

Use Of Chitosan As A Biocoagulant For Treatment Of Water With High Turbidity

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-----ABSTRACT-----

In this study, chitosan was evaluated as a biocoagulant for treatment of very high turbidity water, through bench tests using the jar test. Turbidity (NTU) and apparent color (uC) were used as analytical parameters of operational efficiency, as well as sedimentation and filtration in granular bed were studied as fundamental stages of the process of clarification of synthetic raw water. The operational yields reached maximum removals of turbidity and color of 99.98% (0.42 NTU) and 99.37% (5 uC), respectively, applying 12 mg.L⁻¹ of the biopolymer. In all the tests, the filtration was able to reduce turbidity of 20 to 55% of the supernatant, being efficient and fundamental in the removal of residual material in suspension to obtain treated water with turbidity below 0.5 NTU. During the sedimentation, a rapid deposition velocity of flakes and aggregates in the water with the formation of a dense, compact sludge of homogeneous distribution was observed in the bottom of the vessel, which gave the low values of residual turbidity. The results point to a significant operational efficiency proportional to water turbidity; the more blurred the better the clarification process yields, thus demonstrating the potential of using chitosan as a biocoagulant for the removal of suspended particulates present in the water.

KEYWORDS: Chitosan, Biocoagulant, Treatment of turbid water.

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I. INTRODUCTION

The quality of natural waters has been constantly affected by the various human activities of the contemporary era, causing serious environmental impacts that directly affect the dynamics of ecosystems. Soluble organic matter, nutrients, surfactants, oils and greases, suspended solids and inorganic ions (Cl⁻, NO₃⁻, PO₄³⁻) are the main pollutants of surface waters (rivers and lakes) [1]. Large-scale natural disasters and anthropogenic environmental accidents also contribute to the current phenomenon of deterioration of water quality, many of which are used as sources of public supply [2].

One of the main analytical parameters of environmental and sanitary monitoring of the quality of natural and treated waters is turbidity, characterized by the presence of suspended materials (clay, silt, organic matter) capable of causing absorption/dispersion of light [3]. High levels of turbidity can induce significant changes in aquatic ecosystems by limiting the entry of light into the environment. Water with turbidity above 300 NTU can be classified as having very high turbidity and difficult conventional treatment through coagulation with aluminum salts, which besides the operational limitations also present the constant concerns with the metallic residual in the treated water, associated to the development of neurodegenerative diseases such as Alzheimer's disease [4-7].

An alternative for the removal of suspended solids present in the turbid waters is the use of biocoagulants, characterized as materials derived from natural and renewable sources capable of interacting with the particles of the medium, removing them from the water column [8]. Chitosan is a linear copolymer derived from chitin when it is subjected to deacetylation reactions in strongly alkaline media. Its main uses include applications in the pharmaceutical, food, agriculture and tissue engineering sectors, as it is a non-toxic, easily biodegradable material with good compatibility with human cells; the biopolymer also presents a significant potential of industrial production from the chemical processing of shellfish and exoskeletons of marine crustaceans (rich in chitin), generated as by-products of the seafood chain [9-11].

Although abundant, a number of biocoagulants described in the literature present disadvantages, such as the need for prior treatment of material (coagulant isolation), development of characteristic staining in water after treatment, use of significant dosages and low yields, contribute to the increase in the amount of organic matter in the water and are subject to the presence of substances possibly toxic to humans [4,12,13,14]. In this

study, chitosan was evaluated as a biocoagulant for the treatment of water of high turbidity through bench tests using the jar test. Turbidity (NTU) and apparent color (uC) were used as analytical parameters of operational efficiency. Electrical conductivity ($\mu\text{S}/\text{cm}$) and pH were evaluated in parallel to discuss the results of coagulation/flocculation assays. Sedimentation and filtration in granular bed were also studied as fundamental stages of the process of clarification of the raw water.

II. MATERIALS AND METHODS

2.1. Preparation of synthetic raw water

Synthetic crude water was prepared by the dispersion of silt in distilled water by intense agitation (10% w/v) for 20 minutes and subsequent decantation for 6h. After this time, the supernatant was transferred to another vessel by siphoning and stored until the time of jar testing. The prepared raw water had the following physico-chemical characteristics: Turbidity in the range of 2,450 to 2,500 NTU (turbidimeter HANNA), Apparent Color between 700-800 uC (Aquatest APHA), Electrical conductivity at 25°C of 52,59 $\mu\text{S}/\text{cm}$ (conductivitymeter TECNOPON), total alkalinity of 40 $\text{mg}\cdot\text{L}^{-1}$ CaCO_3 (acid base titration) and pH equal to 7.15 (pHmeterHANNA). The methodologies adopted in the physical-chemical evaluation of each parameter before and after treatment are described in Standard Methods for the examination of the water and wastewater [15].

