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Chitosan as a Strategy in the Treatment of Effluent

Quitosana como Estratégia no Tratamento de Efeluentes

El Chitosan como Esatrategia en el Tratamiento de Aguas Residuales

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Abstract
The treatment of effluents requires new methodologies for the treatment of the tailings. One option is the use of natural coagulants. Chitosan has amino groups in the polymeric chains that allow it to act as a cationic polyelectrolyte and present a high density of charges, which are easily adsorbed on negatively charged surfaces, which is the case for most colloidal impurities present in water. Thus, this work used chitosan in the coagulation/flocculation process to remove color, turbidity and suspension of solids, as a strategy in the treatment of effluents. For that, samples of effluents from the textile industry in the of State of Rio Grande do Norte and samples of effluents from stabilization Lagoons in the municipalities of Touros and Santa Cruz were used in the coagulation/flocculation tests using jar-test. The results proved to be efficient for the removal of color, turbidity and suspension of solids from the samples. The best dosages were 22.5 mg/L and 37.5 mg/L for textile industry effluents, 52.5 mg/L and 60 mg/L for Santa Cruz lagoon effluent; 30 mg/L and 37.5 mg/L for effluent from Touros lagoon. It was observed in this work that chitosan presented in an optimal proportion, that is, the addition of more chitosan did not provide greater removal and that it can be used as a coagulant/flocculant in the treatment of effluents from both the textile industry and domestic effluents, replacing the synthetic coagulants or being used together with them.
Keywords: Chitosan; Textile effluent; Stabilization lagoon.

Resumo
O tratamento de efluentes requer novas metodologias para o tratamento dos rejeitos. Uma opção é o uso de coagulantes naturais. A quitosana possui grupos amino nas cadeias poliméricas que lhe permitem atuar como um polieletrólito catiônico e apresentar alta densidade de cargas, que são facilmente adsorvidas em superfícies carregadas negativamente, como é o caso da maioria das impurezas coloidais presentes na água. Assim, este trabalho utilizou quitosana no processo de coagulação/floculação para remoção de cor, turbidez e suspensão de sólidos, como estratégia no tratamento de efluentes. Para tanto, amostras de efluentes da indústria têxtil do Estado do Rio Grande do Norte e amostras de efluentes de lagoas de estabilização dos municípios de Touros e Santa Cruz foram utilizadas nos testes de coagulação/floculação utilizando jar-test. Os resultados mostraram-se eficientes na remoção de cor, turbidez e suspensão de sólidos das amostras. As melhores dosagens foram 22,5 mg/L e 37,5 mg/L para efluentes da indústria têxtil, 52,5 mg/L e 60 mg/L para efluentes da lagoa Santa Cruz; 30 mg/L e 37,5 mg/L para o efluente da lagoa dos Touros. Observou-se neste trabalho que a quitosana apresentou-se em proporção ótima, ou seja, a adição de mais quitosana não proporcionou maior remoção e que pode ser utilizada como coagulante/floculante no tratamento de efluentes tanto da indústria têxtil como doméstica efluentes, substituindo os coagulantes sintéticos ou sendo utilizados em conjunto com eles.
Palavras-chave: Quitosana; Efluente têxtil; Lagoa de estabilização.

Resumen
El tratamiento de efluentes requiere de nuevas metodologías para el tratamiento de los relaves. Una opción es el uso de coagulantes naturales. El chiotosán tiene grupos amino en las cadenas poliméricas que le permiten actuar como un polielectrolito catiónico y presentar una alta densidad de cargas, las cuales son fácilmente adsorbidas en superficies cargadas negativamente, como es el caso de la mayoría de las impurezas coloidales presentes en el agua. Así, este trabajo utilizó chiotosán en el proceso de coagulación/floculación para remover color, turbidez y suspensión de

sólidos, como estrategia en el tratamiento de efluentes. Para eso, se utilizaron muestras de efluentes de la industria textil en el Estado de Rio Grande do Norte y muestras de efluentes de Lagunas de Estabilización en los municipios de Touros y Santa Cruz en las pruebas de coagulación/floculación utilizando el jar-test. Los resultados demostraron ser eficientes para la remoción de color, turbidez y suspensión de sólidos de las muestras. Las mejores dosificaciones fueron 22,5 mg/L y 37,5 mg/L para efluentes de la industria textil, 52,5 mg/L y 60 mg/L para efluentes de la laguna Santa Cruz; 30 mg/L y 37,5 mg/L para efluentes de la laguna de Touros. Se observó en este trabajo que el chitosán se presentó en una proporción óptima, es decir, la adición de más chiotosán no proporcionó mayor remoción y que puede ser utilizado como coagulante/floculante en el tratamiento de efluentes tanto de la industria textil como domésticos. efluentes, reemplazando a los coagulantes sintéticos o utilizándose junto con ellos.
Palabras clave: Chitosán; Efluente textile; Laguna de estabilización.

