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Chlorine Reactivity with Organic Matter: A Modelling Approach for Surface Waters in Portugal and Angola

Ramiro J. E. Martins[1]
[1]Technology and Management School, Bragança Polytechnic University, 5300-253 Bragança, Portugal. Centro de Investigação de Montanha (CIMO) and Laboratório Associado para a Sustentabilidade e Tecnologia em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, Bragança, 5300-253, Portugal.
rmartins@ipb.pt

Abstract— *Water quality is an essential requirement for human consumption. One of the key quality criteria is the absence of bacterial contamination, necessitating disinfection as the final step in water treatment, which is commonly achieved through chlorination. During chlorination, chlorine is consumed through the oxidation of the organic compounds present in water. This study focused on examining chlorine consumption in raw water from the Bengo River (Angola) and water at the outlet of the Lever Water Treatment Plant (Portugal). Specifically, the decay kinetics of chlorine in water samples were investigated through a series of experiments. In the first series, the chlorine concentration was varied while maintaining a constant level of organic matter (expressed as oxidability using* $KMnO_4$*) at temperatures of 25 and 35°C. In the second series, the chlorine concentration was held constant while the oxidability varied. Various kinetic models have been applied to the experimental data to describe the decay of chlorine and organic matter. The parallel first-order model yielded the most satisfactory representation of chlorine consumption kinetics.*

Keywords— *chlorine consumption, organic matter oxidation, surface water, water quality*

INTRODUCTION

Water is an essential element in all forms of life, particularly in humans. It plays a vital role in a wide range of human activities, including public and industrial water supply, agriculture, electricity generation, recreational pursuits, and preservation of aquatic ecosystems (World Bank, 2020; United Nations, 2019). As the quality of life of populations has improved, there has been an increasing focus on essential resources. Water, once considered virtually limitless, has now become a critical resource that requires preservation. This shift in mindset has prompted heightened concern regarding water quality. The sources and origins of water have undergone significant changes over the past several decades, primarily owing to rapid industrial development and agricultural practices. These changes have led to notable alterations in the water quality parameters. For instance, the expansion of agricultural activities near water sources has raised concerns regarding potential pesticide contamination. Agriculture is a significant contributor to environmental pollution and is often associated with the introduction of various pollutants (Grutzmacher et al., 2008).

Several rivers and springs in Angola serve as water sources for human consumption in different cities across the country. In the capital city, the two main rivers supply water to the city. Water in Rio Bengo is treated at the Kifangondo Water Treatment Plant, located in the northeastern part of the capital, in the municipality of Cacuaco. The Rio Kwanza's water is treated at the Kikuxi Water Treatment Plant, situated southeast of Luanda, in Viana. In Portugal, the study focused on the Douro River, specifically on the water at the outlet of the Lever Water Treatment Plant (Águas do Douro e Paiva, SA), which supplies the municipalities of Porto and Vila Nova de Gaia, among others.

Water quality plays a crucial role in ensuring suitability for consumption. An essential requirement is the absence of bacteriological contamination, which necessitates water disinfection. Chlorination is a widely adopted method that is typically employed as the final step of the treatment process. During chlorination, chlorine is consumed through the oxidation of the organic compounds present in water. In addition, chlorine is consumed through reactions in the distribution system.

In Water Treatment Plants (WTPs), the pre-oxidation of surface waters with chlorine or sodium hypochlorite is employed to enhance subsequent treatment processes, with particular emphasis on the chemical coagulation/flocculation process (Hidayah et al., 2019). This pre-oxidation step contributes to improving the overall performance and effectiveness of the treatment process, ensuring the removal of contaminants, and enhancing water quality for consumption.

The added chlorine undergoes a series of chemical reactions with naturally occurring organic substances, predominantly humic and fulvic substances, that originate from bacterial activity on lignites and tannins found in plant organisms. These organic compounds, particularly humic acids, exhibit higher reactivity than fulvic acids, resulting in a reduction in their initial concentrations during the chlorination process. Consequently, the presence of chlorine leads to the formation of oxidation by-products, with trihalomethanes (such as chloroform, dichlorobromomethane, chlorodibromomethane, and bromoform) being the most notable. Trihalomethanes are known to pose potential health risks and therefore require quantification and control measures to ensure water safety (Sadeghi et al., 2019; EPA, 2011).

Therefore, it is important to understand the chlorine consumption rate in surface waters subjected to pre-oxidation (Paschoalato et al., 2008) in order to design pre-chlorination tanks and calculate the appropriate chlorine dosage for application. The chlorine consumption rate depends on water composition, initial chlorine concentration, temperature, and other factors. Through laboratory experimental results, it is possible to select, among various models commonly used for chlorine decay (Kohpaei and Sathasivan, 2011), models that adequately model the evolution of chlorine concentration. This selected model, along with known kinetic parameters, can then be used to size a pre-chlorination unit.

