



Comparison of commercial disinfectants and an *in loco*-produced solution: free residual chlorine decay in human supply waters

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ABSTRACT

The disinfection process is used in the treatment of water for human supply to promote sanitary safety and provide users with drinking water that meets potability standards. Thus, it is necessary to sustain a minimal concentration of free residual chlorine (FRC) throughout the entire distribution system. The present study investigated the decay process of FRC concentration in water destined for human supply. The decay was evaluated in bench-scale testing, using sodium hypochlorite, calcium hypochlorite, sodium dichloroisocyanurate (organic chlorine) as disinfectant agents, and also an alternative disinfectant solution (ADS) produced *in loco*, with oxidizing and disinfectant properties, which is being used in Brazilian sanitation industry. To evaluate the decay, four models were fitted: first-order, *n*th-order, limited first-order and parallel first-order, hence determining the corresponding parameters which describe the decay speed of the FRC concentration in water. Achieved results demonstrated that all models were statistically significant and predictive. However, the parallel first-order model produced the best fit. Regarding the evaluated disinfectants, there was preeminence of the ADS solution when compared to the others, since it imparted a higher FRC over time, a behavior indicated by lower values for reaction rate constant in all models and when compared to other disinfectants used in this study.

Key words: chlorine decay, kinetic models, water disinfection

HIGHLIGHTS

- Alternative disinfectant solution (ADS) tends to maintain a greater residual chlorine over time.
- Chlorine decay over time is best described by the first-order parallel model.
- The use of disinfectants that contain not only chlorine derivatives guarantees a greater residual-free chlorine over time.

INTRODUCTION

For water to play its role in society, it is necessary to take a lot of care, from the abstraction in springs and aquifers to the use and disposal by the population (Salvatierra *et al.* 2010). Such care is related not only to aspects of water quality, but also to safety regarding its availability to meet human, industrial, commercial, agricultural, livestock, and recreational needs, as well as electricity generation, among other supplies. Thus, the distribution must be carried out rationally, avoiding degradation and water losses (Santos *et al.* 2011).

In Brazil, the procedures for the control and surveillance of water quality and potability standards for human consumption were reviewed and established in the Consolidation Ordinance No. 5, Annex XX, of September 28, 2017 of the Ministry of Health (Brasil 2017).

To protect public health, disinfection is applied to water with the secondary objective of maintaining a disinfectant residual throughout the distribution system, ensuring this residual even at the ends of the networks, limiting microbial growth (Silva *et al.* 2019).

The chlorination process introduced in the early nineteenth century aims to reduce the spread of diseases through water. It decisively contributed to this purpose; however, due to the use of chlorine as the main disinfectant in water supply systems

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around the world, microorganisms acquired resistance to it over time, enabling outbreaks of water-borne diseases (Souza & Daniel 2005). When applied in the form of gas, chlorine poses high risk of leakage; because of that, it has been replaced by other less dangerous products.

A proven technology available in the Brazilian market is the *in loco* sodium hypochlorite generator, which uses water, salt (sodium chloride) and electricity as inputs. The production of this disinfectant agent includes the electrolysis of sodium chloride present in brine prepared at a concentration of 3%, which is soon after subjected to a direct current in an electrolytic cell containing anode and cathode (Pacheco *et al.* 2018). The result of the electrolytic reaction of sodium chloride is a solution that contains hypochlorite ion, hypochlorous acid, other chlorine species and traces of other oxidizing agents such as hydrogen peroxide, hydroxyl radicals and oxygen free radicals. The solution can be produced continuously, dosed directly in water, or in batch (Garcia 2018).

When it comes into contact with water, chlorine undergoes hydrolysis and this reaction results in the hypochlorite ion and hypochlorous acid, substances that are responsible for the free residual chlorine (FRC) content in the waters for human supply. The control of water pH is an important factor for disinfection, since hypochlorous acid is a weak acid and the main disinfectant agent, showing bactericidal power up to 80 times greater than that of hypochlorite ion. Its predominance occurs at pH between 2 and 8 (Sanabria & Julio 2013; Libânio 2016).

Due to the diversity of water characteristics, FRC species react with various substances such as iron, manganese, ammonia (inorganic matter) and organic matter in general, which causes two stages of decay of their concentrations: first reacting with inorganic material and then with organic material (Vieira *et al.* 2004; Gallandat *et al.* 2019; Nono *et al.* 2019).

Over the years, several studies on FRC decay have been conducted seeking to effectively describe, through mathematical models, the behavior of decay in various water supply systems for human consumption and which model has the best fit in these systems, reflecting the studied conditions (Brown *et al.* 2011; Fisher *et al.* 2011).

The first-order model, due to its simplicity, has been widely used in the simulation of the FRC decay in water supply systems (Rossman *et al.* 1994). For Munavalli & Kumar (2004), FRC decay is defined and it may be appropriate to admit first-order reactions in the models. However, several authors have reported that this kinetic approach is often not the most accurate to describe the decay of chlorine concentration for water used in public supply (Clark 1998; Kastl *et al.* 1999; Jonkergouw *et al.* 2009; Monteiro *et al.* 2014). Other models were proposed, in addition to first-order kinetics, aiming at a description with greater accuracy of the decay of chlorine concentration in water (Sanabria & Julio 2013).

According to Vieira *et al.* (2004), the first parallel order model is the one that was best adjusted to the consumption of FRC in the liquid mass by presenting two stages of FRC degradation, the first being the fastest, in which reactions with inorganic matter and the second slower stage occur, in which chlorine reacts with the organic material present in water.

According to Figueiredo (2014), the factors that influence chlorine decay, such as natural organic matter concentration, initial chlorine concentration, temperature and hydraulic conditions, need to be added to the models, in order to make them more robust.

In this perspective, the aim of this study was to evaluate the decay of FRC concentration over time and to determine the kinetic coefficients of FRC decay for four disinfectant agents: sodium hypochlorite, calcium hypochlorite, sodium dichloroisocyanurate (organic chlorine) and an alternative disinfectant solution (ADS) produced *in loco*, in view of the need for conducting studies that evaluate the efficiency of new disinfectant agents and disinfection processes alternative to chlorine, which contribute to guaranteeing the quality of water for supply and allow greater safety to the communities served.

METHODS

Experimental conditions and procedures

The water used in the experiments came from the Water Treatment Plant of Gravatá (WTP-Gravatá) and was collected shortly after the filtration stage. Located in the municipality of Queimadas, PB, Brazil, and responsible for the treatment of the waters of the Epitácio Pessoa reservoir (Figure 1), this station is the conventional type and has the following configuration: Parshall trough, mechanical flocculants, horizontal flow decanters, gravity filters, chlorine contact tank and a complete chemical treatment facility, with the use of aluminum sulfate as coagulant agent and chlorine gas in the disinfection step.

