BREAKPOINT REACTION OF CHLORINE JETS IN AMMONIA NITROGEN AND TREATED PRIMARY EFFLUENT: MODELING AND EXPERIMENTAL STUDY

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ABSTRACT

Chlorine is extensively used in disinfection processes in water and wastewater treatment. In the chemically-enhanced primary treatment (CEPT) plant of the Hong Kong Harbour Area Treatment Scheme, high concentration (10 percent) chlorine solution is dosed into the treated sewage flow (2×10^6 m^3/d) by jet mixing. Due to the fast reaction of chlorine with organic and inorganic nitrogen compounds, field observations have demonstrated significant loss of chlorine within a short distance or travel time from the dosing point (in the order of 0.1 m or 1 second or less). It is essential to understand the mixing and reaction of chlorine jet with ammonia nitrogen for disinfection dosage optimization.

In this paper, an integral reacting chlorine jet model for predicting the changes in free chlorine, chloro-amine and ammonia nitrogen is developed for the first time. The model is validated against measurements in a bench-scale "toy" model experiment of chlorine jet discharging in coflowing ammonia nitrogen solution and CEPT effluent. The results suggest that in ammonia solution, the dosed chlorine predominantly reacts with ammonia to form combined chlorine with negligible chlorine demand. In CEPT effluent, the chlorine demand is mainly due to the preferential oxidation of organic debris by free chlorine. Combined chlorine is then formed due to the reaction of remaining free chlorine with ammonia nitrogen under jet mixing.

Keywords: Chlorine disinfection, chlorine demand, breakpoint chlorination, ammonia

1. INTRODUCTION

In the Stonecutters Island Sewage Treatment Works (SCISTW) of the Hong Kong Harbour Area Treatment Scheme, municipal sewage receives chemically enhanced primary treatment (CEPT). Before being discharged into coastal waters via a submarine outfall, the CEPT effluent is chlorinated to protect the bacterial water quality for the nearby bathing beaches. Concentrated ten percent chlorine solution (in sodium hypochlorite, specific gravity of 1.2) is injected in the form of coflowing dense jets into a sewage flow of approximately 2×10^6 m^3/d, with a target (full mixing) dosage of 10-20 mg/L. It is expected that most of the chlorine dosage would be used for inactivation of pathogens, and the bacterial concentration of the disinfected sewage effluent would meet the environmental regulations before discharging. However, operational experience and in-plant records reveal large spatial and temporal fluctuation of total residual chlorine (TRC) and *E. coli* concentration in the chlorinated CEPT effluent. Field monitoring data show that most of dosed chlorine is rapidly lost after injection in the chlorine dosing chamber (Lee et al., 2014).

The chlorine demand of CEPT sewage depends on factors including sewage characteristics, septicity, pH and temperature, and most importantly the chlorine concentration which changes continuously in the jet mixing process. Field experiments (Lee et al., 2017) have shown significant chlorine demand occurred within a short distance (in the order of 0.1 m, or 1 second or less of travel time) from the dosing position due to the turbulent mixing and reaction with ammonia nitrogen and organic impurities. In view of the importance of sewage disinfection on the environmental impact, it is essential to understand the mixing and reaction of chlorine with sewage for disinfection dosage optimization.

A tractable mathematical model of a reacting dense chlorine jet in CEPT effluent is highly useful in exploring different options to optimize chlorine dosage. Chan et al. (2017) has developed an integral jet model to predict the jet mixing in the initial contact region of chlorine and coflowing sewage, employing an empirical lumped second order kinetic model to account for the chlorine demand by sewage. Yang et al. (2019) developed an integral jet model that accounts for the breakpoint reaction with ammonia. The model is validated with chlorine jet experiments in stagnant and coflowing ambient CEPT effluent. However, the modeling of the reactions between chlorine and ammonia in terms of the individual chemical species has hitherto not been attempted.

In this paper, we present an integral reacting jet model which incorporates the reaction of chlorine with ammonia, both above and below the breakpoint to account for the loss of free chlorine and formation of combined chlorine. The model is validated against experimental observations in a bench-scale "toy" model of chlorine jet discharging in coflowing ammonia solution and CEPT effluent. The ammonia concentration and the chlorine concentration in the flume outflow are also measured.

