Journal of
Water, Sanitation & Hygiene for Development

IWA PUBLISHING

 Journal of Water, Sanitation and Hygiene for Development Vol 12 No 11, 803 doi: 10.2166/washdev.2022.120

Practical Paper

Application of tannin-based coagulant for high-range turbidity surface water clarification

Camila de Oliveira, Viviane Trevisan and Everton Skoronski*

Departamento de Engenharia Ambiental e Sanitária, Laboratório de Tratamento de Água e Resíduos, Universidade do Estado de Santa Catarina, Av. Luís de Camões, 2090, Lages, Santa Catarina CEP 88520-000, Brasil
*Corresponding author. E-mail: everton.skoronski@udesc.br

VT, 0000-0003-4826-0269; ES, 0000-0002-8554-8272

ABSTRACT

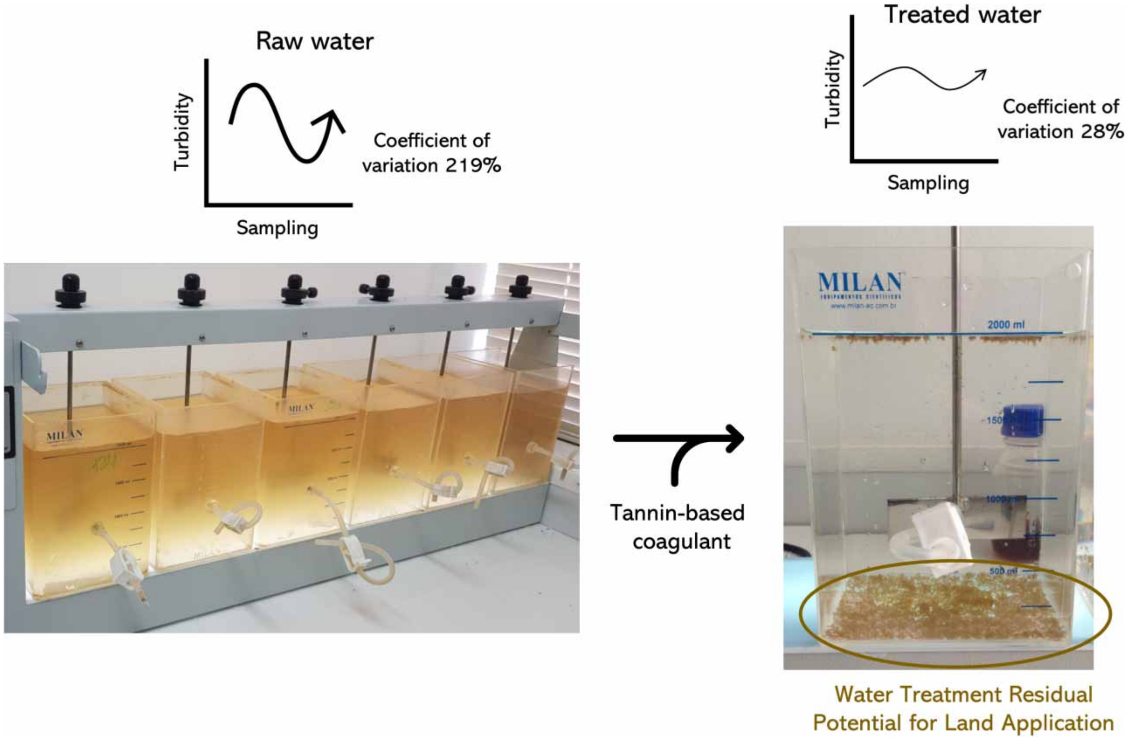
This study aimed to evaluate the performance of a tannin-based coagulant in clarifying drinking water from a high-range turbidity river and characterizing the sludge. Tanfloc MTH product was selected for this investigation. The study site was surface water located in southern Brazil (Caveiras River, Brazil). Samples were collected just before the Parshall flume in the municipal water treatment plant in Lages (Brazil) for nine months, at least once a week. Jar testing evaluated turbidity removal, alkalinity consumption, optimal coagulant dosage, and settling velocity. After flocculation and settling, the sludge generated from the jar test was submitted to metal and thermogravimetric analyses. The use of tannin reduced the average water turbidity from 26.1 ± 56.1 to 0.94 ± 0.26 NTU, apparent color from 145 ± 190 to 3 ± 3 Pt-Co, and there was no variation in the pH. Additionally, the settling velocity of the flocs reached a maximum turbidity removal at 3.5 cm·min^{-1}. Furthermore, the metal concentrations in the sludge showed a majority of aluminum and iron, and thermogravimetric analysis revealed 64% weight loss. In conclusion, Tanfloc presented the potential to be used in surface water clarification from the Caveiras river, and the extensive turbidity range observed during this study did not affect the operational stability.

