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Environmental Control

Synthesis and efficiency of cationic chitosan in the physical-chemical treatment of water

Síntese e eficiência da quitosana catiônica no tratamento físico-químico da água

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ABSTRACT

Water for human consumption must comply with legal potability standards, involving treatments that often use chemical agents that have impacts on the environment and human health. An alternative is to use organic polymers, such as chitosan, but in some situations, its structure should be modified to improve its applicability. This is achieved by adding reagents such as CHPTAC to make it cationic. This research aimed to create a cationic polysaccharide derived from chitosan using the CHPTAC reagent and apply it in water treatment, varying dosages and pH. The results showed that the synthesized chitosans achieved good efficiency in removing turbidity and color, in which some dosages were more effective. Furthermore, each flocculant performed better in a specific pH range, often in an acidic pH. The research highlighted that both cationic and non-cationic chitosan are effective in water treatment, providing a viable alternative to commonly used inorganic coagulants.

Keywords: Organic flocculant; Structural modification; Cationic polysaccharides

RESUMO

A água para consumo humano deve obedecer aos padrões legais de potabilidade, envolvendo tratamentos que muitas vezes utilizam agentes químicos com impactos no meio ambiente e na saúde humana. Uma alternativa é utilizar polímeros orgânicos, como a quitosana, mas em algumas situações sua estrutura deve ser modificada para melhorar sua aplicabilidade. Isto é conseguido adicionando reagentes como CHPTAC para torná-lo catiônico. Esta pesquisa teve como objetivo criar um polissacarídeo catiônico derivado da quitosana utilizando o reagente CHPTAC e aplicá-lo no tratamento de água, variando dosagens e pH. Os resultados mostraram que as quitosanas sintetizadas obtiveram boa eficiência na remoção de turbidez e cor, sendo algumas dosagens mais eficazes. Além disso, cada floculante teve melhor desempenho em uma faixa específica de pH, muitas vezes em pH ácido. A pesquisa destacou que tanto a quitosana catiônica quanto a não catiônica são eficazes no tratamento de água, proporcionando uma alternativa viável aos coagulantes inorgânicos comumente usados.

Palavras-chave: Floculante orgânico, Modificação estrutural; Polissacarídeos catiônicos

1 INTRODUCTION

Water is fundamental for life on the planet, determining territories and resources, including its importance for the health of species (Bacci; Pataca, 2008). Regarding water intended for human use in Brazil, potability standards and procedures for quality control and surveillance are regulated by Ordinance GM/MS No. 888/2021 (Brasil, 2021).

Conventional water treatment involves processes such as coagulation and flocculation, commonly using inorganic coagulants, despite generating waste and environmental impacts, such as sludge production (Botero *et al.*, 2009). Furthermore, inorganic coagulants present other disadvantages, such as the toxicity of residual ions (Noor *et al.*, 2019). However, the use of inorganic coagulants can be justified due to their low cost and high efficiency (Silveira *et al.*, 2019).

A viable alternative is to replace inorganic coagulants with organic coagulants based on natural polymers, which offer advantages due to their wide availability, low cost, low toxicity, biodegradability, and short lifespan, thereby respecting the environment (Huang *et al.*, 2016; Ibrahim; El-Zairy, 2015; Lee; Robinson; Chong, 2014; Lin *et al.*, 2020; Lu *et al.*, 2014).

The processes such as heterogeneous photocatalysis and adsorption by nanocomposites have received special attention in the scientific community due to their unique properties and ability to degrade and remove several organic pollutants, including pesticides (Bruckmann *et al.*, 2022). One new study demonstrate the efficiency of using compounds as alternatives at emerging contaminant chloroquine (CQN) removal through adsorption and employing a low-cost activated biochar from *açai* fruit endocarp (Santos et al., 2023). In another study, the furosemide (FUR) adsorption was performed employing magnetic carbon nanotubes ($CNT \cdot Fe_3O_4$) with different amounts of incorporated magnetite (Salles *et al.*, 2023).

Of particular note is the growing exploration of alternative materials, such as starch, chitosan, nanoscale structures like zeolites and metal-organic frameworks, magnetic materials, and carbon-based substances for the development of inorganic adsorbents. These materials, with their remarkable capacity for nanoscale structural adjustment, possess extraordinary capabilities for effective contaminant removal, facilitating swift water purification (Badran *et al.*, 2023).

Among the natural polymers used as flocculants, chitosan can be mentioned, which exhibits high performance in flocculation and possesses antimicrobial properties (Huang et al., 2016; Ibrahim; El-Zairy, 2015; Strand *et al.*, 2001). Chitosan is derived from the world's second most abundant organic polymer, chitin, ranking only behind cellulose (Ibrahim; El-Zairy, 2015).

In this context, this research aimed to chemically modify chitosan through cationization in different aqueous mediums (acidic, basic, and neutral), evaluating the degree of substitution in the chitosan monomers for each process, as well as the properties of the obtained products as flocculation agents in treating water with high turbidity (100-180 NTU).

