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Chlorine dioxide bulk decay prediction in desalinated drinking water

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HIGHLIGHTS

- We propose a novel empirical mathematical model for chlorine dioxide decay prediction.
- Model covers decay at a wide range of both temperature and ClO_2 concentrations.
- Model provides an unprecedented opportunity to properly design disinfection systems.
- Model verifications indicate good agreement between calculated and measured values.

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ABSTRACT

Chlorine dioxide is one of the most promising disinfectants though usually used as a secondary disinfectant. Several studies addressed the decay rate of chlorine while no study so far tackled the chlorine dioxide decay. This work provides a novel mathematical equation for chlorine dioxide decay prediction in desalinated water.

The study was performed at five different chlorine dioxide dosages; 1.4, 1.2, 1.0, 0.8 and 0.6 mg/L (to cover the most frequently used dosages within both production facilities "as primary disinfectant" and/or the distribution system "as secondary disinfectant"). Each dosage had been tested at four different temperatures; 20°, 27°, 35° and 45 °C.

To confirm the validity of the proposed decay rate model/equation, site verification was performed (real concentration vs. predicted concentration) and then t-test formula was used to indicate the similarity of both test results.

As an overall conclusion, the study's proposed a novel model/equation that shows reasonable levels of robustness. Furthermore, it covers the chlorine dioxide decay at a wide range of temperature profiles as well as a wide range of chlorine dioxide initial concentration dosages.

The proposed model provides an unprecedented opportunity to more realistically plan and model distribution systems to achieve disinfection; among other water quality; goals. Network modelling software such as EPANET provides the platform where the proposed chlorine dioxide decay model can be implemented. Moreover, the model can aid in the decision variables (design, placement, number of stations and operation control & operation optimization) for disinfection boosters in water distribution systems.

1. Introduction

Drinking water is generally disinfected to protect public health. The goal of secondary disinfection is to maintain a disinfectant residual throughout the distribution system. This allows for a nominated residual even at system extremities [1]. This provides some degree of protection against contamination, as well as limits bacterial re-growth [2].

Chlorine dioxide is an oxidant that can be reduced in a variety of ways, depending on the system conditions and the nature of the reducing agent [3]. Chlorine dioxide (ClO_2) demonstrated promising behavior as a secondary disinfectant in full-scale distribution systems [4].

Several studies using chlorine dioxide as a secondary disinfectant in a full-scale distribution system [4] have shown that residuals can be maintained throughout these specific systems, without booster stations. Other studies [4] have demonstrated the opposite, being that residuals disappear at the ends of the system without booster addition. Residuals decrease faster as the water temperature increases and the size and complexity of the distribution system increases.

Chlorine dioxide decay in the distribution system is the result of auto-decomposition reactions and reactions with organic and inorganic compounds, including biofilms, pipe materials, and scales. Chlorine dioxide is also subjected to photolytic decomposition [5].

The immediate redox reactions with natural organic matter play the dominant role in the decay of chlorine dioxide into chlorite in drinking water [6]. Chlorite ion is generally the primary product of chlorine

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dioxide reduction. The distribution of chlorite and chlorate is influenced by pH and sunlight. Approximately 50 to 70% of the chlorine dioxide consumed by oxidation reactions is converted to chlorite under conditions typical in water treatment [6,7]. Ultraviolet light and even fluorescent lights can lead to photolysis [8,9].

Numerous inorganic and biological materials found in raw water will react with chlorine dioxide [10]. The concentration and types of various chemical and biological constituents that exert a chlorine dioxide demand, as well as the temperature variance, will both impact the decay coefficient. The decay coefficient for specific bulk water can be determined using bottle decay tests. The coefficient for pipe wall decay however, must be determined in the field or with pipe segments taken from the distribution system piping. Overall, the relative importance of decay at the pipe wall increases as the pipe diameter decreases because the ratio of water volume to pipe surface area decreases [11–20].

Based on the order of the reaction, the mathematical form for alternative decay models can be proposed as [11–20]:

$$\text{Zero order reaction}: \quad [A]_t = -kt + [A]_0$$

$$\text{First order reaction}: \quad [A]_t = [A]_0 \ \exp(-kt).$$

Where:

$[A]_t$	Concentration of disinfectant in mg/L at time t
$[A]_0$	Initial concentration of disinfectant in mg/L at $t = 0$
t	Time in days
k	Decay coefficient day^{-1}
n	Order of reaction.