Key words: coagulation and flocculation, sludge, tannin-based coagulant, water clarification

HIGHLIGHTS

- Tannin-based coagulant was applied to clarify a high-range turbidity superficial freshwater.
- Treated water showed a lower coefficient of variation for turbidity than raw water.
- Flocs have a settling velocity comparable to the design criteria value for settling tanks.
- Potential land application of sludge in terms of metal concentration.
- Thermogravimetric analysis revealed a weight loss of 64% up to 800 °C.

GRAPHICAL ABSTRACT



INTRODUCTION

The central technology used in water treatment plants (WTP) comprises coagulation and flocculation, sedimentation, gravity filtration, and disinfection. In this context, the most frequent coagulants applied in WTPs are aluminum sulfate, ferric chloride, and polyaluminum chloride (PAC). Aluminum sulfate and PAC are widely employed in coagulation due to their low prices, simplicity, and significant efficiencies. However, since these chemicals are aluminum-based coagulants, they are frequently associated with the potential risk of developing Alzheimer's or other diseases (Bondy 2016).

Many natural organic substances are being studied and validated as potential sources of coagulants/flocculants for water treatment. Among these, chitosan (Lertsutthiwong *et al.* 2009), moringa (extracted from the *Moringa oleifera* seeds) (Camacho *et al.* 2017), and tannins (Beltrán Heredia & Sánchez Martín 2009; Sánchez-Martín *et al.* 2010a; Bacher *et al.* 2017; Bello *et al.* 2020) may be mentioned, among others. Tannins are macromolecular polyphenols extracted from different vegetable sources such as *Schinopsis balansae* Engler, *Castanea sativa* Miller, and Wildeman's *Acacia mearnsii*. Since tannin is obtained from various sources, its chemical structure varies for all vegetable species from which they are extracted, making it challenging to determine their chemical structures (Crestini *et al.* 2016; Messini *et al.* 2017).

Tannin is not a coagulant in its natural form. Hence, it must undergo cationization via the Mannich reaction (Bello & Leiviskä 2022). According to Ibrahim *et al.* (2021), this reaction may involve adding formaldehyde, ammonium chloride (NH_4Cl), and hydrochloric acid. Thus, the produced compound has additional characteristics relative to the original tannin, especially for application as a coagulant. This chemical compound's other essential technical elements consist of its stability in a wide pH range, lower alkalinity consumption, non-release of metals into the treated water, and capacity to form complexes with metals present in the water (Saleem & Bachmann 2019; Okoro *et al.* 2021; Tomasi *et al.* 2022).

Tannin-based coagulants have been tested in the drinking water clarification of surface water in rivers in Spain, Brazil, and Finland, and their potential was assessed by many authors (Sánchez-Martín *et al.* 2010a, 2010b; Bacher *et al.* 2017; Bello & Leiviskä 2022). Although several studies related to tannin-based coagulants for water treatment have been published, there are still some points to be addressed, considering the variation in water quality over time and the evaluation of the generated byproduct. The present study was conducted in a river used as a water source for a drinking water supply system in southern Brazil under different climatic conditions, resulting in water samples with large-range characteristics.

Given this context, this study aimed to evaluate the performance of a commercial tannin-based coagulant in treating water from the Caveiras river in the city of Lages/SC, Brazil, and characterizing its sludge.

MATERIALS AND METHODS

Study site

The city of Lages (Brazil) is in the Santa Catarina mountainous region and has approximately 160,000 inhabitants. The Caveiras river is the primary source of water in the city. Rafaeli Neto *et al.* (2019) studied the hydrology of the Caveiras river and obtained information about its 2,416 km^2 watershed and 232 km of length from its source to the mouth. The authors claim this river has a sinuosity of 2.5 $Km{\cdot}Km^{-1}$ in the sector where the raw water is captured. Additionally, they characterized the land adjacent to the river as a floodplain. Rafaeli Neto *et al.* (2013) built a map of the use and occupation of the Caveiras river basin, which is used as a water supply source for the city of Lages. According to the authors, the river spring area is where there is the highest forest index, decaying as the river advances. The fields represent 40–50% of the basin, with 4–5% reforesting. There is surface runoff of pollutants and the water itself when it rains, which increases the river flow and leaches sediments, increasing the turbidity and, consequently, the apparent color of the water. The region's climate is temperate (Köppen, Cfb), with evenly distributed rainfall and average annual rainfall ranging from 1,100 to 2,000 mm, with no dry season. Different conditions of raw water were found as the work was carried out over nine months because there was a significant change in the parameters when it rained due to solids being carried into the river. Therefore, the water quality varies, as demonstrated in the raw water characterization section (Table 1).

