

COMPARATIVE STUDY OF THE PRE-OXIDATION STAGE IN WATER TREATMENT USING DIFFERENT OXIDANTS

ESTUDO COMPARATIVO DA ETAPA DE PRÉ-OXIDAÇÃO NO TRATAMENTO DE ÁGUA UTILIZANDO DIFERENTES OXIDANTES

ESTUDIO COMPARATIVO DE LA ETAPA DE PREOXIDACIÓN EN EL TRATAMIENTO DE AGUA UTILIZANDO DIFERENTES OXIDANTES



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ABSTRACT

In this study, the pre-oxidants tested (sodium hypochlorite, sodium dichloroisocyanurate, hydrogen peroxide, and potassium permanganate) were analyzed regarding their behavior at different concentrations and contact times. The objective was to optimize the pre-oxidant dosage and observe how contact time affected the efficiency of the process. The concentration of 1.5 mg/L was effective for the first three oxidants (sodium hypochlorite, sodium dichloroisocyanurate, and hydrogen peroxide), resulting in good removal of color and turbidity, with residual values close to the recommended levels. For potassium permanganate, the concentration of 0.2 mg/L proved to be the most efficient. Regarding the contact time in the pre-oxidation stage, the increase in oxidation time resulted in a greater amount of oxidized sample, indicating an increase in oxidant demand. In conclusion, the application of all tested oxidants in the pre-oxidation stage significantly contributed to improving the efficiency of water treatment. Subsequently, the different stages of water treatment were evaluated through physicochemical parameters using different oxidants in the pre-oxidation stage. Jar tests were conducted to evaluate the behavior of each stage (pre-oxidation, coagulation, flocculation, sedimentation, and filtration), and water quality was monitored. Water treatment with pre-oxidants showed greater treatment efficiency than samples without the use of oxidants. Pre-oxidation, combined with coagulation and flocculation, contributed to better performance in solid removal. When comparing the treatments, sodium hypochlorite showed the best results.

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Keywords: Water Treatment. Pre-Oxidation. Oxidants. Jar Test.

RESUMO

Neste trabalho, os pré-oxidantes testados (hipoclorito de sódio, dicloroisocianurato de sódio, peróxido de hidrogênio e permanganato de potássio) foram estudados quanto ao seu comportamento em diferentes concentrações e tempos de contato. O objetivo foi otimizar a dosagem do pré-oxidante e observar como o tempo de contato afetou a eficiência do processo. A concentração de 1,5 mg/L foi eficaz para os três primeiros oxidantes (hipoclorito de sódio, dicloroisocianurato de sódio e peróxido de hidrogênio), resultando em boa remoção de cor e turbidez, com valores residuais próximos aos recomendados. Para o permanganato de potássio, a concentração de 0,2 mg/L mostrou-se a mais eficiente. Em relação ao tempo de contato na etapa de pré-oxidação, o aumento do tempo de oxidação resultou em uma maior quantidade de amostra oxidada, inferindo um aumento na demanda de oxidante. Em conclusão, a aplicação de todos os oxidantes testados na etapa de pré-oxidação contribuiu significativamente para a melhoria da eficiência do tratamento de água. Em seguida foram avaliadas as diferentes etapas do tratamento de água por meio de parâmetros físico-químicos utilizando diferentes oxidantes na etapa de pré-oxidação. Foram realizados Jar Test para avaliar o comportamento de cada etapa (pré-oxidação, coagulação, floculação, decantação e filtração) e a qualidade da água foi monitorada. O tratamento da água com pré-oxidantes apresentou maior eficiência de tratamento do que as amostras sem o uso de oxidantes. A pré-oxidação, combinada com coagulação e floculação, contribuiu para um melhor desempenho na remoção de sólidos. Ao comparar os tratamentos, percebe-se que o hipoclorito de sódio apresentou os melhores resultados.

Palavra-chave: Tratamento de Água. Pré-Oxidação. Oxidantes. Teste de Jarros.

RESUMEN

En este trabajo, los preoxidantes evaluados (hipoclorito de sodio, dicloroisocianurato de sodio, peróxido de hidrógeno y permanganato de potasio) fueron analizados en relación con su comportamiento a diferentes concentraciones y tiempos de contacto. El objetivo fue optimizar la dosificación del preoxidante y observar cómo el tiempo de contacto afectaba la eficiencia del proceso. La concentración de 1,5 mg/L fue eficaz para los tres primeros oxidantes (hipoclorito de sodio, dicloroisocianurato de sodio y peróxido de hidrógeno), resultando en una buena remoción de color y turbidez, con valores residuales cercanos a los recomendados. Para el permanganato de potasio, la concentración de 0,2 mg/L resultó ser la más eficiente. En cuanto al tiempo de contacto en la etapa de preoxidación, el aumento del tiempo de oxidación resultó en una mayor cantidad de muestra oxidada, lo que indica un aumento en la demanda de oxidante. En conclusión, la aplicación de todos los oxidantes evaluados en la etapa de preoxidación contribuyó significativamente a mejorar la eficiencia del tratamiento de agua. Posteriormente, se evaluaron las diferentes etapas del tratamiento de agua mediante parámetros fisicoquímicos utilizando distintos oxidantes en la etapa de preoxidación. Se realizaron pruebas de jarras (Jar Test) para evaluar el comportamiento de cada etapa (preoxidación, coagulación, floculación, decantación y filtración) y se monitoreó la calidad del agua. El tratamiento del agua con preoxidantes presentó mayor eficiencia que las muestras sin el uso de oxidantes. La preoxidación, combinada con coagulación y floculación, contribuyó a un mejor desempeño en la remoción de sólidos. Al comparar los tratamientos, el hipoclorito de sodio presentó los mejores resultados.

Palabras clave: Tratamiento de Agua. Preoxidación. Oxidantes. Prueba de Jarras.

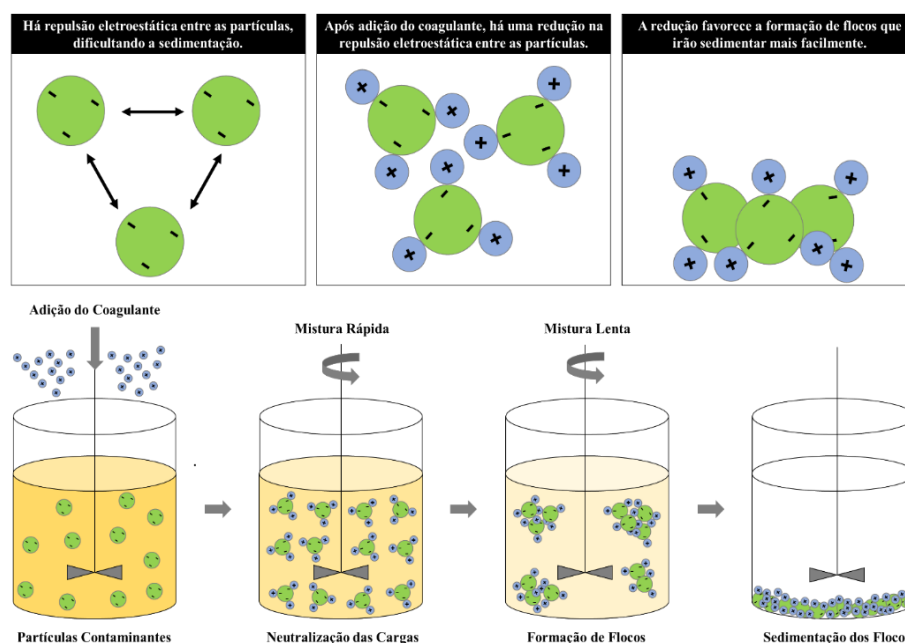
1 INTRODUCTION

In Brazil, Water Treatment Plants (WTPs) generally use a conventional treatment system, composed of the following steps: capture, adduction, alkalization, coagulation, flocculation, decantation, filtration, pH correction, disinfection, fluoridation and reservation.¹⁻³ All these steps are conducted before distributing the water to the population.

The coagulation-flocculation stage promotes the removal of turbidity and suspended particles, in addition to the reduction of color, organic matter and microorganisms. In summary, in the coagulation process, chemicals are added that will cause the colloidal particles in the raw water to become destabilized. Then, the particles coalesce to form flocs in the flocculation process (see Figure 1). The flakes continue to clump together during mixing, forming larger and heavier flakes that will settle more easily.² The basic requirement for a coagulant chemical, whether it is a metallic salt or an organic polymer, is that they discharge the usually negative charges into colloidal solids present in the water, giving rise to a precipitate.⁴

Figure 1

Illustrative explanation of the functioning of coagulation, flocculation and decantation

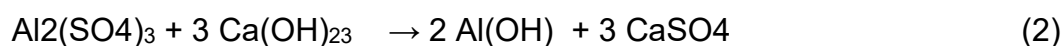
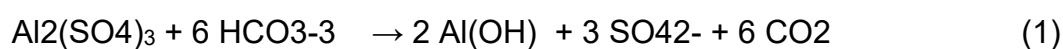


Colloidal particles, due to their size, naturally decant very slowly. Therefore, it is necessary for them to agglomerate in order to form larger particles to be efficiently eliminated in the decantation stage.⁴ In raw water with a pH range between 5.0 and 8.0, colloidal particles are mostly negatively charged. These repulsions make the possibility of forming larger clusters very unlikely. Thus, since repulsive electric forces are the basis of the stability

of colloidal particles, neutralizing them entails their agglomeration. This step occurs in coagulation, where the destabilization of colloidal and suspended particles is processed, with the removal of the forces that keep them apart (neutralization of the negative electrostatic charges on the surface of the particles).^{2,5}

Coagulation begins right after the application of coagulants, through a rapid mixing process and lasts a few seconds. The added coagulants rapidly hydrolyze and form insoluble precipitates that destabilize the negatively charged colloidal particles. It is common knowledge that polyvalent cations in water, such as Al^{3+} , Fe^{3+} , Fe^{2+} , neutralize the electrical charges of the particles.²

Aluminum Sulfate is probably the most widely used coagulant in water treatment. The classic chemical formula of Aluminum Sulfate is $Al_2(SO_4)_3 \cdot 18 H_2O$, but the versions used in water treatment contain varying amounts of crystallization water.² When aluminum sulfate reacts with the natural alkalinity of raw water, usually in the form of bicarbonates, Equation (1) occurs. After this reaction, a decrease in pH is observed due to the production of CO_2 . When alkalinity is reduced, calcium hydroxide is added, where there is a reaction between calcium hydroxide and aluminum sulfate, according to Equation (2).



When aluminium sulphate is added to water, the monomeric form, Al^{3+} undergoes various hydrolysis and polymerisation reactions, forming different aluminium species, such as soluble aluminium monomeric complexes (e.g. Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_3$ (soluble) and $Al(OH)_4^-$), soluble polymeric aluminium complexes (e.g. $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}(OH)_{24O_47}^{+}$) and solid precipitates (e.g., $Al(OH)_3(s)$). These species formed with high positive charges are responsible for coagulation. The formation of these species depends on the pH and dosage of the coagulant.^{2,6}

When the coagulation pH is lower than 5.0, there is an inhibition of polymerization reactions, forming mostly monomers. At pH values above 8.0, the formation of $Al(OH)_4^-$ occurs, a negative species that makes it difficult to destabilize the particles. Therefore, the ideal would be to maintain coagulation at pH between 6.0 and 8.0, where the polymeric species formed highly positively charged better induce the neutralization of charges, have greater efficiency in removing color and turbidity.^{2,6}

Following this approach, a high amount of coagulant can cause a change in the surface charge of the particle, making it stable again. However, when the concentration is

further increased, the phenomenon of destabilization by sweeping occurs. When high concentrations of coagulant are used, the precipitation of metal hydroxide $\text{Al}(\text{OH})_3$ occurs. In this process, the precipitate generated can capture the colloidal particles as it forms, leading to their precipitation.^{2,6}

Soon the neutralized colloidal particles are agglutinated into larger particles, causing the formation of larger flocs, in the stage called flocculation.¹³ This step consists of the aggregation of these neutralized particles, which increase in weight and size over time, in order to enable their separation by decantation and/or filtration. The contact time is usually 10 to 20 minutes, where there is a slow mechanical stirring that promotes contact between the particles and the flakes.⁷

Finally, settling separates the solid particles suspended in the water through gravitational forces, where particles with a density higher than water settle to the bottom of the settling tank. While filtration removes the remaining particles from the coagulation, flocculation and decantation stages, ensuring the quality of the treated water.⁷⁻¹⁰

Regarding pre-oxidation, there are several advantages of its application in water treatment, such as the oxidation of organic matter, the reduction of the presence of algae, the increase in the efficiency of coagulation and filtration processes, the removal of metals and other particulate matter, in addition to reducing the taste and odor of water.^{8,9}

The pre-oxidation step breaks the bonds between the particles and the adsorbed organic compounds, promoting the reduction of the molecular mass of the organic matter. This process favors the desorption of previously stabilized organic coatings, facilitating the aggregation of particles. In the presence of metal ions, pre-oxidation can break up complexes formed with these metals, resulting in the *in situ generation* of coagulants that aid in the treatment. In addition, pre-oxidation contributes to the reduction of the negative surface charge of the matter, increasing the probability of collisions between particles.

