An Empirical Model for Bulk Chlorine Decay in Drinking Waters


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The current chlorine decay models involve complex calculations, and they are impractical for rapid chlorine dose/decay product calculations. This problem limits their applicability to treatment systems. Previously, less attention was paid to developing empirically based bulk chlorine decay models for predicting chlorine decay pathways. In order to bridge this gap, we developed a chlorine decay model based on kinetic data. The model was calibrated using well-characterized humic substances to simulate the natural organic matter content in water. Subsequently, the decay model was utilized to make chlorine decay predictions in the water of the Greater Kandy Water Treatment Facility, Sri Lanka. The chlorine decay predictions are in accordance with model calculations on a short-time scale (less than 5 h). Accordingly, it was noted that the chlorine dose of 1.6 mg/L was found to be inadequate for maintaining the mandatory residual chlorine balance at 0.2 mg/L at distribution. Furthermore, the reported average total of trihalomethanes (TTHMs) below 20 µg/L leaves room to increase the initial chlorine dose.

Key Words: empirical model, chlorine decay, residual chlorine, humic acid

1. Introduction

In drinking water systems, the water quality generally deteriorates due to the decay of disinfectants, which enhances the regrowth of microorganisms. On the other hand, the presence of chlorine and natural organic matter (NOM) also leads to the formation of disinfection byproducts, such as trihalomethanes (THMs), that require stringent regulation. THMs are well known for their toxic and carcinogenic activities1)-4).

However, chlorine is still used as a disinfectant in water treatment because of its high performance and oxidation capacity, which ensure a minimal level of residual chlorine throughout the distribution system, thus protecting against microbial recontamination1). Therefore, it is crucial to optimize the chlorine dosage at the treatment plant or boost chlorination points to ensure adequate chlorine residual while maintaining minimal or zero concentrations of THM. The proposed empirical model will provide a rapid method of predicting residual chlorine concentrations on a short timescale. The robustness and simplicity of the chlorine decay model were ensured by validating its performance against those of controlled natural samples.

Chlorine decay can mainly be categorized by two processes: bulk decay (reactions in the aqueous phase) and wall decay (reactions that occur on particulate/pipe wall surfaces). Due to a lower ratio of (water volume: wall area) treatment plant to service reservoirs, wall decay does not contribute significantly to the initial chlorine decay. Thus, bulk chlorine decay plays a major role until water reaches its distribution points.

For instance, in the water supply process, chlorine wall decay happens subsequently, whereas bulk decay occurs at the treatment plant and service reservoirs initially. For almost 20 years, numerical models have been available to generate hypothetical chlorine profiles and to compare alternative ways of achieving an adequate residual in a distribution system. By far, the most commonly applied chlorine bulk decay model is the (pseudo-) first-order model. It was based on the assumption that chlorine reacts with excess chlorine demanding reactants at a constant rate5)-6). However, recent studies have found that bulk decay was not strictly first order, and other alternatives have been presented7)-9).

Moreover, chlorine decay in single sources of bulk
water has been described by various mathematical models; however, these models have become increasingly complex\(^{(10)}\). Recently, numerical models to reduce complexity have been proposed with encouraging results\(^{(11,12)}\). However, providing a total solution for workers operating small-scale water treatment plants is not feasible due to the lack of highly technological instruments, specific knowledge, and training. Therefore, it is timely to investigate alternative methods to meet the stringent requirements.

To address this issue, we developed a simple empirical model of chlorine decay to determine the characteristics of chlorine decay as a function of time. However, it is important to note that bulk chlorine decay does not take place without light and organic matter in water. Thus, without light, only dissolved contamination (bulk) reactions are involved in decay. It is known that soil-derived humic materials are ubiquitous, comprising 40% to 60% of dissolved organic matter\(^{(3,14,15)}\). Therefore, we spiked the sample with well-characterized humic substances as the main precursor of chlorine decay. Validation of the empirical model was performed at the Greater Kandy Water Treatment Plant (location: 80.6203\(^{\circ}\)E, 7.3166\(^{\circ}\)N, hereafter referred to as GKWTP) located in Kandy, Sri Lanka.

