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# Evaluation of second order and parallel second order approaches to model temperature variation in chlorine decay modelling

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## ABSTRACT

All drinking water receives some form of disinfection and a minimum residual should remain at the customer's tap. Most popular disinfectant of all is chlorine. Chlorine reacts with compounds in water and hence leads to decay. Temperature is one of the important factors that control the rate of decay. Annual water temperature variations of more than 20°C are common in distribution systems, so that dosing needs to be adjusted substantially between seasons to maintain residuals within desired limits. Arrhenius equation has been successfully used to estimate the temperature effects on chlorine decay reactions, especially when temperature is below 30°C. The temperature dependence parameter estimated is activation energy ($E$)/universal gas constant ($R$). A number of chlorine decay tests were conducted, by varying temperature from 15–50°C. Resulting chlorine measurements were input into AQUASIM, data fitting was performed using the parallel second order model (PSOM) proposed by Kastl et al. [1] and second order model (SOM) proposed by Clark [2]. The model parameters for all modelling approaches were estimated using AQUASIM. PSOM has two reactants and two respective decay coefficients. Results showed that PSOM fitted the data very well when either single or two $E/R$s were used. On the contrary, the SOM did not show a good fit to the experimental chlorine decay profile for the same data sets. The results, therefore, indicated PSOM is more convenient to describe chlorine decay profile over a wide range of temperature.

*Keywords*: Disinfection; Chlorine decay; Second order model (SOM); Parallel second order model (PSOM); Temperature; Parameter estimation

## 1. Introduction

Drinking water supplies are disinfected primarily to inactivate micro-organisms that are harmful to human health, before water reaches any consumer [3]. Chlorine has been widely employed as a disinfectant in the treatment of water supplies for more than one hundred years, due to its low cost and high efficacy. Chlorine, as a non-selective oxidant, reacts with both organic and inorganic chemical species in water; therefore it functions as a highly effective antimicrobial agent to reduce the risk of water-born and infectious disease.

Typically, disinfectant, here chlorine, is applied in the clearwell as the final stage of treatment. This stage must achieve an adequate inactivation of microorganisms before the treated water reaches the first customer (primary disinfection), and be large enough to ensure an adequate residual at the periphery of the distribution system to inhibit microbial regrowth (secondary disinfection) [4]. As a result, and according to water quality regulations, it is essential to have a minimum chlorine residual over the whole distribution system and at all

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times. However, while reacting with different species, depending on the quality of water, the type of treatment processes and the condition of distribution system, chlorine decay behaviour significantly varies. Thus the chlorine demand, the retention time, its required set point and initial dosing vary from one water source to another and also over different water networks. On the other hand, the reaction between chlorine and natural organic matters (NOMs) contributes to production of disinfection by-products (DBPs) which has been identified as potentially carcinogenic, mutagenic or toxic substances. The latter, along with the need to limit the maximum chlorine concentration below certain level for aesthetic reasons, force operators to optimise the treatment/chlorine dosing. In addition, as temperature has been proved to have a significant effect on chlorine decay behaviour, any change in this parameter should also be considered. Consequently, the important role of having a robust mathematical modelling approach to address all above-mentioned inter-twinned issues, regarding chlorination, for both planning and management applications is being broadly emphasized [3].

### 1.1. First order model (FOM)

Traditionally, chlorine decay in bulk waters used to be modelled by first order kinetic:

$$\frac{d\mathrm{Cl}}{dt} = -k \cdot \mathrm{Cl} \tag{1}$$

where Cl is chlorine concentration [mg/L] and $k$ is the decay constant [$\mathrm{h}^{-1}$].

Despite the simplicity and easiness of this model, it has not presented a good data fitting in different applications. Initially, several attempts were made to compensate the defects of the simple first order model (FOM) ignoring the role of other important influencing factors on chlorine decay especially reactant species. These include:

- Power-law decay model ($n$th order)
- First-order decay with stable components
- Power-law decay with stable components (nth order)
- Parallel first-order decay model

A minor empirical improvement upon this situation was extended to the models by including some affecting factors such as initial chlorine concentration, dissolved organic carbon (DOC), pH and temperature.