The drinking water supplied to Lages is treated in a WTP which operates at a flow rate of 600 $L{\cdot}s^{-1}$. This plant is a single conventional water treatment plant located 5,000 m from the raw water intake of the Caveiras river (coordinates 27°49′59.6″S and 50°16′07.9″W). Figure 1 shows the processes involved in the WTP. Polyaluminum chloride (PAC) is currently applied as the coagulant, and a polyacrylamide-based polymer is the flocculant. Calcium hydroxide is used for pH correction. Chlorination and fluoride addition are the final steps before the treated water is stored and distributed to the population. The produced sludge is disposed of in the Caveiras river. In this study, a tannin-based coagulant was tested as an alternative coagulant.

Raw water characterization

To characterize the raw water, the turbidity, apparent color, pH, and alkalinity parameters were evaluated. Table 1 presents the average values for all samples taken and each parameter's maximum and minimum values.

The raw water turbidity used in the dosage optimization tests presented an average value of 26.1 $\pm$ 57.1 NTU, varying from 4.71 to 350 NTU. The associated coefficient of variation was 219%, which means that the turbidity of water considered in this study accounts for high variance. Furthermore, the apparent color was also observed, which varied from 45 to 1,051 Pt-Co (average of 145 $\pm$ 190 Pt-Co), also presenting a high coefficient of variation of 131%. This variation is related to the data obtained from the analyses performed in which various climatic conditions were observed, such as abundant rainy and dry periods. Furthermore, the pH varied between 5.89 and 7.78, while the average alkalinity was 17 $\pm$ 3 $mgCaCO_3{\cdot}L^{-1}$, and the coefficient of variation for these parameters was lower and accounted for 5 and 17%, respectively.

Tannin-based coagulant

We selected a commercial product called Tanfloc MTH (Tanac, Brazil), among others available. According to the supplier, this is a tannin-based coagulant with a higher molecular weight, producing larger and heavier floc. In terms of tests, we initially ran preliminary jar tests comparing different tannin-based coagulants and considered the highest turbidity removal

Table 1 | Raw water characterization of Caveiras River (Lages/SC – Brazil)

Parameter	*n*	Average	CV	Minimum	Maximum
Turbidity (NTU)	47	26.1 $\pm$ 57.1	219%	4.71	350
Apparent color (Pt-Co)	47	145 $\pm$ 190	131%	45	1,051
pH	47	7.08 $\pm$ 0.39	5%	5.89	7.78
Alkalinity ($mg{\cdot}L^{-1}$ $CaCO_3$)	11	17 $\pm$ 3	17%	10	20

n, number of samples; CV, coefficient of variation.

