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Effectiveness of parallel second order model over second and first order models

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ABSTRACT

The chlorine decay is usually described by the first order model (FOM) due to its easiness, although its weaknesses are well known. In this work, two better models, second order model (SOM) and parallel second order model (PSOM), are compared for their accuracy to predict chlorine residuals for a single dosing scenario. Results showed that SOM model provided a better prediction compared to FOM. However, SOM had two important shortcomings. Firstly, it overly predicted residuals in the lower end of chlorine decay curve, implying false sense of security in achieving secondary disinfection goals. Secondly, when higher initial dose was practiced, chlorine residual prediction was poorer. PSOM on the other hand provided the best fit for the experimental data in the initial as well as the later part of the decay curve for any doses. Compared to SOM which had two parameters, PSOM is more complex as it uses four parameters. Comparing to the advantages, complexity of PSOM is not an issue as EPANET-MSX can be used for full scale system simulation.

Keywords: Disinfection; Chlorine decay; First order model (FOM); Second order model (SOM); Parallel second order model (PSOM); Parameter estimation; EPANET-MSX

1. Introduction

Chlorine is broadly used as an effective disinfectant in the final process of the most water treatment schemes, 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 [1].

Disinfection must achieve two important goals: an adequate inactivation of microorganisms before the treated water reaches the first customer (primary disinfection); and a minimum concentration of disinfectant should always be maintained at the periphery of the distribution system to inhibit microbial regrowth or accidental contamination (secondary disinfection) [1].

However, because of reasonably high oxidation potential, chlorine also reacts with other organic and inorganic matters in the bulk water. This phenomenon of reaction with different species other than microorganisms (bacteria and viruses) is known as the main reason for chlorine decay over time. Therefore, more chlorine is usually required than necessary to satisfy the primary and secondary disinfection goals.

On the other hand, the reaction between chlorine and natural organic matters (NOMs) results in the production of disinfection by-products (DBPs), some of which has been recognised as potentially carcinogenic or toxic substances. Hence, chlorine concentration should be limited in order to decrease the disinfection by-products formation. In addition, aesthetic consideration requires a maximum residual to be maintained at the customer tap. Furthermore, chlorine decay behaviour has been proved to be significantly affected by water quality character-

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istics such as total organic carbon (TOC) or dissolved organic carbon (DOC), pH and temperature. There are also several evidences of how different types of treatment processes and hydraulic and non-hydraulic conditions of the distribution system (such as corrosion, biofilm) may influence the chlorine decay profile [2]. Therefore the chlorine demand, the retention time and its required set point and initial dosing vary from one water source to another, over different water networks or different seasons within the same network [1].

Consequently, meeting this complex requirement is an optimization problem that needs robust models [3]. So far, several empirical as well as theoretical models for the prediction of chlorine decay in bulk water have been presented. While empirical models are based on the relationship of chlorine consumption with certain water characteristics such as TOC, DOC, pH and temperature, theoretical models attempt to relate the chlorine decay to the time throughout a set of dynamic process equations. These equations are based on physical and chemical principles such as conservation of mass for water and chemical constituents and mass-action kinetics in chemical reactions. The latter (theoretical models) have been presented to be more suitable for both planning and management applications [3]. Therefore, those models, which are dependent on the chemical reactions of chlorine with different constituents in the water, have been paid more attention in the literature.

The objective of this research is to investigate and to compare effectiveness of the most popular modelling approaches (first order, second order, and parallel second order models) for the prediction of chlorine decay in the bulk water. For this purpose, initially, existing models are reviewed for its accuracy. Then, both our own laboratory experimental data and literature data were used to compare effectiveness. The effectiveness is defined in terms of accuracy and simplicity.

2. Modelling background

2.1. First order models

One of the earliest, simplest and initially most popular mechanistic or theoretical approaches for modelling chlorine decay was the first order kinetics. According to the first order kinetics, chlorine concentration is assumed to react with infinite source of reactant, which never depletes with time. The general first order kinetic expressions for chlorine decay in bulk water would be expressed as follows:

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

$$\mathrm{Cl}(t) = \mathrm{Cl}_0 \exp(-kt) \tag{2}$$

where c_{Cl} is chlorine concentration at time t, Cl_0 is initial chlorine concentration [mg/L] and k is the decay constant [h^{-1}].

