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Investigation of new natural coagulant - cationic hemicellulose associated with cationic tannin - for coagulation/dissolved air flotation (C/DAF) in the treatment of industrial effluent

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ABSTRACT

The use of plant-based coagulants (natural coagulants) in wastewater treatments has potential advantages over the inorganic coagulants used commercially. This study evaluated organic coagulants cationic hemicelluloses (CH) synthesized from peanut shell and associated with commercial cationic tannin (TSG) for use as the primary coagulation/flocculation treatment, followed by solid-liquid separation via sedimentation/flotation by dissolved air (DAF). The assay was carried out in a jar test on effluent from a multinational industry in the grain processing sector, located in the city of Uberlândia-MG. Coagulation diagrams were determined using the data spatial interpolation method of the Kringing regression model and the Tukey test was used to assess the difference in the results obtained. The optimum removal points of turbidity removal efficiency (TRE), greater than 98%, were achieved for the TSG/CH association with 200 mg L^{-1} (pH 10.72), 350 mg L^{-1} (pH 9.72), 500 mg L^{-1} (pH 9.56) in sedimentation. For the separation by DAF, the association of TSG/CH resulted in TRE values greater than 95% at dosages of 350 mg L^{-1} (pH 9.59) and 500 mg L^{-1} (pH 7.92). Furthermore, the results indicate that the associated use of TSG/CH, a coagulation aid, favored the coupling of the DAF bubble-particle, resulting in a smaller volume of sludge. In addition, CH expanded the action of TSG to the basic region.

Keywords: agroindustry residue, natural organic coagulants, primary physical chemical treatment.

Investigação de um novo coagulante natural - hemicelulose catiônica associada ao tanino catiônico – na coagulação/flotação por ar dissolvido (C/DAF) no tratamento de efluente industrial

RESUMO

O uso de coagulantes à base de plantas (coagulante natural) em tratamentos de efluentes tem potencial contra coagulantes inorgânicos utilizados comercialmente. Este trabalho teve como objetivo avaliar os coagulantes orgânicos hemiceluloses catiônicas (CH) – sintetizadas a partir da casca de amendoim – associadas ao tanino catiônico (TSG) – comercial – para coagulação/floculação como tratamento primário, seguido de separação sólido-líquido via sedimentação/flotação por ar (DAF). O ensaio foi realizado em *jar test* em efluente de uma indústria multinacional do setor de beneficiamento de grãos, localizada na cidade de Uberlândia-MG. Os diagramas de coagulação foram determinados pelo método de interpolação espacial de dados do modelo de regressão de *Kringing* e o teste de Tukey foi utilizado para avaliar a diferença nos resultados obtidos. Os pontos ótimos de eficiência de remoção de turbidez (TRE), superiores a 98%, foram alcançados para a associação TSG/CH com 200 mg L^{-1} (pH 10,72), 350 mg L^{-1} (pH 9,72), 500 mg L^{-1} (pH 9,56) na sedimentação. Para a separação por DAF, a associação de TSG/CH resultou em valores de TRE superiores a 95% nas dosagens de 350 mg L^{-1} (pH 9,59) e 500 mg L^{-1} (pH 7,92). Além disso, os resultados obtidos indicam que o uso associado de TSG/CH como auxiliar de coagulação, favoreceu o acoplamento bolha-partícula, resultando em menor volume de lodo, além disso, o CH expandiu a ação do TSG para a região básica.

Palavras-chave: coagulantes orgânicos naturais, resíduo agroindustrial, tratamento primário físico-químico.

1. INTRODUCTION

Effluent treatment technologies to better preserve the quality of water resources and conserve aquatic ecosystems have been developed and improved in recent decades. In general, effluent treatment can be divided into physical (sedimentation, flotation, filtration, membrane, adsorption), chemical (coagulation, oxidation, catalytic reduction, ion exchange) and biological (bioreactors, microbial biodegradation, phytoremediation) processes. Furthermore, the application of joint technologies for the purpose of obtaining better water quality parameters is common, resulting in the following treatment stages: primary, secondary and tertiary (Pioltine and Reali, 2015; Ang and Mohammad, 2020).

Coagulation is one of the oldest treatment technologies and continues to be constantly investigated and improved. The commonly used coagulants are inorganic and non-biodegradable, such as aluminum sulfate ($Al_2(SO_4)_3$, iron chloride ($FeCl_3$) and polyaluminium chloride ($Al_n(OH)_mCl_{3n-m}$). Despite their proven chemical efficiency, when dosed incorrectly these inorganic coagulants can cause residual concentrations of aluminum, iron, sulfate and chlorides that remain in the treated water, thus impacting aquatic ecosystems. Furthermore, there are reports that the increase in aluminum concentration in treated water, due to the use of coagulants containing aluminum, contributes to the increase in cases of diseases such as: Alzheimer's, Parkinson's and Down's syndrome (Shak and Wu, 2015; Silva, 1999).

In view of the consequences associated with the use of inorganic coagulants, natural coagulants have been introduced as alternatives having safety advantages for human health and ecosystems (Shak and Wu, 2015; Franco *et al.*, 2017). When compared to the aforementioned inorganic coagulants, these have lower toxicity and higher biodegradability, thus following the principles of green chemistry (Lima Júnior and Abreu, 2018).

