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Removal of Chlorine Residual in Tap Water by Boiling or Adding Ascorbic Acid

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ABSTRACT

Society's preference for bottled water mainly comes from a dislike of the mildly pungent taste and odor of tap water. Such odor and taste may be caused by chlorine residual (in the form of free chlorine or chloramines), which is maintained in a water distribution system to prevent regrowth of microorganisms and is thus present in tap water. To encourage individuals who drink bottled water to shift to tap water, which affords numerous financial and environmental advantages, a simple, effective and low-cost method of reducing chlorine residual in tap water is essential. Two methods of reducing chlorine residual, boiling tap water and adding ascorbic acid to tap water, were tested. The results showed that, for free chlorine, a quick and cheap way to reduce chlorine residual is to add ascorbic acid, which if added in an equal molar amount to free chlorine would completely eliminate chlorine residual within 1 min. For monochloramine, a quick and cheap way to reduce chlorine residual is also to add ascorbic acid, but in greater quantity due to some ascorbic acid being oxidized by oxygen in the air. Although boiling is slower, it is effective in removing low concentrations of chlorine residual.

***Keywords*:** Drinking Water, Tap Water, Chlorine Residual, Boiling, Ascorbic Acid.

I. INTRODUCTION

Chlorine is widely used to disinfect raw water in drinking water treatment plants. It is low in cost and effective in inactivating harmful microorganisms and eliminating waterborne diseases, such as the cholera-causing bacteria *Vibrio cholerae* [1]. Treated water from a treatment plant is distributed to households via a public drinking water distribution system. During distribution, a low concentration of chlorine is maintained to prevent regrowth of microorganisms in the water, especially due to possible leaks and other weaknesses in the system [2]. Thus, household tap water contains chlorine residual.

Like its effect on pathogens and parasites, chlorine attacks delicate body tissues when tap water is consumed. Many concerns have been raised about the safety of chlorine residual in tap water, which has been linked to adverse health effects, including dementia in elderly patients [3] and heightened food allergies [4]. More significantly, chlorine residual in tap water causes a mildly pungent odor and taste, which may be one of the primary reasons for people to consume bottled water. It is known that bottled water is considerably more expensive than tap water. Aside from financial costs, purchasing bottled water or delivered water induces environmental costs, mainly associated with packaging, transportation and disposal. In any given year in the United States, 17 million barrels of crude oil is used to make plastic for 29 billion bottles of water, which require 50 million barrels of oil to transport and result in 2 million tons of non-biodegradable plastic waste [5]. Accordingly, a simple, effective and low-cost method of reducing chlorine residual in tap water is essential for sustainable and palatable drinking water.

Two forms of chlorine residual exist in tap water, free chlorine and combined chlorine. When chlorine gas (Cl_2) is applied to water, it undergoes a disproportionation reaction to form hypochlorous acid (HOCl) and hydrochloric acid (HCl). Hypochlorous acid is known as free chlorine. In the presence of ammonium ions, monochloramine (NH_2Cl) is also formed. Monochloramine is a species of combined chlorine. Combined chlorine also includes dichloramine ($NHCl_2$) and trichloramine (NCl_3), but these two species exist in very low concentrations in tap water, ranging from 0.0003 to 0.0025 mg/L [6]. In this investigation, only monochloramine is tested. The U.S. Environmental Protection Agency [7] stipulates that the annual average concentration of chlorine residual in tap water must not exceed 4.0 mg/L.

It is known that chlorine residual may decompose when exposed to sunlight and that ascorbic acid (in the form of vitamin C tablets, an essential nutrient and a reducing agent) may reduce chlorine residual to chloride ions. However, the reduction of chlorine residual in tap water by heating and boiling tap water or by adding ascorbic acid to tap water has not previously been investigated systematically and quantitatively. Either method is safe and could be a quick and easily accessible means to reduce chlorine residual in households. Therefore, boiling tap water and adding ascorbic acid to tap water were systematically tested and compared in this investigation.

II. EXPERIMENTAL METHODS

2.1 Chemicals and Reagents

All chemicals used were of analytical grade. All solutions used were prepared with ultrapure water (18.2 MΩ·cm) supplied by a NANOpure system (Barnstead). Ascorbic acid was purchased from Sigma, and a stock solution (17600 mg/L) was freshly prepared before use. A free chlorine stock solution (NaOCl, ~2000 mg/L as Cl_2) was prepared by diluting a commercial sodium hypochlorite solution (15% active chlorine, Allied Signal) and standardized using the N,N-diethyl-p-phenylene diamine (DPD) ferrous titration method [8] prior to use. An monochloramine stock solution was prepared just before use by adding the free chlorine stock solution to an ammonium chloride solution at a chlorine to ammonia mole ratio of 0.8:1.0.