There are several general mechanisms that may explain how preoxidation can improve coagulation. Of course, the influence varies according to the oxidant used, however, as a general rule, oxidation usually causes a change in the Zeta potential by removing the organic coating on the surface of the particles.⁷⁻⁹ BED

However, research has shown that the oxidation of water with a large amount of Natural Organic Matter (MON) can produce several compounds that pose health risks, the Disinfection Byproducts (SPDs). MON includes a complex matrix of organic compounds from natural sources that are present in water.¹⁰ Together with algae and cyanobacteria, these compounds are the main precursors that halogens react to form by-products.^{11,12}

An alternative to try to minimize the formation of SPDs includes replacing the chemical agent used, since most of them are the result of the reaction with chlorine. Some research suggests the use of Hydrogen Peroxide (H₂O₂) and Potassium Permanganate (KMnO₄).

Pre-oxidation damages the bond between the particles and their adsorbed organic compounds, reducing the molecular mass of organic matter, which would result in the desorption of stabilized organic coatings, and the reduction of the steric effect and the electrostatic barrier. In the presence of iron or manganese, pre-oxidation can disrupt metal ion complexes, resulting in an *in situ* production of coagulant.⁷⁻⁹ BED

In addition, pre-oxidation is effective in reducing the negative charge of organic matter, increasing the probability of collisions between particles in the coagulation stage. And due to the loss of CO₂ during oxidation, there is a greater potential to induce CaCO₃ precipitation and particle aggregation.⁸⁻¹⁰

However, it is necessary to compare the results of each pre-oxidant to the reality of each WTP. Each station has its peculiarities and procedure for treating water, in addition to the characteristics of raw water being unique. Therefore, to make its application viable, it is necessary to evaluate the quality of the water after treatment, quantify the by-products generated, the cost, the efficiency of oxidation, and other indicators.

2 OBJECTIVE

The objective of this work was to evaluate the behavior of different oxidants in the pre-oxidation stage of raw water in a WTP. The pre-oxidants chosen for this study were: sodium hypochlorite, sodium dichloroisocyanurate, hydrogen peroxide and potassium permanganate. Several *Jar-test* tests were performed in order to evaluate the behavior of pre-oxidation, where the water quality was monitored using several physicochemical parameters. Afterwards, the different stages of water treatment were evaluated through analysis parameters using different oxidants in the pre-oxidation stage. Several *Jar-test* tests were performed in order to evaluate the behavior of each step (pre-oxidation, coagulation, flocculation, decantation and filtration) and the water quality was monitored using physicochemical parameters. The raw water samples used in this project come from the Dr. João Penido and Chapéu D'uvas dams. The waters of these dams are treated at the Marechal Castelo Branco Water Treatment Plant (ETA MCB) by the Municipal Sanitation Company (Cesama) of Juiz de Fora/MG.

3 METHODOLOGY

All materials, inputs and equipment used in the development of this work, along with explanations of the techniques used, standards used as a basis and other pertinent information are found below. The reagents and analysis kits used are shown in Table 1.

Table 1

Data of the reagents used in the physicochemical assays of this work

REAGENT	BRAND	LOT
Sodium Hypochlorite (NaOCl)	Own Synthesis *	-
Sodium Dichloroisocyanurate (C ₃ Cl ₂ N ₃ NaO ₃)	GR Chemical Industry	1620241013AL
Hydrogen Peroxide (H ₂ O ₂)	Anhydrol (35%)	50619-1
Potassium Permanganate (KMnO ₄)	Kinetics	15605
Alkalizing - Calcium Hydroxide (Ca(OH) ₂)	Geocalcium	-
Coagulant - Aluminum Sulfate (Al ₂ (SO ₄) ₃)	Coagulan 20	67L0619122
Sodium Hydroxide (NaOH)	Scientific ACS	202203095
Potassium Hydroxide (KOH)	LS Chemicals	127058
Sodium Hypochlorite (NaOCl) 8%	BH	063/24
Ferric Chloride (FeCl ₃ .6H ₂ O)	Dynamics	115622
Methyl Alcohol (CH ₃ OH)	Quimis	13082079
Anhydrous Dibasic Sodium Phosphate (Na ₂ HPO ₄)	Exodus	2207204457
Sodium Borate (Na ₂ B ₄ O ₇ .10H ₂ O)	Impex	566-M
Ferrous Ammonia Sulphate (NH ₄) ₂ (SO ₄) ₂ .6H ₂ O)	LS Chemicals	0121574
Potassium Iodide (KI)	Exodus	2303011133
Sulfuric Acid 98% (H ₂ SO ₄)	Exodus	2301190368
Ammonium Thiocyanate (NH ₄ SCN)	Vetec	1102249
Sodium Oxalate (Na ₂ C ₂ O ₄)	LS Chemicals	124588
Calcium Chloride (CaCl ₂)	Dynamics	117846
Sodium Thiosulfate (Na ₂ S ₂ O ₃)	LS Chemicals	2009165795
Alkalizing - Calcium Hydroxide (Ca(OH) ₂)	Geocalcium	-
Coagulant - Aluminum Sulfate (Al ₂ (SO ₄) ₃)	Coagulan 20	67L0619122
Determination of Aluminum: 0.10 - 1.20 mg/L	Merck	HC280992
Determination of Chlorine 0.10 - 5.00 mg/L	Policontrol	494

*Using Liquid Chlorine Generator Systems (Hidrogenon) that through brine electrolysis. # Wet synthesis from sodium hydroxide, sodium hypochlorite and ferric chloride.

3.1 WATER TREATMENT PLANT

The raw water samples used in this work come from the Dr. João Penido and Chapéu D'uvas dams, both located in the region of the municipality of Juiz de Fora, in Minas Gerais. The waters of these dams are treated at the Marechal Castelo Branco Water Treatment Plant (ETA MCB) in Juiz de Fora/MG. The ETA MCB has an installed capacity to treat up to 1300 liters of water per second. The station performs a conventional type treatment, with coagulation, flocculation, decantation, rapid filtration (6 filters with two cells per filtration unit)

and disinfection, in addition to fluoridation and pH correction. The collection for the *Jar-test* tests was done at the ETA just before the addition of the alkalizer/coagulant, and at that time the composition of the waters from the Dr. João Penido and Chapéu D'uvas dams had already been made.

3.2 JAR-TEST TESTS

The *Jar-test* assay provides information on the optimal conditions for the execution of coagulation-flocculation. Generally, the optimized coagulation pH value and coagulant dosage are chosen. Then the collected samples are evaluated for apparent color and turbidity or removal of organic matter.¹¹ These assays are procedures widely used in WTPs to determine the optimal dosages of the agents to be used. The *Jar-test* apparatus consists of six jars that simulate the agitation conditions and contact and settling time used in the treatment of raw water. Afterwards, different analysis parameters must be performed to evaluate the quality of the water after treatment. In this work, the *Jar-test* was used to test different oxidation conditions, which will be explained in more detail in the topic of the results. The model used was the *Jar-test* Microcontrolled 6 Tests - JT303M/6 (Brand: Milan) (see Figure 2).

In summary, the tests are carried out as follows: start by adding 2 L of raw water to each jug. Then the coagulant and alkalizer are added to the jugs at the same time and rapid stirring (100 rpm) is carried out for 1 minute. Up to this point, the coagulation stage is simulated. Afterwards, the stirring speed decreases (70 rpm) and is maintained for another 19.5 minutes. This stage is marked by the formation of larger flakes and agglomerates (flocculation). Finally, the decanting stage begins for 4 minutes where there is no agitation, then the flakes settle.¹³

For this study, the pre-oxidation stage was added. The summary of the programming of the equipment used is shown in Figure 2. The rapid mixing, slow mixing and sedimentation steps were kept fixed so that it was possible to evaluate only the contribution of pre-oxidation. The pre-oxidation velocity gradient was also not changed. All *Jar-test* tests were performed in short periods so that the springs did not change their characteristics significantly.

Figure 2

Example of a Jar-test test next to the summary of the equipment programming



FASE	PARÂMETROS	CONDIÇÕES
PRÉ-OXIDAÇÃO	Tempo de Contato:	2 - 8 minutos
	Gradiente de Velocidade:	40 rpm
	Dosagem:	0,1 - 2,50 mg/L
COAGULAÇÃO (Mistura Rápida)	Tempo de Contato:	1,0 minutos
	Gradiente de Velocidade:	100 rpm
	Dosagem:	20 mg/L
	pH:	6,38
FLOCULAÇÃO (Mistura Lenta)	Tempo de Contato:	19,5 minutos
	Gradiente de Velocidade:	70 rpm
DECANTAÇÃO (Sedimentação)	Tempo de Contato:	4,0 minutos
	Gradiente de Velocidade:	0 rpm

3.3 TECHNIQUES

The tests were carried out at Cesama's Central laboratory, which has recognition of competence in the standard in ABNT NBR ISO/IEC 17025:2017, and at the ETA MCB laboratory.

The determination of Free Residual Chlorine (mg/L) was made using the *4500-Cl G. DPD Colorimetric Method, 2023*. In slightly acidic solutions the free chlorine reacts with n-n-diethyl-p-phenylenediamine (DPD) to form a pink color.¹⁵

The colorimetric method, *4500- H2O2 Hydrogen Peroxide (Residual) (Proposed)*, is suitable for measuring Hydrogen Peroxide (mg/L) in the presence of Paraacetic Acid. The method, which takes 1 minute, is based on the reaction of ferric thiocyanate. Under acidic conditions, H₂O₂ oxidizes ferrous iron to the ferric state, resulting in the formation of an orange ferric thiocyanate complex.¹⁶

The concentration of potassium permanganate (mg/L) is directly proportional to the absorbance measured at 525 nm. Concentrations are best determined from the light absorption characteristics of a sample filtered by means of a spectrophotometer. The color

of the solutions ranges from light pink (diluted) to deep purple (concentrated). The method of determination is *the 4500-KMnO₄ Potassium Permanganate, 2023*.¹⁷

The potentiometric determination of pH is made based on the *4500-H+ B pH method - Electrometric Method, 2023* with the aid of a combined glass electrode.¹⁸

The determination of Apparent Color (CU) in waters was made by the *2120 E. Tristimulus Spectrophotometric Method, 2023*. Apparent Color includes not only the color due to substances in solution, but also due to the suspended matter, determined in the original sample without filtration. This procedure is based on the Tristimulus method.¹⁹

Turbidity (NTU) was measured by the nephelometric method, based on a comparison of the intensity of the light scattered by the sample under defined conditions with the intensity of the light scattered by a reference standard suspension. The standard used was *2130 B Nephelometric Method, 2023*. Formazin suspension was used as the primary reference standard.²⁰

The determination of Electrical Conductivity is made by the *2510 B Conductivity - Laboratory Method, 2023* with the aid of a conductivity meter with sensitivity in the order of $\mu\text{S}/\text{cm}$.²¹

The Dissolved Oxygen (mg/L) determination was made based on the *4500-O G. Membrane-Electrode Method, 2023* through the use of an oximeter with a galvanic electrode.²² Temperature ($^{\circ}\text{C}$) was measured with the aid of the same oximeter, based on the *2550 B Temperature - Laboratory and Field Methods, 2023*.²³

The Pre-Oxidation Demand tests were performed using the *2350 Oxidant Demand/Requirement method, 2023*. Oxidant demand corresponds to the difference between the amount of oxidant added and the concentration of residual oxidant measured after a specific contact time, considering a defined pH and temperature. Oxidant consumption, on the other hand, refers to the amount of oxidant needed to reach a given oxidant residue, in a given contact time, pH, and temperature.²⁴

The aluminum residual (mg/L) test is colorimetric and was performed with the aid of the *Hach kit*. The calibration curve was already pre-programmed in the spectrophotometer used.

3.4 EQUIPMENT

In the present study, several equipment were used to determine physicochemical parameters in the samples under analysis. All instruments were calibrated, ensuring the accuracy and reliability of the measurements taken during the study. To determine pH, a pH meter was used - Brand: Milwaukee, Model: MW151 max. Turbidity was determined by

means of a Colorimeter - Brand: Policontrol, Model: AP 2000 WT, while Apparent Color was analyzed with the aid of a Tristimulus Colorimeter (0 – 500 UC) - Brand: Digimed, Model: DM-Color. The quantification of Free Residual Chlorine was performed using a Colorimeter - Brand: Policontrol, Model: AquaColor Chlorine FE. Conductivity was measured with a Conductivity Meter - Brand: Thermo Scientific, Model: Orion Star A212. An Oximeter was used to determine Dissolved Oxygen and Temperature - Brand: Hanna, Model: HI 98193. For the Colorimetric Methods, the Spectrophotometer (340 to 900 nm) - Brand: Hach, Model: DR2800 - was used.

4 RESULTS AND DISCUSSION

For the execution of the work, the *Jar-test* was used to simulate the coagulation/flocculation process in a water treatment plant. The tests were always carried out in short periods, with the objective that the raw water used maintained the most similar characteristics. In the development of this work, the concentrations of pre-oxidants were varied, along with the contact time, and the samples obtained were compared by means of different physicochemical parameters.

4.1 EVALUATION OF PRE-OXIDANTS

In this stage, the tested pre-oxidants (sodium hypochlorite, sodium dichloroisocyanurate, hydrogen peroxide and potassium permanganate) were studied for behavior at different concentrations and contact time. The objective was to optimize the dosage of the pre-oxidant and observe how the contact time affected the efficiency of the process.

After the *Jar-test* assays, the samples were collected and analyzed for the following parameters: Apparent Color (CU), pH, Conductivity ($\mu\text{S}/\text{cm}$), Turbidity (NTU), Dissolved Oxygen (mg/L), Temperature ($^{\circ}\text{C}$). The samples were always evaluated in comparison to the raw water used. Since pre-oxidation is applied in the Water Treatment Plant before the alkalization step, it is not possible to control the pH of the reaction. Therefore, the pH was kept fixed in all *the Jar-test* tests performed. As the coagulation/flocculation step is strongly influenced by pH, by keeping the pH fixed it was possible to minimize its influence, focusing only on the action of the different pre-oxidants.