There are several authors who report the use of biopolymers with natural coagulant, tannins (Justina *et al.*, 2018; Ribeiro *et al.*, 2017a), oil moringa (Ntibrey *et al.*, 2020), chitosan (Jagaba *et al.*, 2021), okra and passion fruit seeds (Muniz *et al.*, 2020a). One of the advantages of natural coagulants is that their synthesis reactants may come from agro-industrial residues, as in the case of cellulosic derivatives such as Cationic Hemicellulose (Ren *et al.*, 2006; Landim *et al.*, 2013; Ribeiro *et al.*, 2017a; 2017b).

Agro-industrial production stands out as one of the main economic activities in the country, mainly for promoting the production of food, fibers, bioenergy, among other products and by-products. In this sector, the production of peanuts is attracting attention and, according to the National Supply Company (CONAB), 165.1 thousand hectares were planted in the country's first crop. Brazil currently occupies the 12th position in the world ranking of largest peanut producers and reached record levels of production in 2020 (CONAB, 2021). As for the total Brazilian production, again according to CONAB (2021), the 2020/21 crop corresponded to 574.4 thousand tons, representing a productivity of 3,479 kg/ha. Furthermore, the foreign market purchases from 60% to 70% of the total amount of peanuts produced in Brazil, with Russia, Holland and Algeria being its main buyers.

Considering the size of production, one of the biggest concerns of the agro-industrial sector is the generation of enormous residues. As an example of the dimension of this activity, according to data from Vaz Junior (2020) it is estimated that world agricultural production is around 7.26 Gt and that the volume of dry residue from plant biomass reaches the equivalent of 140 Gt. This huge amount of waste becomes an aggravating environmental factor. According to Ribeiro (2017), peanut shells are tailings consisting mainly of cellulose (from 20% to 30%), hemicelluloses (from 10% to 15%) and lignin (from 40% to 45%), presenting itself as source of biomass for the obtaining of natural coagulants.

Furthermore, the association of coagulation by natural biopolymers, followed by solid-liquid separation via dissolved air flotation (C/DAF) has been highlighted as a more sustainable method, as it allows both the formation of smaller volumes of sludge in shorter separation times and Biochemical oxygen demand (BOD) reduction. The use of dissolved air flotation (DAF) occurred in the mid-1920s and there are records of it being used in two factories located in Sweden as early as the 1970s (Pioltione and Reali, 2015). Subsequently, its use was extended to several other European countries and today it is widely used in countries such as the United States, (Creamer *et al.*, 2010), Canada (Gudmundur *et al.*, 2020), China (Wang *et al.*, 2021), South Korea (Oh *et al.*, 2019), New Zealand (Okoro *et al.*, 2017), Iran (Behin and Bahrami, 2012), Malaysia (Rozainy *et al.*, 2014), Brazil (Muniz *et al.*, 2020b), among others.

The main objective of the present study was to carry out the C/DAF with a natural organic coagulant obtained by the association of cationic hemicellulose, extracted and synthesized from the agroindustrial residue of peanut shell by the authors, and commercial cationic tannin in the treatment of effluent generated by a multinational in the grain processing sector, located in the city of Uberlândia, Minas Gerais, in order to obtain a more sustainable and effective technology.

2. MATERIAL AND METHODS

2.1. Synthesis of cationic hemicelluloses (CH) from agroindustrial peanut shell residue

The holocellulose was extracted from the lignocellulosic agroindustrial residue of peanut shells according to the procedure described by Vieira *et al.* (2012), in which the peanut shells were mixed with distilled water at a ratio of 1:20 (g mL^{-1}) and heated at 75°C for 30 min. Then, acetic acid and sodium chlorite were added to the system in a ratio of 1:1.5 (mL g^{-1}) and kept under stirring for 1 h. This process was repeated 3 times and every 1 hour the same amount of these reagents was added to the system, adding up to a digestion period of 4h. Then, the reaction mixture was cooled to 10°C and filtered. The fibrous residue, composed of holocellulose, was washed with distilled water at 5°C for 20 min, at which point it displayed a whitish color. At the end of the washing step, it was dried in an oven at 75°C for 6 h.

The procedure established by Morais *et al.* (2010) was followed for the isolation of natural hemicelluloses, in which a 17.5% (m v^{-1}) NaOH solution was added to the holocelluloses in a proportion of 15:1 (mL g^{-1}). The material was then ground for 8 min and the mixture filtered in a nylon strainer to separate the celluloses, the fibrous residue of the hemicelluloses (liquid part). Acid solution 1:1 (v v^{-1}) ethanol/acetic acid (CH_3COOH/Ethanol (C_2H_5OH)) was added to the liquid part to precipitate the material which, after 12 h, was filtered in a porous plate funnel and dried in an oven at 75°C for 6 h.

Cationic hemicelluloses were synthesized according to procedures adapted from Ren *et al.* (2006; 2007) and Landim *et al.* (2013), in which a 10% (w v^{-1}) solution of hemicelluloses was kept under stirring at 60°C for 30 min. Subsequently, a NaOH solution was added to the reaction medium in a proportion of 14% (m v^{-1}) and kept under stirring for 20 min. After this time, a solution of (2,3-Epoxypropyl) trimethylammonium chloride 6.8% (v v^{-1}) was added and again the reaction medium was kept under stirring for 30 min. Afterwards, a 2.2% NaOH solution (m v^{-1}) was added and the reaction medium was kept under stirring at 60°C for 5 h. The resulting mixture was cooled in an ice bath and neutralized with HCl solution. Then, the Cationic Hemicelluloses were precipitated with 98% ethanol and filtered in a porous plate funnel. The final material was oven dried at 75ºC for 6 h.