It is also a prerequisite for accurately modelling associated disinfection byproducts, such as THMs, which are now strongly regulated. Water workers are required to invest substantial resources in controlling such byproducts with additional treatment or more intensive operations within the distribution system. Such measures are likely to be inefficient unless they are devised with the assistance of accurate chlorine modelling tools. Since no data of THM levels in GKWTP were available, TTHMs (totals of CHCl\(_3\), CHCl\(_2\)Br, CHClBr\(_2\), and CHBr\(_3\)) were studied in conjunction with the empirical model of chlorine decay.

### 2. Materials and Methods

All the experiments were conducted in year 2015. Laboratory experiments were conducted with chlorine, purified Sigma-Aldrich humic acid (SHA), and filtered water collected from conventional process of GKWTP before chlorination (i.e.; Conventional process; Aeration\(\rightarrow\) Conagulation\(\rightarrow\) Settling\(\rightarrow\) Rapid Sand Filtration\(\rightarrow\) Chlorination\(\rightarrow\) Distribution). The humic acid (SHA) fraction was used as an organic precursor; it was obtained in its proton form, freeze dried, and stored in a glass container. Several studies have reported the characteristics of this SHA. SHA reflects many characteristics normally found in naturally occurring humic substances. Vermeer et al. (1998) and Vermeer (1996)\(^{(19,13)}\) documented the characterized data of SHA. Elemental analysis on an ash-free basis of purified SHA is as follows (wt%): C\(\_\)55.8%, O\(\_\)38.9%, H\(\_\)4.6%, and N\(\_\)0.6%. The H:C ratio was 0.99; the O:C ratio was 0.52. The concentration of trace metals was below the detection limit of inductively coupled plasma (ICP) measurements. The concentrations of Si and P were much smaller than 0.01%. The characterized chemical total acidity of the humic acid was 5.00x10\(^{-3}\) mol/g, of which 3.70x10\(^{-3}\) mol/g consisted of carboxylic groups, and 1.30x10\(^{-3}\) mol/g consisted of phenolic groups.

As a first step, a series of SHA (as a measure of total organic carbon (TOC) concentration) was interacted with varying doses of free chlorine. According to previous data, the TOC concentration in water is around 5 mg/L; during periods of rain or conditions of faulty plant operation, this can increase to as much as 10 mg/L\(^{(19)}\)\(^{-25}\). Therefore, for the SHA reaction sequences of 1.0, 2.0, 4.0, 6.0, 8.0, and 10 mg/L (as TOC), solutions were prepared by dissolving an adequate amount of SHA in water.

To maintain the standard residual chlorine level of 0.2 mg/L at consumer end points, as recommended by the World Health Organization\(^{(22)}\) and Sri Lankan standards\(^{(23)}\), water workers use higher chlorine doses at the treatment plant, usually between 0.5 mg/L and 3.0 mg/L. Further, as a rule of thumb, chlorine was added to achieve residual chlorine values between 0.5 and 1.5 mg/L after contact times of 20 minutes. Therefore, by keeping in the 0.5 mg/L to 3.0 mg/L concentration range, SHA was chlorinated with a commercial solution of sodium hypochlorite (NaOCl, 4% active chlorine, Sigma-Aldrich). Reactions were performed in amber-colored glass reactors as a closed system at 25 \(^{\circ}\)C. At particular time intervals, samples were collected for THM and residual chlorine (RCl) measurements. Data were fitted with the empirical equation \(C_t = (C_0 - C)e^{-kt} + C/(1 + kt)\). The reaction series performed are summarized in Table 1. To simplify calculations constants were plotted as contours as a function of the initial chlorine dose and TOC.