2. INTEGRAL MODEL FOR REACTING CHLORINE JET

Figure 1 shows a chlorine jet discharging in a sewage coflow with ambient velocity U_a, density ρ_a. The jet (diameter D, discharge Q_0, velocity U_0, density ρ_0 and free chlorine concentration C_0) mixes with the ambient sewage by turbulent entrainment induced by the velocity and density differences between the jet and ambient fluid. The chlorine concentration in the jet is rapidly reduced by the entrainment process. In addition, the reaction of the chlorine with the ammonia nitrogen (NH_3-N) and organic debris in the ambient sewage results in further concentration reduction and/or transformation of the chemical species. The chlorination kinetics is principally dependent on the relative concentration of chlorine and ammonia. When the molar ratio of available chlorine to ammonia nitrogen (Cl/N) is less than 1 (or mass ratio of 5.1), ammonia reacts with free chlorine (HOCl or OCl^-) to form monochloramine (NH_2Cl):

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \tag{1}$$

As Cl/N increases beyond 1, free chlorine can further react with NH_2Cl to produce other combined chlorine species of dichloramine ($NHCl_2$) and trichloramine (NCl_3). When Cl/N is greater than 1.5 (or mass ratio of 7.6), the reaction of chlorine with ammonia forms nitrogen gas and resulted in the loss of the chlorine (the "breakpoint reaction", White, 1986; Jafvert and Valentine, 1992):

$$2NH_3 + 3HOCl \rightarrow N_2 + 3Cl^- + 3H^+ + 3H_2O \tag{2}$$

Only free chlorine remains after the ammonia has been exhausted. Both reactions (1) and (2) are very rapid and can be considered as instantaneous (Wei and Morris, 1974; Stenstrom and Tran, 1983).

An integral reacting jet model (Fig. 1) is developed for the reaction of chlorine with ammonia based on the general integral theory of dense jets in coflowing fluid (Lee and Chu, 2003; Chan et al., 2017; Yang et al., 2019). As the toy model flume has a narrow width of only about four jet diameters (w = 1.5 cm, see next section), the jet can be modelled by a two-dimensional (2D) dense jet in a coflow (with equivalent jet momentum and buoyancy flux per unit width) (e.g. Jirka, 2006). Assuming self-similar jet velocity and concentration profiles, the conservation of horizontal (M_x) and vertical (M_z) kinematic jet momentum fluxes can be written in terms of the jet properties as:

$$\frac{dM_x}{ds} = \frac{d[2BV(U - U_a)]}{ds} = 0, \qquad \frac{dM_z}{ds} = \frac{d[2BVW]}{ds} = \frac{F_0}{U_a} \tag{3}$$

where B is the top-hat jet half width, $V = (U, W)$ is the average jet velocity in the streamwise direction s. The specific buoyancy flux per unit width $F_0 = (Q_0/w)[(\rho_0 - \rho_a)/\rho_a]g$ (g = 9.81 m/s^2) is conserved and assumed to be unaffected by the chemical reaction. A jet spreading hypothesis is used for turbulent closure to account for the increase in jet width B by shear entrainment, buoyancy-induced mixing and ambient turbulence (Chan et al., 2017):

$$\frac{dB}{ds} = \beta_s \frac{(V - U_a \cos\phi)}{V} + \beta_n \frac{U_a \sin\phi}{V} + \beta_* I \tag{4}$$

where $\beta_s = 0.14$, $\beta_n = 0.6$, $\beta_* = 0.8$; $\phi = \tan^{-1}(W/U)$; $I = 0.16(U_a w/\nu)^{-1/8} = 0.064$ is the ambient flow turbulent intensity; $\nu = 10^{-6}$ m^2/s is the kinematic viscosity of water.