2.2. Determination of the degree of substitution (DS) of CH by elementary analysis

The synthesized CH was previously dried at a temperature of 60ºC for 24 h. The determination of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) was performed by elemental analysis in an EA 1110-CHNS/O equipment from CE Instruments. The degree of substitution (DS) of CH was calculated using Equation 1 (Ren *et al.*, 2006; 2007).

$$DS = \frac{60\%\,N}{14\%\,C - 72\%\,N} \tag{1}$$

In which:

%N = percentage of nitrogen determined by elemental analysis;

%C = percentage of carbon determined by elemental analysis;

60 = molar mass of carbons of the xylose molecule;

14 = molar mass of nitrogen present in the cationic substituent group; and

72 = molar mass of carbons of the cationic substituent group.

2.3. Analytical characterization of industrial effluent

The raw effluent was collected in a composite sample in a grain processing (corn and soybean) plant of a multinational food industry, located in the city of Uberlândia, Minas Gerais. For the analytical characterization of the effluent, the turbidity index/NTU was measured in an Ap 2000 Policontrol turbidimeter, the initial pH in a Hanna instruments® pHmeter and the sedimentable solids in an *Imhoff* Cone® (mL L^{-1}) for 45 min. These control parameters were adopted as standards of comparison for the evaluation of the treatment effectiveness and for the determination of the turbidity removal (%) efficiency. Another aim was to analyse the volume of sludge formed after sedimentation and solid-liquid separation by DAF.

2.4. Preparation of natural organic coagulant solutions

The coagulant studied in this work, based on cationic tannin, was TANFLOC SG (TSG), a commercial organic-cationic polymer, from black Acassia bark, provided by the company TANAC S/A. Considering that TANFLOC SG has a non-volatile content between 30-34%, an average of 32% was considered for the amount of cationic tannin in this solution (31.25 g), the solution was diluted to 10%.

The coagulant for the TSG/CH association was obtained at the ratio of 3:1 (v v^{-1}), adapted from Ribeiro (2017), by mixing 75 mL of a 10% TANFLOC SG solution (v v^{-1}) with 25 mL of a 10% CH solution (m v^{-1}), resulting in TSG/CH 3:1 (v v^{-1}). Assays were performed for TANFLOC SG and TANFLOC SG/Cationic Hemicellulose (TSG/CH) with the following dosage variations: 200; 350 and 500 mg L^{-1}.

2.5. Grain processing effluent treatability tests

The physical-chemical treatment tests were carried out at the Laboratory of Energy Storage and Effluent Treatment (LAETE/UFU) in jar tests (PolyControl brand Jartest) for coagulation/flocculation, followed by sedimentation. Assays were performed for TANFLOC SG and TANFLOC SG/Cationic Hemicellulose (TSG/CH) with the following dosage variations: 200; 350 and 500 mg L^{-1}. The variation of the coagulation pH was carried out by the addition of a 1 mol L^{-1} sodium hydroxide solution. Jar tests were carried out with the following steps: (i) 1 L of effluent was added to each jar; (ii) rapid agitation in a mean agitation gradient (G_{mr}) of 300 s^{-1} (250 rpm) for 30 s, where a 40 mL sample was collected from each jar and the coagulation pH was measured; (iii) a slow mixing occurred in a mean flocculation gradient (G_f) of 35 s^{-1} (30 rpm) for 15 min; (iv) the treated effluent was transferred to *Imhoff* Cones® after 30 min of decantation, the volume of sludge formed by sedimentation was measured and the remaining turbidity was measured.

After selecting the points with TRE greater than 98%, the points were repeated in triplicate using the solid-liquid separation method by C/DAF, through a stainless steel saturation chamber and modified jars for flotation. The treatment was carried out for 1 L of effluent and the water went through a saturation time of 20 min. Thus, the saturated water was injected at a pressure of 5.0 Kgf cm^{-2} and administered in the effluent in a 25%/75% (saturated water/effluent) proportion. Finally, the turbidity measurements of the raw effluent were compared with those obtained after sedimentation or DAF, using Equation 2.

$$turbidity\ removal\ efficiency\ (TRE\ \%)\ =\ \left(1-\left(\frac{final\ turbidity}{initial\ turbidity}\right)x\ 100\right) \quad (2)$$

2.6. Determination of coagulation diagrams

The coagulation diagrams were determined in 18 tests for 10% TSG (v v^{-1}) (dosages: 200, 350 and 500 mg L^{-1}) and 18 tests for 10% TSG/CH (v v^{-1}) (dosages: 200, 350 and 500 mg L^{-1}), by design 3 dosages and 3 repetitions. For each batch with 6 jars (in each jar 1 L of effluent were added), the coagulant dosage was maintained in all jars, the pH was varied by the addition of HCl (1 mol L^{-1}), as acidifier, or NaOH (1 mol L^{-1}), as alkalinizing, in different volumes to obtain the desired pH values, between 4 at 12 (for each dosage studied, pH tests were performed that were near 4, 5, 7, 9, 11 and 12).

The records of coagulation pH readings, coagulant dosage and the respective percentages of apparent color removal were tabulated in electronic spreadsheets in Microsoft Excel and later transferred to the computer program Surfer ® (Golden Software, 2018). The aim was to estimate percentages in non-sampled points and draw the curves of the same removal efficiency, called the "coagulation diagram".

The Kriging regression method was selected as a mathematical model for the spatial interpolation and estimation of the mean turbidity removal percentages. The model is characterized by isolines, which represent the removal percentage level curves. In this study, ordinary Kriging was used, so the estimate to determine an average value in a non-sampled region was made from neighboring points.