1. Introduction

The disorderly growth of cities, combined with population growth and a consumerist model, has generated a very large volume of effluents. The word effluent comes from the Latin effluente that emanates that flows (Informal Dictionary, 2022). All fluid waste (liquid and gaseous) from various human activities, when discarded into the environment are called effluents. Liquid effluents constitute the biggest polluters of water bodies and therefore there is a great effort in trying to control their quality. The qualitative erosion and irreversible consumption of supply sources, including, here, water sources for consumption, domestic use and agriculture have contributed to the degradation of water sources (Jordão et. al. 1995)

According to their origin, effluents can be classified as domestic, industrial, agricultural, urban rainwater and solid waste deposit effluents. In this work, two types of effluent were used, domestic and industrial. Domestic effluent is characterized by having a high load of organic matter and substances used as cleaning material. The industrial effluent varies according to the industrial activity. Effluents from agroindustry and the food industry, in general, are rich in organic matter, while other industrial branches tend to produce effluents richer in diverse and varied elements and chemical compounds, such as the textile industry. This is a generator of a large volume of highly polluting discharges with an accentuated color and various products that are toxic to man and the environment.

The main environmental problems of the textile industries are related to the use of azo-dyes, which are synthetic and resistant to natural degradation, in addition to being mutagenic and carcinogenic. The concern with the aesthetics and quality of the environment affected by colored effluents leads to the search for discoloration alternatives, which constitutes one of the great challenges faced nowadays (Pinheiro et. al., 2004).

Due to the extreme complexity and diversity of the compounds that can be found in effluents, there is a constant concern to develop processes aimed at a more appropriate application of treatments. Due to this fact, many alternatives have been studied. The conventional methods used for the treatment of liquid effluents can be generically classified as primary or mechanical, secondary or biological and tertiary or physical-chemical (Zamora et. al. 2002).

One of the alternatives being used for the treatment of effluents is chitosan. It has been used in the treatment of effluents from the textile industry, in the coagulation/flocculation/ultrafiltration process for the production of drinking water, in bioremediation and in the treatment of water containing trace metals. This is possible due to its cationic polyelectrolytic action. Being a polycation, chitosan can form electrostatic complexes with negatively charged species that constitute the majority of colloidal impurities in water, thus making cationic coagulants an alternative for the treatment of water and industrial effluents (Moraes et. al., 2005).

Chitosan has been adopted by many countries such as Japan, China, India and the United States, presenting numerous advantages in relation to chemical products, mainly regarding biodegradability, low toxicity and low rate of production of residual sludge (Moraes et. al., 2005).

In this context, Kawamura states that:

> No disadvantages are known in relation to the use of chitosan, and it can be a promising substitute for synthetic products. It can also be used to increase the action of inorganic coagulants such as aluminum sulfate, acting as an auxiliary polyelectrolyte, resulting in lowering the dose of each compound (Kawamura, 1991).

Melo et. al. (2022) evaluated the use of chitosan as a coagulant for fishing industry effluents. In the work in question, chitosan with a pH of 5.5 and 6.0 showed the best responses. Costa et. al (2017) prepared a porous composite of dry coconut fiber with chitosan and observed that this mixture with a pH of 6.0 and 7.0 has active sites that increase the probability of adsorption of chromium ions. Furthermore, he found that the greater the amount of chitosan in the composite there is a tendency to improve the adsorption of chromium ions. Vaz et. al (2010) tested different coagulant/flocculant agents to remove color and turbidity from the electroplating effluent, chitosan with low concentrations obtained high efficiencies, proving to be a coagulant agent. Most promising flocculant for the treatment of this type of effluent.

Rego, O. C (2022) made use of chitosan nanoparticles as a reagent in the flotation of chalcopyrite in a Hallimond tube and observed that the microflotation tests with the chitosan collector the floatability of the copper ore was equal to 67.53%, 72.34% and 84.86%. With the chitosan collector for the tests carried out at pH's 11, 10 and 9. The results of this work confirm that chitosan has efficiency in the recovery process in the floatability of chalcopyrite, having a behavior similar to that of inorganic polymers. In relation to the collector with chitosan, the highest values of floatability were greater than 60% at dosages of 500 g/t and 1000 g/t, with the highest values of 84.9% for tests carried out at pH 9 and dosage of 500 g/t t.