### 1.2. Second order model (SOM)

Considering the effect of reactants, Clark [2] introduced a two-component second order chlorine decay model which is based on the concept of reaction between chlorine and another notional substance on the assumption that the balanced reaction equation can be represented by:

$$aA + bB \rightarrow pP \tag{2}$$

where $A$ and $B$ are reacting substances; $A$ could be representative for chlorine and $B$ would be a summation of all individual organic and inorganic species which potentially react with chlorine. $P$ is an overall representative for the product of the reaction.

An analytical solution for the second order model has been proposed by Clark [3]. The proposed solution was the first prosperous trial for a second-order model:

$$C_A = \frac{K}{1 - \mathrm{R}e^{-ut}} \tag{3}$$

where $C_A$ is the initial chlorine concentration and $K$, $R$ and $u$ are constant parameters to be estimated.

Because chlorine reacts with variety of organic and inorganic compounds with different complicated mechanisms and stoichiometry, having a and b as stoichiometric parameters, to be estimated, is not appropriate [3]. The Clark's equation can be written as follows if the simple stoichiometry of the chlorine reaction is assumed:

$$\mathrm{Cl}_2 + RA \xrightarrow{k} \text{inert product} \tag{4}$$

$$C_{\mathrm{Cl}}(t) = \frac{\mathrm{Cl}_0 - RA_0}{1 - \frac{RA_0}{\mathrm{Cl}_0} \cdot e^{-(\mathrm{Cl}_0 - RA_0)\cdot k \cdot t}} \tag{5}$$

where $\mathrm{Cl}_0$ and $RA_0$ are initial concentrations of chlorine and notional reactant, respectively, and $k$ is the rate coefficient.

One disadvantage for the second order model is that it considers only one individual species to react with chlorine. This is very important since in most cases at least two different reactions with chlorine, the initial fast and later slower one, have been reported. Analysing single chlorine decay curves, Jabari Kohpaei et al. [6] made two important conclusions regarding SOM's ability to predict chlorine residuals. First, they showed that SOM overly predicted residuals in the lower end of chlorine decay curve, implying false sense of security in achieving secondary disinfection goals. Secondly, they noted that when higher initial dose was practiced, chlorine residual prediction was poorer.

### 1.3. Parallel second order model (PSOM)

Probably one of the best two-constituent chlorine decay models introduced so far is the one proposed by Kastl et al. [1]. Their model was expressed as a new "parallel reactant" scheme assuming two notional constituents — fast and slow reducing agents — to react with chlorine. This parallel second order decay model (PSOM) consists of two simultaneous parallel reactions with an overall second order kinetics as follows:

$$\mathrm{Cl}_2 + \mathrm{FRA} \rightarrow \mathrm{Cl}^- + \text{inert product} \tag{6}$$

$$Cl_2 + CRA \rightarrow Cl^{-} + \text{inert product} \tag{7}$$

where FRA stands for the fast reacting reducing agents and SRA represents the slow reacting reducing agents in the water.

The second order reaction rates for different reactants in this model could be given as follows:

$$\frac{d\text{FRA}}{dt} = -k_{\text{FRA}} \cdot \text{Cl} \cdot \text{FRA} \tag{8}$$

$$\frac{d\text{SRA}}{dt} = -k_{\text{SRA}} \cdot \text{Cl} \cdot \text{SRA} \tag{9}$$

where FRA and SRA are the concentration of fast and slow reacting agents and $k_{\text{FRA}}$ and $k_{\text{SRA}}$ are their reaction rate constants respectively.

$$\frac{d\text{Cl}}{dt} = \frac{d\text{FRA}}{dt} + \frac{d\text{SRA}}{dt} \tag{10}$$

where Cl is free chlorine concentration.