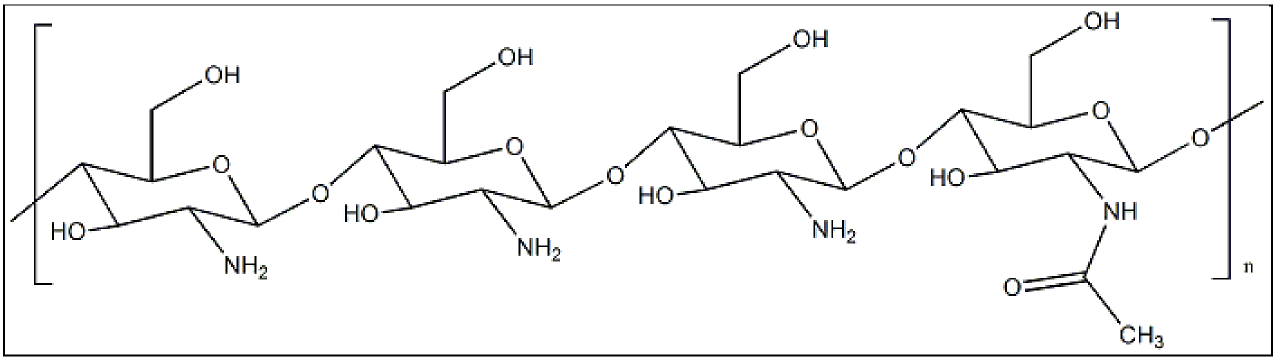
1.1 Chitosan

The most important derivative of chitin is chitosan. It is obtained from distinct techniques, two of which are noteworthy: the partial deacetylation of chitin under alkaline conditions and enzymatic hydrolysis (Pontius, 2016; Song *et al.,* 2018). The development of these methods is necessary because although chitin is widely found, chitosan is only present in nature in small quantities, specifically in some fungi (Aranaz et al., 2021; Ibrahim; El-Zairy, 2015).

Both chitin and chitosan comprise a family of linear polysaccharides made up of varying amounts of D-glucosamine, the constituent of the amino group, and N-acetyl-D-glucosamine, which is the acetylated unit of the molecule, linked by β-(1→4) glycosidic bonds (Aranaz *et al.*, 2021). In chitin, the predominance is in the acetylated units, whereas in chitosan, the deacetylated units are prominent (as illustrated in Figure 1) (Wang *et al.*, 1991).

The chitosan molecule contains amino groups that enable its protonation, ensuring some solubility in aqueous solutions (Ibrahim; El-Zairy, 2015). Therefore, to improve the properties of chitosan, chemical modifications need to be carried out in its structure. Over the years, various cationization techniques have been developed for chitosan. By using these techniques, the positive electrical charge of the molecules compared to pure chitosan is increased while maintaining its biodegradability and other characteristics (Lu *et al.*, 2014).

Figure 1 – Molecular structure of chitosan



Adapted the Spinelli (2001)

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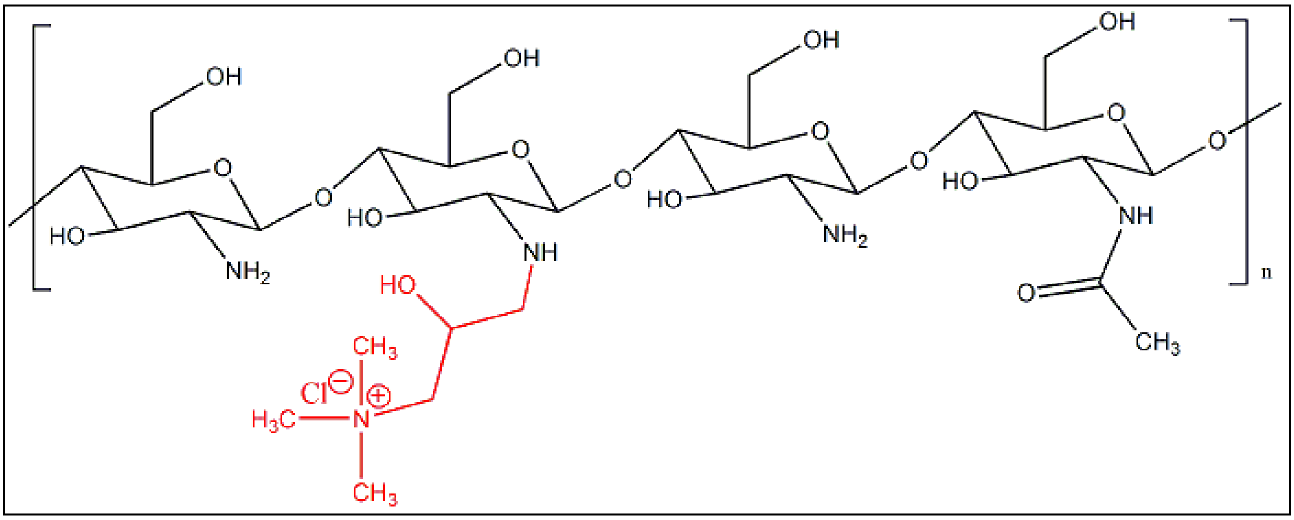
Cationization is a technique that aims to introduce positive charges throughout the polymeric chain of the molecules, thus inducing a polyelectrolyte cationic effect, regardless of the aqueous medium's pH (Aranaz; Harris; Heras, 2010).

In chitosan, cationization generally occurs through N-substitution reactions (Figure 2), that is, there is substitution in the NH_2 group, which is more reactive than the OH- groups. Substituting NH_2 and/or OH- groups enhances the hydrophilic characteristics of chitosan (Madera-Santana; Herrera-Méndez; Rodríguez-Núñez, 2018). However, the type and degree of modification substitution can affect the water-soluble activity of chitosan (Song *et al.*, 2018).