Despite the simplicity and easiness of this model, it has not presented a good data fitting in different applications. In fact, the rate coefficient, k, is highly dependent on water source and type of treatment process. Most specifically, the model is not capable of handling the higher decay rates observed in the initial stages of chlorination nor the slow tailing off the decay at very long reaction times [1–4].

Initially, several attempts were made to compensate the defects of the simple first order model. These attempts, however, were to ignore the role of other important influencing factors on chlorine decay, especially reactant species. Hass and Karra [5] evaluated some of these models against first order and a new method called parallel first order model. The models were labelled as follows:

- Power-law decay model (*n*th order)
- First-order decay with stable components
- Power-law decay with stable components (*n*th order)

For the decay models with stable components, it was assumed that a portion of the initial chlorine residual does not decay and only the remainder decays. They concluded that except for the parallel first order model, all other rate laws resulted in unsatisfactory fits to the data.

In the parallel first order model, chlorine is divided into two parts and each part decays independently, according to a first order reaction with its own individual decay rate. From a theoretical viewpoint, however, separating chlorine into two constituents, one part is being decayed fast while the decay of another part is slow, is not fundamentally valid.

In all first order kinetic models, only two variables, chlorine concentration and time, are considered. In fact, in these modelling concepts, the effect of reacting agents is either neglected or their amount assumed to be much larger than chlorine. Therefore, it is assumed that the concentration of reacting agents does not significantly change during the reaction with chlorine; and the reaction rate is only proportional to the chlorine concentration. This leads to the so-called pseudo-first-order reaction. However, this assumption is not necessarily valid for all applications.

2.2. Second order model

In order to involve the effect of reactant constituents, Clark [6] proposed a two-component second-order chlorine decay model for prediction of chlorine decay in bulk water. The model is based on the concept of reaction between chlorine and another notional substance assuming that the balanced reaction equation could be represented as follows:

$$aA + bB \rightarrow pP \tag{3}$$

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 product of the reaction.

An analytical solution for the second order model was proposed by Clark [6]. The proposed solution was the first prosperous trial for a second-order model:

$$C_A = \frac{K}{1 - \mathrm{R}e^{-ut}} \tag{4}$$

where C_A is the initial chlorine concentration [mg/L] and K [mg/L], R [dimensionless] and u [h^{-1}] are constant parameters to be estimated.

The Clark's equation can be written as follows if the simple stoichiometry of the chlorine reaction is assumed:

$$\mathrm{Cl}_2 + RA \xrightarrow{k} \text{inert product} \tag{5}$$

$$\frac{dC_{RA}}{dt} = -k \cdot C_{\mathrm{Cl}} \cdot C_{RA} \tag{6}$$

$$C_{\mathrm{Cl}}(t) = \frac{C_{\mathrm{Cl}_0} - C_{RA_0}}{1 - \dfrac{C_{RA_0}}{C_{\mathrm{Cl}_0}} \cdot e^{-\left(C_{\mathrm{Cl}_0} - C_{RA_0}\right) \cdot k \cdot t}} \tag{7}$$

where C_{Cl_0} and C_{RA_0} are the initial concentrations of chlorine and notional reactant [mg/L], respectively, and k [(mg/L)$^{-1}$h^{-1}] 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 the later slow one, have been reported.

2.3. Parallel second order model

Probably the earliest second order model for the prediction of chlorine decay in natural water has been proposed by Qualls and Johnson [7]. They used this model for the prediction of chlorine decay in the first five minutes after dosing, which was the timescale for cooling water to pass through a power plant. They assumed two types of reactions — initial fast reaction followed by a slow one — occurring between chlorine and fulvic acids as NOM representative:

$$\frac{dC_{\mathrm{Cl}}}{dt} = k_1[\mathrm{Cl}][F_1] + k_2[\mathrm{Cl}][F_2] \tag{8}$$

where dC_{Cl}/dt is the rate of free chlorine disappearance, [Cl] is the free chlorine concentration, k_1 and k_2 are the rate constants for the fast and slow reactions, respectively, and [F_1] and [F_2] are the concentrations of sites on the fulvic acids for the fast and slow reactions, respectively.