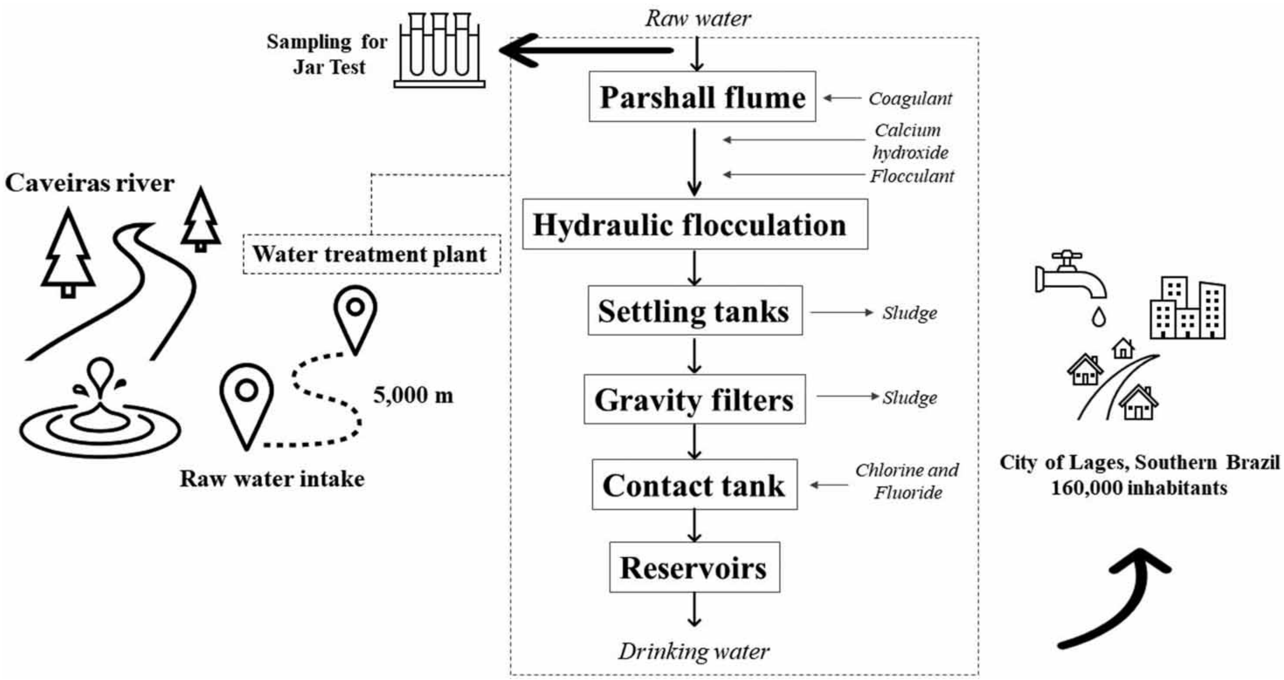


Figure 1 | Schematic diagram of the water treatment plant and the raw water intake location.

to select this ideal coagulant for further use. Then, Tanfloc MTH 2% (m·v^{-1}) stock solution was prepared and stored in a glass container for use in the jar tests.

Analytical methods

The raw water was sampled before the Parshall flume in the water treatment plant (Figure 1), as it is hydraulically transported from the Caveiras river to the WTP. It is worth mentioning that no coagulant, flocculant, or other chemicals were added at this point. The turbidity, pH, and alkalinity parameters were initially monitored. The sampling and analyses were carried out for nine months, and the analyzed parameters followed standardized methodologies according to the Standard Methods for the Examination of Water and Wastewater (APHA *et al.* 2005). The turbidity measurements (NTU) were conducted in a turbidimeter (Hach, model 2100Q), following method 2130 B. Apparent color was measured using a spectrophotometer (model DR 3900, Hach) (method 2120 C). In addition, pH was measured in a pH meter (Hach, model Sension pH3) (method 4500 H^+ B). Finally, the alkalinity was determined via titration with H_2SO_4 0.02 N using a 0.1% methyl orange indicator (method 2320 B).

Performance evaluation of the tannin-based coagulant

The coagulation and flocculation in jar tests were conducted to evaluate the performance of the tannin-based coagulant. The jar test was used to study the effect of chemical additives on the stability of particles and to establish coagulant dosages for water treatment (Howe *et al.* 2012). We took 47 samples of raw water for the treatability experiments in the jar test. These tests were accomplished in an appropriate device containing six jars with 2-liter capacities (MILAN, model JT-203). The volume of water in the jar tests was 2 liters. Different Tanfloc MTH dosages (8–38 mg·L^{-1}) were added using a transferpette to define the optimal dosage responsible for the higher reduction in turbidity and apparent color. The coagulation step (rapid mixing) was performed at a rotational speed of 120 rpm for 1 minute. The flocculation (slow mixing step) was conducted at 51 rpm for 20 minutes. The sedimentation period was fixed at 20 minutes. Jar testing was carried out according to these parameters, given that they are already used during the routine operation of the studied WTP. The treatment performance was evaluated by pH, turbidity, apparent color, and total alkalinity measured in the raw and treated water.

Additionally, the pH of the raw water was varied with values between 4 and 9, using a 0.1 N NaOH or 0.1 N HCl solution to assess the effect of pH in the coagulation and flocculation tests. The raw water turbidity and apparent color for these tests were 8.22 NTU and 79 Pt-Co, respectively. First, a jar test was performed to determine the best dosage, which was 19 mg·L^{-1}, and this condition was used in the following tests. Each experiment was carried out in triplicate. After the sedimentation time, aliquots were taken to analyze the turbidity, apparent color, and pH. Removal was defined by Equation (1):

$$\text{Removal (\%)} = \frac{X_0 - X}{X_0}.100 \tag{1}$$

in which:

$X_0 =$ is the turbidity (NTU) or apparent color (Pt-Co) or metal in the raw water;
$X =$ is the turbidity (NTU) or apparent color (Pt-Co) or metal in the water after jar test.

Sedimentation tests

The sedimentation tests were carried out after the coagulation and flocculation process performed at the condition which provided the highest turbidity removal. Therefore, only the turbidity in water was measured, and the settling time was varied to obtain the sedimentation curve. The apparatus used for this experiment was another jar test (Ethik, model 218–3LDB), provided by a sampler to accomplish this experiment. The volume of each sample removed was 3 mL, and the water volume used in jar testing was 2 L. Turbidity was measured using a photometer (Model Spectroquant NOVA 60, Merck). The samples were collected from the position 7 cm below the water surface, available in our jar test. The sampling time intervals were defined at 1, 2, 3.5, 7, and 14 minutes, resulting in settling velocities of 7, 3.5, 2, 1, and 0.5 cm·min^{-1}, respectively. Therefore, the residual turbidity was applied to estimate the amount of suspended solids (Tse *et al.* 2011), which presents a settling velocity below the value computed by Equation (2).

$$\text{settling velocity}\left(\frac{\text{cm}}{\text{min}}\right) = \frac{7\ \text{cm}}{\text{time interval (min)}} \tag{2}$$

The settling velocity was correlated to the residual turbidity (Figure 3). Jar tests were carried out in triplicate, and results are expressed as average and standard deviation.