Giannetti-Morandim- et. al. (2017) studied the treatment of tannery effluents using chitosan associated with the ionic liquid of sec-butylammonium acetate and through the analysis of the results obtained, the effectiveness in the adsorption of chromium was verified, obtaining results within the standards established by CETESB. Finally, the work presents an innovative, low-cost, ecologically favorable method, alternative to the conventional methods currently used and, the continuation of the research and experiments, can be considered promising, always aiming at its application in the industry and in the large-scale treatment of chromium in liquid effluents, such as those from tanneries.

Lucena et. al (2016) researched the effect of chitosan associated with thioacetamide in relation to the adsorption of reactive textile dyes (reactive yellow GR, blue R 160% remazol and olive green colloisal indranthren). the modification of chitosan with thioacetamide favored the adsorptive process, obtaining an increase in the percentage of dye removal, with values greater than 90% in all dyes studied, in addition to reducing the contact time so that the system tended to reach equilibrium with 60 minutes of the beginning of the adsorptive process. According to the study of the adsorption isotherms by the Langmuir method, it was verified that the modification of chitosan with thioacetamide promoted an increase in the adsorption capacity about twice as much as that of pure chitosan.

Barcellos et. al (2008) states that in the treatment of waste from the dyeing of nylon 6,6 fabrics with acid dyes, the blend nylon 6,6/chitosan 80/20 (flakes) showed a high affinity with the dyes acids (erionyl A-3B red, erionyl rxl yellow and erionyl R marine), obtaining color removal rates greater than 95%. However, it was found that the reproducibility of dyeing is better when using waste treated with only one dye (monochrome). When waste treated with dye mixtures is reused (trichrome), yellowish dyeing is affected.

In the work of Janegitz et. al. (2007) Chitosan previously solubilized in an acid medium and subsequently precipitated with the metal cation in a basic medium was more efficient in removing the metal cations. The proposed method was effective for removing Cu2+, Cr3+, Pb2+, Cd2+ and Hg2+ ions in solution, and the remaining concentrations of these cations were below the LDs of the analytical technique employed, which are lower or close to those concentrations established by CONAMA.

Laus, R. et. al (2006) studied the use of chitosan microspheres cross-linked with tripolyphosphate (QTS-TPF) for the treatment of coal-contaminated water. by coal mining. The results obtained in relation to the removal of iron and manganese are interesting, since there are few existing alternatives for the recovery of water with this type of contamination, with QTS-TPF microspheres being a new adsorbent for the treatment of water contaminated by mining. coal. Another advantage would be that the biopolymer containing nitrogen and phosphorus, which was used in the treatment of water, can be discarded in the environment after the desorption of the metals, without harming the ecosystems.

Silva et al. (2001) studied chitosan and moringa oleifera for decolorizing textile industry effluents and found that these products function as a natural coagulant that can be used in the physical-chemical treatment of textile industry effluents. Optimum concentrations of moringa and chitosan are around 400 and 3 mg/L, respectively.

Spinelli et.al (2001) tested chitosan in the treatment of drinking water using chitosan as a coagulant for river water with low turbidity. The efficiency of chitosan in the treatment was evaluated by analysis of pH, apparent color and remaining turbidity. The best chitosan dosage found for river water was 1.5mg/L.

Valentini et. al (2000) prepared chitosan capsules complexed with dimethylglyoxime (DMG) and with tetraacetic ethylenediamine and observed that there was an increase in the capacity of metal retention by the capsule. The value obtained for retention of Ni metal in the capsules after DMG adsorption is twice as high; for the case of Cu, we observed that the adsorption capacity increased by about eighteen times after the adsorption of EDTA. The insolubility of the capsules in an acid medium was also observed, making it possible to use them at a pH in which the chitosan polymer was previously soluble.

Thus, this work aimed to use chitosan to remove color, turbidity and suspension of solids from effluents from the textile industry and raw effluents (EB) from the stabilization ponds of Touros/RN and Santa Cruz/RN, with the aim of using the as a strategy in the treatment of effluents.

