

THM formation during chlorination of treated municipal wastewater

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Abstract Chlorination batch experiments were conducted in order to estimate the concentration of THM and their formation potential in nitrified and partially nitrified secondary effluent. The role of contact time (up to 2 hours), chlorine dose (3 levels), pH and temperature on the formation of THM was evaluated. THM formation, as measured by individual concentration as well as formation potential, was high for the nitrified secondary effluent, while for the partially nitrified effluent the respective concentrations were low, due to the reaction of chlorine with ammonia to form chloramines. In general, THM concentrations progressively increased as contact time, pH and chlorine dose increased. Increase in temperature (from 15–25°C) showed a rather limited effect. In addition, coagulation tests were applied prior to chlorination of the nitrified effluent for removing organic carbon and thereby controlling the formation of THM. Alum was used as the coagulant in doses varying from 0.1 mM to 2.5 mM. As the coagulant dose increased, the removal of both DOC and absorbance at 254 nm increased, while THM formation decreased. The reduction in THM formation was more pronounced for coagulant doses higher than 1.5 mM.

Key words THM; wastewater chlorination

Introduction

Wastewater disinfection is generally considered as the last barrier for the protection of the receiving waters from pathogens. As the population increases, greater demands are placed on the use of reclaimed water so that the probability of human exposure to treated wastewater significantly increases. Chlorine is the most widely used disinfectant applied directly to treated wastewater.

The presence of chlorinated organic contaminants in drinking water, as a result of chlorination, has been extensively studied during the past 25 years. These by-products are produced by the reaction of aqueous chlorine with natural organic matter (e.g. humic substances) present in water (Rook, 1974; Oliver and Lawrence, 1979; Reckhow and Singer, 1990). Trihalomethanes (THM) which were first identified in drinking water, constitute a major class of chlorination by-products and have drawn significant attention due to their potential harmful effects on human health. Their formation potential is influenced by the amount and chemical characteristics of Dissolved Organic Carbon (DOC) (Galapate *et al.*, 1999). Parameters that affect their formation, increasing their reaction rate, include: chlorine dose, contact time, pH and temperature (El-Dib and Ali, 1995; Garcia Villanova *et al.*, 1997). Several ways to control THM formation by removing their precursors have been proposed (Oliver and Lawrence, 1979; Ivancez-Tumbas *et al.*, 1999) with coagulation showing a high removal efficiency for DOC and THM precursors.

In treated wastewater disinfection, a complete study of the above THM formation parameters as well as of THM control strategies is lacking. The most significant factor restricting THM formation is ammonia nitrogen due to the preferential consumption of chlorine by chloramine formation reactions (WEF, 1996; Winstrom *et al.*, 1996). However, nitrification may reduce the amount of ammonia to very low levels allowing the possible formation of chlorination by-products.

The aim of this study was to evaluate the formation of THM during laboratory chlorination of treated municipal wastewater and examine the role of ammonia nitrogen, chlorine dose, contact time, pH and temperature on it. In addition, coagulation treatment prior to chlorination took place to estimate its efficiency to control THM formation.

Methods

Nitrified secondary effluent was collected from the Chania Municipal Wastewater Treatment Plant prior to chlorination. Sample 1 was used for three series of direct chlorination experiments, while sample 2 for the coagulation runs prior to chlorination. Their general characteristics, summarised in Table 1, were determined immediately after sampling according to standard procedures (*Standard Methods*, 1998). Partially nitrified (synthetic) sample was prepared by adding an appropriate amount of an ammonium stock solution to sample 1. The final concentration of $\text{NH}_4\text{-N}$ in the partially nitrified sample was 5.24 mg/L.

