Membrane Water Treatment, *Vol. 9, No. 3 (2018) 173-179*
DOI: https://doi.org/10.12989/mwt.2018.9.3.173

Developing numerical method to predict the removal of Microcystin-LR in a clear well

Inhee Yeo[1], Yong-Gyun Park[2] and Dooil Kim*[1]

[1]*Civil and Environmental Engineering, Dankook University, Yonginsi, 448-701 Korea*
[2]*Environmental Process Engineering Team, GS E&C, 33, Jong-ro, Jongro-gu, Seoul, 03159, Korea*

(Received November 5, 2017, Revised May 3, 2018, Accepted May 7, 2018)

Abstract. Microcystin-LR, one of algal toxins induced by the eutrophication of a reservoir, is known to be harmful to human by adversely affecting our liver and brain. Hypochlorous acid is very efficient to remove Microcystin-LR in a clear well. The previous researches showed that CT, pH and temperature affected removal rate in batch tests. It was noted that hydrodynamic properties of clear well could also influence its removal rate. A mathematical model was built using an axial dispersion reactor model and software was used to simulate the removal rate. The model consisted of the second order differential equations including dispersion, convection, Microcystin-LR reaction with chlorine. Kinetic constants were obtained through batch tests with chlorine. They were 0.430×10^{-3} L/mg/sec and 0.143×10^{-3} L/mg/sec for pH 7.0 and 8.1, respectively. The axial dispersion reactor model was shown to be useful for the numerical model through conservative tracer tests. The numerical model successfully estimated the removal rate of Microcyctin-LR in a clear well. Numerical simulations showed that a small dispersion number, low pH and long hydraulic retention time were critical for higher removal rate with same chlorine dosage. This model could be used to optimize the operation of a clear well during an eutrophication season.

Keywords: Microcystin-LR; clear well; chlorine; axial dispersion reactor model; numerical simulation; dispersion number

1. Introduction

Eutrophication occurs in a river due to the addition of artificial or natural nutrients. It generally induces the increase of pH, the reduction of dissolved oxygen (DO) and visual nuisance in a water system (Choi *et al.* 2006). Also, it has various negative impacts on water treatment processes, representatively blocking filters and reducing the efficiency of coagulation and sedimentation (Shen *et al.* 2011). And more public attention can be paid if eutrophication occurs in a drinking water resource because the growth of Cyanobacteria, known as blue-green algae, generates toxic compounds such as Microcystins (Hakim *et al.* 1970). It has been reported that Microcystins' poisonings can cause mass stranding of fish and shellfish and bleeding of mammals' liver (Galey *et al.* 1987, Carmichael 1992). They are also highly toxic to human beings; even the small amount in drinking water is very harmful to the liver because it stimulates the growth of cancerous tumors on it (USEPA 2015).

The molecular weight of Microcystins is around 1,000 daltons with low polarity. They are very stable to temperature (Lawton and Robertson 1999). Microcystins is a cyclic heptapeptide consisted of seven amino acids linked by peptide bonds and it is differentiated into above 80 types by substitution of two L-amino acid (Harada *et al.* 1991). Among them, Microcystin-LR (MC-LR) is known as the most toxic compound (Sivonen *et al.*). Because of the toxicity of MC-LR, the World Health Organization (WHO) suggests 1.0 μg/L of a drinking water guidance value (WHO 1998). The maximum allowable concentrations in Germany, Canada and Japan are ranged from 1.0 to 1.5 μg/L (WHO 1998).

The effective removal methods of MC-LR are an oxidation process with ozone, chlorine and TiO_2; coagulation and filtration followed by sedimentation; and a treatment process with granular activated carbon or powdered activated carbon (Lawton and Robertson 1999, Lawton and Edwards 2001, Rapalaa *et al.* 2002). Since Hoffman investigated the removal of MC-LR with chlorine, there have been various studies of the effective oxidants including ozone, hydroxyl radical, hydrogen peroxide and permanganate (Tsuji *et al.* 1997, Hoffmann 1976, Miao and Tao 2009, Rodriguez *et al.* 2007). Even though the advanced water treatment technologies with ozone, activated carbon and TiO_2 were proved as an effective method of MC-LR removal, the more efficient technologies and materials are required to further enhance the construction and operation cost effectiveness (Tsuji *et al.* 1997). Compared with these technologies, chlorination doesn't require any additional facility in an existing water treatment plant because most water treatment plants generally have a chlorination system at a clear-well for disinfection with residual chlorine. Therefore, chlorination could be a very efficient option to remove MC-LR (Choi *et al.* 2001).

