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Quantifying chlorine-reactive substances to establish a chlorine decay model of reclaimed water using chemical chlorine demands

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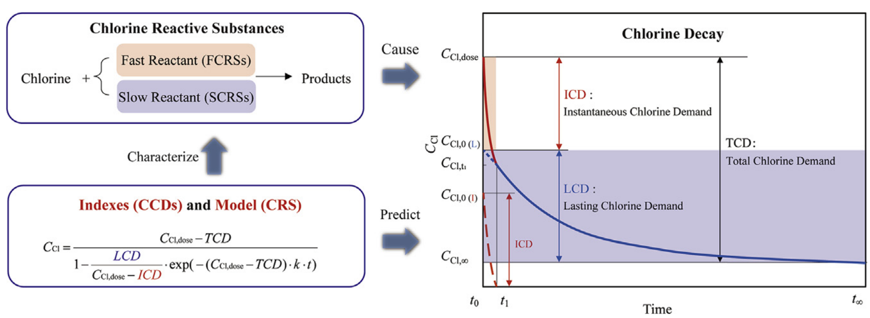
HIGHLIGHTS

- Chlorine-reactive substances (CRSs) were quantified by chemical chlorine demand (CCD).
- The CRS model was established to predict chlorine decay of reclaimed water.
- The data fitting results of this model were promising for reclaimed water samples.
- Key independent parameters of the model was related to chlorine consumption and UV_{254}.
- Chlorine decay of reclaimed water was predicted precisely by measuring water quality.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to guarantee the water quality of reclaimed water in pipeline system, a chlorine bulk-decay model is required for simulation and prediction of chlorine profiles in networks. Conventional chlorine decay models of drinking water are not applicable to reclaimed water due to its complex and varying water quality. In this study, the chlorine decay of reclaimed water was investigated under different operational conditions. Based on these results, different chlorine-reactive substances (CRSs) in reclaimed water were quantified by total chlorine demand (TCD), instantaneous chlorine demand (ICD) and lasting chlorine demand (LCD), respectively. A stoichiometric model (CRS model) of chlorine decay of reclaimed water was established using ICD, TCD and reaction rate constant (k) as key independent parameters. The experimental data were fitted to the CRS model with promising results under various initial chlorine concentrations (3–10 mg-Cl_2/L) and temperatures (8–35 °C). The ICD, TCD and k of different reclaimed water samples were in the range of 0.23 to 2.85 mg-Cl_2/L, 1.07 to 4.73 mg-Cl_2/L, and 0.04 to 4.06 L/(mg·h), respectively. Furthermore, the ICDs, TCDs and k could be determined directly by measuring the chlorine consumption at 5 min ($\Delta C_{Cl,5min}$) and 8 h ($\Delta C_{Cl,8h}$) after the addition of chlorine into reclaimed water, and the UV_{254} of reclaimed water, respectively. The relationships between ICD, TCD, k and the

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corresponding water quality indexes were further validated. In this way, the chlorine decay profile of reclaimed water could be predicted rapidly and precisely by measuring the $\Delta C_{Cl,5min}$, $\Delta C_{Cl,8h}$, and UV_{254} of reclaimed water.

1. Introduction

Wastewater reclamation and reuse is an effective way to solve the problem of water shortage. Reclaimed water such as high-quality secondary effluent which meets the corresponding national standards is widely reused in many ways in Beijing, China, including flushing, landscape and scenic environmental use [1]. Compared with drinking water, reclaimed water contains a larger amount and wider variety of harmful microorganism and pollutants, which might expose the users of reclaimed water to more potential risks. Maintaining a minimum concentration of disinfectants is a practical way to guarantee the safe reuse of reclaimed water [2]. Chlorine is commonly used in pipe networks to control microbial regrowth. Therefore, many countries and regions have issued relevant regulations to guarantee the chlorine concentration in or at the end of reclaimed water pipes [3]. For reclaimed water suitable for urban miscellaneous reuse in China, chlorine concentration should exceed 1 mg-Cl_2/L after 30 min retention in chlorine contact tanks, and 0.2 mg-Cl_2/L at the outlet of pipe networks [4].

However, compared to drinking water distribution, chlorine decays more rapidly in reclaimed water pipes, making it a challenge to maintain the residual chlorine concentration throughout the distribution system. It is important to understand the kinetics of chlorine decay and to be able to predict the chlorine concentration in pipe networks. Therefore, a suitable chlorine decay model is required.

In general, the overall decay of chlorine within a pipe system involves bulk decay and pipe wall decay. In reclaimed water, pollutants with high concentration in the bulk water performs more important roles in consuming residual chlorine. Thus, this study mainly focuses on the bulk decay of chlorine.