Chlorination experiments

Stock chlorine solution was prepared from a commercial sodium hypochlorite 9%w/v in active chlorine, as measured by the iodometric method (*Standard Methods*, 1998). 0.3, 0.75 and 1.5 ml of stock chlorine solution were diluted to 100 ml total volume sample to produce chlorine doses of 2, 5 and 10 ppm, respectively. Effluent samples and chlorine doses were mixed in closed Erlenmeyer flasks for contact times of 5, 15, 30, 60 and 120 min., which are typical residence times in chlorination tanks. Mild agitation was provided by an orbital shaker operating at 75 rpm, inside an incubator in order to maintain a constant temperature during each experiment. At first, chlorination at three chlorine levels took place, for both nitrified sample 1 and partially nitrified sample at 20°C and effluent pH = 7.25 (ambient pH). No addition of buffer solution was necessary since the wastewater samples were well buffered and the pH remained stable during the chlorination experiment. A second series of experiments was performed for the same contact times and temperature, using the nitrified effluent and a chlorine dose of 10 ppm, after adjusting the effluent pH to 6.0 and 8.5 by adding sufficient amounts of concentrated solutions of HCl and NaOH, respectively. In the third series of experiments, the pH remained unchanged while the temperature in the incubator was set at 15°C and 25°C. Finally, chlorination experiments were applied under similar conditions (20°C, ambient pH and 10 ppm chlorine dose) to the nitrified sample 2 after coagulation.

At the end of the specified contact times, the chlorinated samples were carefully transferred to 40 ml glass screw-cap vials with TFE-faced silicone septum in which 0.5 ml $\text{Na}_2\text{S}_2\text{O}_3$ 0.1N had been added, as a dechlorinating agent. The vials were filled completely and the caps were placed in a way to ensure no air bubbles or empty space was left, after adding 4 drops of HCl 6N to prevent hydrolysis of intermediates. Finally, the vials were wrapped in aluminium foil and stored at 4°C. Analysis for THM was completed within one week at the latest.

Table 1 General characteristics of the nitrified secondary effluents

Parameter	pH	TSS (mg/L)	BOD (mg/L)	COD (mg/L)	TOC (mg/L)	$\text{NH}_4\text{-N}$ (mg/L)	N-Kjeldahl (mg/L)	UV-Abs. at 254 nm
Sample 1	7.25	4.2	8	32.1	7.74	0.17	0.57	
Sample 2	7.22	4	21	41.5	9.86	0.62	1.86	0.256

Coagulation experiments

Coagulation tests were performed with a Velp jar test apparatus with six rectangular jars. Each jar was filled with 1 L of nitrified sample 2. Alum was used as the coagulant in doses of 0, 0.5, 1, 1.5, 2 and 2.5 mmol Al³⁺/L, added under stirring. Rapid mix took place for 5 min. at 200 rpm, followed by a slow mix for 10 min. at 45 rpm. The settling stage lasted for 30 min. Prior to chlorination of the coagulated effluents, filtration through Gelman fibre glass filters (type A/E) took place.

THM formation potential

Both nitrified and partially nitrified secondary effluents as well as the coagulated samples were chlorinated in duplicate in 40 ml glass vials by an adequate amount of stock chlorine solution to provide a chlorine residual of at least 1 mg/L at the end of the test. The incubation period was 7 days at 25°C in darkness. The excess chlorine after incubation was quenched with Na₂S₂O₃ and the samples were preserved as above.

Analytical methods

Residual chlorine and ammonium nitrogen measurements. Both free available chlorine (HOCl, OCl⁻) and total chlorine (sum of free chlorine and chloramines) residuals were determined using the DPD colorimetric method (Standard Methods, 1998). The concentration of NH₄⁺-N was measured using the phenate method (Standard Methods, 1998). Absorbances at 557 nm and 712 nm for the DPD and the phenate methods, respectively, were measured on a Shimadzu UV-1200 spectrophotometer.

DOC and absorbance at 254nm measurements. DOC was determined with a Shimadzu 5000A TOC analyser, while the UV absorbance with a Shimadzu UV-1200 spectrophotometer using quartz cells with a light path of 10 cm.