2.2. Preparation of the chitosan coagulant solution

Coagulant solution of chitosan was prepared by previously dissolving 500 mg of the biopolymer (Polymar-Brazil) in 50 mL of 0.1M HCl and being shaken for 18h. After this period, the mixture was transferred to a 100 mL volumetric flask and calibrated with the same acid, yielding a stock solution of 5,000 $\text{mg}\cdot\text{L}^{-1}$.

2.3. Coagulation/Flocculation Assays – Jar Test

The coagulation/flocculation assays were performed in Milan Jar-Test equipment, JT 102 model, provided with 03 acrylic vats. In each test, the evaluated coagulant was added to 1L of synthetic crude water, which was subjected to rapid mixing at 200 rpm for 2 min, and then slow mixing at 40 rpm for 20 min. Soon after, the system was switched off and allowed to settle for 20 min. Samples of the supernatant (2 cm below the surface) were carefully removed for physico-chemical evaluation and measurement of the efficiency of each process.

2.4. Construction of the granular filtration system.

Filtering beds were constructed by obtaining granular material collected from the river banks. The granulometric separation was done in automatic sieving machine using sieves of 4.80, 2.40 and 0.85 mm (\varnothing) of pore diameter. The system was assembled by overlaying three layers of equal volume and with decreasing ascending particle size, having as support a glass chromatographic column of 500 mm in height and 25 mm in diameter. After assembly, the system was rinsed with distilled water in a continuous stream and down to constant turbidity (0.10 NTU). Figure 1 shows the assembly of the filters used in this work.



Figure 1: Construction of the granular filtration system. Initial mechanical separation of the sand collected in river bed (a); details of the granulometric fractions used in the construction of the filters (b) and assembly of the filter column (c).

III. RESULTS AND DISCUSSIONS

3.1. Coagulant effect

Chitosan was highly efficient as a biocoagulant (Figure 2), allowing residual turbidity values in treated water below 1.0 NTU and apparent Color lower than 15 uC, consuming low dosages of the biopolymer. The operational yields reached maximum removals of turbidity and color of 99.98% (0.42 NTU) and 99.37% (5 uC), respectively, applying 12 $\text{mg}\cdot\text{L}^{-1}$ of the biopolymer.

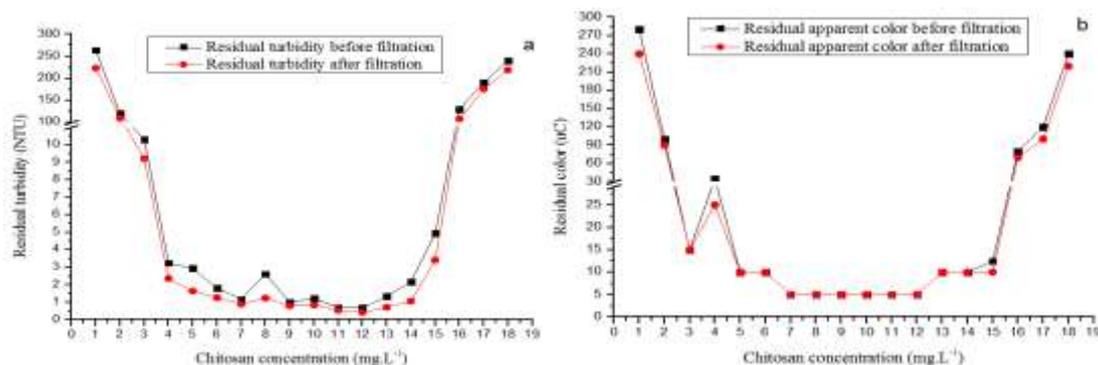


Figure 2: Turbidity (a) and Apparent color (b) residuals obtained before and after filtration of chitosan treated water, using dosages of 1 to 18 mg.L⁻¹ (considering a sedimentation time of 20 minutes).

