Chloramine demand estimation using surrogate chemical and microbiological parameters

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ABSTRACT

A model is developed to enable estimation of chloramine demand in full scale drinking water supplies based on chemical and microbiological factors that affect chloramine decay rate *via* nonlinear regression analysis method. The model is based on organic character (specific ultraviolet absorbance (SUVA)) of the water samples and a laboratory measure of the microbiological (F_m) decay of chloramine. The applicability of the model for estimation of chloramine residual (and hence chloramine demand) was tested on several waters from different water treatment plants in Australia through statistical test analysis between the experimental and predicted data. Results showed that the model was able to simulate and estimate chloramine demand at various times in real drinking water systems. To elucidate the loss of chloramine over the wide variation of water quality used in this study, the model incorporates both the fast and slow chloramine decay pathways. The significance of estimated fast and slow decay rate constants as the kinetic parameters of the model for three water sources in Australia was discussed. It was found that with the same water source, the kinetic parameters remain the same. This modelling approach has the potential to be used by water treatment operators as a decision support tool in order to manage chloramine disinfection.

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Introduction

A key goal of drinking water treatment plants is to supply water that is safe and is also aesthetically acceptable to customers. As a stage in water treatment processes, disinfection of drinking water has been regularly carried out since the early 20th century to destroy pathogenic organisms and prevent waterborne diseases (Elshorbagy et al., 2000). In order to meet regulations regarding formation of disinfection by-products (DBPs) in drinking water, chloramine is commonly used as a disinfectant instead of chlorine, particularly in Australia and the USA (Moradi et al., 2016; Sarker et al., 2015). The main advantage of using chloramine over chlorine is the slow decay rate of chloramine since it is less reactive with natural organic matter (NOM). Therefore, the use of chloramine also reduces the formation of regulated DBPs, such as trihalomethanes and haloacetic acids (Goslan et al., 2009; Jafvert and Valentine, 1992; Vikesland et al., 2001). The dose of chloramine is crucial, to ensure that the water is safe to drink, but also needs to be properly considered to prevent taste and odour problems

arising from the use of high chloramine doses. Chloramination requires careful control of the chlorine to ammonia ratio, and pH to avoid nitrification that will deplete chloramine residuals, particularly in storage tanks and outer extremities of a distribution system. Maintaining a disinfectant residual throughout the water distribution system is important in ensuring microbiologically safe water which is supplied at the customer's tap (Fitzgerald et al., 2006). Control of disinfectant residual in Australian water distribution systems is challenging due to high levels of dissolved organic matter (DOM) that can be present (which therefore results in high disinfectant demand), seasonal variation in flow demands and varying water temperatures (Fitzgerald et al., 2006; Hua et al., 1999).

In chloraminated drinking water systems, monochloramine decay occurs due to chemical and microbiological reactions (Krishna and Sathasivan, 2010; Sathasivan et al., 2005). In order to manage disinfection residuals in drinking water, it is important to discriminate between chemical and microbiological decay processes. Chemical factors affecting monochloramine decay include DOM measured as dissolved organic carbon (DOC) concentration, pH, nitrite, organic nitrogen compounds, chlorine to ammonia ratio and temperature (Cook et al., 2012; Sathasivan et al., 2005; Zhang et al., 2010). In addition, the presence of dead microbial cells and abiotic particles in water may also affect monochloramine decay. The impact of microbiological decay on monochloramine decay can be determined by the analysis of F_m. This simple strategy involves comparing monochloramine decay rates in processed (0.2 μm membrane filtered) and unprocessed samples (Sathasivan et al., 2005).