Analysis of metals in the sludge

Jar tests were repeated with the optimized conditions to produce sludge samples. The concentration of metals was analyzed using the inductively coupled plasma optical emission spectrometry technique (ICP-OES). The digestion of dried samples was performed using nitric acid and sodium peroxide in a Multiwave 3,000 microwave equipment for 20 minutes. Then, the solution was added to a 50-ml plastic Falcon tube, and the volume was adjusted with distilled water up to 30 ml. The analysis was executed in triplicate, and the results are expressed as average and standard deviation

We also performed 13 jar tests to study iron, manganese, and aluminum removal from the raw water. Jar tests were carried out once, and the results are expressed as average and standard deviation. The conditions for the jar test are the same as detailed before. Removal was computed by Equation (1).

Thermogravimetric analysis

The thermogravimetric analysis (TGA) was carried out with a thermo-microbalance (model STA-449C Jupiter, Netzsch-Gerätebau GmbH). This characterization is essential for further studies on the disposal or valorization of this material. The sample was heated from room temperature to 800 °C at a constant 10 °C·min^{-1} rate, under an airflow equal to 40 mL·min^{-1}. The TGA data were transformed into derivative thermogravimetry (DTG) by calculating the first mass loss derivative as a temperature function.

Statistical analysis

The graphs were plotted using the Sigmaplot 14.0 software program (Systat). In addition, raw water characterization and jar tests were carried out once for long-term evaluation (Table 1 and Figure 2), and turbidity, apparent color, and optimal dosage data were submitted for statistical analysis regarding the coefficient of variation.

RESULTS AND DISCUSSION

Evaluation of the optimal coagulant dosage

Jar tests were carried out to simulate the treatment of 47 samples collected for nine months.

