Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1023850

57 (2016) 8696–8704
April

Taylor & Francis
Taylor & Francis Group

Development and validation of a simulation model to determine the reaction rate constant of chlorine disinfection process at a wastewater treatment plant

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Received 7 July 2014; Accepted 22 February 2015

ABSTRACT

Chlorine disinfection of wastewater was investigated to determine the reaction rate constant of the disinfection process at the Kanapaha Water Reclamation Facility in Gainesville, FL. Chlorine reactions with wastewater occurred in the contact basin, and they could be characterized by partial differential equations (PDEs). In addition to the difficulties of the solution of these PDEs, the determination of the reaction rate constant of chlorine disinfection is also difficult because of complex reactions with ammonia and the dynamic behavior of wastewater. These vary depending on the influent ammonia concentration, chlorine dosage, and wastewater content and flow rate. A method of characteristics and an odometric transformation technique were applied to these equations to more easily obtain a solution. The method of characteristics is a mathematical solution technique that transforms a PDE into an ordinary differential equation (ODE). Because the disinfection reaction also has a large and variable time delay, the odometric transformation technique was introduced to eliminate this obstacle. The application of these mathematical solution and transformation techniques converted the dynamics of the system into a constant time-delay model and a set of ODEs. To validate the model and determine the reaction rate constant by simulation, the resulting equations were coded in Matlab and solved numerically. The validation was performed by a comparison of the simulated response of the developed model with the experimental data using Matlab software packages. The validation criterion was the obtainment of the highest fit (%) for the simulated result. The simulation results revealed that the fit (%) was the highest when the reaction rate constant was 0.0074 h^{-1}.

Keywords: Chlorine disinfection; Reaction kinetics; Modeling and simulation; Model validation; Parameter estimation; Wastewater treatment

1. Introduction

Chlorination is the most widely applied disinfection process for the inactivation of pathogenic micro-organisms in water and wastewater treatment plants. In this process, most of the micro-organisms remaining from the previous part of the treatment plant are killed before the water is discharged. The effectiveness of chlorine in wastewater depends on the chlorine demand of the water, the length of time that chlorine is in contact with the pathogens, the water quality, the exposure of water to sunlight, and the temperature and pH of the water. In comparison with other

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disinfection methods, such as ozone and UV, chlorine use has many advantages, such as its low cost, well-known technological effects for many water problems (bacteria, metal ions, etc.), applicability to a large volume of water, and residual bactericidal effect [1–3]. Although it has more advantages than other disinfectants, the main drawback of the use of more chlorine is that the reaction of chlorine with natural organic matters causes the generation of toxic, mutagenic, and carcinogenic disinfection by-products (DBPs), and haloacetic acids (HAAs), which are dangerous for humans and the environment [4–7]. The formation of these DBPs and HAAs is related to chlorination and is an unintentional result of wastewater treatment. More than 600 DBPs have been reported as a result of using chlorine, including chloramines and chlorine dioxide [8]. A drawback of the use of less chlorine is that it does not have a sufficient residual bactericidal effect after the disinfection process and does not provide residual chlorine throughout the distribution system [9]. Moreover, the pathogenic micro-organisms present in wastewaters cannot be totally inactivated in the use of less chlorine. Because of these drawbacks, treatment plants that use a chlorination basin are required to have a specified effluent concentration of chlorine to guarantee a minimum level of disinfection.

Another important concern related to chlorine disinfection at a wastewater treatment plant is the large and variable time delay or time constant that is due to the long duration of disinfection, the variable flow rate, and slow disturbances such as variations in sunlight intensity and temperature. This varies, depending on the wastewater flow rates, and it can change from 1 to 2 or 3 h. This significantly affects the dynamics of the chlorine disinfection systems of the plant [10,11].

