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Can microbes significantly accelerate chloramine decay without severe nitrification?

Bhagya S. Herath, Arumugam Sathasivan*, Hoi Ian Lam

School of Computing Engineering and Mathematics, University of Western Sydney, Kingswood, NSW, 2747, Australia

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ABSTRACT

The ability of microbes to accelerate chloramine decay to the same degree as under severe nitrification, but without the signs of severe nitrification is reported. Traditionally, only nitrification is believed to microbiologically challenge the stability of chloramine. Chloraminated water containing high amount of natural organic matter (10–12 mg L^{-1} of dissolved organic carbon (DOC)) was fed to four lab scale reactors connected in series. Each reactor had one day retention time with a total of four days in total. The decay coefficient was observed to be a maximum of 0.06 h^{-1} without substantial changes in ammonia, nitrite or nitrate levels. Despite very low chloramine residuals, nitrite only increased to less than 0.012 mg-N L^{-1}, indicating a mildly nitrifying condition. Previously reported decay coefficient (0.001–0.006 h^{-1}) for the condition was an order less. Changing of the feed to a new water from the same source, but with a low DOC (of 4 mg L^{-1}) led to the onset of nitrification complying biostability. The maximum observed chloramine decay coefficient with severe nitrification was 0.085 h^{-1}. Therefore, microbes present under mildly nitrifying condition can be as destructive as that in severely nitrifying condition. For better control of chloramine, attention on microbes present under mild nitrification is needed.

Introduction

Chloramine especially monochloramine, behind chlorine, is the second most popular disinfectant used in water supply systems. The typical purpose of chloramine is to provide a longer-lasting residual as the water moves through pipes to consumers. Chloramine is formed when ammonia and chlorine is combined. Subsequently chloramine is not as reactive as chlorine, it forms fewer regulated disinfection by-products such as the Trihalomethanes (THMs) and Halo acetic acids (HAAs) (Bond et al., 2011). The longer lasting nature provides enhanced protection against bacterial regrowth in systems with large storage tanks. Apart from that, ability to minimise taste and odour is an additional advantage (Zaitsev and Dror, 2013).

Maintaining an effective chloramine residual throughout a distribution system can be a challenge at times due to accelerated chloramine decay occurring through chemical and microbial reactions (Sathasivan et al., 2005). Auto-decomposition and direct reaction with chloramine demanding compounds including natural organic matter (NOM) present in water distribution system contribute towards chemical decay of monochloramine (Vikesland et al., 2001).

Usually, nitrification is associated with chloramine loss or difficulty in maintaining an adequate disinfectant residual (Wolfe et al., 1990; Cunliffe, 1991; Skadsen, 1993; Odell et al., 1996; Wilczak et al., 1996) and hence nitrification related parameters and disinfectant residual are measured to judge the stability of a disinfectant. Nitrification is the biological oxidation of ammonia with oxygen into nitrite followed by the oxidation of nitrite into nitrate. The first step is performed by ammonia-oxidizing bacteria (AOB) and the second by nitrite oxidizing bacteria (NOB). However, recent findings have shown that other species – e.g., *Nitrosomonas oligotropha* (Regan et al. 2002), nitrifying Archaea (Hoefel et al., 2011), and heterotrophic nitrifiers (Daum et al., 1998) can be present and contribute to nitrification.

In a chloraminated system, the highest residual at which onset of nitrification occurs for a given free ammonia and temperature is reported to follow biostability concept (Sathasivan et al., 2008; Sarker and Sathasivan, 2011; Sarker et al., 2013). According to the biostability concept (Woolschlager et al., 2001) the regrowth of

* Corresponding author.
E-mail addresses: 17914941@student.uws.edu.au (B.S. Herath), A.Sathasivan@uws.edu.au (A. Sathasivan), hoiian114@gmail.com (H.I. Lam).

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AOB can be prevented if the inactivation rate equals or exceeds the bacterial growth rate at each location within the distribution system (Sarker et al., 2013). A biostable residual concentration (BRC) is the chloramine residual below which potential for nitrification occurrence exists. The equation for BRC was implemented by Fleming et al. (2005) and further modified by Sathasivan et al. (2008) as follows:

$$BRC = \frac{\mu_m}{k_d} \cdot \left(\frac{free\ ammonia\_N}{K_s + free\ ammonia\_N} \right) \quad (1)$$

where μ_m is the maximum specific growth rate of AOB (d^{-1}); free ammonia_N = ammonia (NH_3–N) plus ammonium (NH_4^+-N) concentrations (mg-N L^{-1}); K_s = half saturation constant for AOB (mg-N L^{-1}); k_d = the rate constant for inactivation of AOB by disinfectant (L d^{-1} mg-Cl_2^{-1}); BRC is measured as total chlorine concentration (mg Cl_2 L^{-1}). Sathasivan et al. (2008) proposed the values for μ_m/k_d = 2 mg-Cl_2 $L^{-1}$and K_s = 0.18 mg-N L^{-1} at 20 °C.

In addition to nitrification, Sathasivan et al. (2005, 2008) and later Bal Krishna et al. (2012) observed microbiologically assisted chloramine decay with a lower but a steady production of nitrite until the onset of nitrification. The former authors termed this behaviour as mild nitrification. Bal Krishna et al. (2013) identified the microbes present under mildly nitrifying conditions; Microbes include heterotrophic bacteria such as *Solibacteres, Sphingomonas, Actinobacteria, Psuedomonas* and *Methylobacterium.* These results confirmed the findings of Williams et al. (2004) who analyzed the heterotrophic bacterial community in a chloraminated system and reported the dominance of *Alphaproteobacteria*. Sequences aligned with *Alphaproteobacteria* including *Afipia*, *Sphingomonas*, *Brevundimonas*, *Blastomonas*, *Hyphomicrobium*, *Methylocystis* and *Bradyrhizobium* were reported in the systems.