4.1.1 Sodium hypochlorite

The pre-oxidation stage in WTPs is often called pre-chlorination, due to the frequent use of chlorine derivatives in this phase of treatment, due to the high oxidizing power. Among the derivatives, Sodium Hypochlorite (NaClO) is the most used.

When sodium hypochlorite is dissolved in water, it undergoes a chemical reaction forming hypochlorous acid and the hypochlorite ion. Hypochlorous acid has a high disinfection power, being the main responsible for disinfecting water.²⁴

The sodium hypochlorite used in this work was generated in a chlorine-generating equipment called 'Hidrogenon' installed in the MCB WTP. Its operation is based on the electrolysis reaction of brine (water and sodium chloride). The 3% brine solution is continuously and automatically injected into the electrolytic cell, where electrochemical reactions for the conversion of sodium chloride to sodium hypochlorite take place.²⁵ The final solution obtained is 1000 mg/L of sodium hypochlorite.

Hypochlorite interacts with sample components through three main mechanisms: oxidation, addition, and substitution. Initially, chlorine can oxidize reducing species, such as Fe^{2+} , Mn^{2+} and sulfide, being reduced to inorganic chloride (Cl^-) during these reactions. Then, chlorine can be added to olefins and other organic compounds containing double bonds, resulting in the formation of chlorinated organic compounds. Finally, chlorine can replace chemical groups in substrates, generating addition and substitution reactions forming organochlorine species.¹⁵

In this assay, first the pre-oxidation time was fixed and the concentration of sodium hypochlorite was varied. Then, the optimized concentration value was kept fixed, and the contact time varied. The tests were performed in the *Jar-test*, where the conditions of each jar are shown in Figure 2. After the *Jar-test* was performed, the final samples were collected and analyzed together with the raw water for the following parameters: Free Residual Chlorine (CRL), Apparent Color, pH, Conductivity, Turbidity, Dissolved Oxygen and Temperature.

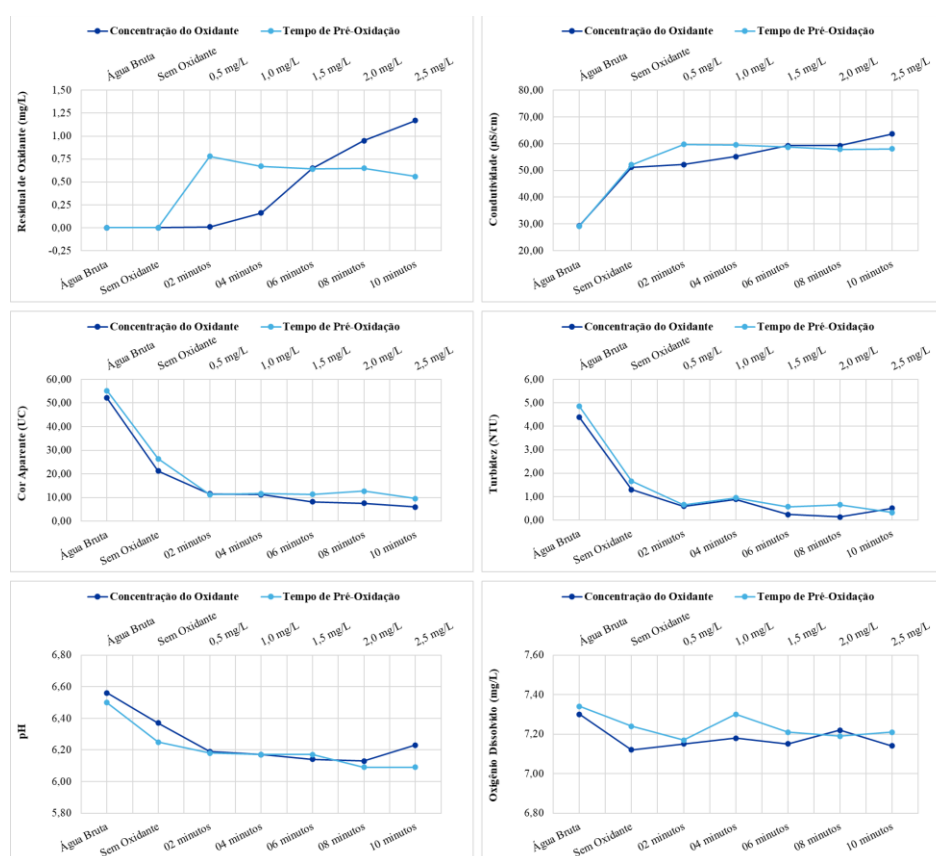
Initially, it was necessary to determine the volume of alkalizing agent used in each jar. The sodium hypochlorite solution (1000 mg/L) used in the assays is alkaline, so the required amount of the 1% geocalcium alkalizing agent was reduced as the dosage of the oxidant was increased. In this step, the volume of alkalizing agent needed to reach the ideal pH of 6.38 was tested for each oxidant concentration. The volumes found are in Table S2.1.1 (Supplementary Material). It is interesting to note that from the results, it can be concluded that the use of sodium hypochlorite as a pre-oxidant can cause a reduction in the amount of alkalizing agent used in WTP.

Afterwards, the pre-oxidation time was set at 6 minutes and the sodium hypochlorite concentration was varied from 0.5 to 2.5 mg/L. Then, the optimized concentration value was kept fixed (1.5 mg/L), and the time was varied from 2 to 10 minutes. The results of the analyzed parameters are in Table S2.1.II and S2.1.III (Supplementary Material) and organized in graphs in Figure 3.

The first analyzed parameter of CRL provides us with an insight into the oxidation behavior of the sample. As the oxidant concentration increases, an increase in the residual CRL is observed. This behavior is expected when using the same raw water sample, which has a certain oxidant demand. The higher the oxidant concentration, the higher the residual CRL value. Therefore, the CRL varies from 0.01 to 1.17 mg/L, with the increase in the concentration of oxidant. The same occurs with the increase in oxidation time. Since the longer the contact time, the greater the amount of oxidized sample and oxidant consumed, there is a decrease in the CRL residual (ranging from 0.78 to 0.56 mg/L).

Figure 3

Graphs showing the behavior of different water analysis parameters after application of different sodium hypochlorite concentrations and pre-oxidation times



In addition, by considering CRL values, it is also possible to evaluate the efficacy of sodium hypochlorite in meeting oxidant demand (see Table S1.1). It was verified that at the concentration of 0.5 mg/L of oxidant, the sample consumed 0.49 mg/L (98.0% / 6 minutes) and at the concentration of 1.0 mg/L, the sample consumed 0.84 mg/L (84.0% / 6 minutes). These high results indicate that perhaps there was still matter for oxidation, but the oxidant had already been depleted or was very low. Therefore, these concentrations would not be meeting the demand of the raw water sample. In addition, the residual CRL was below the recommended limit of 0.30 mg/L after pre-oxidation.²⁶

At concentrations of 2.0 and 2.5 mg/L of oxidant, the results were quite similar, with an intake of 1.05 mg/L (53% / 6 minutes) and 1.33 mg/L (53% / 6 minutes), respectively. This indicates that there was still enough CRL to meet the oxidant demand of the sample in both cases. However, the problem observed was that the oxidant residuals were significantly above the recommended limit of 0.30 mg/L after oxidation.²⁶

At the concentration of 1.5 mg/L, the sample consumed 0.85 mg/L (57% / 6 minutes), a result that apparently satisfies the oxidant demand of the sample, keeping the residual closer to the recommended value, compared to the other assays.

Regarding the study of oxidation time, the intake ranged from 0.72 mg/L (48% / 2 minutes) to 0.94 mg/L (63% / 10 minutes). The variation was not so significant when compared to concentration studies. However, a predicted pattern is observed: the increase in oxidation time, resulting in a greater amount of oxidized sample, inferring an increase in oxidant demand.

Regarding conductivity, the result of the raw water sample was initially at 29.36 and 29.15 $\mu\text{S}/\text{cm}$ and increased to 51.20 $\mu\text{S}/\text{cm}$ (increase of 43%) and 52.10 $\mu\text{S}/\text{cm}$ (increase of 44%) after the coagulation/flocculation stage (without pre-oxidation), in the tests of oxidant concentration and contact time, respectively. The increase in electrical conductivity after coagulation/flocculation is a result of dissociation of the coagulant producing ions that increase conductivity.²⁷

According to the graph, it was observed that the electrical conductivity increased as the dose of oxidant increased. The conductivity ranged from 51.20 $\mu\text{S}/\text{cm}$ to 63.70 $\mu\text{S}/\text{cm}$, representing a growth of 20%, as the concentration of sodium hypochlorite increased from 0.0 to 2.5 mg/L. The samples that went through the pre-oxidation process had different concentrations of sodium hypochlorite added to the water. The resulting CRL dissociates into ions, mostly in the form of hypochlorite ions (OCl^-) or chloride ions (Cl^-), depending on the pH of the water. This dissociation increases the concentration of charged particles in the water, which results in a higher electrical conductivity compared to the sample that did not

go through the pre-oxidation step. The increase in the concentration of oxidant results in an increase in conductivity. Therefore, it is possible to infer a directly proportional relationship between the residual of CRL and conductivity.²⁷⁻²⁹

Considering the same principle, in the contact time test, the conductivity varied from 59.75 $\mu\text{S}/\text{cm}$ to 58.10 $\mu\text{S}/\text{cm}$, a reduction of 2.8%, as the oxidation time increased from 2 to 10 minutes. In this interval, the CRL value decreased from 0.78 to 0.56 mg/L. This was an expected result, considering the directly proportional relationship, previously postulated.

Among the objectives of water treatment is the removal of colloidal substances, that is, solid material in suspension (color) and/or dissolved (turbidity). Thus, it is possible to evaluate the efficiency of the treatment based on the apparent color and turbidity of the final sample, in relation to the raw water sample. Color and turbidity removal is calculated as a percentage (%), comparing the results obtained after treatment compared to raw water. After the addition of aluminum sulfate (coagulation) to bind impurities, where the formed particles group into larger flocs (flocculation) and settle, it is possible to observe a decrease in color and turbidity. This was the behavior observed in all sample results at the end of the *Jar-test*, as shown in Figure 3. As shown in the graph, as a general rule, the increase in the concentration of oxidant and oxidation time causes a reduction in apparent color and turbidity, since these variables act to optimize the performance of the treatment.

The apparent color decreased from 52.10 UC to 21.20 UC (59% color removal) and 55.20 UC to 26.40 UC (52% color removal) after the coagulation/flocculation step (without pre-oxidation), in the oxidant concentration and contact time assays, respectively. Turbidity reduced from 4.38 NTU to 1.30 NTU (70% turbidity removal) and from 4.85 NTU to 1.66 UC (66% turbidity removal). This result is consistent with the execution of the *Jar-test*.

However, there is a very attractive result in this test when comparing samples that have undergone pre-oxidation. Pre-oxidation helps break down undesirable substances such as organic matter, metal compounds such as iron and manganese, and compounds that generate taste and odor. This makes it easier to clot, as contaminants can be removed more easily in the following steps.²

This was observed with the increase in the concentration of the oxidant, where the apparent color reduced from 21.20 UC to 6.00 UC, representing a reduction of 72% and a color removal of 88.5%, as the concentration increased from 0.0 to 2.5 mg/L. Turbidity, on the other hand, decreased from 1.30 NTU to 0.51 NTU, representing a reduction of 61.8% and a turbidity removal of 88%.

Regarding the pre-oxidation time, the apparent color reduced from 26.40 UC to 9.60 UC, representing a reduction of 64% and a color removal of 83%, as the oxidation time

increased from 2 to 10 minutes. Turbidity reduced from 1.7 NTU to 0.33 NTU, representing a reduction of 80% and a turbidity removal of 93%. Both results corroborate the premise that pre-oxidation increases the efficiency of water treatment. Since the higher the concentration of oxidant and pre-oxidation time, the greater the decomposition, which causes an increase in the efficiency of color removal and turbidity.

The color is usually caused by the presence of organic matter, mainly humic and fulvic acids. In addition, the color is also strongly influenced by the presence of iron salts and other metals. The color value of a water sample can also depend greatly on the pH of the sample. Generally, waters with a higher pH, especially in aquatic systems with a high load of organic matter, tend to have higher color values.³¹

In the results of Figure 3, it is observed that the pH decreases subtly as the color of the water decreases. Therefore, there is a positive correlation between pH and apparent color. The coefficient of variation (%) of the pH results in the oxidant concentration study was 1.4% and in the oxidation time study was 1.0%. Therefore, despite the correlation, it can be stated that the results do not present such a significant variation as that shown in the other parameters evaluated.

The last parameter analyzed was dissolved oxygen. According to the graph, there is no evident relationship between dissolved oxygen and other variables. The coefficient of variation (%) of the dissolved oxygen results in the oxidant concentration study was 0.5%, and in the oxidation time study it was 0.6%. Therefore, it can be concluded that the results do not present such an expressive variation as those observed in the other parameters evaluated.

In conclusion, in this stage it was observed that the application of the pre-oxidation stage positively influenced the efficiency of water treatment. The oxidant concentration and contact time increased the color and turbidity reduction, as well as the conductivity due to the higher CRL residual. Among the results analyzed, the concentration of 1.5 mg/L apparently satisfied the oxidant demand of the sample, keeping the residual closer to the recommended value (0.30 mg/L). It also showed a color removal of 84% and a turbidity removal of 95%. Therefore, pre-oxidation with sodium hypochlorite at 1.5 mg/L is recommended.