To characterize chlorine disinfection in terms of the reaction kinetics, many studies have been performed in the past for water and wastewater treatment plants. Because wastewater includes large amounts of ammonia-nitrogen compounds, researchers have developed kinetic equations based on the reaction between ammonia-nitrogen compounds and chlorine [12–15]. Ammonia-nitrogen compounds are usually present in wastewater in the form of ammonia gas (NH_3), ammonium ions (NH_4^+), or nitrogen-containing organic compounds [16,17]. When an aqueous solution of chlorine comes into contact with any of these species, chloramines are produced. This reaction occurs by chlorine transfer from HOCl to the nitrogen amine species [18]. As long as chlorine is added, all amine nitrogen species will react with chlorine, and their hydrogen atoms will be replaced by chlorine. Nitrogen gas will eventually be released. Further addition of chlorine results in free chlorine residuals. Reactions of free chlorine with ammonia based on the breakpoint chlorination by Morris and Isaac [12] are summarized in Table 1 with the forward and reverse reaction rate constants [12,13,19].

Although many studies on the kinetics of chlorine reactions with ammonia have been performed by many researchers, only a few have involved the determination of the reaction rate constant between chlorine and wastewater in the disinfection process. To investigate the disinfection process for wastewater, researchers have studied the kinetics of the aqueous chlorination of certain pharmaceuticals and their elimination from water matrices (reservoir water, groundwater, and secondary effluents from two municipal wastewater treatment plants) [20]; the kinetics of inactivation for the disinfection effectiveness of three organic N-chloramines on the bacteria *Escherichia coli* under various pH conditions [18]; and modeling and parameter estimation for optimal chlorination [21]. Other researchers have investigated the reactivity of organic contaminants and amines with free chlorine in terms of the kinetics for wastewater [22,23], the chlorination kinetics of ametryn over a wide range of pH conditions and a calculation of the rate constants in chlorination reactions [24], and the chlorination kinetics of chlortoluron and the determination of the rate constants for each of the elementary reactions [25]. Cai et al. [26] have studied the reaction kinetics and transformation of antipyrine chlorination with free chlorine and determined several rate constants for water. Chusaksri et al. [27] have studied the mechanism of the reaction of chlorine with phenylurea compounds and determined the role of the substituents on the reactivity of the compounds in terms of the reaction

Table 1
Summary of the reaction kinetics of chlorine with ammonia [12,13,19].

Reaction	Forward-rate constant	Reverse-rate constant
$NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O$	$6.6 \times 10^8 \exp\left(-\frac{1{,}510}{T}\right)$	$1.38 \times 10^8 \exp\left(-\frac{8{,}800}{T}\right)$
$NH_2Cl + HOCl \leftrightarrow NHCl_2 + H_2O$	$3 \times 10^5 \exp\left(-\frac{2{,}010}{T}\right)$	7.6×10^{-7} (L mol^{-1} s^{-1})
$NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O$	$2 \times 10^5 \exp\left(-\frac{3{,}420}{T}\right)$	$5.1 \times 10^3 \exp\left(-\frac{5{,}530}{T}\right)$
$2NH_2Cl \leftrightarrow NHCl_2 + NH_3$	$80 \exp\left(-\frac{2{,}160}{T}\right)$	24.0 (L mol^{-1} s^{-1})

kinetics. Similarly, the reaction kinetics of the disinfection process using aqueous chlorination has been studied to determine the kinetic parameters or the reaction mechanisms for water and wastewater [28–43]. However, no reaction rate constants are available for the entire disinfection process of a wastewater treatment plant. Because of the significance of disinfection using chlorine and the limited information on the reaction kinetics for the entire disinfection process of a wastewater treatment plant, it is the focus of this study.

The Kanapaha Water Reclamation Facility (KWRF) is an advanced wastewater treatment plant in Gainesville, FL and uses chlorine for disinfection [11,44]. The wastewater is treated at the plant to the standards for drinking water, and most of the water effluent is used for irrigation, reuse, and injection into groundwater. It has a current allowable capacity of 14.9 million gallons per day. The disinfection process is performed in two chlorine contact basins that are open to the atmosphere [45].

