Comparison of dechlorination rates and water quality impacts for sodium bisulfite, sodium thiosulfate and ascorbic acid

Onita D. Basu and Nigel P. De Souza

ABSTRACT

The impact of water quality parameters such as organic and inorganic matter as well as chlorine species (free chlorine and monochloramine) on the rate of dechlorination by sodium bisulfite (SBS), sodium thiosulfate (STS) and ascorbic acid (AA) were studied. Reaction rate constants determined for the various dechlorination reactions showed that SBS and AA achieved dechlorination at a faster rate than STS. Organic matter present in the test solution increased the rate of dechlorination by STS but not SBS and AA. AA was found to be ineffective for the removal of monochloramine. The effect of dechlorination chemicals on water quality with respect to pH, turbidity and total organic carbon (TOC) was investigated along with the acute toxicity of the chemicals on the aquatic indicator species *Daphnia magna*. SBS was determined to have an LC_{50} of 68 mg/L with no toxicity impacts observed when the concentration was $\leq$ 20 mg/L for *D. magna.* AA increased the TOC levels in the treated water and resulted in some *D. magna* mortality at higher levels. STS had the least impact on daphnia mortality rates, but the use of STS for dechlorination resulted in the largest pH change of test waters compared to the other dechlorination chemicals.

Key words | acute toxicity, ascorbic acid, *Daphnia magna*, sodium bisulfite, sodium thiosulfate, water dechlorination

Onita D. Basu (corresponding author)
Nigel P. De Souza
Dept of Civil and Environmental Engineering,
1125 Colonel By Drive,
Ottawa, ON,
K1S 5B6, Canada
E-mail: *onita_basu@carleton.ca*

INTRODUCTION

Disinfection using chlorine is a common treatment process employed by municipal and private industries for the disinfection of both potable water and wastewater effluent. The drawback to chlorine disinfection is the production of disinfection by-products (DBPs) and aquatic toxicity. It is well established that chlorine reacts with organic matter typical of raw water and wastewater to produce various DBPs (Guanghui & Reckhow 2007; Zhang *et al.* 2008). These DBPs include trihalomethanes and haloacetic acids, some of which are carcinogens (Singer 2002). The formation of by-products can be minimized by reducing excess residual chlorine levels in a process called dechlorination. Furthermore, the presence of chlorine in wastewater effluent has been linked with the mortalities of aquatic species at discharge sites, signifying the toxicity of chlorine to aquatic

environments (Helz & Nweke 1995). Wastewater effluent with total residual chlorine values greater than 0.02 mg/L have been reported to have deleterious impacts on the receiving environment (MSSC 1993). Dechlorination can be used to remove excess residual chlorine before it enters the receiving waters thus reducing chlorine-associated water toxicity.

Dechlorination is most typically achieved by the addition of chemical dechlorination agents to chlorinated waters. These agents include sulfite salts – sodium metabisulfite, sodium bisulfite and sodium sulfite; thiosulfates – calcium thiosulfate and sodium thiosulfate; and even ascorbic acid (Connell 2002). While the aforementioned agents are all capable of reducing residual chlorine levels, sulfite salts are commonly used due to the ease of handling

and control. Various studies have investigated the effectiveness of the sulfite salts, thiosulfates and ascorbic acid for dechlorination. Sulfite salts were found to require less time for dechlorination reactions than thiosulfates (Environment Canada 2006) but were also less effective than thiosulfates for the reduction of chloramines (Bedner et al. 2004). While Peterka (1998) concluded that ascorbic acid was effective in reducing the free chlorine and chloramine components of residual chlorine, Bedner et al. (2004) found that ascorbic acid was not as efficient as sulfite salts for dechlorination purposes. However, a systematic assessment of these three chemical options has not been carried out making it difficult to compare them against each other.

Studies have also shown that most dechlorination systems in use fail to provide sufficient dechlorination to meet the stringent regulatory requirements for residual chlorine concentrations (Bedner et al. 2004; Environment Canada 2006). This insufficient provision of dechlorination could be due to interference of water quality components with the reaction of dechlorination agents and residual chlorine. Apart from microbial pathogens, the raw water source may also contain other components such as natural organic matter, or high levels of suspended inorganic solids. The presence of these components as well as the type of residual chlorine present in the treated water could both have an impact on the rate of dechlorination as well as completion of the dechlorination reaction.

Two different types of experiments were employed during the course of the study. Firstly, dechlorination experiments were performed to investigate the impact of small changes in water quality on the rate of dechlorination of three chemicals with respect to free chlorine and monochloramine solutions. Dechlorination chemicals tested were sodium bisulfite (SBS), sodium thiosulfate (STS) and ascorbic acid (AA). Sodium bisulfite was chosen to represent the sulfite salts as it is the more frequently used salt due to its relative efficiency in terms of speed of dechlorination (Kirmeyer et al. 2004). While STS was selected due to its common use in wastewater applications in the USA (Tikkanen et al. 2001), AA was chosen due to its emergence as an environmentally friendly alternative for dechlorination agent (Peterka 2002).