The mass conservation equations for the molar concentrations (mol/L) of free chlorine C (Eq. 5), monochloramine M (Eq. 6) and ammonia N (Eq. 7) along the jet are solved with the stoichiometric reactions according to reactions (1) and (2), dependent on the ratio between jet free chlorine concentration and ambient ammonia concentration, $R = C/N_a$:

$$\frac{d[2BVC]}{ds} = \begin{cases} -\dfrac{dq}{ds}C & \text{for} \quad R < 1 \\ -1.5\dfrac{dq}{ds}N_a & \text{for} \quad R > 1.5 \end{cases} \tag{5}$$

$$\frac{d[2BVM]}{ds} = \begin{cases} \dfrac{dq}{ds}C & \text{for} \quad R < 1 \\ 0 & \text{for} \quad R > 1.5 \end{cases} \tag{6}$$

$$\frac{d[2BVN]}{ds} = \begin{cases} \dfrac{dq}{ds}(N_a - C) & \text{for} \quad R < 1 \\ 0 & \text{for} \quad R > 1.5 \end{cases} \tag{7}$$

where dq/ds is the entrained volume flux per unit length of a jet element ds. For $R > 1.5$, there is a net consumption of free chlorine without the increase of NH_2Cl and NH_3-N, as NH_3-N is limiting. For $R < 1$, there is a net increase in NH_3 and NH_2Cl concentration with a net consumption of free chlorine. Eqs. (3)-(7) are solved by numerical integration marching from the initial conditions at the jet nozzle (Fig. 1). Linear interpolation is used for the reaction terms of Eqs. (5)-(6) for $1 < R < 1.5$.

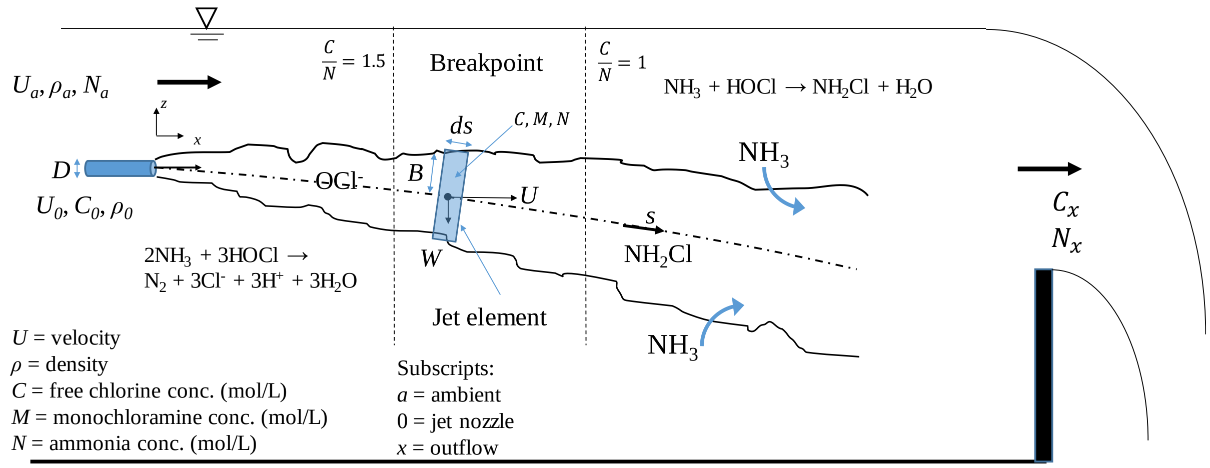


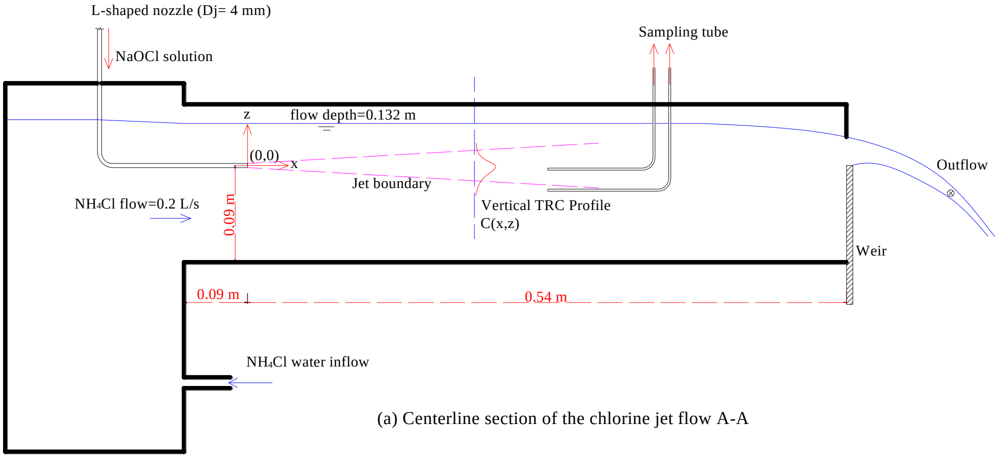
Figure 1. Integral model of chlorine jet in a coflowing ambient and the reaction of chlorine with ammonia nitrogen.