The kinetics of the disinfection mechanism at the KWRF was developed for a water stream containing ammonia and micro-organisms. In addition, a plug-flow reactor model is presented to describe the dynamics of the disinfection portion of the plant. In modeling the reaction of chlorine with wastewater using kinetics, several difficulties arose. These difficulties stemmed from a set of partial differential equations (PDEs), which were obtained from kinetic models in the time domain. A solution of the PDEs of the plug-flow model was pursued using the well-known "method of characteristics," which yielded an equivalent set of ordinary differential equations (ODEs). The odometric transformation technique was applied to the concentration field to eliminate the large and variable time-constant obstacle [11]. Following the implementation of the techniques yielded an equivalent set of ODEs with constant time delay and hence made the solution much easier.

The purpose, and novelty, of this study is to develop and validate a model for the entire chlorine disinfection process at the KWRF, as well as determine the reaction rate constant numerically using the method of characteristics and odometric transformation by overcoming the large and variable time constant and PDEs of chlorine reactions with wastewater.

2. Materials and methods

2.1. Wastewater sampling and characterization

The KWRF chlorine dosage and flow rates were used in this study. A schematic representation of the disinfection process at the KWRF is shown in Fig. 1. The sampling points for the free chlorine residual concentrations are the chlorine injection point at the post-aeration basin, the north probe at the north chlorine contact basin, and the final probe at the effluent of the wastewater. The treated wastewater is first filtered before entering the contact basin for disinfection. Chlorine gas is added into the pipe, and this pipe transfers the wastewater from the post-aeration basin to the north chlorine contact basin. The flow of wastewater is split immediately into two parallel streams after it enters the contact basin in the north basin. The influent pH does not change significantly from a neutral pH, and it was approximately 7. The total suspended solid concentration was measured using EPA method 160.2 in the effluent wastewater sample. The water parameters determined in the field were pH, water temperature, conductivity, and dissolved oxygen. The results are given in Table 2.

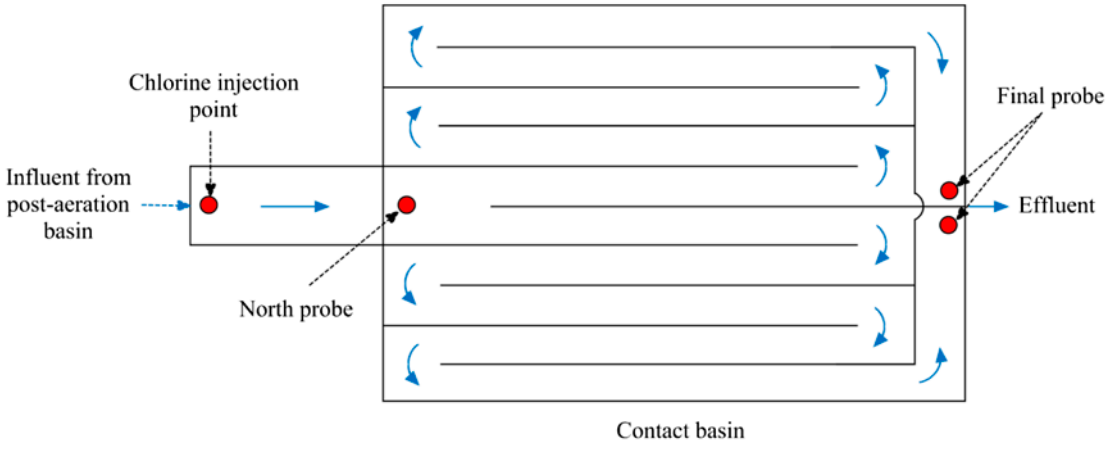

Fig. 1. Sampling points for the chlorine disinfection contact basin at the KWRF.