The robustness of the model is more understood when its way of characterising different chlorine reacting agents, FRA and SRA, is given more attention. Additionally, the model does not suffer from the same theoretical imperfection that exists in the parallel first order modelling methods in which chlorine is divided into two fractions while reacting with compounds in NOM. However, like every mathematical model, when there is certain number of parameters to be estimated, uncertainty may arise as to the parameter values or more than one value for a single parameter may satisfy a given set of data. This should be minimised by increasing the number of experiments and data sets.

Jabari Kohpaei et al. [6] evaluated the efficacy of the parallel second order model (PSOM) against the most popular models including FOM and SOM. They concluded that PSOM is the most accurate modelling methods among the mentioned chlorine decay models.

### 1.4. Temperature effect

Depending on the climate of the network region as well as the type of water storage and distribution system (either over or underground) and the material used for that purpose, water temperature could vary over the year. For several years, Arrhenius equation has been proposed as the best method to describe the way in which temperature alterations affect the chlorine decay. Fisher and Kastl [5] preferred to use a relative form of Arrhenius equation to keep the temperature relationship independent of any other variables. They assumed the temperature dependence relationship to be described by a single value of activation energy in this relative form of Arrhenius equation:

$$k_T = k_{T_0} \cdot \exp\left( \frac{-\frac{E}{R} \cdot (T_0 - T)}{(273 + T_0)(273 + T)} \right) \tag{11}$$

where $k_T$ and $k_{T0}$ are the reaction constants at temperatures $T$ and $T_0$ [°C] respectively. $E/R$ is the ratio of activation energy to the universal gas constant [K], which expresses the sensitivity of all reactions to the temperature.

The objective of this research is to investigate and to compare the temperature effect on chlorine decay at normal and high temperatures. For this purpose, after conducting all necessary laboratory experiments for the nominated water sample, obtained data was analysed with the presented parallel second order model (PSOM). The results, afterwards, were compared to the ones analysed with the second order model (SOM).

## 2. Material and methods

### 2.1. Water samples and analytical methods

Water samples taken from Pilbara Water Treatment Plant influent, labelled as "Pilbara Raw Water", were used for the tests. Prepared chlorine-demand-free HDPE bottles were used to store the water samples. Table 1 presents the water quality characteristics of the samples used in the experiments.

Before beginning any sampling for the experiments, all involving containers and glassware were cleaned with de-ionized water to ensure that no chlorine demand was present. Disposable PET bottles were used to keep the samples in a water bath to maintain the temperature condition constant during the test period. All chlorine measurements were conducted with the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method using Lovibond pocket colorimeter. Samples were examined at the temperatures of 15, 20, 25, 30, 35, 40, 45 and 50°C. To minimise the effects water quality variations, repeated tests were done and the results were compared for consistency. Diluted standard sodium hypochlorite solution was used for chlorination of the samples. Several experi-

Table 1
Water quality characteristics of the samples

| Sample label | Description | Water quality characteristics | | |
|---|---|---|---|---|
| | | DOC ($mgL^{-1}$) | $UV_{254}$ | pH |
| PRW | Pilbara Raw Water | 3.27 | 0.055 | 8.35 |

ments with de-ionized water were conducted before the main tests to ensure the initial chlorine concentrations. Duplicate analysis was performed on each sample to get an accuracy of ±0.05 mg/L, and the average was reported.

### 2.2. Data analysis

Employing previously explained chlorine decay modelling approaches (PSOM and SOM), data analysis was performed using one of the powerful softwares for water quality simulation, AQUASIM [7].

AQUASIM contains a dynamic equation solver, which is capable of finding best fit parameters [7]. The fitting was performed based on the numerical solution of all defined reaction schemes. The weighted error between experimental and model data ($\mathrm{Chi}^2$) can be used as a measure of goodness of fit between experimental and predicted data and can be defined as follows:

$$\mathrm{Chi}^2(p) = \sum_{i=1}^{n} \left( \frac{f_{\mathrm{meas},\,i} - f_i(p)}{\sigma_{\mathrm{meas},i}} \right)^2 \tag{12}$$

where $f_{\mathrm{meas},i}$ is the $i$th measured value, $f_i(p)$ is the calculated value from the model using parameter values $p$ and $\sigma_{\mathrm{meas},i}$ is the estimated standard deviation of $f_{\mathrm{meas},i}$.