*Corresponding author, Professor
E-mail: dikim21@dankook.ac.kr

http://www.techno-press.org/?journal=mwt&subpage=7
ISSN: 2005-8624 (Print), 2092-7037 (Online)

Oxidation methods for blue-green algae removal before a coagulation process, such as pre-chlorination and pre-ozonation induce the increase of the amount of coagulants necessary for treating the released intercellular organic matters of algal cells (Brookea *et al.* 2006, Park *et al.* 2006). If the toxic compounds of blue-green algae existed inside cells are released to water by oxidation, it is needed to remove the compounds as well as blue-green algae from water (Park *et al.* 2006). Therefore, it was reported that chlorination and ozonation after a coagulation process were more appropriate (Park *et al.* 2006, Nicholson *et al.* 1994). The MC-LR removal rate by chlorination depends on chlorine concentration, contact time, pH, temperature and its chemical structures (Brookea *et al.* 2006, Nicholson *et al.* 1994). According to the experimental results of MC-LR removal with aqueous chlorine, 100% removal of 10 μg/L of MC was achieved within 60 minutes with less than 3.0 mg Cl_2/L of chlorine concentration (Choi *et al.* 2001). As pH decreased, the ratio of hypochlorous acid (HOCl) is increased. And it can enhance MC-LR removal rate (Nicholson *et al.* 1994, Acero *et al.* 2005). The removal rate of MC-LR was known to be lower than the ones of MC-RR and MC-YR because it was a relatively stable compound compared with the others (Choi *et al.* 2001, Moreno *et al.* 2004). The temperature effect on Microcyctins' removal varies depending on its species. Although the removal rates of MC-RR and MC-YR were not affected by temperature from 15.0 to 35.0°C, the removal rate of MC-LR is proportional to temperature. The other study of MC-LR removal with 0.5 to 10.0 mg Cl_2/L found that with above 3.0 mg Cl_2/L and by increasing CT, the intracellular MC-LR concentration was decreased and the dissolved MC-LR was increased (Park *et al.* 2006). Therefore, the total amount of all toxic compounds was not changed, which means that the intracellular toxin was released out of cell. Acero *et al.* estimated the reduction coefficients of MC-LR, -RR and -YR depending on pH using a secondary reaction equation (Acero *et al.* 2005). As pH was increased from 4.8 to 8.8 at 20°C, the reduction coefficient was reduced 50 times but the temperature effect was not significant (Acero *et al.* 2005). Xagoraraki *et al.* conducted batch tests with reagent-grade and surface water samples (Xagoraraki *et al.* 2006). As CT (concentration × contact time) was increased at all levels of pH, the concentration of MC-LR in the sample decreased and it had a 1-log removal ratio at pH 6.0 (Xagoraraki *et al.* 2006).

Numerical simulation was required to predict effluent concentration at a clear well since experiments in a clear well was impossible because of the toxicity of MC-LR. Hydraulic and chemical decay kinetic terms were coupled to build a mathematical model (Kim *et al.* 2015). The hydraulics of the clear well at a water treatment plant could be described by a continuous stirred-tank reactor (CSTR) with complete mixing and a plug flow reactor (PFR) with perfect mixing in the radial direction but no mixing in the axial direction. CSTR and PFR are ideal flow and could not represent hydraulics of the clear well since flows in a reactor involves non-ideal patterns such as short-circuiting flow, rotational flow and dead zone (Kim *et al.* 2007).

A plug flow model with axial dispersion is called as Axial Dispersion Reactor (ADR) model. Tracer test is often used to verify if ADR model is suitable for mathematical model or not (Kim *et al.* 2007). The numerical ADR model for simulating MC concentration in a clear well is expressed by Eq. (1). Its dimensionless form is shown at Eq. (2). Hydraulic characteristics of a reactor affect the reaction efficiency. The dispersion number is one of critical factors for flow hydrodynamics in the ADR model. Low dispersion number is beneficial for enhancing removal efficiency under same operation conditions of a clear well.

$$\mathrm{E}\cdot\frac{d^2[\mathrm{MC}]}{dx^2}-\mathrm{U}\frac{d[\mathrm{MC}]}{dx}-k_R\cdot[\mathrm{MC}]\cdot[\mathrm{Cl_2}]=0 \qquad (1)$$

$$d\cdot\frac{d^2[\mathrm{MC}]}{dx^2}-\frac{d[\mathrm{MC}]}{dx}-k_R\cdot[\mathrm{MC}]\cdot[\mathrm{Cl_2}]=0 \qquad (2)$$

$$d=\frac{D}{UL} \qquad (3)$$

where [MC] is MC-LR concentration, $[Cl_2]$ is residual chlorine concentration as Cl_2, E (m^2/s) is diffusivity, x(m) is the distance from the inlet of each chamber in the axial direction, k_R (L/mg/sec) is a second-order MC-LR decay rate constant, U (m) is axial velocity, L (m) is the axial distance from inlet to outlet and d is a dispersion number.