2.2 Removal of Chlorine Residual in Tap Water by Boiling

A fresh tap water sample was collected locally. The chlorine residual in it was measured immediately using the DPD ferrous titration method [8]. As shown in Results and Discussion, the chlorine residual in the tap water sample was mainly free chlorine. Two L of the tap water was heated on a magnetic stirring heater with temperature monitoring. A series of 100-mL aliquots of water were sampled at the temperature of 40, 60, 70, 80, 90, and 100 °C, and cooled with an iced water bath. The chlorine residual in each aliquot was measured once it was cooled to room temperature [8].

To better observe the effect of boiling on chlorine removal, free chlorine was added to two L of the tap water at ~4 mg/L as Cl_2 (to simulate the maximum chlorine residual level that is allowed in the distribution system). The measured chlorine residual was 4.01 mg/L as Cl_2. Then the tap water with added free chlorine was heated to boiling. A series of aliquots (~110 mL each) of the boiled water were sampled at the boiling time of 0 (the moment when the water reached 100 °C), 2, 5, 10, 15, 20, 30, 60 min, and cooled with an iced water bath. Once an aliquot was cooled to room temperature, the chlorine residual in it was measured using the DPD ferrous titration method [8]. To investigate the effect of boiling on monochloramine removal, monochloramine was added to two L of the tap water at ~4 mg/L as Cl_2. The measured chlorine residual was 3.98 mg/L as Cl_2. The above experiment was repeated except that a series of aliquots were sampled at the boiling time of 0, 5, 10, 20, 30, 45, and 60 min.

2.3 Removal of Chlorine Residual in Tap Water by Adding Ascorbic Acid

Tikkanen et al. [9] reported that ascorbic acid could complete reduce free chlorine rapidly at a mole ratio of 1:1. However, there is rare research on using ascorbic acid to remove monochloramine. Thus, the purpose of this experiment is to determine the stoichiometric amount of ascorbic acid and the optimal reaction time for removing monochloramine in tap water. To better observe the effect of ascorbic acid on monochloramine removal, monochloramine was added to five 2-L tap water samples at ~4 mg/L as Cl_2. The measured chlorine residuals in the samples were in the range of 3.98−4.31 mg/L as Cl_2. Then the five samples were added with ascorbic acid at the chlorine to ascorbic acid mole ratio of 1:1.00, 1:1.37, 1:1.50, 1:2.00, and 1:2.50. The addition of ascorbic acid did not significantly change the pH of the five samples. For each sample, after the addition of ascorbic acid, a series of aliquots (100 mL each) were sampled after a reaction time of 0 (without the addition of ascorbic acid), 2, 5, 10, 15, 20, 30, 45, and 60 min, and the chlorine residual in each aliquot was measured immediately [8].

III. RESULTS AND DISCUSSION

3.1 Reduction of Chlorine Residual in Tap Water with Temperature

Figure 1 shows the reduction of chlorine residual in the tap water with heating temperature. The temperature in this experiment was directly proportional to the heating time. The magnetic stirring heater was kept at a constant stirring speed and a constant heating rate. This means that the reduction of chlorine residual was not simply due to longer heating time.

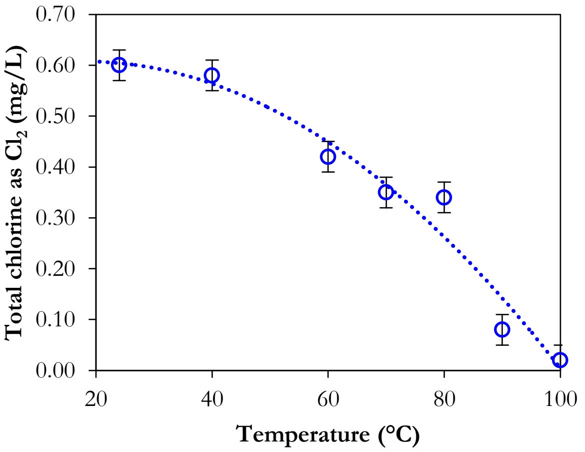

Figure 1. Reduction of chlorine residual in the tap water with heating temperature.

As shown in Figure 1, the chlorine residual decreased faster at higher temperatures. At room temperature (24 °C), the chlorine residual was 0.60 mg/L as Cl_2. At the boiling temperature of water (100 °C), the chlorine residual fell to 0.02 mg/L as Cl_2.

3.2 Reduction of Free Chlorine and Monochloramine in Tap Water through Boiling

Heating the water from room temperature (about 24 °C) to 98 °C required about 30 min. A small portion of the water (less than 5%), including its chlorine residual content, was vaporized in this period. Therefore, the starting concentration of free chlorine or monochloramine was lower than the original “elevated” concentration.

