Wastewater Disinfection Efficiency Using One-Step and Two-Step Chlorination

Brilyana Bela Islami[1], C*indy Rianti* Priadi[1,*], *Sandyanto* Adityosulindro[1], and *Ayik* Abdillah[1]

[1]Environmental Engineering Study Program, Department of Civil Engineering, Faculty of Engineering, Universitas Indonesia, Indonesia

Abstract. One-step chlorination (OSC) is a common method, generally implemented as the last step of wastewater treatment plants (WWTPs) and water treatment plants (WTPs). Improving disinfection efficiency is necessary to increase pathogen and organic matter removal. Two-step chlorination (TSC) has been studied as a new method of chlorination. This study aimed to compare OSC and TSC efficiency for coliform and organic matter removal. Chlorination was performed in a batch system and at laboratory scale using calcium hypochlorite. Samples were collected from WWTP effluent in an industrial estate located in Indonesia. The samples underwent the adsorption process beforehand. Chlorine dosage at 10–110 mg/L, at a 10–200-second time interval, and with a dosage ratio of 3:1–7:1 were evaluated. Results showed that the optimum dose for OSC is 80 mg/L. The optimum condition for TSC is a 50-second time interval and a 5:1 dosage ratio between the two steps. With the same total dose as in OSC, TSC improved efficiency for COD, BOD, and coliform removal up to 12%, 35%, and 0.39-log reduction, respectively ($p < 0.05$). Moreover, trihalomethane (THM) formation was reduced up to 13% by using the TSC method. However, an increasing ammonia concentration occurred because of the OSC and TSC processes ($p < 0.05$).

1 Introduction

Clean water scarcity can be resolved by sustainable water management, such as water reclamation and water reuse [1]. Implementation of water reuse could reduce raw water intake, wastewater disposal to the environment, and operating cost, all while achieving green industry [2], [3]. Chlorination has the potential to form disinfection by-products (DBP) by the reaction between chlorine and precursor compounds, such as natural organic matter (NOM), humic acid, bromide, and iodide [4]. Previous studies have found that multistage chlorination is more effective than conventional methods, called one-step chlorination (OSC) [5]–[7]. These studies explained the effects of disinfection efficiency by modifying the chlorination dosing technique in several stages. Multistage chlorination is a new chlorine dosing technique, which is divided into several stages or steps. The allocation of dosing depends on dosage ratio and time interval. Types of multistage chlorination that

*Corresponding author: cindy.priadi@eng.ui.ac.id

have been studied are two-step chlorination (TSC) and three-step chlorination (TrSC). TSC is performed by dosing chlorine two times according to the dosage ratio and the time interval between the first and second dosing. The same technique is applied to TrSC, which requires three dosing times. In the OSC mechanism, there is a rapid decrease in chlorine concentration in the first 10 seconds after the first chlorine dosing. The background substances in water react with chlorine to form one of several types of chloramine, which will depend on the pH and chlorine concentration [6]. Monochloramine is generally formed at pH > 7 [8]. If formed, monochloramine will help oxidize the residual organic matter in water so that chlorine consumption is reduced during subsequent dosing [6]. This mechanism could result in higher residual-free chlorine concentrations in TSC and TrSC effluents than in OSC effluent. Consequently, disinfection efficiency in TSC and TrSC can lead to the higher removal of organic matter and pathogens [6], [7].

A previous study reported that a two-step addition of chlorine could reduce chlorine demand for the same level of *E.coli* removal [5]. However, the study was conducted at a preliminary stage and only one condition was reported: a 5-minute time interval and 20 minutes of contact time with the first and second chlorine dose at 2.5 and 2.5 mg/L. Other studies reported that TSC and TrSC could enhance *E. coli* removal with the same dose and contact time as OSC. The increasing efficiency of *E. coli* removal via TSC has resulted in a 1.02-log reduction when compared to OSC [6], while TrSC has resulted in a 0.73-log reduction [7]. To achieve the same efficiency as OSC, TSC is able to reduce the chlorine dose demand by up to 13%. Thereby, operational costs of up to 17% can be saved [6], and DBP formation can be reduced by up to 23% [7]. Based on these previous studies, the potential to improve chlorination efficiency by the TSC method is clear.