In addition, Figure 1 schematically shows the effluent treatment carried out by sedimentation or DAF from the use of coagulant synthesized from agro-industrial residues. The cationic hemicellulose has a dark brown visual color, the intrinsic viscosity corresponds to viscosity 8.06 mL g^{-1} (Ribeiro, 2017), solubility 20.00 g L^{-1} (Ribeiro *et al.*, 2017a) and density 0,1 g mL^{-1}.

2.7. Selection of optimal points

To select the best points of the coagulation diagram, the conditions (dosage and pH) resulting from the percentages of turbidity removal (> 98%) associated with a lower sludge formation were chosen. Therefore, 3 points were selected for TSG coagulant and 3 points when TSG/HC was applied. These same points were used in DAF.

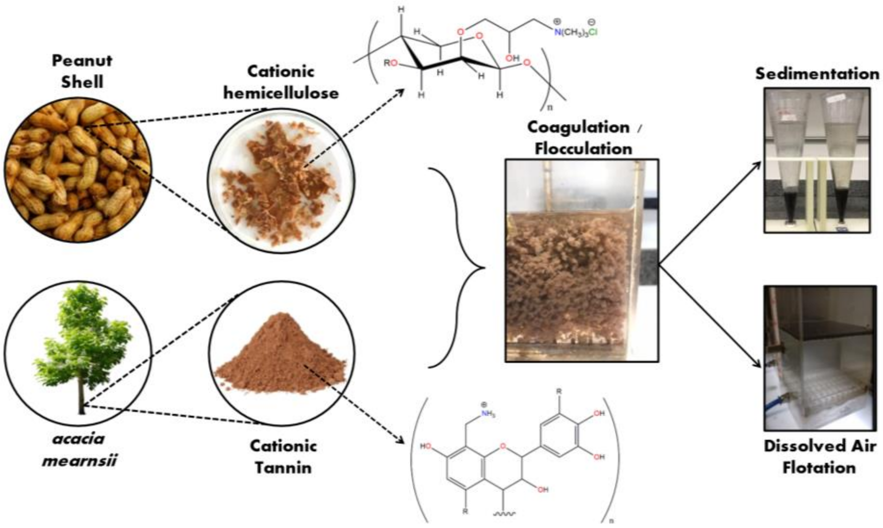

Figure 1. Schematic representation of coagulant synthesis from agro-industrial waste and effluent treatment.

2.8. Statistical analysis

The statistical treatment of the results obtained in this study was developed using the computer program Sivar and Rbio. To verify the existence of significant differences between different treatments, the analysis of variance (ANOVA) was applied. When identifying the occurrence of significant difference between treatments, the Tukey was applied, with a significance level of 5% and 95% confidence for analyses.

3. RESULTS AND DISCUSSION

3.1. Determination of the degree of replacement of cationic hemicelluloses

Peanut shells have xylan as their main sugar, which makes the hemicellulose from peanut shells contain, mostly, two hydroxyls per unit of xylose available to be etherified (Martin *et al.*, 2007). Thus, according to Ribeiro *et al.* (2017a), for the molar ratio calculation, the hemicellulose was considered to only be constituted of xylose (MM=132 g mol^{-1}).

Cationic hemicelluloses were synthesized from hemicellulose extracted from the agro-industrial residue of peanut shells. Elemental analysis data and the DS calculation are shown in Table 1 for the duplicates. From Equation 1, it was possible to estimate a DS of 0.410 ± 0.06, similar to that obtained by Ribeiro (2017) (0.410), which was extracted from the same agro-industrial waste. Furthermore, Ren *et al.* (2006), who studied the effect of the variation of NaOH/ETA molar ratio from 0.1 to 3 on this synthesis, obtained materials with DS for cationic hemicelluloses that ranged from 0.01 at 0.52. These values are similar to those obtained by Ribeiro *et al.* (2017a), Castro (2020) and Landin *et al.* (2013), materials were obtained by the same synthesis method, as shown in Table 2.

3.2. Grain processing effluent treatability tests

The coagulation/flocculation tests were carried out to evaluate the effect of the coagulant dosages on the turbidity removal efficiency from the raw effluent, in order to determine the most appropriate coagulation concentration and pH for the two studied coagulants (TSG and association of TSG/CH 3:1 v v^{-1}). Firstly, dosages were investigated in order to assess the range of values in which the coagulants had the greatest turbidity removal, and then which of these points provided the smallest amount of sedimentable solids (sludge volume). The analytical characterization of the raw effluent from grain processing presented the following results, shown in Table 3. These were adopted as the standards of comparison for the analysis of the treatment efficiency, which was based on the removal of turbidity and the amount of sludge volume.

Table 1. Percentages and DS obtained from the elemental analysis of CH.

Sample	%C	%H	%N	DS
Cationic Hemicelluloses (CH 1)	14.17	2.97	0.92	0.410 ± 0.06
Cationic Hemicelluloses (CH 2)	14.03	3.02	0.87	

Table 2. Comparison of the Degree of Substitution of Cationic Hemicellulose calculated in the present work and from other residue sources.

Reference	Source	Degree of substitution (DS)
Landim *et al.* (2013)	Corn straws	0.430
Ribeiro *et al.* (2017a)	Corn straws	0.520
Ren *et al.* (2006)	Peanut Shells	0.540
Ribeiro (2017)	Peanut Shells	0.410
Castro (2020)	Peanut Shells	0.295
Present work	Peanut Shells	0.410 ± 0.06

Table 3. Analytical characterization of the raw effluent collected from the grain processing food industry before carrying out the treatability test.