During parameter estimation for all sets of experimental data, the initial values of all involving parameters were adjusted by AQUASIM software until $\mathrm{Chi}^2$ reaches a minimum value. In order to have the highest level of accuracy in parameter estimation process, after assigning the initial values of the parameters, parameter estimation was first performed using the 'simplex' method. The process did continue until the difference between new $\mathrm{Chi}^2$ and the old one became zero. Then, the process was performed using the 'secant' method several times until $\mathrm{Chi}^2$ reached its lowest value.

To model temperature variation, two different methods of analysis for PSOM were exercised. The reason for considering these methods was due to their broadly used applications in the literature.

In the first method of analysis, one single temperature-dependence parameter for both fast and slow reactants, defined as the ratio of activation energy to the universal gas constant ($E/R$), was added to other parameters ($\mathrm{FRA}_0$, $\mathrm{SRA}_0$, $k_{\mathrm{FRA}}$ and $k_{\mathrm{SRA}}$) in AQUASIM. $\mathrm{FRA}_0$ and $\mathrm{SRA}_0$ are the initial concentrations of the fictional fast and slow reacting agents. Using this method, the software estimated the parameter to make a linear relationship between rate coefficients according to Arrhenius equation.

In the second modelling attempt, two different $E/R$ parameters were defined for the involving reactions; one for the fast reacting agents labelled as $(E/R)_{\mathrm{FRA}}$ and another for the slow ones labelled as $(E/R)_{\mathrm{SRA}}$. The latter method of temperature analysis is more valid fundamentally, according to Arrhenius equation. However, it adds one more parameter to the model and makes it more complex.

Using the second order model (SOM), since only one reaction is assumed to occur between the chlorine and other reacting agents, only one $E/R$ parameter was needed.

## 3. Results and discussion

Parameter estimation and the results of the first and second modelling procedures for the temperature analysis with PSOM are presented in Tables 2 and 3 as well as in Figs. 1 and 2. Similarly, Table 4 and Fig. 3 show the parameter estimation and data fitting on PRW sample with the second order model (SOM).

The comparison of two mentioned methods for temperature analysis with PSOM shows that both methods present a reasonably good data fitting over the given range of temperatures. As can be seen from Figs. 1 and 2, the second method of temperature analysis with two E/R parameters is slightly better than the first approach with only one parameter. Similar conclusion can be drawn from Tables 2 and 3, i.e. the weighted error between experimental and model data ($\mathrm{Chi}^2$) of the first method is very close to the one in the second approach.

According to Table 2, considering only one temperature dependence parameter for both notional reactions in PSOM, ($E/R$) is observed to be $8037°\mathrm{K}^{-1}$. The $\mathrm{Chi}^2$ value for this experiment is shown to be 0.8797, which is not considered to be too high compared with the summation of experimental errors for all data points. The temperature-dependence parameters for the second method of temperature analysis with PSOM are shown to be 2853 and 8374 for the fast and slow reacting agents (FRA and SRA), respectively, according to Table 3. This method presents a better fit to the experimental data and gives a $\mathrm{Chi}^2$ value of 0.6283.

Fisher et al. [8] estimated E/R to be between 5000 and 8000 K for a treated mixed groundwater/artesian source on 3 different occasions and 5600 and 9800 K for conventionally treated reservoir and river sources respectively. This confirms that the estimated $E/R$ for the authors' experiment with a single temperature parameter is within the reported range.

Although, the first method for the temperature analysis, which considers only one $E/R$ value, is not fundamentally valid according to the Arrhenius equation, it gives a reasonably low weighted error for the parameter estimation, while having one less parameter to be estimated than the second method.

