

## Modeling and validation of chlorination breakpoint with nitrite in wastewater treatment

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### ABSTRACT

Chlorination in wastewater treatment is regarded as a complicated process due to its ammonia and nitrite content. Chlorine added to such systems reacts with ammonia undergoing episodes of complex reactions resulting in the chlorination breakpoint behavior. Most of the available chlorination mechanistic models are not easily applied which has restricted their practical utilization in treatment plants. In this study, a new mechanistic model for the chlorination breakpoint in ammonia-nitrite systems is suggested with a user-friendly interface and to be applicable with conditions occurring in wastewater treatment plants. The model was validated against laboratory studies reported in the literature and was also applied to forecast chlorine residual in a wastewater treatment plant in the region. The model simulated both experimental and field data reasonably well.

**Key words** | ammonia-nitrite system, breakpoint chlorination, chlorination, disinfection, wastewater treatment

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### INTRODUCTION

Recently, the implementation of disinfection in water and wastewater treatment has been regarded as a major public health measure as it is responsible for a huge reduction in waterborne diseases worldwide. The most commonly used disinfectant for water and wastewater treatment worldwide is chlorine (Casteel *et al.* 2008). Not only employed as a primary disinfectant in water and wastewater treatment processes, chlorine is also added to provide a minimum disinfectant residual to maintain the water quality throughout the distribution system (Casteel *et al.* 2008). Although the chemistry of the chlorination process is fundamentally the same in water and wastewater treatment, the reactions differ owing to the various interfering substances, organic and inorganic, that exist in considerable amounts in the wastewater discharge and exert an extra chlorine demand or impair the bacterial disinfection efficiency of the added chlorine (Watson *et al.* 2012). The most important among

these interfering substances are ammonia and nitrite forming nitrogenous compounds (Hong *et al.* 2013).

The behavior of chlorine in ammonia contaminated water is described through a series of reactions, often called 'breakpoint chlorination', which, discovered in the 1940s in the course of research, attempted to destroy ammonia in wastewater or natural water and accomplish disinfection via free chlorine residual (Hui *et al.* 2013). The finding of breakpoint chlorination then led to the discovery of chloramine as a possible disinfectant (McGuire 2006).

Although monochloramine, one of the products of the chloramination process, is considered as a more stable disinfectant than free chlorine and more importantly a by-product-free disinfectant, it is not yet widely implemented owing to the poor understanding of the breakpoint chlorination profile and its changing behavior in the presence of different water quality or operating process parameters

(Kool *et al.* 1999). This is partially because the formation of chloramines is followed by subsequent decay involving a complex series of chemical reactions (Duirk *et al.* 2005).

The lack of an easy-to-implement approach for modeling and forecasting the variation in the breakpoint behavior resulted in the limited use of monochloramine and also led to the deficient prediction and control of free chlorine disinfection in the presence of ammonia (Vikesland 2001). This difficulty in modeling and hence optimizing the chlorination performance can be linked to various problems commonly recognized at wastewater and municipal water treatment facilities, from acute odor up to disinfection by-products (DBPs) (Maier *et al.* 2000).

The complexity and ambivalence of the chloramination system has given rise to various research putting forward new mechanisms and kinetic studies for the formation and decay of chloramines (Weil & Morris 1949; Granstrom 1954; Wei 1954; Jafvert 1976; Saunier 1976; Morris & Issac 1983). While some of these studies explore individual reactions, many of them have proposed different reaction schemes of this complicated reactive system. This study will shed light on the most recognized and comprehensive models for the chlorination process, which will serve to create a platform for the development of the model proposed in this study.

The aim of this work is to establish a real-time approach to optimize the chlorination process for wastewater and municipal water effluents where fluctuating ammonia and nitrite content exists. A mechanistic model will be developed based on previous kinetic studies data. This will be done by reviewing the most well-known chlorination reaction mechanisms, from which a model will be proposed for the current study. The breakpoint chlorination will be validated in the presence of nitrite using field data and literature experimental data.

## REVIEW OF CHLORINATION REACTIONS MECHANISMS AND KINETICS

### Morris and Wei's model

Wei and Morris were among the very first researchers to propose an overall mechanism for the breakpoint reactions (Wei & Morris 1974). They performed extensive experimental

studies at different levels of pH and temperature, with a fixed chlorine to ammonia molar ratio of 1.8 to calibrate the proposed mechanism. The reactions of the proposed mechanism are presented in Table 1.

Reactions R-2 and R-5 were the rate limiting steps in the Morris and Wei reaction scheme with nitroxyl radical (NOH) considered as the key intermediate to account for the loss of chlorine and ammonia. Not all the reactions in the proposed mechanism were real; some were only hypothetical ones at that time. The assumed reactions were R-6, R-7 and R-8 with NOH involved in all of them reacting with  $\text{NH}_2\text{Cl}$ ,  $\text{NHCl}_2$ , and HOCl, respectively. The assumption that these reactions were much more rapid than R-5 made their reaction rates of little concern. These reactions were considered important due to their competitive and simultaneous production of  $\text{N}_2$  and  $\text{NO}_3^-$  and their re-generation of hypochlorous acid, which were all end products of the reaction system. Reaction R-5 combined with reaction R-6 are considered the major trigger for the breakpoint, since they describe the interaction between  $\text{NHCl}_2$  and  $\text{NH}_2\text{Cl}$  (Wei & Morris 1974).