One of the reagents used to produce organic cationic, as well as to prepare synthesized chitosan, is 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC), demonstrated in Figure 2. It increases the cationic content of the flocculant, and thus enhances its flocculation efficiency during water treatment (Momeni *et al.*, 2018).

Figure 2 – Molecular structure of cationized chitosan.



Adapted from Madera-Santana; Herrera-Méndez; Rodríguez-Núñez (2018) and Song et al., 2018

2 MATERIALS AND METHODS

2.1 The chitosan cationization technique

Chitosan cationization was carried out following adaptations of the techniques described by Gruškiene, Deveikyte, and Makuška (2013), which are detailed in the following topics.

2.1.1 Cationization in neutral solution

In a becker, 5 g (30.73 mmol) of chitosan (brand Sigma-Aldrich) was dissolved in 100 mL of distilled water. The mixture was taken to a heating plate and constantly stirred, gradually raising the temperature until it reached 80 °C.

Subsequently, 23 mL of CHPTAC (brand Sigma-Aldrich) was added dropwise to the neutral solution containing chitosan. This process lasted approximately 30 minutes on average. The solution was maintained under these conditions for about 2 hours and 30 minutes.

After this period, the reaction mixture was cooled to room temperature (± 20 °C), and 50 mL of previously chilled acetone was added. The resulting reaction mixture was left in refrigeration (±5 °C) for approximately 12 hours.

Upon refrigeration, product precipitation occurred, which was vacuum filtered, washed several times (±3) with acetone, and placed in an oven at 60 to 65 °C. The dried product was kept in sealed containers until the subsequent steps of the research were conducted.

2.1.2 Cationization in basic solution

In a becker flask, 5 g (30.73 mmol) of chitosan (brand Sigma-Aldrich) was dissolved in 100 mL of 1% NaOH (brand Dinâmica). The mixture was placed on a heating plate with constant stirring, gradually raising the temperature until it reached 70 °C on a magnetic stirrer (brand RBR). After the temperature stabilized, the solution was left stirring under these conditions for 30 minutes.

Next, 23 mL of CHPTAC (brand Sigma-Aldrich) was added dropwise. This process took approximately 30 minutes. The reaction solution was maintained under these conditions for about 4 hours. Subsequently, the reaction mixture was cooled to reach room temperature (±20 °C).

When the reaction temperature matched the room temperature, 100 mL of methanol (brand synth) was added. The new mixture was placed on a magnetic stirrer o (brand RBR), maintaining constant agitation for 3 hours. After this period, 100 mL of previously chilled acetone (brand synth) was added to the solution, and the resulting reaction mixture was left in refrigeration (±5 °C) for approximately 12 hours.

Upon refrigeration, product precipitation occurred, which was vacuum filtered, washed several times (±3) with acetone, and placed in an oven at 60 to 65 °C. The dried product was stored in sealed containers until the subsequent steps of the research were conducted.

2.1.3 Cationization in acidic solution

In a becker flask, 5 g (30.73 mmol) of chitosan (brand Sigma-Aldrich) was dissolved in 250 mL of 1% acetic acid. The mixture was placed on a heating plate and constantly stirred, gradually raising the temperature until it reached 70 ºC. After the temperature stabilized, the solution was left stirring under these conditions for 30 minutes.

Next, 23 mL of CHPTAC (brand Sigma-Aldrich) was added dropwise. This process took approximately 30 minutes. The reaction solution was maintained under these conditions for about 4 hours. Subsequently, the mixture was cooled to reach room temperature (±20 ºC), and 100 mL of previously chilled acetone was added. Then, the acidic solution containing chitosan was left in refrigeration (±5 ºC) for approximately 12 hours.

Upon refrigeration, product precipitation occurred, which was vacuum filtered, washed several times (±3) with acetone, and placed in an oven at 60 to 65 °C. The dried product was stored in sealed containers until the subsequent steps of the research were conducted.

2.3 Substitution degree analysis

In order to determine the degree of substitution (DS) of the synthesized chitosan derivatives in the three different solutions (neutral, acidic, and alkaline), the titration process was carried out with silver nitrate according to adaptations in the techniques developed by Lu *et al.* (2014), as described below.

For the titration process, 0.10 g of each cationized chitosan (HTCC) sample was dissolved in 50 mL of deionized water, and 1 mL of potassium chromate (K_2CrO_4) indicator was added to the HTCC solution. It was titrated with a standard solution of 0.1000 mol/L $AgNO_3$ until a red precipitate formed in the HTCC solution. An additional 50 mL of deionized water was used to perform a blank titration under the same conditions.

In order to verify the degree of substitution through the titration method, Lu *et al.* (2014) developed the following equation:

$$DS(\%) = ((V2-V1) \times M \times 314)/(G \times 10^3)) \times 100 \qquad (1)$$

Where:

DS is the degree of substitution of HTCC;

V1 and V2 are the volumes (mL) of the $AgNO_3$ standard solution used in the 50 mL of deionized water and the HTCC solution, respectively,

314 is the molar mass (g/mol) of HTCC;

G is the mass (g) of HTCC, and

M is the molar concentration (mol/L) of the $AgNO_3$ standard solution.