Referring to the results of parameter estimation for $k_{\mathrm{FRA}}$ in Table 2 and comparing them with the corresponding results in Table 3, it is realised that the rate of increase for $k_{\mathrm{FRA}}$ with the temperature in the first method is noticeably higher than the ones in the second method. This is an unwanted result from an extra parameter reduction which leads to having higher $k_{\mathrm{FRA}}$ values in higher temperatures

Table 2
Parameter estimation for PRW sample with the parallel second order model (PSOM); using single *E*/*R* value

| Parameter | Value | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Temperature | | | | | | | |
| | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 |
| $FRA_0$, mg/L | 1.1064 | 1.1064 | 1.1064 | 1.1064 | 1.1064 | 1.1064 | 1.1064 | 1.1064 |
| $SRA_0$, mg/L | 2.4483 | 2.4483 | 2.4483 | 2.4483 | 2.4483 | 2.4483 | 2.4483 | 2.4483 |
| $k_{FRA}$, $(mg/L)^{-1}h^{-1}$ | 2.7610 | 4.4451 | 7.0431 | 10.9912 | 16.9063 | 25.6496 | 38.4077 | 56.7974 |
| $k_{SRA}$, $(mg/L)^{-1}h^{-1}$ | 0.0242 | 0.0390 | 0.0617 | 0.0963 | 0.1482 | 0.2248 | 0.3366 | 0.4978 |
| $E/R$, $K^{-1}$ | 8037 | 8037 | 8037 | 8037 | 8037 | 8037 | 8037 | 8037 |
| $Chi^2$ | 0.8797 | 0.8797 | 0.8797 | 0.8797 | 0.8797 | 0.8797 | 0.8797 | 0.8797 |

Table 3
Parameter estimation for PRW sample with the parallel second order model (PSOM); using two E/R values

| Parameter | Value | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Temperature | | | | | | | |
| | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 |
| $FRA_0$, mg/L | 1.1998 | 1.1998 | 1.1998 | 1.1998 | 1.1998 | 1.1998 | 1.1998 | 1.1998 |
| $SRA_0$, mg/L | 2.8546 | 2.8546 | 2.8546 | 2.8546 | 2.8546 | 2.8546 | 2.8546 | 2.8546 |
| $k_{FRA}$, $(mg/L)^{-1}h^{-1}$ | 3.3515 | 3.9688 | 4.6732 | 5.4730 | 6.3769 | 7.3938 | 8.5332 | 9.8045 |
| $k_{SRA}$, $(mg/L)^{-1}h^{-1}$ | 0.0157 | 0.0258 | 0.0417 | 0.0663 | 0.1039 | 0.1604 | 0.2443 | 0.3672 |
| $(E/R)_{FRA}$, $K^{-1}$ | 2853 | 2853 | 2853 | 2853 | 2853 | 2853 | 2853 | 2853 |
| $(E/R)_{SRA}$, $K^{-1}$ | 8374 | 8374 | 8374 | 8374 | 8374 | 8374 | 8374 | 8374 |
| $Chi^2$ | 0.6283 | 0.6283 | 0.6283 | 0.6283 | 0.6283 | 0.6283 | 0.6283 | 0.6283 |