In the study of bulk decay in drinking water pipe networks, a pseudo first-order model [5–7] is firstly proposed to simulate the decay curves. Alternative excessive reactants models are the pseudo second-order model [8], pseudo n-order model [7,8] and parallel first-order model [7,9]. It is worth mentioning that since these models are based on the assumption that the reactants with chlorine are excessive, the decay rate depends only on the concentration of chlorine in the apparent kinetic equation. However, even in reclaimed water the reactants with chlorine are not excessive enough in most cases, because residual chlorine decay but still can be detected in reclaimed water even after a long reaction time.

Furthermore, investigations have also been done to determine the functional relationships between the pseudo reaction rate constant (k) and conventional water quality indexes, such as total organic carbon (TOC), dissolved organic carbon (DOC), UV absorption, Exciting-Emission-Matrix (EEM) fluorescence intensity, initial chlorine, NH_4^+ concentration, temperature and pH value. The more organic matters bring more kinds of chlorine-reactive substances, so that the k of reaction of chlorine and reactants was increased [10–12]. The k was effected by temperature with Arrhenius equation generally [10,12]. The higher concentration of NH_4^+ changes more free chlorine into combined chlorine which has slower reaction rate, so that decreases the k of reaction of chlorine and reactants [13]. However, the effects of factors are so complicated that the relationship between the conventional indexes and the parameters of the models is applicable only under certain simple water quality conditions and there is no universal quantitative method to describe them clearly.

Other chlorine decay models are limited reactants models, which are based on the assumption of reactions between chlorine and limited fictive reactive components, including single reactant (SR) second-order model [14], two reactants (2R) second-order model [10,15,16], and variable rate coefficients model [11]. Several fictive chlorine-reactive components were proposed and needed to be calculated in these models, making the limited reactants models much more complicated compared with the excessive reactants models [17]. Though these models are much more accurate in predicting chlorine decay curves of drinking water. The concentration of the fictive reactive components cannot be measured directly, which means all the parameters in these models need to be obtained by fitting the experimental data to these models, or some parameters might be omitted to simplify the model [16]. Thus, these models are only practical to predict chlorine decay in drinking water distribution system with simple and stable water quality. When the water quality changes frequently and complicatedly, the parameters obtained by model fitting under certain water quality might not be applicable.

To simulate chlorine decay under changeable water quality conditions, parameters of the chlorine decay models in drinking water usually contain DOC, UV_{254}, NH_4^+-N and other conventional water quality indexes [11,18]. However, these indexes are not sufficient to describe the complexity of water quality in reclaimed water. Furthermore, these indexes cannot characterize the substances reacted with chlorine directly.

Compared with the studies in drinking water, research on chlorine decay of reclaimed water is limited. Using the theories in drinking water for reference, the pseudo first-order model [7] has been applied in reclaimed water pipe network after reverse osmosis (RO) system [19]. However, RO effluent is just one type of reclaimed water with few pollutants, which cannot be considered as the representative of all types of reclaimed water. For flushing, landscape and scenic environmental use, secondary effluent is more widely used and more economical. Chlorine decay model specific for secondary effluent and some other types of reclaimed water has not been established yet. What's more, the quality of reclaimed water are essentially different from drinking water. The substances able to react with chlorine are generally more varied and abundant in reclaimed water. So the applicability of the chlorine decay models mentioned above requires investigation. Further study on chlorine decay of reclaimed water is necessary.

In this study, the substances that can react with chlorine in reclaimed water are defined as chlorine-reactive substances (CRSs). To establishing a practical chlorine decay model of reclaimed water, the key is to find suitable and measurable indexes to characterize and quantify CRSs and integrate the indexes with the model.

The main objective of this study was to investigate the chlorine bulk decay of reclaimed water samples with different water quality. Based on the data analysis, a series of indexes were proposed to directly characterize and quantify CRSs in reclaimed water. Furthermore, a promising model using these indexes as key parameters was established and validated.

2. Materials and methods

2.1. Water samples

A total of 38 secondary effluent samples were collected from four (A, B, C and D) wastewater treatment plants (WWTPs) in Beijing, China. Secondary effluent water which satisfying standard can be used as reclaimed water for landscaping or agriculture [20,21]. Membrane bioreactor (MBR) technology was used in plant A and D, and Anaerobic-Anoxic-Oxic (AAO) technology was used in plant B and C. In each WWTPs, 8 to 12 samples were collected. For a better control of types and doses of disinfectants, samples were collected before the addition of