Grab sample monitoring of disinfectant residual in drinking water systems can lead to delay in corrective response in disinfectant dosing at the treatment plant. Consequently, applied doses that are either too high or too low are often identified too late for an operator to react and to take corrective action (Hua et al., 1999; Rodriguez and Sérodes, 1998). When considering the tools that operators might utilise to manage disinfection, models are potential options (Gnos et al., 2013). Modelling of disinfectant demand in treated water is aimed at creating a better understanding of the effect of raw water quality on the disinfection consumption and can serve as a decision making tool for effective water quality control (Abdullah et al., 2009; Gnos et al., 2013). Some researchers developed several models for prediction of chlorine demand and the formation of DBPs using different methods such as multiple regression analysis (Abdullah et al., 2009; Uyak et al., 2007), or neural networks (Janes and Musilek, 2007). In addition, kinetic models describing the formation of different group of DBPs during chloramination have been addressed in some studies (Alsulaili et al., 2010; Duirk and Valentine, 2007; Zhai et al., 2014). Zhu and Zhang (2016) studied the formation kinetics of DBPs during chloramination through formation of total organic chlorine (TOCl), total organic bromine (TOBr), and total organic iodine (TOI). They incorporated a series of reactions into two kinetic models which provided valuable insight into reactions that control the formation of DBPs in chloramination. The formation and decay of bromochloramine as a function of operating conditions, such as pH and Cl_2/N ratio were examined by Alsulaili et al. (2010), and they refined a chemical kinetic model to predict haloamine concentrations over time. Zhai et al. (2014) studied the kinetics of formation of

brominated DBPs during chloramination and developed a quantitative empirical model based on major reactions involved.

The development of reliable models is increasingly recognised as an essential methodological basis for predicting chloramine demand because it is one of the main factors in determining the chloramine dosage during chloramination. Due to the complexity of the chloramine properties, surrogate parameters have been developed to predict its demand and estimate its reactivity toward DBP formation. These surrogate parameters include DOC, ultraviolet absorbance (UVA), and specific ultraviolet absorbance (SUVA) (Chow et al., 2007; Fitzgerald et al., 2006; Hua et al., 2015). SUVA is defined as the ultraviolet (UV) absorbance at 254 nm/m divided by the DOC concentration (mg/L). SUVA represents the average absorptivity at 254 nm from all the organic molecules that comprise the DOC (Weishaar et al., 2003). Strong correlation between SUVA and different classes of DBPs during chlorination (Chu et al., 2010), and chloramination (Chu et al., 2013; Hua et al., 2015) was observed, and therefore SUVA can be a useful surrogate parameter to characterise NOM during drinking water treatment. Fitzgerald et al. (2006) predicted the chlorine and chloramine demand based on chemical water quality parameters. They found that surrogate chemical water quality parameters such as DOC and UVA_{254} can be used for chlorine demand prediction. However, Fitzgerald et al. (2006) reported that chloramine demand did not correlate well with the DOC or UVA_{254} for three day demand prediction. Their focus was just on chemical based water quality parameters. To the best of our knowledge, a predictive model that considers the effects of both chemical and microbiological effects together for the determination of disinfectant demand has not been developed.

The aim of this study was to develop a model for prediction of chloramine demand under different water quality conditions using surrogate chemical and microbiological parameters in waters of different quality as measured by DOC and UVA_{254}. A mathematical model to predict chloramine demand at later times was developed *via* nonlinear regression analysis based on chemical and microbiological parameters determined from 2-day chloramine decay tests. Fast and slow decay rate constants of three Australian water sources with different organic matter character (SUVA) and microbiological decay rate (F_m) were determined and the model was evaluated for water samples from these water sources that had not been included in the regression analysis. This numerical approach for chloramine demand estimation based on the water quality and dosing conditions can be considered as a pre-warning method to control disinfection dosing process in drinking water system. This has potential to be applied within the water industry as a decision support tool for drinking water system management.

1. Experimental

1.1. Sampling locations

Water samples were taken prior to disinfection from different water treatment plants supplied with water sourced from

Maryborough, Victoria (VIC), Mundaring Weir in Western Australia (WA), and Murray River in South Australia (SA) from 2010 to 2015. The description of water treatment plants, their water sources and abbreviations are described in Appendix A Table S1. This selection produced a database of varying water qualities throughout Australia and incorporated seasonal variation. The database facilitated the determination of surrogate parameters for the prediction of disinfection demand that would hold over a range of water qualities and seasons. Water samples prior to disinfection have been taken from different water treatment plants that are sourced from aforementioned water sources, chloraminated in laboratory and the rate of monochloramine decay over time was studied. The chloramine decay tests were completed using operational conditions as follows: target NH_2Cl 4.0 ± 0.1 mg/L as Cl_2, Cl_2 dose 4.0 mg/L, $NH_3 - N$ dose 0.89 mg/L, order of dosing is ammonia + chlorine, $Cl_2:NH_3 - N$ ratio 4.5:1, temperature 30 ± 1°C, and pH 8.2 ± 0.1.