Furthermore due to the lack of literature on the effect of the dechlorination agents on the final quality of the treated water, the impact of the dechlorination chemicals on the final quality of water with respect to pH, total organic carbon (TOC) and turbidity were compared during the dechlorination experiments. Acute toxicity tests were also conducted using the indicator aquatic species *Daphnia magna* to determine the toxic effects of each of the three chemicals on the aquatic environment.

METHODS AND MATERIALS

Dechlorination experiments

A schematic diagram of the experimental set up for dechlorination experiments with respect to free chlorine and monochloramine is shown in Figure 1. The setup made use of a DULCOMETER® D1C continuous pH and chlorine analyzer to measure changes in total and free chlorine (mg/L Cl_2) as well as pH of the test solutions during dechlorination experiments. Test solution stored in an 18 L mixing reactor was pumped to the DULCOMETER® D1C probe chamber and back to the reactor using a Cole Parmer – Masterflex peristaltic pump (model # 7024-20). The test solution was continuously mixed in the reactor at 550 rpm (G-value = 717 s^{-1}) using a VWR™ overhead mechanical stirrer (Power Max Elite Dual Speed Meter) to maintain the homogeneity of the test solution.

Secondary chlorine measurements were collected and analyzed using the HACH® DR2800 spectrophotometer and HACH analysis methods DPD Method 8021, DPD Method 8167 and the Indophenol Method 10171 to measure free chlorine (mg/L Cl_2), total chlorine (mg/L Cl_2) and monochloramine (mg/L as Cl_2) respectively for the various test solutions. Total organic carbon was measured using the TOC-V CPN unit of a SHIMADZU TOC-VCPH/CPN total organic carbon analyzer while turbidity of the test solutions was measured using a HF Scientific Inc. MicroTPW/MicroTPI portable turbidity meter.

Two stoichiometric dosages, namely 1× and 3× stoichiometric dosage of each dechlorination chemical, were employed during the experiments. The dosages required to remove 1 mg of free chlorine from chlorinated waters were 1.45 mg for SBS and 2.5 mg AA, based on reactions 1 and 2 for SBS and AA respectively. In the case of STS, due to the pH dependency of STS for the removal of chlorine in
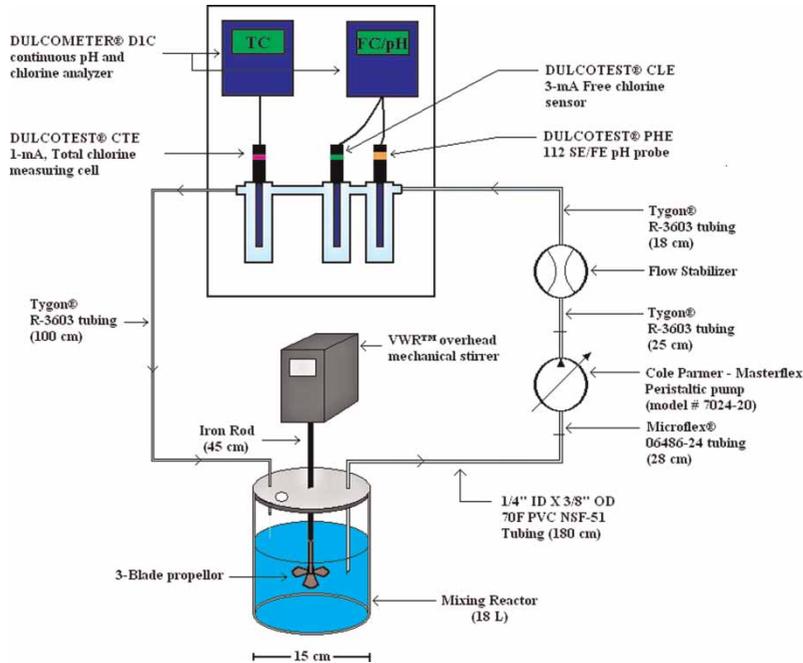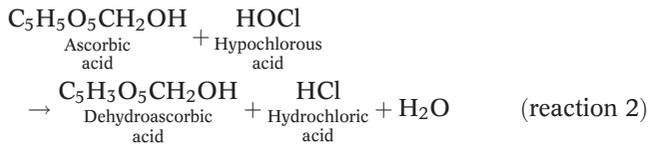
Figure 1 | Schematic diagram of experimental set up for dechlorination experiments.

water, a dosage of 2.23 mg of STS was utilized to remove 1 mg of chlorine with STS dosage being dependent at a pH of 6 (Wang *et al.* 2006).

$$\underset{\substack{\text{Sodium}\\\text{bisulfite}}}{NaHSO_3} + \underset{\substack{\text{Hypochlorous}\\\text{acid}}}{HOCl} \rightarrow \underset{\substack{\text{Sodium}\\\text{bisulfate}}}{NaHSO_4} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{HCl} \qquad (\text{reaction 1})$$

$$\underset{\substack{\text{Ascorbic}\\\text{acid}}}{C_5H_5O_5CH_2OH} + \underset{\substack{\text{Hypochlorous}\\\text{acid}}}{HOCl}$$

$$\rightarrow \underset{\substack{\text{Dehydroascorbic}\\\text{acid}}}{C_5H_3O_5CH_2OH} + \underset{\substack{\text{Hydrochloric}\\\text{acid}}}{HCl} + H_2O \qquad (\text{reaction 2})$$