In this study, a mathematical model for predicting MC-LR concentration in a clear well was developed and applied to six clear wells with kinetic parameters obtained from batch tests from pH 7.0 and 8.1. MC-LR decay kinetic constants were obtained from batch tests. Dispersion numbers were obtained from six clear wells from tracer tests. The applicability of ADR model for MC-LR numerical simulation was verified and factors affecting on the MC-LR removal efficiencies at a clear well were revealed. Also, simulations were carried out to predict MC-LR concentration for six clear wells at pH 7.0 and 8.1.

2. Experimental method

2.1 Clear well and tracer tests

The dimension, flow rate, depth of each clear wells are shown at the Table 1. A tracer test was performed to evaluate the applicability of the ADR model and to estimate its dispersion number at each clear well. Tracer was injected by pulse and then tracer concentration was measured at the outlet of a clear well. High purity sodium fluoride was used as a tracer because it was non-reactive in a clear well. The fluoride concentration applied for the tests did not exceed 1.0 mg/L of drinking water quality standard in South Korea. The stock solution was injected into filtrated water holding tank before transferred to a clear well. Fluoride concentration was measured at the outlet of a clear well with an ion sensor (Thermo Scientific, USA) at every one hour.

2.2 MC-LR extraction

MC-LR was extracted from an algae solution collected from a lake in South Korea. The algal cell in a 500 mL

Table 1 Dimension, flow rate and water level of clear wells

	Size (m^2)	Flow (m^3/hr)	Water Level (m)
A	W 22.0m × L 35.0m × H 4.0m × 2	2,239	2.8 ~ 3.7
B	W 15.0m × L 22.1m × H 5.0m × 6	2,359	2.5 ~ 4.5
C	W 15.0m × L 25.0m × H 4.5m × 2	510	3.0 ~ 4.3
D	W 24.4m × L 27.8m × H 4.0m × 2	2,005	2.0 ~ 2.5
E	W 12.0m × L 12.0m × H 4.5m × 2	163	3.5 ~ 4.2
F	W 15.0m × L 25.0m × H 4.5m × 2	1,722	2.2 ~ 2.25

beaker was destroyed by an ultra sonicator for 60 minutes. And then, 300 mL of the sample was filtrated by a nylon membrane filter with a 0.8 μm pore size and with a vacuum pump (Welch 2522C-10, USA). The remained sample in a 100 mL square volumetric flask (Pyrex, USA) was extracted with 10 mL of 80% methanol solution for 30 minutes. To increase the extraction efficiency, 0.1% trifluoroacetic acid (Sigma-Aldrich, USA) and surfactant (Tween 20, Sigma-Aldrich, USA) was added while agitating it with a magnetic stirrer. The extracted MC-LR solution was separated with a centrifugal separator (Smart 15, Hanil, Korea) at 6,800 RPM for 5 minutes and then, the supernatant solution was filtrated with GF/C filters (Whatman, USA). The extracted MC-LR concentration was 2.94 μg/L.

2.3 Batch test for decay coefficient of MC-LR

The decay coefficient (k_R) of MC-LR by residual chlorine was estimated from batch tests. The experiments were conducted at room temperature (20±3°C) and residual chlorine solution was prepared with sodium hypochlorite (Sigma-Aldrich, USA). The extracted MC-LR was diluted in a 250 mL amber bottle with DI water and then the test was conducted for 30 minute after the injection of a chlorine solution. MC-LR concentrations from samples were measured after removing residual chlorine with ascorbic acid (Showa, Japan).

2.4 Residual chlorine and MC-LR analysis

The residual chlorine concentration was measured with a DPD reagent and an UV-VIS spectrophotometer (Hach DR5000, USA). The EnviroLogix QualiTube kit was used for MC-LR analysis, which used a competitive Enzyme-Linked Immuno Sorbent Assay (ELISA). MC-LR concentration was measured with an UV-VIS spectrophotometer (Hach DR5000, USA) after serial processing. The effective analysis concentration with the kit was ranged from 0.5 to 3 μg/L.