This equation allows the assessment of the percentage of D-glucosamine units in chitosan that underwent substitution due to the addition of CHPTAC and the estimation of the cationized material's quality based on the volume of $AgNO_3$ used in the titration.

2.3 Coagulation assays

The following describes the methods used in the coagulation tests, from the development of the coagulants to their evaluation process. Initially, it presents the techniques for preparing all the tested coagulants/flocculants. It also provides specific information about the raw water used and the synthetic water, along with the procedure to alter turbidity.

Subsequently, it clarifies the control parameters for the analyses, the dosages used for each tested coagulant, and the procedures developed during the coagulation tests in the Jar test. The data obtained from these processes were used to analyze the color and turbidity removal index provided by each coagulant and to create coagulation diagrams.

2.3.1 Flocculants and coagulants

Unadulterated, pure chitosan (QP), and the synthesized chitosans (QCSA, QCSB, and QCSN) were diluted in distilled water at a concentration of 2% (20 g/L). For dilution, the raw materials were added to a becker on a heating plate with constant stirring, which was maintained for 5 minutes after the mixture reached 80 °C. Subsequently, the heating was stopped, and the flocculant was cooled down only with agitation until it reached room temperature (±20 °C). Finally, the desired volume of the coagulant was completed using a volumetric instrument.

2.3.2 Collection of raw water

The raw water used to prepare the synthetic water with high turbidity (100-180 NTU) was directly collected from Lajeado Pardo (27°23'31.35"S; 53°25'32.31"W) in the municipality of Frederico Westphalen (RS), located approximately 2.5 km upstream from the water collection point by pumping from Companhia Riograndense de Saneamento (CORSAN-AEGEA). The collections were made using plastic jugs, where typically 40 to 50 liters of water were stored before starting the experiment. The water was kept at room temperature (±20 °C) until use, which occurred on the same day as the collection.

2.3.2 Synthetic water preparation

To create turbidity in the raw water used in studies, it is common to use suspensions based on clay minerals. Based on this and to increase the turbidity of the raw water, in this study, the methodology proposed by Di Bernardo (2004) was adapted as follows:

The clay mineral selected for making the suspension is kaolinite. To do this, 22 g of this material was dissolved in 1 L of distilled water. Then, the solution was taken to the Jar test for agitation at a speed of 200 RPM for 2 hours. Subsequently, the resulting solution was allowed to stand for 12 hours. After this period, a supernatant material formed, which was collected from the mother suspension to remove larger particles, thus reducing errors in the preparation of the study water.

The water used in the study, synthetic water, was prepared by gradually adding the supernatant from the kaolinite solution to the raw water until the desired turbidity values, 100-180 NTU, were reached.

2.3.3 Control parameters

For the control analyses, the following parameters were evaluated: color, pH, alkalinity, temperature, and turbidity in the raw water and synthetic water. The same analyses and methods, except for alkalinity evaluation, were performed after the clarification test for each proposed treatment. The analyses followed the methodologies developed by the Standard Methods for the Examination of Water and Wastewater (American Public Health Association; American Water Works Association; Water Environment Federation, 2017).

2.3.4 Coagulant dosages

After preparing the synthetic water and the control parameter analyses, 2 L of synthetic water was added to each Jar test flask. Fixed dosages of coagulant/flocculant were then added to each jar through the test tubes attached to the device, enabling synchronized application of the coagulant/flocculant to all the flasks.

For chitosans (QCSA, QCSB, QCSN, and QP) at a concentration of 2%, the tested dosages were 15, 25, 35, 45, 55, and 65 mg/L, and the tests were conducted at pH 3, 4, 5, 6, 7, and 8. All tests were conducted under the same time and agitation conditions, as listed in the next item of this work.

2.3.4 Coagulant dosages

Table 1 – Operational Parameters in Coagulation Tests

Treatment stage	Operation
Coagulation	The rapid mixing, coagulant addition, began at a speed of 350 RPM (average velocity gradient of 700 s^{-1}), maintained for 60 seconds
Flocculation	Programmed to change the speed to 50, 40, 30, and 20 RPM (average velocity gradient of 40, 30, 18, and 10 s^{-1}), lasting 5 minutes in each stage.
Decantation	Initiated by turning off the device, the settling velocity is 0.35 cm/min. The process lasted 20 minutes, and samples were collected and analyzed at 0 and 20 minutes.
Filtration	Performed using qualitative filter paper, weighing 80 g/m^2, with a diameter of 150 mm, FIL model P80150, Qualividros brand.

Source: the authors

To evaluate the efficiency of the developed coagulants/flocculants, coagulation tests were conducted using the Jar test micro controlled equipment from PoliControl®, Floc Control III model, with automatic programming of the tests and a capacity of 6 jars of up to 2 L each.

The clarification test stages using the Jar test were defined based on previous works by the research team, which used different operational parameters presented in Table 1.

2.3.5 Efficiency of removal

After conducting the water treatment simulation (coagulation, flocculation, sedimentation, and filtration), the study water was reanalyzed for color and turbidity parameters to calculate the efficiency of removing these parameters. Therefore, the removal efficiency was determined using the equation below:

$$\text{Removal efficiency (\%)} = (VAB-VAT)/VAB \times 100 \qquad (2)$$

Where:

VAB: represents the color (uC) or turbidity (uT) values for the raw water.

