

## **APPLICATION OF PRE-OZONATION FOR REMOVAL OF DISINFECTION BY- PRODUCTS PRE-CURSOR FROM SAIGON RIVER WATER**

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Received: 1 April 2016; Accepted for publication: 15 June 2016

### **ABSTRACT**

This study aimed to apply pre-ozonation for removal of disinfection by-products precursors to reduce the formation of trihalomethanes (THMs) in Saigon river water. The pre-ozonation process was conducted in a lab-scale ozone contactor. The raw water sample was collected from Saigon River at the Hoa Phu pump station in Cu Chi District, Ho Chi Minh City. The suitable condition for pre-ozonation was found. At ozone dose of 1.5 mgO<sub>3</sub>/mgDOC, pH of 8.5, and contact time of 15 minutes, the removal efficiency of turbidity, color, iron, manganese, dissolved organic carbon (DOC), trihalomethanes formation potential (THMFP) were 36 %, 25 %, 56 %, 81 %, 35 %, and 46 %, respectively. These results indicated that the pre-ozonation could reduce DOC concentration and thus resulted in significant mitigation of THMs formation. In comparison with pre-chlorination, THMFP of raw water pretreated by pre-ozonation was lower. Moreover, this study showed that the pre-ozonation was more effective than pre-chlorination in terms of turbidity, color, manganese, and DOC removals.

*Keywords:* disinfection by-products (DBPs), THMFP, pre-ozonation, pre-chlorination.

### **1. INTRODUCTION**

Disinfection is a significant step in drinking water treatment to eradicate and inactivate pathogens for public health protection but may cause other issues to human health due to its disinfection by-products (DBPs) [1]. The major DBPs found in water supply are trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles, chlorophenols, and chloral hydrate, which are products formed during the oxidation of natural organic matters (NOMs) in water by chlorine (Cl<sub>2</sub>). Analytical and epidemiological studies have shown that DBPs may cause various

health when using water for drinking and other purposes [2, 3]. Various techniques have been applied for DBPs control, such as removal of DBPs precursors, using disinfection alternatives, and DBPs removals. Among these techniques, the removal of DBPs precursors (e.g. removal of NOMs in water source) appears to be one of the best candidates for DBPs reduction and pre-ozonation seems to be an effective method for NOMs removal in various water sources [4, 5]. The application of ozonation in water treatment system also have several other advantages, such as disinfection, removal of taste and odor, oxidation of iron and manganese, enhancement in coagulation and filtration, and increase in the biodegradability of NOMs [6, 7].

With the industrialization in the South East of Vietnam, water quality of Saigon River, the main source for water supply of Ho Chi Minh City, has been degraded with increasing concentration of iron, manganese, nitrogen, pathogen and organic compounds due to the poor wastewater management in the upstream. In order to maintain the supply water quality, Tan Hiep Water Treatment Plant (THWTP) used chlorine for pre-oxidation purpose. Our previous study assessed THMs formation potential at unit operations of THWTP and results showed that average total THMs after disinfection were 155.8 µg/L [8]. This value was higher than the allowable value in drinking water quality standards of The European Communities but lower than that of Vietnam. However, with the increasing of organic and ammonia pollution of Saigon River, it is necessary to look for alternatives for chlorine use in pre-oxidation process to ensure both the water quality and the reduction of THMs formation in the future.

In this work, a lab-scale ozone contactor was used as the pre-oxidation step to remove DBPs precursors in Saigon River water. The optimum operational condition such as pH, reaction time, and ozone dose was obtained for this water source. Water quality was evaluated based on the removal efficiency of turbidity, color, iron, manganese, dissolved organic carbon (DOC), and trihalomethanes formation potential (THMFP). The performances of ozone and chlorine as pre-oxidants for water treatment and THMFP removal were evaluated for raw water sample.

## 2. MATERIALS AND METHODS

Raw water used in the experiments was collected directly from Saigon River (Hoa Phu Pumping Station - THWTP). Water quality parameters including pH, turbidity, color, ferrous ion, total iron, manganese, alkalinity, total organic carbon (TOC), DOC, THMFP, and O<sub>3</sub> in water/air were analyzed using Standard Methods [9]. Details on water treatment processes at THWTP, water sampling and analysis, and raw water characteristics can be found in our previous study [8].