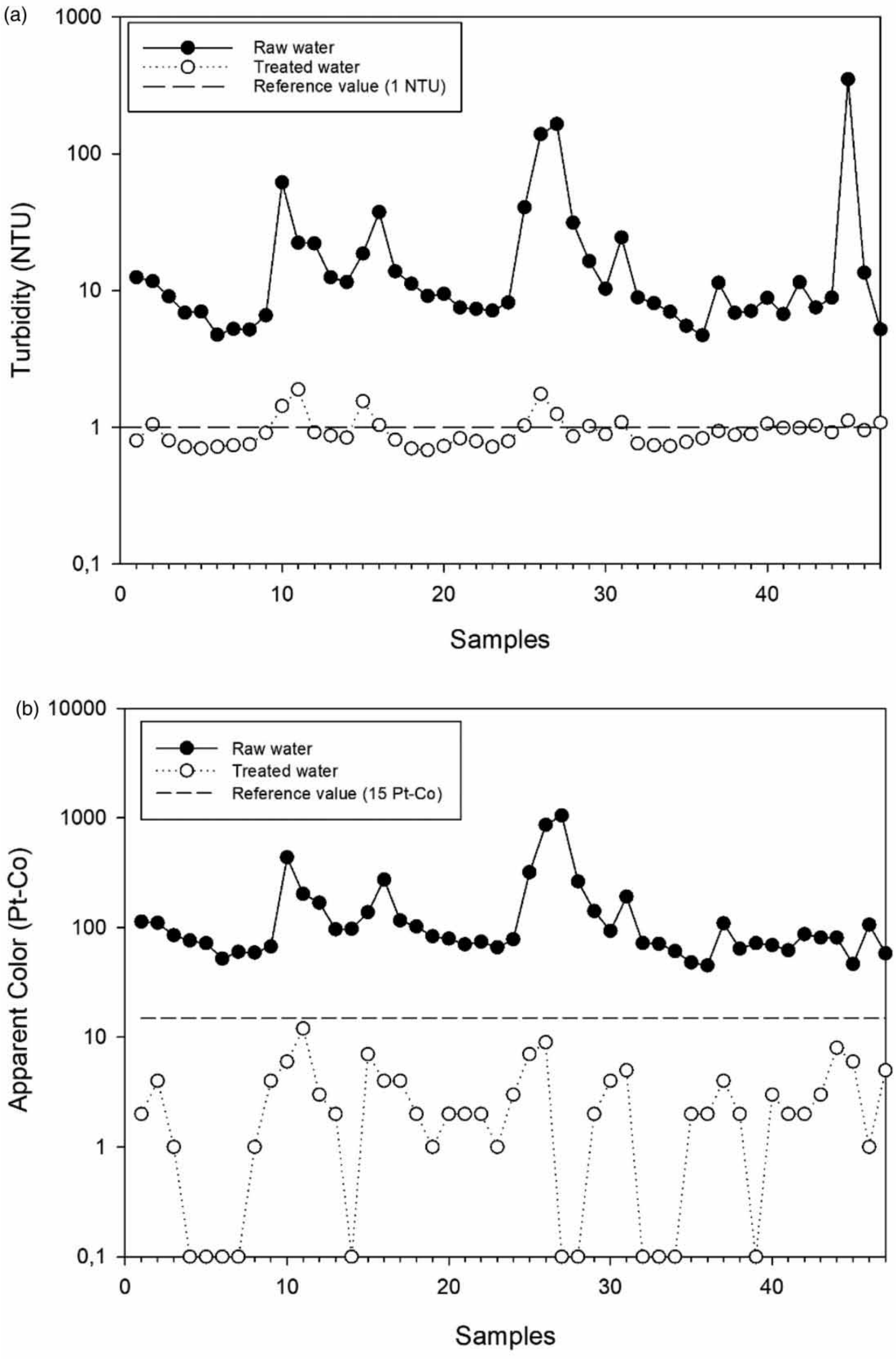


Figure 2 | (a) Turbidity and (b) apparent color of raw and treated water using Tanfloc MTH.

The treatability tests using Tanfloc MTH produced water turbidity of 0.94 ± 0.26 NTU (Figure 2(a)). In this case, the turbidity varied from 0.68 to 1.89 NTU, resulting in a coefficient of variation of 28%. Although the studied raw water showed high variance in the turbidity (Table 1), the water turbidity of treated water showed more homogeneous data, as the coefficient of variation was as little as 7-fold lower. Additionally, the tannin-based coagulant dosages remained between 12 and 36 $mg{\cdot}L^{-1}$. The average optimal dosage for all tests was 18 ± 5 mg·L^{-1} and the coefficient of variation was 28%. Hence, we also observed a narrower range for coagulant dosage from a high variance in the raw water turbidity. According to Sánchez-Martín *et al.* (2010b), a low tannin concentration may remove most suspended solids in surface waters. Therefore, this suggests operational stability for drinking-water quality control in terms of coagulant dosage and following international guidelines for drinking water (WHO 2017). This relevant guideline recommends maximum turbidity of 1.0 NTU after filtration to accomplish efficient disinfection. In this case, using a tannin-based coagulant produced water with average turbidity of 0.94 NTU, reducing the demanding credit of turbidity removal by the filtration process. Thus, an increase in the filter run may be observed when put into operation at a WTP, given that the most significant portion of particles will already be removed in the sedimentation process.

The apparent color was also efficiently reduced using Tanfloc MTH as a coagulant. As a result, we observed a decrease from 145 ± 190 Pt-Co to 3 ± 3 Pt-Co (Figure 2(b)), and the average apparent color removal was 97.34%. Most importantly, even though the raw water had apparent color as high as 1051 Pt-Co, the treated water presented values ranging from 0 to 12 Pt-Co. This value follows the Brazilian drinking water guidelines, establishing a maximum reference value of 15 Pt-Co (BRASIL 2021). Similarly, international guidelines define a value of 15 TCU (true color unit) (WHO 2017), less restrictive than Brazilian guidelines as TCU only measures dissolved substances. Also, the coefficient of variation for apparent color was reduced from 131 to 97% in the raw and treated water, respectively. Nevertheless, considering this parameter, we noticed a higher variation in the data than turbidity. Additionally, other studies focused on using tannin-based coagulants for water treatment have not measured apparent color or true color to measure the treatability performance.

Additionally, since tannin is naturally colored (brown), we observed that Tanfloc MTH did not increase the apparent color of water, and it conversely reduced more than 97% of this parameter. Similarly, Bongiovani *et al.* (2016) applied tannin to treat surface water and demonstrated that this coagulant removed turbidity, enhanced natural organic matter removal, and minimized trihalomethane formation.

In terms of pH, the average value of the treated water was 6.99 ± 0.52, and the coefficient of variation was 7%, which means that pH remained stable after the treatment. Also, there was an average reduction of fewer than 0.10 units compared to the pH of raw water (7.08 ± 0.39). The lowest value found using Tanfloc MTH was 4.76. Similarly, the pH of the raw water in this test was 5.89, and the correction in this value would be requested regardless of the treatment. It is worth mentioning that this result is out of the range recommended by Brazilian drinking water guidelines, from 6.0 to 9.5 (BRASIL 2021).