2. Methodology

Powdered chitosan with a degree of deacetylation of 90%, according to the manufacturer, and a molar mass of 2.0 x 105 Da (Dalton), determined by the vicosimetry method, using the authorization of Mark-Howink-Sakurada (Tsaih et.al.; 1999; Tonhi et.al.; 2002). The chitosan solution (1.5% m/v) was prepared from a 2% aqueous acetic acid solution. This solution was kept constant for 24 hours at 150 rpm, in order to homogenize the solution. A part of the chitosan solution was used pure and another part was mixed with iron chlorine (iron perchloride – FeCl¬3). FeCl3 is also used in water and sewage treatment.

Coagulation tests were carried out in jar-tests with raw samples from the textile industry of Norte Rio Grandense and from stabilization ponds in the city of Touros and Santa Cruz, located in the state of Rio Grande do Norte. The following parameters were determined: Color, Turbidity and Suspended Solids. The rapid mixing was carried out with a rotation of 100 rpm for 30 seconds and the flocculation with a rotation of 30 rpm for 10 minutes. The settling time was 15 minutes. After sedimentation, the samples were analyzed in a HACH DR 2010 spectrophotometer. The dosages used are shown in Table 1.

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Table 1 - Concentration of coagulants used for each Type of samples and amount of coagulant used in the jar-test.

Samples	***Coagulants***
Textile Effluent	Chitosan (7,5; 15; 22,5; 30; 37.5; 45; 60; 75; 90 mg/L) e Chitosan + $FeCl_3$ (7,51; 22,5; 37.5 mg/L)
Santa Cruz Lagoon	Chitosan (7,5; 15; 22,5; 30; 37.5; 45;52,5;60; 67,5; 75 mg/L)
Touros Lagoon	Chitosan (7,5; 15; 22,5; 30; 37.5; 45;52,5;60; 67,5; 75 mg/L)

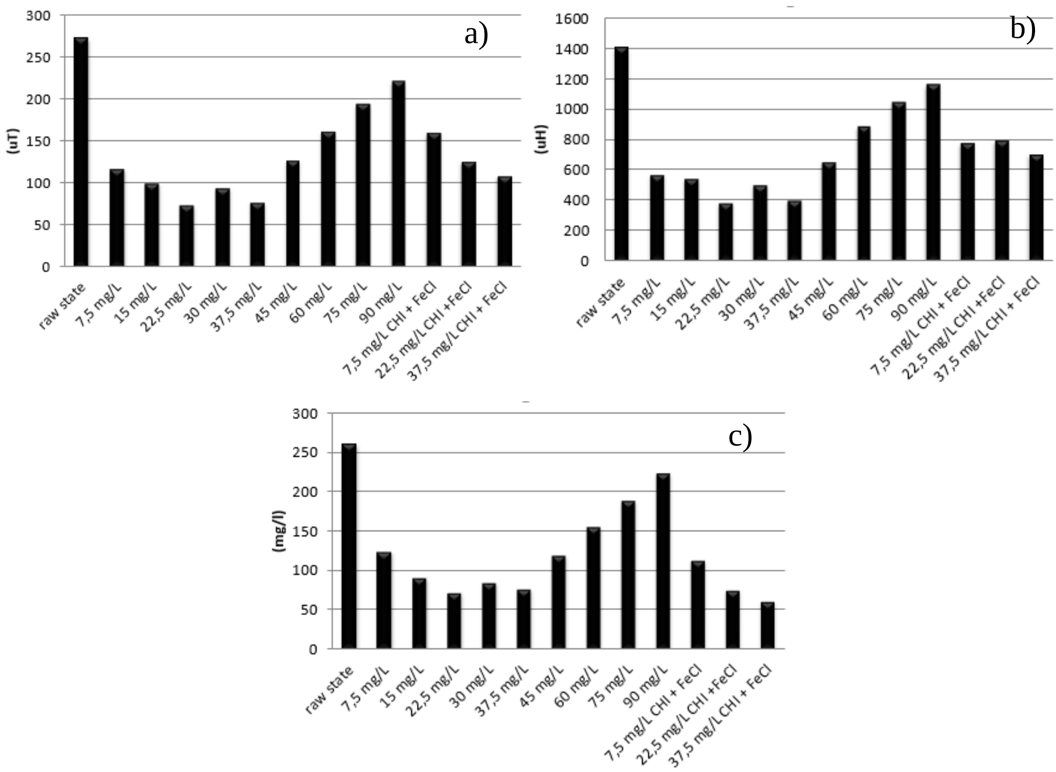
Source: Authors.