Dechlorination by $1\times$ and $3\times$ stoichiometric dosage of each dechlorination chemical was performed in duplicate or triplicate on four different test solutions. In the instance where simultaneous experiments achieved similar results, the tests were only performed twice. The constituents of the four test solutions differed based on the water quality parameters being tested which included dissolved organics (TOC), inorganic particulate matter (turbidity – nephelometric turbidity units (NTU)) and residual chlorine species concentrations (free chlorine and monochloramine). The formula of the test solutions with respect to the water quality parameter

tested is shown in Table 1. Hardness chemicals were incorporated in the formula for each test solution to simulate the hardness of natural source waters and receiving waters. The chemical composition was as follows: sodium bicarbonate ($NaHCO_3$ – 192 mg/L), calcium sulfate ($CaSO_4$ – 120 mg/L), magnesium sulfate ($MgSO_4$ – 120 mg/L) and potassium chloride (KCl – 8mg/L) allowing for a final expected hardness in the range 160–180 mg/L $CaCO_3$.

Table 1 | Constituents of test solutions for dechlorination experiments

Test parameter	Test solution	Formula
Free chlorine (baseline test)	Test solution 1	8L Distilled water + hardness chemicals + free chlorine
Free chlorine + dissolved organic matter (mg/L TOC)	Test solution 2	8L Distilled water + hardness chemicals + free chlorine + glucose (20 mg/L TOC)
Free chlorine + inorganic particulate matter (NTU)	Test solution 3	8L Distilled water + hardness chemicals + free chlorine + kaolin clay (~5 NTU)
Monochloramine	Test solution 4	8L Distilled water + hardness chemicals + monochloramine

Free chlorine was added to test solutions 1, 2 and 3 in the form of sodium hypochlorite (NaOCl) to achieve free chlorine concentrations of 2.0 mg/L Cl_2. In test solution 4, monochloramine concentrations of 2.0 mg/L as Cl_2 were achieved by combining sodium hypochlorite with ammonium chloride (NH_4Cl) in a 4:1 weight ratio of Cl_2:NH_3-N. For experiments using SBS and AA, this combination was performed at a pH of 8.5, which is ideal for the formation of monochloramine in solution. In the case of experiments using STS, monochloramine concentrations were achieved at a lower pH of 6.5 to enable the consistent use of the stoichiometric dosage of STS for all STS experiments. Organic matter for test solution 2 was added in the form of glucose to achieve concentrations of 20 mg/L TOC which can be experienced in wastewater effluent. A turbidity value of 5 NTU representing the maximum turbidity acceptable for unrestricted urban reuse such as toilet flushing and fire protection (USEPA 2004) was used for test solution 3 and was achieved by adding kaolin clay to the test solution. When required, the pH of the various solutions was altered using hydrochloric acid (HCl) to lower the pH of solutions and sodium hydroxide (NaOH) to increase the pH of test solutions. The baseline measurements for water quality parameters in the test solutions can be seen in Table 2.

Acute toxicity tests

Acute toxicity tests were performed to identify the impact of the three dechlorination chemicals with respect to the aquatic environment (Environment Canada 1990). These tests made use of the aquatic indicator species *D. magna* and assessed the percentage mortality of the organism when in contact with the three dechlorination chemicals (Table 3).

The cultured *Daphnia* were maintained in deionized water as required by the standard procedure, with hardness added as described previously. The temperature of the culture solutions was maintained at $20 \pm 1\,^{\circ}C$ by placing them in an incubator with a photo-period of 16 h light: 8 h dark of 'cool-white' fluorescent light of 400–800 lux. Dissolved oxygen (DO) levels in the culture media were maintained at > 80% by aerating if necessary. The pH of the culture medium was adjusted to between 6.5 and 8.5, if necessary. Monthly 48 hour reference toxicity tests were conducted using zinc sulfate as the reference toxicant to investigate the general health of the cultures. Stock cultures received daily water changes, and laboratory cultured algae feed of 12 mL/L of dilution water, consisting of a mixture of *Selenastrum capricornutum* and *Chlorella pyrenoidosa*, and 4 mL/L of dilution water of laboratory prepared yeast-cerophyl-trout chow, made-up according to the method outlined by USEPA (2002) using Fleishmann's® Yeast, Tetramin® fish flakes and rabbit pellets made of alfalfa leaves. Algal culture medium was also prepared according to the method outlined in the USEPA method 13 (2002).