Taking inspiration from Qualls and Johnson's work, Kastl et al. [4] simplified the model they had previously used and developed the parallel second order model for the entire reaction time of a typical distribution system (up to 7 days). They considered two parallel simultaneous reactions occurring between chlorine and two notional constituents in the water with the overall second order kinetics, assuming that one of the reactions is much faster than the other:

$$\mathrm{Cl}_2 + \mathrm{FRA} \xrightarrow{k_{\mathrm{FRA}}} \mathrm{Cl}^- + \text{inert product} \tag{9}$$

$$\mathrm{Cl}_2 + \mathrm{SRA} \xrightarrow{k_{\mathrm{SRA}}} \mathrm{Cl}^- + \text{inert product} \tag{10}$$

where FRA and SRA are the fast reacting reducing agents and slow reacting reducing agents in the water and k_{FRA} and k_{SRA} are their reactions' rate constants, respectively.

The second order reaction rates for the above-mentioned reactions in this model could be given as follows [3]:

$$\frac{dC_{\mathrm{FRA}}}{dt} = -k_{\mathrm{FRA}} \cdot C_{\mathrm{Cl}} \cdot C_{\mathrm{FRA}} \tag{11}$$

$$\frac{dC_{\mathrm{SRA}}}{dt} = -k_{\mathrm{SRA}} \cdot C_{\mathrm{Cl}} \cdot C_{\mathrm{SRA}} \tag{12}$$

where C_{FRA} and C_{SRA} are concentration of the two reacting agents (fast and slow), respectively.

$$\frac{dC_{\mathrm{Cl}}}{dt} = \frac{dC_{\mathrm{FRA}}}{dt} + \frac{dC_{\mathrm{SRA}}}{dt} \tag{13}$$

where C_{Cl} is free chlorine concentration.

Realizing the need for having a more accurate modelling approach for chlorine decay prediction, some researchers started to apply the parallel second order model for the assessment of the effects of different treatment processes on the chlorine decay profile [8,9,11].

3. Material and methods

3.1. Water samples and analytical methods

Two water samples taken from Pilbara Water Treatment Plant, labelled as "Pilbara Raw Water (PRW)" and "Pilbara Post-Filtration Water (PPFW)", were used for the tests. Prepared chlorine-demand-free amber bottles were used to store the water samples.

All chlorine measurements were conducted with the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method using Lovibond® pocket colorimeter. To minimise the effects of variations in the water quality, repeated tests were done and the results were compared for consistency. Diluted standard sodium hypochlorite solution was used for chlorination of the samples. Several experiments with de-ionized water were conducted before the main tests to confirm the initial chlorine concentrations. Prepared chlorine-demand-free plastic bottles were used to store the water samples. The samples were kept in a water bath to maintain the temperature condition constant.

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. Duplicate analysis was performed on each sample to get an accuracy of ±0.05 mg/L, and the average was reported.

3.2. Selection and extraction of literature (independent) data

The literature data was extracted from the research work performed by Gang et al. [10]. In this study, different samples from surface water of the rural Missouri agricultural watersheds (Garden City, Maysville and Lake Vandalia) and Mississippi River were reported to be dosed by different concentrations of chlorine. A 120-h chlorine demand preliminary study was said to be performed using a series of chlorine dosages based on Cl_2 : DOC ratios. Among the data sets of this research work, three of them were selected for the analysis. The data for the residual free chlorine concentrations was accurately extracted from provided figures in this publication using graphical methods. Table 1 shows water quality characteristics of the samples chosen from the literature as well as the ones obtained from the authors' experiments.

3.3. Data analysis

In order to compare the accuracy of the parallel second order model (PSOM) with the first and the second order modelling methods, the data of free chlorine readings from laboratory experiments as well as literature data were put into three files to be run in AQUASIM® software, each one was allocated for each modelling approach. In the first AQUASIM file, which was allocated for the parallel second order model, four program parameters (C_{FRA_0}, C_{SRA_0}, k_{FRA} and k_{SRA}) and two reaction schemes (fast and slow) were defined for each data set. Similarly, another two AQUASIM® files were generated for the first order model (FOM) and the second order model (SOM). Parameter estimation was conducted for each group of measured data and for each modelling methods.