4.1.2 Sodium dichloroisocyanurate

Sodium Dichloroisocyanurate (DIC) is a chemical compound widely used as a disinfectant agent. It is an organic salt of the halogen family, derived from isocyanuric acid, containing two chlorine atoms.³² IHD also promotes water disinfection through the release of

free chlorine, in the form of hypochlorous acid (HClO). The DIC, in the presence of water, releases two molecules of hypochlorous acid and forms sodium isocyanurate.³³ One of its commercial advantages is versatility, and it can be used in powder form, in addition to having greater stability during storage.

In the first part of the study, the pre-oxidation time was fixed and the concentration of sodium dichloroisocyanurate was varied. Afterwards, the optimized concentration value was kept fixed, and the contact time varied. The assays were performed in the *Jar-test* (as shown in Figure 2) and after the assays, the samples were collected and analyzed as performed in the studies with sodium hypochlorite.

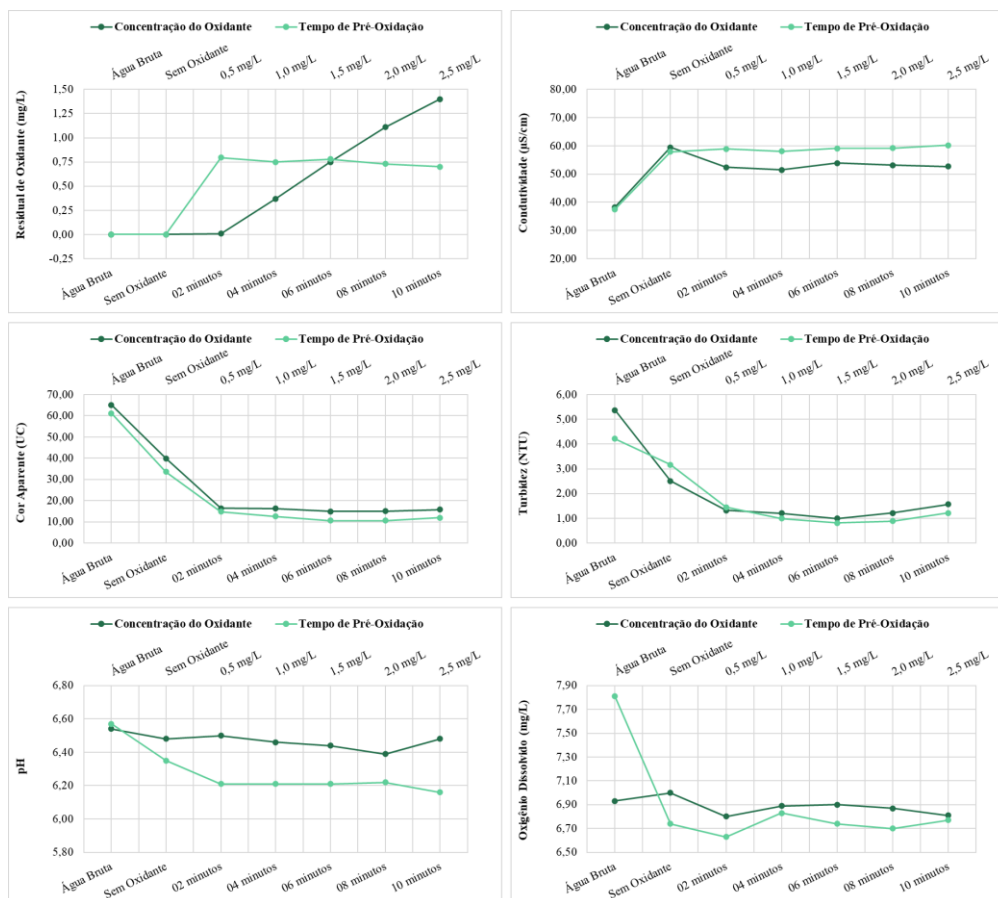
First, the volume of alkalizing agent needed to reach the ideal pH of 6.38 for each oxidant concentration was determined. The volumes found are in Table S2. I (Supplementary Material). Then, the pre-oxidation time was set at 6 minutes and the concentration at 0.5 to 2.5 mg/L. Then, the concentration was set (1.5 mg/L), and the time varied from 2 to 10 minutes. The results are in Table S2.II and A2. III (Supplementary Material) and are organized in graphs in Figure 4.

As already explained in the previous topic, the higher the oxidant concentration, the higher the CRL value. Therefore, the CRL ranged from 0.01 to 1.40 mg/L in this study. The longer the time, the greater the amount of oxidized and oxidant sample consumed, so there is a decrease in the CRL value (ranging from 0.80 to 0.70 mg/L).

Subsequently, the efficacy of sodium dichloroisocyanurate in meeting the oxidant demand was evaluated (see Table S1.2). At concentrations of 2.0 and 2.5 mg/L of oxidant, the results were quite similar, with an intake of 0.89 mg/L (45% / 6 minutes) and 1.10 mg/L (44% / 6 minutes), respectively. The demand for oxidant has not increased significantly. This indicated that there was still enough CRL to meet the oxidant demand of the sample in both cases. However, the problem observed was that the oxidant residuals were significantly above the recommended limit of 0.30 mg/L after oxidation.²⁶

Figure 4

Graphs showing the behavior of different analysis parameters applying different concentrations of sodium dichloroisocyanurate and different pre-oxidation times



At a concentration of 1.5 mg/L, the sample consumed 0.75 mg/L (50.0% / 6 minutes), a result that apparently satisfies the oxidant demand of the sample, keeping the residual close to the recommended limit of 0.30 mg/L.²⁶ At lower concentrations (0.5 and 1.0 mg/L) the oxidant residuals were significantly above the recommended limit. Regarding the oxidation time, the intake ranged from 0.71 mg/L (47.0% / 2 minutes) to 0.80 mg/L (53.3% / 10 minutes). The variation maintains the pattern of increased oxidant demand as the oxidation time increases.

As shown in the electrical conductivity, the raw water result increased from 38.30 and 37.50 $\mu\text{S}/\text{cm}$ to 59.50 $\mu\text{S}/\text{cm}$ (38.3% increase) and 57.90 $\mu\text{S}/\text{cm}$ (37.5% increase), in the oxidant concentration and contact time assays, respectively, after the coagulation/flocculation step (without pre-oxidation), due to the dissociation of the coagulant producing ions that increase electrical conductivity.²⁷

According to the graph in Figure 4, the conductivity varied between 51.50 and 59.50 $\mu\text{S}/\text{cm}$ when changing the concentration of sodium dichloroisocyanurate (0.0 to 2.5 mg/L),

representing a coefficient of variation of 5.3%. And a variation between 57.90 and 60.20 $\mu\text{S}/\text{cm}$ when changing the oxidation time (2 to 10 minutes), representing a variation of 1.4%.

When analyzing the results of the apparent color and turbidity of the final sample, in relation to the raw water sample, it is observed that the increase in the concentration of oxidant and in the oxidation time, causes a reduction in apparent color and turbidity. Initially, the apparent color decreased from 65.10 UC to 39.90 UC (38.7% color removal) and from 61.10 UC to 33.60 UC (45.0% color removal) after the coagulation/flocculation stage (without pre-oxidation), in the oxidant concentration and contact time assays, respectively. Turbidity reduced from 5.37 NTU to 2.51 NTU (turbidity removal of 53.3%) and from 4.21 NTU to 3.16 UC (turbidity removal of 24.9%).

The increase in the concentration of the oxidant (0.0 to 2.5 mg/L) resulted in the apparent color reducing from 39.90 UC to 15.80 UC (color removal of 75.7%) and turbidity reducing from 2.51 NTU to 1.56 NTU (turbidity removal of 70.9%). Regarding the pre-oxidation time, the apparent color decreased from 33.60 CU to 12.00 CU (80.4% color removal), as the oxidation time increased from 2 to 10 minutes. Turbidity reduced from 3.16 NTU to 1.22 NTU (turbidity removal of 71.0%).

Regarding pH and dissolved oxygen, it is observed in Figure 4 that they decrease subtly with the increase in the concentration of the oxidant and oxidation time. The coefficient of variation (%) of the pH results in the oxidant concentration study was 0.6% and in the oxidation time study was 1.0%. While the coefficient of variation (%) of the dissolved oxygen results in the oxidant concentration study was 1.1% and in the oxidation time study was 1.0%. Therefore, it can be concluded that the results do not present such an expressive variation as those observed in the other parameters evaluated.

In conclusion, in this stage it was observed that the application of the pre-oxidation stage positively influenced the efficiency of water treatment. The oxidant concentration and contact time increased the reduction of color and turbidity. Among the results, the concentration of 1.5 mg/L satisfied the oxidant demand of the sample, keeping the residual close to the recommended value (0.30 mg/L). It also showed a color removal of 77.1% and a turbidity removal of 81.6%. Therefore, pre-oxidation with sodium dichloroisocyanurate at 1.5 mg/L is recommended.

4.1.3 Hydrogen peroxide

Hydrogen Peroxide (H_2O_2) is a versatile and highly efficient oxidizer. Through catalysis, it can be converted into hydroxyl radical (OH), which are even more reactive species. In addition to its high oxidizing power, it has several advantages for not introducing

contaminants to the water, since it spontaneously decomposes into water and oxygen. According to Huang, Dong and Tang (1993), hydrogen peroxide oxidizes organic contaminants by abstraction of hydrogen atoms, electron transfer and addition of radicals. ·

³⁴ As physical characteristics, hydrogen peroxide is transparent, with the appearance of water and a characteristic odor. It is non-flammable, is miscible with water in all proportions and is usually sold as an aqueous solution with concentrations between 20 and 60% (w/v). In this study, a 35% (w/v) solution was used. At this concentration the compound is usually stable, however, the increase in temperature makes it very unstable.³⁵

The assay evaluated the effects of H₂O₂ concentration and pre-oxidation time on parameters such as hydrogen peroxide residual, pH, turbidity, conductivity, dissolved oxygen and temperature. Initially, the volume of alkalizing agent needed to adjust the ideal pH of 6.38 was determined. The volumes found are in Table S3. I (Supplementary Material). Then, the pre-oxidation time was set at 6 minutes and the hydrogen peroxide concentration was varied between 0.5 and 2.5 mg/L. The contact time was also changed from 2 to 10 minutes, maintaining the optimized concentration of 1.5 mg/L. The results of the analyzed parameters are recorded in Table S3.II and S3. III (Supplementary Material) and are organized in the form of graphs in Figure 5.

Figure 5

Graphs showing the behavior of different analysis parameters applying different concentrations of hydrogen peroxide and different pre-oxidation times



The results showed that with the increase in the concentration of the oxidant, the hydrogen peroxide increased from 0.00 to 0.17 mg/L, due to the greater amount of oxidant used in the process. While with the increase in time, hydrogen peroxide showed a reduction, ranging from 0.18 to 0.02 mg/L, due to the higher consumption of the oxidant. This is also consistent with the fact that peroxide is unstable and decomposes quickly.³⁶ These results suggest that both concentration and oxidation time apparently affect the efficiency of water treatment.

By analyzing the peroxide residual, it is possible to assess the effectiveness of hydrogen peroxide in meeting oxidant demand. The results are in Table S1.3. At a concentration of 0.5 mg/L, the sample consumed 0.50 mg/L (100.0% in 6 minutes). Therefore, since all the oxidant was consumed, it is inferred that there was still matter for oxidation and that this concentration did not meet the demand.

While at concentrations of 1.0, 1.5, 2.0 and 2.5 mg/L the consumption was very similar: 0.84 mg/L (84.0% in 6 minutes), 1.32 mg/L (88.0% in 6 minutes), 1.85 mg/L (92.5% in 6 minutes) and 2.33 mg/L (93.2% in 6 minutes), respectively. Regarding the oxidation time,

the oxidant consumption ranged from 1.32 mg/L (88.0% / 2 minutes) to 1.48 mg/L (98.7% / 10 minutes). A variation that maintains the pattern of the longer the oxidation time, the greater the oxidant demand.

The initial raw water conductivity of 27.28 and 26.73 $\mu\text{S}/\text{cm}$ increased to 47.20 $\mu\text{S}/\text{cm}$ (42.2% increase) and 44.40 $\mu\text{S}/\text{cm}$ (39.8% increase) after coagulation/flocculation, due to coagulant dissociation. With the increase in peroxide concentration from 0.0 to 2.5 mg/L, the conductivity decreased from 47.20 $\mu\text{S}/\text{cm}$ to 44.40 $\mu\text{S}/\text{cm}$ (variation of 4.1%).

In the time test, the conductivity varied from 44.40 $\mu\text{S}/\text{cm}$ to 43.20 $\mu\text{S}/\text{cm}$, a variation of 1.7%, as the oxidation time increased from 2 to 10 minutes. The variations were not relevant to support a conclusion.

The efficiency of the treatment was evaluated based on the apparent color and turbidity of the final sample, in relation to the raw water sample in percentage (%). After coagulation and flocculation, a reduction in color and turbidity was observed. While the increase in oxidant concentration and oxidation time contributes to the reduction of color and turbidity, optimizing the treatment.

In coagulation/flocculation, color decreased by 64.4% and 62.5%, and turbidity decreased by 74.5% and 63.7% in the oxidant concentration and contact time assays, respectively. Pre-oxidation, by decomposing undesirable substances, facilitated coagulation. With the increase in the concentration of the oxidant, the color reduction and the turbidity reduction reached the maximum efficiency at 1.5 mg/L (73.1% apparent color and 81.3% turbidity). Regarding the pre-oxidation time, the color and turbidity reduction reached the maximum efficiency in 6 minutes (71.0% of apparent color and 75.2% of turbidity).