In all coagulation/flocculation/sedimentation/filtration tests performed at different concentrations (Figure 2), the filtration was able to reduce turbidity of the supernatant from 20 to 55%, being efficient and fundamental in the removal of residual material in suspension and obtaining turbid treated water below 0.5 NTU. This value is stipulated by the World Health Organization (WHO) and by many countries as the maximum acceptable limit for drinking water [16]. It is suggested that the high filtration efficiency may be associated with the surface adhesion capacity presented by the biopolymer [17] and the particle size exclusion promoted by the pores of the filter bed on the residual chitosan polymer chains. The optimal dosages of the acid solution of chitosan (12 mg.L⁻¹) did not cause significant variations in the pH (7.15 → 6.59) and the electrical conductivity of the medium (52.59 μS/cm → 60.93 μS/cm). The mechanisms involved in coagulation/flocculation do not involve the consumption of alkalinity of water (constant throughout the tests), but rather the neutralization of loads and the formation of intracardial bridges adsorbent to impurities [18]. When evaluating the results obtained with other studies in the literature, a significantly higher efficiency of chitosan is observed when compared to other biocoagulants. Magaji et al [19] studied the coagulant effect of *Moringaoleifera* seeds on the turbidity removal of raw waters from rivers, obtaining yields of 75.67% (38.93 NTU of residual turbidity) with consumption of 100 mg.L⁻¹ of plant material. Qureshi, Bhatti and Shaikh [20] applied biocoagulants derived from the fruits of *Mangiferaindica* in the treatment of turbid waters, obtaining 98% efficiency in the removal of turbidity by the application of 25 mg.L⁻¹ of biomass. This highlights the high operational performance of chitosan, which promoted greater turbidity removal with lower material consumption.

Chitosan also stands out compared to traditional inorganic coagulants, such as those based on aluminum. Hu et al [21] applied AlCl₃ as a highly turbid water coagulant (10,000 NTU), requiring dosages of 135 mg.L⁻¹ to obtain water with residual turbidity below 10 NTU.

3.2. Influence of the HCl solution on the color removal and turbidity efficiency

Figure 3 shows the influence of the 0.1M HCl solution used in the preparation of the chitosan coagulant solution (blank test). The assay was performed by adding the same amounts of acid (without the presence of chitosan) applied in the tests with the stock solution of the biopolymer. It was noticed that there were no significant interferences on the removal of color and turbidity from the water, being these directly associated with the action of the biopolymer when protonated in acid medium. The discrete decrease in turbidity may be associated with the natural sedimentation of the suspended particles present in the water column throughout the period of the tests.

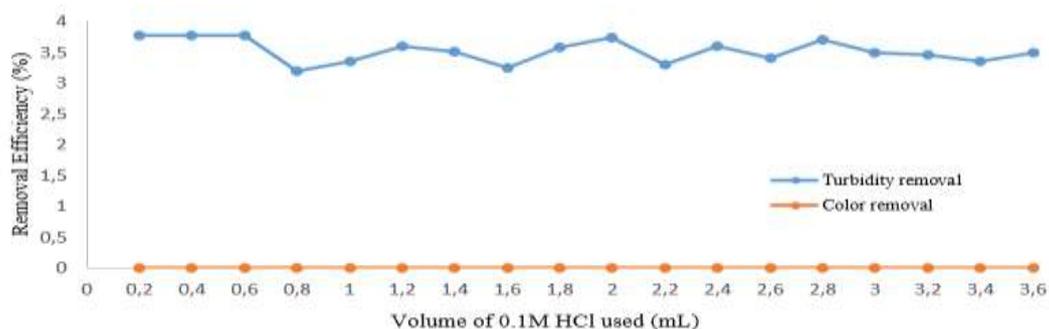


Figure 3: Influence of the solution of 0.1M HCl used in the protonation of chitosan on the removal of color and turbidity.

3.3. Sedimentation Time Study

Figure 4 shows the influence of sedimentation time on water turbidity after coagulation/flocculation (measured in the supernatant). Even in the initial instants (1 to 5 min) it was possible to obtain turbidity values lower than 10 NTU, which favors the sequential rapid filtration process [21]. The best relationship between time and residual turbidity was achieved after 20 minutes of sedimentation. After this period, a stabilization of the system was observed, resulting from particles still remaining in the water.

