PAPER • OPEN ACCESS

Effectiveness of Breakpoint Chlorination and Rechlorination on Nitrified Chloraminated Water

To cite this article: N. B. Karthik *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **464** 012001

IOP Conf. Series: Earth and Environmental Science **464** (2020) 012001 doi:10.1088/1755-1315/464/1/012001

Effectiveness of Breakpoint Chlorination and Rechlorination on Nitrified Chloraminated Water

N. B. Karthik[1,a], Bal Krishna KC[1,b] & Arumugam Sathasivan[1,c]

[1]School of Computing, Engineering and Mathematics, Western Sydney University, Penrith 2757

[a]19237419@student.westernsydney.edu.au, [b]B.Kc@westernsydney.edu.au, [c]S.Sathasivan@westernsydney.edu.au

Abstract. Chloramine is used as a secondary disinfectant in water distributions system (WDS). However, nitrification is a major concern involved in the chloraminated WDS as it leads to the accelerated decay of chloramines. After the onset of nitrification, breakpoint chlorination followed by rechlorination is generally practiced in WDS to reinstate chloramine residuals in the WDS. In this study, two different control strategies re-chlorination and breakpoint chlorination followed rechloramination were applied on the severely nitrified water collected from the laboratory-scale reactor system. Results showed that breakpoint chlorination followed by rechloramination is highly stable as the chloramine residual was maintained up to 300 hours and is highly effective than rechlorination alone as it could maintain residue only up to 50 hours even with repeated re-dosing.

1. Introduction

Chloramine is formed due to the reaction between chlorine and ammonia. Many developed countries such the USA, Australia and other European countries started replacing chlorine with chloramine as a cheaper alternative, due to its better stability and less disinfection by-product formation (DBPs) such as Trihalomethanes (THMs) and Haloacetic acids (HAAs) formation [1] due to its less reactive nature with natural organic matter, iodide and bromide present in the water [2].

Besides its vast benefits, chloramine decays due to chemical and microbial pathways [3]. Ammonia oxidizing bacteria (AOB) oxidize free-ammonia present in the system to nitrite which is further oxidized to nitrate by nitrite oxidizing bacteria (NOB). In distribution system it is generally believed that ammonia oxidation takes place which leads to partial nitrification [4]. Hence, nitrite concentration is used as an indicator for of nitrification status. Nitrification accelerates the chloramine decay [5] due to the production of nitrite and soluble microbial products (SMPs). To control nitrification, free chlorine is dosed to the residual ammonia to maintain the ratio towards five and occasional breakpoint chlorination is carried out [6, 7]. The previous studies of breakpoint chlorination done after eliminating the microbes (by filtration) showed that breakpoint chlorination destroy the SMPs and improve chloramine residual [8]. Rechloramination alone on nitrified water is not effective as it only delays the onset of nitrification but does not prevent nitrification from happening [9]. This study investigated the effectiveness of two control strategies (breakpoint chlorination followed by rechloramination and rechlorination) to improve the chloramine stability after the onset of nitrification and to prevent the nitrification from happening. The microbes were not filtered during the experiment to understand the direct effect of control strategies on them.

2. Materials and methods

2.1. Stock chemical solutions, sample bottle and glassware preparation
All the stock solutions were prepared using Milli-Q ultrapure water. Polyethylene terephthalate (PET) bottles (500 mL each) were used for the decay test. The bottles were cleaned by immersing into 2% sodium hypochlorite for more than 24 hours and rinsed with Milli-Q water for six times to ensure they were free of any residual chlorine. All the glassware used for experiment was rinsed with Milli-Q water and autoclaved.

2.2. Rechlorination and Breakpoint chlorination followed by rechloramination
The breakpoint chlorination was performed by dosing chlorine more than 5:1 chlorine to TAN ratio where it reacts with nitrogen compounds present in the water sample. The same sample was rechloraminated by dosing both chlorine and ammonia to maintain the required ratio of 4.2:1. Rechlorination was done by dosing chlorine only to the sample to maintain the required chlorine to TAN ratio of 4.2:1.