Parameter Analyzed	Value ± standard deviation	Equipment	Procedure
Visual Color	Opaque Dark Gray	-	-
Turbidity (NTU)	196 ± 10.11	Turbidimeter Ap 2000 Policontrol	APHA *et al.* (2017) nephelometric method (2130 B)
Sedimentable Solids (mL L^{-1})	2 ± 1.00	*Imhoff* Cone®	NBR 10561/1988 (ABNT, 1988)
pH	3.91 ± 0.58	pHmeter Hanna instruments	APHA *et al.* (2017) electrometric method (4500 H^+ B)
Temperature (ºC)	23.00 ± 1.50	pHmeter Hanna instruments	APHA *et al.* (2017) (2550 B)

The coagulation diagrams map the effectiveness of turbidity removal, considering the pH range from 4 to 12. The coagulation diagrams (Figure 2) were determined for both tested coagulants, TSG (a) and TSG/CH (b) using the Kriging method for interpolation of points. On the abscissa axis are the coagulation pH values measured after 30 seconds of rapid mixing (250 rpm), on the ordinate axis are the coagulant dosages in mg L^{-1}, and the curves indicate isoefficiency points for turbidity removal (%). A color scale of similar hue has been adopted to simplify viewing, with the lighter areas having the highest turbidity removal efficiency values.

Figure 2a shows the results of applying only TSG. In the pH 6 to 10 region, there is a predominance of high turbidity removals (90 to 100%) for the application of coagulant dosages of 200 mg L^{-1} up to 500 mg L^{-1} of TSG 10%. For these pHs, the turbidity removal index appears to have been more effective. Furthermore, it is observed that at pHs greater than 10, removals were not satisfactory (from 40% to 70%) with the increase of the effluent basicity, showing that high pHs may not be appropriate for the performance of TSG in the studied effluent.

For the application of the TSG/CH 3:1 (v v^{-1}) coagulant, the results presented in Figure 2b show that the most effective coagulation pH range occurred between 8 and 12 for the entire dosage range analysed, with turbidity removals between 90% and 100%. Thus, it is inferred that the association with CH expanded the range of action of TSG in basic environments. These data corroborate those observed by Ribeiro *et al.* (2017b), that the performance range of tannin associated with cationic hemicelluloses, when applied in dosages above 400 mg L^{-1}, led to an increase in turbidity removals in basic pHs. The performance of tannin as a primary coagulant in that region was limited, so being able to achieve turbidity removals above 95% suggests a synergistic effect between the coagulants. Furthermore, the coagulant TSG/CH 3:1 (v v^{-1}) proved to be more efficient when compared to TSG, resulting in turbidity removals greater than 80% for all investigated dosages.

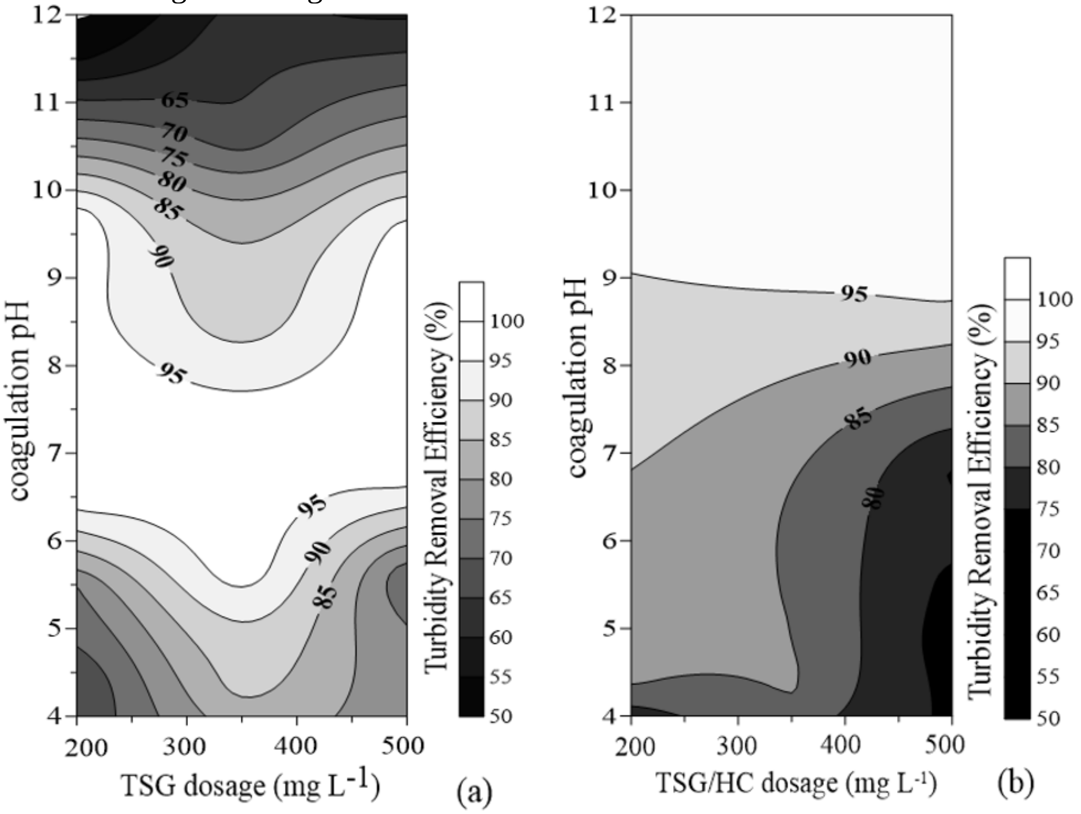

Figure 2. Coagulation diagrams for turbidity removal (%) from the industrial grain processing effluent using the coagulant: (a) TSG and (b) Tanfloc SG associated with Cationic Hemicellulose (TSG/CH 3:1 (v v^{-1})).