3. Results and Discussion

The treatment carried out with the chitosan solution was effective in removing turbidity (Figure 1a), color (Figure 1b) and suspended solids (Figure 1c) from textile effluent in all proportions used, however specific amounts of chitosan (22.5 mg/L, 30 mg/L and 37.5 mg/L) showed a better result, indicating an optimal ratio.

When chitosan was mixed with FeCl3, there was also removal, especially for suspended solids (Figure 3). In the turbidity and color tests, this removal was not so great (Figures 1 and 2). This is believed to have occurred because ferric chloride is orange in color, which may have influenced the turbidity and color result. Among the chitosan and FeCl3 mixtures, the best result was 37.5 mg/L of chitosan plus 37.5 mg/L of FeCl3.

Figure 1 - a) Test to remove turbidity from textile effluent using a chitosan and chitosan solution mixed with FeCl3; b) Assay for removing color from textile effluent using chitosan solution mixed with FeCl3; c) Assay to remove suspended solids from textile effluent using chitosan solution and chitosan plus FeCl3 mixture.



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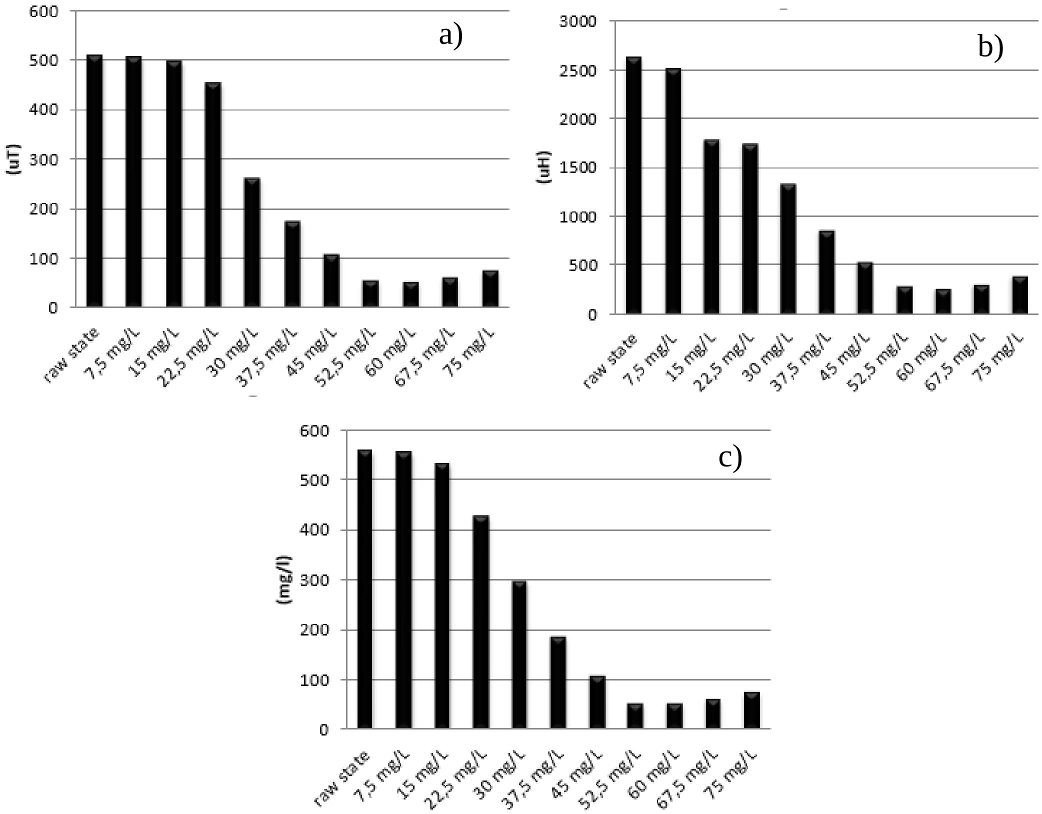
Observing the three graphs (Figures 1a, 1b and 1c) one can still see that the increase in chitosan concentration induces a loss of the ability to remove these parameters.

In the EB samples from the Santa Cruz lagoon, it is observed that the untreated sample has much higher values of color, turbidity and solid suspension than the textile effluent samples. In this case, the proportions of chitosan that presented the best results were much higher than those used in the textile effluent. The most prominent proportions were 52.5 mg/L, 60 mg/L, 67.5 mg/L and 75mg/L, in other words, twice the most prominent proportions for the treatment of effluent from the textile industry. The removal in this case was also much greater than the removal of the textile effluent (Figures 2a, 2b and 2c).

