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Hansen, Kamilla Marie Speht; Spiliotopoulou, Aikaterini; Cheema, Waqas Akram; Andersen, Henrik Rasmus

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Laboratory studies on the effect of ozonation on THM formation in swimming pool water

K. M. S. Hansen^{*}, A. Spiliotopoulou^{**}, W. A. Cheema^{*}, H. R. Andersen^{*}

^{*} Department of Environmental Engineering, Technical University of Denmark, Miljøvej 113, 2800 Kgs. Lyngby, Denmark

(E-mail: kmsh@env.dtu.dk; wche@env.dtu.dk; hran@env.dtu.dk)

^{**} Water ApS, Farum Gydevej 64, 3520 Farum, Denmark

(E-mail: katspil@windowslive.com)

Abstract

Water samples from indoor swimming pool were ozonated at different pH values to evaluate the effect of pH on decomposition of ozone in swimming pool water. Furthermore, drinking and pool water were repeatedly ozonated followed by chlorination to evaluate THM formation.

Decomposition of ozone was not affected by pH in the range relevant to swimming pools (pH 6.8 – 7.8) and a half-life time at 10-12 min was obtained. Repeating the ozonation, the decomposition of ozone increased at the second dose of ozone added ($t_{1/2,2}=8$ min) and then decreased again at the third and fourth dose of ozone ($t_{1/2,3}=17$ min; $t_{1/2,4}=18$ min). For drinking water, ozone decomposition was fast for the first dose of ozone ($t_{1/2,1}=4$ min) and then decreased for the second and third dose of ozone ($t_{1/2,2}=19$ min; $t_{1/2,3}=17$ min). Chlorination after ozonation revealed that ozone removed reactivity of the dissolved organic carbon toward chlorine for drinking water as lower TTHM formation occurred than in non-ozonated samples. For pool water, a higher TTHM formation was observed in ozonated than non-ozonated pool water. Thus, it was observed that ozone reacts markedly different in swimming pool water from the known pattern in drinking water production.

Keywords

Swimming pool; ozonation; DIN; trihalomethane.

INTRODUCTION

Chlorine is the most common disinfectant for public swimming pools. However, chlorine reacts with pollutants brought into the water by bathers and forms disinfection by-products (DBPs). Actually, the main removal processes of the dissolved organic pollutant are oxidation and mineralization through oxidation by chlorine. Ozone is a strong oxidizing agent, which if applied to swimming pool water could oxidize the dissolved pollutant and reduce their ability to form disinfection by-products (DBPs) with chlorine. In a Korean study, ozone/chlorine treated swimming pools had lower levels of DBPs than chlorinated pools (Lee et al., 2010).

Generally, most ozonation treatment of swimming pools is built based on the German DIN standard where all or a part of the water is ozonated with a contact time of 3-10 min before deozonation on an activated carbon filter. The deozonation is done to prevent ozone escaping to the air in the swimming pool, but it results in that only a small part of the ozone reacts with the treatment targets while the main part will be destroyed. A radical different treatment principle which emerges from USA is the slip-stream ozonation method which applied a low dose of ozone into a side stream of the filter flow. The low dose of ozone is consumed fast by reaction with organic in the main recirculation flow. The ozone dosing is controlled by a redox probe to ensure ozone is not added in excess to dissolved organic matter thus ensuring that ozone does not reach the pool.

Literature on effect of ozone on DBP formation in swimming pool water is limited. However, general knowledge about ozone and reactivity can be found in literature on the topic of ozonation of drinking water and wastewater e.g. von Gunten (2003) where it is seen that the most common DBPs, THM and HAA react very slowly with ozone. Ozone's reaction with nitrogen compounds and chloramine is also relative slow (Eichelsdörfer and Jandik, 1985). However, in a field application of ozone treatment of swimming pool water according to DIN standard, 34-48 % decrease in chloroform formation potential was achieved depending on ozone contact time (Eichelsdörfer and Jandik, 1988). While in laboratory batch experiment, Glauner et al. (2005) obtained 12 % reduction of absorbable organohalogen (AOX) formation potential and 3% reduction in total trihalomethane (TTHM) formation potential after 10 min oxidation by ozone.

An increased understanding of ozonation in swimming pools e.g. half-life time could help in making a more cost effective ozone treatment and minimize the occurrence of disinfection by-products in swimming pools. Thus, the aim was to determine the half-life time of ozone in pool water and investigate the effect of ozonation on TTHM formation.