The efficiency of tannins as a primary coagulant has been studied in the physicochemical treatment of various types of industrial effluents, such as those from industrial laundry companies (Ribeiro *et al.*, 2017a), dairy products (Justina *et al.*, 2018) and breweries (Tonhato Junior *et al.*, 2019), as can be seen in Table 4. The treatability efficiencies achieved in this study, either by applying TSG or the TSG/CH association, are comparable to values found in the literature and demonstrate a progress towards promoting greater efficiency for the entire pH range investigated.

Table 4. Main studies selected in the bibliographic survey on the application of Cationic Tannin in Effluent and Water Treatment.

References	Nature of Coagulant	Type of Effluent	Effluent Turbidity (NTU)	Coagulant Dosage (mg L^{-1})	pH	Sedimentation Time (min)	Turbidity Removal Ef. (%)
Ribeiro *et al.* (2017a)	Tannin (TANFLOC SL)	Industrial laundry	>1100	3000	5	-	82
Justina *et al.* (2018)	Tannin extracted from Acacia *Mearnsii* (TANFLOC)	Dairy industry	763.84	600	-	60	92
Ribeiro *et al.* (2017a)	Tannin and cationic hemicellulose	Industrial laundry	>1100	3200	5	-	95
Pacheco *et al.* (2022)	Tannin (TANFLOC SG)	Synthetic dairy wastewater	553	400	7.38	30	98.67
Present work	Tannin (TANFLOC SG)	Grain processing	391	350	5.65	30	100
Present work	Tannin (TANFLOC SG) and cationic hemicellulose (3:1 v v^{-1})	Grain processing	391	200	10.72	30	100

Turbidity has been studied as one of the main previous parameters for comparing efficiency after physicochemical treatment. In the study by Ribeiro *et al.* (2017a) the physicochemical treatment enabled 82% of turbidity removal in an industrial laundry effluent, when 3000 mg L^{-1} at pH 5 was applied. Justina *et al.* (2018) reported removals of 92% from a dairy effluent, for a dosage of 600 mg L^{-1}. Tonhato Junior *et al.* (2019) reported turbidity removal of 99% for the application of 0.23 mL L^{-1} of vegetable tannin at pH 4.9. Pacheco *et al.* (2022) reported turbidity removal of 94.79 and 98.67%, for the dosage of 400 mL L^{-1} (coagulation pH 9 and 7.35) for Cationic Hemicellulose and TANFLOC SG, respectively.

The results showed that the association between tannin and cationic hemicelluloses (3:1 v v^{-1}) achieved turbidity removals greater than 80% for the investigated coagulation pH ranges, including the alkaline regions. To choose the best treatment efficiency point, the volume of sludge formed after the flocculation process was also analysed by sedimentation. The 3 points selected were the ones where removals greater than 98% were achieved with the use of both coagulants and at the same time with the smallest amount of sludge volume formation (mL L^{-1}) in an *Imhoff* Cone®. The results are shown in Figure 3; it can be seen that there are different points (coagulation pH x dosage) for each coagulant (TSG and TSG/CH). The points with the greatest removal were selected for analysis and to proceed with the studies for DAF.

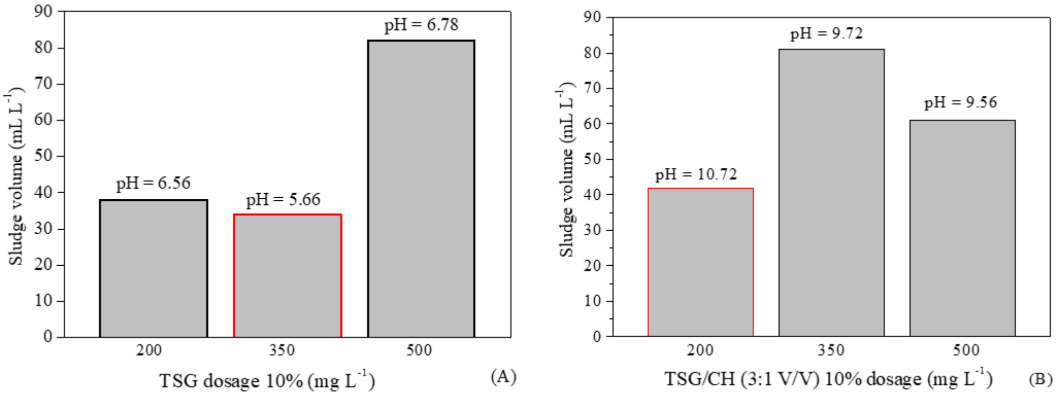

Figure 3. Sludge volume formation (mL L^{-1}) after solid-liquid separation by physical-chemical treatment of the industrial effluent with sedimentation, for TSG and TSG/CH coagulants, respectively.

As can be seen in Figure 3, from the 3 points with the highest TRE for TSG and TSG/CH, the one with the smallest volume of sludge formed was when 350 mg L^{-1} (pH 5.66) was applied. The amount of sludge formed was 34 mL L^{-1} showing the best performance. For TSG/CH 3:1 (v v^{-1}), it was noted that the lowest volume of sedimentable solids occurred after treatment with dosage 200 mg L^{-1} (pH 10.72), forming a sludge volume of 60 mL L^{-1}. With the association of CH with TSG, there was a significant reduction in the dosage used. Therefore, it is noted that when TSG/CH is applied at a higher pH above 10, there was a reduction in dosage compared to when only TSG is applied, which does not have an efficient action at basic pH.