VAT: represents the color (uC) or turbidity (uT) values for the treated water.

In addition to the removal efficiency, the results were compared and discussed based on the maximum allowable values for color and turbidity in supply waters after treatment, as determined by the Ordinance GM/MS Nº. 888, dated May 4, 2021.

2.3.7 Coagulation diagrams

One way to assess whether the treatment used is satisfactory is by using coagulation diagrams. Analyzing coagulation diagrams enables visual representation of the remaining dosages, pH, remaining turbidity, color, and other parameters evaluated (Bartiko; Julio, 2015; Valverde *et al.*, 2013).

The use of coagulation diagrams is ideal and adds credibility to the study, confirming the efficiency of the analyzed coagulant (Silveira *et al.*, 2019; Valverde *et al.*, 2015). As coagulation diagrams combine different conditions and mechanisms, they are crucial for planning, analyzing, and interpreting the data obtained in the Jar test (Kim; Moon; Lee, 2001).

Coagulation diagrams were created in the Minitab Statistical Software 20. Using the tools available in the software, contour graphs were developed with color and remaining turbidity isopleths for the studied flocculants (QP, QCSA, QCSB, and QCSN).

3 RESULTS AND DISCUSSION

3.1 Degree of substitution

The results obtained for the degree of substitution by evaluating the percentage content of chloride are presented in Table 1, and the analyses were performed in triplicate.

Table 2 – Degree of Substitution (DS) values, CHPTAC cationization

Sample	DS (1:3)	%DS
QCSA	1.39	46.33
QCSB	1.03	34.33
QCSN	0.80	26.66
Pure chitosan (QP)	0	0

Source: the authors

The DS values classified according to the degree of substitutions attained for the cationic chitosans can be classified as medium/high substitution. Thus, the DS values obtained were considered satisfactory for the continuation of the study.

The three chitosan solutions subjected to the reaction with CHPTAC differed in terms of the calculated DS, an expected result due to the different chemical reactions that occurred in each developed aqueous solution.

The study results align with those found by Song *et al.* (2018), who obtained a substitution degree of 16.5% to 46.8% at variable concentrations of the CHPTAC reagent. In this study, the lowest DS value, 26.66% in QCSN, was higher than that found in the previous study. However, this result might be justified by the lower concentration of CHPTAC. With identical reagent values, the substitution degree remained similar, especially for QCSA.

Similarly, adopting a similar methodological procedure adapted for our study, Gruškiene, Deveikyte, and Makuška (2013) used GTMAC as a reagent and obtained DS values for QCSA ranging from 36% to 72%. In the same study, they also assessed the

DS for solutions prepared in neutral and alkaline conditions, with results varying from 29% to 66% and from 2.6% to 95%, respectively. The wide variation observed might be attributed to discrepancies in the molar ratio between chitosan and the reagent, as well as factors such as the concentration of the base used and the choice of different bases.

The values of QCSN were the lowest obtained in this study, 26.66%. This might have been influenced by how the reaction was conducted, given that chitosan was only dispersed in distilled water, and the gradual addition of the etherification reagent took place. Peng et al. (2010) obtained DS values ranging from 6, 18, and 44% in chitosan solution with distilled water, where higher reagent concentrations increased the DS of the product.

The relatively low DS value for QCSB (1.03 and/or 34.33%) may be associated with the low solubility of chitosan in an alkaline medium, restricting epoxide reactions to the molecule's surface layers (Gruškiene; Deveikyte; Makuška, 2013). Using acetic acid facilitates the opening of epoxide groups, intensifying the reaction rate and elevating the DS (Prado; Matulewicz, 2014; Seong; Whang; Ko, 2000). This aligns with the obtained result, as the highest DS was found for the coagulant formulated in an acidic solution (46.33%), showing that diluting chitosan in acetic acid enhances cationization.

Additionally, DS values may be linked to the cationizing agent used in the study, CHPTAC. Prado and Matulewicz (2014) reported that both DS and the reaction's efficiency are lower when using CHPTAC compared to the cationizing agent EPTAC. However, in a study utilizing EPTAC and acetic acid as modifying agents, the optimal DS value found was 1.04 after 18 hours of reaction (Seong; Whang; Ko, 2000), which is lower than that of the present study, even when using a less efficient reagent.

Furthermore, in comparison with the etherification reagent, contrasting CHPTAC with a study conducted by Mao et al. (2021), which carried out the grafting of citronellol into the chitosan molecule, relatively lower DS values (0.165, 0.199, and 0.182) were obtained. Hence, the reagent used in the study, CHPTAC, proved to be more efficient in chitosan cationization. However, when compared to GTMAC and/or EPTAC, CHPTAC showed lower efficiency, but the results are still satisfactory.

As mentioned, several factors can influence the DS value, including the type of reagent used, the molar ratio between the reagent and the solution, temperature, and reaction time. Generally, an increase in reaction time and the quantity of the cationizing reagent leads to an increase in DS, both possibly due to the increased availability of reagent molecules near the polysaccharide and/or a longer exposure time to the material (Prado; Matulewicz, 2014; Song *et al.*, 2018).

Therefore, based on the obtained results, it can be observed that even though the processes for modifying the chitosan structure are challenging, it has been modified and cationized in the different initially proposed aqueous solutions. This was confirmed through the obtained degrees of substitution in the silver nitrate titration and chloride analysis.

