Combined UV treatment and ozonation for the removal of by-product precursors in swimming pool water

Waqas A. Cheema [a, b], Kamilla M.S. Kaarsholm [a], Henrik R. Andersen [a, *]

[a] Department of Environmental Engineering, Technical University of Denmark, 2800 Kongens Lyngby, Denmark
[b] National University of Sciences & Technology, H-12, Islamabad 44000, Pakistan

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ABSTRACT

Both UV treatment and ozonation are used to reduce different types of disinfection by-products (DBPs) in swimming pools. UV treatment is the most common approach, as it is particularly efficient at removing combined chlorine. However, the UV treatment of pool water increases chlorine reactivity and the formation of chloro-organic DBPs such as trihalomethanes. Based on the similar selective reactivity of ozone and chlorine, we hypothesised that the created reactivity to chlorine, as a result of the UV treatment of dissolved organic matter in swimming pool water, might also be expressed as increased reactivity to ozone. Moreover, ozonation might saturate the chlorine reactivity created by UV treatment and mitigate increased formation of a range of volatile DBPs. We found that UV treatment makes pool water highly reactive to ozone. The subsequent reactivity to chlorine decreases with increasing ozone dosage prior to contact with chlorine. Furthermore, ozone had a half-life of 5 min in non-UV treated pool water whereas complete consumption of ozone was obtained in less than 2 min in UV treated pool water. The ozonation of UV-treated pool water induced the formation of some DBPs that are not commonly reported in this medium, in particular trichloronitromethane, which is noteworthy for its genotoxicity, though this issue was removed by UV treatment when repeated combined UV/ozone treatment interchanging with chlorination was conducted over a 24-h period. The discovered reaction could form the basis for a new treatment method for swimming pools.

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1. Introduction

Swimming pools are used for recreational activities, and it is necessary to disinfect swimming pool water in order to protect against infection by microbiological pathogens. Chlorine is the most commonly used disinfectant in swimming pool water. However, a general problem with maintaining chlorine concentrations for hygiene reasons is that the chlorine reacts continuously with organic matter in the water to form chloramines (combined chlorine) and chloro-organic by-products. A general concern about chloro-organic disinfection by-product (DBP) formation is the effect on human health, because some are carcinogenic (Richardson et al., 2007). There has been identified more than 100 DBPs in pool water (Richardson et al., 2010) where the most frequently investigated DBPs are chloramines, haloacetonitriles (HANs), haloacetic acids (HAAs) trihalomethanes (THMs), chloral hydrates

and nitrosamines (Chowdhury et al., 2014; World Health Organisation, 2006). Both types of by-product can be reduced through water exchanges or different treatment methods. Combined chlorine concentration can be reduced with UV treatment via direct photolysis (PWTAG, 2009). It is an efficient way of removing chloramines to photolyse them with UV treatment in the return flow. Soltermann et al. (2014) reported that trichloroamine is the easiest of the combined chlorine species to be removed by UV.

A reduction in the combined chlorine level via medium pressure UV treatment has been reported by several full-scale studies (Beyer et al., 2004; Cassan et al., 2011, 2006; Kristensen et al., 2009). However, these studies do not agree regarding the effect of UV treatment on trihalomethane (THM) formation. An increase (Cassan et al., 2006) and decrease (Beyer et al., 2004) of THM formation has been reported in short-term full-scale studies. In contrast, Kristensen et al. (2009) observed no effect on THM levels in a swimming pool treated with UV in a long-term full-scale study. However, Liviac et al. (2010) illustrated that UV treatment might be beneficial for the reduction of genotoxicity and cytotoxicity in chlorinated swimming pool water. Hansen et al. (2013b) reported

that photolysis is less important than volatilization for some volatile DBPs e.g. chloroform. Moreover, Zare Afifi and Blatchley (2016) demonstrated that concentration of most volatile DBPs decreased with both MP and LP UV treatment. A recent laboratory study (Spiliotopoulou et al., 2015) reported that UV treatment appears to break down relative non-reactive organic molecules into smaller molecules which react quickly with chlorine and accelerated DBP formation but did not clearly increase the total amount formed. Ozone is difficult to use for pool water treatment, as there is a lack of a good reliable sensor for ozone detection in water and ozone cannot be allowed in the pool due to toxicity to swimmers. Different authors have mentioned ozone dosage of 1 ppm (Eichelsdörfer and Jandik, 1985), 0.8—1.2 ppm (Eichelsdörfer and Jandik, 1988) and 1.6 ppm (Hamil, 2011) for swimming pool water treatment. There is limited literature on the effect of ozonation on formation of chlorination DBPs in recirculated water, but knowledge about ozone and its kinetics can be found in the drinking water and wastewater ozonation literature (von Gunten, 2003). It has been found that the most common DBPs, along with nitrogen compounds and chloramine, react very slowly with ozone (Eichelsdörfer and Jandik, 1985); however, according to DIN standards for swimming pool water ozonation, a decrease (34—48%) in chloroform formation potential can be achieved, depending on ozone contact time (Eichelsdörfer and Jandik, 1988). Alternatively, Glauner et al. (2005) achieved 12% absorbable organohalogen (AOX) reduction and 3% reduction of total trihalomethane (TTHM) formation potential after 10 min of ozone oxidation compared with untreated pool water. An investigation of several pools (Lee et al., 2010) found that ozone/chlorine-treated swimming pools had lower levels of DBPs than chlorinated pools. A laboratory study (Hansen et al., 2016) reported that ozone reacts well with freshly added organic matter but slowly with organic matter that remains after extended chlorination. Additionally, it was reported that reaction with fresh organic matter decreases formation of volatile chlorination by-products, while a slow reaction with already chlorinated organic matter produces more volatile by-products with further chlorination.