Temperature, DO, pH and conductivity of the test solutions were measured at least once at the beginning, and at the end of the tests as recommended (Environment Canada 1990). The pH and the DO of the test solutions were not adjusted after the addition of the dechlorination chemical during the test setup, since suppression of pH and DO is one of the indirect effects of some chemicals on the aquatic environment (Environment Canada 2006; Ryon *et al.* 2002). The daphnids were not fed during the tests and were visually observed in terms of mortality and

Table 2 | Baseline measurements of water quality parameters in test solutions

| Test parameters | Test solution | | | |
	1	2	3	4
Baseline measurements				
pH	6.5–8.5	6.5–8.5	6.5–8.5	6.5–8.5
Turbidity (NTU)	0.02	0.02	5.0	0.02
TOC (mg/L)	0.70	20.00	0.70	0.70
Free chlorine (mg/L Cl_2)	2.0	2.0	2.0	0
Monochloramine (mg/L as CL_2)	0	0	0	2.0

Table 3 | Concentrations of dechlorination chemicals used in 48 hours *Daphnia magna* mortality testing

Dechlorination chemical	Concentrations tested (mg/L)[a]
SBS	0, 4.6, 10, 20, 22, 50, 100, 200
STS	0, 4.6, 10, 20, 22, 46, 100, 150, 200
AA	0, 1, 10, 20, 100, 200
Chlorine	0, 0.1, 1, 5, 10

[a] For all of the dechlorination chemicals, a control solution was tested with dilution water and no dechlorination chemical (0 mg/L).

movement at the beginning (0–1 hours) and at the end of the test (48 ± 2 hours). Tests were run in triplicate.

RESULTS AND DISCUSSION

Dechlorination of free chlorine

Two options for the analysis of experimental data were considered for the identification of the order and dechlorination reaction rate constants: the integral method and the differential method for analyzing kinetic data. Experimental data consisting of measured chlorine concentrations over time required a time dependent method of data analysis. The integral method was selected as it accounts for the time dependency of the decrease in chlorine concentrations (Levenspiel 1999).

For each of the dechlorination chemicals the order and rate of reaction was determined using the integral method. Therefore each reaction was initially considered to be an irreversible bimolecular second order reaction. In the event of the reactions failing a second order test, the data were put through zero and first order tests to determine the possible pseudo-zero order or pseudo-first order of the reactions. Reaction rates constants obtained for the dechlorination of the three test solutions for 3× stoichiometric dosage of each dechlorination agent are shown in Table 4.

The rates of dechlorination of test solutions 2 and 3 were compared to those of the control solution for each dechlorination chemical. This comparison was performed to study the impact of organic and inorganic matter on dechlorination. The presence of inorganic particulate matter (5 NTU) was found to have no impact on the rate of dechlorination

for any of the three chemicals. The presence of dissolved organics (20 mg/L) was found to have conflicting results with an increase in the rate of dechlorination for STS, but no similar increase for SBS or AA was noted.

Results from dechlorination tests using SBS showed that a 1× stoichiometric dosage of SBS was insufficient for complete dechlorination of test solutions irrespective of their constituents. Considering that water and wastewater treatment plants employ a stoichiometric dosage a little higher than 1×, these results are consistent with the finding of incomplete dechlorination by most dechlorination systems as reported by Bedner *et al.* (2004) and Environment Canada (2006). However, the complete removal of residual total chlorine from test waters was achieved at the 3× stoichiometric dosage (Figure 2). In the case of 1× stoichiometric dosage of SBS, a lower overall removal of total chlorine was observed in test solutions containing organic and inorganic matter compared to the control. While the differences between the post dechlorination chlorine levels of solutions 1 and 2 and solutions 1 and 3 are relatively small, the findings suggest that organic and inorganic matter may be responsible for inhibiting dechlorination at low stoichiometric dosages of SBS.

The 3× stoichiometric dosage of SBS was successful in achieving complete dechlorination. When comparing the pseudo-zero order reaction rate constant of 0.10 mg/L.s determined for test solution 1 with 0.12 mg/L.s determined for test solution 2 (Table 4), it was found that the presence of organic matter did not result in a noticeable change in reaction rate constants. Similarly, on comparing the rate constants for solution 1 and solution 3 (Table 4), it was concluded that the presence of inorganic particles in the test solution did not impact the rate of dechlorination by SBS.