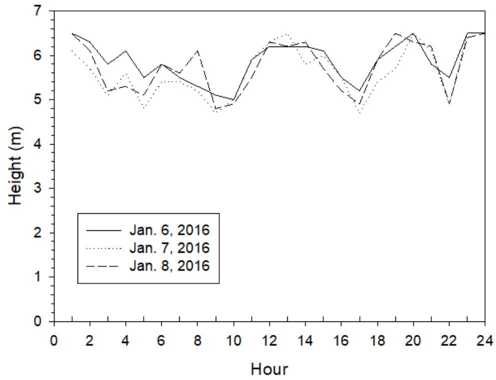


Fig. 1 Water height variation of a representative clear well in Korea over 24 hours in a clear well

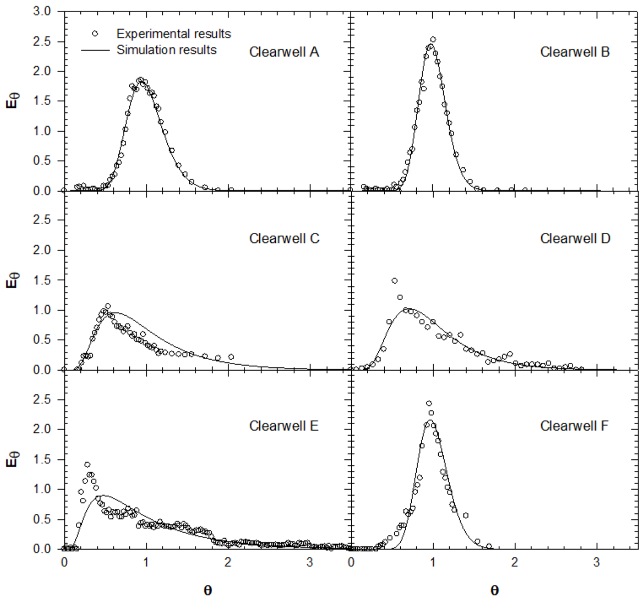


Fig. 2 Tracer test results from six clear wells with dimensionless axis

Table 2 Dispersion number, R^2, average residence time and fluoride recovery rate

Clear well	Dispersion number	R^2	$T_{average}$ (min)	Fluoride recovery rate(%)
A	0.0300	0.9637	186.00	87.5
B	0.1060	0.7986	157.36	83.1
C	0.2093	0.9615	252.86	84.3
D	0.1422	0.8902	149.05	77.5
E	0.4102	0.7857	383.13	86.7
F	0.0269	0.8826	71.09	84.7

3. Results and discussion

3.1 Tracer tests

Tracer test results were obtained from six clear wells in drinking water treatment plants. The purpose of tracer test was to investigate hydrodynamic characteristics in each clear well. A clear well is a reservoir in a water treatment plant and used to store treated water for several hours before transmitted to a distribution reservoir. Chlorine was injected just before a clear well for pathogen disinfection and reacted with MC-LR.

The depth of a clear well was varied according to pumping schedule to a distribution reservoir. Fig. 1 shows the depth variation of a representative clear well in Korea over 24 hours for the date of Jan. 6th, 7th and 8th of 2016. The average depths were 5.88 m, 5.64 m and 5.76 m, respectively. The standard deviations were 0.47 m, 0.60 m and 0.59 m respectively, which were around 10% of water depths. The depth fluctuations were not severe because residence time in a clear well required to be secured to guarantee marginal CT (Concentration×Residence Time) for disinfection credit. Hence, it was assumed that the effect of depth variation might be minor.

Although diverse hydrodynamic model could be applied to a clear well for numerical simulation, the ADR model was selected and its adaptability needed to be verified. The ADR model was fitted to normalized tracer results as shown at Fig. 2. While tracer results of clear wells fitted well with the ADR model, clear well C and E were not fitted well with the ADR model. Their tracer pattern implied that there might be short circuiting and recursive flow in the clear well (Kim *et al.* 2010). The existence of such non-ideal flow resulted in high dispersion number as shown at Table 2. Table 2 shows the dispersion number, T_{10} and average residence time of clear wells. Dispersion numbers were ranged from 0.0269 to 0.4102, which reflected diverse hydrodynamics according to internal geometry of each clear well. The R^2 ranged from 0.7857 to 0.9634, which showed that axial dispersion model could be applied to simulate hydrodynamics of clear wells.