Accordingly, this study aimed to compare the disinfection efficiency of OSC and TSC on coliform and organic matter removal. Ammonia and THM formation were also studied to further compare the two methods.

2 Research Methodology

2.1 Experimental set-up

Wastewater samples were collected from WWTP effluent in an industrial estate located in Indonesia. WWTP has a treatment capacity of 10,800 m^3/day with 4,900 ± 1,025 m^3/day used. Wastewater was derived from industrial, commercial, and residential sites. Unit treatment installed in WWTP included a grit chamber, primary sedimentation treatment, an oxidation ditch, and a secondary sedimentation tank. For the purpose of this study, the WWTP effluent was processed using a pilot-scale adsorption column before chlorination. This adsorption process was aimed at optimizing the chlorination process by controlling turbidity in samples to remain under 5 NTU [9]. Based on a previous study, coconut shell-activated carbon and silica sand were used as the media in the reactor with a contact time of 26 minutes and a flowrate of 4 L/min [10]. The effluent of the adsorption process used for chlorination was sampled using the grab method. Samples were stored in a cooler box without direct contact from sunlight and were immediately transferred to prevent any changes of the constituents. Chlorination experiments were performed in a batch experiment and at laboratory scale using a calcium hypochlorite solution.

2.2 Experimental procedures

Initially, a preliminary test was conducted to obtain the optimum dose of chlorination. The chlorination test was adapted to APHA 4500-Cl B. Aliquots of the sample were chlorinated using the reported estimation dose for a batch experiment of 1.0–4.5 mg/L in a previous

study [5]. However, the dose of disinfectant had to be increased, with a new range of 10–110 mg/L, when the doses were considered too low, which was indicated by no change in color after the addition of starch solution. After 20 minutes of contact time, the chlorinated sample was titrated by 0.10 M natrium thiosulfate to halt the reaction. The optimum chlorine dose for the OSC experiment was identified by plotting residual-free chlorine in the breakpoint chlorination (BPC) curve. However, the optimum dose for TSC was not performed to determine the difference between OSC and TSC with the same chlorine dose. Residual-free chlorine was determined using equation 1, where *A* corresponds to the volume of titration for the sample, *B* corresponds to the volume of titration for blank (positive or negative), and *N* corresponds to the normality of $Na_2S_2O_3$.

$$mg\ Cl\ as\ Cl_2/L = \frac{(A \pm B) \times N \times 35{,}450}{mL\ sample} \quad (1)$$

To perform the TSC process, the time interval and chlorine dosage ratio were needed to obtain the optimum condition for the process. Initially, various time intervals of 10, 20, 50, 100, and 200 seconds with a dosage ratio of 1:1 were evaluated. Afterward, the optimum dosage ratio was assessed by varying the dosage ratio from 3:1 to 5:1 to 7:1. The selection of the optimum operating condition was based on the highest removal efficiency of coliform. After the optimum dose and operating condition were obtained, a comparison test of OSC and TSC was conducted. For the OSC test, aliquots of the sample were dosed with calcium hypochlorite solution for a 20-minute contact time; whereas the samples for the TSC test were chlorinated with the same total chlorine dose, but the dose was split into two portions at dosage ratios obtained in the preliminary test. The OSC and TSC tests were performed to determine the effect of the different methods on disinfection efficiency and DBP formation. Then, the samples were compared in terms of the removal efficiency of coliform, organic substances (BOD and COD), and ammonia. To further compare the efficiency of OSC and TSC, measurements of THM formation were conducted. Additionally, the temperature, turbidity, and pH parameters were measured to determine the parameters of the chlorination process.

2.3 Analytical method

The major portion of the samples were used for OSC and TSC, while the remaining samples were used for water quality analysis. The analysis was adapted to APHA (2012), as shown in Table 1. Interpretation was statistically analyzed to validate the analysis results through an independent sample *t*-test for the parametric test and a Mann Whitney test for the non-parametric test.