Table 4 │ Dechlorination rate constants for SBS, STS and AA

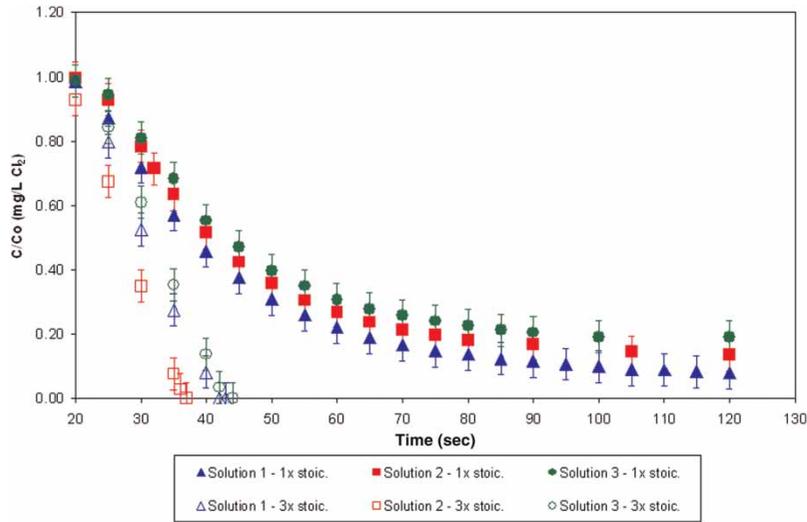|	Constituents in test solution		
	Test Solution 1 – control	Test solution 2 – TOC (20 mg/L)	Test Solution 3 – turbidity (5 NTU)
Sodium bisulfite – pseudo-zero order			
3× Stoich.	0.10 mg/L.s	0.12 mg/L.s	0.10 mg/L.s
Ascorbic acid – pseudo-zero order			
3× Stoich.	0.12 mg/L.s	0.12 mg/L.s	0.10 mg/L.s
Sodium thiosulfate (STS) – second order			
3× Stoich.	0.0043 L/mg.s	0.0066 L/mg.s	0.0044 L/mg.s

Figure 2 | Chlorine removal using SBS.

As in the case of SBS, a $1\times$ stoichiometric dosage of AA was found to be insufficient for the complete removal of total chlorine from test solutions (Figure 3). Similar to the results observed with SBS, organic and inorganic matter in the test solutions resulted in a slightly lower overall removal of total chlorine suggesting that the presence of organic and inorganic matter inhibit dechlorination at low stoichiometric dosages of AA. The $3\times$ stoichiometric dosage of AA resulted in complete dechlorination while the presence of organic and inorganic particles in test solutions did not have any evident impact on the pseudo-zero order rate constants determined for the dechlorination reactions at this dosage.

While complete dechlorination was not achieved using $1\times$ stoichiometric dosage of STS, the complete removal of total chlorine was achieved using $3\times$ stoichiometric dosage of STS (Figure 4). The reaction time using STS as dechlorination chemical was approximately 75–100 s compared to SBS (37–44 s) and AA (39–42 s) over the different test solutions at the $3\times$ stoichiometric level. Other studies have also found STS to be slower than SBS and AA for dechlorination purposes (Ryon et al. 2002) The presence of organic matter had an impact on the determined reaction rate constant for STS, specifically the 53% increase of the reaction rate constant compared to the control test solution (refer to Table 4). This increase in the
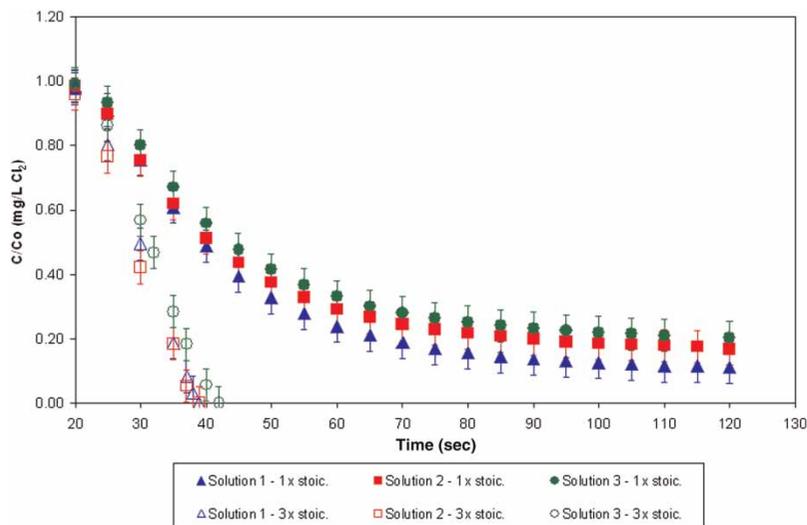

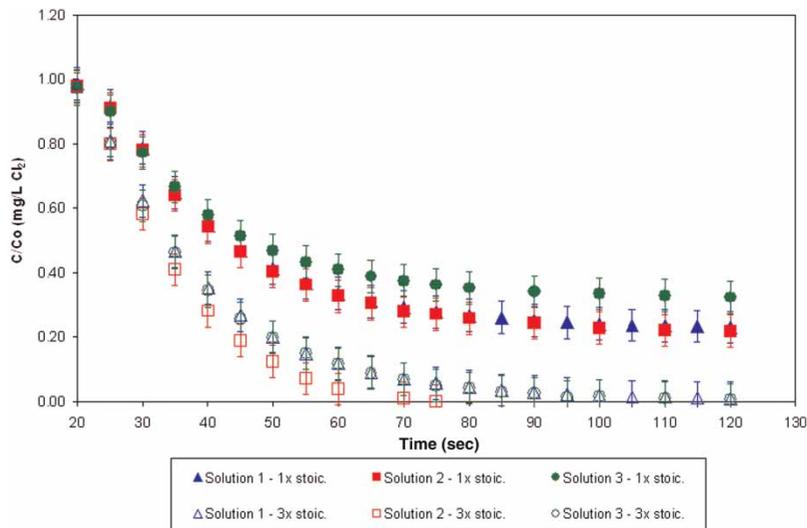**Figure 3** | Chlorine removal using AA.