The organic matter content in water treated through chemical coagulation/flocculation is generally quite low, which poses challenges in studying the kinetics of chlorine consumption. However, chlorine is often used in the initial step of direct pre-oxidation of raw surface water.

The main objective of this study was to investigate the decay kinetics of chlorine in water samples from two different sources: the Bengo River (Angola) and the outlet of the Lever Water Treatment Plant (Portugal). The specific objectives were as follows: (1) fitting different kinetic models to the experimental data of chlorine decay in water samples, (2) comparing and selecting the most appropriate model, and (3) assessing the influence of temperature on the kinetic parameters.

1. MATERIALS AND METHODS

2.1 Samples

The surface water used in this study was collected from the Bengo River near the Kifangondo Water Treatment Plant in Luanda, Angola. It was then transported in 5 L containers to the Laboratory of Separation Engineering, Chemical Reaction, and Environment at Agostinho Neto University (LESRA), where the experimental tests were conducted. The samples were stored in a refrigerator at 4°C until laboratory experiments were performed. For the tests in Portugal, the samples were collected at the outlet of the Lever Water Treatment Plant before the final disinfection (chlorination), following a procedure similar to that described above.

2.2 Analytical methods and reactants

The residual chlorine in the water samples was determined using the titration with ammonium ferrous sulfate (DPD) method, as outlined in the Standard Methods for the Examination of Water and Wastewater (APHA, 2022).

To quantify the amount of organic matter present in the raw water samples, the oxidability by $KMnO_4$ was measured. The volumetric oxidation-reduction method was employed, where the oxygen equivalent to the organic matter was assessed by the consumption of a potassium permanganate oxidizing agent.

For the experiments, a sodium hypochlorite stock solution was prepared by diluting bleach with 5.25% NaOCl, resulting in a final concentration of 64.3 mg Cl_2 L^{-1}.

Solutions of ammonium ferrous sulfate (FAS), phosphate buffer, and N, N-diethyl-p-phenylenediamine (DPD) indicator were prepared according to the instructions provided in the Standard Methods (APHA, 2022).

2.3 Chlorine decay models

In recent years, considerable research has focused on chlorine consumption in both surface water and drinking water, resulting in the development of various models to characterize chlorine decay (Liu et al., 2020; Zhang et al., 2020; Xie et al., 2019; Charron and Sadiq, 2019; Li et al., 2018). The modeling of chlorine decay aims to understand the changes in chlorine concentration over space and time, accounting for its physical movement and the chemical reactions it undergoes with other species present in the solution.

In this study, the following models were chosen to investigate chlorine decay:

a) Pseudo second-order model

$$C = C_0/(1 + C_0 . K . t) \quad (1)$$

b) Limited first-order model

$$C = C^* + (C_0 - C^*) . e^{-kt} \quad (2)$$

c) Parallel first-order model

$$C = C_0 . x . e^{-k_1 t} + C_0 . (1 - x) . e^{-k_2 t} \quad (3)$$

where:

C; chlorine concentration at time t (mg L^{-1})
C_0; initial chlorine concentration (mg L^{-1})
C^*; initial residual chlorine fraction that does not react (mg L^{-1})
k; kinetic decay constant (min^{-1})
k_1; velocity constant (min^{-1})
k_2; velocity constant (min^{-1})
K; kinetic decay constant (L mg^{-1} min^{-1})
x; fraction of initial chlorine

2.4 Experimental procedure

The decay of chlorine due to reactions occurring within the water was studied using the so-called "bottle test," which allows for the evaluation of the effects of reactions occurring solely within the water. Water samples with known initial chlorine concentrations were introduced into Winkler bottles, and chlorine measurements were performed at predetermined time intervals to assess the kinetics of the reactions.

In the first experiment, the initial chlorine concentration was varied while maintaining the initial organic matter concentration constant. The second experiment consisted of a series of tests with a constant initial chlorine concentration, while varying the initial organic matter concentration. All experiments were conducted in duplicate at two different temperatures, 25°C and 35°C. The methodology used for the bottle tests was adapted from Costa et al. (2021).

2.RESULTS AND DISCUSSION

3.1 Chlorine concentration 0.65 – 4.7 mg Cl_2 L^{-1} (T = 25ºC)

Four experiments were conducted at 25°C, with variable initial chlorine concentrations ranging from 0.65 to 4.7 mg Cl_2 L^{-1}, while maintaining a constant initial organic matter concentration (initial oxidability of 4.6 mg O_2 L^{-1}). The objective of these experiments was to study the decay of residual chlorine in water from the Bengo River over a specific period of time. The experimental results obtained at predetermined time intervals are listed in Table 1. Additionally, for the experiments conducted with water from the Lever Water Treatment Plant (LWTP), only the conclusions are discussed.