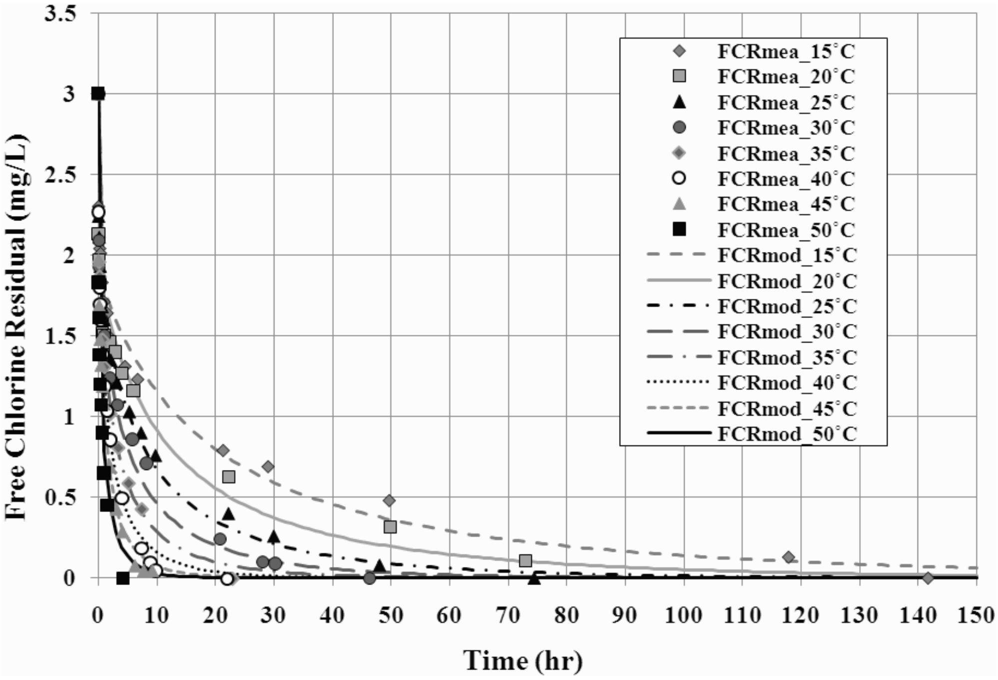

Fig. 1. Data fitting for PRW sample with the parallel second order model (PSOM), using single *E*/*R* value.

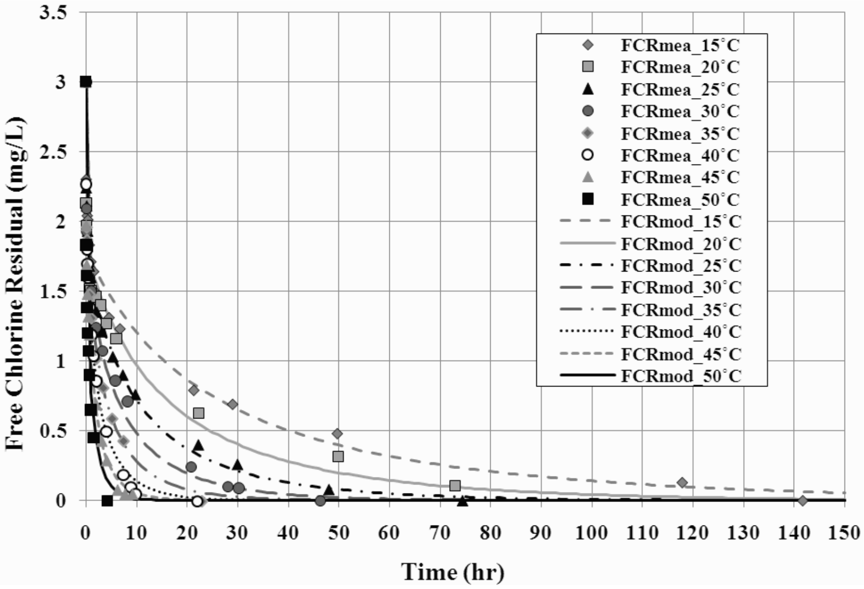

Fig. 2. Data fitting for PRW sample with the parallel second order model (PSOM), using two *E*/*R* values.