In addition, Morris and Wei attempted to determine the rate law of those reactions by recognizing their orders. Orders of some reactions were known with high certainty, as is the case with reactions R-1 and R-2. The decomposition of dichloramine, as described by reaction R-3, was observed in the experiments to be of second-order, with respect to the concentration of dichloramine, and proportional to the activity of hydroxyl ion. Finding the rate laws for the remaining reactions was not achievable in the absence of computer modeling in order to fit the experimental data to representative rate laws. Accordingly, R-4 and R-5 were considered to be first-order reactions, while R-3, R-6, R-7, and R-8 were considered as second-order reactions (Wei & Morris 1974).

### Saunier's model

Before the work of Saunier in 1976, most of the experimental work concerning breakpoint chlorination was performed in batch reactors (Saunier 1976). Saunier, in contrast, has considered different types of reactors to perform a series of experiments. He studied the chlorination system in four different types of reactors, namely batch, plug flow,

**Table 1** | Morris and Wei proposed reaction scheme (Wei & Morris 1974)

Reaction	Rate coefficient	Reaction reference
$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	$k_1$	R-1
$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$	$k_2$	R-2
$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$	$k_3$	R-3
$NCl_3 + H_2O \rightarrow NHCl_2 + HOCl$	$k_4$	R-4
$NHCl_2 + H_2O \rightarrow NOH + 2H^+ + 2Cl^-$	$k_5$	R-5
$NOH + NH_2Cl \rightarrow N_2 + H_2O + H^+ + Cl^-$	$k_6$	R-6
$NOH + NHCl_2 \rightarrow N_2 + HOCl + H^+ + Cl^-$	$k_7$	R-7
$NOH + 2HOCl \rightarrow NO_3^- + 3H^+ + 2Cl^-$	$k_8$	R-8

continuous flow stirred tank reactor (CSTR), and a non-ideal tubular reactor. However, the data collected were mainly from the plug flow reactor, assuming an ideal plug flow and using N,N-diethyl-p-phenylene diamine (DPD-FAS) as the analytical technique for free and combined chlorine measurements (Saunier 1976).

The experimental outcomes that Saunier reported from the plug flow reactor type did not match the outcomes predicted by the model of Wei and Morris. Saunier reported a much faster rate for the disappearance of monochloramine, and a large difference in nitrogen trichloride concentrations (Saunier 1976; Switzer *et al.* 2006). Accordingly, Saunier established a new mechanism proposing  $NH_2OH$  as an intermediate. The new mechanism established by Saunier accounted for nitrite, which appeared to be significant especially when the molar ratio is sufficient for nitrate production. The new developed model after Saunier is summarized in Table 2 (Saunier 1976).

Saunier revised some of the rate coefficients adopted by Wei and Morris to provide a better match with the experimental results (Saunier 1976). This model predicted the free chlorine residual with high accuracy, but failed to determine the concentration of nitrogen trichloride. The kinetic rate laws predicted the results at pH values ranging from 6 to 8, but failed to provide adequate prediction at pH values dwelling outside this range (Saunier 1976).

### Stenstrom and Tran's model

Stenstrom and Tran contributed to the improvement of the model of Wei and Morris. Stenstrom and Tran adopted

the same mechanism as Wei and Morris, but performed an extensive experimental study to modify the kinetic parameters using an estimation technique (Stenstrom & Tran 1984). Around 23 experiments were implemented at different pH values ranging from 4 to 8.4, performed in a plug flow reactor and two dispersed flow reactors. Initial values for the reaction rate coefficients were necessary for each reaction for the successful application of the estimation technique. The parameter estimation technique was analogous to that proposed by Becker & Yeh (1972), which includes sequential estimation and linearization of the objective function, based on an initial set of parameter values.

As a result of the experimental work performed by Stenstrom & Tran (1984), the following results were concluded: free chlorine was not detected until the chlorine breakpoint

**Table 2** | Reaction scheme of Saunier (1976)

Reaction	Reaction reference
$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$	R-1
$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$	R-2
$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$	R-3
$NCl_3 + H_2O \rightarrow NHCl_2 + HOCl$	R-4
$NHCl_2 + 2H_2O \rightarrow NH_2OH + HOCl + HCl$	R-5
$NH_2OH + HOCl \rightarrow NOH + HCl + H_2O$	R-6
$NHCl_2 + H_2O \rightarrow NH_2OH + HCl$	R-7
$NOH + NH_2Cl \rightarrow N_2 + HCl + H_2O$	R-8
$NOH + NHCl_2 \rightarrow N_2 + HCl + HOCl$	R-9
$NOH + HOCl \rightarrow NO_2 + H^+ + HCl$	R-10
$NO_2^- + HOCl \rightarrow NO_3^- + HCl$	R-11

dosage was passed; before the breakpoint, monochloramine was present at a much higher concentration than dichloramine; at a pH value as low as 6.5, dichloramine was detected at higher concentrations than monochloramine; only at high chlorine to ammonia ratio did nitrogen trichloride exist in substantial concentration; and at a pH value of 4, 90% of the initial chlorine dose existed as a residual. The residual percentage dropped down to 65% of the initial dose at a pH value of 6; while it decreased to 35% of the initial dose for pH values between 7.5 and 8.4.