As WTP-Gravatá operates in full cycle, upon arriving at WTP, the raw water receives hydrated lime for pH correction, then in the coagulation stage, the aluminum sulfate is added to the Parshall trough, where the rapid mixing occurs. Then the water

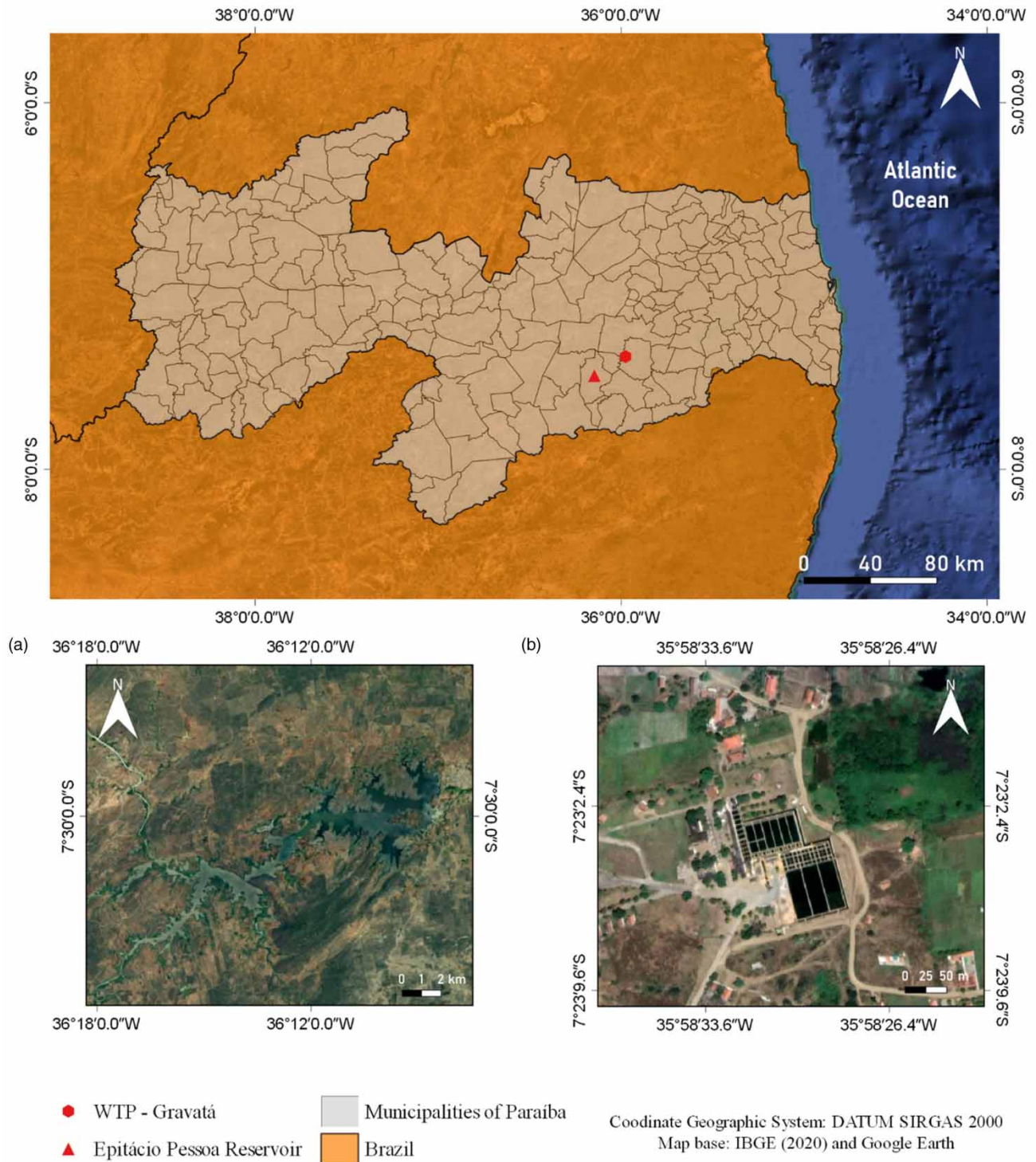


Figure 1 | Location of the Epitácio Pessoa Reservoir (a) and WTP-Gravatá (b).

proceeds to the stages of flocculation, decanting, filtration and disinfection with gaseous chlorine. Finally drinking water is distributed.

Thus, this station is responsible for supplying nine municipalities in the state of Paraíba, including Campina Grande, which has a medium-sized supply system and benefits 156,298 economies, through 135,532 home connections (Nascimento *et al.* 2016) with an estimated population of 409,731 inhabitants for the year 2019 (IBGE 2020).

Some physical–chemical and microbiological characteristics of the water used to conduct the tests are presented in Table 1, with their respective average values.

In the present study, the disinfectant agents used were sodium hypochlorite, calcium hypochlorite, sodium dichloroisocyanurate (organic chlorine) and the agent produced from an electrochemical reactor, which will be described later and which, for discussion purposes here, will be called ADS (Alternative Disinfectant Solution), in order to verify the decay of its FRC species in the water volume.

The experiments were carried out as follows: (i) 5-L samples of filtered water were added in gallons with the same volume; (ii) doses of the different disinfectant solutions were added until reaching FRC concentrations of approximately $5.0 \text{ mgCl}_2 \cdot \text{L}^{-1}$, simulating the value maximum value allowed by Consolidation Ordinance No. 5, in Annex 7 of the Annex XX, of the Ministry of Health, at the exit of the water treatment station; (iii) FRC was determined at regular time intervals. The experiments were conducted at room temperature. Figure 2 illustrates the experimental apparatus of the decay test.

As illustrated in Figure 2, the experiments were conducted in triplicate for each disinfectant agent. Each test took a total duration of 1,440 minutes, with FRC determinations performed at times of 0, 10, 20, 40, 80, 160, 720 and 1,440 minutes. In parallel, the determinations of FRC were performed to monitor pH and temperature, in order to verify the variability of these parameters during the execution of the experiments, as these parameters are directly related to the degradation of FRC in water (Gallandat *et al.* 2019; Li *et al.* 2019; Goodarzi *et al.* 2020).

FRC concentrations were determined using the DPD-SFA titrimetric method, as described in the Standard Methods for the Examination of Water and Wastewater (APHA *et al.* 2012). Temperature and pH monitoring during the experiments was performed with a MS TECNOPON[®] mPA-210 benchtop pH meter.

Alternative disinfectant solution (ADS) produced *in loco*

The solution with disinfectant potential is produced from the electrolysis process in aqueous medium of sodium chloride (non-iodized common salt).

