Removal of Hexamethylenetetramine by Advanced Water Treatment

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INTRODUCTION

In May 2012, water quality accident occurred with detecting formaldehyde (FA) at water purification plants in the Tone River system (**Figure 1**). As a result, eight purification plants suspended water intake and water supply to approximately 360,000 houses, which affected approximately 870,000 people. The causative substance of the accident was hexamethylenetetramine (HMT) , which reacts with chlorine to form FA, not FA itself (**Figure 2**).

In this study, Bureau of Waterworks, Tokyo Metropolitan Government (hereafter called "Tokyo Waterworks") investigated time-dependent change in reaction of HMT with chlorine, presence of reaction products other than FA, and removal capacity of HMT in water treatment process including advanced water treatment.

Figure 1 Map of Kanto region in Japan

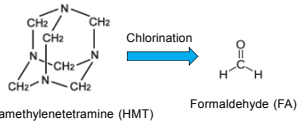

Figure 2 Formation of formaldehyde

METHODS

Reactivity of HMT with chlorine

Reaction rate of HMT with chlorine and conversion ratio to FA were investigated. Tokyo Waterworks prepared mineral water injected with HMT and raw water in the purification plant at the time of the accident with FA formation potential. After adding sodium hypochlorite acid to them, Tokyo Waterworks monitored the time-dependent change in concentrations of HMT and FA.

HMT is hydrolyzed to FA and NH_4^+ as shown below [1]:

$$(CH_2)_6N_4 + 4H^+ + 6H_2O \rightarrow 4NH_4^+ + 6HCHO$$

Chloramines were formed via the reaction of chlorine with HMT. Therefore, chloramines, which were formed by the reaction sodium hypochlorite with raw water adding with HMT, were measured by DPD colorimetric method and investigated time-dependent change.

Removal of HMT on water treatment

Removal of HMT by powdered activated carbon (PAC) was evaluated. Removal ratio was determined by jar test by using 0.08 mg/L HMT, was added to raw water without FA formation potential.

Removal of HMT by ozonation and biological activated carbon (BAC) treatment was evaluated. Investigation was carried out at the pilot plant composed with **Figure 3**. Filtered water was used as supplied water.

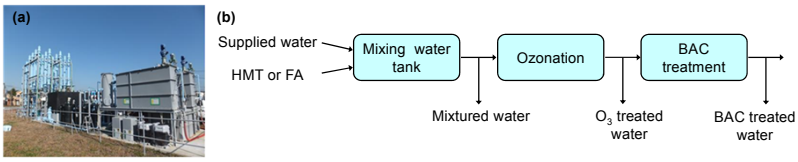

Figure 3 (a) Overall view of the pilot plant, **(b)** Schematic diagram of the pilot plant

RESULTS and DISCUSSION

Reactivity of HMT with chlorine

Figure 4 shows the time-dependent change of HMT and FA concentration after addition of sodium hypochlorite to HMT aqueous. After 30 minutes of adding sodium hypochlorite, more than 95% of HMT was no longer detected. Moreover, the theoretical maximum amount of FA from HMT was detected.

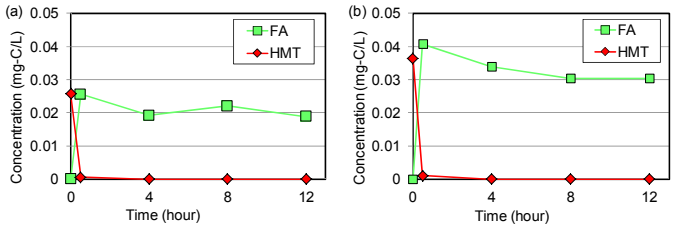

Figure 4 Time-dependent change of HMT and FA concentration with the reaction of HMT and chlorine in different solution (a) in mineral water; (b) in raw water

Figure 5 shows the time-dependent change of HMT and chloramines concentration in the reaction of HMT and chlorine. At the reaction of chlorine with ammonia, when the ratio of Cl_2/NH_3-N exceeds 10, trichloramine become the main reaction product [2]. In this study, despite the ratio of Cl_2/NH_3-N reaching approximately 60, monochloramine and dichloramine were main reaction products. Therefore, it is assumed that the reaction of HMT with chlorine has the complicated process such as forming chloramines and/or generating various intermediates instead of generating chloramines after generation of ammonia simply.

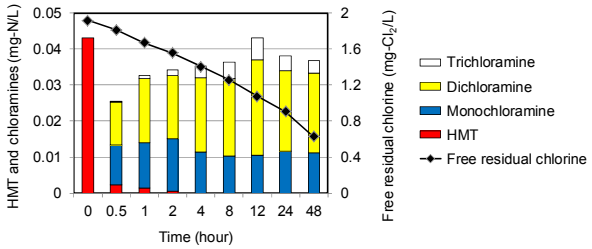

Figure 5 Formation of chloramines from the reaction of HMT and chlorine

Removal of HMT on water treatment

Figure 6 shows the result of jar test in removal of HMT by PAC. HMT could not be removed despite injection of as much as 60 mg/L PAC. Hence, purification plants without advanced water treatment would be difficult to remove HMT with high hydrophilicity.

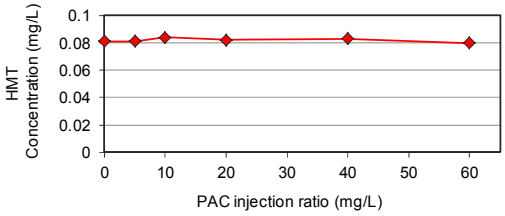

Figure 6 Removal of HMT in aqueous solution by PAC only by jar test

Figure 7 shows removal ratio of HMT and FA on advanced water treatment. Removal ratio in HMT was approximately 90% by simplex ozonation and approximately 75% by simplex BAC treatment respectively. Furthermore, the combination of ozonation and BAC treatment could remove HMT perfectly. Meanwhile, FA did not decomposed by ozonation. However, it was completely removed on BAC treatment.

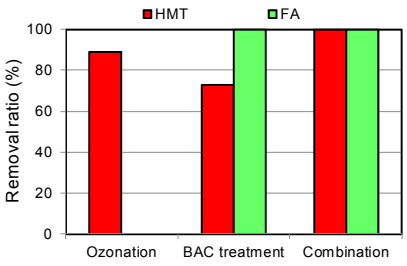

Figure 7 Removal ratios of HMT and FA on Ozonation, BAC treatment and combination (Ozonation+BAC treatment) at the pilot plant

CONCLUSIONS

1. Under the presence of free residual chlorine, chlorination quickly decomposed over 95% of HMT to FA after 30 minutes from reaction. Besides, the conversion ratio to FA was approximately 100%.
2. Reaction of chlorine with HMT formed chloramines other than FA.
3. Since PAC treatment could not remove HMT, conventional water treatment would be difficult to the removal of HMT. In contrast, advanced water treatment composed with ozonation and BAC treatment could perfectly remove HMT and FA.

References

[1] Bodik, I., Derco, J., & Drtil, M. (1991). Hexamethylenetetramine removal in single-sludge activation system. *Std. Environ. Sci.*, 71-76.
[2] White, C. (2010). *White's Handbook of Chlorination and Alternative Disinfectants, 5th Edition,* John Wiley & Sons, New Jersey USA: Black & Veatch Corporation,