Table 2
Water parameters of the KWRF at the chlorine contact basin

Water parameters	
pH	≈7
Water temperature (°C)	≈27
Conductivity (μmhos cm^{-1})	≈500
Dissolved oxygen O_2 (mg L^{-1})	≈3.5
Average total suspended solids (mg L^{-1})	0.367
Average total chlorine residual in the effluent (mg L^{-1})	2.8

To determine the ammonia concentration in the influent, undisinfected wastewater samples were collected slightly in front of the north basin (at the north probe). After the samples were carefully collected, they were immediately transferred to the laboratory in the KWRF, and the ammonia concentrations were measured with a Hach DR 2000 VIS Spectrophotometer. Compatible Hach test kits were used with a wavelength range of 340–900 nm.

The chlorine measurements were performed online at the chlorine injection point, at the north probe and at the final probe. A step change was made at the chlorine injection point, and its effect was observed along the entire reactor. All measured data were recorded and used for the simulation.

2.2. Reaction kinetics of the disinfection process

The kinetic study of free chlorine with ammonia reported by Morris and Isaac [12] showed the experimental conditions for the determination of the reaction rate constant. The proposed reaction rate expressions of free chlorine with ammonia and micro-organisms at the wastewater treatment plant include the following:

$$r_{HOCL} = -k_1[NH_3][HOCl] + k_2[NH_2Cl] - k_3[NH_2Cl][HOCl] + k_4[NHCl_2] - k_5[NHCl_2][HOCl] + k_6[NCl_3] - k_{Disinfection}\,[HOCl] \quad (1)$$

$$r_{NH_3} = -k_1[NH_3][HOCl] + k_2[NH_2Cl] + k_7[NH_2Cl]^2 - k_8[NHCl_2][NH_3] \quad (2)$$

$$r_{NH_2CI} = k_1[NH_3][HOCl] - k_2[NH_2Cl] - k_3[NH_2Cl][HOCl] + k_4[NHCl_2] - k_7[NH_2Cl]^2 + k_8[NHCl_2][NH_3] \quad (3)$$

$$r_{NHCl_2} = k_3[NH_2Cl][HOCl] - k_4[NHCl_2] - k_5[NHCl_2][HOCl] + k_6[NCl_3] + k_7[NH_2Cl]^2 - k_8[NHCl_2][NH_3] \quad (4)$$

$$r_{NCl_3} = k_5[NHCl_2][HOCl] - k_6[NCl_3] \quad (5)$$

The reaction rates in these expressions are in units of L mol^{-1} s^{-1}, the concentrations of the species are in mol L^{-1}, and the water temperature is room temperature. The kinetic rate constants of these reactions are k_1, k_2 … , k_8. The term $k_{Disinfection}$ [HOCl] represents the chlorine consumed during disinfection. This process was viewed as a pseudo-first-order reaction, and $k_{Disinfection}$ as the rate constant for the entire disinfection process in the contact basin [11].

2.3. Model transformation techniques

2.3.1. Method of characteristics

The method of characteristics is a method that can be used to solve PDEs by reducing them to a set of ODEs [11,46–48]. The goal of the method is to change coordinates from (x, y) to a new coordinate system, in which the PDE becomes an ODE along certain curves in the x–y plane. To apply this method to a PDE, the independent variable should be transformed to a new variable. The method can be explained using the general expression of a PDE as follows:

$$P\frac{\partial z}{\partial x} + Q\frac{\partial z}{\partial y} = R(x, y) \quad (6)$$

where P and Q are constants and R can be a function of x and y. P and Q define a characteristic line, and the angle between this line and the x-axis is expressed as follows:

$$\theta = \tan^{-1}\left(\frac{Q}{P}\right) \quad (7)$$

The following transformations are introduced:

$$x = r + s \cdot \cos(\theta) \quad (8)$$

$$y = s \cdot \sin(\theta) \quad (9)$$

where r and s are variables that are geometrically interpreted in Fig. 2.