1.2. Analytical methods

Water samples were chloraminated under laboratory conditions using a free chlorine stock solution prepared by the addition of gaseous chlorine to ultra-pure water and analytical grade liquid ammonia (1000 mg/L as N). Chloramine residuals, pH, temperature and ammonia concentration for all water samples were analysed at different times. Free chlorine and bound chlorine were determined using N,N-diethyl-p-phenylenediamine (DPD)–ferrous ammonium sulphate (FAS) titrimetric procedure (APHA et al., 1998). Ammonia concentrations were determined using ammonia-selective electrode Standard Method 4500-NH_3 (D) (APHA et al., 1998). UVA_{254} was measured through a 1 cm quartz cell using an Evolution 60 Spectrophotometer (Thermo Scientific, USA). DOC was measured using a Sievers 900 Total Organic Carbon Analyser (GE Analytical Instruments, USA). Measurements of pH and temperature were conducted using a portable pH meter with a sealed, gel filled reference electrode with temperature compensation (pH 320, WTW, Germany). Ultra-pure water was obtained from a Milli-Q purification system (Millipore, France). All water samples were processed to determine the relative contribution of microbiological mediated monochloramine decay to the overall monochloramine decay in the bulk water, by determination of a microbial decay factor (F_m) described by Sathasivan et al. (2005). Briefly, the microbial decay factor is determined from the ratio of the monochloramine decay rate of unfiltered water to filtered (0.2 μm membrane) water. In this test, the filtered water has micro-organisms removed that are responsible for monochloramine decay, and represents decay by chemical means only. Conversely, the unfiltered water will have chloramine decay by both microbial and chemical processes.

1.3. Model development

The kinetic behaviour of chloramine decay has been described by first-order, second-order, power and parallel first-order decay functions (Haas and Karra, 1984; Harrington and Noguera, 2003; Yang et al., 2008). Since a significant loss of chloramine happens in the first few minutes of contact time with NOM, chloramine decay was assumed to be described by the sum of two first-order equations, in which the first part describes a rapid decay and the second simulates a slower decay.

$$C = C_0 \cdot x \cdot \exp(-k_1 t) + C_0 \cdot (1-x) \cdot \exp(-k_2 t) \tag{1}$$

In this equation, C is chloramine concentration (mg/L) at time t (hr), C_0 is initial chloramine concentration (mg/L), x is fraction of fast reacting agents with chloramine, and k_1 and k_2 are rate constants (L/(mol·hr)) for the fast and slow reactions, respectively. Duirk et al. (2002) assumed that chloramine directly reacted with both the fast reactive fractions in the NOM structure through a direct reaction of monochloramine with NOM and the slow reactive fractions in the NOM structure through reaction of free chlorine from chloramine hydrolysis. The parallel first-order decay model assumes that decay proceeds through two mechanisms, each consisting of first-order reactions, and involving a different component of the chloramine residual (that is, component x with concentration $C_0 x$, is subject to first-order decay with a rate constant of k_1 (fast reactive fractions) and the remainder, the initial chloramine residual without component x, $C_0 \cdot (1-x)$, is subject to first-order decay with a rate constant of k_2 (slow long-term reactive fractions)-by definition, x is limited to a range between zero and unity) (Haas and Karra, 1984).

To have two parallel first-order decays for chloramine residual, the chloramine demand is described in a differential equation as follows (the derivation of the differential equation is given in Appendix A):

$$\frac{\partial C_{Demand}}{\partial t} = C_0 \cdot x \cdot k_1 \cdot \exp(-k_1 t) + C_0 \cdot (1-x) \cdot k_2 \cdot \exp(-k_2 t) \tag{2}$$

The strategy here is to predict chloramine demand (C_{Demand}) at different times based on chemical and microbiological water quality data obtained from a 2-day chloramine decay test and water quality (SUVA). By taking the integral of Eq. (2), and setting the lower limit of the integral at 2-days, chloramine demand can be determined according to Eq. (3).

$$C_{Demand}(t) = C_{Demand}^{t=2} - \frac{C_0 \cdot x \cdot k_1}{k_1} \cdot \exp(-k_1 t)\Big|_{t=2}^{t} - \frac{C_0 \cdot (1-x) \cdot k_2}{k_2}$$
$$\cdot \exp(-k_2 t)\Big|_{t=2}^{t} \tag{3}$$