METHODS

Reagents

All reagents and chemicals were purchased at Sigma-Aldrich (Denmark). The experimental set-up for the ozonation was based on a 20 g/h ozone generator from O3-Technology AB (Vellinge, Sweden) which was supplied with dry oxygen gas. The generated ozone was dispersed through a diffuser in a collection bottle containing ultra-pure water which was immersed in an ice bath so that ozone solubility is increased. To further increase the solubility of the ozone a manometer and a valve were placed after the collection bottle and a pressure at 1.4 barg was established. Based on these experimental conditions, the concentration of ozone in the stock solution was between 70 and 90 mg/L.

Analysis of ozone, TOC, chlorine, H₂O₂

Ozone. Ozone concentration was quantified with the indigo method (Bader and Hoigné, 1981). The reagents used were 0.5 M phosphate buffer at pH 2 and 1.00 g/L indigo trisulphate dissolved in 20 mM phosphoric acid. For the ozone decomposition profile, the volumes from Bader and Hoigné (1981) were downscaled to fit into a 3 mL cuvette. Specifically, 0.100 mL indigo trisulphonate (1.0 g/L) and 0.250 mL phosphate buffer (0.5 M at pH 2) were added to the cuvette. Then ultra-pure water and sample were added so the total volume was 2.5 mL. The amount of sample and ultra-pure water were varied depending on ozone concentration. The absorbance of the unreacted indigo trisulphonate was measured at 600 nm. By comparing the absorbance of a blank with the sample and using $\Delta A = -20000 \text{ l}/(\text{cm} \cdot \text{mol ozone added per L})$, the ozone concentration was determined.

The delivered ozone dose was determined by adding sufficient amount of indigo and 10 mL phosphate buffer into 100 mL. Eg. A water sample (100 mL) was ozonated with an ozone dose of 2 mg/L. To determine the delivered ozone dose, four mL indigo trisulphate (1.0 g/L) and 10 mL phosphate buffer were added in a 100 mL volumetric flask and then filled to the mark with ultra-pure water and poured into a glass bottle. The same amount of ozone stock solution was then added to the glass bottle as added to the water sample. The absorbance of the unreacted indigo trisulphonate was measured at 600 nm and compared to the absorbance of a blank. The ozone dose was then determined using $\Delta A = -20000 \text{ l}/(\text{cm} \cdot \text{mol ozone added per L})$.

Total organic carbon. A Shimadzu ASI-V UVC/Persulphate analyzer was utilized for the quantification of the remaining total organic carbon (TOC) in the samples. Sample injection volume

was 3.00 mL and a calibration curve was formed using standards with concentrations ranging from 50-2000 µg/L ($R^2 = 0.9994$). The method quantification limit is 50 µg/L.

Chlorine. The concentration of chlorine and combined chlorine in the swimming pool samples were quantified at the arrival using DPD based test kit (LCK 310, Hach Lange, Denmark). The concentration of chlorine during experiments was quantified using ABTS method (Pinkernell et al., 2000).

Hydrogen peroxide. Hydrogen peroxide was analysed by colorimetric method using potassium TiOxalate (Antoniou and Andersen, 2014).

Chlorination assay and THM analysis

After ozonation, water samples were transferred to 40 mL glass vials where chlorine and boric acid were added to samples based on chlorine consumption measured by ABTS. Chlorine consumption was determined in pre-experimental tests. The aim was to achieve a chlorine residual after 24 h of 1-3 mg/L. After 24 h at 25 °C, residual chlorine was determined and samples analyzed the same day for THM by purge and trap (purge temperature = 30 °C, Velocity XPT Purge and Trap Sample Concentrator, Teledyne Tekmar, with auto-sampler: AQUATek 70, Teledyne Tekmar) coupled with a GC-MS (HP 6890 Series GC System, 5973 Mass selective detector, Hewlett Packard).

Experiments

Life time at different pH. A swimming pool water sample was divided into 4 subsamples and pH was adjusted to 6.8, 7.0, 7.3, and 7.8. The subsamples were placed in a circulation bath with controlled temperature at 28 °C and the samples were ozonated with approximately 2.3 mg/L by adding ozone stock solution. The ozone concentration was measured over time.

Repeated ozonation. A swimming pool water sample was divided into 5 subsamples (300 mL each) and placed in a circulation bath with controlled temperature at 28 °C. Four of the subsamples were ozonated with 2 mg/L ozone. The delivered ozone dose was determined as previously described. In one of the subsamples the ozone concentration was measured over time. When the ozone was decomposed, the ozonation was repeated but this time only with the remaining three samples. Again the ozone concentration was determined over time in one of the samples. The samples used for ozone profiles and the non-ozonated sample were utilized in the chlorination assay and THM analysis.