Table 1. Methodology for wastewater characteristics test

Parameter	Methodology
Temperature	APHA. 2550 B
pH	APHA. 4500-S^{2-} D
BOD	APHA. 5210 B
COD	APHA. 5220 C
Coliform	APHA. 5220 C
Turbidity	APHA 2130 B
Ammonia	APHA. 4500 F
THM	APHA. 6232 B

3 Results and Discussion

3.1 Optimum dosage

Chlorination was performed at the temperature, pH, and turbidity of 28.0 °C, 7.25, and 4.80 NTU, respectively. Samples were chlorinated using the chosen chlorine dose with 20 minutes of contact time. After 20 minutes, the chlorination process was halted by dechlorination, and the residual chlorine was obtained. The results were plotted in a BPC curve (shown in Figure 1). The BPC curve showed that three zones were divided in the chlorination process. Each zone represents the reaction that occurred at the range dose of the disinfectant. Zone I represents the process of chloramine and chloro-organic compound formation. In this zone, the amount of residual-free chlorine increased until all organic compounds that could be oxidized by chlorine had been exhausted [11]. Thus, the dose added in Zone I was not sufficient to oxidize organic compounds in the samples.

Zone II represents the destruction process of chloramines and chloro-organics by the oxidization of organic matter and microorganisms, called chloramination [11]. Chloramination produced nitrogen gas, nitrates, and chloride ions. The process continued until the BPC occured. The chlorine dose at BPC was used as an optimum chlorine dose for chlorination, which occurred when all ammonia and nitrogen compounds had been fully oxidized [12]. The optimum dose occurred at 80 mg/L, exactly at the transition point from Zone II to Zone III. The optimum dose at 80 mg/L was used for the OSC and TSC processes in the following experiments. Zone III represents the remaining unreacted chloro-organics and free chlorine. These remaining compounds were left when the oxidized organic compounds had been exhausted by chlorination. In other words, the chlorine dose used in this zone exceeded chlorine demand.

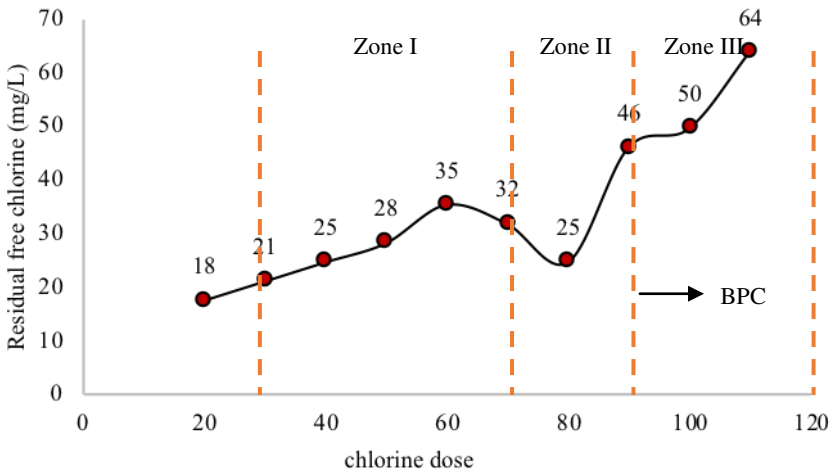


Fig. 1. BPC curve at determination of optimum chlorine dose for OSC.