### Table 1: Reaction series of SHA with chlorine

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>SHA concentration as TOC (mg/L)</th>
<th>Initial chlorine dose (mg/L)</th>
<th>Exp. no.</th>
<th>SHA concentration as TOC (mg/L)</th>
<th>Initial chlorine dose (mg/L)</th>
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<td>C-a</td>
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</tr>
<tr>
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<td>C-b</td>
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<td>A-c</td>
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<td>C-c</td>
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<td>A-d</td>
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<td>C-d</td>
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<tr>
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<td>C-e</td>
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<td>B-b</td>
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<td>D-b</td>
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<td>D-c</td>
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<td>B-d</td>
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For model validation, filtered water was collected from GKWTP before being subjected to disinfection. Water was stored in amber-colored glass bottles. Reactions with chlorine disinfection were performed in 500 mL amber-colored glass bottles at 25 °C in a closed system. By following the same chlorine dose (viz. 1.0 mg/L to 3.0 mg/L), filtered water was chlorinated. THMs and RCl values were measured at particular time intervals, and the data were used to validate the empirical model.

2.1 Materials and Reagents
Reference SHA (Sigma-Aldrich Chemie: code H1, 675-2) was purchased from Sigma-Aldrich (USA) in its proton form; it was freeze dried and stored in a glass container. HPLC-grade methanol of THM-certified standards (4S8746); analytical grades of NaOCl, HF, HCl, H2SO4, C8H5KO4, and Na2S2O3; and diethyl-p-phenylenediamine-1 (DPD-1) were also from Sigma-Aldrich (USA).

2.2 Analytical Method
The head space analysis method, as proposed by Kuivinen & Johnson (1999) was used for THM analysis using a dedicated headspace gas chromatography—electron capture detector system with a built-in auto sampler (Thermo Scientific Trace 1300 GC-ECD and TriPlus RSH autosampler) coupled with a capillary column (TRACE-TR5) under a split/splitless injector mode. The autosampler system consists of agitation and an incubation oven. Data processing and instrument conditions were set and monitored with dedicated software (Chromelion 7, version 7.2, USA). For TOC analysis, a 680 °C combustion, catalytic oxidation method developed by Shimadzu was used. A TOC analyzer (Shimadzu L series) coupled with a non-dispersive infrared (NDIR) gas analyzer was configured as described in Shimadzu (2015). Free chlorine was measured using the DPD-1 standard colorimetric method, 4500-C1 with a DR 5000 colorimeter (Hach, USA). pH was measured using a pH meter (Hach sensION+ pH3, USA). Sampling sites were identified using a Garmin global positioning system (Garmin eTrex, USA).

2.3 Sample Collection and Preservation
Water samples were collected from the GKWTP, service reservoirs, and distribution outlets for THM analysis. Since samples contained residual chlorine, a reducing agent, sodium thiosulfate (10 mg per 40-mL sample for up to 5 mg/L chlorine), was added to the empty amber-colored sample bottles prior to sampling. Samples were taken from cold tap water at the point nearest the main pipeline. Before sampling, tap water was allowed to run for 5 min, and sample bottles were filled without leaving a headspace. Free chlorine measurements were performed at the point of sample collection.

3. Results and Discussion

3.1 Empirical Model Development for Chlorine Decay
A chlorine decay model was developed that employed an SHA-mediated system. The experimental conditions were 25 °C and 6.9 pH in a closed system. Most suitable empirical equation was obtained by trial and error method with the several empirical equations. Equations were developed to meet the criteria where $t \to \infty$, $C_0$ goes to zero. The minimum number of variable constants were also considered. By referring $R^2$ values for the fitted curves, most suitable equation was selected. First and second terms were separated for simplification. As shown in the data, the chlorination decay behavior was modeled according to the equation shown below,

$$C_t = (C_0 - C)e^{-kt} + \frac{C}{1+kt} \quad (1)$$

where $C_t$ is the concentration of the substance at time $t$; $C_0$ is the initial chlorine concentration; $t$ is the time; and $k, C$ are empirical constants. The experimental data were used to optimize the empirical constants ($k, C$) goodness of curve fitting ($R^2$).