2.3. Analytical Procedure
Samples were analyzed for total chlorine (TCl), total ammoniacal nitrogen (TAN) and nitrite (NO_2^-) prior and during the application of control strategies. TAN is the integration NH_3-N, NH_4^+-N and nitrogen associated with chloramines. Thermo scientific gallery discrete analyzer (automated analyzer) was used for the measurement of TAN and nitrite. TAN concentration is measured spectrophotometrically using salicylate ion method. Nitrite is measured by reacting it with sulphanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride to form a coloured azo dye and is analyzed spectrophotometrically. Colorimetric DPD method was used for the measurement of total chlorine using hach pocket chlorimeter (HACH DR 1900). HACH HQ40d pocket meter was used to measure pH of water sample during the experiment.

2.4. Experimental procedure
After the collection of severely nitrified sample from the laboratory-scale reactor, it was divided into five subsamples where one was used as control, two of them were rechlorinated with chlorine to TAN ratio of 4.5:1 and 4:1. The other two samples were breakpoint chlorinated at 5.5:1 and 6:1 total chlorine to TAN ratios and later rechloraminated with 4.2:1 chlorine to TAN ratio. The samples were dosed with sodium hypochlorite (1000 mg Cl_2/L) and ammonium chloride (500 mg-N/L). Later, all the samples were incubated at constant temperature (22 ± 1 °C) and total chlorine, TAN and nitrite were periodically monitored. The chloramine decay coefficient was determined by plotting total chlorine versus time. The exponential slope value of the trend line gives the chloramine decay coefficient. The flow chart of the experimental procedure is shown in Figure 1.

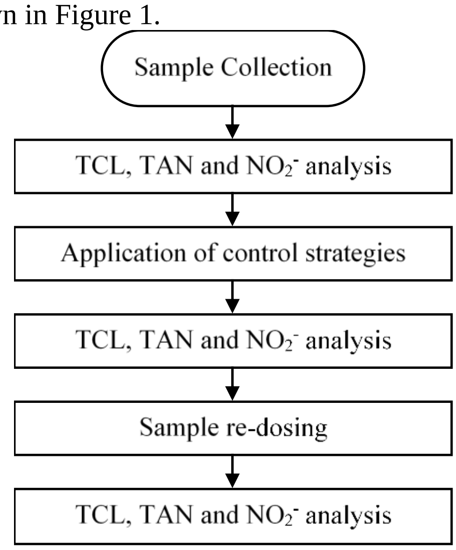

Figure 1: Experimental procedure flow chart

3. Results and Discussion

3.1. Effect of breakpoint chlorination followed by rechloramination and rechlorination on total chlorine levels

The initial conditions of the sample were as follows TCL 0.64 mg/L, TAN 0.279 mg/L, pH 7.85 and nitrite 0.173 mg/L. It can be seen in Figure 1 that the rechlorinated samples besides four re-doses the chloramine residue couldn't be maintained and it diminished by 100 hours. In the breakpoint chlorinated (total chlorine to TAN ratios of 5.5:1 and 6:1) followed by rechloraminated samples, the residue can be maintained up to 300 hours with three re-doses (Figure 2). Even breakpoint chlorination at a ratio of 5.5:1 suppressed the nitrification and was almost as efficient as 6:1 ratio. The control sample could not sustain and disinfectant diminished very early.

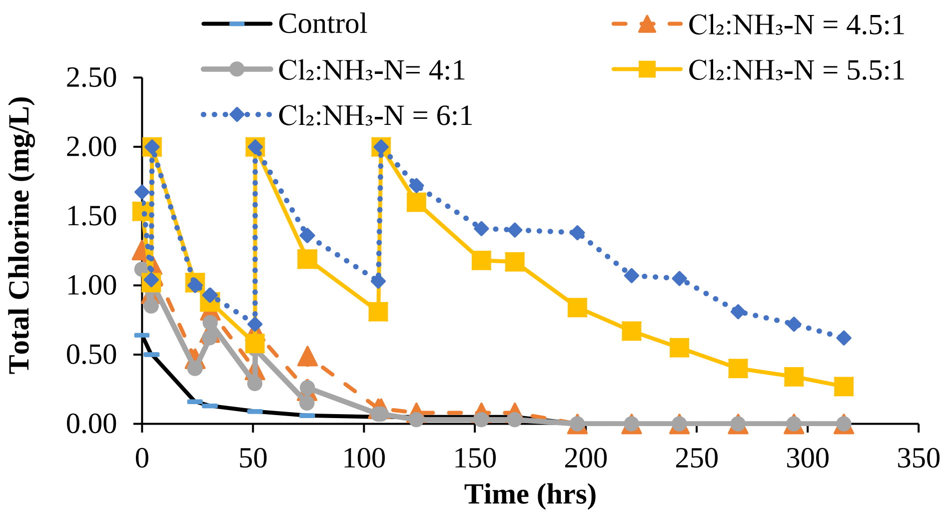

Figure 2. Total chlorine profile of breakpoint chlorinated followed by rechloraminated and rechlorinated samples