RESULTS AND DISCUSSION

Effect of pH

Pool water from a swimming pool in Copenhagen area was used to evaluate the effect of pH on decomposition of ozone in a pH range relevant for swimming pools. Four subsamples were pH adjusted and ozonated. Ozone concentration was measured over time (Figure 1). As seen, decomposition of ozone did not vary in the investigated range. Half-life time of 10-12 min was estimated based on the measured ozone concentrations. According to Rice (1995) the expected half-life time should be approximately 10 min, which fits well with our findings.

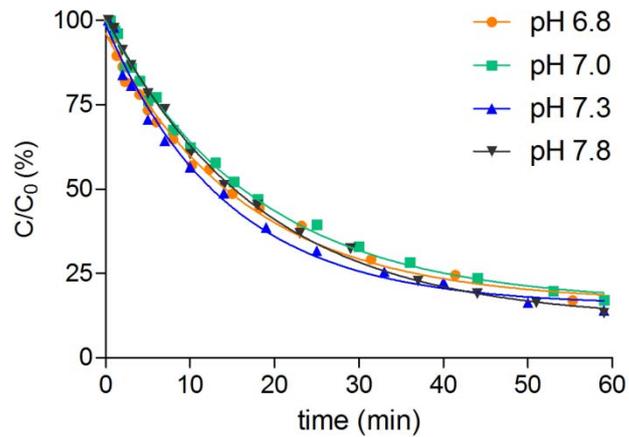


Figure 1. Concentration profile of ozone in swimming pool water samples where pH was adjusted (Ozone dose approximately 2.3 mg/L).

Repeated ozonation

Ozonation experiments were performed with filling water (unchlorinated groundwater) and pool water from a swimming pool in Copenhagen area. Concentration of ozone was measured over time (Figure 2). In the case of filling water, it can be seen that the first dose disappeared faster ($t_{1/2} = 3.8$ min) than the second and third ($t_{1/2,2nd} = 19$ min and $t_{1/2,3rd} = 17$ min). So the first dose reacts with the easily ozonated DOC while at second and third dose the ozone reacts with more slowly reactive DOC. For the pool water, the first ozone dose reacted slower ($t_{1/2} = 11$ min) compared to filling water. However, the second dose disappeared even faster ($t_{1/2} = 8$ min). So the first dose reacted with some DOC and made it more reactive towards ozonation during the second dose. The half-life time of the third and fourth dose ($t_{1/2,3rd} = 17$ min, $t_{1/2,4th} = 18$ min) were similar to the ones (2nd and 3rd) for the filling water.

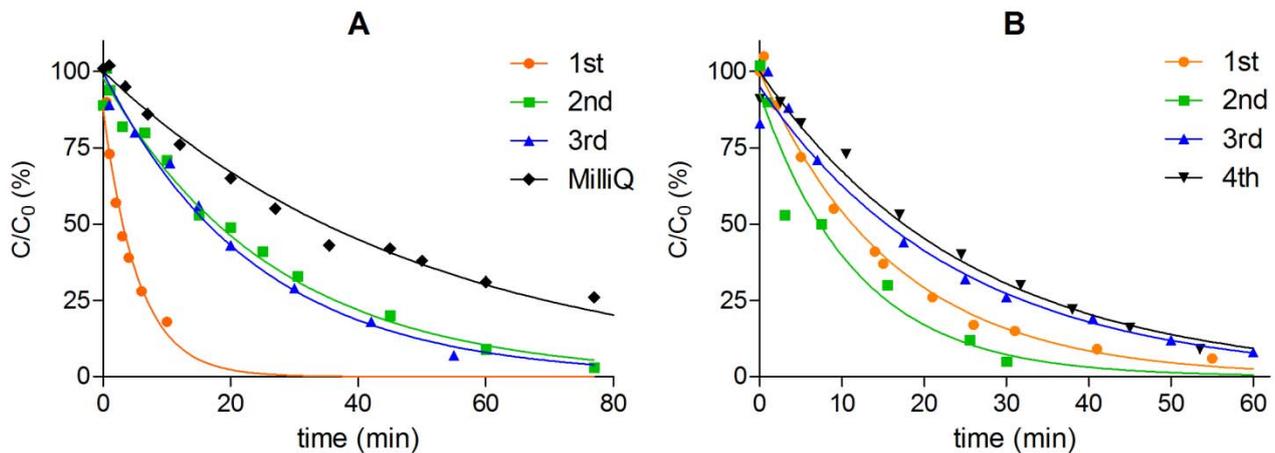


Figure 2. Concentration profile of ozone in A) filling water (pH = 7.9, DOC = 2 mg/L) and MilliQ water (buffered at pH 7.3 with phosphate) and B) swimming pool water (pH = 7.3, DOC = 1.5 mg/L). The water samples were treated repeatedly with an ozone dose of approximately 2 mg/L.