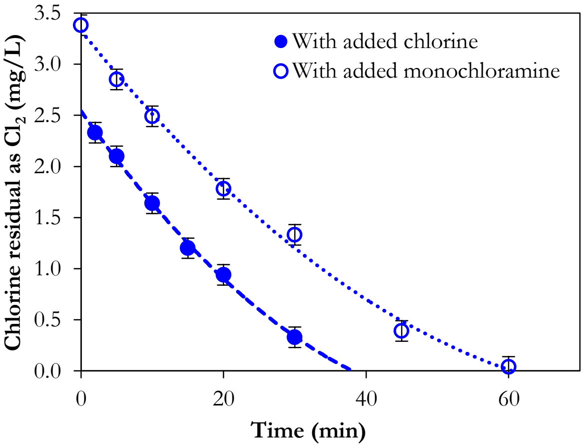

Figure 2. Reduction with boiling time of free chlorine and monochloramine in the tap water with elevated free chlorine and monochloramine.

Figure 2 shows the reduction with boiling time of free chlorine and monochloramine in the tap water with elevated free chlorine and monochloramine. In the set of data for boiling the tap water with elevated free chlorine, the chlorine residual refers predominantly to free chlorine. In the set of data for boiling the tap water with elevated monochloramine, the chlorine residual refers predominantly to monochloramine. However, there was a small concentration of free chlorine in the tap water with elevated monochloramine and of monochloramine in the tap water with elevated free chlorine owing to the presence of free chlorine and monochloramine in tap water itself.

As shown in Figure 2, both residuals of free chlorine and monochloramine decreased with boiling time, and the residual of free chlorine decreased slightly faster than that of monochloramine. A second degree polynomial was used to model the curve of best fit for each set of data.

For the tap water with elevated free chlorine, the best fit equation of chlorine residual (mg/L as Cl_2) versus boiling time (t, min) can be expressed as

$$\text{Free } Cl_2 \text{ residual} = 0.000843t^2 - 0.09881t + 2.5414$$

For the tap water with elevated monochloramine, the best fit equation of chlorine residual (mg/L as Cl_2) versus boiling time (t, min) can be expressed as

$$NH_2Cl \text{ residual} = 0.000522t^2 - 0.08656t + 3.3282$$

According to the equations, when the concentration of chlorine residual was 2.00 mg/L as Cl_2, the reduction rates of free chlorine and monochloramine were 0.0891 and 0.0687 mg/L-min, respectively. Also, when the chlorine residual was 2.00 mg/L as Cl_2, the boiling time required to completely remove free chlorine was about 33 min, and the boiling time required to completely remove monochloramine was about 44 min.

The decomposition of free chlorine through boiling is most likely due to the following reaction [10]:

$$3OCl^- \rightarrow ClO_3^- + 2Cl^-$$

The decomposition of monochloramine through boiling is most likely due to the following reaction:

$$3NH_2Cl + 3H_2O \rightarrow ClO_3^- + 3NH_4^+ + 2Cl^-$$

3.3 Effect of Ascorbic Acid on Free Chlorine and Monochloramine

Ascorbic acid added in a molar ratio of 1:1 (free chlorine to ascorbic acid) completely eliminated free chlorine. The DPD indicator did not produce a red color when added within 1 min after the addition of ascorbic acid. Reduction of free chlorine by ascorbic acid can be expressed as follows:

$$C_6H_8O_6 + HOCl \rightarrow C_6H_6O_6 + HCl + H_2O$$

Ascorbic acid ($C_6H_8O_6$) is oxidized to dehydroascorbic acid ($C_6H_6O_6$) (Bedner et al., 2004). Simultaneously, free chlorine (HOCl) is reduced to chloride ions (HCl).

Five tap water samples with added monochloramine were tested for the effect of ascorbic acid. Each sample was conducted with a different molar ratio of monochloramine to ascorbic acid. Monochloramine was completely eliminated in a short period of time after the addition of ascorbic acid. However, 2 min later, the concentration of monochloramine partially rebounded in 4 of the 5 samples (Figure 3).

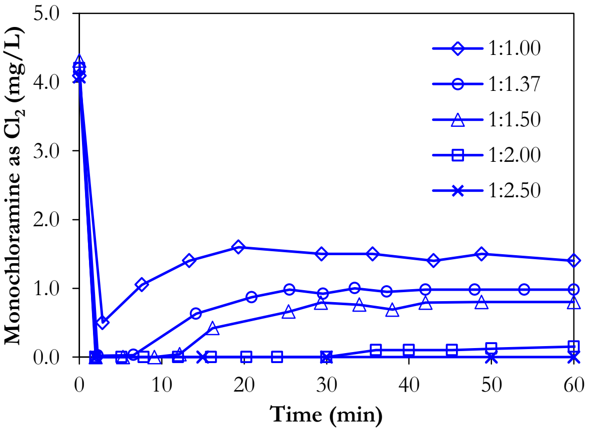

Figure 3. Change with time of monochloramine in the tap water with elevated monochloramine when different monochloramine to ascorbic acid mole ratios were used.