AQUASIM® contains a dynamic equation solver, which is capable of performing parameter estimation to find the best fit of the model output to the experimental data [12]. The fitting procedure, however, is performed based on the numerical solution of all defined reaction schemes. The weighted error between experimental and model data (χ^2) can be used as a measure of goodness of fit between experimental and predicted data and can be defined as follows:

$$\chi^2(p) = \sum_{i=1}^{n} \left(\frac{f_{\mathrm{meas},i} - f_i(p)}{\sigma_{\mathrm{meas},i}} \right)^2 \tag{14}$$

where $f_{\mathrm{meas,i}}$ is the ith 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 the fitting of the model to the experimental data, the initial values of all parameters were adjusted by AQUASIM® software until χ^2 reached a minimum value.

4. Results and discussion

The results of parameter estimation for both data sets from Pilbara Water Treatment Plant (PPFW and PRW) and literature data when they were fitted to three most popular chlorine decay models (FOM, SOM and PSOM) are presented in Tables 2–4 and Figs. 1–6.

As can be seen from Figs. 2 and 4, the first order model does not properly predict the chlorine residuals of any dataset. This can also be noticed from the fitting parameter (chi-squared) in Table 2, as FOM gave the highest chi-squared which is indicative of poorest fitting. The only FOM parameter to be estimated is k (the rate constant), which is listed for each water in Table 2.

According to Table 3, Fig. 3 and Fig. 5, the SOM represents a much better description of the chlorine decay than FOM for all data sets. For SOM, chi-squared values were smaller than half that of FOM. SOM contains two parameters to be estimated (the rate constant, k, and the initial concentration of the total reacting agents, RA_0), which gives more degree of freedom in chlorine residual prediction compared to FOM. Despite a better fitting than FOM, SOM model had the poor ability to fit the lower end of the decay curve.

Table 4 shows the model and fitting parameters estimated by PSOM for the water samples taken from Pilbara

Table 1
Water quality characteristics of the samples

Sample label	Description	Water quality characteristics		
		DOC (mg/L)	UV_{254}	pH
PPFW	Pilbara post-filtration water	2.43	0.024	7.78
PRW	Pilbara raw water	3.87	0.063	8.50
LWR	Gang et al. [10]	9.89	0.1574	—
GWT	Gang et al. [10]	2.8	0.0284	—
CWT	Gang et al. [10]	3.09	0.0518	—

Table 2
The results of parameter estimation for the experimental data with the first order model

Sample label	Initial dosing (mg/L)	Software	Estimated and fitting parameters		
			k (h^{-1})	Chi^{2*}	No. of data points
PPFW	3.20	AQUASIM	0.088	4.24	18
PRW	8.40	AQUASIM	0.105	39.659	18
LWR	12.20	AQUASIM	0.036	32.889	11
GWT	4.03	AQUASIM	0.025	5.001	11
CWT	3.62	AQUASIM	0.066	3.99	11

Table 3
The results of parameter estimation for the experimental data with the second order model

Sample label	Initial dosing (mg/L)	Software	Estimated and fitting parameters			
			k (mg/L)$^{-1}$h^{-1})	C_{RA_0} (mg/L)	Chi^{2*}	No. of data points
PPFW	3.20	AQUASIM	0.058	2.92	2.189	18
PRW	8.40	AQUASIM	0.036	7.10	19.469	18
LWR	12.20	AQUASIM	0.012	10.05	10.755	11
GWT	4.03	AQUASIM	0.055	2.90	1.354	11
CWT	3.62	AQUASIM	0.077	2.93	1.136	11

Table 4
The results of parameter estimation for all data using the parallel second order model