3. EXPERIMENTS

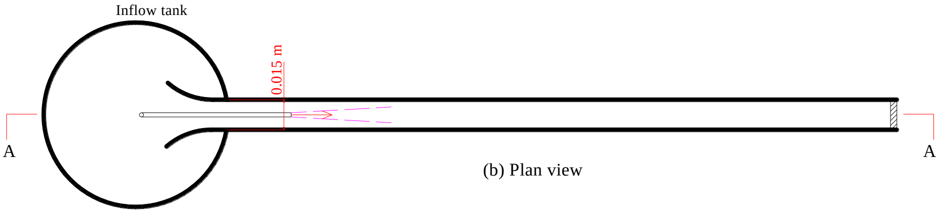
A bench-scale physical model is used to study the chlorine jet mixing and chlorine demand in coflowing deionized (DI) water, ammonia solution and CEPT effluent (Fig. 2). This once-through flow system consists of a test flume of 0.63 m long × 0.015 m wide × 0.15 m high. The chlorine solution is discharged through a nozzle of D=4 mm at the upstream end of the flume. The jet discharge velocity U_0 varies in the range of 0.1-0.5 m/s, while the ambient flow is kept at Q = 0.2 L/s with an average velocity U_a of around 0.1 m/s. The (full mixing) chlorine dosage can be expressed as $C_d = q_j C_0/(Q + q_j)$. For all experiments, C_d ranges from 10-100 mg/L depending on the jet discharge q_j and source concentration C_0.

Experiments of chlorine jet in DI water and ammonia solution are carried out in the hydraulic laboratory of HKUST. The ambient ammonia nitrogen concentration is about 30 mg/L at pH 6.0, similar to that of CEPT sewage. The source chlorine solution is prepared by diluting commercially available bleach (~20,000 mg/L) to a nominal concentration of C_0 = 200, 800 and 5000 mg/L. Tests of the chlorine jet in CEPT effluent flow are carried out on site in the treatment works (SCISTW), using fresh CEPT effluent from a nearby sedimentation tank. The NH_3-N concentration of CEPT sewage is measured to be 30-40 mg/L.

Samples are collected at the flume outflow using 2 L plastic bottles for measurement of TRC and NH_3-N concentrations. In selected experiments, the vertical profiles of TRC and NH_3-N at the jet centerline are measured using suction sampling. TRC concentration is measured with a Lovibond Mini-100 photometer with appropriate dilution of samples. The NH_3-N concentration is determined with standard Nessler's reagent method.



(a) Centerline section of the chlorine jet flow A-A



(b) Plan view

Figure 2. Schematic diagram of the bench scale model test flume for chlorine jet in coflowing ambient.

4. RESULTS AND DISCUSSION

4.1 Structure of a chlorine jet in ammonia solution

The vertical TRC concentration at the jet centerline can be well described by a Gaussian profile (Fig. 3a):

$$\frac{C(x,z)}{C_m} = \exp\left[-\left(\frac{z-z_m}{b_{gc}}\right)^2\right] \tag{7}$$

where C_m is maximum TRC concentration; z_m is the vertical position of C_m; b_{gc} is the concentration half width ($C/C_m = e^{-1}$). The vertical NH_3-N concentration profile shows a minimum (N_m) near the centerline of the jet and attains a maximum at the jet edge. The normalized concentration “deficit” can be described as:

$$\frac{N_a - N(x,z)}{N_a - N_m(x)} = \exp\left[-\left(\frac{z-z_m}{b_{gc}}\right)^2\right] \tag{8}$$