The higher values in concentration and time probably reacted in excess of hydrogen peroxide, which can cause competitive reactions with hydroxyl radicals (OH), causing an inhibitory effect on the degradation of organic matter. In excess, peroxide acts by capturing radicals, consequently reducing their oxidation power. ³⁴

As noted in Figure 5, there is a positive trend between the pH and color of the water, with the pH decreasing as the color decreases. However, this variation is small, with a coefficient of variation of 0.4% in the oxidant concentration study and 0.3% in the oxidation time study. The last parameter analyzed, dissolved oxygen, does not present a clear relationship with the other variables. The coefficient of variation of dissolved oxygen was 1.1% in the oxidant concentration study and 1.3% in the oxidation time study, indicating that there were no significant variations.

In summary, at this stage, pre-oxidation with hydrogen peroxide had a positive effect on the efficiency of water treatment. The concentration of the oxidant and the contact time

contributed to the reduction of color and turbidity, in addition to influencing conductivity. Among the results obtained, the concentration of 1.5 mg/L seems to have adequately met the oxidant requirement of the sample, keeping the residual closer to the ideal value. Above this concentration, pre-oxidation showed an inhibitory behavior that decreased the efficiency of the process. This value also provided a color reduction of 73.1% and turbidity of 81.3%. Thus, it is recommended to use pre-oxidation with hydrogen peroxide at 1.5 mg/L.

4.1.4 Potassium permanganate

Potassium Permanganate (KMnO_4) can be used as an oxidant in water treatment plants. There are some advantages to its use, such as taste and odor control and the removal of color, iron and manganese. In addition, pre-oxidation with potassium permanganate can help reduce natural organic matter, while reducing the formation of SPDs.^{36,37}

Its use is usually done in liquid form, dosing directly in raw water. In an aqueous medium, potassium permanganate dissociates. However, at neutral pH, the formation of the manganese dioxide precipitate can occur.^{37,38} Therefore, when a plant uses pre-oxidation with potassium permanganate, care should be taken to remove this precipitate during the remainder of the treatment.^{39,40}

In the first part of the study, the concentration of potassium permanganate was varied, keeping the pre-oxidation time fixed. After optimizing concentration, the contact time was changed. After the tests, the samples were collected and analyzed for: Potassium Permanganate, Apparent Color, pH, Conductivity, Turbidity, Dissolved Oxygen and Temperature.

In Table S4. I (Supplementary Material) are the volumes of alkalizing necessary to reach the ideal pH of 6.38 for each concentration of oxidant. First, the pre-oxidation time was set at 6 minutes and the concentration ranged from 0.1 to 0.5 mg/L. The potassium permanganate solution has a vibrant purple color. Therefore, if it is used in excess, it gives color to the water. Therefore, permanganate concentrations were chosen that after oxidation did not leave a large residual of color. In the chosen range, it was observed that after the addition of permanganate, the raw water lost its yellowish color and turned pink, which disappeared after the end of oxidation.

Then, the concentration was fixed (0.2 mg/L), and the time varied from 2 to 10 minutes. The results are in Table S4.II and A4. III (Supplementary Material) and are organized in graphs in Figure 6.

The higher the oxidant concentration, the greater the permanganate residual, ranging from 0.00 to 0.14 mg/L. Regarding the contact time, it was not possible to establish a directly

or inversely proportional relationship between the potassium permanganate residual and the time parameter, since the concentration decreased (0.08 to 0.04 mg/L) and then increased again (0.04 to 0.06 mg/L).

Table S1.4 evaluates the efficacy of potassium permanganate in meeting oxidant demand. At concentrations of 0.1 to 0.3 mg/L, the samples consumed 0.10 mg/L (100.0% / 6 minutes), 0.20 mg/L (100.0% / 6 minutes) and 0.30 mg/L (100.0% / 6 minutes), respectively. While at concentrations of 0.40 and 0.50 mg/L, the results were quite similar, with the samples consuming 0.35 mg/L (87.5% / 6 minutes) and 0.36 mg/L (72.0% / 6 minutes).

According to the conductivity results, the raw water showed an increase from 27.52 and 26.95 $\mu\text{S}/\text{cm}$ to 47.30 $\mu\text{S}/\text{cm}$ (71.9% increase) and 42.00 $\mu\text{S}/\text{cm}$ (55.8% increase) in the concentration and contact time assays, respectively, after coagulation/flocculation (without pre-oxidation). With different concentrations (0.1 to 0.5 mg/L), there was a variation between 45.20 and 43.70 $\mu\text{S}/\text{cm}$, representing a variation of 3.0%. The variation with time (2 to 10 minutes) was between 41.60 and 41.90 $\mu\text{S}/\text{cm}$, a change of 0.3%.

Regarding the apparent color and turbidity results, it was observed that after coagulation/flocculation without oxidants, the color results reduced from 56.50 UC to 20.40 UC (63.9% color removal) and from 53.10 UC to 20.00 UC (62.3% color removal), in the oxidant concentration and contact time assays, respectively. Turbidity reduced from 5.07 NTU to 1.60 NTU (turbidity removal of 68.4%) and from 3.82 NTU to 1.19 NTU (turbidity removal of 68.8%).

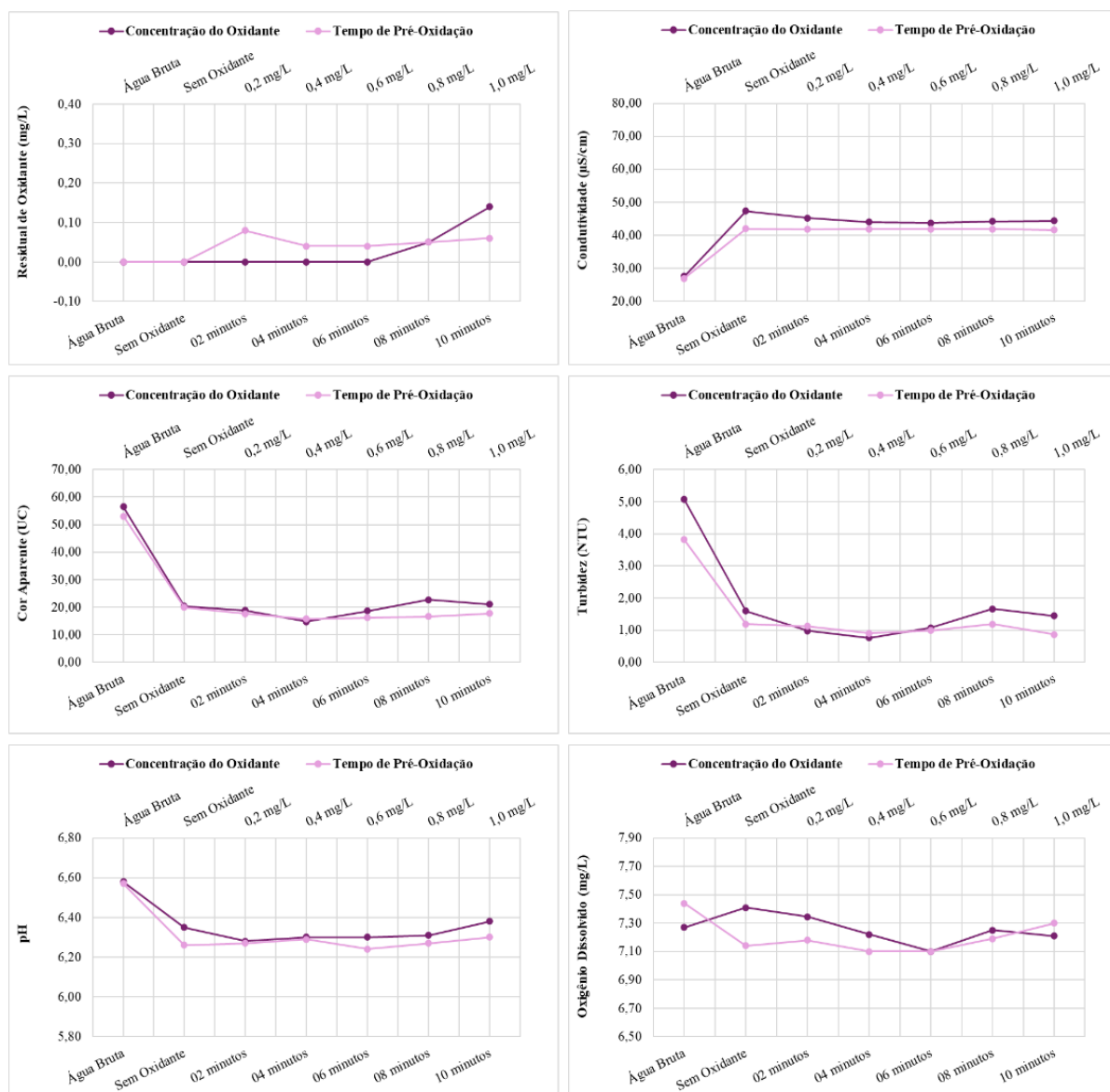
With the increase in the concentration of the oxidant from 0.0 to 0.2 mg/L, the apparent color reduces from 20.40 UC to 14.80 UC (73.8% color removal) and the turbidity from 1.60 NTU to 0.76 NTU (85.0% turbidity removal). However, from the concentration of 0.2 to 0.5 mg/L, the apparent color actually increases from 14.80 UC to 21.10 UC (42.6% color increase) and the turbidity from 0.76 NTU to 1.44 NTU (89.5% turbidity increase). This increase is expected considering that the potassium permanganate solution has a vibrant purple color and the higher the concentration of oxidant, the greater its residual in the final sample. Regarding the pre-oxidation time, in the increase of 2 to 4 minutes the apparent color decreased from 17.65 UC to 15.70 UC and the turbidity, in turn, reduced from 1.12 NTU to 0.90 NTU. On the other hand, in the oxidation time of 4 to 10 minutes, the behavior of the apparent color and turbidity was increasing, probably due to the lower oxidation efficiency.

Both pH and dissolved oxygen decreased moderately with increasing oxidant concentration and oxidation time. The coefficient of variation of the pH results was 0.6% in the oxidant concentration study and 0.3% in the oxidation time study. The coefficient of variation of the dissolved oxygen results was 1.5% in the oxidant concentration study and

1.0% in the oxidation time study. These results indicate that the variations in these parameters were not as expressive as those observed in the other parameters analyzed.

Figure 6

Graphs showing the behavior of different analysis parameters applying different concentrations of hydrogen peroxide and different pre-oxidation times



Thus, the addition of permanganate in pre-oxidation increased the efficiency of the treatment. Pre-oxidation contributed to a greater reduction in color and turbidity. The concentration of 0.2 mg/L was the most effective, with color removal of 73.8% and turbidity removal of 85.0%. At higher concentrations, due to the higher residual potassium permanganate, water coloration and turbidity increased. Therefore, the use of 0.2 mg/L of potassium permanganate in pre-oxidation is recommended.

4.2 EVALUATION OF THE STAGES OF WATER TREATMENT

In order to better understand the execution of water treatment using different oxidants, *Jar-Test assays were used*. The *Jar-test* was used to simulate the process of pre-oxidation/coagulation/flocculation/decantation in a water treatment plant. This test was carried out by placing the same sample of raw water in all the jars. In jars 2 to 6, the different pre-oxidizers were placed under their optimized analysis conditions. In jar 1, the pre-oxidation stage was not performed. The execution of the assay is summarized in Table 2, including the concentrations of pre-oxidants, together with the contact time, coagulant volume, coagulant dosage and alkalizing volume used in the assays.

Table 2

Summary of the Jar-Test run using different oxidants

Jug	Oxidant	Oxidizing Concentration (mg/L)	Pre-Weather Oxidation (min)	Vol. (mL) Coagulant	Conc. Coagulant (mg/L)	Vol. (mL) Alkalizing
1	Oxidant Free	-	-	4,0	24,0	1,3
2	Sodium Hypochlorite	1,5	8,0	4,0	24,0	0,3
3	Sodium Dichloroisocyanurate	1,5	8,0	4,0	24,0	1,0
4	Hydrogen Peroxide	1,5	8,0	4,0	24,0	1,0
5	Potassium Permanganate	0,2	8,0	4,0	24,0	1,0
6	Potassium Ferrate	2,0	8,0	4,0	24,0	1,0

The pre-oxidation time used was 8 minutes. This time was kept fixed for all oxidants. In this stage, the pre-oxidants tested were: sodium hypochlorite, sodium dichloroisocyanurate, hydrogen peroxide and potassium permanganate.

After the *Jar-Test assays*, the samples were collected at the following moments: (1) raw water, (2) after pre-oxidation, (3) after flocculation/coagulation, (4) after decantation and (5) after filtration. The samples obtained were compared by means of different physicochemical parameters: Conductivity ($\mu\text{S}/\text{cm}$), Aluminum Concentration (mg/L), Apparent Color (CU), Turbidity (NTU), pH, Dissolved Oxygen (mg/L) and Temperature ($^{\circ}\text{C}$). Figures 7, 8 and 12 show graphs of the results after each stage of the treatment: pre-oxidation, coagulation/flocculation, decantation and filtration in the different parameters.