Table 1 | Physical-chemical and microbiological characteristics of the study water

Parameter	Value	Method
Turbidity	0.71 NTU	Nephelometric
Apparent color	12.30 uH	Colorimetric
True color	8.90 uH	Colorimetric
Absorbance 254 nm	0.135	Ultraviolet absorption method
pH	7.51	Potentiometric
Alkalinity	$23.0 \text{ mg CaCO}_3 \cdot \text{L}^{-1}$	Titrimetric
Total hardness	$99.0 \text{ mg CaCO}_3 \cdot \text{L}^{-1}$	Titrimetric
Total coliforms	Presence	Chromogenic substrate
<i>E. Coli</i>	Absence	Chromogenic substrate

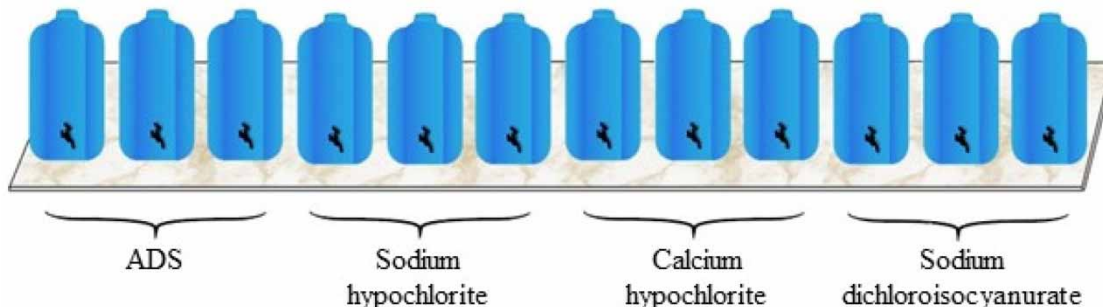


Figure 2 | Experimental apparatus.

The reactor produces *in loco* a solution that contains sodium hypochlorite and hydrogen peroxide, with oxidizing potential greater than that of commercial sodium hypochlorite. Figure 3 illustrates in a schematic way the production process and its respective chemical species.

In this study, the static chlorine generator Hidrogeron[®] GE-15 was used. The generator's operation to produce the solution (Figure 4) was started with the addition of 15 liters of water (Figure 4(I)), preferably slowed down to avoid electrodeposition of calcium and magnesium salts in the electrodes, with subsequent addition of 600 g of non-iodized sodium chloride (salt) (Figure 4(II)) and homogenization of brine solution (Figure 4(III)). Then, the reactor was closed and connected to the electrical power source. After 8 hours, the source was turned off automatically and the ADS was ready (Figure 4(IV)). At the end,

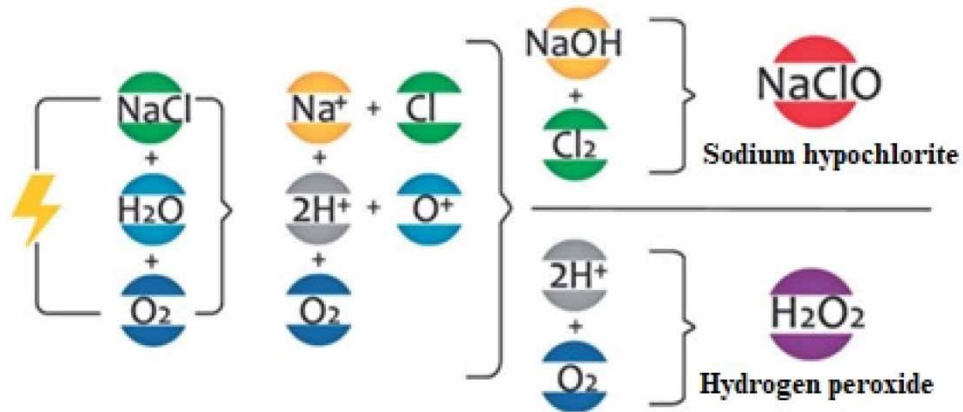


Figure 3 | ADS production process via electrolysis. Source: Dantas *et al.* (2017).

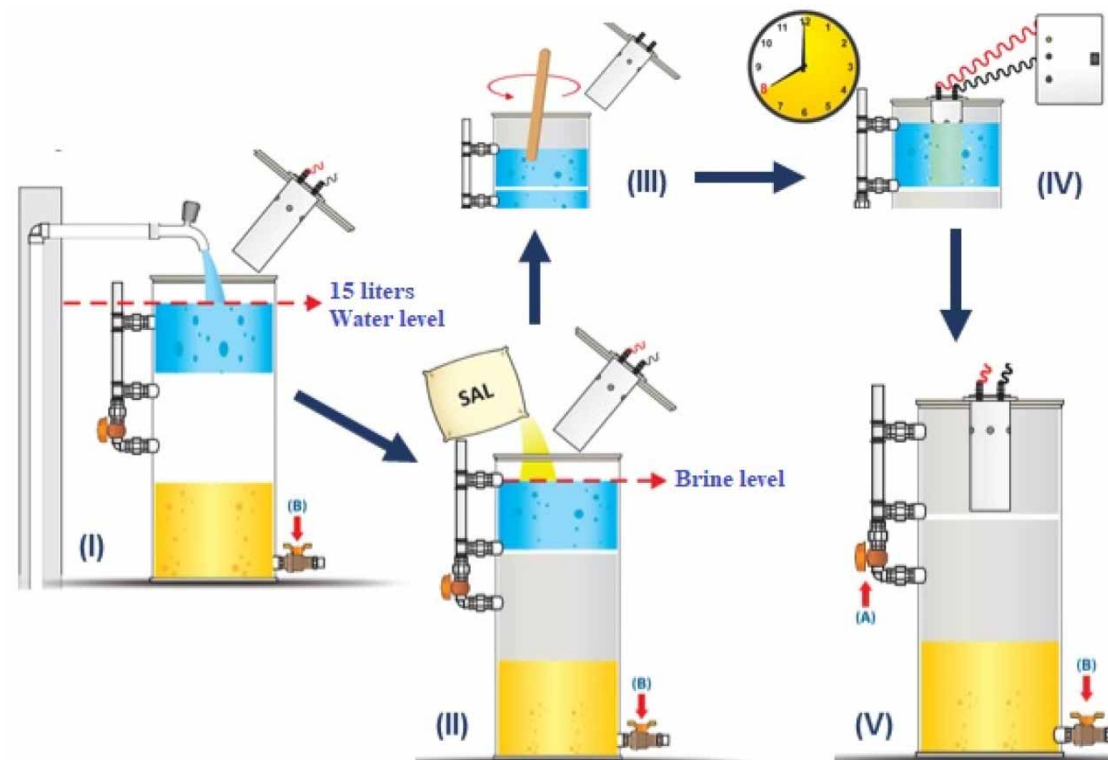


Figure 4 | Operation of static chlorine generator for ADS production.

the valve (A) that connects the upper and lower chambers was opened so that the solution was collected by the output valve (B) of the lower reservoir (Figure 4(V)). With this, the upper reservoir was emptied and a new batch could be produced.