### Jafvert and Valentine's model

The breakpoint chlorination profile comprises of three main regions; in the first region, disinfection is maintained by monochloramines, while combined chlorine (i.e. monochloramine, dichloramine, and trichloramine) provides the disinfection action in the second region, and free chlorine is the main disinfectant in the third one (Weil & Morris 1949; Stenstrom & Tran 1984; Switzer *et al.* 2006). Preceding Jafvert and Valentine, researchers focused on the breakpoint region, where free chlorine residual is detected (Weil & Morris 1949; Becker & Yeh 1972; Jafvert & Valentine 1992). Jafvert and Valentine, on the other hand, studied the entire chlorination profile putting forward a unified model suitable for any chlorine to ammonia ratios (Jafvert & Valentine 1992). They re-examined the previous chlorination mechanisms to develop their own reaction scheme. The model of Jafvert and Valentine is represented by a series of 14 reactions as shown in Table 3 (Jafvert & Valentine 1987).

Reactions R-1 through R-4 justify the formation of monochloramine, while reactions R-5 and R-6 account for its disproportionation and reverse disproportionation reactions, respectively. Prediction of the residuals in the combined region was attainable through reaction R-7. Reactions R-9 through R-11 described the decay of dichloramine in excess of ammonia, while reactions R-8 and R-13 were adopted from the mechanisms of Hand and Margerum, to account for the decay of dichloramine in excess of HOCl (Hand & Margerum 1983; Jafvert & Valentine 1987). Reactions R-12 and R-14 explained the formation of nitrate and nitrogen gas, respectively (Jafvert & Valentine 1987).

Jafvert and Valentine have performed a series of experiments aiming to appraise their model. The experiments

**Table 3** | Reaction scheme of the unified model (Jafvert & Valentine 1987)

Reaction	Reaction reference
$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	R-1
$NH_2Cl + H_2O \rightarrow HOCl + NH_3$	R-2
$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$	R-3
$NHCl_2 + H_2O \rightarrow HOCl + NH_2Cl$	R-4
$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$	R-5
$NHCl_2 + NH_3 \rightarrow NH_2Cl + NH_2Cl$	R-6
$NHCl_2 + H_2O \rightarrow NOH + 2HCl$	R-7
$NHCl_2 + NOH \rightarrow HOCl + N_2 + H_2O + HCl$	R-8
$NH_2Cl + NOH \rightarrow HOCl + HCl + N_2$	R-9
$NH_2Cl + NHCl_2 \rightarrow N_2 + 3HCl$	R-10
$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$	R-11
$NHCl_2 + NCl_3 + 2H_2O \rightarrow 2HOCl + N_2 + 3HCl$	R-12
$NH_2Cl + NCl_3 + H_2O \rightarrow HOCl + N_2 + 3HCl$	R-13
$NHCl_2 + 2HOCl + H_2O \rightarrow NO_3^- + H^+ + 4HCl$	R-14

were categorized into different sets, each of which was dedicated to studying a certain region in the breakpoint chlorination profile. All of the experiments were performed at pH ranging from 6 to 8 using a batch type reactor. Their model was successfully able to predict chlorine ammonia behavior within a wide range of chlorine to ammonia ratios (Jafvert & Valentine 1987).

Some researchers stretched the work of the Jafvert and Valentine model to make it applicable to distribution system water quality forecasting accounting for nitrification, corrosion, and pipe surface (Woolschlager 2000; Yang *et al.* 2008). The implementation of such models requires a well-calibrated hydraulic model (Yang *et al.* 2008).

## METHODOLOGY OF CHLORINATION BREAKPOINT MODEL SET-UP AND DEVELOPMENT

The involvement of sophisticated programming languages and the requirement of extensive field measurements and hydraulic calibration parameters left the vast majority of the available chlorination mechanistic models non-user friendly, and restricted their practical utilization in treatment plants (Rauen *et al.* 2012; Nejari *et al.* 2014). Currently, control of the chlorination system typically

relies on operators' experience and qualitative guidelines (Rauen *et al.* 2012; Nejari *et al.* 2014).

### Selection of the reactions and coefficients

In the current study, the model of Jafvert and Valentine is modified based on outcomes of other studies to develop a new mechanistic model empowered with the following capabilities and characteristics:

- Accounts for the effect of nitrite in chlorine-ammonia systems.
- Applicable mainly for the ranges of pH and temperature at which the chlorination process typically occurs in the treatment plants (i.e.  $6 < \text{pH} < 8$ , and  $25^\circ\text{C} < \text{Temperature} < 35^\circ\text{C}$ ) (Hua & Reckhow 2008).
- Incorporates updated rate coefficients wherever applicable.
- Requires the minimal inputs to ease its usage in plants and ill-defined systems.
- Introduced in a user-friendly interface.