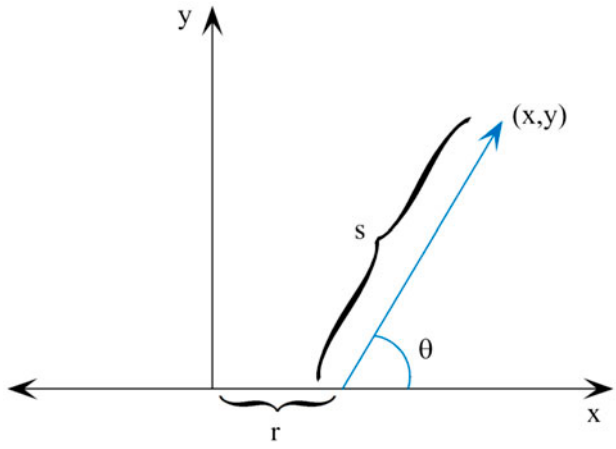

Fig. 2. Geometric interpretation of the method of characteristics.

Substituting Eqs. (8) and (9) into Eq. (6) and integrating along the characteristic line to solve the PDE yields the following:

$$z(x,y) = z(x - y\cot(\theta)) + \int_0^{y\,\mathrm{cosec}(\theta)} R(x - y\cot(\theta) + s'\cos(\theta), s'\sin(\theta))\frac{\mathrm{d}s'}{\sqrt{P^2+Q^2}} \quad (10)$$

This equation is now transformed into an ODE by taking the derivative relative to the variables. The result represents a system of ODEs along their corresponding characteristics.

2.3.2. Odometric variable (β)

This transformation was first introduced by Harmon et al. [49] and Svoronos and Lyberatos [50]. They claimed that "variability in the effective time constant can be considerably reduced if one considers, instead of time, the cumulative amount of a quantity generated, consumed, or fed as the independent dynamic model variable" [49]. Thus, the cumulative distance travelled by wastewater in the contact basin was defined as a new variable (β) and called the odometric transformation. This new variable replaces time with (β). The mathematical representation of this transformation is as follows:

$$\frac{\partial\beta}{\partial t} = v(t) \quad (11)$$

$$\beta = \int_0^t v(t)\mathrm{d}t \quad (12)$$

The advantage of (β) is that it obtains a constant delay equal to the length of the contact basin and time-independent model equations.

2.4. Application of the transformation techniques to solve the kinetic models of disinfection

Chlorine disinfection reactions occur in the contact basins of the plant, and the contact basins are called the reactors. The reactors are assumed to be plug-flow reactors with constant cross-sectional areas. The other assumption is that no diffusion exists in the direction of the flow. The model for the disinfection reactor is based on a material balance. These assumptions result in the following first-order PDE for six species that appear during chlorine disinfection in a plug-flow reactor [11]:

$$\frac{\partial c_i}{\partial t} = -v(t)\frac{\partial c_i}{\partial z} + r_i(\underline{c}(t,z)) \quad (13)$$

where

$i = 1, 2, \ldots, 6$, c_i is the concentration of species i, c is a vector, the components of which are the compositions (c_i), z is the location along the length of the reactor, v is the linear flow velocity, and, t is the time variable.

The solution of these dynamic models are difficult because of the variability of the influent, the complexity of chlorine reactions with ammonia and microorganisms, and the large and variable time delays. The time delays are approximately 2 h depending on the wastewater flow rates of the KWRF. They significantly reduce the effluent quality and affect the dynamics of the chlorine disinfection systems of the plant. To overcome their unfavorable effects, Demir and Woo [11] applied the odometric transformation to the concentration field by substituting Eq. (11) into Eq. (13), and they transformed the dynamics of the system into a constant time-delay model. The resulting equation is as follows:

$$\frac{\partial c_i}{\partial \beta} = -\frac{\partial c_i}{\partial z} + \frac{1}{v(\beta)} r_i(\underline{c}(\beta,z)) \quad (14)$$