4.2.1 Electrical conductivity and aluminium

The first stage of the water treatment used was pre-oxidation. As noted in Figure 7, the electrical conductivity of the raw water decreased when using all the different oxidants. Potassium permanganate showed the highest conductivity variation from 52.60 to 30.10 $\mu\text{S}/\text{cm}$ (42.8%) and sodium hypochlorite the smallest variation from 52.60 to 46.40 $\mu\text{S}/\text{cm}$ (11.8%). The concentration of aluminum remained unchanged.

Oxidation can result in the formation of products that affect the ionic composition of water, causing decreased electrical conductivity. The oxidation of organic matter, heavy metals or other compounds present in water can cause the formation of less ionic or insoluble products, such as chlorides, oxychlorides or chlorinated organic compounds, reducing the free ions in the solution. In addition, oxidation can precipitate some compounds, such as metal hydroxides, which can form due to the change in pH during the oxidation process.⁷⁻⁹

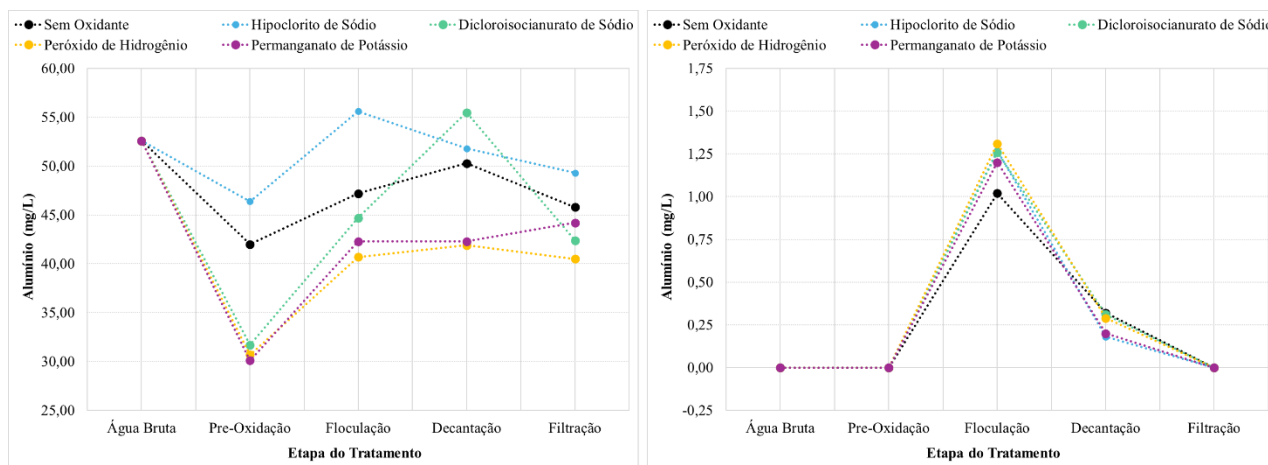
BED

After coagulation/flocculation there is an increase in conductivity in the use of all oxidants. Sodium dichloroisocyanurate showed the highest range of conductivity from 31.70 to 44.70 $\mu\text{S}/\text{cm}$ (41.0%) and the treatment without oxidant the lowest range from 42.00 to 47.20 $\mu\text{S}/\text{cm}$ (12.4%).

The increase in electrical conductivity may be a result of the addition of aluminum sulfate. After dosing the coagulant, there is dissociation of the reagent producing aluminum ions that increase electrical conductivity. This behavior is observed in the samples due to the presence of residual aluminum in the water. The dissociated aluminum sulfate releases ions into solution after the formation of the flakes, helping to increase electrical conductivity.^{27,28} This behavior is in accordance with the concentration of aluminum, which increased from 0.00 mg/L to 1.02 - 1.31 mg/L. These results are consistent with the conductivity values. For example, the non-oxidant treatment, which showed the least variation in electrical conductivity, also has the lowest aluminum residual.

Figure 7

Graphs showing the behavior of Electrical Conductivity ($\mu\text{S}/\text{cm}$) and Aluminum (mg/L) when using different oxidants in all stages of water treatment.



Then the decantation is carried out. The behavior was variable depending on the type of oxidant. Decantation can cause a decrease in the electrical conductivity of water due to the removal of suspended solid particles by the action of gravity. However, while decanting generally reduces conductivity by removing suspended solids, in some specific circumstances, it can result in an increase in conductivity.^{27,28} This was observed in samples without oxidants (47.20 to 50.30 $\mu\text{S}/\text{cm}$ - 6.6%), with sodium dichloroisocyanurate (44.70 to 55.50 $\mu\text{S}/\text{cm}$ - 24.2%) and with hydrogen peroxide (40.70 to 41.90 $\mu\text{S}/\text{cm}$ - 2.9%). As shown in the graph, these three samples were also the ones that obtained the highest aluminum residual after decantation (0.32, 0.31 and 0.29 mg/L, respectively). Therefore, they have a higher concentration of aluminum ions, contributing to increased conductivity.

After that, the sample is filtered, where the water passes through filters in order to retain the remaining impurities from the decantation stage.^{2,41} The conductivity behavior was also variable depending on the type of oxidant used. It is not possible to infer further conclusions.

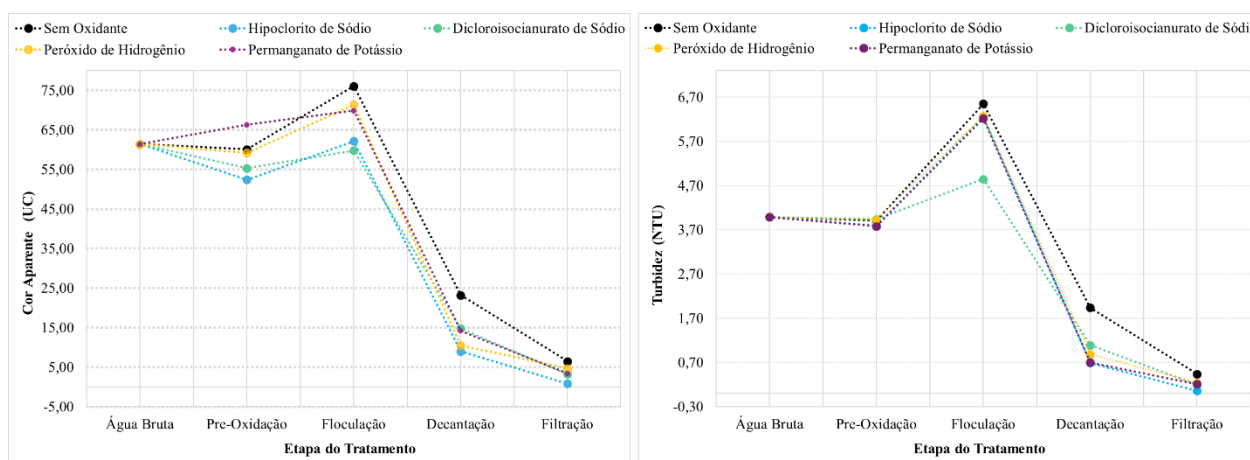
According to the standards established by the Ministry of Health, the maximum allowed limit of aluminum in drinking water is 0.20 mg/L. The presence of high concentrations of aluminum can cause intoxication, which by cumulative effect leads to degenerative processes, such as Alzheimer's disease.^{42,43} Therefore, water treatment must take into account the monitoring of aluminum levels to ensure compliance with standards. As observed, the aluminum residues were equal to 0.00 mg/L in all samples after filtration, ensuring the removal of coagulant remnants.

4.2.2 Apparent colour and turbidity

After pre-oxidation, the following samples showed apparent color and turbidity reduction: no oxidant, sodium hypochlorite, sodium dichloroisocyanurate, and hydrogen peroxide, with apparent color reduction - turbidity of 2.1 - 2.0%, 14.7 - 5.0%, 9.9 - 1.3%, and 3.6 - 1.5%, respectively. Pre-oxidation with these oxidants aided in the decomposition of organic matter, causing color reduction and turbidity. The results are shown in Figure 8.

Figure 8

Graphs showing the behavior of Apparent Color (CU) and Turbidity (NTU) when using different oxidants in all stages of water treatment.



The potassium permanganate sample, on the other hand, showed an apparent increase in color. This result is consistent considering that this oxidizer gives color to the water. The potassium permanganate solution has a vibrant purple color. Therefore, the addition of this oxidant at this stage of treatment can cause an increase in apparent color or turbidity in relation to raw water. See Figure 9.

Figure 9

Photo of the samples during the pre-oxidation stage, where the sample with sodium permanganate gives a moderate addition of color to the water.



Next came the coagulation/flocculation stage, which as a general rule caused an increase in color and turbidity in all samples. The addition of the coagulant causes a change in the surface charge of the particles, which are agglutinated into larger particles, causing the formation of larger flakes. Therefore, the sediments are still in suspension, forming a highly heterogeneous solution, as shown in Figure 10.

According to the results, an increase in apparent color between 5.4 - 26.6% and an increase in turbidity of 23.1 - 67.5% is observed. The sample without oxidant showed the greatest increase (26.6% of apparent color and 67.5% of turbidity). It was observed during the experimental stage that the samples with oxidants showed the formation of flocs faster than the sample without oxidant, in addition to resulting in larger and heavier flakes. Refer to Figure 11 to observe this phenomenon in samples without oxidant and with sodium hypochlorite as an example.

This phenomenon may be an indication of why there was a greater increase in the sample without oxidant, especially in turbidity. The tests were carried out with the same raw water, so they have the same amount of suspended solids. However, the sample without oxidant resulted in a greater increase in turbidity than the others. Since turbidity is proportional to the shape, size, and composition of the particle, the difference in particle size may explain this difference. The sample without oxidant had a higher amount of smaller particles (lower mass) with a strong ability to reflect and scatter light. The samples with oxidants, on the other hand, resulted in a smaller number of larger particles (greater mass) giving the water a lower turbidity. ^{Pages 44-46}

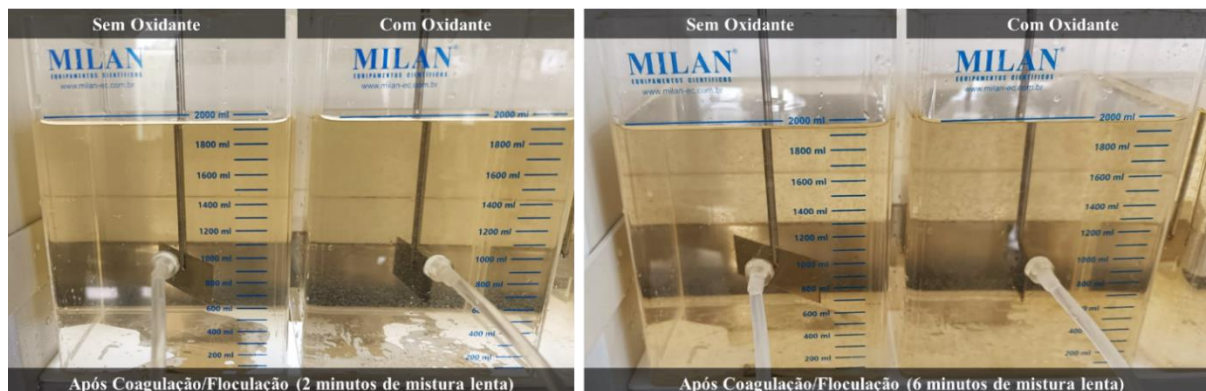
Figure 10

Photo of the samples after the coagulation/flocculation stage and after decantation



Figure 11

Photo of the sample without oxidant and with oxidant (sodium hypochlorite), after 2 minutes of slow mixing in the coagulation/flocculation step and after 6 minutes of slow mixing.



Then, decantation occurs that separates the suspended solid particles through gravitational forces. At this stage, a great change in the apparent color and turbidity results is observed, since particles with a density higher than water are deposited at the bottom of the jug. Therefore, as expected, all samples showed a large reduction in apparent color (between 69.5% and 85.5%) and turbidity (between 70.4% and 89.0%). The sample without oxidant showed the smallest reduction (69.5% of apparent color and 70.4% of turbidity), indicating that there was a less efficient sedimentation of the particles in relation to the other samples with oxidants.

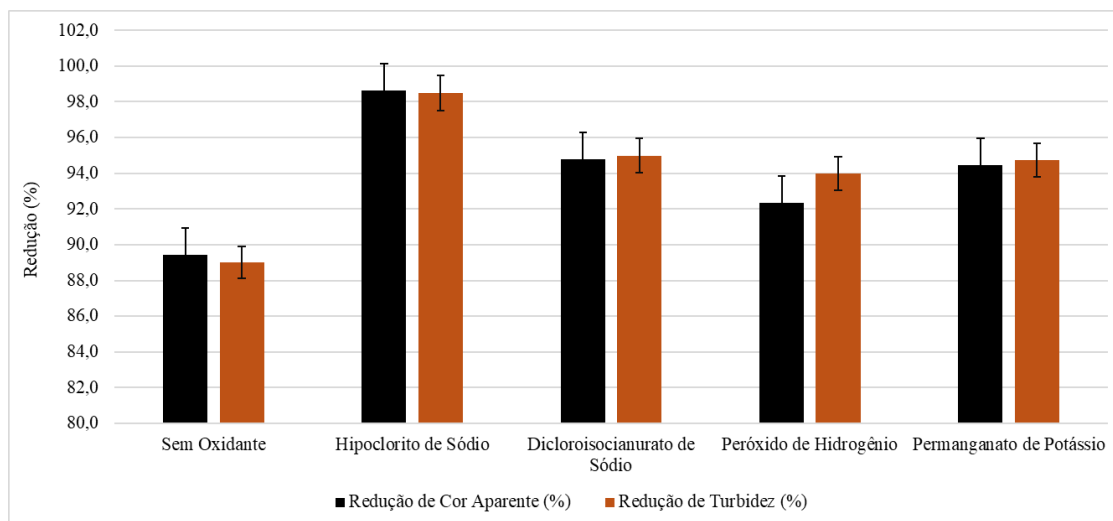
Finally, filtration is carried out, where the remaining particles from the previous steps are removed. The samples were filtered on Whatman 40 quantitative filter paper. As observed in the results, all samples resulted in a large reduction in apparent color (between 55.2% and 90.6%) and turbidity (between 70.0% and 91.3%).