Determination of the kinetic coefficients of FRC decay and data analysis

The kinetic coefficients of FRC decay were determined by fitting first-order, n th-order, limited first-order, parallel first-order models (Equations 1, 2, 3 and 4, respectively) to the experimental data, based on the least squares method, and the parameters of each model were estimated by minimizing the sum of the residuals. These models were proposed by Haas & Karra (1984) to describe the decay of chlorine in the disinfection of wastewater, but have also been reported in the literature as capable of representing FRC decay in supply waters:

$$C = C_0 \times e^{-kt} \quad \text{1st order} \quad (1)$$

$$C = \left[kt(n-1) + \left(\frac{1}{C_0} \right)^{(n-1)} \right]^{-\frac{1}{n-1}} \quad \text{nth order} \quad (2)$$

$$C = C^* + (C + C^*)e^{(-kt)} \quad \text{1st limited order} \quad (3)$$

$$C = xC_0e^{(-k_1t)} + (1-x)C_0e^{(-k_2t)} \quad \text{1st parallel order} \quad (4)$$

where:

C = FRC concentration at a given time, in $\text{mg}\cdot\text{L}^{-1}$;

t = time, in min;

k = chlorine decay rate constant, in min^{-1} for the first-order and limited first-order models and in $\text{mg}^{1-n}\cdot\text{L}^{n-1}\cdot\text{min}^{-1}$, for the n th-order model;

C^* = chlorine limit concentration, in $\text{mg}\cdot\text{L}^{-1}$;

n = reaction order, dimensionless;

C_0 = initial concentration of FRC, in $\text{mg}\cdot\text{L}^{-1}$;

x = FRC fraction, dimensionless;

k_1 and k_2 = respectively, fast and slow chlorine decay rate constants, in min^{-1} .

The adequacy of the models to the decay data was evaluated through the coefficient of determination (R^2) and by the Fisher test (F test). For the fit of the models to the observed data, the statistical analyses were performed using Statistica software version 12.0 (Statsoft 2011).

RESULTS AND DISCUSSION

The decay behavior of the FRC concentration over time, for each disinfectant, was used to determine the kinetic coefficients of FRC decay in the volume of water, which describe the speed at which chlorine reactions occur in water destined for human supply.

Hypochlorous acid and hypochlorite ion are the main oxidizing agents that make up the FRC, and react with other substances present in the water, thus, once added to water, chlorine initiates several interactions resulting in the decay of its concentration. Several substances present in water is able to react with chlorine simultaneously at different speeds. Inorganic substances such as ammonia, nitrite, iodides and bromides, sulfites, iron (II) are responsible for interacting with chlorine at faster speeds, while manganese (II) reacts more slowly. In turn, because they present more complexity and variety of species, organic substances present reaction velocities with chlorine from fast to very slow, according to their composition (Deborde & Vonguten 2008; Sanabria & Julio 2013).

Figure 5 illustrates the FRC decay curve for the different disinfectant agents evaluated. It is observed that the free chlorine residual in the water mass tends to be consumed more quickly in the first minutes of the test, reaching a greater stability of its concentration over time. This is due to water quality conditions, as organic and inorganic substances will react with FRC and generate higher initial consumption. After all these substances are oxidized, the FRC will tend to decay more slowly. This behavior is consistent with that observed in other studies described in the literature (Gallandat *et al.* 2019; Nono *et al.* 2019).

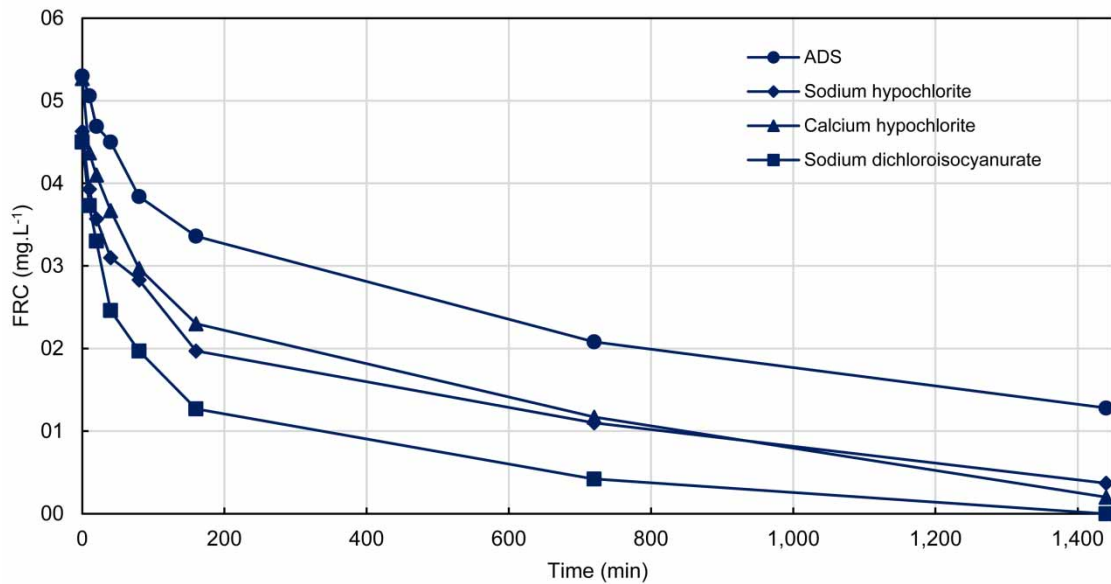


Figure 5 | FRC decay in the volume of water for different disinfectants.

Among the decay curves illustrated in [Figure 5](#) for the different disinfectant agents, it is noticed that the ADS showed a more stable behavior, with a lower decay of the portion of rapid consumption at the beginning and a higher concentration of FRC throughout the test.

The water used in the tests has an apparent color of 12.30 uH and true color of 8.90 uH, however a low absorbance value was verified 254 nm ([Table 1](#)) that indicated a low concentration of organic matter in suspension. According to the obtained values, the true color represents about 70% of the apparent color, indicating that dissolved solids and colloidal particles in water are in greater proportion than suspended solids, and this apparent color value may represent the by-products of the decomposition of organic matter in the reservoir, as well as the possible presence of dissolved inorganic substances, such as iron, manganese and chemicals, such as lime hydrates and aluminum sulfate, used for pH correction and coagulation, in the process of water treatment ([Libânio 2016](#)).

[Wang et al. \(2020\)](#) comment that the presence of biofilms is frequent in water supply systems and results mainly from organic matter not removed in conventional water treatment and from the aging of the distribution network. The authors point out that the control of the biofilm depends heavily on the residual levels of disinfectant in the system and that FRC values equal to or below $0.5 \text{ mg}\cdot\text{L}^{-1}$ are not effective for this purpose. Based on this, the present study showed the potential of ADS for greater network security, as, even after 1,440 min, the FRC level in water was above $1.0 \text{ mg}\cdot\text{L}^{-1}$.