Given that several studies addressed the decay rate of chlorine while no study so far tackled the chlorine dioxide decay, the objective of this work was to determine an empirical predictive novel model for chlorine dioxide bulk decay prediction in desalinated water over both a wide range of temperatures and a wide range of chlorine dioxide concentrations.

2. Materials and methods

2.1. Sampling bottle selection, preparation and cleaning

1.0 l amber glass bottles were used. As laboratory glassware can potentially exhibit a demand for chlorine dioxide which could bias the analytical results and lead to poor accuracy and/or precision, all bottles were thoroughly cleaned with soap and water and rinsed several times with reagent water. Vials (without caps) were dried in an oven at 140 °C.

2.2. Standard chlorine dioxide solution [21]

Since chlorine dioxide is a relatively unstable gas, it cannot be compressed and liquefied, and must, therefore, be generated "on-site" and dissolved in water.

Today's technology utilizes chlorite and hydrochloric acid reactions to produce chlorine dioxide through a system called: "Chlorine dioxide under water generating system" (manufactured by ISIA®). As this special generator works "under water", the formation of chlorine dioxide takes place in water only, limiting the possibility for chlorine dioxide to be released from the water. For that reason it is often times considered 100% safe fulfilling the most diversified requirements in terms of usage, safety, reliability, yield, purity of ClO_2 solution and ease of conduction. This system was used to get a chlorine dioxide solution.

The generated chlorine dioxide solution was used for preparing the temporary chlorine dioxide standards to the desired strengths and the solution was stored in a refrigerator at 4 °C (±0.5 °C). For standardization, the Iodometric Method (4500 ClO_2-B) was used.

2.3. Raw water source [21]

Given that the raw water should contain zero levels of chlorine dioxide but also should represent water in the distribution system, that being, re-mineralized desalinated water, before the addition of any disinfectant; was selected.

2.4. Chlorine dioxide concentration and temperature testing profile

Bulk decay may be isolated from wall decay by carrying out chlorine decay experiments on the source water under controlled conditions in the laboratory. In order to investigate the effects of chlorine dioxide concentration and water temperature on the bulk decay, experiments were carried out at five different chlorine dioxide concentrations; 1.4, 1.2, 1.0, 0.8 and 0.6 mg/L. Each concentration was tested at four different temperatures; 20°, 27°, 35° and 45 °C. Those specific temperatures were maintained by incubating the 1.0 l amber glass bottles. The five different chlorine dioxide concentrations were selected to cover the most frequently used dosages within both production facilities "as primary disinfectant" and/or the distribution system "as secondary disinfectant" while the four temperature regimes were selected in order to ascertain the relationship between the bulk decay coefficient and water's temperature so that appropriate values for the winter and summer condition simulations are derived.

The chlorine dioxide concentrations were measured on duplicate sub-samples using ChlorodioXense® instrument with disposable amperometric sensors (the US EPA's approved instruments). The accuracy of the instrument was checked regularly against the standards set provided by the manufacturer and were always found to be within the acceptable tolerance level.

2.5. Experiment

One bulk raw water sample (50 L) was collected and the following procedure was performed at the five different temperatures:

Five blank samples were prepared and then dosed with the standardized chlorine dioxide (prepared from the on-site generator) to attain 1.4, 1.2, 1.0, 0.8 and 0.6 mg/L in the five bottles respectively. The chlorine dioxide concentration promptly measured at each bottle and the time was registered as the zero time.

2.6. Bulk decay coefficient estimation & model verification

For each temperature (20°, 27°, 35° and 45 °C), five graphs were plotted illustrating the chlorine dioxide concentration (mg/L) variance "until non-detectable levels" vs. time (hrs) at each dosage. The natural logarithmic for chlorine dioxide concentrations was calculated to estimate the bulk decay coefficient (K_b). Several types of trend line were examined to choose the type of trend line most appropriate to the results. The best fit trend line type was chosen based on the highest R^2 (Pearson Coefficient of Determination). Then, model's precision was verified vs. samples collected (within

Table 1
Site parameter results for the raw water.

Parameter	Unit	Result
Temperature	°C	39
pH	–	7.9
Electrical conductivity (EC)	μS/cm	164
Turbidity	NTU	0.1
Chlorine dioxide	mg/L	ND