemical oxidation of cyanotoxins in natural water. For example, the presence of natural organic matter (NOM) would influence the effectiveness of the oxidation of cyanotoxins (Rodríguez et al., 2007). Therefore surface waters with high NOM require higher chlorine doses to oxidize released cyanotoxins (Acero et al., 2005). If higher doses of a disinfectant are needed to degrade cyanotoxins, the chlorination in the distribution system must still maintain sufficient residuals and comply with the disinfection by-product standard.

In addition, temperature has an effect on toxin degradation. As water temperature increased, the toxin degradation from ozone and chlorine increased and CT requirements were reduced (Al Momani & Jarrah 2010).

The CT analysis in this study is based solely on the reaction rate constant of MC-LR and should be used with great caution. In a full-scale application of chemical oxidants for the degradation of MC-LR, a site-specific investigation should be conducted to account for those influencing factors.

Reference

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