Jafvert and Valentine have categorized the reactions of the unified model into five main categories: substitution reactions, monochloramine disproportionation, redox reactions in the first zone, redox reactions in the second zone,

and other reactions (Hand & Margerum 1983; Jafvert & Valentine 1987). This work utilizes the same categories that were adopted in the unified model; however, one more category is added to account for the reactions of nitrite, and the reactions included in each category are modified, which makes up a total of six categories to be considered in this study.

Table 4 provides a summary of the reactions considered in each of the six categories as given by the unified model and the corresponding modifications adopted in this study. The reactions in each category and the basis of the modifications are detailed in the next sections.

### Substitution reactions

The substitution reactions are the major pathways in the chlorine-ammonia reaction system through which monochloramine, dichloramine, and trichloramine are produced (Vrček & Meštrić 2009). They are represented by Reactions 1, 3 and 11. Reaction 3, in which dichloramine is formed, has been studied extensively to determine its rate coefficient (Palin 1949; Canty 1950; Morris 1950; Saunier 1976; Hand & Margerum 1983). Morris and Isaac re-evaluated the data reported in preceding studies and achieved an updated rate expression (Table 5), which is used in this study

**Table 4** | Summary of the modifications applied to the reaction in Jafvert and Valentine's model

Reactions category	Reactions in Jafvert and Valentine's model (i.e. the unified model) (Trogolo & Arey 2017)	Modification considered in this study
Substitution reaction	<ul style="list-style-type: none"> <li>• Monochloramine, dichloramine, and trichloramine formation (reactions 1, 3 &amp; 11)</li> <li>• Hydrolysis of monochloramine and dichloramine (reactions 2 &amp; 4, respectively)</li> </ul>	<ul style="list-style-type: none"> <li>• Inclusion of trichloramine hydrolysis</li> <li>• Exclusion of dichloramine hydrolysis (reaction 4)</li> </ul>
Monochloramine disproportionation	<ul style="list-style-type: none"> <li>• Monochloramine disproportionation (reaction 5)</li> <li>• Monochloramine disproportionation back reaction (reaction 6)</li> </ul>	<ul style="list-style-type: none"> <li>• Exclusion of monochloramine disproportionation back reaction (reaction 6)</li> </ul>
Redox reaction in the first zone	<ul style="list-style-type: none"> <li>• Decomposition of dichloramine considering NOH the intermediate (reactions 7, 8 &amp; 9)</li> </ul>	<ul style="list-style-type: none"> <li>• No modifications</li> </ul>
Redox reaction in the second zone	<ul style="list-style-type: none"> <li>• Breakpoint reactions (reactions 12, 13 &amp; 14)</li> </ul>	<ul style="list-style-type: none"> <li>• No modifications</li> </ul>
Reactions with nitrite	<ul style="list-style-type: none"> <li>• Not considered in the unified model</li> </ul>	<ul style="list-style-type: none"> <li>• Free chlorine and monochloramine demand caused by nitrite are considered</li> </ul>
Other reactions	<ul style="list-style-type: none"> <li>• Reaction 10 is included to improve the fitting between predicted and experimental data</li> </ul>	<ul style="list-style-type: none"> <li>• Reaction 10 is excluded</li> </ul>