Pre-ozonation tests were conducted using a batch ozone contactor as illustrated in Figure 1. Ozone source was from an ozonator (70W, Lino, Vietnam). Water was pumped from raw water tank (1) into the ozone contactor (2) using a water pump (3). The ozone contactor in cylindrical shape (D × H = 0.04 m × 2 m and volume of 1.5 L) was made from acrylic. Ozone was bubbled at the bottom of the contactor with flowrate controlled by a flowmeter (maximum flowrate of 1 L/min). pH values were controlled using a pH controller with a pH probe (Hana Instrument) placed inside the contactor, a chemical pump, and a Ca(OH)<sub>2</sub> solution tank.

The pre-ozonation study was divided into two sets of experiments. In the first set, optimum experiments were conducted by varying operational conditions such as ozone doses of 0.5 - 3.0 mgO<sub>3</sub>/mgDOC, pH values in range of 6.5 - 9.0, and contact time from 5 to 30 minutes. After each experiment, water parameters such as excess ozone in water and in air, pH, turbidity, color, alkalinity, DOC, and BDOC were analyzed. The optimum ozone dose, pH value, and contact

time were chosen based on the highest DOC removal efficiency. In the second set, the optimum condition was then applied to investigate the performance of pre-ozonation on raw water sample. The pre-chlorination test was also conducted the chlorine dose of 3.86 mgCl<sub>2</sub>/L for 30 minutes (according to the operational condition at THWTP in 2015). The parameters for evaluation included turbidity, color, alkalinity, iron, manganese, DOC, and THMFP after pre-ozonation and pre-chlorination.

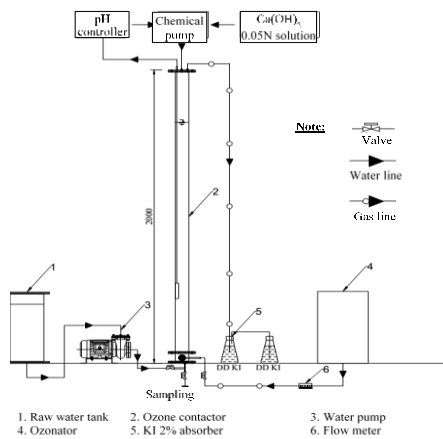


Figure 1. Lab-scale pre-oxidation system using ozone.

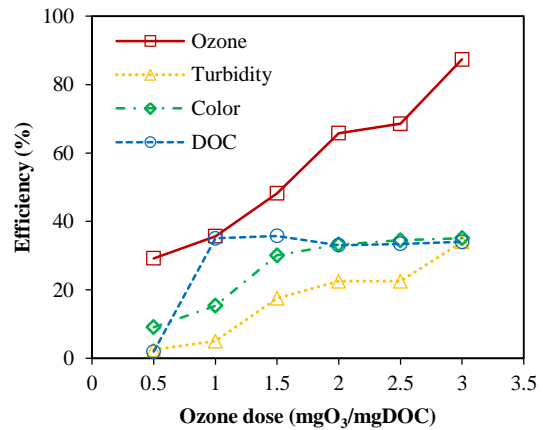


Figure 2. Water treatment efficiency at pH 8.5, contact time of 15 minutes, and different ozone doses.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effects of ozone dose, pH, and contact time on pre-ozonation

The effect of ozone dose on water treatment efficiency is presented in Figure 2. Ozone consumption efficiency increased from 29 % to 87 % when ozone dose increased from 0.5 to 3 mgO<sub>3</sub>/mgDOC, which may be due to the mixing condition caused by ozone flow at the bottom of the contact column. The removals of turbidity and color were also increased with the increase of ozone dose from 0.5 to 1.5 mgO<sub>3</sub>/mgDOC and slightly increased to reach the highest values at 34 % and 35 %, respectively, when ozone dose reached 1.5 mgO<sub>3</sub>/mgDOC. The increase of ozone consumption and the reaction of ozone with humic/fulvic acid and suspended solids could be the reasons for this [10]. Surface water contains NOMs, which cause color, turbidity, and THMs formation after disinfection process using chlorine. NOMs were reported to be effectively removed by ozonation and usually evaluated by using DOC [11, 12]. As seen in Figure 2, DOC removal was very low with efficiency of 2 % at low ozone dose (0.5 mgO<sub>3</sub>/mgDOC) while it reached the highest efficiency of 36 % at ozone dose of 1.5 mgO<sub>3</sub>/mgDOC. This was consistent with results reported in the literature about the limit of ozone dose in pre-oxidation processes, where ozone dose above this value had almost no effect on DOC removal [11, 13].