THM analysis. THM identification analysis was done by the purge-and-trap/GC/MS method using a CDS 6000 purge-and-trap apparatus connected to a Shimadzu 17A GC with a QP5050 MS. The time of purging was 8 min. (2 min. for dry purging). During the desorption step, the trap temperature was set at 225°C for 2 min. The GC column was a Supelco capillary column (MDN-5 30 m length × 0.32 mm internal diameter × 0.25 μm film thickness). The temperature programme of the oven was: 33°C (10 min.), 33–130°C (6°C/min.), 130°C (5 min.). The interface temperature was set at 190°C and the detector voltage was 1.15 kV. Helium was used as carrier gas with a flow rate of 3 ml/min., and the split ratio was 1:30. Data was acquired in the full-scan detection mode from 45–300 amu at a rate of 0.5 scan/sec.

For the quantitative analysis, the CDS 6000 purge-and-trap apparatus was connected to a Carlo Erba 5360 GC with an ECD detector. The ECD temperature was set at 300°C. Nitrogen gas (ECD quality) was used as carrier (8 ml/min.) and make-up gas (40 ml/min.) and the split ratio was 1:10. The rest of the analytical conditions were the same as above. The quantification was made using calibration curves, for each measured concentration range, based on external reference standards for each THM. Standards were made by diluting aliquots of stock solutions, weekly prepared in methanol and stored at -5°C, in ultrapure water and analysed under the same conditions.

Results and discussion

Prior to chlorination the nitrified effluent samples were analysed in triplicate and no THM were detected. Figure 1 presents the amount of total and free chlorine residuals in nitrified and partially nitrified secondary effluent chlorinated with 10 ppm dosage versus time. As

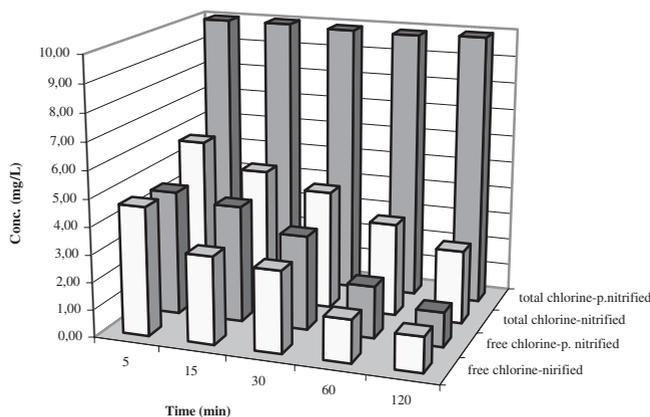


Figure 1 Free and total chlorine in chlorinated (10 ppm dose) nitrified and partially nitrified effluent

time proceeded, chlorine was consumed and the concentration of free available chlorine decreased in both nitrified and partially nitrified samples. The significant difference between the two samples was that the concentration of total chlorine residual in the partially nitrified wastewater remained stable (around 10 mg/L), while in the nitrified effluent it progressively decreased (from 5.8–2.7 mg/L). This was due to ammonia or organic nitrogen chloramines formed which exist in equilibrium with hypochlorous acid and are termed “combined available chlorine”. Although the detected amounts of free and total chlorine residuals were relatively low in the other two chlorine doses, similar trends were observed. In all partially nitrified samples the concentration remained fairly stable, decreasing from 5.24 mg/L (at the time of preparation) to 4.69 mg/L (after 2 hours of chlorination).

In Figures 2–5 the formation of THM versus time is shown. Among the individual compounds, chloroform and bromodichloromethane constituted more than 90% of Total THM (TTHM), with the chloroform concentration being twice as much as that of bromodichloromethane. Bromoform was identified in traces (< 0.3 ppb) in only a few samples. For all cases, the concentration of each THM progressively increased as contact time increased.

The effect of chlorine doses of 2, 5 and 10 ppm on the formation of trihalomethanes in sample 1 (nitrified effluent) is shown in Figures 2(a), 2(b) and 2(c), respectively. THM production was greatest for the dose of 10 mg/L chlorine: 52.3 ppb for the TTHM (64% of which was chloroform) after 2 hours contact time. A lower THM production was observed at 5 ppm dose followed by 2 ppm for all specified contact times. The rate of formation was relatively rapid; the concentration of each THM reached two-thirds of the final measured concentration within the first 30 min. of the reaction for all chlorine doses.