3.2 Coagulation assay

To simulate the water treatment system using cationic chitosans and pure chitosan as organic flocculants, the Jar test equipment was adopted, followed by the filtration process using filter paper with a grammage of 80 g/m^2. This allowed the determination of turbidity and color values after treatment, as well as the treatment's efficiency.

For the construction of coagulation diagrams, the synthetic water pH ranged from 3 to 8 (on a one-unit scale), and the chitosan-based flocculant concentrations varied from 15, 25, 35, 45, 55, and 65 mg/L.

To facilitate comprehension, tables containing the main data from the treatment assays, such as initial and final color/turbidity, and treatment efficiency, were created. The comprehensive tables with all the data obtained during the Jar test assays at all collection times and for all the utilized coagulants/flocculants are presented in the Appendices of this work.

Combining the pH variations and the flocculant concentrations used with the final values obtained for color and turbidity, coagulation diagrams were developed to facilitate the observation and identification of combinations (pH and concentration) that showed the best treatment efficiency. Figure 3 presents the coagulation diagrams for the turbidity parameter for the flocculant agents produced in the study (QCSA, QCSB, QCSN, and QP).

From the data obtained for the remaining turbidity values, it is evident that pH influenced the treatment efficiency. Subsequently, the values in NTU that most closely approached those established by Brazilian regulations for each of the coagulants/flocculants tested in the study will be highlighted.

The first analyzed coagulant was based on QCSA. The best turbidity results were achieved at pH 7 and 8, with values of 5.63 and 2.75 NTU, respectively, both at a dosage of 15 mg/L, showing removal rates of 95.9% and 97.9%, respectively. For the QCSB-based coagulant, the closest results were obtained at pH 4, with values of 6.30 and 6.43 NTU at concentrations of 15 and 25 mg/L, achieving removal rates of 94.9% and 94.8%, respectively.

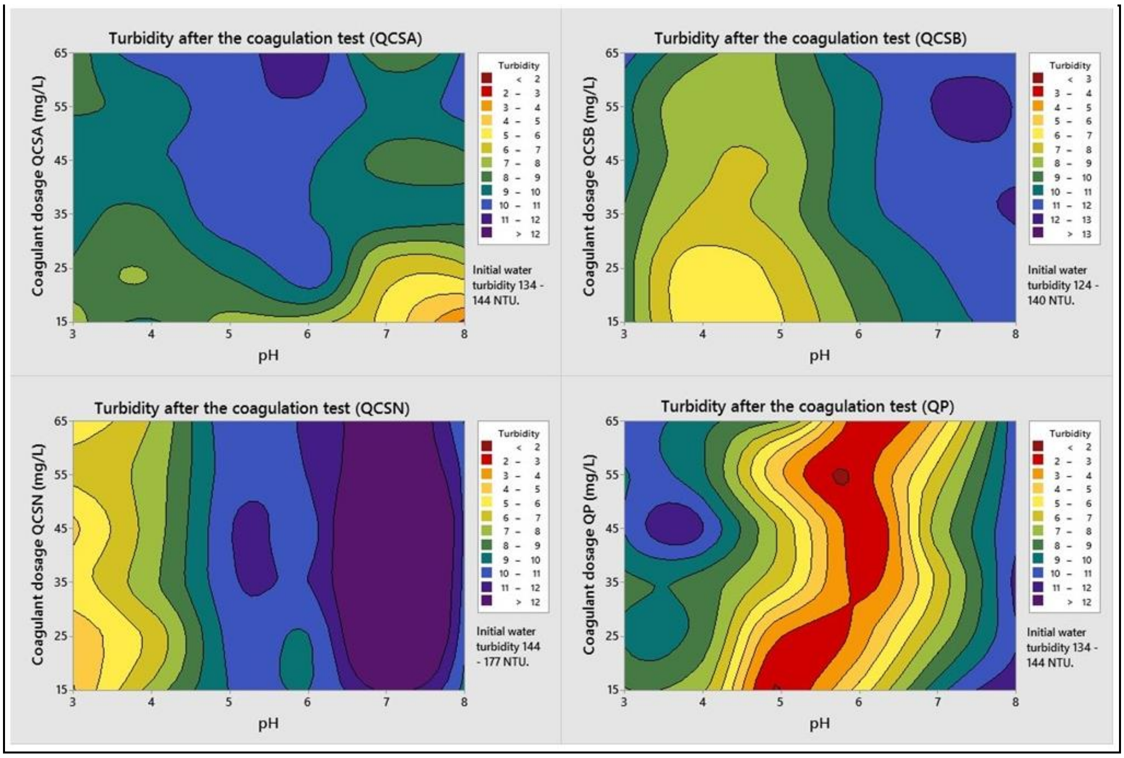
Upon analyzing the QCSN-based coagulant, the most favorable outcomes were observed at pH 3, showing turbidity values of 4.59 and 3.89 NTU at dosages of 25 and 15 mg/L, achieving removal efficiencies of 97.4% and 97.8%, respectively. However, the remaining turbidity values for the synthesized chitosans did not meet the parameters listed in Annex 2 of Ordinance Nº. 888/2021, where the maximum allowed value for water turbidity after the filtration process is 1 uT.

Reviewing the collective results for the remaining turbidity of the study water concerning "dosage x pH," the best values achieved overall were at acidic pH levels. Regarding the cationic chitosan dosage, the lower dosages showed more significant outcomes, especially at 15 mg/L.