**Table 5** | Summarized reaction scheme adapted in this study with rate expressions and rate constants

RxnRef	Reaction	Rate expression	Rate constant*	Reference
1	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	$k_1 [HOCl] [NH_3]$	$k_1 = 4.1 \times 10^4 \text{ mM}^{-1} \text{ s}^{-1}$	Morris (1950)
2	$NH_2Cl + H_2O \rightarrow HOCl + NH_3$	$k_2 [NH_2Cl]$	$k_2 = 1.27 \times 10^{-3} \text{ s}^{-1}$	Hand & Margerum (1983)
3	$HOCl + NH_2Cl \rightarrow NHCl_2 + H_2O$	$k_3 [HOCl] [NH_2Cl]$	$k_3 = 0.35 \text{ mM}^{-1} \text{ s}^{-1}$	Morris (1950)
4	$NHCl_2 + H_2O \rightarrow HOCl + NH_2Cl$	$k_4 [NHCl_2]$	$k_4 = 0$	
5	$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$	$k_5 [NH_2Cl] [NH_2Cl]$	$k_5 = 5.6 \times 10^{-2} \text{ mM}^{-1} \text{ s}^{-1}$	Trogo & Arey (2017)
6	$NHCl_2 + NH_3 \rightarrow NH_2Cl + NH_2Cl$	$k_6 [NHCl_2] [NH_3] [H^+]$	$k_6 = 0$	
7	$NHCl_2 + H_2O \rightarrow NOH + \text{Products}^*$	$k_7 [NHCl_2] [OH^-]$	$k_7 = 1.67 \times 10^{-1} \text{ mM}^{-1} \text{ s}^{-1}$	Jafvert & Valentine (1987)
8	$NHCl_2 + NOH \rightarrow HOCl + \text{Products}^*$	$k_8 [NOH] [NHCl_2]$	$k_8 = 27.7 \text{ mM}^{-1} \text{ s}^{-1}$	Jafvert & Valentine (1987)
9	$NH_2Cl + NOH \rightarrow \text{Products}^*$	$k_9 [NOH] [NH_2Cl]$	$k_9 = 8.3 \times 10^3 \text{ mM}^{-1} \text{ s}^{-1}$	Jafvert & Valentine (1987)
10	$NH_2Cl + NHCl_2 \rightarrow N_2 + 3HCl$	$k_{10} [NH_2Cl] [NHCl_2]$	$k_{10} = 0$	
11	$HOCl + NHCl_2 \rightarrow NCl_3 + H_2O$	$k_{11} [HOCl] [NHCl_2]$	$k_{11} = 5.05 \text{ mM}^{-1} \text{ s}^{-1}$	Hand & Margerum (1983)
12	$NHCl_2 + NCl_3 + 2H_2O \rightarrow 2HOCl + \text{Products}^*$	$k_{12} [NHCl_2] [NCl_3]$	$k_{12} = 35.56 \times 10^3 \text{ mM}^{-1} \text{ s}^{-1}$	Jafvert & Valentine (1992)
13	$NH_2Cl + NCl_3 + H_2O \rightarrow HOCl + \text{Products}^*$	$k_{13} [NH_2Cl] [NCl_3]$	$k_{13} = 1.39 \times 10^{-2} \text{ mM}^{-1} \text{ s}^{-1}$	Jafvert & Valentine (1992)
14	$NHCl_2 + 2HOCl + H_2O \rightarrow NO_3^- + \text{Products}^*$	$k_{14} [NHCl_2] [HOCl]$	$k_{14} = 2.31 \times 10^2 \text{ mM}^{-1} \text{ s}^{-1}$	Jafvert & Valentine (1992)
15	$HOCl + NO_2^- \rightarrow NO_3^- + Cl^- + H^+$	$k_{15} [HOCl] [NO_2]$	$k_{15} = 1.386 \times 10^3 \text{ mM}^{-1} \text{ s}^{-1}$	Soltermann et al. (2015)
16	$NH_2Cl + NO_2^- + H_2O \rightarrow NO_3^- + NH_4^+ + Cl^-$	$k_{16} [NH_2Cl] [NO_2]$	$k_{16} = 3.58 \times 10^{-3} \text{ mM}^{-1} \text{ s}^{-1}$	Work & Smith (2004)
17	$NCl_3 + H_2O \rightarrow HOCl + NHCl_2$	$k_{17} [NCl_3]$	$k_{17} = 3.24 \times 10^{-5} \text{ s}^{-1}$	Kumar et al. (1987)

\*Products may include:  $N_2$ ,  $H_2O$ ,  $Cl^-$ ,  $H^+$ ,  $NO_3^-$ .

(Morris 1950). Reaction 11 is the predominant reaction after the breakpoint region is passed, where free chlorine concentration is quite high. Hand and Margerum reported the rate coefficient with good fit to the linear free energy relationship through conducting base catalytic experiments, at various pH values ranging from 6 to 12 (Hand & Margerum 1983). Their reported rate expression will be used in this study.

Reaction 2 is the hydrolysis of monochloramine, the reverse of Reaction 1, which was first proposed by Granstrom in 1954 to be the first order part of monochloramine disproportionation (Granstrom 1954). He studied this reaction for pH less than 5.2 and temperature range of 5 to 50°C. Hand and Margerum later re-evaluated the  $k_2$  expression using the hydrolysis constant and  $k_1$  at 25°C and a broader range of pH (6 to 8); they estimated  $k_2$  to be  $1.9 \times 10^{-5} \text{ s}^{-1}$  (Hand & Margerum 1983). This value will be used in this study.

Reaction 4 is the hydrolysis of dichloramine; its coefficient rate was studied mainly by Palin (1949) and Huang (2008). Morris and Isaac obtained the rate constant of this reaction through thermodynamic calculations based on

equilibrium constants of Reactions 1 and 5, and it was reported as  $7.6 \times 10^{-7} \text{ s}^{-1}$  (Morris & Issac 1983). On the other hand, Hand and Margerum experimentally determined the same parameter to be  $6.5 \times 10^{-7} \text{ s}^{-1}$  at 25°C (Hand & Margerum 1983). However, this hydrolysis reaction is experimentally difficult to measure, which caused a high uncertainty in both reported rates (Driss & Bouhelassa 2013). Hence, this reaction was excluded in the proposed reaction mechanism scheme.

The hydrolysis of trichloramine was not incorporated in the unified model (Palin 1949). Saguinsin and Morris (Saguinsin & Morris 1975; Saunier 1976) first proposed this reaction and it was also included in the reaction scheme of Saunier, as shown in Equation (1).