Figure 3 displays the effect of pH on the performance of ozonation. It was stated that pH value of water sample is an important parameter because it relates to hydroxide ion (OH<sup>-</sup>) concentration in water, which enhances the reaction of ozone [14]. As can be seen in Figure 3, the ozone consumption increased with the increase of pH value. As results, the removal efficiencies of turbidity and color were low in pH range of 6.5 – 7.5 but then quickly increased when pH increased from 7.5 to 8.5. However, these efficiencies decreased when pH further

increased from 8.5 to 9, which may be due to the comparative consumption of  $\text{OH}^*$  radical by alkalinity (i.e.  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) at high pH values. For NOMs removal, pH appeared to have a little effect on the removal of DOC, which slightly increased from 23 % at pH = 6.5 to 33 % at pH = 9.0. Results from these experiments demonstrated that pH 8.5 was the optimum condition for ozonation, whereby the highest removal efficiencies for turbidity, color, and DOC were achieved.

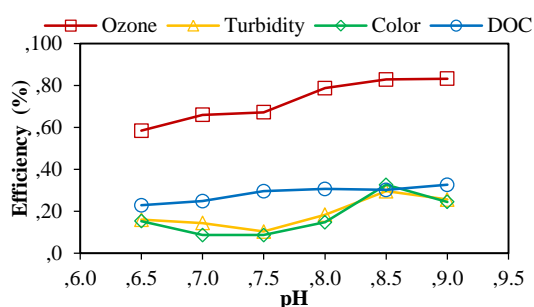


Figure 3. Water treatment efficiency at ozone dose of  $1.5 \text{ mgO}_3/\text{mgDOC}$ , contact time of 15 minutes, and different pH values.

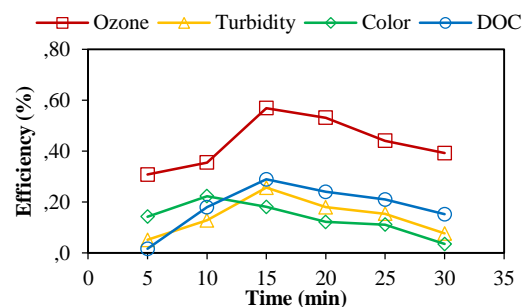


Figure 4. Water treatment efficiency at ozone dose of  $1.5 \text{ mgO}_3/\text{mgDOC}$ , pH 8.5, and different contact times.

The effect of contact time on the ozonation is exhibited in Figure 4. Ozone consumption increased when contact time increased from 5 to 15 minutes, but decreased when contact time further increased from 15 to 30 minutes. The fixed ozone dose in this experiment was controlled by the flowrate and the contact time (i.e. the total ozone amount in the inlet was not changed). Therefore, the mixing condition should be the limiting factor for long contact time (low flowrate) while mass transfer could be the controlling factor for short contact time (high flowrate). The removals of turbidity and DOC were in accordance with the ozone consumption, both reached highest efficiencies at contact time of 15 minutes.

The removal of color was slightly different from that of DOC (Figure 4). At contact time of 5 minutes, the removal efficiency of DOC was only 2 % while that of color was 14 %. In contrast, the removal efficiency of DOC was 15 % while that of color was only 3 % at contact time of 30 minutes. These could be due to the oxidation level of ozone with different contact times. With long contact time of 15 minutes, reaction conditions (e.g., the highest ozone consumption, mixing condition, and reaction time) were sufficient for completed oxidation of NOMs, which gave high DOC removal. Meanwhile, short contact time of 5 minutes could partially convert humic/fulvic acids to simple compounds instead of completed oxidation, which resulted in low color but high DOC content. At this contact time, ozonation had high removal of color and the highest efficiencies for ozone consumption, DOC and turbidity removal; therefore, it was chosen as optimum condition.