The removal efficiency varied significantly among the tested cationic chitosans, but optimal values were around 97%, with the most notable value being 97.9% for QCSA, resulting in remaining turbidity close to 3.0 uT. The coagulant that exhibited a reduction in turbidity close to values compliant with the current legislation across different concentrations and a wide pH range was QP, as shown in Table 2.

The results achieved for QP approached the values stipulated by the current legislation; however, they still do not comply with the criteria established in Annex 2 of Ordinance Nº 888/2021. Although the results for QP showed a significant performance, the dosages used were generally higher than those used for the synthesized chitosans.

Figure 3 – Coagulation diagram for turbidity in treated water with QCSA, QCSB, QCSN, and QP



Source: the authors

Based on the conducted tests, it can be stated that all the tested chitosans have considerable flocculating potential. However, QP proved to be more favorable in reducing turbidity over a wide pH range. It is easily found in nature, in comparison to the pH ranges of 3 and 4, for instance, to which QCSN and QCSB adapted better. This may have occurred due to the insoluble properties of the chitosan molecule. For the creation of this coagulant, its complete dilution did not occur, and its granules may have influenced the flocculation process.

Table 3 – QP coagulant results: turbidity (uT), pH, and the percentage of reduction in relation to initial turbidity

Concentration (mg/L)	pH	Turbidity (uT)[1]	Reduction (%)
15	5	2.02	98.5
25	5	3.04	97.8
55	5	4.10	96.9
25	6	3.47	97.5
35	6	2.77	97.9
45	6	2.23	98.4
55	6	2.34	98.3
65	6	2.46	98.2
65	7	4.38	96.7

Source: the authors

NOTE:

(1) 1 uT, maximum value allowed after the filtration process according to Ordinance GM/MS Nº 888/2021, annex 2

Based on the conducted tests, it can be stated that all the tested chitosans have considerable flocculating potential. However, QP proved to be more favorable in reducing turbidity over a wide pH range. It is easily found in nature, in comparison to the pH ranges of 3 and 4, for instance, to which QCSN and QCSB adapted better. This may have occurred due to the insoluble properties of the chitosan molecule. For the creation of this coagulant, its complete dilution did not occur, and its granules may have influenced the flocculation process.

Consequently, it can be said that the commercialized chitosan (QP) performed better as a flocculant when not cationized by the method used in this study. This may have occurred due to the insolubility of chitosan. As the granules remain partially intact, they may better attract the anionic particles present in the water.

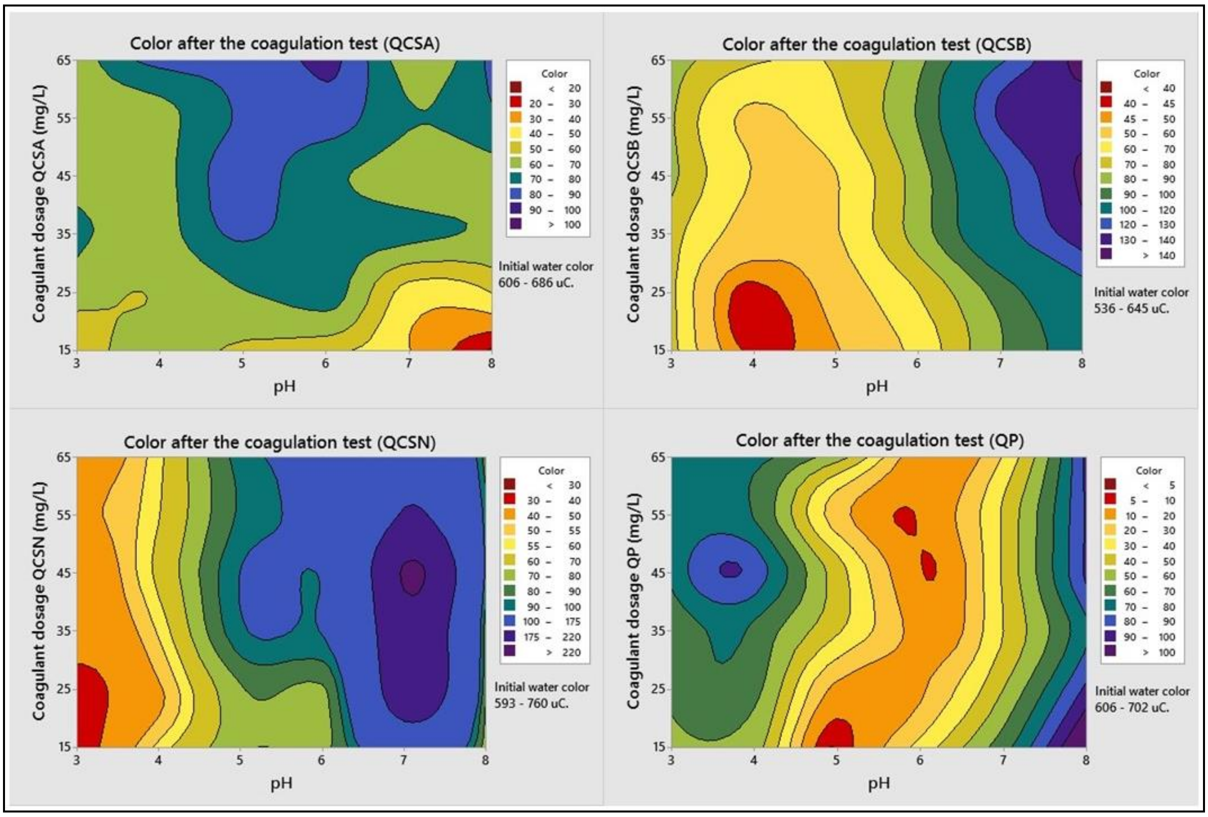
The required coagulant concentration in the study was higher than that used by Hamdon et al. (2022), who assessed the capacity to reduce algae, turbidity, BOD, among other parameters, in water treatment, obtaining turbidity removal results of 96.5 to 99.5% at a concentration of 2 to 2.7 mg/L. The authors also assessed the optimal pH for treatment and found that a pH of 7 to 7.49 is most suitable. Pontius (2016) also used a lower chitosan concentration, 8 mg/L, and achieved a removal efficiency of 96.9%, a value similar or equal to the most promising results of this study.