Saguinsin & Morris (1975) used an empirical rate coefficient for this reaction. Another study was conducted for the decomposition of trichloramine through hydrolysis reaction along with Reaction 12 (i.e. reaction with

dichloramine). Kumar *et al.* (1987) investigated this reaction under pseudo first order conditions and reported the overall stoichiometry of trichloramine decomposition, as presented in Equation (2).



The study by Kumar and his research group considered the trichloramine hydrolysis to be the rate controlling reaction, since Reaction 12 is very rapid (Kumar *et al.* 1987). Various research papers have also reported that trichloramine hydrolysis is the main route through which trichloramine is decomposed (Driss & Bouhelassa 2013; Trogolo & Arey 2017). Accordingly, this reaction is deemed important to introduce to the reaction scheme of this study, referred to as Reaction 17 in Table 5, with a rate coefficient based on a pH value of 7.

### Monochloramine disproportionation

Monochloramine disproportionation, Reaction 5, is considered to be the major pathway through which dichloramine is formed when excess ammonia is available (Hand & Margerum 1983; Jafvert & Valentine 1987, 1992; Wooschlagler 2000). Before the development of the unified model, Granstrom studied Reaction 5 along with Reaction 2 (i.e. hydrolysis of monochloramine) and suggested the rate law to be as given by Equation (3) (Granstrom 1954).

$$\frac{d[\text{NHCl}_2]}{dt} = k_1[\text{NH}_2\text{Cl}] + k_2[\text{NHCl}]^2 \quad (3)$$

The first term in Equation (3) (i.e. first order rate) refers to monochloramine hydrolysis while the second term (i.e. second order rate) refers to monochloramine disproportionation (Nejjari *et al.* 2014). Jafvert later investigated the work presented by Granstrom and deduced that monochloramine hydrolysis is not fast enough to compete with monochloramine disproportionation, and hence the latter can be isolated and studied separately (Jafvert & Valentine 1987). The rate expression reported for monochloramine disproportionation in the unified

model was not used in this study as it was based on a catalyzed pathway (Jafvert & Valentine 1987). In a recent study, Trogolo & Arey (2017) explored the uncatalyzed pathway for this reaction and reported the rate coefficient to be  $5.6 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ . Reaction 6, the reverse of Reaction 5, was reported as insignificant for pH range from 7 to 9 in a sensitivity study presented in Huang's (2008) dissertation. Since this range of pH is conflicting with that considered for the model development in this study, this reaction is excluded from the developed model in this work.

### Redox reactions in the first zone

Weil and Morris were among the first researchers to propose Reactions 7 through 9 to be the episodes through which dichloramine decomposition occurs with NOH as the hypothesized intermediate (Weil & Morris 1949). The rate coefficients at 25°C were reported as  $k_7 = 1.12 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_8 = 2.46 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_9 = 2.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . Over a decade later, Jafvert & Valentine (1987) set up a computer code in FORTRAN to study the three reactions and re-estimate their rate constants. The estimated coefficients were:  $k_7 = 1.62 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_8 = 2.78 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_8/k_9 = 3.3$ . These values are believed to be of high certainty, as evident from the numerous studies that have confirmed and utilized them, including the unified model (Jafvert & Valentine 1987; Vikesland *et al.* 1998; Huang 2008; Luh & Mariñas 2014). Accordingly, these values are incorporated in this study.

### Redox reactions in the second zone

Reactions 12 to 14 are the main reactions occurring in the breakpoint region, where free chlorine starts to be available (Stenstrom & Tran 1984; Kim & Stenstrom 1997; Driss & Bouhelassa 2013; Soltermann *et al.* 2015). In Reaction 12, trichloramine reacts with dichloramine, especially when the concentration of the latter is more than that of free chlorine (Kumar *et al.* 1987; Soltermann *et al.* 2015). Kumar *et al.* (1987) studied this reaction under base catalytic conditions, using  $\text{HPO}_4^{2-}$ . However, Jafvert and Valentine re-studied this reaction assuming only  $\text{OH}^-$  catalysis and determined the rate coefficient empirically through data fitting (Jafvert

& Valentine 1992). Since the pathway of  $\text{HPO}_4^{2-}$  catalysis is not applicable in this study, the approach of the unified model will be embraced here.

Reaction 13 is similar to Reaction 12, in which an empirical rate coefficient was reported in the unified model,  $k_{13} = 1.39 \times 10^{-2} \text{ mM}^{-1} \text{ s}^{-1}$  (Jafvert & Valentine 1987). Reaction 14 is the only trail leading to the formation of nitrate in the unified model, since it did not account for chlorine reaction with nitrite. Jafvert reported the most updated rate expression, which was used in the unified model and other studies as well (Jafvert & Valentine 1987; Kim & Stenstrom 1997; Driss & Bouhelassa 2013; Trogolo & Arey 2017).

### Reactions with nitrite

Chlorine demand caused by nitrite-nitrogen was not part of the unified model reaction scheme. However, since wastewater effluent is typically an ammonia-nitrite system, the nitrite demand of chlorine should be revealed here. The main chlorine demand reactions are characterized by the nitrite demand of free chlorine and monochloramine, which are represented by Reactions 15 and 16 in Table 5, respectively (Hand & Margerum 1983).

