Chemosphere 117 (2014) 692–700

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effectiveness of breakpoint chlorination to reduce accelerated chemical chloramine decay in severely nitrified bulk waters

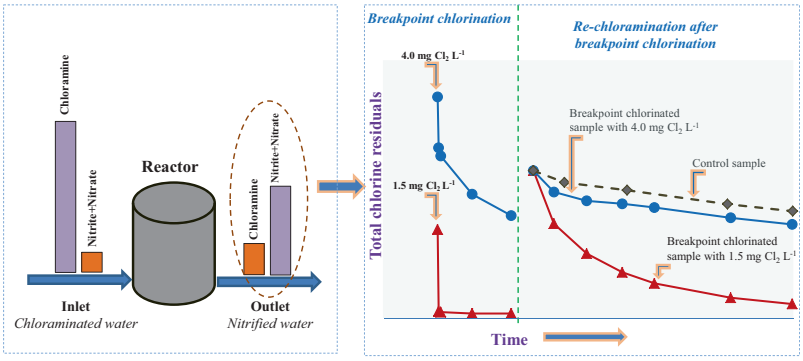
K.C. Bal Krishna [a], Arumugam Sathasivan [a,b,*], George Kastl [b]

[a] Department of Civil Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[b] School of Computing, Engineering and Mathematics, University of Western Sydney, Locked Bag 1797, Penrith, NSW 2751, Australia

HIGHLIGHTS

- Breakpoint chlorination does more than killing nitrifying bacteria in controlling chloramine decay.
- Rapid chloramine loss cannot be stopped by adding just enough chlorine to oxidise ammonia and nitrite.
- Chlorine preferentially reacts with nitrite and ammonia before inactivating SMPs.
- Effectiveness of breakpoint chlorination rely on satisfying demand exerted by SMPs.

GRAPHICAL ABSTRACT



(A) Laboratory Scale System (B) Experimental Results

ARTICLE INFO

Article history:
Received 12 August 2014
Received in revised form 21 September 2014
Accepted 22 September 2014
Available online 1 November 2014

Handling Editor: O. Hao

Keywords:
Breakpoint chlorination
Chlorine
Chloramine
Re-chloramination
Nitrification
Soluble microbial products

ABSTRACT

Rectifying the accelerated chloramine decay after the onset of nitrification is a major challenge for water utilities that employ chloramine as a disinfectant. Recently, the evidence of soluble microbial products (SMPs) accelerating chloramine decay beyond traditionally known means was reported. After the onset of nitrification, with an intention to inactivate nitrifying bacteria and thus maintaining disinfectant residuals, breakpoint chlorination followed by re-chloramination is usually practiced by water utilities. However, what actually breakpoint chlorination does beyond known effects is not known, especially in light of the new finding of SMPs. In this study, experiments were conducted using severely nitrified chloraminated water samples (chloramine residuals <0.5 mg Cl_2 L^{-1}, nitrite residuals >0.1 mg N L^{-1} and an order of magnitude higher chloramine decay rate compared to normal decay) obtained from two laboratory scale systems operated by feeding natural organic matter (NOM) containing and NOM free waters. Results showed that the accelerated decay of chloramine as a result of SMPs can be eliminated by spiking higher free chlorine residuals (about 0.92 ± 0.03 to 1.16 ± 0.12 mg Cl_2 L^{-1}) than the stoichiometric requirement for breakpoint chlorination and nitrite oxidation. Further, accelerated initial chlorine decay showed chlorine preferentially reacts with nitrite and ammonia before destroying SMPs. This study, clearly demonstrated there is an additional demand from SMPs that needs to be satisfied to effectively recover disinfection residuals in subsequent re-chloramination.

* Corresponding author at: School of Computing, Engineering and Mathematics, University of Western Sydney, Locked Bag 1797, Penrith, NSW 2751, Australia. Tel.: +61 02 4736 0941; fax: +61 02 4736 0833.
E-mail address: A.sathasivan@uws.edu.au (A. Sathasivan).

http://dx.doi.org/10.1016/j.chemosphere.2014.09.080
0045-6535/

1. Introduction

Chloramine is often used as a secondary disinfectant instead of chlorine to maintain a longer lasting residual and/or a reduction in the formation of chlorinated disinfection by-products within drinking water distribution systems (Russo, 1979; Cotruvo, 1981). Better stability, ability to penetrate biofilm (LeChevallier et al., 1990) and minimal objectionable taste and odor are major advantages of chloramine over chlorine. In addition, its lower reactivity than chlorine (Wolfe et al., 1985) makes chloramine a popular choice for water utilities with long retention times.

Chloramine unfortunately has some additional challenges. Besides auto-decomposition, its direct reaction with chloramine demanding compounds present in water distribution systems and microbial activities including nitrification were shown to accelerate chloramine decay (Sathasivan et al., 2005). Nitrification is a two-step microbial process. Initially, ammonia-oxidizing bacteria (AOB) convert free ammonia to nitrite and then nitrite-oxidizing bacteria (NOB) convert nitrite to nitrate. Based on chloramine decay rates and prevailing nitrite levels nitrification in chloraminated distribution systems was defined as mild or severe nitrification (Sathasivan et al., 2008). In the front parts of the system, chloramine was reasonably stable and nitrite production was low (nitrite < 0.01 mg N L^{-1}). This phase was termed as mild nitrification. When chloramine residuals dropped below 0.5 mg Cl_2 L^{-1}, a sharp drop in chloramine and ammonia residuals were noted. In this phase, nitrite residual was more than 0.1 mg N L^{-1} and total chlorine decay was about an order higher than that noted in a mildly nitrifying phase and this phase was termed as a severely nitrifying phase.