Although the effect of chlorine doses was similar for both types of effluent, ammonia had a large impact on THM production. The quantity of THM present after chlorination of partially nitrified effluent was one order of magnitude smaller. Since the partially nitrified sample was prepared from the nitrified sample 1 by adding NH_4Cl and the two samples contained the same type and concentration of precursors, this effect was due to the ammonia reaction selectivity and the slow kinetics to form by-products in the presence of both chlorine forms, free or combined available chlorine. In Figure 2(d), the THM concentrations versus contact time for partially nitrified samples chlorinated with 10 ppm dosage at 20°C are shown. All measured concentrations were significantly lower than the respective concentrations obtained after chlorination of nitrified effluent: after 2 hours contact time TTHM concentration was 3.1 ppb (95% of that was chloroform). Similar trends were

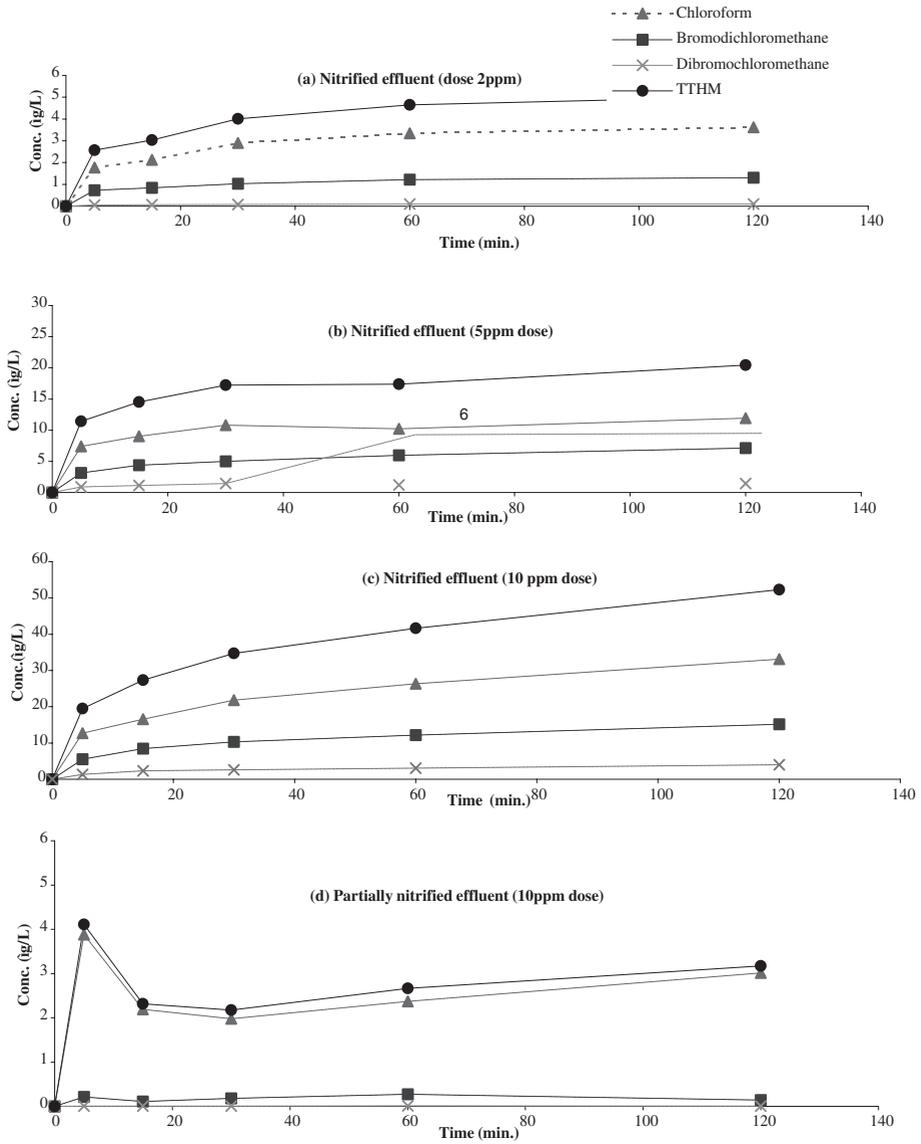


Figure 2 THM formation during chlorination of nitrified and partially nitrified wastewater with different chlorine doses (TOC = 7.74 mg/L, 20°C and ambient pH)