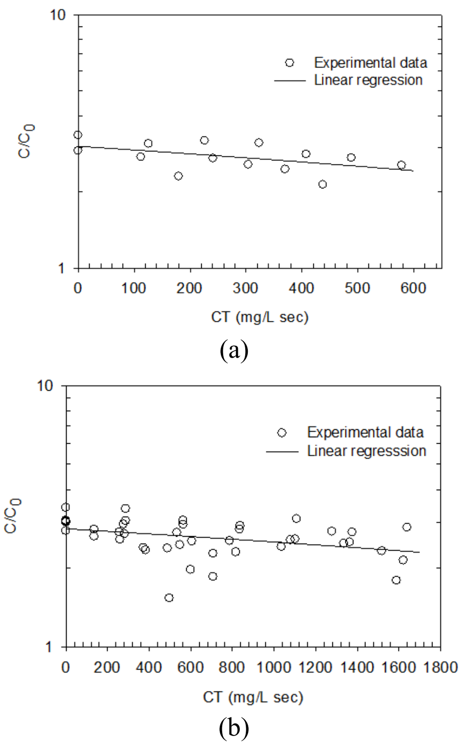


Fig. 3 MC-LR decay kinetics at pH 7.0 (a) and 8.1 (b) at 20°C

Table 3 Kinetic constants obtained from batch tests

pH	Temperature (℃)	$C_{MC\text{-}LR}$ (μg/L)	k_{Cl} (1/sec)	k_R (L/mg/sec)
7.0	20.4	3.12	12.60×10^{-3}	0.430×10^{-3}
8.1	23.8	3.15	2.140×10^{-3}	0.143×10^{-3}

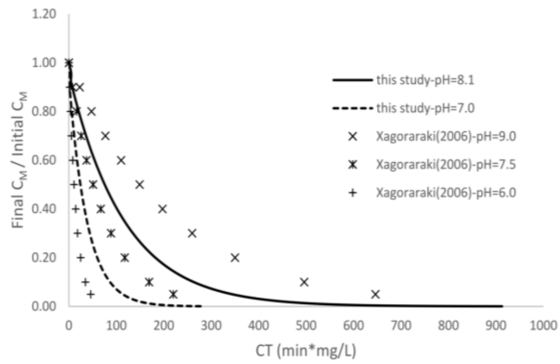


Fig. 4 Comparison of MC-LR decay kinetics with previous research results (Xagoraraki *et al.* 2006)

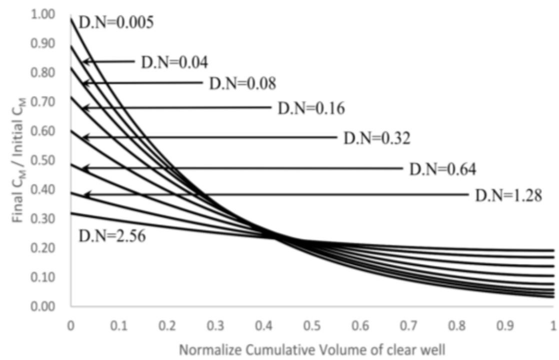


Fig. 5 The effect of a dispersion number on the MC-LR concentration profiles

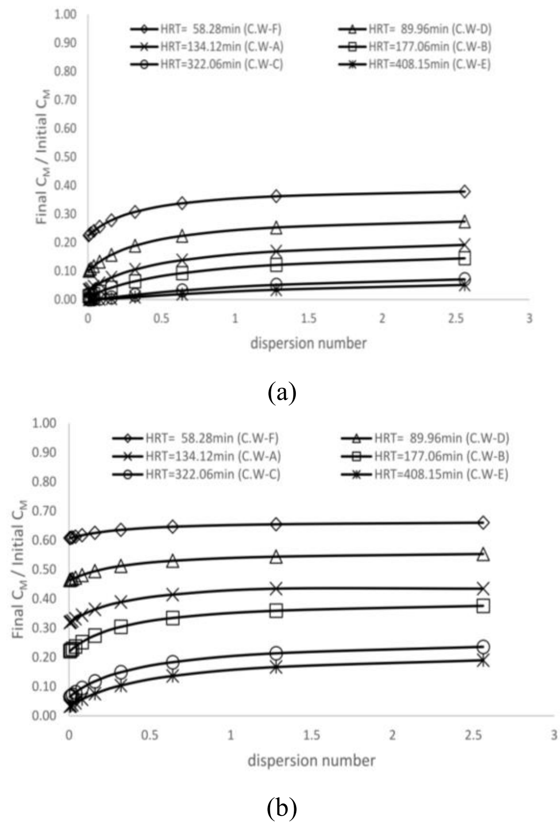
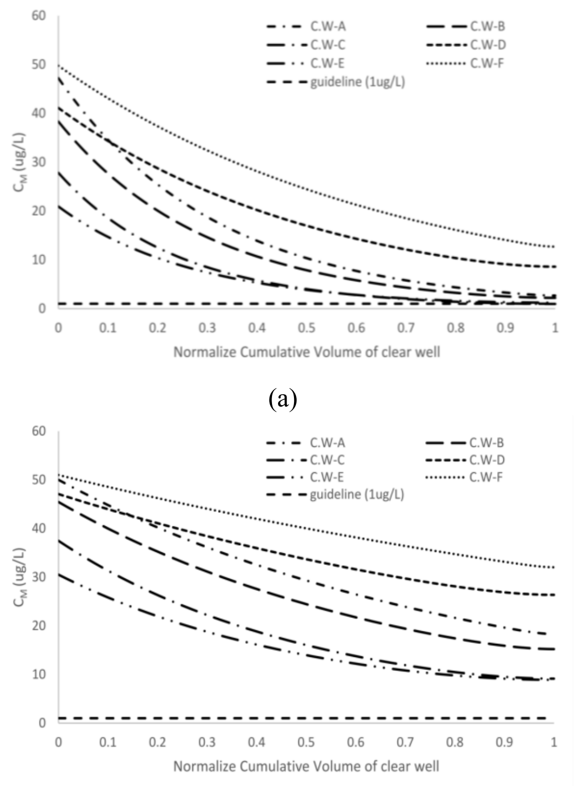