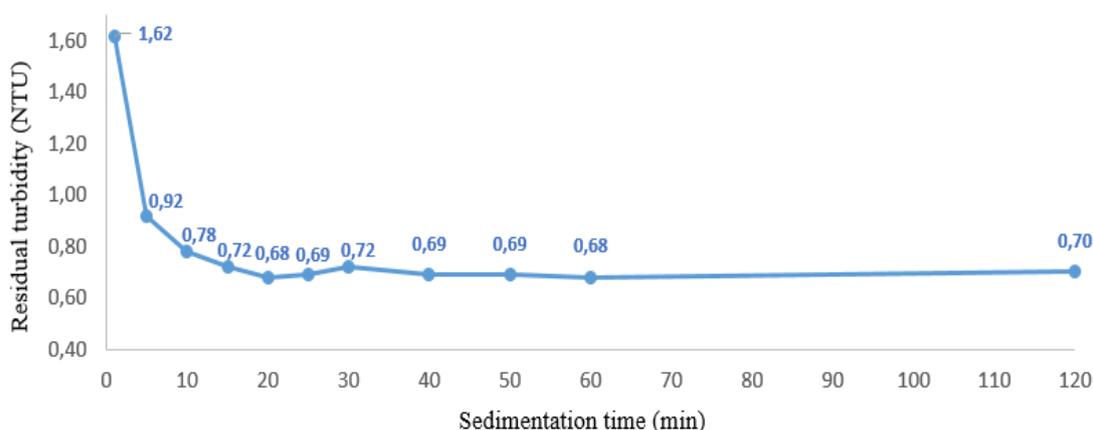


Figure 4: Influence of the sedimentation time on the turbidity of the water treated with chitosan.

3.4. Sludge formation at the end of the process

An important characteristic observed during sedimentation, which provided low values of residual turbidity, was the rapid deposition rate of flakes and aggregates present in the water, with the formation of a dense, compact sludge with a homogeneous distribution at the bottom of the vessel, as shown in Figure 5.

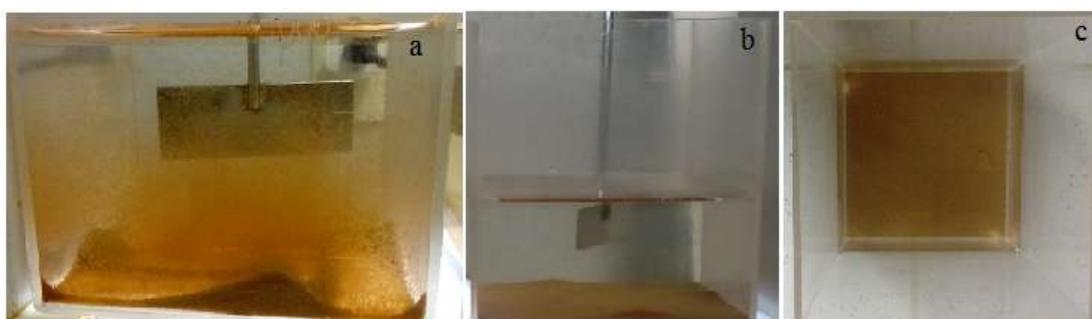


Figure 5: Rapid sedimentation of flakes and formation of dense and compact sludge in the bottom of the vessel. Beginning of the sedimentation process (a); aspect of the system after 20 min of sedimentation (b); top view of compacted sludge and uniform distribution (c).

The sludge generated in the process presents environmental advantages when compared to that obtained by inorganic coagulants. Produced in less quantity (more compact and dense), the sludge resulting from the use of chitosan is predominantly organic, has a lower environmental impact, has nutritional potential for later use, and can be degraded naturally by microorganisms [5]. As for treated water, it was shown to be safe in toxicological tests in rats, with no deaths, macroscopic lesions and clinical signs being observed during a 14 days evaluation period [22].

IV. CONCLUSION

Chitosan was highly efficient in the removal of turbidity (99.98%) and apparent color (99.37%) of highly turbid waters, without drastically affecting the pH of the medium. The obtained results point to an operational efficiency proportional to the turbidity of the water; the more blurred, the better the clarification process yields. The amount of biocoagulant required to obtain satisfactory results was small (12 mg.L^{-1}) when compared to other coagulants of the same nature. Filtration presented as a fundamental step of the treatment process, as it promoted the removal of residues still present in the water after coagulation/flocculation. The generation of a sludge of fast sedimentation allows to reduce the time necessary to obtain water with levels of turbidity within the recommended by the WHO and by several nations. Even preliminary, these and other studies show the potential of using chitosan as a coagulant for water treatment for public supply.

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