In relation to the parameters pH and temperature, [Figure 6](#) illustrates their variability for the data obtained in the decay tests with the disinfectant agents evaluated. Based on these parameters, and on the FRC concentration present in water, the Consolidation Ordinance No. 5, Annex XX of September 28, 2017 of the Ministry of Health, establishes the minimum contact time for disinfection performed through chlorination.

Water pH is a factor that significantly influences the efficiency of disinfection with chlorine compounds, as it promotes the dissociation of hypochlorous acid (HOCl) and the formation of hypochlorite ion (OCl^-). The sum of the HOCl and OCl^- species constitutes the FRC, with OCl^- being the weakest disinfectant and prevailing at higher pH (>8.0), while HOCl is more reactive and prevails at lower pH (<8.0) ([Libânio 2016](#)).

For this reason, research studies have indicated that pH is a parameter that strongly influences the rate of chlorine decay, as well as the stability of the disinfectant and the formation of disinfection by-products ([Gallandat et al. 2019](#); [Li et al. 2019](#)). In the present study, the decay of FRC for the four disinfectant agents occurred at pH values lower than 8.0, without large variations, which according to [Libânio \(2016\)](#) ensures a prevalence higher than 80% of hypochlorous acid.

Chlorine decay is a reaction that also depends directly on temperature. Thus, the higher this parameter, the faster the FRC self-decay will occur ([Li et al. 2019](#); [Goodarzi et al. 2020](#)). This observation was confirmed by [Kim et al. \(2019\)](#), who found

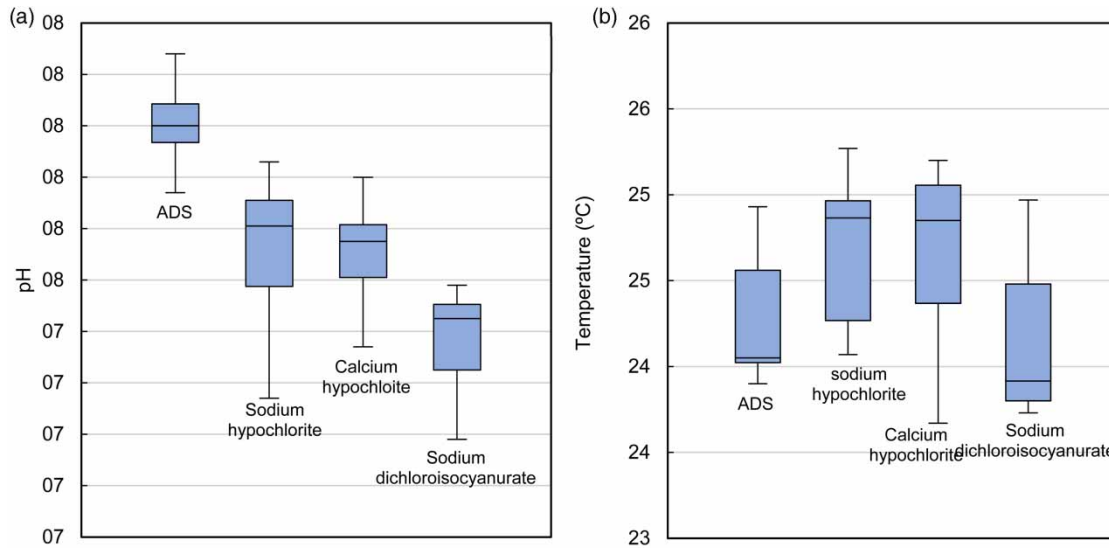


Figure 6 | Variation of pH (a) and temperature (b) in FRC decay tests.

that the decay of FRC in supply water occurred more accelerated at 23 °C than at 18 °C. However, in the present study, no significant variations in temperature were observed between the tests.

An alternative disinfectant that has been studied is peracetic acid, considered quite efficient for water disinfection. Its behavior in the supply water was evaluated by [Zhang *et al.* \(2020\)](#), who observed a decay of 10% from an initial concentration of 5.0 mg·L⁻¹, after 60 min in water with pH of 7.0–7.5 and temperature of 20 °C. Under similar conditions of initial concentration, time and pH, in this study, the decay of ADS was similar to that of peracetic acid, even with the higher water temperature (24 °C), which highlights its stability.

First-order, nth-order, limited first-order and parallel first-order models were fitted to the data obtained from the FRC decay experiments in the water volume.

The first-order model (Equation (1)) is widely applied in studies on chlorine decay in water distribution systems ([Maier *et al.* 2000](#); [Sanabria & Julio 2013](#); [Rodrigues & Scalize 2019](#)), where it is assumed that the concentration, C , of FRC decreases exponentially over time, t , and k is the decay rate constant of chlorine.

For the limited first-order model (Equation (3)), C^* is considered a part of the initial concentration that does not react with any species of organic or inorganic nature present in the water, and the first-order exponential decay is dependent on the complementary part ($C_0 - C^*$). In the nth-order model (Equation (2)), the decay rate constant is proportional to the umpteenth power of the concentration C .

In turn, the parallel first-order model (Equation (4)) assumes that there are two specific rate constants: one part (αC_0) of the initial chlorine concentration decays exponentially with specific rate constant k_1 , and the other $(1-\alpha)C_0$ decays exponentially with specific rate constant k_2 .

[Figure 7](#) presents the fits of the models to the experimental data, for which it is possible to verify that the parallel first-order model showed the best fit for all disinfectant agents.

Some authors used the correlation coefficient (R) as a criterion for hierarchization in the process of choosing the best kinetic model ([Powell *et al.* 2000](#); [Vieira *et al.* 2004](#); [Beleza 2005](#)). However, here, to evaluate the best fit, a statistical analysis was performed, adopting as a criterion for choosing the best model the highest values of the coefficients of determination (R^2) and F test.

[Table 2](#) shows the statistical values of R^2 and F test, as well as the values of the parameters fitted for each model analyzed.

Although all models showed satisfactory fits, with coefficients of determination above 0.83 and $F_{\text{calculated}}$ higher than $F_{\text{tabulated}}$, the parallel first order model presented the best values for the F test ($F_{\text{calculated}} > F_{\text{tabulated}}$) and higher values of the coefficients of determination, when compared with the models for each disinfectant agent. The model is statistically significant if $F_{\text{calculated}} > F_{\text{tabulated}}$ and, if the $F_{\text{calculated}}/F_{\text{tabulated}}$ ratio (F test) is greater than 10, the model is not only statistically significant but also predictive ([Barros Neto *et al.* 2001](#)), which can be observed for all models evaluated for different experiments with 95% confidence interval.