Figure 4 │ Chlorine removal using STS.

rate of dechlorination by STS can be attributed to a chlorine demand brought about by reactions between chlorine and STS as well as the rapid reaction of chlorine and organic compounds at lower pH levels (Svenson *et al.* 2002).

Dechlorination of chloramine

Dechlorination tests of monochloramine instead of free chlorine provided intriguing results. These tests measured the effect of the three dechlorination chemicals on the rate of change of monochloramine as mg/L Cl_2. In contrast to results reported by Helz & Nweke (1995), SBS was found to be effective in reducing monochloramine from test waters. Dechlorination was found to be quick and complete at a $3\times$ stoichiometric dosage but not at a $1\times$ stoichiometric dosage. Complete dechlorination was also achieved using $3\times$ stoichiometric dosage of STS but at a much slower rate than SBS. Interestingly, AA was found to be completely ineffective for the removal of chloramines in test solutions even at the higher $3\times$ stoichiometric dosage. These results contradict the findings of Peterka (1998) who reported that AA was effective in reducing chloramine levels.

The removal of monochloramine using $3\times$ stoichiometric dosage of SBS occurred quickly with a completion time of approximately 32 s compared to 42 s for the control solution (only free chlorine) with a pseudo-zero order reaction rate constant of 0.23 mg/L.s (see Table 4). These results suggest that the presence of monochloramine in the test

solution had a positive impact on dechlorination using SBS. In the case of $3\times$ stoichiometric dosage of STS, dechlorination was comparable to that of the control solution with a second order reaction rate constant of 0.0038 L/mg.s indicating that the presence of monochloramine versus free chlorine did not influence the rate of reaction for STS.

Dechlorination using AA was found to be completely ineffective for the removal of chloramines as can be seen in Figure 5. The pseudo-zero order reaction rate constant of 0.001 mg/L.s is much smaller than the reaction rate constant of the control test. Ascorbic acid has been reported to be an effective and environmentally friendly option for dechlorination in place of sulfur based dechlorination (Peterka 2002). While this is true for free chlorine, dechlorination of monochloramine using AA must be viewed more cautiously.

Impact of dechlorination agents on water quality

Three water quality parameters namely pH, turbidity and TOC were monitored for changes with the different test solutions employed. Experimental results showed that the pH of the solution was only affected when a $3\times$ stoichiometric dosage of STS was used to dechlorinate solution containing monochloramine. Results also showed that the use of AA led to an increase in the TOC of the solution which could be of concern in natural waters receiving dechlorinated
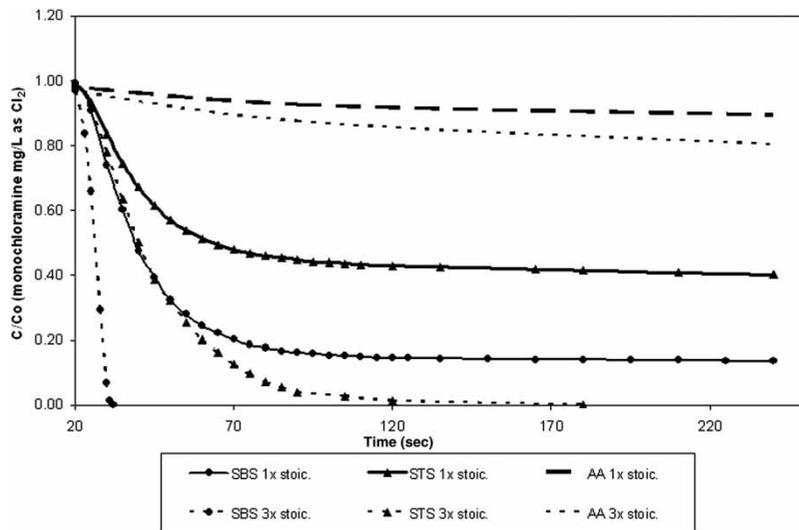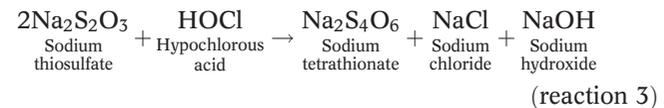
Figure 5 │ Removal of monochloramine using SBS, AA, and STS.

effluent and also in drinking water distribution systems. Turbidity was not impacted during any of the tests performed.