3.2 Time interval and dosage ratio of chlorine for TSC

Time interval and dosage ratio tests were performed for two days consecutively. The parameters of temperature, pH, and turbidity for the first and second test were 28.3 °C, 7.13, and 6.45 NTU, and 29.5 °C, 7.10, and 6.70 NTU, respectively. Both tests did not meet the chlorination requirements (< 5 NTU) because of the high loading of influent wastewater

at the WWTP. The range of the chlorine dose, at 1.0–4.5 mg/L, with a contact time of 20 minutes was tested to obtain an optimum dose for OSC. The optimum dose obtained in the previous test (80 mg/L) was used in the operating parameter test for TSC. The operating parameter tests for TSC were time interval and dosage ratio of chlorine. The first test was performed to obtain the time interval, with the assumption of a 1:1 dose (first step 40 mg/L, second step 40 mg/L), a contact time of 20 minutes, and various time intervals: 10, 20, 50, 100, and 200 seconds. The optimum time interval was 50 seconds, with a coliform removal efficiency by up to 1.87-log reduction (Figure 2a). After the time interval was obtained, the second test was performed to determine the dosing ratio using the same optimum dose and contact time as the first test, but with a time interval of 50 seconds. As shown in Figure 2b, the highest coliform removal was achieved using a dosage ratio of 5:1 (first step 67 mg/L, second step 13 mg/L) with 2.40-log reduction. Both of these variables were used for the TSC process in subsequent experiments.

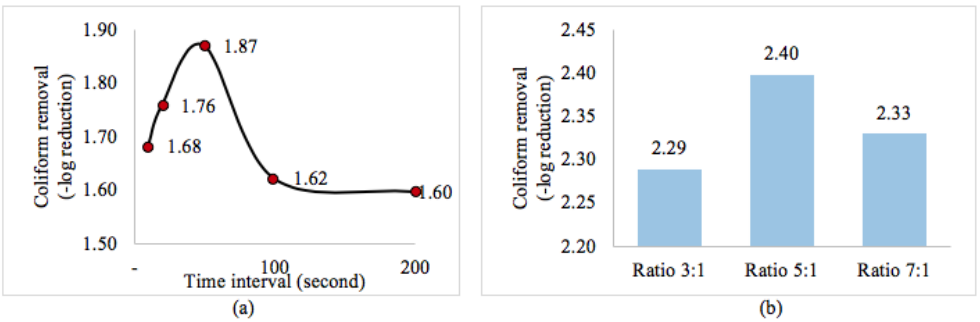
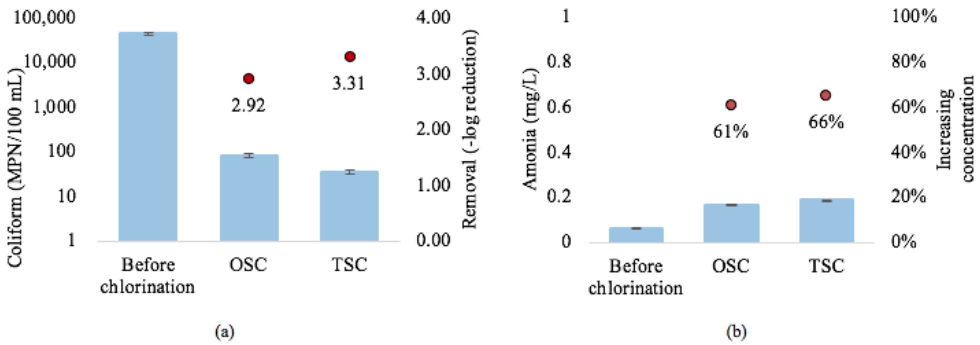


Fig. 2. Effect of (a) time interval, (b) dosage ratio between the first and second dosing on coliform removal efficiency in the TSC method (contact time: 20 minutes; chlorine dose: 80 mg/L).

3.3 Comparison of disinfection efficiency

During the OSC and TSC experiments, several experimental parameters, such as temperature, pH, and turbidity, were at 28.2 ± 0.0002 °C, 7.54 ± 0.02, and 2.42 ± 0.0002 NTU, respectively. The efficiency of the chlorination method was evaluated based on total coliform, ammonia, and organic substances (COD and BOD) removal.