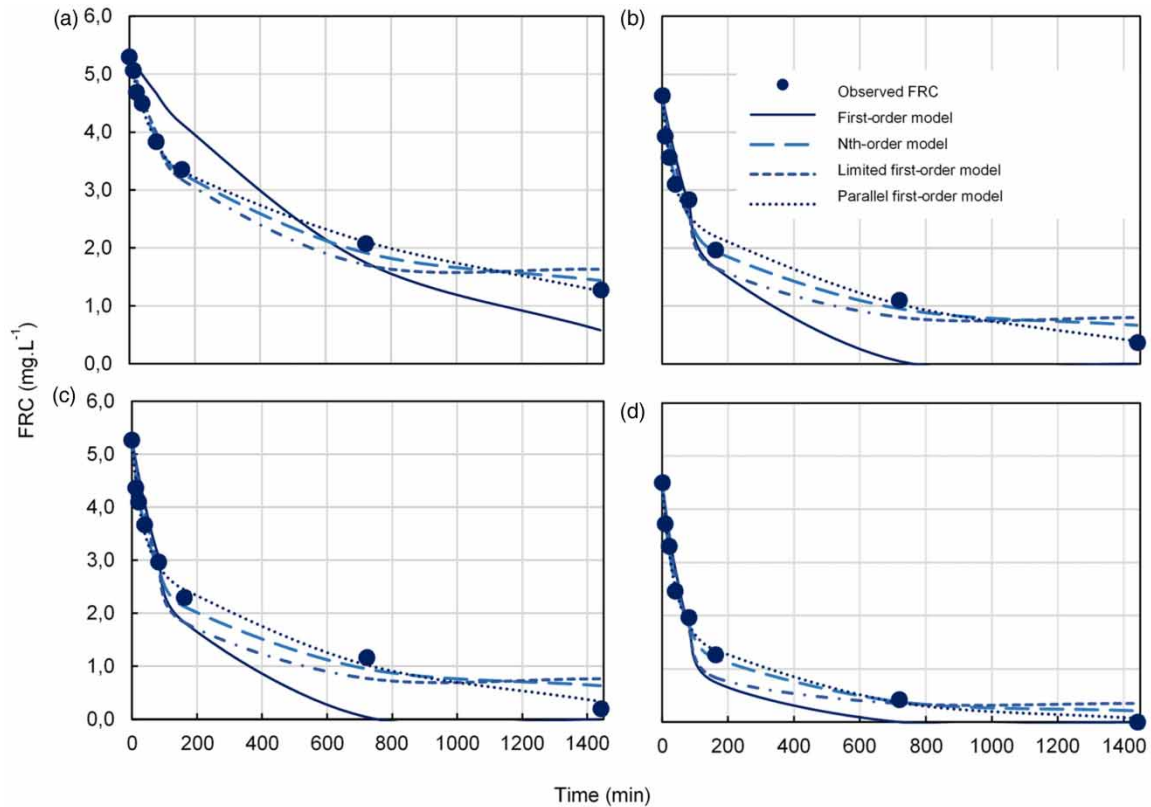


Figure 7 | Fit of models for the disinfectants ADS (a), sodium hypochlorite (b), calcium hypochlorite (c) and sodium dichloroisocyanurate (d).

Table 2 | Comparison of the parameters of the studied models

Kinetic model	Adjustable parameter	ADS	Sodium hypochlorite	Calcium hypochlorite	Sodium dichloroisocyanurate
First-order	k (min^{-1})	0.0015	0.0064	0.0066	0.0112
	R^2	0.8365	0.8642	0.8885	0.9548
	F test	65.3202	44.1404	49.8021	87.0246
Nth-order	n	3.2160	2.8720	2.6321	2.1383
	k ($\text{mg}^{1-n} \cdot \text{L}^{n-1} \cdot \text{min}^{-1}$)	0.0001	0.0008	0.0009	0.0035
	R^2	0.9943	0.9833	0.9804	0.9952
	F test	890.8570	171.6385	135.0281	385.5136
Limited first-order	C^* ($\text{mg} \cdot \text{L}^{-1}$);	1.6315	0.8020	0.7672	0.3507
	k (min^{-1})	0.0054	0.0093	0.0090	0.0133
	R^2	0.9733	0.9439	0.9409	0.9684
	F test	189.4623	50.6714	44.3657	58.1400
Parallel first-order	k_1 (min^{-1})	0.0150	0.0336	0.4068	0.0301
	k_2 (min^{-1})	0.0007	0.0013	0.0337	0.0023
	x	0.3297	0.4114	0.0015	0.5694
	R^2	0.9983	0.9901	0.9925	0.9975
	F test	1,537.7678	152.9764	185.9471	387.9774

An accurate analysis of the parallel first-order model, in relation to the adjustable parameters k_1 and k_2 , reveals the coherence of the results obtained ($k_1 > k_2$), since these coefficients describe the speed of fast and slow reactions of FRC in water, respectively. The high values of k_1 are justified by the direct relationship of this parameter with the reactions between chlorine and inorganic substances present in water, which are more easily degraded than organic ones.

Table 3 | Analysis of variance for the parallel first-order model applied to different disinfectant agents

Disinfectant	Source of variation	SS	DF	MS	F _{calculated}	F _{tabulated}	F test	R ²
ADS	Regression	127.8218	3	42.6073	8,318.4800	5.4095	1537.7678	0.9983
	Residual	0.0256	5	0.0051				
	Total	127.8474	7					
Sodium hypochlorite	Regression	72.3643	3	24.1214	827.5181	5.4095	152.9764	0.9901
	Residual	0.1457	5	0.0291				
	Total	72.5100	7					
Calcium hypochlorite	Regression	92.3991	3	30.7997	1,005.8717	5.4095	185.9471	0.9925
	Residual	0.1531	5	0.0306				
	Total	92.5522	7					
Sodium dichloroisocyanurate	Regression	56.7252	3	189,084	2,098.7451	5.4095	387.9774	0.9975
	Residual	0.0450	5	0.0090				
	Total	56.7702	7					

Thus, the high values of k_1 obtained in the fit of the models to the data are coherent. In addition, the value of the kinetic constant associated with reactions involving organic compounds in the raw water of the water supply system of Campina Grande is 5% (Nascimento *et al.* 2016), attesting that inorganic compounds are responsible for most of the chlorine demand.

Table 3 presents the analysis of variance for the parallel first-order model, which showed the best values of R^2 (>0.99) and F test (>152.9764). It is observed that the disinfectant agent ADS was superior to the others, mainly in relation to the components of the F test.

Regarding the FRC decay rate in the water volume, for the parallel first-order model, it can be observed that the values of the kinetic constants of reaction speed (k_1 and k_2) were lower for ADS. That is, for this disinfectant agent the concentration of FRC decays more slowly, leaving a greater residual over time and, consequently, making the water safer for consumption by users of the supply system.

This fact can be attributed to the characteristics of the chemical species that make up the ADS solution: hydrogen peroxide, which has a great oxidative power capable of oxidizing substances present in water, and sodium hypochlorite, which is responsible for maintaining FRC for longer in the water mass.