The method of characteristics is very well suited for the numerical solutions of PDEs that occur when modeling chlorine disinfection reactions in the contact basin as shown in Eq. (14). The method reduces them from PDEs to ODEs. These are first-order PDEs with constant delay and are independent of time. Furthermore, the coefficients of $\partial c_i/\partial\beta$ and $\partial c_i/\partial z$ are

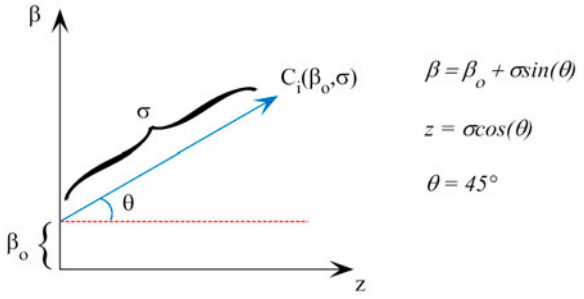

Fig. 3. Graphical representation of the odometric transformation.

constants equal to 1. Applying the method of characteristics, as shown in Fig. 3, gives first-order ODEs. The resultant ODE equations are as follows:

$$\frac{\partial c_i\left(\beta_\circ + \frac{\sigma}{\sqrt{2}}, \frac{\sigma}{\sqrt{2}}\right)}{\partial \sigma} = \frac{1}{\sqrt{2}} \frac{1}{v\left(\beta_\circ + \frac{\sigma}{\sqrt{2}}\right)} r_i\left(\underline{c}\left(\beta_\circ + \frac{\sigma}{\sqrt{2}}, \frac{\sigma}{\sqrt{2}}\right)\right) \tag{15}$$

where

β is the odometric transformation variable (cumulative distance travelled by water), (m), β_o is the constant, and σ is the variable.

Use of the method of characteristics and the odometric transformation produced efficient ODE equations for numerical integration.

3. Results and discussion

3.1. Simulation of the model

To find the reaction rate constant of the chlorine disinfection process, measurements of ammonia nitrogen were performed first. After collecting samples at the north probe, the concentrations of ammonia nitrogen were immediately measured using a Hach DR 2000 VIS Spectrophotometer at the laboratory in the KWRF. However, the measurements showed that there was no ammonia in the water at the north basin. This is probably due to the fast reactions of chlorine with ammonia nitrogen compared to those with micro-organisms. A large amount of chlorine added at the beginning of the chlorine contact basin or at the chlorine injection point immediately reacts with ammonia-nitrogen in the water due to the ammonia-nitrogen–chlorine demand, leaving the rest for disinfection with micro-organisms. The ammonia-nitrogen–chlorine demand can also vary with loading of the wastewater plant, and it fluctuates with the daily usage cycle. Therefore, to eliminate chemical reactions with ammonia, we assumed that the disinfection reaction is a pseudo-first-order reaction between chlorine and micro-organisms at all points located between the north and the final probe, namely the ammonia-free part of the disinfection process.

The chlorine concentrations measured online at the chlorine injection point, at the north probe, and at the final probe were used for the simulation. A step change in the chlorine dosing was performed at the chlorine injection point, and its effect was observed along the entire contact basin. All measured data were recorded for each sampling point for use in the simulation studies.

In order to solve the model numerically, Eq. (15) was coded in the Matlab programing language. The simulation program was run using the north probe chlorine concentration measurements to estimate the final probe chlorine concentrations.

3.2. Comparison of the simulation response with the experimental measurements

The simulated and experimental results are shown in Fig. 4. The figure shows the measured chlorine concentration at the north probe (blue-dashed line), at the final probe (cyan solid line), and the simulated results (black circles). Since the reaction rate constant was not exactly identified, an exact numerical match between the simulated response of the model and the experimental measurements was not observed (Table 3).