Sample label	Initial dosing (mg/L)	Software	Estimated and fitting parameters					
			C_{FRA0} (mg/L)	C_{SRA0} (mg/L)	k_{FRA} ((mg/L)$^{-1}$h^{-1})	k_{SRA} ((mg/L)$^{-1}$h^{-1})	Chi^{2*}	No. of data points
PPFW	3.20	AQUASIM	0.89	2.99	2.82	0.014	0.167	18
PRW	8.40	AQUASIM	2.71	5.86	1.35	0.007	0.561	18
LWR	12.20	AQUASIM	2.68	9.99	0.32	0.004	0.140	11
GWT	4.03	AQUASIM	1.22	2.89	0.535	0.007	0.034	11
CWT	3.62	AQUASIM	1.3	3.16	0.557	0.009	0.021	11

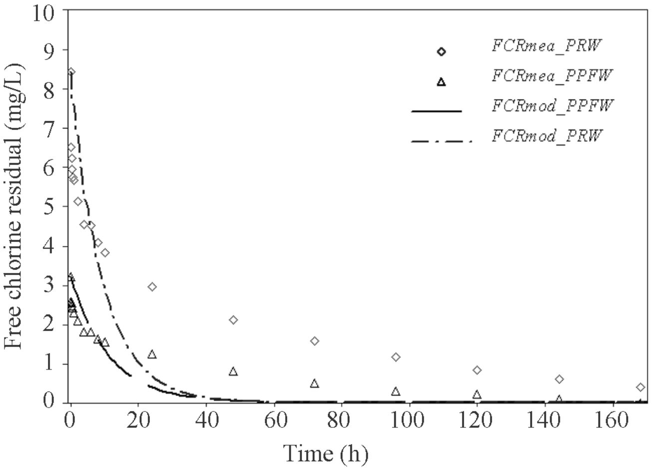

Fig. 1. Goodness of data fitting for Pilbara water samples (PPFW and PRW) using the first order model (FOM).

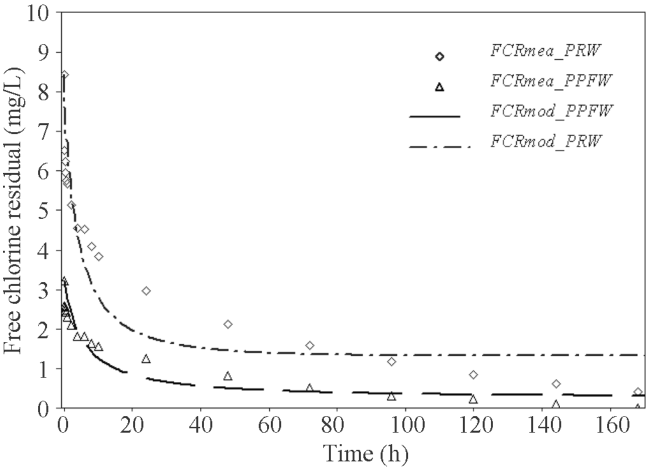

Fig. 2. Goodness of data fitting for Pilbara water samples (PPFW and PRW) using the second order model (SOM).

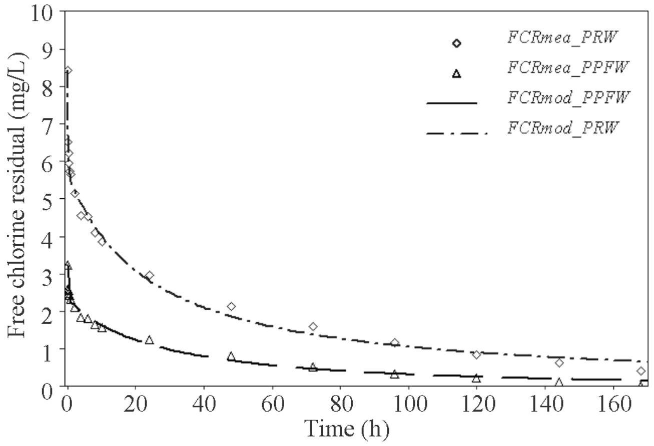

Fig. 3. Goodness of data fitting for Pilbara water samples (PPFW and PRW) using the parallel second order model (PSOM).