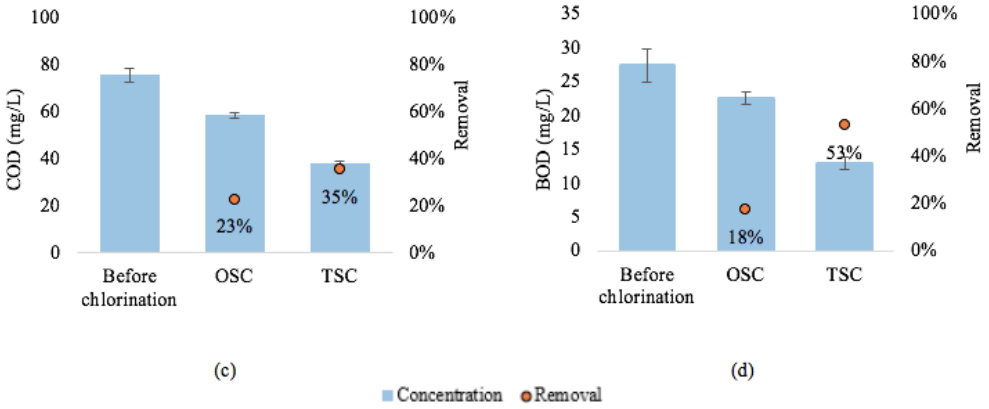


Fig. 3. Effect of OSC and TSC on (a) coliform inactivation (logarithmic scale), (b) ammonia concentration, (c) COD, and (d) BOD removal.

The efficiency of removal of microorganisms, such as coliform, was generally represented by a log-reduction scale or percentage [12]. The comparison of coliform between OSC and TSC is shown in Figure 3a. The coliform concentration was then tested statistically through an independent *t*-test. The results of the statistical estimation showed that TSC had the capacity to increase the efficiency of coliform removal by up to 0.39-log reduction when compared to OSC (sig. 2-tailed = 0.001). The higher removal efficiency observed in TSC can be explained by the formation of monochloramine after the first dosing [6]. Monochloramine is one of the inorganic chloramines [13] formed when pH is above 7 [11] and is considered a secondary disinfectant, but it is 200 times less effective than free chlorine [8]. However, its existence cannot be neglected, because the combination of monochloramine and free chlorine might create a synergistic effect in disinfection [14]. Free chlorine has the ability to injure cell walls and plasma membranes such that the first line of defense for microorganisms became weaker or damaged. Afterward, monochloramine might penetrate cells to inactivate microorganisms by attacking the cells' internal components [12], [15], [16]. The impact of disinfection varies depending on the type of microorganism, ranging from partial injury to severe damage that leads to death. However, partial damage to the cells of some microorganisms is reversible, such that the cell can heal and react by itself [6], [17].

Monochloramine is formed by the reaction of free chlorine and ammonia in water. The ideal chlorine to ammonia-nitrogen (Cl:N) ratio to form monochloramine is 3:1 to 5:1 [18]. However, the Cl:N ratio in this case was not adjusted to determine the mechanism under actual effluent conditions. With a Cl:N ratio at 80:0.065 or equivalent to 1,230:1, inorganic chloramine formation potential could be too low. Besides monochloramine, there was the possibility that other chloramine types could be formed, such as organic chloramine [13], [19]. To further examine the chlorination mechanism, the concentration of total Kjehdahl nitrogen (TKN) in the WWTP effluent was studied. The initial concentration of TKN in the effluent samples was 19.6 ± 4.99 mg/L (April–May 2018). Moreover, there was a possibility that organic nitrogen may have increased alongside coliform death, because coliform cells have protein component considered to be organic nitrogen [20], [21]. In addition, organic nitrogen can react with free chlorine to form organic chloramine compounds [19]. TKN represented organic and inorganic nitrogen in the samples. However, no specific data were measured for organic nitrogen in the sample used for chlorination. Organic chloramine was a weaker type of disinfectant than inorganic monochloramine and free chlorine [13], [19]. Based on previous research, the inactivation rate for *E. coli* parameters was 0.09 L/mg.min for organic chloramine (N-monochloramine

acids), 2.56 L/mg.min for free chlorine, and 0.72 L/mg.min for inorganic monochloramine. Organic chloramine provided a low inactivation effect compared to the other two disinfectants [22].