3.2. Effect of breakpoint chlorination followed by rechloramination and rechlorination on TAN

Due to the nitrifying activity, TAN present in the rechlorinated samples depleted by 100th hour. In breakpoint chlorinated followed by rechloraminated samples, TAN levels were more stable after the third redosing at 100th hour (Figure 3). In a control sample, TAN residues dropped below the detection limit after the 25th hour.

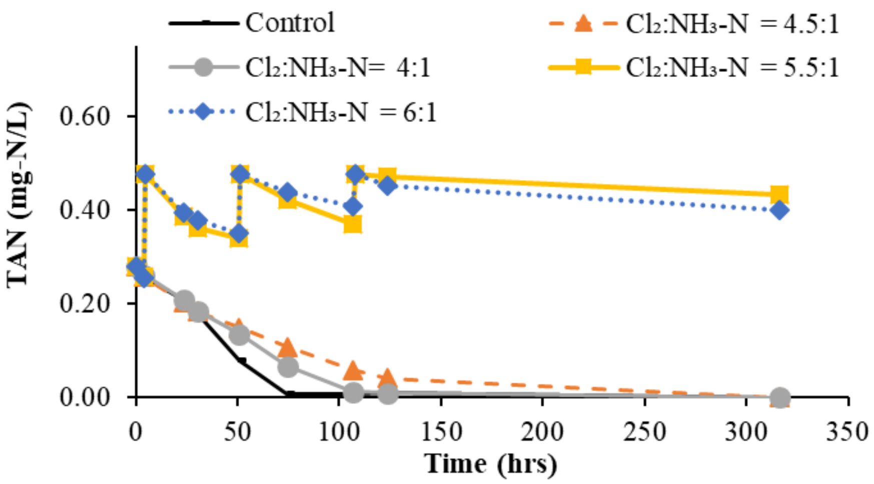

Figure 3. Total ammoniacal nitrogen (TAN) profile of breakpoint chlorination followed by rechloramination and rechlorinated samples

3.3. Effect of breakpoint chlorination followed rechloramination and rechlorination on nitrite

The nitrite in the control sample increased up to 0.5 mg-N/L showing the severe nitrifying activity. In the rechlorinated samples, at the first dosing, the nitrite dropped due to high chloramine residuals but overall as the time progressed the nitrite increased up to 0.2 mg-N/L in the rechlorinated samples. The nitrite completely diminished in the breakpoint chlorinated samples and no recurrence was seen (Figure 4).

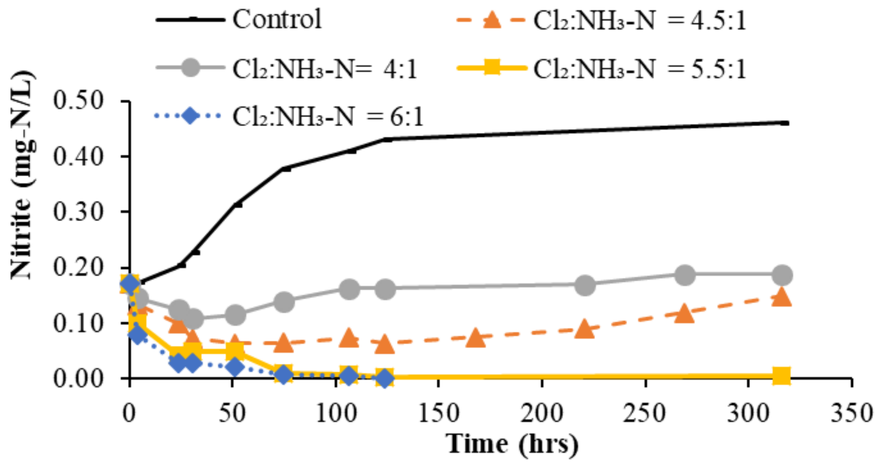

Figure 4. Nitrite profile of breakpoint chlorination followed by rechloramination and rechlorinated samples

3.4. Effect of breakpoint chlorination on decay rate

The decay rate after the breakpoint chlorination supressed in both the samples. Although there is a significant difference in 5.5:1 and 6:1 sample during 0 to 50 hours. After every rechloramination doses the decay rate of the disinfectant was seen to be supressing. During 100 to 320 hours the decay rate in both the samples were supressed greatly and 5.5:1 sample demonstrated to be equally effective as 6:1 sample after the re-dosing (Figure 5).