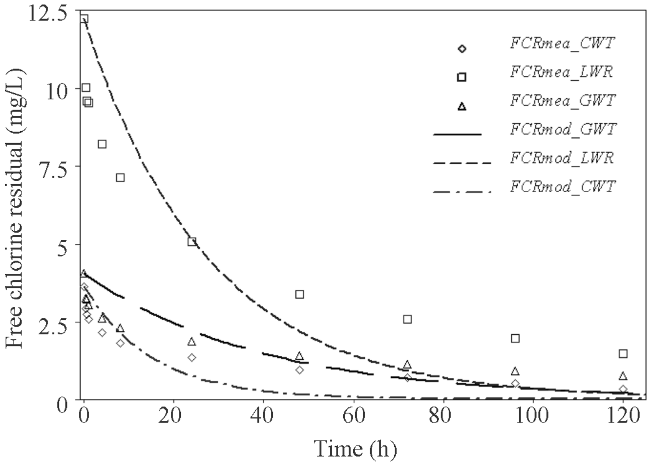

Fig. 4. Goodness of data fitting for the literature data from Gang et al. (2003)'s work using the first order model (FOM).

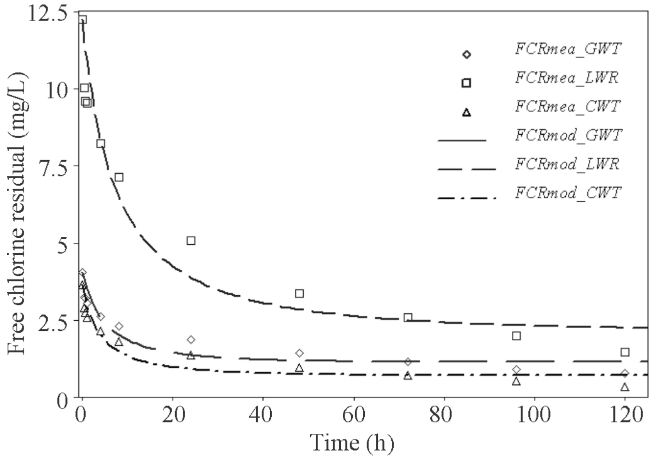

Fig. 5. Goodness of data fitting for the literature data from Gang et al. (2003)'s work using the second order model (SOM).

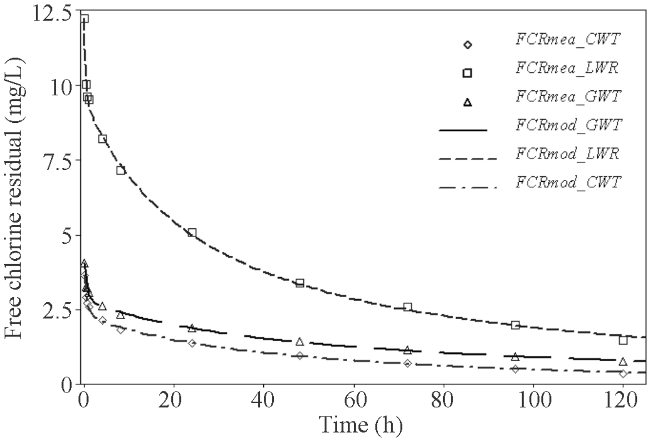

Fig.6. Goodness of data fitting for the literature data from Gang et al. (2003)'s work using the parallel second order model (PSOM).

Water Treatment Plant (PPFW and PRW) and the selected literature data. As indicated in Table 4, chi-squared values were much smaller than any of the values obtained for either FOM or SOM. Such fitting was possible mainly because PSOM separates the decay curve into two parts, one with a much higher decay rate than the other. Moreover, Fig. 3 and Fig. 6 present very good fit for all data sets (at the beginning as well as the end of the decay period), indicating that PSOM provides a much better prediction of chlorine residuals of all models.