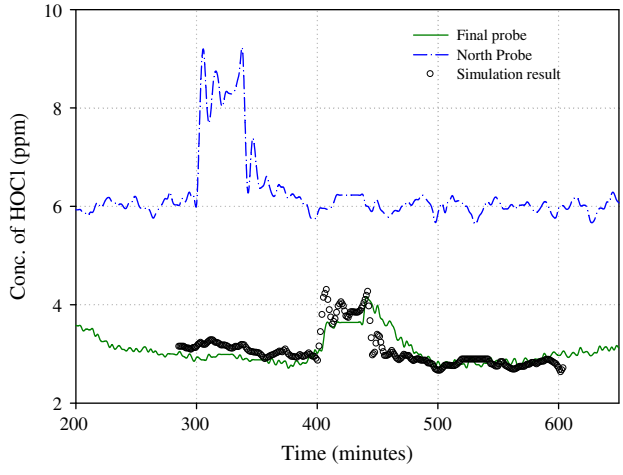

Fig. 4. Comparison of the simulation results with experimental measurements for $k_{Disinfection}$ = 0.0074 h^{-1}.

3.3. Model validation

In order to validate the model and determine the reaction rate constant more precisely, the validation of the model was performed by the comparison of the simulated responses of the model with the measurements of chlorine concentration at the final probe using the Matlab software packages. To fit the simulation results to the experimental data, various trial values of $k_{Disinfection}$ were used in the simulation model changing from 0.006 to 0.0085 h^{-1}. Comparison of the simulation results with the experimental data and the corresponding fit (%) values are shown in Figs. 5–7. The results suggest that the value of $k_{Disinfection}$ = 0.0074 h^{-1} yields the highest fit (%) and are in agreement with the experimental data shown in Fig. 6.

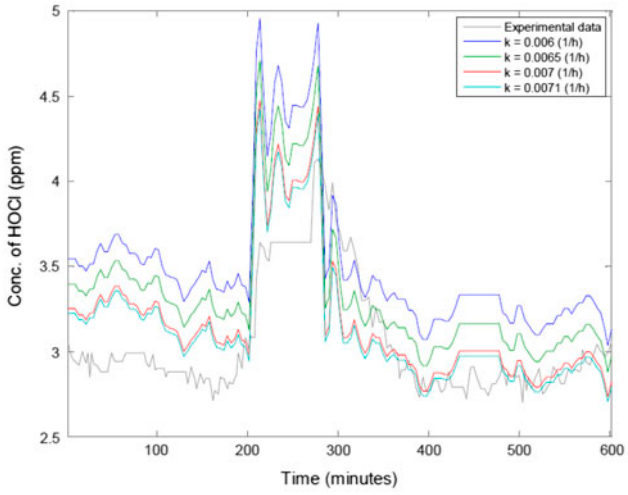

Fig. 5. Comparison of the simulated response of the model with the experimental measurements. $k_{Disinfection}$ = 0.006 h^{-1}, $k_{Disinfection}$ = 0.0065 h^{-1}, $k_{Disinfection}$ = 0.007 h^{-1}, $k_{Disinfection}$ = 0.0071 h^{-1}.