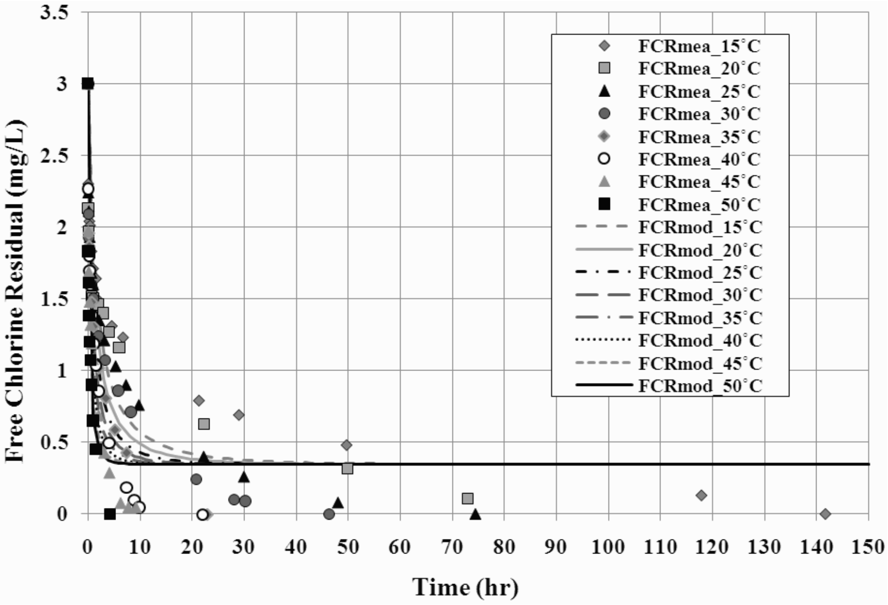

Fig. 3. Data fitting for PRW sample with the second order model (SOM).

compared to the second method. However, the $\text{Chi}^2$ values are not much different in these two methods, which shows that having an extra parameter for temperature analysis does not have a major influence on the accuracy of the chlorine decay prediction.

The details of parameter estimation for the chlorine decay modelling with SOM over a wide range of temperature (from 15 to 50°C) are presented in Table 4. According to this table, the weighted error between experimental and model data ($\text{Chi}^2$) was 10.2496 for PRW sample with SOM. It shows the failure of this method in comparison with the parallel second model. This can also be seen from visual inspection of Fig. 3.

Earlier results pointed out that SOM is weaker in predicting the chlorine concentration at farther ends of distribution system [6]. It especially over predicts the residual at farther ends of distribution system, providing a false sense of security. When results of our previous works and this paper are combined, PSOM has appeared to be a better method to describe chlorine decay behaviour.

Table 4
Parameter estimation for PRW sample with the second order model (SOM)

| Parameter | Value | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Temperature | | | | | | | |
| | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 |
| $RA_0$, mg/L | 2.6533 | 2.6533 | 2.6533 | 2.6533 | 2.6533 | 2.6533 | 2.6533 | 2.6533 |
| $k$, $(\text{mg/L})^{-1}\text{h}^{-1}$ | 0.2349 | 0.3225 | 0.4382 | 0.5893 | 0.7850 | 1.0361 | 1.3556 | 1.7589 |
| $E/R$, $\text{K}^{-1}$ | 5351 | 5351 | 5351 | 5351 | 5351 | 5351 | 5351 | 5351 |
| $\text{Chi}^2$ | 10.2496 | 10.2496 | 10.2496 | 10.2496 | 10.2496 | 10.2496 | 10.2496 | 10.2496 |

## 4. Conclusion

The aim of this study was to evaluate two better chlorine decay models for their ability to represent temperature. The models tested were parallel second order model (PSOM) and second order model (SOM). For this purpose, raw water samples from Pilbara Water Treatment Plant were collected for conducting chlorine decay tests over a wide range of temperatures from 15 to 50°C, as water temperature in the system could vary between 20 and 40°C.

The obtained data was used to analyse the temperature effect on chlorine decay with the parallel second order model (PSOM) proposed by Kastl et al. [4] as well as the second order model (SOM) offered by Clark [3].

Using PSOM for the modelling procedure, two methods of temperature analysis were examined. In the first one, one temperature dependence parameter ($E/R$) was used for both fast and slow reaction schemes. In the second method, however, one single $E/R$ value was used for each reaction pathway between chlorine and two fictional reacting agents; $(E/R)_{\text{FRA}}$ for the fast reacting agents and $(E/R)_{\text{SRA}}$ for the slow one.

Results showed that both methods of analysis with PSOM presented a good fit to the measured chlorine decay profile over the tested range of temperatures. On the contrary, SOM did not fit the experimental data properly.

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