The chloramines, both organic and inorganic, that were formed might redecompose when the chloramination process occurs and reforms ammonia based on reaction in equations 2 and 3. This statement related to ammonia measurement shown in Figure 3b. The results statistically demonstrated that the ammonia in TSC effluent was 3% higher than in OSC effluent (sig. 2-tailed = 0.043).

$$3NH_2Cl \rightarrow N_2 + NH_3 + 3Cl^- + 3H^+ \quad (2)$$

$$4NH_2Cl + 3H_2O \rightarrow 4Cl^- + 3NH_3 + NO_3^- + 5H^+ \quad (3)$$

With the help of chloramines as a secondary disinfectant, the amount of free chlorine required can be reduced. Thus, there was a possibility that free chlorine availability in TSC was higher than in OSC. The higher efficiency in TSC was a result of the larger amount of free chlorine remaining in the samples [6] that could oxidize more organic substances [23]. Compared to OSC, TSC has been statistically proven to have a higher efficiency on COD and BOD than OSC (sig. 2-tailed = 0.046 and 0.000), with an enhanced efficiency of up to 12% and 35%, respectively (shown in Figure 3c and 3d).

3.4 THM formation

The largest amount of DBP formed is THM and haloacetic acid (HAA), together comprising almost 50% of total DBP [24]. In this study, THM was measured to compare the difference between THM formation in OSC and TSC. The results showed that the formation of THM in OSC and TSC samples was 48.3 and 42.0 ppb, respectively (Table 2). TSC was able to reduce THM formation concentrations by up to 13%. However, the THM concentrations in both methods do not represent the overall THM total. This is due to chloroform and bromoform compounds, whose values were lower than the detection limit. Total THM in TSC was lower than in OSC due to the existence of chloramine. As explained before, the chloramine formed in TSC was higher than in OSC, so it reduced the risk of THM formation [8]. However, it should be noted that disinfection with chloramine can produce a DBP similar to chlorinated DBP, but in lower concentrations [25]. The possible types of DBP formed through the chloramination process with inorganic chloramine disinfectants are HANs, cyanogen chloride, chloramino acids, chloral hydrate, and haloketones [19].

Table 2. THM components and total THM in OSC and TSC effluents

Parameter	Unit	Concentration	
		OSC	TSC
Chloroform	Ppb	< 4.00	< 4.00
Bromodichloromethane	Ppb	36.7	28.9
Dibromochloromethane	Ppb	11.6	13.1
Bromoform	Ppb	< 1.00	< 1.00

4 Conclusion

The efficiency of conventional one-step chlorination (OSC) and two-step chlorination (TSC) were compared in terms of disinfection efficiency and THM formation. The results showed that TSC was generally more efficient in terms of disinfection than OSC, specifically in the case of total coliform and organic matter parameters. TSC reached its

maximum efficiency at a 50-second time interval and a 5:1 dosage ratio with a disinfectant dose of 80 mg/L and a contact time of 20 minutes. Compared to OSC, TSC increased total coliform, COD, and BOD efficiency up to 0.39-log reduction, 12%, and 35%, respectively. Additionally, TSC reduced THM formation to 13%. The results suggest that to fulfill the same disinfection goal, TSC might consume less chlorine as a disinfectant than OSC while reducing the operational cost of chlorination.

Acknowledgement

The author would like to thank Universitas Indonesia for financially supporting this research by *Grant of Indexed International Publications for Student Final Project (Hibah PITTA)*, Number 2408/UN2.R3.1/HKP.05.00/2018.