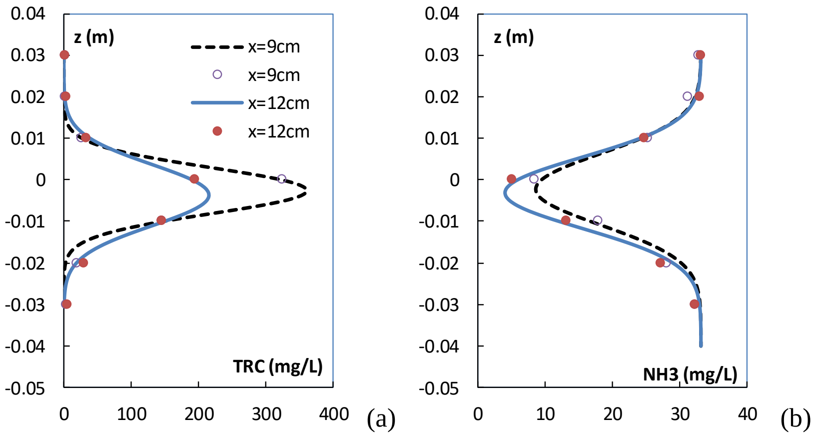
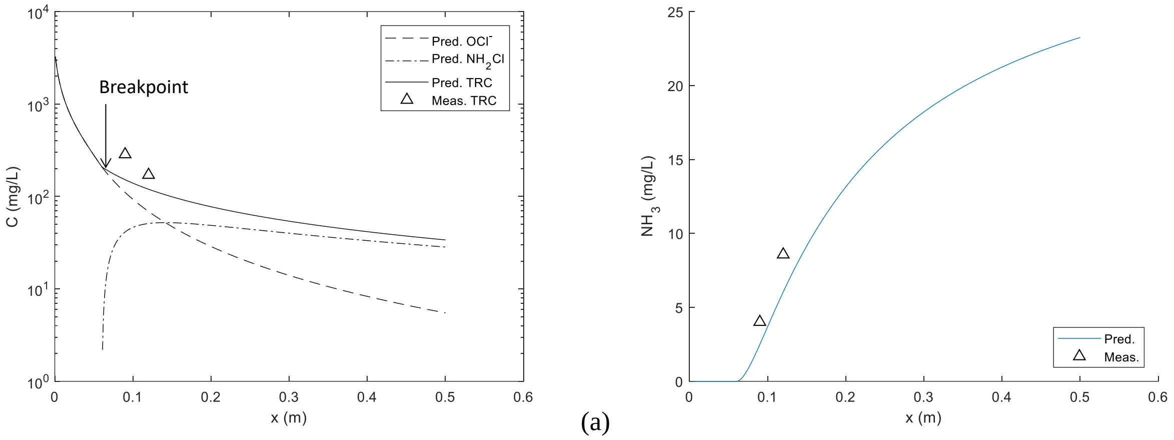


Figure 3. (a) Vertical distribution of TRC and (b) NH_3-N concentration at x = 9 cm and x = 12cm. (U_a = 0.1 m/s, U_j = 0.14 m/s, C_0 = 4000 mg/L, N_a = 33.1 mg/L, jet densimetric Froude number Fr = 16.1). Symbols: measurement, line: best fit.

The average TRC and NH_3 concentrations along the jet can be predicted using the integral model of reacting chlorine jet with ammonia. For a chlorine jet with source concentration C_0 = 3800 mg/L (Fig. 4), it is seen that the jet TRC concentration decreases along the jet due to turbulent entrainment and reaction with entrained ammonia. At $x < 8$cm, the dominant form of residual chlorine is free chlorine as the reaction with ammonia causes the net loss of total chlorine. For $x > 8$cm, combined chlorine forms quickly and dominates the TRC concentration. Ammonia concentration starts to increase from zero below the breakpoint ($x > 8$cm). The model is in reasonable agreement with the measurements.