In the work of Pacheco *et al*. 2022, the sludge was analyzed by energy dispersive X-ray spectroscopy indicating a pattern in elemental composition. When CH is applied to the treatment of a dairy effluent, the sludge presented the following elements: carbon (92.16 ± 1.13%), followed by oxygen (6.23 ±0.91), Na (0.53 ± 0.04) and P (0.39 ±0.02). The order of TSG elements is Carbon (75.36 ± 4.57), Oxygen (20.31 ± 4.27), P (1.06 ± 0.01) and Na (0.53 ± 0.04). The sludge composition provides organic coagulants such as cationic hemicelluloses and Tanfloc SG, a potential application in agriculture as a fertilizer.

3.3. Solid-Liquid Separation by Dissolved Air Flotation

From the results obtained with sedimentation, the separation by DAF was performed in triplicate for the points with the greatest turbidity removals (99.00, 98.10 and 98.27% of TRE). They were reached for TSG with: 200 mg L^{-1} (pH 6.56), 350 mg L^{-1} (pH 5.66), 500 mg L^{-1} (pH 6.78), for dosages and coagulation pH, respectively. For the TSG/CH association, the TREs (97.08, 98.20 and 97.90%) were achieved with 200 mg L^{-1} (pH 10.72), 350 mg L^{-1} (pH 9.72), 500 mg L^{-1} (pH 9.56), for dosages and pH respectively. The results are shown in Figure 4.

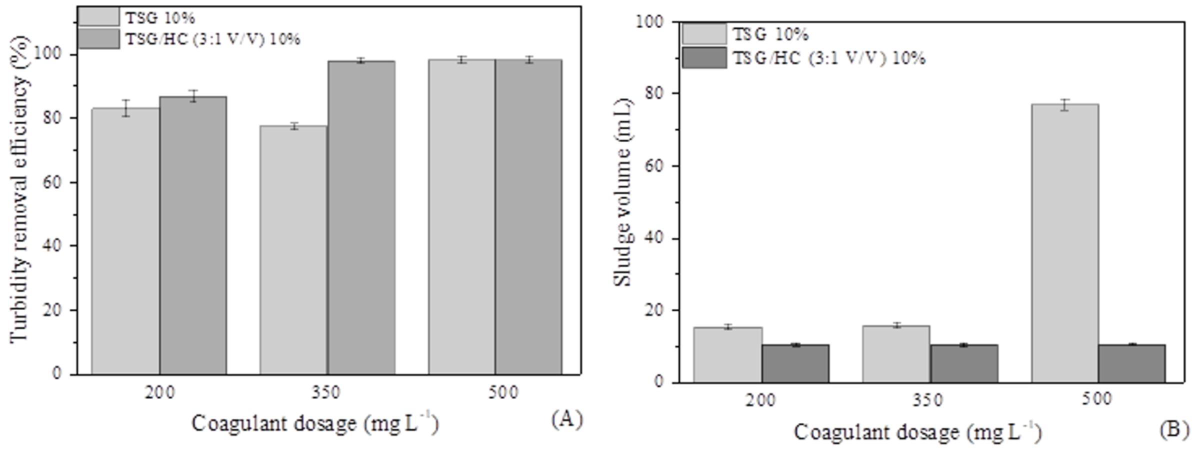

Figure 4. Turbidity removal efficiency (A) and Sludge volume formed (mL L^{-1}) (B) for dissolved air flotation (DAF) applied after coagulation by TSG 10% and TSG/CH (3:1 v v^{-1}) 10%.

In order to assess whether the results obtained in C/DAF from the use of TSG and TSG/CH presented significant differences, the Tukey statistical test was performed. First the Analysis of Variance (ANOVA) was performed. It is shown in Table 5 with a significance level of 95%.

Table 5. Test of Variance (ANOVA) with two factors and repetition applied to the turbidity removal efficiency and sludge volume data when applied: TSG and TSG/CH.

ANOVA						
Source of variation	*SQ*	*gl*	*MQ*	*F*	*P-value*	*Critical F*
Sample	4782.857	5	956.5713	236.0435	1.38508E-19	2.620654148
Columns	46206.55	1	46206.55	11401.93	1.19007E-33	4.259677273
Interactions	2388.104	5	477.6208	117.8577	4.42675E-16	2.620654148
Inside	97.2605	24	4.052521			
Total	53474.77	35				

With the ANOVA test it was possible to infer that there were significant differences between the analysed variables. From Tukey Test, was calculated the minimum significant difference (MSD) resulting in a value of 5.0790 at 95% significance level with a total studentized amplitude (q) of 4.37 (tabled variable obtained a from the studies carried out by Snedecor, 1934), the description of the statistic from the Tukey Test was attached as supplementary material.

Regarding the sludge volume, when only the Cationic Tannin (TSG) was applied at a dosage of 500 mg L^{-1}, it resulted in the formation of the largest sludge volume, while 350 mg L^{-1} of TSG resulted in the smallest volume (Figure 4 (b)), which represents an amplitude of 51 mL. However, the same did not occur when varying the dosages of the association between TSG/CH. There was no significant difference, or tendency, between the sludge volumes since the results obtained had very similar values, with a variation of ± 0.031 mL. When comparing the TSG and TSG/CH variations, only the dosage of TSG 350 mg L^{-1} did not differ significantly from the results obtained for the association of cationic hemicelluloses with cationic tannin.