It is known that increasing the SUVA and F_m as chemical and microbiological effects may result in a greater monochloramine decay rate (Hua et al., 2015; Sathasivan et al., 2005). Therefore, it is assumed that chloramine demand for water samples after 2-days can be represented by Eq. (4):

$$C_{Demand}^{t=2} = a \cdot F_m + b \cdot SUVA + c \cdot F_m \cdot SUVA \tag{4}$$

By substituting Eq. (4) to Eq. (3), and doing a set of mathematical operations, the final equation for prediction of chloramine demand with 3 model variable of F_m, SUVA, and time is as follows (Eq. (5)).

$$C_{Demand}(t) = a \cdot F_m + b \cdot SUVA + c \cdot F_m \cdot SUVA - C_0 \cdot x \cdot \exp(-k_1 t)$$
$$-C_0 \cdot (1-x) \cdot \exp(-k_2 t) + d \tag{5}$$

where, a is the contribution factor of microbiological parameter on chloramine demand, b is the contribution factor of chemical parameter on chloramine demand, c is the contribution of

combined effects of microbiological and chemical parameters, $d = C_0 \cdot x \cdot \exp(-2 \cdot k_1) + C_0 \cdot (1-x) \cdot \exp(-2 \cdot k_2)$, C_0 is the initial chloramine residual at time zero, x is the fraction of fast reacting agents in chloramine demand ($0 < x < 1$), k_1 is the fast reacting kinetic coefficient of chloramine demand, and k_2 is the slow reacting kinetic coefficient of chloramine demand.

As shown in Eq. (5), the model output is chloramine demand at different times. The initial concentration of chloramine, time, chemical (SUVA) and microbiological water quality parameters (F_m), measured from a 2-day chloramine decay test were used as inputs to the model. Model parameters such as fast and slow reacting kinetic coefficients of chloramine demand were estimated by regression analysis.

1.3.1. Model calibration and validation

Model calibration was performed by estimating selected parameters *via* nonlinear regression analysis of 70% of the experimental data from one of the water treatment plants of each water sources (~250 water samples). Model verification was conducted with experimental data from the other water samples, which had not been included in the regression analysis. Residual plots were used to check the validity and precision of the calibrated models. A multiresponse regression determinant criterion method was programmed in MATLAB 8.5 to calibrate the chloramine demand model with optimal parameters that best matched simulations with the experimental data based on minimization of the sum of the square of differences between the experimental data and the predicted values for the chloramine demand model (Bates and Watts, 1985). For validation, a plot of predicted values *versus* measured values was evaluated through statistical test analysis and the best fit line was determined from the coefficient and slope of the regression equation.

2. Results and discussion

2.1. Water quality characteristics of selected water samples

Water samples with a wide range of water quality characteristics were examined in this study as described in Table 1. It should be noted that all water samples used for this study were collected before disinfection. Some raw water samples before any drinking water treatment steps were used to expand the range of water qualities examined. The averaged value of water quality parameters for studied raw and treated (before disinfection) water samples is presented in Table 1.

2.2. Model calibration and verification

The model uses F_m, SUVA, time and initial chloramine dosage as independent parameters. The model parameters determined *via* nonlinear regression analysis based on 70% of water samples from Tailem Bend water treatment plant (T.B.WTP), Mundaring water treatment plant (M.WTP), and Maryborough water treatment plant (Ma.WTP) that are sourced from Murray River, Mundaring Weir, and Centenary Reservoir, respectively are shown in Table 2.