observed for the two other chlorine doses. The above results are in agreement with literature reports on partially nitrified secondary effluents with 13–15 mg/L TOC, which showed that reaction with 5 and 10 mg/L chlorine produced 1–4 ppb chloroform, and 1–5 ppb TTHM at a chlorine dosage of 15 mg/L. In addition, during chlorination of raw wastewater (high nitrogen and total organic carbon content) TTHM concentration was at the greatest, 16 ppb (Oliver and Lawrence, 1979; Winstrom *et al.*, 1996). Although the chloramines formation reactions are generally faster than by-product formation reactions, they seem to be competitive during the early stages as the observed concentrations of THM were a little higher in the first 5 min.: 3.9 and 4.1 ppb for chloroform and TTHM, respectively (Figure 2d). A similar pattern for TTHM concentration produced after chlorination of partially nitrified secondary effluent and raw wastewater during the early stages has also been reported in the literature (Winstrom *et al.*, 1996).

Figure 3 presents the pH effect on TTHM formation during chlorination of nitrified secondary effluent 1 with 10 ppm chlorine dose at 20°C. Increase in pH (from 6–8.5) of treated wastewater exhibited a large impact on THM yield, increasing their formation rate. Measured THM concentrations showed an increase or decrease of up to 50% after adjusting the effluent pH from 7.25 (ambient pH) to 8.5 or 6, respectively, for almost all specified contact times.

The effect of temperature on THM formation is presented in Figure 4. As temperature increased, the THM concentration increased as well. An increase in temperature from 20–25°C resulted in a 20–40% increase in THM concentration, while a decrease from 20–15°C resulted in a 5–20% decrease, for all specified contact times. However, the temperature effect was less severe as compared to the presence of ammonia or the pH variation. In chlorination of river water a small temperature effect has also been reported (Galapate *et al.*, 1999), while in drinking water a non-linear increase in chloroform formation as temperature increased up to 17.3°C, and a decrease after further temperature increase was observed (Garcia Villanova *et al.*, 1997).

The removal of organic matter from the nitrified effluent, as measured by both DOC and absorbance at 254 nm, was accomplished by coagulation treatment. As the coagulant dose increased, the DOC removal increased (Table 2). The highest removal (from 10–5.84 mg/L) was observed at the coagulant dose of 2 mM, while a further increase to 2.5 mM did not affect the DOC value. A similar pattern was observed for the reduction of the absorbance at 254 nm. Figure 5 presents the total THM formed during chlorination of nitrified effluent sample 2, without and after coagulation with various coagulant doses versus time. Although generally the THM formation decreased as the DOC content of the sample decreased, this reduction was significant for coagulant doses higher than 1.5 mM. At the 1.5 mM dose, a 50% restriction on TTHM formation had been observed after 2 hour contact time, while when the coagulant dose increased to 2 mM the restriction was more than 70%.

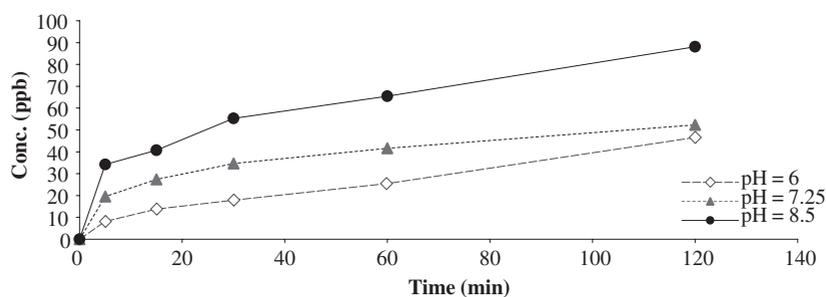


Figure 3 Effect of pH on THM formation during nitrified secondary effluent chlorination (TOC = 7.74 mg/L, 10 ppm dose and 20°C)