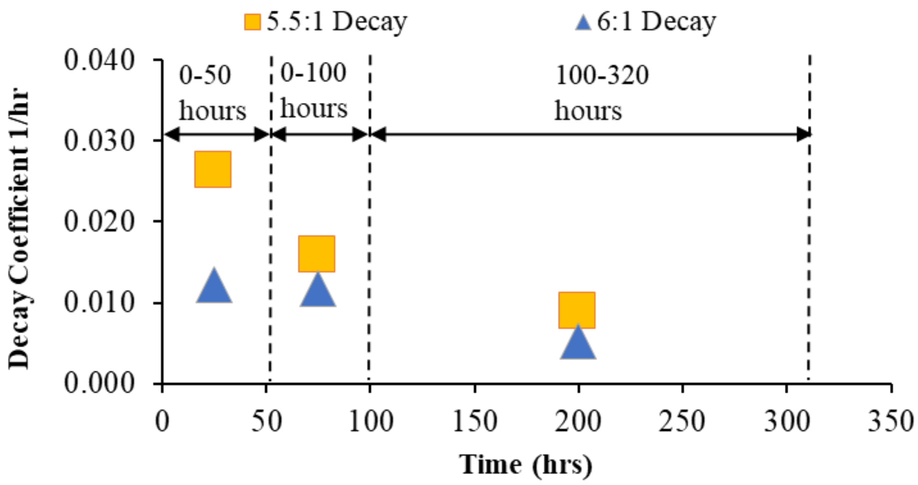

Figure 5. Decay coefficient profile of breakpoint chlorination followed by rechloramination.

4. Conclusion

Rechlorination at water distribution systems did not suppress the nitrifying activity besides; it led to rapid decay of chloramine. Breakpoint chlorination followed by rechloramination greatly suppresses the nitrification and the lower ratio of chlorine to ammonia-nitrogen (5.5:1) is a sustainable option to control nitrification rather than using higher resources at higher ratios.

5. References

[1] Norman T S, Harms L L and Looyenga R W 1980 The Use of Chloramines To Prevent Trihalomethane Formation *Journal - American Water Works Association* **72** 176-80

[2] Bichsel Y and Von Gunten U 2000 Formation of Iodo-Trihalomethanes during Disinfection and Oxidation of Iodide-Containing Waters *Environmental Science & Technology* **34** 2784-91

[3] Sathasivan A, Fisher I and Kastl G 2005 Simple method for quantifying microbiologically assisted chloramine decay in drinking water *Environmental science & technology* **39** 5407

[4] Wolfe R L, Lieu N I, Izaguirre G and Means E G 1990 Ammonia-oxidizing bacteria in a chloraminated distribution system: seasonal occurrence, distribution and disinfection resistance *Applied and Environmental Microbiology* **56** 451

[5] Cunliffe D A 1991 Bacterial nitrification in chloraminated water supplies *Applied and Environmental Microbiology* **57** 3399

[6] Wolfe R L, Iii E G M, Davis M K and Barrett S E 1988 Biological Nitrification in Covered Reservoirs Containing Chloraminated Water *Journal - American Water Works Association* **80** 109-14

[7] Lieu N I, Wolfe R L and Iii E G M 1993 Optimizing Chloramine Disinfection for the Control of Nitrification *Journal - American Water Works Association* **85** 84-90

[8] Bal Krishna K C, Sathasivan A and Kastl G 2014 Effectiveness of breakpoint chlorination to reduce accelerated chemical chloramine decay in severely nitrified bulk waters *Chemosphere* **117** 692-700

[9] Bal Krishna K C, Bhullar G S, Sathasivan A and Henderson R 2015 Effectiveness of re-chloramination to control nitrification in chloraminated bulk waters *Desalination and Water Treatment* **57** 1-9