As it can be seen from Table 2, that water samples from Mundaring Weir (WA) have lower kinetic coefficient for fast reacting agents (0.01×10^4 (L/(mol·hr)) but higher kinetic coefficient for slow reacting agents (5.9 (L/(mol·hr)) in comparison with water samples from SA and VIC. WA water is partly treated water which includes desalinated water, and a small amount of local run-off, therefore compounds producing faster chloramine decay have been removed in the treated water to a greater extent than the other two sites using conventional treatment, as evidenced by a lower x (fraction of fast reacting agents in chloramine demand). In other words, the percentage of fast reactive sites in the NOM structure of WA water that can directly react with chloramine is less than water samples from SA and VIC. The values for the fraction of fast reacting agents (x) of the WA and SA samples were similar. In order to determine if there was any statistical difference in the fraction of fast reacting agents in chloramine demand (x) between WA water with water samples from Tailem Bend (SA), a two-sample t-test conducted, and t results are presented in Appendix A Table S2. The p-value of $\ll 0.05$ was obtained, showing that there is less than 5% chance that the two sets of x values from WA and SA are statistically the same. The t-value in this study is 6.03, and the critical t-value (the minimum t-value required to have p-value less than 0.05) is 2.09. Because the t-value is more than the critical t-value, it is concluded that the difference between the x values of WA and SA samples is significant. Less percentage of fast reactive agents (x), and also higher slow long-term reaction constant (k_2) in WA water implied that there is more reaction of free chlorine (HOCl) derived from monochloramine hydrolysis with NOM compared to water samples from SA and VIC (Duirk et al., 2002; Vikesland et al.,

Table 1 – The averaged value of water quality parameters for studied raw and treated (before disinfection) water samples.

Variable	Raw water samples			Treated water samples before disinfection		
	T.B.WTP (SA)	M.WTP (WA)	Ma.WTP (VIC)	T.B.WTP (SA)	M.WTP (WA)	Ma.WTP (VIC)
Turbidity (Nephelometric Turbidity Unit; NTU)	120 ± 5	80 ± 5	85 ± 5	0.150 ± 0.1	0.135 ± 0.1	0.175 ± 0.1
Conductivity (μS/cm)	480 ± 20	627 ± 20	553 ± 20	526 ± 20	688 ± 20	571 ± 20
Colour (Hazen Unit; HU)	55 ± 5	20 ± 5	35 ± 5	5 ± 1	2 ± 1	4 ± 1
UVA$_{254}$ (cm^{-1})	0.477 ± 0.05	0.312 ± 0.05	0.187 ± 0.05	0.095 ± 0.03	0.031 ± 0.01	0.085 ± 0.02
DOC (mg/L)	11.8 ± 0.2	6.31 ± 0.1	9.36 ± 0.1	5.25 ± 0.1	2.60 ± 0.1	4.95 ± 0.1
F_m	4.8 ± 0.2	4.01 ± 0.2	4.25 ± 0.2	0.67 ± 0.1	0.51 ± 0.1	1.23 ± 0.1

SA: South Australia; WA: Western Australia; VIC: Victoria; UVA: ultraviolet absorbance; DOC: dissolved organic carbon.

Table 2 – Coefficients of the proposed model of chloramine demand for water samples from T.B.WTP, M.WTP, and Ma.WTP.						
Model parameter	a	b	c	x	k_1 $((mol/L)^{-1}\cdot hr^{-1})$	k_2 $((mol/L)^{-1}\cdot hr^{-1})$
T.B.WTP (SA)	1.62	0.40	−0.48	0.85±0.03	$0.03\times10^4\pm0.005\times10^4$	4.2±0.05
M.WTP (WA)	1.74	0.53	−1.16	0.82±0.04	$0.01\times10^4\pm0.004\times10^4$	5.9±0.06
Ma.WTP (VIC)	1.95	0.35	−0.91	0.98±0.01	$0.11\times10^4\pm0.007\times10^4$	2.4±0.06

SA: South Australia; WA: Western Australia; VIC: Victoria.

1998). In order to check whether calculated model parameters (presented in Table 2) can predict chloramine demand of water samples from these three water treatment plants that were not included in parameter optimisation, the experimentally measured and predicted chloramine demand at different times for water samples with different water quality, collected at different seasons from 2011 to 2015, from T.B.WTP, M.WTP and Ma.WTP are compared (as shown in Fig. 1). The comparison shows that the model can predict the chloramine demand of water samples with different water quality ranging from raw water with high F_m value to filtered water with lower F_m over 18-day period. It should be noted that F_m value (microbiological effect) is high for raw water sample prior to any treatment process, therefore after three or four days the chloramine residual declined to zero. Once the chloramine residual is depleted, chloramine demand would remain constant over the time.

We hypothesise that there is no need to determine parameters of suggested model to predict chloramine demand at different times for water samples from different water treatment plants that have the same water source. To investigate this idea, water samples from other water treatment plants with different treatment methods, but with the same water sources were studied. In other words, based on the model parameters from T.B.WTP, predictability of chloramine demand for water samples from another water treatment plant (Morgan WTP (Mo.WTP)) that also draws raw water from the Murray River was investigated (Fig. 2).