By presenting a higher oxidation power than the oxidizing agents present in the CRL, hydrogen peroxide will oxidize the organic and inorganic substances present in water. Normally these substances would be oxidized by the chlorine plots, resulting in a higher consumption, and consequently, a greater decay of their concentration in water. Due to the presence of hydrogen peroxide in the SDA, the CRL concentration remains higher throughout the distribution system, making it possible to reach points farther from the network, avoiding the need for a new disinfectant dosage.

Thus, lower doses of disinfectant can be applied in the disinfection stage of the treatment, keeping the network within the safety standards established by Consolidation Ordinance No. 05/2017, Annex XX, which establishes that at any point in the public network there should be at least $0.2 \text{ mg}\cdot\text{L}^{-1}$ of FRC. This reduction in dose can reduce the operating costs. A cost-benefit economic analysis was performed by Pacheco *et al.* (2018), in order to verify the financial viability in the replacement of chlorine gas by sodium hypochlorite produced *in loco* in a water treatment plant in the city of Uberlândia, Minas Gerais, and these authors found an average reduction of 32.22% in the values paid monthly with disinfectant. However, it is necessary to conduct future studies to assess the cost reduction related to the variation of the dose applied to maintain the FRC throughout the supply network.

CONCLUSIONS

The results presented in this article suggest that the adjustable parameters of the different models evaluated indeed represent the decay of FRC in human water supply, as all were statistically significant and predictive. Therefore, they can be used in future studies of modeling of the disinfection process applied to the treatment of water for human consumption.

The parallel first-order kinetic model proved to be the most appropriate model to describe the decay of FRC for the different disinfectant agents tested in this study.

The ADS solution presented itself as a disinfectant agent capable of maintaining a free chlorine residual in water for a long period of time and at a small dose, ensuring the residual within the established by the Ministry of Health for potability, in addition to promoting greater sanitary safety of the water supplied to users of the supply system.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- APHA, AWWA, WEF 2012 *Standard Methods for the Examination of Water and Wastewater*, 22nd edn. Washington, DC, American Public Health Association, pp. 1360. ISBN 978-087553-013-0.
- Barros Neto, B., Scarminip, I. S. & Bruns, R. E. 2001 *Como fazer experimentos: pesquisa e desenvolvimento na ciência e na indústria (How to Experiment: Research and Development in Science and Industry)*. Unicamp, Campinas, p. 401.
- Beleza, J. M. D. E. B. B. 2005 *Simulação das concentrações de cloro residual e tri-halometanos em redes de distribuição de água para consumo humano (Simulation of Residual Chlorine and Trihalomethane Concentrations in Water Distribution Networks for Human Consumption)*. Faculdade de Engenharia da Universidade do Porto, Porto.
- Brasil 2017 Ministério da Saúde. *Portaria de Consolidação nº 5 de 28 de setembro de 2017, Anexo XX*. Dispõe sobre o controle e vigilância da qualidade da água para consumo humano e seu padrão de potabilidade. http://portalsinan.saude.gov.br/images/documentos/Legislacoes/Portaria_Consolidacao_5_28_SETEMBRO_2017.pdf.
- Brown, D., Bridgeman, J. & West, J. R. 2011 *Predicting chlorine decay and THM formation in water supply systems*. *Reviews in Environmental Science and Biotechnology* **10** (1), 79–99. <https://doi.org/10.1007/s11157-011-9229-8>.
- Clark, R. M. 1998 Demanda de cloro e cinética de formação TTHM: Um modelo de segunda ordem. *Revista de Engenharia Ambiental* **124**, 16–24.
- Dantas, A. D. B., Bernardo, L. D., Voltan, P. E. N. & Koyama, M. H. 2017 Avaliação da eficiência do cloro gerado a partir de sal nas etapas de pré e pós-cloração da água do rio Piracicaba (Evaluation of the efficiency of chlorine generated from salt in the pre- and post-chlorination stages of water from the Piracicaba river). In: *Congresso ABES/Fenasan 2017*, São Paulo. Anais do Congresso ABES/Fenasan 2017.
- Deborde, M. & Von Gunten, U. 2008 *Reactions of chlorine with inorganic and organic compounds during water treatment—kinetics and mechanisms: a critical review*. *Water Research* **42**, 13–51.
- Figureiredo, D. M. D. 2014 Modelagem do decaimento do cloro em sistemas de abastecimento de água (Modeling chlorine decay in water supply systems). Técnico Lisboa.
- Fisher, I., Kastl, G., Sathasivan, A. & Jegatheesan, V. 2011 *Suitability of chlorine bulk decay models for planning and management of water distribution systems*. *Critical Reviews in Environmental Science and Technology* **41** (20), 1843–1882. <https://doi.org/10.1080/10643389.2010.495639>.
- Gallandat, K., Stack, D., String, G. & Lantagne, D. 2019 *Residual maintenance using sodium hypochlorite, sodium dichloroisocyanurate, and chlorine dioxide in laboratory waters of varying turbidity*. *Water* **11** (6), 1309. <https://doi.org/10.3390/w11061309>.
- Garcia, R. da C. D. 2018 Avaliação da substituição do cloro g's pela produção eletrolítica de hipoclorito de sódio in loco em estação de tratamento de água de grande porte (Evaluation of the replacement of chlorine gas by the electrolytic production of sodium hypochlorite on site in a large water treatment plant). 2018. 86 pp. Dissertação (Mestrado em Qualidade Ambiental) – Universidade Federal de Uberlândia, Uberlândia. <http://dx.doi.org/10.14393/ufu.di.2018.727>.
- Goodarzi, D., Abolfathi, S. & Borzooei, S. 2020 *Modelling solute transport in water disinfection systems: effects of temperature gradient on the hydraulic and disinfection efficiency of serpentine chlorine contact tanks*. *Journal of Water Process Engineering* **37**, 101411. <https://doi.org/10.1016/j.jwpe.2020.101411>.
- Haas, C. N. & Karra, S. B. 1984 Kinetics demand of wastewater exertion. *Journal of Water Pollution Control Federation* **56** (2), 170–173.
- IBGE 2021 Instituto Brasileiro de Geografia e Estatística. Censo Demográfico 2010 – Características Gerais da População. Resultados da Amostra. IBGE, 2010. <https://cidades.ibge.gov.br/brasil/pb/campina-grande/panorama> Accessed 2021.
- Jonkergouw, P. M. R., Khu, S. T., Savic, D. A., Zhong, D., Hou, X. Q. & Zhao, H. B. 2009 Um modelo de decaimento de cloro de coeficiente de taxa variável. *Ciência Ambiental & Tecnologia* **43**, 408–414.