Fig. 6 The effect of a dispersion number on the MC-LR effluent concentration, (a) for pH 7.0 and (b) for 8.1



(a)

(b)

Fig. 7 Concentration profile in clear wells, (a) for pH 7.0 and (b) for 8.1

3.2 Decay kinetics of MC-LR

MC-LR reacted with free chlorine in a clear well. MC-LR reaction kinetics with free chlorine could be expressed with second order kinetics (Xagoraraki *et al.* 2006).

$$\frac{d[Cl_2]}{dx} = -k_{Cl} \cdot [Cl_2] \tag{4}$$

$$\frac{d[MC]}{dx} = -k_R \cdot [MC] \cdot [Cl_2] \tag{5}$$

where $[Cl_2]$ (mg/L) is chlorine concentration, [MC] (mg/L) is MC-LR concentration, k_{Cl} (1/sec) is a chlorine decay kinetic constant, k_R (L/mg/sec) is a MC-LR decay kinetic constant and x (sec) is time. Fig. 3 shows batch experimental results for MC-LR with chlorine at pH 7.0 and 8.1 at 20^{o}C. The decay kinetics was well expressed with kinetic equations shown at Eq. (4) and Eq. (5). The kinetics results were compared with Xagoraraki *et al.* (2006) and showed good compatibility as shown at Fig. 4 (Xagoraraki *et al.* 2006). Table 3 summarizes the kinetic constants obtained in this study.

3.3 Effect of a dispersion number on MC-LR removal

It was shown that dispersion in a clear well could affect the removal efficiency of MC-LR. The effect of dispersion number was investigated by changing the dispersion number. Simulation results showed that removal efficiencies were affected by dispersion numbers. Fig. 5 shows effects of dispersion numbers on removal of MC-LR at clear well A and pH 7.0. lower dispersion number showed higher removal efficiency in the clear well. Final effluent dimensionless concentrations were 0.033 and 0.192 for dispersion numbers 0.005 and 2.56, respectively. Clear well with a lower dispersion number showed much better capability to remove the MC-LR. At a higher dispersion number, concentration in the initial stage of clear well was low because of the dilution effect in the reactor. From this figure, it was shown that designing a clear well with a low dispersion number was important.

Additional simulations were conducted with six clear wells at pH 7.0 and 8.1 to show the effect of the dispersion number on removal efficiencies as shown Fig. 6. Lower dispersion number showed better removal efficiencies for both pH 7.0 and 8.1. The effects of the dispersion number were critical for both pH 7.0 and pH 8.1. Additionally, higher hydraulic residence time was important for higher removal efficiencies for both pH 7.0 and 8.1 at the Fig. 6.

3.4 MC-LR removal simulation for each clear well

Fig. 7 shows MC-LR concentration profiles in each clear well at pH 7.0 and 8.1, assuming that influent concentration was extremely high (i.e., 51.67μg/L). The initial free chlorine concentration was assumed to be 0.5 mg Cl_2/L. The removal efficiencies of MC-LR were known to be affected by residence time, chlorine concentration, removal kinetic constants and dispersion number. Since the kinetic constant was smaller at higher pH, simulation results at pH 8.1 showed lower removal efficiency than ones at pH 7.0 for each clear well. Clear well F showed the worst performance for MC-LR removal at a short residence time (i.e., 58 min.) even though it had a small dispersion number (i.e., 0.0269). Although all clear wells could not satisfy WHO' MC-LR guideline (i.e., 1.0 μg/L) at both pH 7.0 and pH 8.1 against extremely high influent concentration, some clear wells could remove it less than 1.0 μg/L with same hydraulic residence time, pH and chlorine concentration if the dispersion number is decreased. Clear well B, C and E could satisfy WHO guideline at pH 7.0 if the dispersion number is decreased to 0.04, 0.32 and 0.64, respectively.