In each sample, the concentration of monochloramine fell to zero within 2 min after the addition of ascorbic acid. The only exception was the sample with 1:1.00 monochloramine to ascorbic acid, but this may have been due to a rebound in the concentration of monochloramine before the withdrawal of the aliquot at 2 min. Also, the concentration of monochloramine did not rebound at all within 60 min in the repeat with 1:2.50 monochloramine to ascorbic acid. The rebound in the concentration of monochloramine can be explained in terms of chemical equilibrium. The reduction of monochloramine by ascorbic acid can be expressed as:

$$C_6H_8O_6 + NH_2Cl \rightleftharpoons C_6H_6O_6 + NH_4Cl$$

Ascorbic acid ($C_6H_8O_6$) is oxidized to dehydroascorbic acid ($C_6H_6O_6$) [11]. Simultaneously, monochloramine (NH_2Cl) is reduced to ammonium chloride (NH_4Cl). When ascorbic acid was added in excess, the equilibrium position shifted to the right and monochloramine was initially completely reduced by ascorbic acid to ammonium chloride. The concentration of ascorbic acid then gradually fell as it was oxidized by oxygen dissolved in the solution and present in the air:

$$2C_6H_8O_6 + O_2 \rightleftharpoons 2C_6H_6O_6 + 2H_2O$$

As a result of the decrease in the concentration of ascorbic acid, the equilibrium position of the first reaction shifted to the left and monochloramine was reformed. This occurred until both of the reactions were in equilibrium. For a larger excess of ascorbic acid, the time required for ascorbic acid to be oxidized by air was longer, and thus there was a delay before the rebound in the concentration of monochloramine. In the repeat with 1:2.00 monochloramine to ascorbic acid, the rebound did not occur until 30 min after the addition of ascorbic acid. In the repeat with 1:2.50, the rebound did not occur at all in 60 min after the addition of ascorbic acid; this may have been due to the ascorbic acid being sufficiently in excess to shift the equilibrium position in each reaction to the right.

In contrast, the concentration of free chlorine did not rebound. This is because free chlorine is a much stronger oxidant than monochloramine. The equilibrium constant for the reduction of free chlorine by ascorbic acid is therefore much larger and the equilibrium position lies far to the right of the reaction.

IV. IV. CONCLUSIONS

The quickest way to reduce the concentration of free chlorine in tap water is to add powdered vitamin C (ascorbic acid) tablets. At a ratio of 1:1.00, free chlorine was completely eliminated by ascorbic acid in less than 1 min. For tap water containing 4 mg/L of free chlorine as Cl_2, which is the maximum concentration in the United States [7], it was determined that 10 mg of ascorbic acid is required to treat 1 L of tap water. A common vitamin C tablet weighs 500 mg and is commercially available in bottles of 300 for US $21. Potentially, this is enough to treat 15 m^3 of tap water. For lower concentrations of free chlorine (about 0.5 mg/L as Cl_2), heating the tap water from room temperature to boiling temperature eliminated nearly all of the chlorine residual. For higher concentrations of free chlorine (about 4.0 mg/L as Cl_2), heating the tap water from room temperature to boiling temperature plus additional an boiling time of 30 min eliminated about 95% of the chlorine residual. The latter case is not recommended due to its high energy cost.

Monochloramine is more difficult to treat. A 44-min boiling was required to eliminate 3.33 mg/L of monochloramine. The concentration of mono-chloramine did not rebound. A molar ratio of 1:2.50 monochloramine to ascorbic acid was required to eliminate monochloramine as well as inhibit its re-formation. For tap water containing 4 mg/L of monochloramine as Cl_2, which is the maximum concentration in the United States, it was determined that 25 mg of ascorbic acid is required to treat 1 L of tap water. The same bottle of vitamin C tablets treats 6 m^3 of tap water. In comparison to boiling tap water, adding ascorbic acid to tap water is still quicker, requiring less than 2 min to eliminate 4 mg/L of monochloramine.

This investigation has demonstrated that heating and boiling is effective in reducing of chlorine residual in tap water when the concentration of chlorine residual is relatively low; adding ascorbic acid, on the other hand, affords a much quicker reduction of chlorine residual in tap water when its concentration is relatively high. Both methods are simpler, less expensive and more effective in obtaining palatable drinking water than purchasing bottled water or delivered water.

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