### 3.2. Water treatment using ozone and chlorine as pre-oxidants

Figure 5 presents the performance of pre-oxidation using ozone and chlorine for raw water samples. In Figure 5(a), the removal of turbidity and color using ozone was 15 % and 8 %, respectively. Although the removal efficiencies by chlorination were comparable with those by ozonation, ozone is preferred because it also acts as a coagulant aid, which enhances the removal of turbidity and color during coagulation and flocculation processes [15, 16]. Results also showed that ozone was better than chlorine for manganese removal (i.e., 76 % and 55 %, respectively).

respectively), but not for iron (II) (i.e., 23 % and 41 %, respectively) as well as total iron removals, which may be due to the inhibition of organic compounds in iron oxidation [7]. Moreover, DOC removals was 29 % after ozonation, which was more effective than chlorination for DOC removal (16 %).

The formation of THMs can be reduced by removal of NOMs employing ozonation as pre-oxidation step, which is demonstrated in Figure 5(b). The THMFP of raw water were relatively high at 983  $\mu\text{g/L}$ . After pre-oxidation, these values decreased to 582  $\mu\text{g/L}$  (ozonation) and 685  $\mu\text{g/L}$  (chlorination), corresponding to removal efficiencies of 41 and 30%, respectively. This revealed that pre-ozonation was more effective than pre-chlorination for THMFP reduction, corresponding to DOC removal efficiencies of 29 %, and 18 % (Figure (5a)). The higher efficiencies of THMFP reduction as compared to those of DOC removal implied that THMFP reduction depended not only on the removal of DOC but also on the conversion of organic compounds (e.g. conversion of hydrophobic DOC into hydrophilic DOC instead of DOC removal [17]), which decreased the activity of the organic compounds for THMs formation.

Among the water samples, only pre-chlorinated sample contained initial THMs of 135  $\mu\text{g/L}$ , which meant that chlorine did not exist in raw water of Saigon River. Therefore, pre-oxidation with chlorine would finally produce more THMs than that with ozone, and ozone would be more effective than chlorine in reduction of THMFP. It is also noted that only chloroform was detected when analyzing THMs, which implied that bromide ion was not found in raw water. This could be an advantage for employing ozone as a pre-oxidant without formation of hazardous bromate.

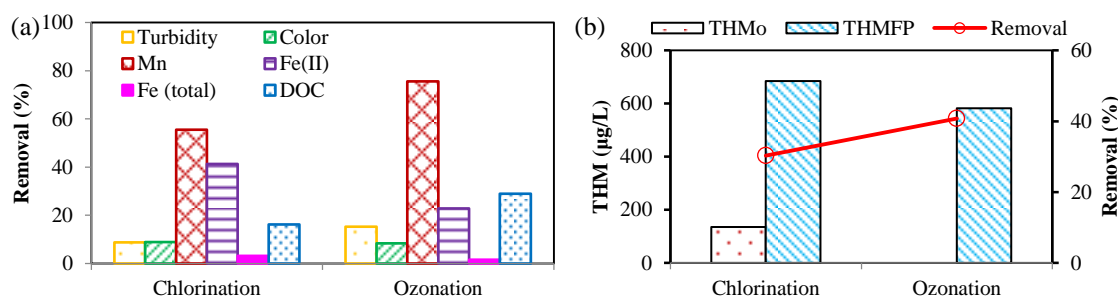


Figure 5. Results of pre-ozonation (1.5  $\text{mgO}_3/\text{mgDOC}$ , pH 8.5, and 15 minutes) and pre-chlorination (3.86  $\text{mgCl}_2/\text{L}$ ): (a) removal efficiency and (b) THMs.

#### 4. CONCLUSIONS

By using a lab-scale ozone contactor, the optimum condition for operation was obtained at ozone dose of 1.5  $\text{mgO}_3/\text{mgDOC}$ , pH 8.5, and contact time of 15 minutes. Under this condition, the removal efficiencies of THMFP, DOC, iron (II), total iron, and manganese were 41 %, 29 %, 23 %, 2 %, and 76 %, respectively. The results also confirmed that ozone was more effective than chlorine as a pre-oxidant in terms of turbidity, color, manganese, DOC, and THMFP removals but not for iron. Pre-ozonation also reduced the activity of organic compounds for THMs formation, which decreased from 180 to 150  $\mu\text{gTHMFP/L-mgDOC}$  after pre-ozonation. Future works may be focus on setting-up a pilot-scale for pre-ozonation placed at Tan Hiep Water Treatment Plant to improve the water quality under continuous increase of pollution in Saigon River.

**Acknowledgements.** The authors gratefully acknowledge the financial support from HCMC Department of Science and Technology and Saigon Water Supply Company (SAWACO).

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