Designing a clear well with a smaller dispersion number is possible by increasing length to width ratio using the equation shown at Eq. (6) (Kim *et al.* 2015, Moustiri *et al.* 2001).

$$d = \frac{E}{UL} = \frac{0.25 \times D_p \times U}{UL} = \frac{0.25}{\left(\frac{L}{D_p}\right)} \tag{6}$$

where, E is diffusivity (m^2/s), U (m) is axial velocity, L (m) is axial length and D_p (m) is wetted perimeter. From Eq. (6), it could be known that a smaller hydraulic diameter and a longer channel length were beneficial for a lower dispersion number. Clear well with an internal baffle along axial direction could decrease the dispersion number (Kim *et al.* 2015). Increasing the number of successive chambers could be another option to decrease a dispersion number in a clear well. The dispersion number of a clear well with multiple successive CSTRs in series could be acquired using Eq. (7), proposed by Villermaux (Villermaux 1982).

$$Pe = \frac{1}{d} = 2.0 \times N + 1 \tag{7}$$

where, Pe is Péclet number and N is the number of chambers.

4. Conclusions

The tracer test showed that the ADR model could be used for numerical simulation of a clear well. Kinetic parameters were obtained through batch tests with residual chlorine and MC-LR. MC-LR decay coefficients were 0.430×10^{-3} L/mg/sec and 0.143×10^{-3} L/mg/sec for pH 7.0 and 8.1, respectively. A numerical model was built with the ADR model which is composed of the second order differential equations including dispersion, convection and the reaction of MC-LR and residual chlorine. The ADR model was successfully applied to estimate the treatability of MC-LR in a clear well. Numerical simulation showed that low dispersion number, low pH and longer hydraulic detention time were preferred for better removal of MC-LR. Assuming the extremely high influent concentration (i.e., 51.76 μg/L and 0.5 mg Cl_2/L of initial chlorine concentration at clear wells, some clear well could satisfy the WHO guideline with low pH, higher chlorine concentration and long hydraulic retention time with a smaller dispersion number. A small dispersion number and low pH were shown to be critical to treat MC-LR in a clear well if the capacity expansion and increasing chlorine concentration were limited. This numerical method could be used to optimize the operation of a clear well during a severe eutrophication season.

References

Acero, J.L., Rodriguez, E. and Meriluoto, J. (2005), "Kinetics of reactions between chlorine and the cyanobacterial toxins microcystins", *Water Res*, **39**(8), 1628-1638.

Brookea, S., Newcombe, G., Nicholson, B. and Klass, G. (2006), "Decrease in toxicity of microcystins LA and LR in drinking water by ozonation", *Toxicon*, **48**(8), 1054-1059.

Carmichael, W.W. (1992) *A Status Report of Planktonic Cyanobacteria (Blue-Green Algae) and Their Toxins*, United States Environmental Protection Agency, Washington, D.C., U.S.A.

Choi, I.H., Kim, S.K., Kim, H.C. and Kim, S.H. (2001), "Removal characteristics of microcystins by chlorination", *Kor. Soc. Environ. Eng.*, **23**(6), 903-910.

Choi, S.K., Lee, J.Y., Kwon, D.Y. and Cho, K.J. (2006), "Settling characteristics of problem algae in the water treatment process", *Water Sci. Technol.*, **53**(7), 113-119.

Galey, F.D., Beasley, V.R., Carmichael, W.W., Kleppe, G., Hooser, S.B. and Haschek, W.M. (1987), "Blue-green algae (Microcystis aeruginosa) hepatotoxicosis in dairy cows", *Am. J. Vet. Res.*, **48**(9), 1415-1420.

Harada, K.I., Ogawa, K., Matsuura, K., Nagai, H., Murata, H., Suzuki, M. and Nakano, M. (1991), "Isolation of two toxic heptapeptide microcystins from an axenic strain of Microcystis aeruginosa, K-139", *Toxicon*, **29**(4), 979-984.

Hakim, K.E., Abbas, M. and Moursi, H. (1970), "Control of algae in Alexandria water treatment plant", *J. Egypt Public Health Assoc.*, **45**(4), 323-340.

Hoffmann, J.R.H. (1976), "Removal of microcystis toxins in water purification processes", *Water SA*, **2**(2), 58-60.

Kim, D., Lee, K.H., Lee, H.S., Kim, Y.J. and Hyun, I.H. (2015), "The hydrodynamics of an ozone contactor with horizontal meandering flow to enhance disinfection efficiency", *Desalin. Water Treat.*, **54**(4-5), 1150-1157.