Gaining an understanding of UV treatment followed by ozonation in swimming pools could help in designing more efficient treatment systems to minimise the occurrence of disinfection by-products. Thus, the aim of the current study is to investigate the effect of a combined treatment system on DBP formation. As both ozone and chlorine preferably react with electrophilic groups in compounds (von Sonntag and von Gunten, 2012; White, 1992), we hypothesise that reactivity to chlorine, created by the UV treatment of dissolved organic matter in pool water, might also mean that there is increased reactivity to ozone and that ozonation might remove the chlorine reactivity created by UV treatment. Therefore, we first performed an experiment to range-find the effect of swimming pool water UV activation on chlorine reactivity. Second, an experiment was carried out to characterise the effect of adding various doses of ozone to pool water, with or without UV pre-treatment, before chlorination to study the effect on chlorine reactivity and the formation of chlorination by-products. Finally, the possible effect on chlorination by-product formation was investigated by a repeated, combined UV-ozone treatment interchanged with chlorination (repeated cycles of UV followed by ozone with subsequent chlorination). Toxicity estimation was used to evaluate water quality.

2. Material and methods

2.1. Reagents and standard analysis

All chemicals and reagents were purchased from Sigma-Aldrich,

Denmark. The experimental set-up for ozonation was based on a 20 g/h ozone generator from O3-Technology AB (Vellinge, Sweden) which was supplied with dry oxygen gas. 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 would be maximised. To increase further the solubility of ozone, a manometer and valve were placed after the collection bottle, and a pressure of 1.4 barG was applied. Based on these experimental conditions, the concentration of ozone achieved in the stock solution was between 80 and 100 mg/L.

Ozone was quantified via a colorimetric method using indigo-trisulfonate (Bader and Hoigné, 1981). Reagents used were 0.5 M phosphate buffer at pH 2 and 1.00 g/L potassium indigotrisulfonate dissolved in 20 mM phosphoric acid and further description can be found in Hansen et al. (2016). Free and total chlorine in the collected pool water samples were measured using the colorimetric method based on the oxidation of diethyl-p-phenylenediamine (DPD), with and without addition of iodide, while residual chlorine during the experiment was determined by employing the colorimetric method, using 2, 2-azino-bis (3-ethylbenzothiazoline)-6-sulfonic acid-diammoniumsalt (ABTS), as described by Pinkernell et al. (2000). Non-volatile organic carbon in the pool water samples was quantified with a Shimadzu ASI-V UVC/Persulphate analyser with a sample injection volume of 3 mL. A calibration curve was formed by using potassium hydrogen phthalate standards, with concentrations ranging from 50 to 2000 μg/L ($R^2 = 0.9994$). The method quantification limit was 50 μg/L. Non-volatile organic carbon is referred to herein as 'dissolved organic carbon' (DOC).

2.2. Pool water

Pool water samples were collected from a public swimming pool and used for experiments on the day of collection. The pool for water collection was the main practice basin in Gladsaxe (Denmark). It is a typical public pool (temperature 26 °C, sand filter with flocculation and a side stream activated carbon filter) with a hydraulic retention time (HRT) of 4 h. The water in the pool is not replaced besides the amount of water which is added due to evaporation and loss during backwash of filters. Water for filling the pool is obtained from the public distribution network, which comprises non-chlorinated groundwater. The pH was measured immediately upon arrival to the laboratory and it was 7.2 ± 0.1.

2.3. Disinfection by-products

Samples were analysed 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), and the analyses were conducted as described by Hansen et al. (2012a).

The employed method detects the following compounds: chloroform, bromodichloromethane, dibromochloromethane, dichloroacetonitrile, bromochloroacetonitrile, trichloropropanone, dichloropropanone and trichloronitromethane. The limit of detection (LOD) and limit of quantification (LOQ) were expressed as $LOD = X_{b1} + 3S_{b1}$ and $LOQ = X_{b1} + 10S_{b1}$, where 'X_{b1}' is the mean concentration of the blank and S_{b1} is the standard deviation of the blank. The LOQ values for all compounds were: chloroform (0.6 μg/L), bromodichloromethane (0.6 μg/L), dibromochloromethane (0.4 μg/L), dichloroacetonitrile (0.6 μg/L), bromochloroacetonitrile (0.2 μg/L), trichloropropanone (1.0 μg/L), dichloropropanone (1.0 μg/L), and trichloronitromethane (0.6 μg/L).