The purpose of these experiments was to determine the kinetic rate constants for the decay of chlorine in water, thereby accurately predicting the rate at which reactions occur between chlorine and the organic matter present in raw water.

Table 1 Chlorine residual concentration as a function of time (initial chlorine concentrations 0.65 to 4.7 mg Cl_2 L^{-1}; oxidability = 4.6 mg O_2 L^{-1}; T = 25ºC).

Time (min)	C (mg Cl_2 L^{-1})			
	C_0 = 0.65	C_0 = 1.3	C_0 = 2.7	C_0 = 4.7
pH	7.5	7.6	7.5	7.6
0	0.65	1.3	2.7	4.7
3	0.20	0.60	1.55	2.9
6	0.15	0.40	1.50	2.4
9	0.05	0.30	1.25	2.2
12	0.02	0.25	1.20	2.1
15	0.02	0.20	1.20	2.05
20	0.02	0.15	1.10	1.95

In this study, the evaluated models (pseudo first-order, limited first-order, and parallel first-order) were fitted to the experimental data using the non-linear optimization software KaleidaGraph version 4.1.3 from Synergy. The obtained values for each kinetic model parameter, along with the statistical parameters, such as the coefficient of determination (R^2) and estimated variance (S^2), are provided in Tables 2 to 4.

Table 2 Parameters of the pseudo second-order model.

C_0 (mg Cl_2 L^{-1})	K ± SE	R^2	S^2
0.65	1.284 ± 0.199	0.986	2.15xE^{-2}
1.3	0.289 ± 0.004	0.999	8.99xE^{-2}
2.7	0.0429 ± 0.0069	0.874	0.307
4.7	0.0248 ± 0.004	0.895	0.932

Table 3 Parameters of the limited first-order model.

C_0 (mg Cl_2 L^{-1})	C^* ± SE	K ± SE	R^2	S^2
0.65	0.025 ± 0.017	0.365 ± 0.049	0.986	2.87xE^{-2}
1.3	0.194 ± 0.058	0.302 ± 0.026	0.994	9.52xE^{-2}
2.7	1.191 ± 0.138	0.393 ± 0.073	0.975	0.164
4.7	2.035 ± 0.086	0.354 ± 0.021	0.997	0.528

Table 4 Parameters of the parallel first-order model.

C_0 (mg Cl_2 L^{-1})	x	k_1	k_2	R^2	S^2
0.65	0.57	0.191	1.000*	0.997	2.65xE^{-2}
1.3	0.41	0.064	0.514	0.999	8.93xE^{-2}
2.7	0.59	0.019	0.926	0.995	0.140
4.7	0.50	0.009	0.444	0.999	0.505

* no statistically significant

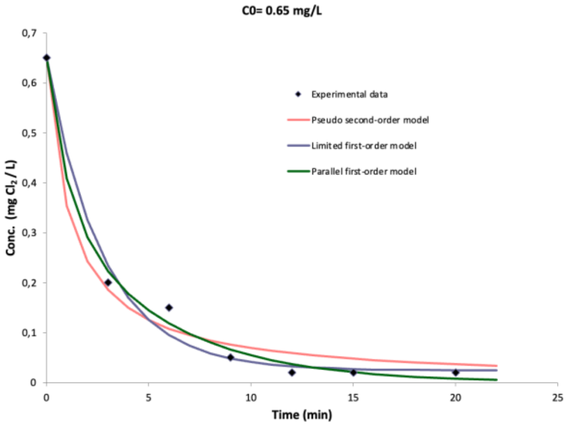
The chosen maximum duration for the experiments proved to be appropriate; after 20 min, the results indicated that the free residual chlorine concentrations stabilized at an approximately constant value. A similar trend was observed for the samples from LWTP, where, starting with an initial chlorine concentration of 0.64 mg L^{-1} (TOC = 4.53 mg L^{-1}), approximately 80% of chlorine decay occurred within 20 minutes.

An analysis of the parameters and their respective standard errors reveals that there is a single experiment (Table 4; C_0 = 0.65 mg L^{-1}) in which one parameter (k_2) was not statistically significant.

Figure 1 (a-d) present the experimental results for the four initial chlorine concentrations studied, along with the kinetic models depicting the decay of chlorine in water.

Table 5 presents the F values obtained from the comparison of the three models: pseudo second-order model (P2), limited first-order model (PL), and parallel first-order model (PP).