Kim, D.I., Hasan, S., Tang, G., Couillard, L., Shijkairy, H. and Kim, J.H. (2007), "Simultaneous simulation of pathogen inactivation and bromate formation in full-scale ozone contactors by computer software", *J. Am. Water Work. Assoc.*, **99**(8), 77-91.

Kim, D., Nemlioglu, S., Roberts, P.J.W. and Kim, J.H. (2010), "Ozone-contactor flow visualization and quantification using three-dimensional laser-induced fluorescence", *J. Am. Water Work. Assoc.*, **102**(1), 90.

Lawton, L.A. and Robertson, P.K.J. (1999), "Physico-chemical treatment methods for the removal of microcystins (cyanobacterial hepatotoxins) from potable waters", *Chem. Soc. Rev.*, **28**(4), 217-224.

Lawton, L.A. and Edwards, C. (2001), "Purification of microcystins", *J. Chromatograh. A*, **912**(2), 191-209.

Miao, H. and Tao, W. (2009), "The mechanisms of ozonation on cyanobacteria and its toxins removal", *Sep. Purif. Technol.*, **66**(1), 187-193.

Moreno, I.M., Maraver, J., Aguete, E.C., Leao, M., Gago-Martínez, A. and Cameán, A.M. (2004), "Decomposition of microcystin-LR, microcystin-RR and microcystin-YR in water samples submitted to in vitro dissolution tests", *J. Agric. Food Chem.*, **52**(19), 5933-5938.

Moustiri, S., Herbrard, G., Thakre, S. and Roustan, M. (2001), "A unified correlations for predicting liquid axial dispersion coefficient in bubble columns", *Chem. Eng. Sci.*, **56**(3), 1041-1047.

Nicholson, B.C., Rositano, J. and Burch, M.D. (1994), "Dessruction of Cyanobacterial peptide hepatotoxins by chlorine and chloramines", *Water Res.*, **28**(6), 1297-1303 .

Park, H.K., Seo, Y.C., Cho, I.H. and Park, B.H. (2006), "Effect of chlorination on disinfection byproducts production and release of microcystins from bloom-forming algae", *J. Kor. Soc. Water Qual.*, **22**(3), 513-520.

Rapala, J., Lahtia, K., Rasanen, L.A., Esalab, A.L., Niemela, S.I. and Sivonen, K. (2002), "Endotoxins associated with cyanobacteria and their removal during drinking water treatment", *Water Res.*, **36**(10), 2627-2635.

Rodriguez, E., Onstad, G.D., Kull, T.P.J., Metcalf, J.S., Aceroa, J.L. and Gunten, U.V. (2007), "Oxidative elimination of cyanotoxins: Comparison of ozone, chlorine, chlorine dioxide and permanganate", *Water Res.*, **41**, 3381 - 3393.

Shen, Q.H., Zhu, J.W., Cheng, L.H., Zhang, J.H., Zhang, Z. and Xu, X.H. (2011), "Enhanced algae removal by drinking water treatment of chlorination coupled with coagulation", *Desalination*, **271**(1-3), 236-240.

Sivonen, K., Jones, G., Chorus, I. and Bartram, J. (1999), *Toxic Cyanobacteria in Water: A Guide to Public Health Significance, Monitoring and Management*, in *Cyanobacterial Toxins*, Chapman & Hall, London, U.K., 41-111.

Tsuji, K., Watanuki, T., Kondo, F., Watanabe, M.F., Nakazawa, H., Suzuki, M., Uchida, H. and Harada, K. (1997), "Stability of microcystins from cyanobacteria-IV. Effect of chlorination on decomposition", *Toxicon*, **35**(7), 1033-1041.

USEPA (2015), *Algal Toxin Risk Assessment and Management Strategic Plan for Drinking Water: Strategy Submitted to Congress to Meet the Requirements of P.L. 114-45*, United

States Environmental Protection Agency, Washington, D.C., U.S.A.

Villermaux, J. (1982), *Genie de la Reaction Chimique*, Lavoisier.

WHO (1998), *Guidelines for Drinking-Water Quality*, World Health Organization.

Xagoraraki, I., Zulliger, K., Harrington, G.W., Zeier, B., Krick, W. and Karner, D.A. (2006), "Ct values required for degradation of microcystin-LR by free chlorine", *J. Water Supply Res. Technol. Aqua*, **55**(4), 233-245.

CC

Abbreviations

ADR Axial dispersion reactor

CSTR Continuous stirred-tank reactor

CT Concentration × Residence Time

ELISA Enzyme-Linked Immuno Sorbent Assay

MC-LR Microcystins-LR

PFR Plug flow reactor

WHO World Health Organization