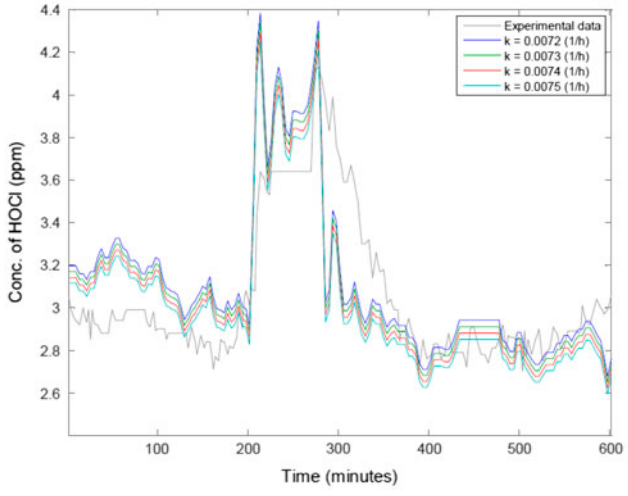

Fig. 6. Comparison of the simulated response of the model with the experimental measurements. $k_{Disinfection}$ = 0.0072 h^{-1}, $k_{Disinfection}$ = 0.0073 h^{-1}, $k_{Disinfection}$ = 0.0074 h^{-1}, $k_{Disinfection}$ = 0.0075 h^{-1}.

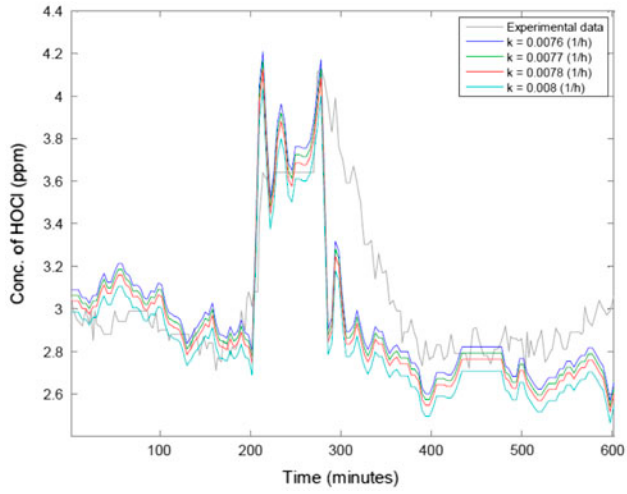

Fig. 7. Comparison of the simulated response of the model with the experimental measurements. $k_{Disinfection}$ = 0.0076 h^{-1}, $k_{Disinfection}$ = 0.0077 h^{-1}, $k_{Disinfection}$ = 0.0078 h^{-1}, $k_{Disinfection}$ = 0.008 h^{-1}.

Table 3
Validation of the simulation results for the various reaction rate constants

Reaction rate constant, $k_{Disinfection}$	Fit (%)
6×10^{-3} h^{-1}	−56.5
6.5×10^{-3} h^{-1}	−14.68
7×10^{-3} h^{-1}	15.46
7.1×10^{-3} h^{-1}	19.25
7.2×10^{-3} h^{-1}	22.06
7.3×10^{-3} h^{-1}	23.83
7.4×10^{-3} h^{-1}	24.52
7.5×10^{-3} h^{-1}	24.13
7.6×10^{-3} h^{-1}	22.7
7.7×10^{-3} h^{-1}	20.33
7.8×10^{-3} h^{-1}	17.12
8×10^{-3} h^{-1}	8.665

4. Conclusions

This study was conducted to evaluate the reaction rate constant of the disinfection process between chlorine and micro-organisms at KWRF by applying

the method of characteristics and the odometric transformation technique to the concentration field. Application of these two techniques transformed the dynamics of the system into the ODE model with constant time delay and made the solution of the resulting equations numerically feasible. The numerical solutions of the resulting equations were validated using Matlab software packages for different trial values of $k_{\text{Disinfection}}$.

According to the simulation result obtained for the $k_{\text{Disinfection}} = 0.0074\ h^{-1}$, the validation of the model provided the highest fit (%) value, and it was confirmed by the experimental data. Furthermore, it showed that a first-order kinetic model is able to describe chlorine consumption by micro-organisms in the ammonia-free part of the contact basin.

Acknowledgments

This work was supported at the University of Florida by a fellowship from the Minister of National Education of the Turkish Government. The author acknowledges this support. The author would also like to acknowledge the Kanapaha Water Reclamation Facility and the University of Florida Wastewater Treatment Plant personnel for their help.

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