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.

METHODS
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.

RESULTS and DISCUSSION

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 NH4+ as shown below [1]:

\[ (CH_2)_6N_4 + 4H^+ + 2OH^- \rightarrow 2NH_4^+ + 6HCHO \]

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.

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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.

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

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