Momeni et al. (2018) synthesized chitosan with CHPTAC and used the product to treat wastewater with an initial turbidity of 60 NTU. In this study, they obtained a removal efficiency of 90.14% with a concentration of 3000 mg/L at a pH close to 6.

The lower DS values obtained for QCSB and QCSN reflect the challenges associated with chitosan synthesis and solubilization due to its strong hydrogen bonds. These properties make the chitosan solubilization process more complex, and these difficulties manifested in the results of this study. Notably, the material that showed the most effectiveness in turbidity removal among the synthesized was chitosan with a higher DS (QCSA).

Regarding the color parameter, Figure 4 represents the coagulation diagram for the remaining color of the treated water with the cationized and non-cationized flocculants in the study.

Figure 4 – Coagulation diagram for color after coagulation test with QCSA, QCSB, QCSN, and QP



Source: the authors

From the obtained results, it can be observed that the lowest color values after water treatment with chitosans were achieved at pH 5 and 6 using the QP coagulant. Within this pH range, a considerable portion of the tested dosages met the organoleptic potability standard listed in Annex 11 of Ordinance Nº. 888/2021, which is up to 15 uC.

The dosage of 15 mg/L of QP yielded the best results, achieving a color of 5.60 uC. Considering the initial color of the study water, the treatment efficiency reached 99.1%. Table 7 presents the values that comply with Annex 11 of Ordinance Nº. 888/2021.

Similar to turbidity, the QP coagulant provided results that were closest to and within acceptable standards for color removal. However, once again, higher coagulant dosages were required, suggesting that the removal effect likely occurred due to the greater availability of insoluble particles with different ionic charges in the water, influencing flocculation and subsequent sedimentation.

The QCSA coagulant did not yield any remaining color values within the acceptable organoleptic standard, with the value closest to the acceptable limit found at pH 8, measuring 18.2 uC, with a removal percentage of 97.2% at a concentration of 15 mg/L.

Similarly, the QCSN coagulant did not achieve any values within the acceptable limits. The closest values were 33.3 uC at a concentration of 15 mg/L at pH 3, with a corresponding removal percentage of 95.2%. Both the QCSA and QCSN values for color and turbidity were obtained at the same coagulant dosage and pH, indicating that these are the values future studies should focus on.

Moreover, concerning the color removal there was a significant variation in the optimal pH. Each coagulant showed more efficient results in a specific pH range. However, the values that comply with the regulations are closer to a neutral pH (pH 5-6).

Momeni et al. (2018) synthesized chitosan with CHPTAC and used the product to treat wastewater with high color. In this study, they achieved a maximum removal efficiency of 76.20% at a concentration of 1000 mg/L at pH 3. This study highlights the challenge that chitosan faces in color removal in water with high turbidity.

Chitosan at a dosage of 7.5 mg/L can remove up to 80% of the color, as indicated in a study conducted with values up to 50 uC for raw water (Eikebrokk; Saltnes, 2002). Given that the initial color value in this study exceeded 500 uC, the achieved results can be considered acceptable.

The flocculants used in the study achieved high removal efficiencies for both color and turbidity. However, in the proposed treatment system (coagulation/flocculation/sedimentation/filtration) in most tests, the treatment itself was not sufficiently efficient to meet the maximum values allowed by ordinance Nº. 888/21, which sets the standards for human consumption water potability.

For the synthesized chitosans, lower coagulant dosages proved to be more efficient, demonstrating the potential of chitosan as a water treatment method. However, due to the generally unsatisfactory values, an option is to conduct or combine the treatment used with a complementary treatment. Furthermore, studies with lower initial turbidity may indicate results that comply with the standards.

4 CONCLUSIONS

The results obtained in this work demonstrate the satisfactory performance and efficiency of cationic chitosans (QCSA, QCSB, and QCSN) for remaining turbidity and color in water with high initial turbidity subjected to coagulation, flocculation, and sedimentation in a laboratory-scale Jar test. The Chitosan cationization resulted in a degree of substitution of 1.39, 1.03, and 0.80 for QCSA, QCSB, and QCSN, respectively. The removal efficiency with the synthesized chitosans reached values of 97.9% for turbidity and 97.2% for color, while QP achieved efficiency of 99.1% and 98.5%, respectively for turbidity and color.

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