Nitrification normally occurs in reservoirs which are situated far from the water treatment plant during warmer months. On other times, i.e., majority of the time, water in reservoirs experience mild nitrification and it is mild nitrification that accelerates chloramine decay to bring chloramine residual below BRC before the onset of nitrification occurs (Sathasivan et al., 2008). Therefore, investigation of accelerated chloramine decay in mild nitrification stage is crucial.

Factors affecting the mildly nitifying microbes are not known but logically it could include organic carbon, chloramine residual and temperature. Organic carbon is known to inhibit nitrification in wastewater treatment systems, but in chloraminated systems the role remains indecisive (Zhang et al., 2009). Others state that nitrifiers are strongly dominated by heterotrophs at a high organic carbon-to-ammonia ratio (Verhagen and Laanbroek, 1991; Ohashi et al., 1995).

As a source of organic carbon, natural organic matter (NOM) may also encourage the growth of microbes present under mildly nitrifying conditions and suppress severe nitrification. The NOM, an integral part of water sources used for drinking water purposes, is derived mainly from decaying vegetation and consists of a complex mixture of organic compounds. Therefore, the amount, character and properties of NOM could differ significantly according to origin and biogeochemical cycles of the surrounding environments. The NOM, which is measured as dissolved organic carbon (DOC) also vary on the same location seasonally (Matilainen et al., 2010). Studying such variation may help understanding the dynamics.

In this paper, an unusually high DOC (10–12 mg-C L^{-1}) observed in natural water and a low DOC (4 mg-C L^{-1}) experienced soon after a few months in the same source are tested for its ability to cause/inhibit nitrification or to encourage microbes causing mild nitrification. The conformance with the bio-stability concept was also tested.

Materials and methods

Analytical procedures

Total chlorine (TCl), total ammoniacal nitrogen (TAN), nitrite and nitrate were measured immediately after collecting the samples. TCl is the total chlorine and TAN is the summation of NH_3–N, NH_4^+-N and nitrogen associated with chloramine. The Gallery (Thermo Scientific), a high precision chemistry automated analyzer, was adopted for measuring TAN, nitrite and NOx concentrations. It performs discrete, spectrophotometric analysis on optical multi-cell cuvette.

Available ammonia reacts with hypochlorite ions generated by the alkaline hydrolysis of sodium dichloroisocyanurate to form monochloramine which reacts with salicylate ions in the presence of sodium nitroprusside at around pH 12.6 to form a blue compound. The compound is measured spectrophotometrically at 660 nm. Nitrite is measured by reaction with sulphanilamide and N-(1-naphthyl)-ethylenediamine dihydorchloride to form a highly coloured azo-dye, thus, the absorbance is measured spectrophotometrically at 540 nm or 520 nm (APHA et al., 1998). The determination of nitrate is by catalytically reducing the nitrate ions into nitrite ions (by nitrate reductive enzyme in the presence of reduced nicotinaminde dinucleotide), the total nitrite ions are then measured by sulphanilamide method as the NOx, and nitrate is obtained by deduction of nitrite from the NOx. The analyzer has the detection limit for TAN, nitratre and nitrite of 0.002 mg-N L^{-1} and NOx has an error of 0.005 mg-N/L. Standard curves for TAN, nitrite and NOx were calibrated for the range 0.0–1.0 mg-N L^{-1} using stock solutions of ammonium chloride, sodium nitrite and sodium nitrate, respectively. The experimental errors were 1.5% for TAN, nitrite and nitrate measurement.

TCl residuals were measured by DPD colorimetric method using a HACH pocket colorimeter. It was assumed that more than 99% of the chloramine was present in the form of monochloramine given that pH was above 8.0 and the Cl to TAN mass ratio was approximately 4.0 or less (Valentine and Wilber, 1987). TCl measurement had an experimental error of ±0.03 mg-Cl_2 L^{-1}. Supplementary details of the analytical methods can be found in Bal Krishna and Sathasivan (2010).

Total organic carbon (TOC) was measured using Shimadzu Total Organic Carbon Analyser with an experimental error for TOC of ±5%. DOC was measured using the same analyser, however the sample was filtered through pre-washed 0.45 μm polycarbonate membrane filter papers. After placing the filter paper on the filtration apparatus, around 100 ml of Milli-Q water was passed through the filter device for minimising the contamination of DOC from filter paper into the sample.

Free ammoniacal nitrogen was determined (Equation (2)) by assuming all total Cl_2 was present as chloramine.

$$Free\ Ammonia\_N = TAN - \frac{Total\ Cl_2}{5} \quad (2)$$

where, free ammonia nitrogen concentration is a function of the TAN concentration and the chloramine concentration is measured as total Cl_2.

Total chloramine decay coefficient was calculated using Equation (3) as defined by Sathasivan et al. (2010).

$$k_{rt} = \frac{1}{\theta}\left(\frac{Cl_{in}}{Cl_{out}} - 1 \right) \quad (3)$$

where, Cl_{out} and Cl_{in} are outlet and inlet chloramine (as TCl) residuals respectively, k_{Rt} is the total chloramine decay coefficient and Θ is the water retention time in the reactors.