Regarding the turbidity removal efficiency, the TSG dosage variations resulted in a significant difference between all points, and only the TSG 500 mg L^{-1} provided a turbidity removal greater than 95%. Furthermore, the use of TSG in comparison to the TSG/CH association, the dosage of TSG 500 mg L^{-1} did not result in a significant difference to: TSG/CH 350 mg L^{-1} and TSG/CH 500 mg L^{-1}. The dosage of TSG 200 mg L^{-1} did not differ significantly when compared only to TSG/CH 350 mg L^{-1}. Finally, when analysing the dosage variation of the association between TSG/CH, only the dosage of 200 mg L^{-1} differed from the others. Thus, the association of TSG/CH enabled a greater TRE at lower dosages when compared to cationic tannin acting alone.

The results suggest that CH in association with TSG, influenced the formation of flakes resulting in a better bubble-particle coupling. That is because when TSG alone was used with dosages of 200 and 350 mg L^{-1}, not only were turbidity removals below 85%, but there were sediment flakes at the bottom of the jar, evidencing a low bubble-particle interaction.

The efficiency of natural coagulants has been studied together with dissolved air flotation for various types of industrial effluents, such as those from dairy industry (Muniz *et al.*, 2020a), laundry effluents, bus washing (Araujo, 2017), effluents from the paper industry (Miranda *et al.*, 2013) and even for spring water (Balbinoti, 2018). Table 6 shows the main comparative studies using C/DAF.

Muniz *et al.* (2020b) used mature okra (Abelmoschus esculentus) as a natural *organic* coagulant in dissolved air coagulation/flotation (C/DAF) experiments treating synthetic dairy wastewater. The optimal conditions found for turbidity removal (91.1%) was an okra dosage of 2.0 g L^{-1} at pH 9.00, indicating that okra seed is a promising source for obtaining the coagulating agent.

Araujo (2017) used the commercial natural *organic* coagulant AQUAFLOC/LS in laundry and bus washing effluent using C/DAF. The optimal conditions found were a dosage of 260 mg L^{-1} at pH 7, resulting in a turbidity removal of 94%. At the same time, Balbinoti (2018) using Moringa Oleifera in spring water obtained an optimal dosage of 40 mg L^{-1} at pH 7.5 providing 85% of turbidity removal. Both studies showed that the use of natural coagulants associated with dissolved air flotation is promising for different types of effluents, including water from springs.

Miranda *et al.* (2013) investigated Chitosan associated with DAF for the treatment of effluent from paper production, resulting in a removal of 89% with an optimal dosage of 100 mg L^{-1} at pH 7.5. The emergence of new natural coagulants is also observed in the literature. Muniz *et al.* (2020b) proposed the use of “mutamba” (Guazuma ulmifolia) as a coagulant agent. The results obtained by the authors demonstrated the material's potential for treatment via C/DAF when applied to dairy effluent at an ideal dosage of 775.8 mg L^{-1} at pH 5.

The results obtained by the aforementioned authors corroborate this study, indicating that CH associated with TSG favours DAF both in relation to the dosage of coagulant to obtain better treatability and in relation to the volume of sludge. Furthermore, as they are natural coagulants, the sludge formed from this effluent is biodegradable and can undergo simple decomposition processes. Thus, the association between CH and TSG is promising for the treatment by C/DAF for grain processing effluent.

Table 6. Main studies selected in a literature review on the application of DAF after the use of natural coagulants.

References	Coagulant	Effluent	Effluent Turbidity (NTU)	Dosage (mg L^{-1})	Ph	Turbidity Removal (%)
Miranda *et al*. (2013)	Chitosan	Effluent from paper production	89	100	7.5	89
Araujo (2017)	AQUAFLOC/LS	Effluent from laundry and bus washing	194	260	7	94
Balbinoti (2018)	Moringa oil	Spring water	30	40	7.5	85
Muniz *et al.* (2020a)	Okra *Abelmoschus esculentus*	Dairy Effluent	698	2000	9	91.1
Muniz *et al.* (2020b)	Guazuma ulmifolia	Dairy Effluent	698	775.8	5	95.8
Present work	Tannin (TANFLOC SG)	Grain processing	391	500	5.65	98
Present work	Tannin (TANFLOC SG) and cationic hemicellulose (3:1 v v^{-1})	Grain processing	391	500	10.72	98

4. CONCLUSIONS

The use of TSG coagulant showed greater turbidity removal (98.10%) when applied to industrial effluent from grain processing in the pH range of 5 to 10. The sludge formation, when applied at a dosage of 350 mg L^{-1} and coagulation pH of 5.65, was of 34 mL L^{-1}. For the association of TSG/CH, the largest range of action occurred for more basic pHs (pH 9 and 10) promoting 97.90% of TRE. With a dosage of 500 mg L^{-1} and pH 10, there was a sludge formation of 60 mL L^{-1}.

In the separation by DAF, only the dosage of 500 mg L^{-1} and coagulation pH of 6.78 promoted turbidity removal greater than 95.00% for TSG. The use of TSG associated with CH, however, resulted in a turbidity removal greater than 95.00% for both 9.72 (350 mg L^{-1}) and 7.92 (500 mg L^{-1}) coagulation pH and dosage, respectively, suggesting a greater bubble-particle interaction. The separation by DAF applied to the effluent from the grain processing industry showed a good performance when evaluated as a function of the turbidity removed and volume of sludge formed. The results of the study indicate that CH as a coagulation aid favours C/DAF, resulting in a smaller volume of sludge, in addition to having an optimal pH range in the basic region.

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