The effect of the three dechlorination chemicals on the final pH of the test solutions after dechlorination can be seen in Table 5. Due to the acidic nature of SBS, studies have shown that dechlorination using SBS results in a pH reduction of receiving waters (Tikkanen *et al.* 2001). Similarly, AA being an acid also contributes to pH reduction of receiving waters (Environment Canada 2006). However, Table 5 shows that at $1\times$ and $3\times$ stoichiometric dosage of AA and SBS, no major change in the pH of the test solutions was observed. On the contrary, the most noticeable effect on the final pH was a 25% increase in pH brought about by the use of STS which was reported to not have any direct

influence on pH by Wang *et al.* (2006). The large increase of pH could be due to the formation of the strong base NaOH as a by-product of one of the dechlorination reactions between STS and chlorine (refer to reaction 3). Such a change in pH of the dechlorinated water could be of concern especially for receiving waters.

$$2Na_2S_2O_3 + HOCl \rightarrow Na_2S_4O_6 + NaCl + NaOH$$

$$\text{Sodium thiosulfate} + \text{Hypochlorous acid} \rightarrow \text{Sodium tetrathionate} + \text{Sodium chloride} + \text{Sodium hydroxide}$$

(reaction 3)

The effect of dechlorination chemicals on turbidity and TOC levels can be found in Table 6. The dechlorination chemicals caused no major change in the turbidity of the test solutions during the dechlorination experiments. A large increase in

Table 5 │ Effect of SBS, AA and STS on the pH of test solutions

Test parameters	Test solution Solution 1 – control	Solution 2 – TOC (20 mg/L)	Solution 3 – turbidity (5 NTU)	Solution 4 – monochloramine
pH readings at $1\times$ stoichiometric				
SBS	No change	No change	No change	No change
AA	No change	No change	No change	No change
STS	No change	−0.41	No change	+0.42
pH readings at $3\times$ stoichiometric				
SBS	No change	No change	No change	−0.52
AA	No change	No change	No change	No change
STS	No change	No change	No change	+1.69

No change indicates change $\leq 5\%$ of initial pH reading.

Table 6 | Changes to turbidity and TOC levels as a result of dechlorination

Test parameters	Test solution Solution 2 – TOC (20 mg/L)	Solution 3 – turbidity (5 NTU)
Turbidity and TOC at 1× stoichiometric		
SBS	No change	No change
AA	+1.97	No change
STS	No change	+0.36
Turbidity and TOC at 3× stoichiometric		
SBS	No change	No change
AA	+6.07	+0.32
STS	No change	No change

No change indicates measure value within 5% of initial measurements.

TOC levels was noticed when both stoichiometric dosages of AA were used to dechlorinate solution 2. This increase in TOC was found to be equal to the amount of TOC in AA added to the test solution for both stoichiometric dosages. Such a high level increase in TOC would not be suitable for a water distribution system, as it might contribute to biofilm growth within the distribution piping network. Depending on the receiving water quality from a wastewater treatment plant effluent, the increase in TOC may or may not be acceptable in these circumstances and would certainly have to be evaluated on a site-specific basis.

Acute toxicity testing

The percentage survival values obtained for *D. magna* under different concentrations of the three dechlorination chemicals tested are illustrated in Figure 6. Sodium bisulfite was observed to be non-toxic at concentrations less than approximately 20 mg/L indicating a toxic threshold below which no adverse impact is observed. Anderson (1946) reported the 48 hour LC_{50} for SBS at 190 mg/L while this research determined the SBS LC_{50} value to be 68 mg/L using the USEPA Graphical Method (USEPA 2002). Previous reports show that a reduction in DO, sufficient to cause a fish kill, is to be expected when the in-stream concentrations of sulfur salts are equal to or exceed ~39 mg/L (Ryon *et al.* 2002). In this study, SBS concentrations greater than 50 mg/L results in approximately a 4–9% DO reduction; it is possible that this reduction in conjunction with the inherent toxicity of the SBS itself resulted in the observed *D. magna* mortality.

Sodium thiosulfate did not cause any mortality at concentrations up to 200 mg/L. The STS EC_{50} for *D. magna* has been previously reported to be as high as 1334 mg/L (Oh *et al.* 2008). Also, pH and DO values (see Table 7) show that the addition of STS did not alter the solution pH or the DO concentration more than 0.3 units and 2%, respectively. Thus, STS was not observed to have any direct or indirect lethal effects on *D. magna*; making STS a good choice of dechlorination chemical for wastewater facilities.

Approximately 15% mortality was observed at 20 mg/L with AA and increased upwards of 80% mortality at 200 mg/L. This result at 200 mg/L was unexpected as it has been reported in the literature as non-toxic at concentrations up to 190 mg/L (NICNAS 2003) whereas in this study the
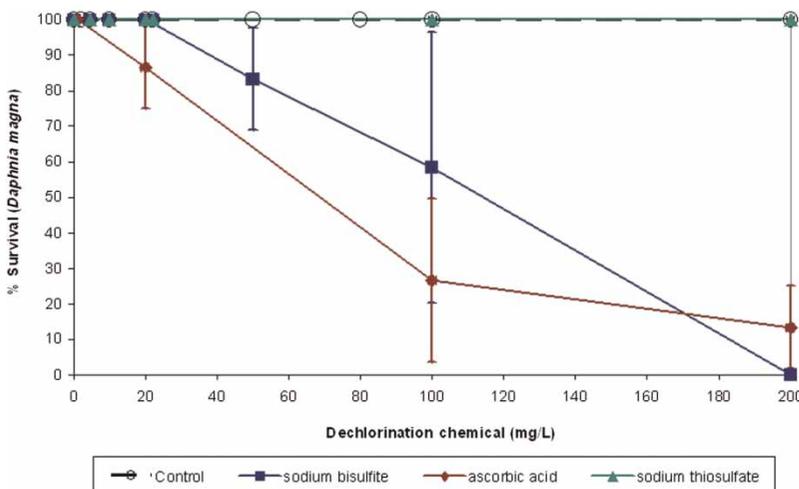
Figure 6 | Acute toxicity of *D. magna* with SBS, STS, and AA.