As it can be seen from Fig. 2, the derived model for the Murray River sourced water is able to predict chloramine demand for water samples from Mo.WTP using the calculated model parameters based on T.B.WTP. It should be noted that

the model parameters taken from Mundaring Weir and Centenary Reservoir were not able to predict chloramine demand at different times for water samples from Mo.WTP due to the different water source. To further confirm that the model can be used to predict the chloramine demand for water samples from different water treatment plants with the same water source, the model was re-applied based on the model parameters from T.B.WTP to predict the chloramine demand for water samples from different water treatment plants on May 2011 (all of them draw their raw water from Murray River, Fig. 3).

According to Fig. 3, it can be concluded that once the model parameters have been determined for a set of water samples, the model can be applied to predict chloramine demand of other water samples that are sourced from the same raw water. However, different water sources in this study are shown to have different model parameters such as fast and slow reacting kinetic coefficients. Therefore, each water source should have a specific percentage of reactive fractions within the organic matter that exhibit reactivity directly with chloramine (for fast disinfectant demand) or HOCl from chloramine hydrolysis (slow long-term disinfectant demand).

2.3. Model validation via statistical data analysis

To determine how well the derived chloramine demand model fits the experimental data, a model validation is carried out. Model validation is a fundamental element to the modelling process and can often lead to the model being reformulated. In order to validate the model, analysis of independent set of data with ~60 water samples is performed. This involved collecting the new set of data and subsequently comparing the data with
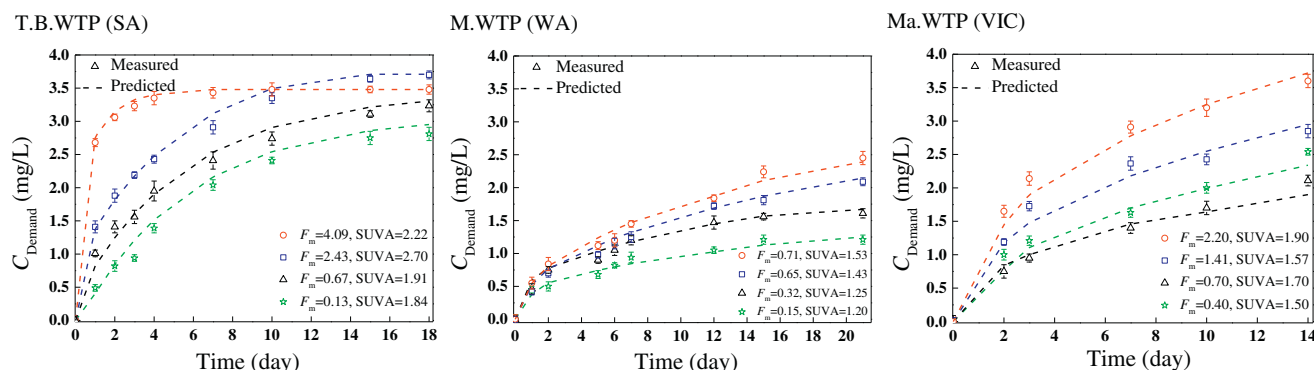
Fig. 1 – Experimental measured and predicted chloramine demand at different times for water samples with different water quality from three studied water treatment plants.
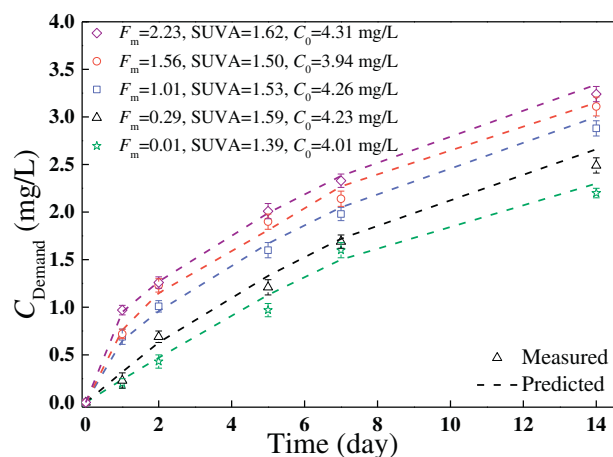
Fig. 2 – The water quality parameters, measured and predicted chloramine demand at different times from 2011 to 2015 for water samples from Morgan water treatment plant (WTP).