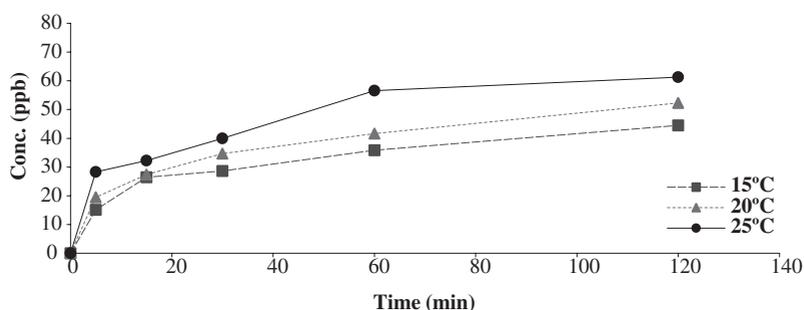
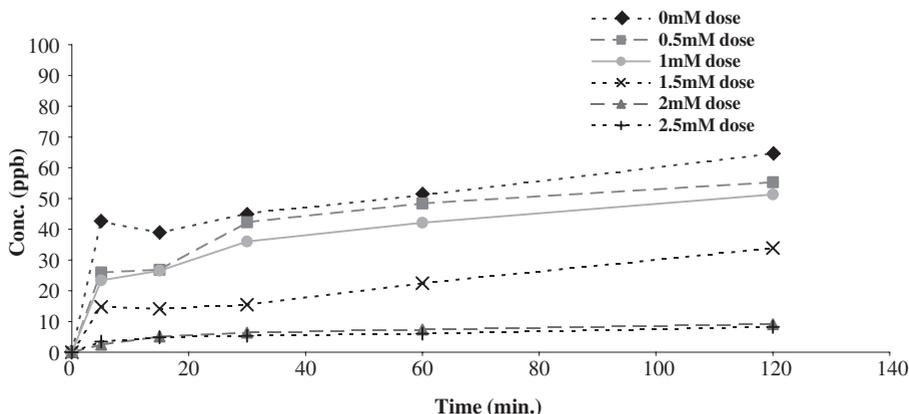


Figure 4 Temperature effect on THM formation during nitrified secondary effluent chlorination (TOC = 7.74 mg/L, 10 ppm dose and ambient pH)

Table 2 DOC values and UV absorbance at 254 nm after coagulation of nitrified sample 2 with different coagulant doses

Dose (mM Al ³⁺)	0	0.5	1	1.5	2	2.5
DOC (mg/L)	10	7.8	6.5	6.15	5.8	5.9
Absorbance at 254nm	0.232	0.203	0.166	0.129	0.109	0.114

**Figure 5** THM formed during chlorination of nitrified effluent 2 treated with various coagulant doses (10 ppm dose, ambient pH and 20°C)

The removal remained almost the same with the higher coagulant dose tested (i.e. 2.5 mM). In the literature, a reduction in THM production more than 60% by the alum treatment (Oliver and Lawrence, 1979) and a similar reduction in chloroform concentration in groundwaters (Ivancez-Tumbas *et al.*, 1999) have been reported.

Conclusions

THM formation and their formation potential, as result of chlorination, were much higher for nitrified secondary effluent as compared to those for partially nitrified effluent due to the consumption of available chlorine by ammonia nitrogen. THM concentrations were greatest for 10 ppm chlorine dose followed by 5 ppm and 2 ppm. Since the greatest amount of THMs was formed within the first 30 min., the reaction rate seems to be rapid. Values of THM increased considerably as the pH was raised from 6 to 8.5, while a 10°C increase in temperature affected THM concentrations to a lesser extent. The use of coagulants decreased THM production by almost 90%. The 2 mmol Al³⁺/L coagulant dose considered as the optimal for DOC and THM removal.

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