Often, WTPs use the apparent color and turbidity results of *the Jar-tests* to evaluate the efficiency of the treatment. Thus, it is possible to compare the results to conclude which was the most efficient treatment, shown in Figure 12.

It is observed that the highest treatment efficiency was observed in the sodium hypochlorite samples, where the apparent color reduced from 61.40 UC to 0.85 UC, representing a color removal of 98.6%. Turbidity reduced from 3.99 NTU to 0.06 NTU, representing a turbidity removal of 98.5%. While the lowest efficiency was in the samples without oxidant, where the apparent color reduced from 61.40 UC to 6.50 UC, representing a color removal of 89.4%. Turbidity reduced from 3.99 NTU to 0.44 NTU, representing turbidity removal of 89.0%.

Figure 12

Graphs showing the behavior of Apparent Color (UC) and Turbidity (NTU) removal when using different oxidants in the pre-oxidation step



As general terms, pre-oxidation improves the coagulation process, increasing the efficiency of water treatment. This is in line with the results, where samples with oxidants (sodium hypochlorite, sodium dichloroisocyanurate, hydrogen peroxide and potassium permanganate) resulted in higher treatment efficiency.

As established by the Ministry of Health, the maximum allowed limit of apparent color and turbidity in drinking water is 15.00 UC and 5.00 NTU, respectively.⁴³ Therefore, all the water treatments carried out in this experiment resulted in water samples in accordance with the established standards of potability.

4.2.3 pH, dissolved oxygen and temperature

In the first stage of the pre-oxidation treatment, the pH of all samples suffered a slight reduction, ranging from 2.1 to 6.9%, and the dissolved oxygen had an increase, ranging from 8.6 to 12.5%. The change in pH after oxidation depends directly on the products formed during the oxidation process and how those products interact with the water or the other components of the solution. However, this change may also be due to the process of shaking the sample during pre-oxidation in the *Jar-test*. So much so that the sample without oxidant also showed a reduction in pH and an increase in dissolved oxygen. The results are shown in the graphs in Figure 13.

To start the coagulation/flocculation stage, the aluminum sulfate coagulant and the calcium hydroxide alkalizing agent are added to the jars. As tested in previous steps, the volumes used are shown in Table 2. Since the goal is to achieve the optimized pH of 6.83, it

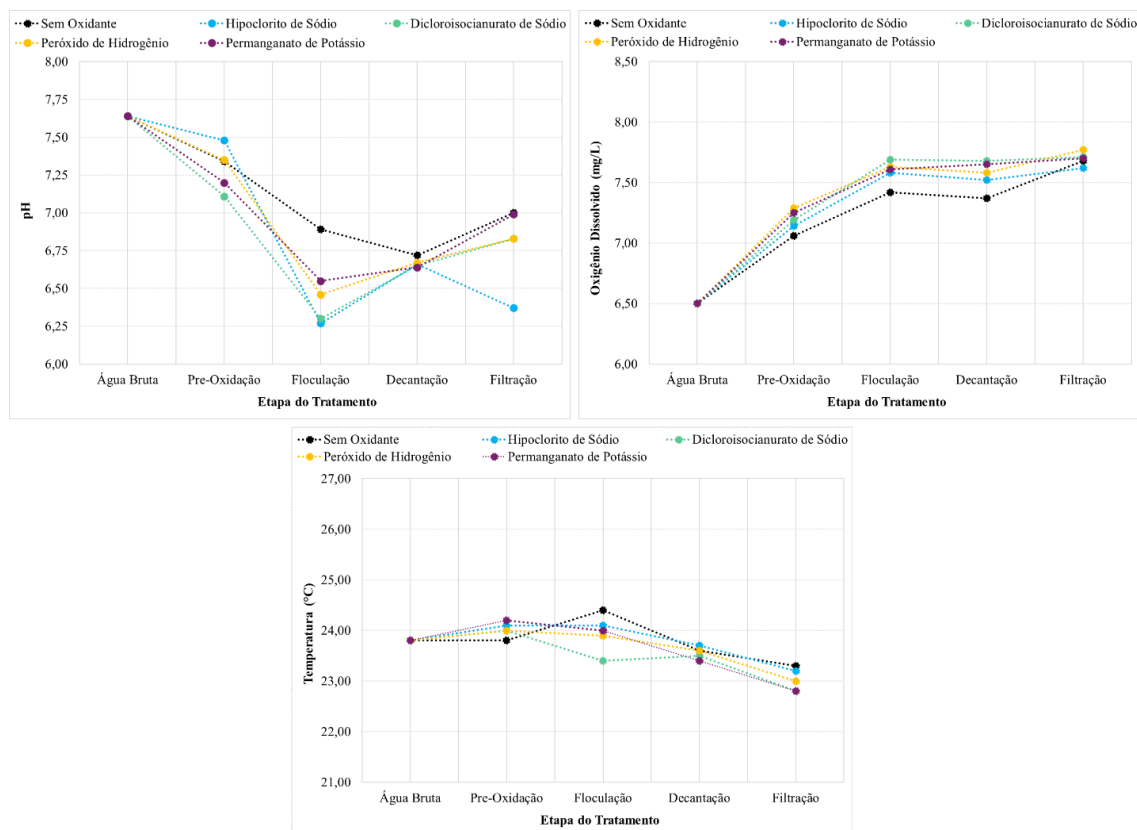
is expected that the pH of all samples will reduce in relation to the raw water in this step. This was the behavior where all samples showed a reduction in pH from 6.1 to 16.2%.

After decantation, a very significant variation in the pH of the samples is not observed, ranging from -6.2 to 2.5%. However, there was a tendency in the variation to have been positive, presenting a slight increase in pH (except in the sample without oxidant). Dissolved oxygen ranged from -0.5 to 0.8% in relation to the samples after coagulation/flocculation.

In filtration, a small increase in pH is observed, ranging from 2.4 to 5.3%. This increase may be related to greater aeration of the sample due to the vacuum filtration process. This can also be based on the results of dissolved oxygen, which increase between 0.4 and 4.2% after filtration, compared to samples after decanting. Aeration causes an increase in dissolved oxygen and a decrease in CO₂, raising the pH.⁴⁷

Figure 13

Graphs showing the behavior of pH, Dissolved Oxygen (mg/L) and Temperature (°C) when using different oxidants in all stages of water treatment



Temperature can influence the analysis of the parameters tested, especially in dissolved oxygen. Thus, temperature was evaluated during all stages of treatment to ensure sample stability. According to the results, the temperature presents a coefficient of variation

of 1.7 to 2.8% among the samples tested. Therefore, the temperature variation can be considered insignificant and its influence disregarded.

5 CONCLUSIONS

The research developed showed how the treatment of water with oxidizing agents under optimized conditions positively affected the treatment of water along the lines of what is practiced in a WTP. The goal of the pre-oxidation step is to improve the efficiency of the process, especially by increasing color and turbidity removal compared to the non-oxidant treatment, which is still practiced in some seasons. As observed, water treatment using different oxidants (sodium hypochlorite, sodium dichloroisocyanurate, hydrogen peroxide and potassium permanganate) showed a higher treatment efficiency than samples without the use of oxidants. Therefore, the results confirmed that all the oxidants used promoted the decomposition of undesirable substances and facilitated the coagulation process.

The concentration of 1.5 mg/L was effective for the first three oxidants studied (sodium hypochlorite, sodium dichloroisocyanurate, hydrogen peroxide), resulting in good color and turbidity removals, with residual values close to those recommended.

In the case of potassium permanganate, the concentration of 0.2 mg/L proved to be the most efficient, with a significant reduction in color and turbidity. This oxidant is naturally colored and can cause an excess of coloration in the water. However, at these optimized concentrations, the natural color of the oxidant did not negatively affect.

Regarding the contact time in the pre-oxidation, a predicted pattern was observed in all oxidants: the increase in the oxidation time resulted in a greater amount of oxidized sample, inferring an increase in the oxidant demand.

In conclusion, the application of all oxidants tested in the pre-oxidation stage presented a significant contribution to improve the efficiency of the treatment, which met the requirements of the main physicochemical parameters: apparent color, turbidity, conductivity and dissolved oxygen.

Pre-oxidation, when combined with coagulation and flocculation, contributed to a better performance in the removal of solids. The presence of residual aluminum, after the use of aluminum sulfate as a coagulant, was duly monitored, with aluminum levels respecting the limits established by the Ministry of Health. In addition, in all treatments performed, the water samples met the standards of potability for color and turbidity.

Thus, it can be concluded that all the processes tested are effective for water treatment. However, when comparing the treatments, it is possible to notice that sodium hypochlorite was the one that presented the best results. The hypochlorite solution did not

impart color to the water and showed a good removal of apparent color and turbidity, demonstrating a significant efficiency in the removal of impurities. However, further investigation of the behavior of oxidants using other parameters is still needed, in particular the formation of disinfection by-products and cyanotoxins when using these oxidants.

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SUPPLEMENTARY MATERIAL S1

Table 1

Oxidant demand as a function of concentration and contact time using sodium hypochlorite (1000 mg/L) as an oxidant (concentration study: fixed time of 6 minutes / oxidation time study: fixed concentration of 1.5 mg/L of oxidant)

	Experimental Conditions	Residual Chlorine Initial Free Kick (mg/L)	Residual Free Residual Chlorine (mg/L)	Oxidant Demand (mg/L)	Oxidant Demand (%)
Concentration	Oxidant Free	0,00	0,00	0,00	0,0
	0.5 mg/L	0,50	0,01	0,49	98
	1.0 mg/L	1,00	0,16	0,84	84
	1.5 mg/L	1,50	0,65	0,85	57
	2.0 mg/L	2,00	0,95	1,05	53
	2.5 mg/L	2,50	1,17	1,33	53
Oxidation Time	Oxidant Free	0,00	0,00	0,00	0,0
	02 minutes	1,50	0,78	0,72	48
	04 minutes	1,50	0,67	0,83	55
	06 minutes	1,50	0,64	0,86	57
	08 minutes	1,50	0,65	0,85	57
	10 minutes	1,50	0,56	0,94	63

Table 2

Oxidant demand as a function of concentration and contact time (for the concentration of 1.5 mg/L of oxidant) using sodium dichloroisocyanurate (1000 mg/L) for pre-oxidation (concentration study: fixed time of 6 minutes / study oxidation time: fixed concentration of 1.5 mg/L of oxidant)

	Experimental Conditions	Residual Chlorine Initial Free Kick (mg/L)	Residual Free Residual Chlorine (mg/L)	Oxidant Demand (mg/L)	Oxidant Demand (%)
Concentration	Oxidant Free	0,00	0,00	0,00	0,0
	0.5 mg/L	0,50	0,01	0,49	98,0
	1.0 mg/L	1,00	0,37	0,63	63,0
	1.5 mg/L	1,50	0,75	0,75	50,0
	2.0 mg/L	2,00	1,11	0,89	44,5
	2.5 mg/L	2,50	1,40	1,10	44,0
Oxidation Time	Oxidant Free	0,00	0,00	0,00	0,0
	02 minutes	1,50	0,80	0,71	47,0
	04 minutes	1,50	0,75	0,75	50,0
	06 minutes	1,50	0,78	0,72	48,0

	08 minutes	1,50	0,73	0,77	51,3
	10 minutes	1,50	0,70	0,80	53,3

Table 3

Oxidant demand as a function of concentration and contact time using hydrogen peroxide (35% v/v) as an oxidizer. (concentration study: fixed time of 6 minutes / oxidation time study: fixed concentration of 1.5 mg/L of oxidant)

	Experimental Conditions	Hydrogen Peroxide (mg/L)	Residual Hydrogen Peroxide (mg/L)	Oxidant Demand (mg/L)	Oxidant Demand (%)
Concentration	Oxidant Free	0,00	0,00	0,00	0,0
	0.5 mg/L	0,50	0,00	0,50	100,0
	1.0 mg/L	1,00	0,16	0,84	84,0
	1.5 mg/L	1,50	0,18	1,32	88,0
	2.0 mg/L	2,00	0,15	1,85	92,5
	2.5 mg/L	2,50	0,17	2,33	93,2
Oxidation Time	Oxidant Free	0,00	0,00	0,00	0,0
	02 minutes	1,50	0,18	1,32	88,0
	04 minutes	1,50	0,10	1,40	93,3
	06 minutes	1,50	0,04	1,46	97,3
	08 minutes	1,50	0,05	1,45	96,7
	10 minutes	1,50	0,02	1,48	98,7

Table 4

Oxidant demand as a function of concentration and contact time using potassium permanganate (1000 mg/L) as an oxidant. (concentration study: fixed time of 6 minutes / oxidation time study: fixed concentration of 0.2 mg/L of oxidant)