Once severely nitrifying conditions are experienced, it is very hard to manage chloramine residuals, even by increasing the residual up to 8.0 mg Cl_2 L^{-1} (Skadsen, 1993) and the mechanisms behind accelerated chloramine loss was unknown. Recently, Bal Krishna et al. (2012) provided a comprehensive evidence (FTIR measurements, protein denaturation) to prove that under the severely nitrifying conditions, microbes release soluble microbial products (SMPs) that catalytically accelerate chloramine decay by expediting auto-decomposition and nitrite oxidation reactions (Sathasivan and Bal Krishna, 2012). They also developed some indicators of the presence of SMPs such as faster ammoniacal nitrogen depletion and simultaneous faster decay of chloramine, least effect from re-chloramination. Such new finding may be used to explain or fine tune some of the control measures traditionally adopted by utilities.

In order to control nitrification and subsequently maintain the chloramine residuals, short-term control methods have been employed by many water utilities. These include: (1) reducing the water retention time in distribution systems (Ike et al., 1988; Wolfe et al., 1988; Lieu et al., 1993), (2) dosing free chlorine to increase the total chlorine to ammonia ratio thus diminishing the free ammonia residual (Wolfe et al., 1988; Lieu et al., 1993; Kirmeyer et al., 2004), (3) regularly carrying out breakpoint chlorination (Wolfe et al., 1988; Lieu et al., 1993), (4) draining and refilling the service reservoir (tank) or diluting the nitrified water with freshly chloraminated water in winter (Lieu et al., 1993; Sathasivan et al., 2010) and (5) frequently flushing the distribution system (Wolfe et al., 1988).

One of the most effective control methods out of all is breakpoint chlorination (Kirmeyer et al., 2004). It is the process of switching from chloramine to free chlorine for a short period (a week to a month), during which time ammonia and nitrite present in the water are oxidized and microbes are disinfected by excessive free chlorine residual. SMPs in those waters may demand additional chlorine, or if not destroyed may accelerate chloramine decay. Although in a full-scale distribution system both microbial and chemical chloramine decay mechanisms prevail, the major aim of this study was to investigate how the presence of SMPs effect on subsequent decay of chloramine or on chlorine demand during breakpoint chlorination. Experiments were conducted on two different severely nitrifying bulk water samples by filtering through 0.2 μm cellulose acetate membrane filters to eliminate microbes followed by successive employment of "breakpoint chlorination and re-chloramination". One severely nitrifying sample was obtained from a system operated with high dissolved organic carbon (DOC) levels (about 3.0 mg L^{-1}). The other was obtained from a system operated with low DOC (<0.15 mg L^{-1}). To distinguish between mildly and severely nitrifying sample behaviors, mildly nitrifying samples were also tested.

2. Materials and methods

2.1. Analytical procedures

Total chlorine, total ammoniacal nitrogen (TAN), nitrite, nitrate and DOC were measured immediately after collecting the samples. The Aquakem 200, a high precision wet chemistry automated analyzer, was employed to measure TAN, nitrite and NOx (nitrite + nitrate) concentrations. The analyzer has a low detection limit for TAN, nitrite and NOx level of 0.002 mg N L^{-1}. Total chlorine residual was measured by DPD colorimetric method using a HACH pocket colorimeter. Total chlorine measurement had an experimental error of ±0.03 mg L^{-1}. DOC was measured using Sievers 5310C Laboratory TOC analyser and an experimental error of ±5% was obtained for DOC concentrations >0.5 mg L^{-1}. A portable pH meter (HACH 40d) with a pH probe (HACH, PHC101) was used to measure pH and the measurement error was ±0.1. The details of measurement methods are given in Bal Krishna and Sathasivan (2010).

2.2. Stock chemical solutions, sampling bottles and glassware preparation

Stock solutions for all chemicals were prepared in RO treated water (IbisIS0006, Ibis Technology, Australia). The RO treated water had DOC and conductivity of <0.15 mg L^{-1} and <1 μS cm^{-1}, respectively. Stock solutions of ammonium chloride (500 mg N L^{-1}) and sodium hypochlorite (500 mg Cl_2 L^{-1}) were used to maintain monochloramine residuals in bulk water samples. The pH was adjusted using 1 M hydrochloric acid and 1 M sodium hydroxide solutions. All the chemicals used in this experiment were of analytical grade.

Sample bottles (500 mL PET – polyethylene terephthalate) and glassware were cleaned by immersing them into a 1.0% sodium hypochlorite solution for 24 h, followed by rinsing five to six times with RO treated water to ensure they were free of chlorine by measuring total chlorine for added RO treated water sample. Before starting the chloramine decay test using PET bottles two tests (chlorine demand by PET bottles and chlorine leaching from PET bottles) were conducted to ensure the conducted chlorine decay tests were not affected (Bal Krishna et al., 2012). Sample collection glassware, the filtration unit and filter papers were autoclaved. Moreover, about 30–50 mL of RO treated water was filtered through 0.2 μm cellulose acetate membrane filter (Sterlitech, USA) before filtering samples to minimize the possible DOC rerelease from the filter membrane.

2.3. Water collection and preparation for feeding into Laboratory Scale System-Raw Water (LSS-Raw Water)

Raw Water was collected from the Mundaring Weir, Western Australia. Mundaring Weir water is composed of rainwater, treated groundwater and river water and water characteristics fluctuated