Except for the experiment for C_0 = 0.65 mg L^{-1}, where statistically insignificant values were obtained for some parameters of the PP model, the parallel first-order model was the best fit for the experimental data (F calculated > 1), confirming the earlier conclusions based on the R^2 values.



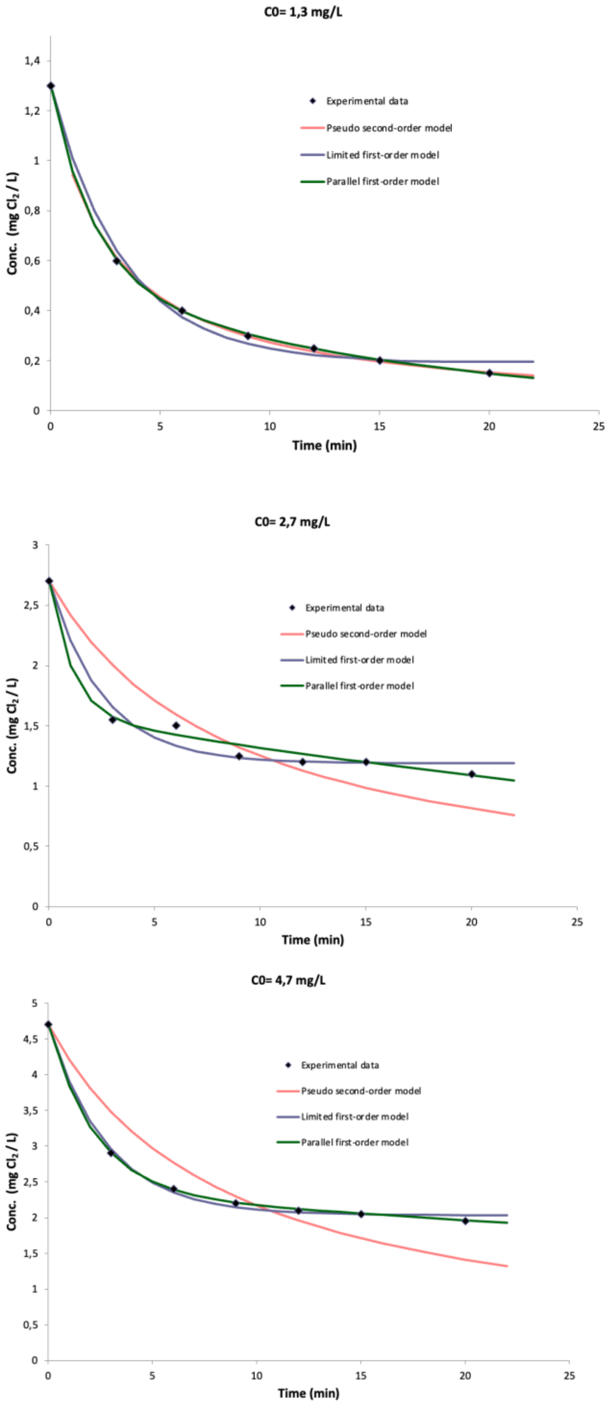


Figure 1 Chlorine decay kinetics at T = 25ºC: (a) C_0=0.65 mg Cl_2 L^{-1}; (b) C_0=1.3 mg Cl_2 L^{-1}; (c) C_0=2.7 mg Cl_2 L^{-1}; (d) C_0=4.7 mg Cl_2 L^{-1}.

Table 5 F-test with a confidence level of 95% applied to chlorine decay in water; degrees of freedom 6:6; $F_{critical}$ = 4.28.

C_0 (mg Cl_2 L^{-1})	F calculated		
	PL/P2	PP/P2	PL/PP
0.65	1.33	1.23	1.08
1.3	1.06	0.99	1.07
2.7	0.53	0.46	1.17
4.7	0.57	0.54	1.05

However, the data in Table 5 indicate that the precision obtained by the parallel first-order model (PP) is not statistically significant at the 95% probability level compared with the PL and P2 models (F calculated < 4.28).

3. CONCLUSIONS

Chlorine decays in water because of reactions that can occur within it.

The chlorine reaction in water is characterized by two phases: a fast phase and a slower second phase. The first group of reactions includes the reaction of more reactive species such as ammonia and certain organic compounds, while the second group involves the reaction of less reactive species such as certain organic compounds and amines.

For both studies - water from the Bengo River and from the Lever Water Treatment Plant, the parallel first-order model accurately represents the kinetics of chlorine consumption, considering the range of initial chlorine concentrations studied and the constant initial organic matter concentration, considering the two phases that characterize the chlorine reaction in the water.

The statistical analysis performed for the study in Angola allows us to conclude that the precision of the parallel first-order model is not statistically significant at the 95% confidence level compared to the pseudo second-order and limited first-order models.

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