	Experimental Conditions	Potassium Permanganate (mg/L)	Residual Potassium Permanganate (mg/L)	Oxidant Demand (mg/L)	Oxidant Demand (%)
Concentration	Oxidant Free	0,00	0,00	0,00	0,0
	0.1 mg/L	0,10	0,00	0,10	100,0
	0.2 mg/L	0,20	0,00	0,20	100,0
	0.3 mg/L	0,30	0,00	0,30	100,0
	0.4 mg/L	0,40	0,05	0,35	87,5
	0.5 mg/L	0,50	0,14	0,36	72,0
Oxidation Time	Oxidant Free	0,00	0,00	0,00	0,0
	02 minutes	0,20	0,08	0,12	60,0
	04 minutes	0,20	0,04	0,16	80,0
	06 minutes	0,20	0,04	0,16	80,0
	08 minutes	0,20	0,05	0,15	75,0

	10 minutes	0,20	0,06	0,14	70,0
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SUPPLEMENTARY MATERIAL S2

Table 5

Evaluation of pre-oxidation with sodium hypochlorite (1000 mg/L) as an oxidant

I. DETERMINATION OF THE VOLUME OF THE ALKALIZER						
Jug	Oxidant Concentration	Oxidant (mL)	Coagulant (mL)	Ideal pH	Alkalinizing (mL)	pH after alkalinizing
1	Oxidant Free	-	4,0	6,38	1,2	6,40
2	0.5 mg/L	1,0	4,0	6,38	0,8	6,40
3	1.0 mg/L	2,0	4,0	6,38	0,6	6,44
4	1.5 mg/L	3,0	4,0	6,38	0,4	6,43
5	2.0 mg/L	4,0	4,0	6,38	0,2	6,43
6	2.5 mg/L	5,0	4,0	6,38	0,0	6,44

II. OXIDANT CONCENTRATION										
<i>Coagulation pH: 6.38. Pre-Oxidation Time: 6 minutes.</i>										
Jug	Oxidant Concentration	Coagulant Volume (mL)	Alkalinizing Volume (mL)	Free Residual Chlorine (mg/L)	Conductivity (μ S/cm)	Apparent Color (UC)	Turbidity (NTU)	pH	Dissolved Oxygen (mg/L)	Temperature ($^{\circ}$ C)
-	Raw Water	-	-	0,00	29,36	52,10	4,38	6,56	7,30	25,10
1	Oxidant Free	4,0	1,2	0,00	51,20	21,20	1,30	6,37	7,12	25,40
2	0.5 mg/L	4,0	0,8	0,01	52,20	11,60	0,60	6,19	7,15	25,60
3	1.0 mg/L	4,0	0,6	0,16	55,20	11,30	0,89	6,17	7,18	25,60
4	1.5 mg/L	4,0	0,4	0,65	59,30	8,20	0,24	6,14	7,15	25,60
5	2.0 mg/L	4,0	0,2	0,95	59,30	7,60	0,14	6,13	7,22	25,60
6	2.5 mg/L	4,0	0,0	1,17	63,70	6,00	0,51	6,23	7,14	25,60

III. PRE-OXIDATION TIME										
<i>Coagulation pH: 6.38. Oxidant Concentration: 1.5 mg/L.</i>										
Jug	Oxidant Concentration	Volume (mL) of Coagulant	Volume (mL) of Alkalinizing Agent	Free Residual Chlorine (mg/L)	Conductivity (μ S/cm)	Apparent Color (UC)	Turbidity (NTU)	pH	Dissolved Oxygen (mg/L)	Temperature ($^{\circ}$ C)
-	Raw Water	-	-	0,00	29,15	55,20	4,85	6,50	7,34	24,80
1	Oxidant Free	4,0	1,2	0,00	52,10	26,40	1,66	6,25	7,24	25,60
2	02 minutes	4,0	0,4	0,78	59,75	11,30	0,65	6,18	7,17	25,75
3	04 minutes	4,0	0,4	0,67	59,60	11,70	0,95	6,17	7,30	25,80
4	06 minutes	4,0	0,4	0,64	58,70	11,40	0,57	6,17	7,21	25,80

5	08 minutes	4,0	0,4	0,65	57,90	12,70	0,65	6,09	7,19	25,80
6	10 minutes	4,0	0,4	0,56	58,10	9,60	0,33	6,09	7,21	25,70

Table 6

Evaluation of pre-oxidation with sodium dichloroisocyanurate as an oxidant

I. DETERMINATION OF THE VOLUME OF THE ALKALIZER										
Jug	Oxidant Concentration	Oxidant (mL)	Coagulant (mL)	Ideal pH	Alkalizing (mL)	pH after alkalizing				
1	Oxidant Free	-	4,0	6,38	1,6	6,38				
2	0.5 mg/L	1,0	4,0	6,38	1,4	6,36				
3	1.0 mg/L	2,0	4,0	6,38	1,4	6,39				
4	1.5 mg/L	3,0	4,0	6,38	1,4	6,41				
5	2.0 mg/L	4,0	4,0	6,38	1,4	6,41				
6	2.5 mg/L	5,0	4,0	6,38	1,4	6,41				
II. OXIDANT CONCENTRATION. Coagulation pH: 6.38. Pre-Oxidation Time: 6 minutes.										
Jug	Oxidant Concentration	Coagulant Volume (mL)	Alkalizing Volume (mL)	Free Residual Chlorine (mg/L)	Conductivity (μ S/cm)	Apparent Color (UC)	Turbidity (NTU)	pH	Dissolved Oxygen (mg/L)	Temperature ($^{\circ}$ C)
-	Raw Water	-	-	0,00	38,30	65,10	5,37	6,54	6,93	25,50
1	Oxidant Free	4,0	1,2	0,00	59,50	39,90	2,51	6,48	7,00	25,60
2	0.5 mg/L	4,0	0,8	0,01	52,40	16,35	1,32	6,50	6,80	25,80
3	1.0 mg/L	4,0	0,6	0,37	51,50	16,30	1,20	6,46	6,89	25,70
4	1.5 mg/L	4,0	0,4	0,75	53,90	14,90	0,99	6,44	6,90	26,00
5	2.0 mg/L	4,0	0,2	1,11	53,20	15,10	1,21	6,39	6,87	25,90
6	2.5 mg/L	4,0	0,0	1,40	52,70	15,80	1,56	6,48	6,81	25,90
III. PRE-OXIDATION TIME. Coagulation pH: 6.38. Oxidant Concentration: 1.5 mg/L.										
Jug	Oxidant Concentration	Coagulant Volume (mL)	Alkalizing Volume (mL)	Free Residual Chlorine (mg/L)	Conductivity (μ S/cm)	Apparent Color (UC)	Turbidity (NTU)	pH	Dissolved Oxygen (mg/L)	Temperature ($^{\circ}$ C)
-	Raw Water	-	-	0,00	37,50	61,10	4,21	6,57	7,81	25,70
1	Oxidant Free	4,0	1,2	0,00	57,90	33,60	3,16	6,35	6,74	26,00
2	02 minutes	4,0	0,4	0,80	58,90	14,75	1,45	6,21	6,63	26,20
3	04 minutes	4,0	0,4	0,75	58,10	12,60	0,99	6,21	6,83	26,00
4	06 minutes	4,0	0,4	0,78	59,11	10,60	0,81	6,21	6,74	26,00
5	08 minutes	4,0	0,4	0,73	59,17	10,60	0,89	6,22	6,70	26,20
6	10 minutes	4,0	0,4	0,70	60,20	12,00	1,22	6,16	6,77	25,70

Table 7

Evaluation of pre-oxidation with hydrogen peroxide (500 mg/L) as an oxidant

I. DETERMINATION OF THE VOLUME OF THE ALKALIZER						
Jug	Oxidant Concentration	Oxidant (mL)	Coagulant (mL)	Ideal pH	Alkalinizing (mL)	pH after alkalinizing
1	Oxidant Free	-	4,0	6,38	1,6	6,39
2	0.5 mg/L	2,0	4,0	6,38	1,6	6,35
3	1.0 mg/L	4,0	4,0	6,38	1,4	6,36
4	1.5 mg/L	6,0	4,0	6,38	1,4	6,36
5	2.0 mg/L	8,0	4,0	6,38	1,4	6,38
6	2.5 mg/L	10,0	4,0	6,38	1,4	6,41

II. OXIDANT CONCENTRATION.										
Coagulation pH: 6.38. Pre-Oxidation Time: 6 minutes.										
Jug	Oxidant Concentration	Coagulant Volume (mL)	Alkalinizing Volume (mL)	Hydrogen Peroxide (mg/L)	Conductivity (µS/cm)	Apparent Color (UC)	Turbidity (NTU)	pH	Dissolved Oxygen (mg/L)	Temperature (°C)
-	Raw Water	-	-	0,00	27,28	53,60	4,16	6,33	7,21	24,90
1	Oxidant Free	4,0	1,6	0,00	47,20	19,10	1,06	6,39	7,11	25,00
2	0.5 mg/L	4,0	1,4	0,00	45,35	17,75	1,05	6,40	7,16	25,30
3	1.0 mg/L	4,0	1,4	0,16	43,00	15,00	1,12	6,33	7,12	25,40
4	1.5 mg/L	4,0	1,4	0,18	42,10	14,40	0,78	6,38	7,18	25,30
5	2.0 mg/L	4,0	1,4	0,15	43,40	14,90	0,78	6,34	7,28	25,40
6	2.5 mg/L	4,0	1,4	0,17	44,40	18,70	1,01	6,37	7,29	25,30

III. PRE-OXIDATION TIME.										
Coagulation pH: 6.38. Oxidant Concentration: 1.5 mg/L.										
Jug	Oxidant Concentration	Coagulant Volume (mL)	Alkalinizing Volume (mL)	Hydrogen Peroxide (mg/L)	Conductivity (µS/cm)	Apparent Color (UC)	Turbidity (NTU)	pH	Dissolved Oxygen (mg/L)	Temperature (°C)
-	Raw Water	-	-	0,00	26,73	54,40	4,55	6,58	7,20	25,10
1	Oxidant Free	4,0	1,6	0,00	44,40	20,40	1,65	6,35	7,21	25,40
2	02 minutes	4,0	1,4	0,18	43,70	17,80	1,00	6,33	7,20	25,60
3	04 minutes	4,0	1,4	0,10	42,60	17,80	1,35	6,34	7,31	25,70
4	06 minutes	4,0	1,4	0,04	42,60	15,80	1,13	6,32	7,36	25,70
5	08 minutes	4,0	1,4	0,05	42,70	19,00	1,09	6,32	7,10	25,70
6	10 minutes	4,0	1,4	0,02	43,20	20,30	1,12	6,30	7,15	25,60

Table 8

Evaluation of pre-oxidation with potassium permanganate (1000 mg/L) as an oxidant

I. DETERMINATION OF THE VOLUME OF THE ALKALIZER						
Jug	Oxidant Concentration	Oxidant (mL)	Coagulant (mL)	Ideal pH	Alkalinizing (mL)	pH after alkalinizing
1	Oxidant Free	-	4,0	6,38	1,4	6,38
2	0.1 mg/L	0,2	4,0	6,38	1,4	6,40
3	0.2 mg/L	0,4	4,0	6,38	1,4	6,40
4	0.3 mg/L	0,6	4,0	6,38	1,3	6,37
5	0.4 mg/L	0,8	4,0	6,38	1,3	6,38
6	0.5 mg/L	1,0	4,0	6,38	1,3	6,40

II. OXIDANT CONCENTRATION.										
Coagulation pH: 6.38. Pre-Oxidation Time: 6 minutes.										
Jug	Oxidant Concentration	Coagulant Volume (mL)	Alkalinizing Volume (mL)	Potassium Permanganate (mg/L)	Conductivity (μ S/cm)	Apparent Color (UC)	Turbidity (NTU)	pH	Dissolved Oxygen (mg/L)	Temperature ($^{\circ}$ C)
-	Raw Water	-	-	0,00	27,52	56,50	5,07	6,58	7,27	25,20
1	Oxidant Free	4,0	1,4	0,00	47,30	20,40	1,60	6,35	7,41	25,30
2	0.1 mg/L	4,0	1,4	0,01	45,20	18,80	0,98	6,28	7,35	25,40
3	0.2 mg/L	4,0	1,4	0,01	44,00	14,80	0,76	6,30	7,22	25,60
4	0.3 mg/L	4,0	1,3	0,00	43,70	18,60	1,07	6,30	7,10	25,60
5	0.4 mg/L	4,0	1,3	0,05	44,20	22,70	1,66	6,31	7,25	25,60
6	0.5 mg/L	4,0	1,3	0,14	44,40	21,10	1,44	6,38	7,21	25,40

III. PRE-OXIDATION TIME.										
Coagulation pH: 6.38. Oxidant Concentration: 0.2 mg/L.										
Jug	Oxidant Concentration	Coagulant Volume (mL)	Alkalinizing Volume (mL)	Potassium Permanganate (mg/L)	Conductivity (μ S/cm)	Apparent Color (UC)	Turbidity (NTU)	pH	Dissolved Oxygen (mg/L)	Temperature ($^{\circ}$ C)
-	Raw Water	-	-	0,00	26,95	53,10	3,82	6,57	7,44	25,80
1	Oxidant Free	4,0	1,6	0,00	42,00	20,00	1,19	6,26	7,14	25,90
2	02 minutes	4,0	1,4	0,08	41,80	17,65	1,12	6,27	7,18	26,20
3	04 minutes	4,0	1,4	0,02	41,90	15,70	0,90	6,29	7,10	26,20
4	06 minutes	4,0	1,4	0,04	41,90	16,20	0,99	6,24	7,10	26,20
5	08 minutes	4,0	1,4	0,05	41,90	16,60	1,19	6,27	7,19	26,20
6	10 minutes	4,0	1,4	0,06	41,60	17,70	0,87	6,30	7,30	26,20