- Kastl, G. J., Fisher, I. H. & Jegatheesan, V. 1999 Avaliação das expressões cinéticas de decomposição de cloro para modelagem de sistemas de distribuição de água potável. *Journal of Water Supply: Research and Technology – AQUA* **48**, 219–226.
- Kim, H., Baek, D. & Kim, S. 2019 Exploring integrated impact of temperature and flow velocity on chlorine decay for a pilot-scale water distribution system. *Desalination and Water Treatment* **138**, 265–269. <https://doi.org/10.5004/dwt.2019.23376>.
- Li, R. A., McDonald, J. A., Sathasivan, A. & Khan, S. J. 2019 Disinfectant residual stability leading to disinfectant decay and by-product formation in drinking water distribution systems: a systematic review. *Water Research* **153**, 335–348. <https://doi.org/10.1016/j.watres.2019.01.020>.
- Libânio, M. 2016 *Fundamentos de qualidade e tratamento de água (Fundamentals of Water Quality and Treatment)*, 4th edn. Editora Átomo, Campinas.
- Maier, S. H., Powell, R. S. & Woodward, C. A. 2000 Calibration and comparison of chlorine decay models for a test water distribution system. *Water Research* **36**, 2301–2309. [https://doi.org/10.1016/S0043-1354\(99\)00413-3](https://doi.org/10.1016/S0043-1354(99)00413-3).
- Monteiro, L., Figueiredo, D., Dias, S., Covas, D., Menaia, J. & Coelho, S. T. 2014 Modeling of chlorine decay in drinking water supply systems using EPANET MSX. *Procedia Engineering* **70**, 1192–1200.
- Munavalli, G. R. & Kumar, M. S. M. 2004 Dynamic simulation of multicomponent reaction transport in water distribution system. *Water Research* **38** (8), 1971–1988.
- Nascimento, R. S., Curi, R. C., Curi, W. F., Oliveira, R., Santana, C. F. D. & Meira, C. M. B. S. 2016 Simulação de alterações numa ETA convencional de portemédio para a produção de água segura (Simulation of changes in a medium-sized conventional WTP for the production of safe water). *Revista Brasileira de Recursos Hídricos* **21**, 439–450. <https://doi.org/10.21168/rbrh.v21n2.p439-450>.
- Nono, D., Odirile, P. T., Basupi, I. & Parida, B. P. 2019 Assessment of probable causes of chlorine decay in water distribution systems of Gaborone city, Botswana. *Water SA* **45** (2), 190–198. <https://doi.org/10.4314/wsa.v45i2.05>.
- Pacheco, I. S., Garcia, R. C. D., Neves, A. S. S., Amaral, F. A. & Canobre, S. C. 2018 Substituição do gás cloro por hipoclorito de sódio produzido in loco em sistema de abastecimento de água: viabilidade econômica e operacional – estudo de caso (Replacement of chlorine gas by sodium hypochlorite produced in loco in a water supply system: economic and operational feasibility - case study). 48° Congresso Nacional de Saneamento da Assemae. May, 2018. Fortaleza-CE.
- Powell, J. C., West, J. R., Hallam, N. B., Forster, C. F. & Simms, J. 2000 Performance of various kinetic models for chlorine decay. *Journal of Water Resources Planning and Management* **126** (1), 13–20. [https://doi.org/10.1061/\(ASCE\)0733-9496\(2000\)126:1\(13\)](https://doi.org/10.1061/(ASCE)0733-9496(2000)126:1(13)).
- Rodrigues, M. F. S. & Scalize, P. S. 2019 Decaimento de cloro residual livre em águas distribuídas em redes de abastecimento (Free residual chlorine decay in water distributed in supply networks). *Brazilian Journal of Development* **5** (9), 16366–16375. <https://doi.org/10.34117/bjdv5n9-187>.
- Rossmann, L. A., Clark, R. M. & Grayman, W. M. 1994 Modelling chlorine residuals in drinking water distribution systems. *Journal of Environmental Engineering ASCE* **120** (4), 803–820.
- Salvatierra, R. V., Oliveira, M. M. & Zarbin, A. J. G. 2010 One-pot synthesis and processing of transparent, conducting, and freestanding carbon nanotubes/polyaniline composite films. *Chemistry of Materials* **22** (18), 5222–5234. <https://doi.org/10.1021/cm1012153>.
- Sanabria, J. M. & Julio, M. 2013 Decaimento do cloro residual em águas de abastecimento do município de Campo Grande/MS (Decay of residual chlorine in supply waters in the municipality of Campo Grande/MS). *Revista de Engenharia e Tecnologia* **5** (4), 92–104.
- Santos, V. D. S., Curi, W. F., Curi, R. C. & Vieira, A. S. 2011 Um Modelo de Otimização Multiobjetivo para Análise de Sistema de Recursos Hídricos I: Metodologia (A multiobjective optimization model for water resources system analysis I: methodology). *RBRH – Revista Brasileira de Recursos Hídricos* **16** (4), 49–60. <http://dx.doi.org/10.21168/rbrh.v16n4.p49-60>.
- Silva, G. A. B., Meira, C. M. B. S., Santana, C. F. D., Coura, M. A., Oliveira, R., Nascimento, R. S. & Santos, W. B. 2019 Simulação do decaimento de cloro residual livre em reservatórios de distribuição de água (Simulation of free residual chlorine decay in water distribution reservoir). *Revista DAE* **67** (218). <https://doi.org/10.4322/dae.2019.036>.
- Souza, J. B. & Daniel, L. A. 2005 Comparação entre hipoclorito de sódio e ácido peracético na inativação de E. coli, colifagos e C. perfringens em água com elevada concentração de matéria orgânica (Comparison between sodium hypochlorite and peracetic acid for E. coli, coliphages and C. perfringens inactivation of high organic matter concentration water). *Revista Engenharia Sanitária e Ambiental* **10** (2), 111–117. <https://doi.org/10.1590/S1413-41522005000200004>.
- Statsoft, Inc 2011 STATISTICA (data analysis software system), version 10. Available from: www.statsoft.com.
- Vieira, P., Coelho, S. T. & Loureiro, D. 2004 Accounting for the influence of initial chlorine concentration, TOC, iron and temperature when modelling chlorine decay in water supply. *Journal of Water Supply: Research and Technology – AQUA* **53** (7), 453–467. <https://doi.org/10.2166/aqua.2004.0036>.
- Wang, Z., Li, L., Ariss, R. W., Coburn, K. M., Behbahani, M., Xue, Z. & Seo, Y. 2020 The role of biofilms on the formation and decay of disinfection by-products in chlor (am) inated water distribution systems. *Science of The Total Environment*, 141606. <https://doi.org/10.1016/j.scitotenv.2020.141606>.
- Zhang, K., San, Y., Cao, C., Zhang, T., Cen, C. & Zhou, X. 2020 Optimising the measurement of peracetic acid to assess its degradation during drinking water disinfection. *Environmental Science and Pollution Research* **27** (27), 34135–34146. <https://doi.org/10.1007/s11356-020-09505-6>.