Fig. 4 – Correlation between the experimental and prediction model results for independent set of studied water samples (R^2 = 0.82).

the model predictions. Using independent set of data obtained from the same water source, the validation is performed through the examination of statistical test, as shown in Appendix A Table S3. Mean square error of prediction is a parameter of measuring the actual predictive capability of the model developed by using a new set of data. It was found that the chloramine demand model had a low prediction error. Fig. 4 illustrates that there was no significant difference between the experimental and predicted data for studied water sources. In general, the statistical coefficients of determination of the model appeared satisfactory (Appendix A Table S3). The R^2 (0.82), standard error of the estimate (0.0435) and the F value (37.799) of the model were found to be statistically significant.
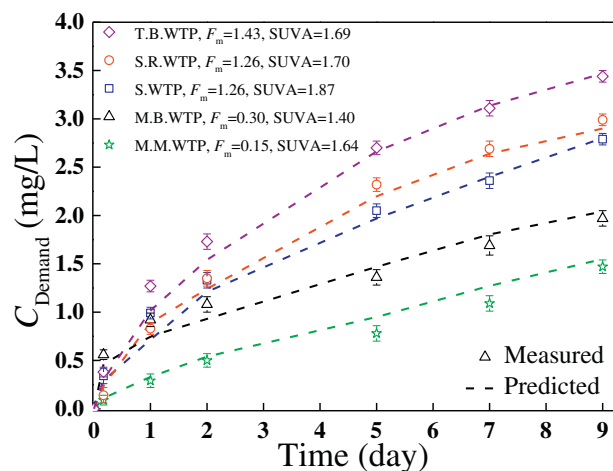

Fig. 3 – Comparison of the measured and predicted chloramine demand based on the model parameters from Tailem Bend water treatment plant (T.B.WTP) for water samples from different WTPs that are sourced from River Murray on May 2011.
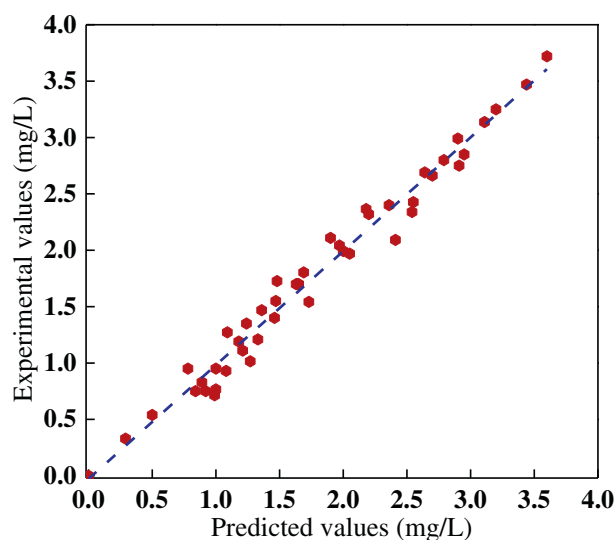
3. Conclusions

This study was conducted to derive a model to predict chloramine demand in water samples using chemical and microbiological parameters that impact on chloramine decay rate. Based on F_m, SUVA, time, and initial chloramine residual determined from 2-day chloramine decay tests, the model can be successfully applied to predict chloramine demand for various water samples from three different water sources, Murray River in SA, Mundaring Weir in WA, and Maryborough in VIC, Australia. The model can also be used to predict the chloramine demand for water samples from different water treatment plants that are sourced from the same water source using the same set of model parameters. Each water source should have a specific percentage of reactive fractions in the NOM that exhibit reactivity directly with chloramine (for fast disinfectant demand) or HOCl from chloramine hydrolysis (slow long-term disinfectant demand). To test the validity and applicability of this model, new set of data were analysed and compared to the predictive values. Validation results showed that there were no significant differences and the errors of prediction were low between the observed and the predicted data. The chloramine demand model could be useful for both the drinking water quality management and treatment plant operational management. In addition the model could be used as a guide in decision making to choose the appropriate strategies to reduce chloramine consumption and improve the disinfection process.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2017.01.010.

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