### Other reactions

Leao was among the first researchers to postulate Reaction 10 in his predictive modeling of the combined chlorine region (Hand & Margerum 1983; Huang 2008). The reaction was not based on a solid mechanism, but rather to have a better fit of the experimental data. Huang deduced, via a sensitivity analysis, that the chlorine-ammonia system does not show any significance towards this reaction under any conditions (Huang 2008). Hence, this reaction was excluded from the reaction scheme of this work.

### Summary of the developed model

In this work, and to maintain consistency, all numbering references for the reactions will remain as per the unified model from Reactions 1 to 14. Excluded reactions will have rate coefficients set to zero, and reactions added to

the model will follow after Reaction 14. The reactions scheme and rate coefficients adopted in this study are summarized in Table 5.

## MATHEMATICAL MODELING

To simulate the reactive scheme adopted in this study, the chemical reactions shown in Table 5 have to be converted to a system of equations of continuity in the following form:

$$\frac{dc}{dt} = r$$

where  $c$  is the solute molar concentration,  $\frac{dc}{dt}$  is the rate of change of species  $c$ , and  $r$  is the reaction rate ( $r > 0$  for rate of formation;  $r < 0$  for rate of consumption). For simplicity, each participating species is given a specific notation as shown in Table 6.

Table 7 displays how each species is involved in each reaction.

Given the rate of reactions provided in Table 6, the set of continuity equations are shown in Table 8.

A MATLAB computer program was developed to calculate the concentration of the species with time and generate the breakpoint chlorination curves for a given contact time. The differential equations presented in

Table 6 | Notations used for the participating chemical species

Symbol	Chemical species
A	[HOCl]
B	[NO <sub>2</sub> ]
C	[NH <sub>3</sub> ]
D	[NH <sub>2</sub> Cl]
E	[NHCl <sub>2</sub> ]
F	[NOH]
G	[NO <sub>3</sub> ]
H	[NCl <sub>3</sub> ]
[ ]	Refers to the molar concentration of the concerned species

**Table 7** | Involvement of the chemical species in each reaction in the adopted model\*

Symbol		$r_1$	$r_2$	$r_3$	$r_4$	$r_5$	$r_6$	$r_7$	$r_8$	$r_9$	$r_{10}$	$r_{11}$	$r_{12}$	$r_{13}$	$r_{14}$	$r_{15}$	$r_{16}$	$r_{17}$
A	$HOCl$	-	+	-					+			-	+2	+	-2	-		+
B	$NO_2$															-	-	
C	$NH_3$	-	+			+												
D	$NH_2Cl$	+	-	-		-2				-				-			-	
E	$NHCl_2$			+		+		-	-						-			+
F	$NOH$							+	-	-								
G	$NO_3$														+	+	+	
H	$NCl_3$											+	-	-				-

\*Where: - means consumption of the species; + means production of the species; blank: means not involved in the reaction.

Table 8 were solved using the fourth order Runge-Kutta-Fehlberg algorithm. The choice of the algorithm was based on the foreseen stiffness of the system caused by the large discrepancies in the values of the rate constants of the reactions.

## RESULTS AND DISCUSSION

### Model validation

The predictive capability of any model may only be proven efficient if it can forecast experimental and field

data to a good extent (Stenstrom & Tran 1984; Chu *et al.* 2012; Gomez Camponovo *et al.* 2014; Ged *et al.* 2015). To examine the projection competency of the proposed model, its output is matched with experimental breakpoint curves reported in literature, and with chlorine residual data obtained from a sewage treatment plant in the region.

### Experimental breakpoint curves validation

Several breakpoint profiles are generated and validated against those reported by Chen & Jensen (2001). In his work, pure water samples were buffered with phosphate (0.1 M total phosphate) to maintain the pH value

**Table 8** | Set of differential equations of the developed model

$$\frac{dA}{dt} = -r_1 + r_2 - r_3 + r_8 - r_{11} + 2r_{12} + r_{13} - 2r_{14} - r_{15} + r_{17}$$

$$\frac{dB}{dt} = -r_{15} - r_{16}$$

$$\frac{dC}{dt} = -r_1 + r_2 + r_5$$

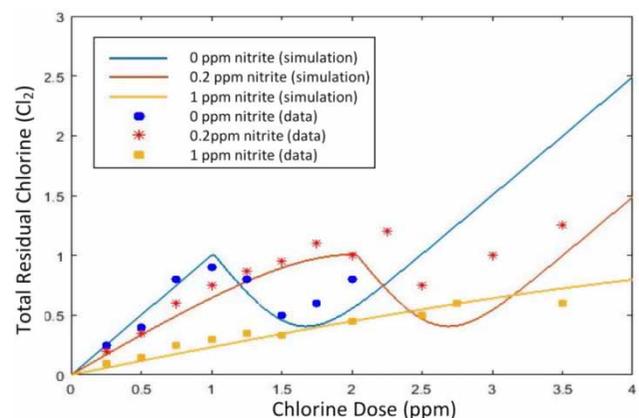
$$\frac{dD}{dt} = r_1 - r_2 - r_3 - 2r_5 - r_9 - r_{13} - r_{16}$$