Conversely, the pH of the other samples was between 6.37 and 7.65; therefore, there is no need for additional alkalinity demand in the water for the treatment using a tannin-based coagulant. Indeed, regarding the raw water alkalinity, the average alkalinity after coagulation and flocculation using Tanfloc MTH was 14 ± 3 mgCaCO$_3$·L^{-1} (coefficient of variation of 21%). In this case, the alkalinity consumption was as low as 3 mgCaCO$_3$·L^{-1} on average, which justifies the pH values for the treated water. According to some authors, the pH variation trend is lower using tannin-based coagulants due to the lower consumption of alkalinity when compared to inorganic coagulants. dela Justina *et al.* (2018) demonstrated that treating dairy wastewater shows that Tanfloc has a lower effect on pH and alkalinity consumption than PAC. Likewise, Hameed *et al.* (2016) stated that there are no significant pH changes caused by tannin in sewage treatment, even at higher coagulant dosages. Therefore, Tanfloc MTH becomes a good option for low-alkalinity raw waters, generating savings with the acquisition, storage, and preparation of the alkalinizes used in WTPs.

According to the supplier, the selling price of tannin-based coagulants is about R$ 8.00 (US$ 1.55) per kilogram. In our study, the optimal coagulant dosage was 18 ± 5 mg·L^{-1}, which accounted for an average clarification cost of R\$.m^{-3} 0.144 ± 0.04 (US\$.m^{-3} 0.027 ± 0.007). However, it is worth mentioning that only the potential of tannin-based coagulant in surface water clarification was demonstrated in our study. Therefore, this information could be used for deeper economic analysis, including reducing or eliminating the use of alkalinity increasers in water treatment plants. Also, the potential alternatives of sludge management besides its disposal in landfills must be studied for cost elaboration. Furthermore, detailed tests on pathogen credit removal due to the clarification are another point to be addressed and considered in the water treatment cost.

Effect of pH on turbidity and apparent color removal

We also studied the effect of pH on turbidity and apparent color removal using Tanfloc MTH. Overall, turbidity removal at pH 4 and 5 did not occur. Also, there was a turbidity removal of 23 and 19% at pH values 6 and 9, respectively. The highest turbidity removal was achieved at pH 7 (94%) (Figure 3(a)). Similarly, the residual color was under the detection limit at pH 7; therefore, the removal was near 100% at this condition. Moreover, color removal was lower than 50% at pH lower than 6 and higher than 9 (Figure 3(b)). According to the tannin-based coagulant supplier, the ideal coagulation pH is 4.5–9.0. According