Fig. 1 shows the best-fit curves for the proposed empirical model used for 1 mg/L, 2 mg/L, 2.5 mg/L, and 3 mg/L initial chlorine dosing systems (Fig. 1 A–D). The variation of chlorine decay was examined as a function of TOC, and the results are shown by letters a–g in Fig. 1 for 10-, 8-, 6-, 4-, 2-, 1-, and 0.5-mg/L TOC concentrations, respectively. As shown in Fig. 1, steep slopes of chlorine decay took place within the first five h, which represents fast-reaction kinetics, followed by a decay rate transition to slow-decaying kinetics for as long as 5 h. The empirical model accounts for most of the observed patterns. However, in some cases, the experimental data showed no convergence. This is not surprising, since the reactive sites of SHA are largely heterogeneous. Furthermore, the empirical constants resulting from optimization are conditional to the initial chlorine dosing and TOC levels. Obtained empirical constants were summarized in Table 2.

Table 2: Summary of empirical constants

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>C</th>
<th>k</th>
<th>Exp. no.</th>
<th>C</th>
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For practical usage, as shown in Fig. 2, contour plots were constructed with respect to the chlorine dosing and TOC levels. Best-fit curve function empirical constants showed different values, correlations complicated by the initial chlorine dose and TOC concentrations. Thus, model calculations for different chlorine doses and TOC levels became more complex. In order to simplify the mathematical complexity, constants were separately plotted as contours (i.e., as a function of the initial chlorine dose and TOC concentration), which can be used as a tool (Fig. 2). Kriging interpolation method with defined boundary conditions (i.e., 0.5, 3.5/0.5, 10) were used to calculate contours. These contour plots can be used to determine the $k$ and $C$ empirical constants with respect to the water TOC level and initial chlorine dose. Once these parameters are known, the residual chlorine concentrations can be deduced at a specific time.

3.2 Validation of the Chlorine Decay Model
To validate the proposed empirical model, water collected from the GKWTP before chlorination (filtered water) was chlorinated (TOC value detected in the collected water was 3.16 mg/L) to the current operational chlorination range in the treatment facility (0.5 mg/L to 1.6 mg/L). Water chlorine and THM concentrations were measured continuously for 72 h (THM level is a limiting factor that must be adjusted with the chlorine dose). Fig. 3 summarizes the decay patterns with respect to the initial chlorine dose (thick black line). As seen in Fig. 2, $k$ and $C$ values were estimated for a 3.16 mg/L TOC level. Visual estimations from Fig. 2 can vary from person to person; therefore, the constant's upper and lower values, with the point (TOC 3.16mg/L) and chlorine
dose (0.6, 0.8, 1.0, 1.2, 1.4, 1.6, and 1.8 mg/L) laid between, were considered for calculations. The values of $k$ and $C$ were substituted in the empirical formula to plot the model decay curves. The dotted lines in Fig. 3 show the upper and lower estimated empirical curve functions of chlorine at the treatment plant other than the water itself; this allows better control of chlorine dosing at the treatment plant, which could reduce the formation of THMs.

Although the analyses from this study have been conducted for filtered water from the GKWTP, seasonal variations were not considered. The model predicts well chlorine decay up to 10 mg/L TOC and 3 mg/L residual chlorine. However, the assessment of model validity for other TOC and chlorine doses is required to understand variations of chlorine decay throughout the year.