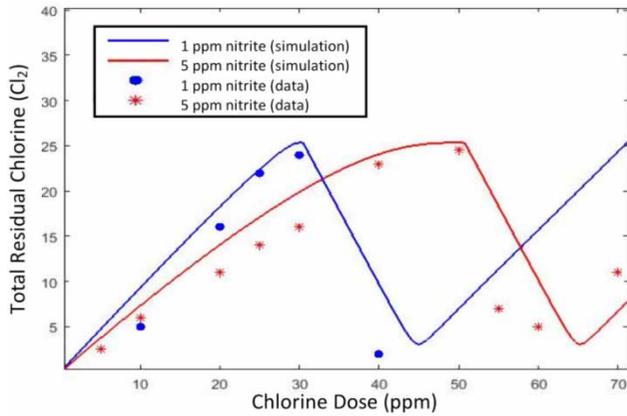
$$\frac{dE}{dt} = r_3 + r_5 - r_7 - r_8 - r_{11} - r_{12} - r_{14} + r_{17}$$

$$\frac{dF}{dt} = r_7 - r_8 - r_9$$

$$\frac{dG}{dt} = r_{14} + r_{15} + r_{16}$$

$$\frac{dH}{dt} = r_{11} - r_{12} - r_{13} - r_{17}$$

**Figure 1** | Experimental and simulated breakpoint curves for 1 ppm ammonia and 30 mins contact time (Chen & Jensen 2001).



**Figure 2** | Experimental and simulated breakpoint curves for 5 ppm ammonia and 30 mins contact time (Chen & Jensen 2001).

at 7. The samples were spiked with ammonia and nitrite, and chlorinated with sodium hypochlorite, allowing different contact periods. The chlorination process was performed in a dark environment, and amperometric titration was used to measure the chlorine residuals, complying with the standard methods (Hunter *et al.* 1998; Chen & Jensen 2001). The breakpoint curves are presented in Figures 1 and 2.

The solid lines shown in Figures 1 and 2 represent predictions using the model proposed in this work. It can be said that the model is able to depict the experimental breakpoint curve to a good extent.

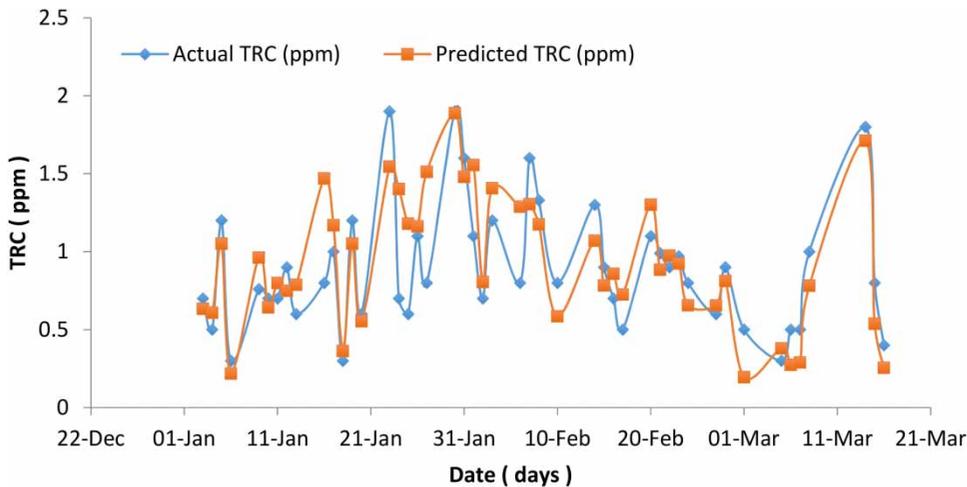
### Validation against field data

The model was also tested for predicting total residual chlorine (TRC) in a wastewater treatment plant. Field data were collected from a sewage treatment plant in the United Arab Emirates (UAE). Ammonia, nitrite, chlorine dose, and TRC data were collected over a period of three months, from 1st January until 1st April 2016. Figure 3 shows the TRC values as predicted by the model and as measured by the plant. The correlation coefficient,  $r$ , between the predicted and the actual data is found to be  $r > 0.88$ , which indicates that the model can predict the plant data fairly well.

The above mentioned results (Figures 1–3) demonstrate that the model used in this work with the proposed reactions scheme can provide a good estimate of the breakthrough points.

### CONCLUSIONS

The developed model has shown excellent agreement with both experimental work reported in literature and plant data. The model accounts for the effect of nitrite in chlorine-ammonia systems. It incorporates updated rate coefficients wherever applicable. The model requires minimal inputs and is introduced in a user-friendly interface.



**Figure 3** | Actual and predicted total residual chlorine (TRC).

Achieving satisfactory outputs with the minimal feeding inputs makes the model deployment very appealing for practical implementation, especially in plants where ill-defined systems exist.

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