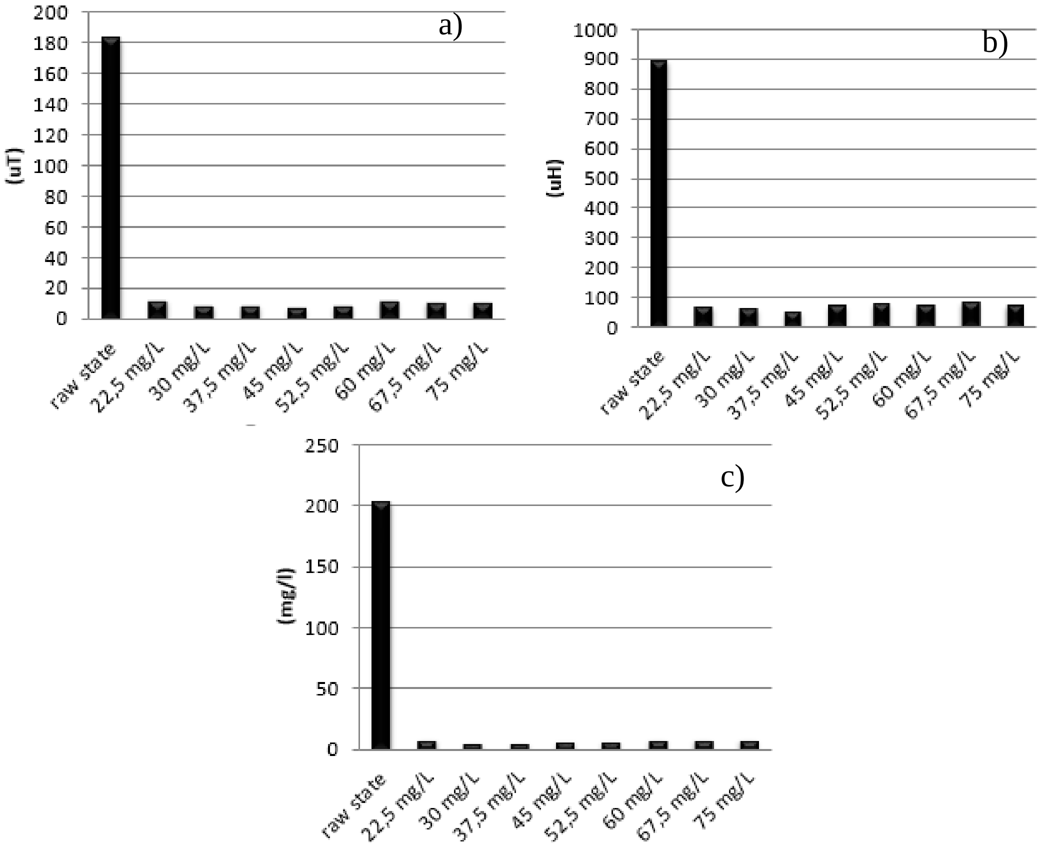
Figure 2 - a) Assay to remove turbidity from the RE of Santa Cruz/RN Lagoon with chitosan solution; b) Assay for color removal of RE from the Santa Cruz/RN Lagoon with chitosan solution; c) Assay for the removal of suspended solids from the RE of Santa Cruz/RN Lagoonwith chitosan solution.



Source: Authors.

The raw sample from Touros lagoon showed the lowest values of turbidity, color and suspension of solids (Figures 3a, 3b and 3c). In the tests carried out with the samples from this lagoon, it was observed that all quantities of natural coagulant used presented good results, with little difference in results between them.

Figure 3 - a) Assay to remove turbidity from the RE of Touros/RN Lagoon with chitosan solution; b) Assay for the removal of RE color from the Touros/RN lagoon with chitosan solution; c) Assay for the removal of suspended solids from the RE from the Touros/RN lagoon with chitosan solution.



Source: Authors.

4. Final Considerations

The chitosan studied is a promising alternative in the physical-chemical treatment of effluents from the textile industry and RE from the stabilization pond. It can be used as an auxiliary in primary treatment, increasing the efficiency of decanters. In addition, chitosan, being a natural coagulant, is ecologically compatible, unlike metallic salts. Another observation is that chitosan works at an optimal ratio, so increasing this ratio does not result in greater efficiency in removing color, turbidity, and suspending solids. Chitosan can also be used as other chemical products such as FeCl3, optimizing its performance.

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