**Fig. 3:** Observed and empirically modeled chlorine decay for filtered water (3.16 mg/L TOC level) (pH = 6.9, Temperature = 25°C)

3.3 Effective Use of a Chlorine Decay Model to Maintain Adequate Residual Chlorine by Minimizing THMs

Corresponding to chlorine decay in filtered water, TTHM formation was monitored during the empirical model validation in the absence of data. As TTHMs are a highly regulated material, it was essential to identify the minute differences in the byproducts formed. The formation of THMs is shown in Fig. 4. Accordingly, TTHMs do not exceed 15 µg/L at the 60-h contact time (WHO limit: 80 µg/L) with the maximum TOC concentration. To identify changes in the residual chlorine, THM residual chlorine levels and TTHM. According to Fig. 3, empirical model results for initial chlorine doses of 1.6 mg/L to 1.0 mg/L are in agreement with the actual chlorine decay patterns within the first five h of contact time. Thus, the decay of chlorine for initial chlorine doses of 1.6 mg/L to 1.0 mg/L levels is validated (GKWTP does not practice post chlorination since it does not have a lengthy distribution and contact time is less than 72 h). Therefore, residual chlorine levels after distribution only depended on the water treatment system’s initial chlorination; thus, the model above could be a good tool for estimating residual chlorine for an initial chlorination range of 1.6 mg/L to 1.2 mg/L.

Furthermore, the model output can also be used to find parameters that contribute to the consumption levels in the GKWTP, service reservoirs, and selected sub-water supply schemes were measured. (i.e., Contact time <5hr/higher demand and lower distance from the GKWTP). The Fig. 5 boxplot summarizes the TTHMs and residual chlorine in the GKWTP and selected sub water supply schemes (SWSS). Fig. 6 shows the spatial distribution of TTHMs in SWSS. According to Fig. 5 c), TTHM levels in the GKWTP after 20 min of contact time and 1.4 mg/L initial chlorine dose (TTHMs: -18.11µg/L) were higher than the experimental data shown in Fig. 4 b) (TTHMs: -3.16µg/L). The water temperature, changes in the initial chlorine dose, and the TOC concentration may contribute to the formation of higher TTHMs than in the experimental results. In the distribution, maximum retention times were less than two days; the increased contact time may contribute to the formation of more THMs. After 30 min of contact time for the treatment,
facility residual chlorine levels were between 0.60 mg/L and 0.80 mg/L. The empirical model calculations were given a reasonable value of 0.56 mg/L–0.76 mg/L (3.16 mg/L TOC and 1.4 mg/L initial chlorine dose).

Fig. 5: Boxplot analysis of GKWSS THMs and residual chlorine (NG: Nugawela; KL: Kulugammana; KH: Kahalla; AS: Asgiriya; KN: Konadeniya)

According to the empirical model values, a maximum initial chlorine dose of 1.6 mg/L was not sufficient to maintain a 0.2-mg/L residual chlorine level when contact time exceeded five hour (see Fig. 3 a). Therefore, increasing the initial chlorine dose at the treatment facility by monitoring THMs levels is recommended.

However, average TTHM concentrations in the distribution were lower than 20 µg/L; hence, the chlorine dose can be increased further. To obtain better results, seasonal variations with respect to THM formation should also be accounted for to assess a treatment facility’s performance throughout the year.

4. Conclusion

An empirical model was developed to assess bulk chlorine decay in water spiked with SHA at short time intervals. Contour plots can effectively be used to estimate empirical parameters with sufficient accuracy in short-term (5 h<) bulk chlorine decay in the range of 1.6–1.2 mg/L at the Greater Kandy Water Treatment Facility. An initial chlorine dose between 1.6 and 0.5 mg/L was not sufficient to maintain residual chlorine levels of 0.2 mg/L.

Comparing the TTHM formation values during the filtered water chlorination at the treatment plant and TTHM distribution levels, the observed TTHM levels than the experimental values. Particularly, the reported average TTHM level (20 µg/L<) leaves room for

Fig. 6: Spatial Distribution of TTHMs in SWSS
increasing the initial chlorine dose to meet the adequate residual. Although the analyses from this study have been conducted for filtered water from the GKWTP, seasonal variations were not considered. The model predicts well chlorine decay up to 10 mg/L TOC and 3 mg/L residual chlorine. However, the model validity for other TOC and chlorine doses must be assessed to understand variations of chlorine decay throughout the year.

Acknowledgments

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