Chlorination of filling water formed a lot of TTHM. Addition of 2 mg/L of ozone, the formation was decreased of 40 % (Figure 3B). However, repeating the ozone treatment did not decrease the THM formation further. The chlorine consumption (Figure 3A) decreased with the first dose and then for the next doses it increases again slowly. A likely explanation is that ozone reacted with the functional groups of NOM which otherwise would react with chlorine resulting in THM formation

and thereby a small amount of ozone decreased the formation potential of the filling water. Furthermore, the filling water contains some bromide which when chlorinated ends up as brominated THM. The ozone oxidized bromide to bromate, which will not end up as brominated THM when chlorinated. However, this is not advantageous as bromate is carcinogenic and should be avoided in swimming pools.

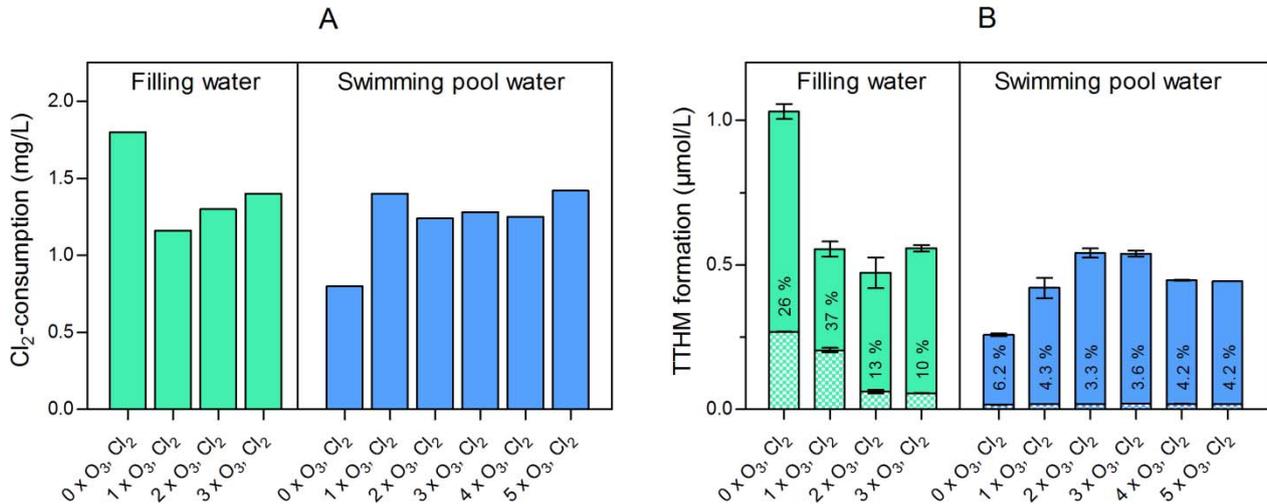


Figure 3. A) The chlorine consumption for filling water and swimming pool water with repeated ozonation. B) The formation of total trihalomethane (TTHM) at repeated ozonation of filling water and swimming pool water. The pattern part represent the amount of incorporated bromine in TTHM; also given as percentages.

For swimming pool water, firstly an increase in THM formation then a decrease was observed. Likewise, there is observed an increase for chlorine consumption at the first ozone dose. But for the following ozone doses, the chlorine consumption remains the same. This means that ozone first makes the DOC more reactive towards chlorine and then removes this reactivity again. The amount of bromine in the pool water is low and the bromine incorporation did not change a lot during the experiments.

Our results are contradicting with findings of previous studies (Eichelsdörfer and Jandik, 1988; Glauner et al., 2005) where a reduction of THM formation potential by ozonation of pool water was found. A likely explanation could be that bather load in our pool was low and only very little fresh (non-chlorinated) organic pollution was present in the pool water. Thus, the organic pollution would already have reacted with chlorine and thereby be less reactive towards ozone. The decomposition of ozone makes hydroxyl radicals which may react with the chlorinated organic pollution and make it more reactive towards chlorine.

CONCLUSION

Our experiments were conducted as batch experiments in the laboratory and the repeated dosing can only give an indication of what might happen in a continuous treatment of pool water where hydraulic retention time of water in the basin is 0.3-6 hours and the water age is normally several month or even years. It was observed that ozone reacts markedly different in swimming pool water from the known pattern in drinking water production. Intermediate dosing levels of ozone increase the THM formation and ozonation increases the chlorine consumption in the entire investigated range of ozone dosing.

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