References

1. UNESCO, "Water for a sustainable world: the United Nations World Water Development Report 2015," France: United Nations Educational. Scientific and Cultural Organization, 2015.
2. J. Lahnsteiner and F. Klegraf, "Industrial water reuse case studies," *Newsl. IWA Spec. Gr. Water Reuse*, pp. 0–3, 2005.
3. C. R. Priadi *et al.*, "Water recycling opportunity in the business sectors of Greater Jakarta, Indonesia," *Int. J. Technol.*, vol. 8, pp. 1031, 2017.
4. S. D. Richardson, M. J. Plewa, E. D. Wagner, R. Schoeny, and D. M. DeMarini, "Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research," *Mutat. Res.,* vol. 1–3, pp. 178–242, 2007.
5. K. Verma, K.D. Gupta, A.B. Gupta, "Disinfection using chlorine with step doses", *Res. Rev. J. Eng. Technol*. 2 (2013) 282–286, ICE-WWISH, ISSN 23199873
6. Y. Li *et al.,* "Two-step chlorination: a new approach to disinfection of a primary sewage effluent," *Water Res.,* vol. 108, pp. 339–347, 2017.
7. Y. Li *et al.,* "Three-step effluent chlorination increases disinfection efficiency and reduces DBP formation and toxicity," *Chemosphere*, vol. 168, pp. 1302–1308, 2017.
8. Water Quality Association, "Chloramine Fact Sheet," 2013.
9. M. W. LeChevallier, T. S. Hassenauer, A. K. Camper, and G. A. McFeters, "Disinfection of bacteria attached to granular activated carbon," *Appl. Environ. Microbiol*., vol. 48, pp. 918–923, 1984.
10. N. Marasabessy and C. R. Priadi, "Treatment efficiency of effluent water from wastewater treatment plant using activated carbon unit in PT. Jababeka Infrastruktur," *Int. J. Energy Technol. Policy*. In review.
11. C. E. Adams *et al., Wastewater Treatment.* Les Ulis: CRC Press LCC, 1999.
12. Q. Yinan, "Monochloramination - fecal coliform inactivation and haloacetic acid formation," Hong Kong University of Science and Technology, Hong Kong, 2003.
13. Z. T. How, I. Kristiana, F. Busetti, K. L. Linge, and C. A. Joll, "Organic chloramines in chlorine-based disinfected water systems: a critical review," *J. Environ. Sci.,* vol. 58, pp. 2–18, 2017.
14. Y. Kouame and C. N. Haas, "Inactivation of E. coli by combined action of free chlorine and monochloramine," *Water Res.,* vol. 25, pp. 1027–1032, 1991.

15. J. G. Jacangelo, V. P. Olivieri, and K. Kawata, "Investigating the mechanism of inactivation of escherichia coli B by monochloramine," *J. Am. Water Work. Assoc*., vol. 83, pp. 80–87, 1991.
16. R. L. Wolfe, N. R. Ward, and B. H. Olson, "Inorganic chloramines as drinking water disinfectants: a review," *J. Am. Water Work. Assoc*., vol. 76, pp. 74–88, 1984.
17. M. R. Salton, "Structure and function of bacterial cell membranes," *Annu. Rev. Microbiol*., vol. 21, pp. 417–442, 1967.
18. WHO, "Chemistry of disinfectants and disinfectant by-products," in *EHC 216: Disinfectants and Disinfectant By-products,* 2000, pp. 27-109.
19. M. M. Donnermair and E. R. Blatchley, "Disinfection efficacy of organic chloramines," *Water Res.,* vol. 37, pp. 1557–1570, 2003.
20. AWWA, *Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources*. New York: McGraw-Hill, 1991.
21. S. E. Manahan, *Environmental Chemistry*, 8th ed. Washington DC: CRC Press LCC, 2005.
22. C. N. Sawyer, P. L. McCarty, and G. F. Parkin, *Chemistry Environmental Engineering Science*, 5th ed., New York: McGraw-Hill, 2002.
23. K. Verma, P. Shukla, A. B. Gupta, and K. D. Gupta, "Hybrid disinfection of sewage effluent—a comparative study of three secondary treatment plants of Jaipur, India," *Desalin. Water Treat*, vol. 57, 2016.
24. E. H. Goslan *et al.,* "A comparison of disinfection by-products found in chlorinated and chloraminated drinking waters in Scotland," *Water Res.,* vol. 43, pp. 4698–4706, 2009.
25. U.S. EPA, "Drinking water criteria document for chloramines," 1994.