Comparing the statistical fitting parameters of the three mentioned methods, i.e. χ^2 (chi-squared), it is clear that PSOM perfectly meets the accuracy criteria compared to FOM and SOM methods. As indicated from the results, the chi-squared value for the modelling of PPFW sample starts from 4.24 using FOM, decreases to 2.189 with SOM modelling approach and gets its lowest value of 0.167 using the parallel second order model. However, the improvement of fitting parameters with the change of modelling methods for PRW sample with higher initial concentration of chlorine is significantly better than that of PPFW. Analysing the data from Tables 2–4, it is found that chi-squared value using SOM are much lower for the lower initial chlorine doses than the higher ones. For example, while the χ^2 values for PPFW, CWT and GWT (with the chlorine dosing of 3.2, 3.62 and 4.03 mg/L) using SOM are 2.189, 1.136 and 1.354, respectively, the χ^2 values for PRW and LWR (with the chlorine dosing of 8.4 and 12.2 mg/L) are 19.469 and 10.755, respectively. This implies that SOM provides a reasonably good fit only when the initial chlorine concentration is low.

Considering the results of chlorine decay prediction by FOM, it is clear that the model is not capable of satisfactorily describing the chlorine profile. The results indicate that in most of times there is a big difference between the measured data and the predicted ones using FOM. This huge gap between the measured and predicted data would significantly increase when other scenarios such as multiple dosing, re-chlorination, temperature effect and wall reaction are to be considered. In some arbitrary cases (i.e. when neglecting initial fast decay), however, FOM would give more accurate results during the end period of considered retention time depending on the initial chlorine doses and/or water quality characteristics (in CWT sample for example). In this case, the starting time for modelling has to be chosen arbitrarily, such as 4 h after the initial dose, implying that model parameters have to be re-evaluated every time characteristics affecting the decay vary.

Looking at the figures, it can be realised that long time chlorine residuals predicted by SOM are always higher than the measured values. This will impact on many important criteria of the model. Firstly, the model will give larger chlorine residuals than actual values in farther ends of distribution systems, providing a false sense of security. This will adversely affect the utility achieving secondary disinfection targets. Secondly, if this model is used to determine the wall coefficients, any error in the model will impact on the estimation of the wall decay coefficient providing a false indication of the wall impact, and thus leads to wrong operational strategies. Moreover, SOM provides less reacted chlorine, which results in less DBPs formation prediction, as DBP formation is often calculated using reacted chlorine [11]. This is not desirable when DBPs formation control is targeted.

As clearly manifested from the results of the tables as well as figures, PSOM shows the best description of chlorine decay profile and presents reasonably low prediction errors compared to FOM and SOM. As mentioned earlier, it is very important to have a very accurate model when only one scenario, i.e. prediction of chlorine decay without having multiple dosing, temperature effect or re-chlorination, is to be considered. This is because any error in a single scenario will accumulate when other scenarios are considered. In addition, PSOM could satisfactorily meet the criteria of secondary disinfection as well as DBPs formation control. That is if, for example, the maximum allowable prediction error is considered to be within experimental error of the instrument for the prediction of chlorine residual after a normal retention time for secondary disinfection, PSOM is the only model amongst the above-mentioned models that could reach this level of accuracy.

PSOM utilises four parameters which is double that of SOM, making it a complex model. Currently, parameter estimation is made via the AQUASIM or other softwares capable of handling numerical solution. To make the model easy to use, it is important that an analytical solution for the PSOM is established. Earlier, there was no software capable of handling complex set of reaction schemes for full scale system simulations [13]. However, availability of EPANET-MSX means that any complex scheme of reactions can be easily incorporated [14]. Therefore, added complexity of PSOM will not be an issue if there was an analytical solution.

5. Conclusion

The aim of this research was to compare performance of the three most popular modelling approaches for the prediction of chlorine decay in bulk water. First order model (FOM), second order model (SOM) and parallel second order model (PSOM) were compared for its accuracy to predict a single dosing scenario. As usually concluded in the literature, FOM performed the weakest. SOM was better than FOM, but in lower end of the decay curve SOM predicted higher concentration indicating that utilities will have trouble satisfying secondary disinfection goals or in identifying how wall reaction is impacting chlorine decay. PSOM, in contrast, provided the best fit to the chlorine decay profiles at any part of the curve. It was concluded that the PSOM is the most accurate modelling method among the three mentioned chlorine decay models, despite its complexity with four parameters compared to two in SOM and one in FOM.

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