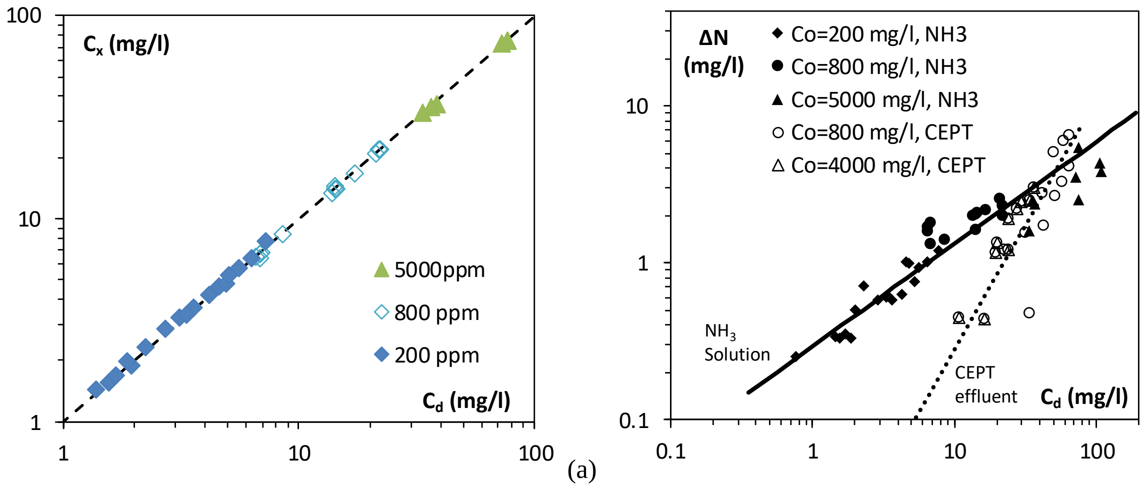


(a) (b)

Figure 4. Comparison of model predictions with data: (a) chlorine (TRC = OCl^- + NH_2Cl) and (b) ammonia concentrations (C_0 = 3800 mg/L, N_a = 33.1 mg/L, U_j = 0.153m/s, U_a = 0.1 m/s).

4.2 Chlorine demand in ammonia solution

The chlorine demand of a chlorine jet can be estimated by measuring the TRC concentrations in the fully mixed outflow of the flume. It can be seen that for a wide range of chlorine dosage (1-100 mg/L) with source chlorine concentration (C_0 = 200-5000 mg/L), the measured chlorine concentration C_x at the outflow is very close to that of the dosage C_d (Fig. 5a). The maximum chlorine demand is only about 5% for an experiment with C_0 = 5000 mg/L and C_d = 100 mg/L.



(a) (b)

Figure 5. (a) Correlation of outflow TRC concentration C_x with chlorine dosage C_d, showing negligible chlorine demand in NH_3-N solution. (b) Correlation of ammonia consumption ΔN with chlorine dosage C_d in NH_3-N solution and CEPT effluent.

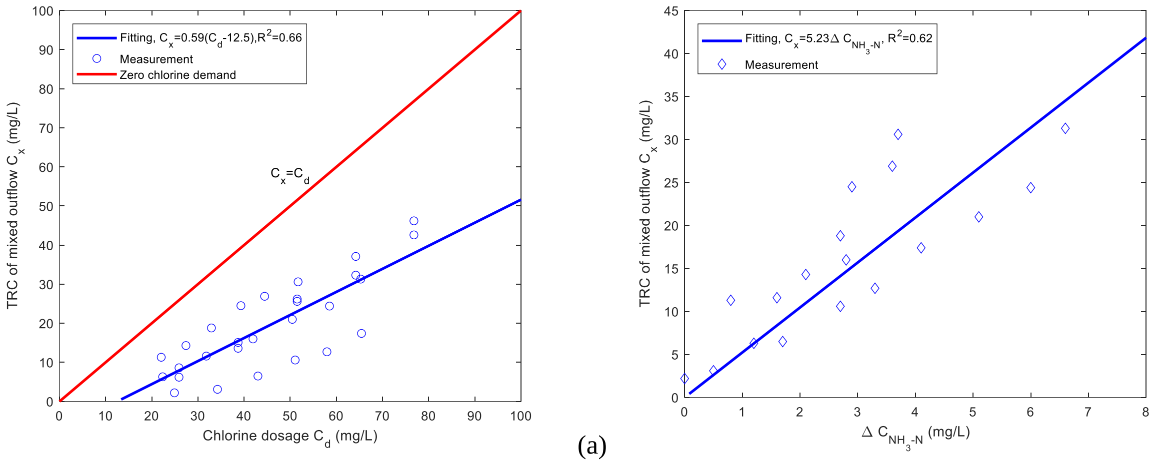
Due to the rapid reaction of free chlorine with ammonia, the TRC concentration in the jet quickly drops below the breakpoint; hence it is not surprising that the measured TRC at the outflow is dominated by combined chlorine. The chlorine dosage is correlated with the overall ammonia-nitrogen consumption by the jet mixing:

$$\Delta N = \frac{Q}{Q + q_j} N_a - N_x \tag{10}$$

where N_x is the measured ammonia nitrogen concentration of flume outflow (Fig. 5b). The correlation of ΔN and C_d can be described by a power law ($\Delta N = aC_x^b$), indicating that the reaction ratio $C_x/\Delta N$ increase with chlorine dosage. For a C_0 of about 200 mg/L, as the entire jet is below the breakpoint, the free chlorine (OCl^{-1}) reacts with ammonia to produce monochloramine, without any loss of TRC. The reaction ratio $C_x/\Delta N$ = 5.4, is about the same as the theoretical value of 5.1. The main end product is NH_2Cl. For a source concentration above the breakpoint (C_0 = 800 and 4000 mg/l), breakpoint reaction of free chlorine with ammonia occurs near the discharge point. For C_0 = 800 and 4000 mg/L, their reaction ratios increase to about 7.2 and about 20 respectively. This probably indicates further consumption of free chlorine by combine chlorine for the formation of $NHCl_2$ and NCl_3.

4.3 Chlorine demand in CEPT effluent

Tests have also been conducted with a chlorine jet in coflowing CEPT effluent with an NH_3-N of 30-40 mg/L. Fig. 6a clearly indicates that there is significant chlorine demand in CEPT effluent, contrary to the negligible chlorine demand in ammonia solution. Despite the large scatter in the data due to variations in sewage quality, the tests show that when C_d is lower than about 10 mg/L, all the chlorine dosed can be effectively consumed. On the other hand, the pattern of ΔN in CEPT effluent is significantly different (Fig. 5b). For low C_d of about 10 mg/L, ΔN is much smaller compared to that in ammonia solution, while for high chlorine dosage (C_d = 40-100 mg/L), ΔN is similar to that in ammonia solution. This suggests that the free chlorine oxidizes other substances in sewage preferentially, causing the loss of free chlorine. At low dosage, as most free chlorine is consumed, there is no oxidant for the ammonia to form combined chlorine, thus the disappearance of TRC. It is seen that ΔNH_3-N is correlated with the TRC at the outflow with a proportionality constant of about 5.2 (Fig. 6b), suggesting that the ammonia reacts with the remaining free chlorine to form monochloramine after the consumption of free chlorine.



(a) (b)

Figure 6. (a) Correlation of outflow TRC concentration C_x with chlorine dosage C_d, showing there is significant chlorine demand in CEPT effluent. (b) Correlation of ammonia consumption ΔN with C_x in CEPT effluent. ($C_0 \approx$ 5000 mg/L)

5. CONCLUSIONS

An integral model is developed for a reacting chlorine jet discharging in co-flowing sewage. The model incorporates the entire range of chlorine-ammonia reactions above and below the breakpoint to account for the loss of free chlorine and formation of combined chlorine. Model predictions of total residual chlorine (TRC) and ammonia nitrogen concentrations are in good agreement with data from experiments in a bench-scale “toy” model of chlorine jet discharging in coflowing ammonia nitrogen solution and CEPT effluent.

Both theory and observations suggest that for the case of pure ammonia solution there is negligible chlorine demand as the breakpoint reaction occurs within only a very short distance (< 0.1m) from the dosing jet source. This indicates that the dosed free chlorine is transformed into combined chlorine by reacting with ammonia in jet mixing process. In contrast, for a chlorine jet discharging into CEPT effluent under the same jet mixing condition, significant chlorine demand is caused by the reaction between free chlorine and organic matters in sewage, before the formation of combined chlorine by the reaction of the remaining free chlorine and ammonia. This work provides insights that are useful for chlorine dosage optimization in practice.

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