Table 7 │ Dissolved oxygen and solution pH changes with dechlorination chemical (DC)

DC	5 mg/L Init.[b]	Avg. Δ	10 mg/L Init.	Avg. Δ	20 mg/L Init.	Avg. Δ	50 mg/L Init.	Avg. Δ	100 mg/L Init.	Avg. Δ	200 mg/L Init.	Avg. Δ
Dissolved oxygen in solution[a]												
Sodium bisulfite	97	−2	97	−1	96	−1	93	−5	94	−4	83	−9
Sodium thiosulfate	97	−1	97	0	97	+2	n/a	n/a	94	−1	83	0
Ascorbic acid	97	−4	97	−2	96	−3	n/a	n/a	90	−5	83	−2
Solution pH												
Sodium bisulfite	6.8	−0.2	7.7	−0.2	7.7	−0.6	6.8	−0.2	6.5	−0.3	6.8	−0.3
Sodium thiosulfate	7.3	−0.3	7.3	−0.4	6.8	−0.1	n/a	n/a	6.8	−0.1	6.8	−0.1
Ascorbic acid	7.7	−0.2	7.3	−0.2	7.7	−0.2	n/a	n/a	7.3	−0.5	6.8	−1.2

The average change (Avg Δ) is indicated as positive (+), if the DO or pH value increased following the addition of the dechlorination agent. If the DO or pH value decreased following the addition of the dechlorination agent, the value is indicated as negative (−).

[a] Dissolved oxygen (DO) as % solution saturation.

[b] Init = initial starting conditions, prior to DC addition.

LC_{50} value was determined to be approximately 70 mg/L. The reason for this observed discrepancy in results may be that the NICNAS (2003) toxicity test study was conducted under controlled pH conditions, which would have masked any indirect toxicity as a result of pH suppression. For instance, at 100 and 200 mg/L the pH of the solution decreased by 0.5 and 1.2 pH units, respectively (see Table 7). The mortality observed for AA concentrations ≥ 100 mg/L could be due to the pH suppression that is caused by AA in solution. Therefore AA indirectly causes toxicity to *D. magna* at higher concentrations. However, the pH and DO did not change appreciably at the 20 mg/L AA dosage and therefore this is either due to AA itself or potentially some degree of experimental error. It is important to note that the concentration of both AA and SBS that lead to significant daphnid mortality would only occur at dosages where an accidental spill occurred. At the low levels used in practice (i.e. 3× stoichiometric dosages) with respect to the anticipated residual chlorine that requires dechlorination, it is not likely that any toxicity impact would be observed from these chemicals.

CONCLUSIONS

Dechlorination reactions were determined to be pseudo-zero order for both SBS and AA and second order for STS. The rate of dechlorination using SBS was found to increase when monochloramine was the main residual chlorine species in solution. While the rate of dechlorination using STS was found to increase in test solutions with spiked organic content, STS generally required a longer time for complete dechlorination compared to SBS and AA. Ascorbic acid was found to be inefficient for the removal of chloramines but comparable to SBS dechlorination rates for the removal of free chlorine.

The use of SBS as dechlorination agent had no impact on the pH, turbidity and TOC of the test waters post dechlorination. Acute toxicity tests identified a threshold of 50 mg/L SBS above which SBS had toxic effects on *D. magna*. Dechlorination using AA was found to increase the TOC of the test waters post dechlorination. This increase in TOC creates a carbonaceous biochemical oxygen demand (cBOD) in receiving waters thus resulting in indirect depletion of oxygen in receiving waters. The increase in readily biodegradable carbon may also contribute to biofilm growth in water distributions systems. Higher levels of AA were found to contribute to some level of mortality with the acute toxicity testing.

While dechlorination using STS did not have any impact on the turbidity and TOC of the test solutions post dechlorination, a major increase in pH was noticed when the 3× stoichiometric dosage of STS was used to dechlorinate the monochloramine solutions. Such an increase in the pH is a source of potential harm to aquatic species in receiving waters. Acute toxicity testing found no negative impact on the *D. magna* test species with within the test range of 200 mg/L STS.

Further research examining the impact of wastewater effluent on the anticipated rates of dechlorination should

be examined. In addition, monitoring low chlorine residuals in wastewater to ensure the appropriate chlorine residual has been obtained should be examined by comparing measurements of excess reagent versus chlorine residual and oxidation reduction potential.

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