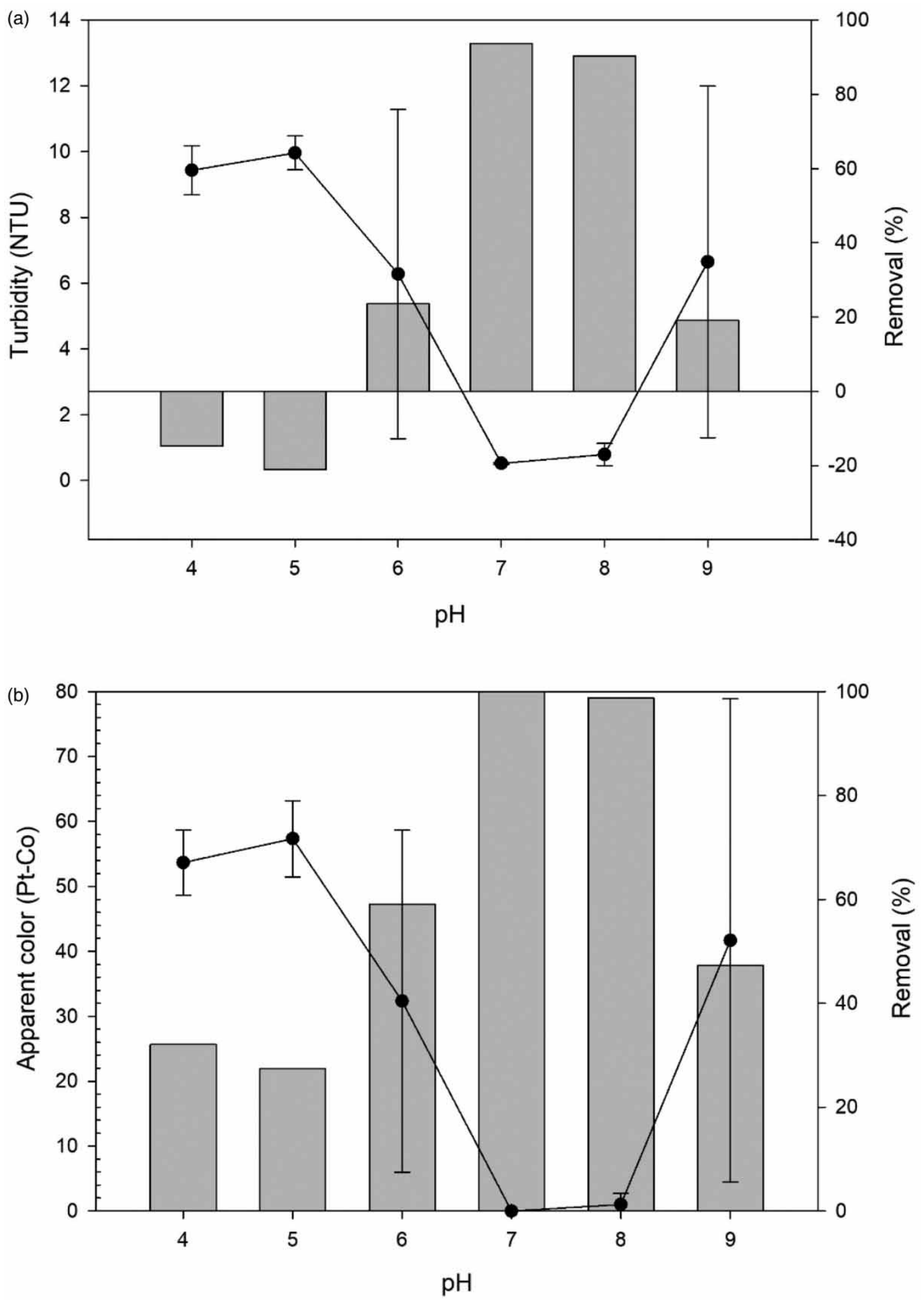


Figure 3 | Effect of pH on (a) turbidity removal and (b) apparent color removal. The raw water had a turbidity of 8,22 NTU and an apparent color of 79 Pt-Co. The circles connected by solid lines are the individual turbidity measurements, and the bars are the removal in percentage.

to Sánchez-Martín *et al.* (2009), who used Tanfloc as a coagulant, the optimal pH value for tannin coagulation is around 5.0 and 8.0. Our study observed that the optimal pH value for coagulation (considering turbidity) was between 7 and 8. It is worth noting that this behavior occurred in the water studied in the current project, and variations may occur in other waters. So, the pH affects the surface charge of colloids and suspended solids (Howe *et al.* 2012), and consequently, the chemical composition of water plays a vital role in the coagulation and flocculation performance.

Sedimentation study

The relation between the residual turbidity after the jar test (T/T_0) and the settling velocity was obtained (Figure 4). The turbidity value of the raw water selected for this experiment was 7 NTU.

It may be noticed that the clearance was achieved at the condition considering settling velocities below 3.5 cm·min^{-1}, resulting in maximum remaining turbidity of 0.17 (turbidity in treated water of 1 NTU). Furthermore, the remaining turbidity considering a settling velocity as high as 7 cm·min^{-1} was 0.24, which means that 76% of flocs can be removed under this circumstance. Likewise, the typical overflow rate design criteria value for horizontal-flow rectangular settling tanks is 1.25–2.50 m·h^{-1}, equivalent to 2.08–4.17 cm·min^{-1} (Howe *et al.* 2012). In this case, the overflow rate numerically equals the critical settling velocity. Our results indicate that the flocs formed by tannin-based coagulants are large and settle quickly. This occurs because the flocs produced by tannin are more oversized and irregular, with large surface areas, rendering the flocculation step more efficient (Hameed *et al.* 2016).

Characterization of the sludge

The data presented in Table 2 are the results of the analyses carried out on the sludge generated. The results are expressed as mg per kg on a dry basis. Table 3 also reports land application reference values according to American (Title 40 of the Code of Federal Regulations, Part 503) and Brazilian (Resolution of CONAMA no.498 of 2020) guidelines. It is worth mentioning that these guidelines consider sewage sludge. Therefore, in the absence of reference for sludge produced in water treatment, we considered these ceiling values to contribute to a discussion about the viability of sludge from WTP using a tannin-based coagulant for land application.

The macronutrients such as phosphorous, calcium, and magnesium presented average values of 17.03 mg·kg^{-1}, 38.00 mg·kg^{-1}, and 49.67 mg·kg^{-1} respectively, which may be attractive for agriculture purposes. Also, potentially toxic metals did not exceed the ceiling values presented in the third and fourth columns of Table 2. This means that barium and zinc

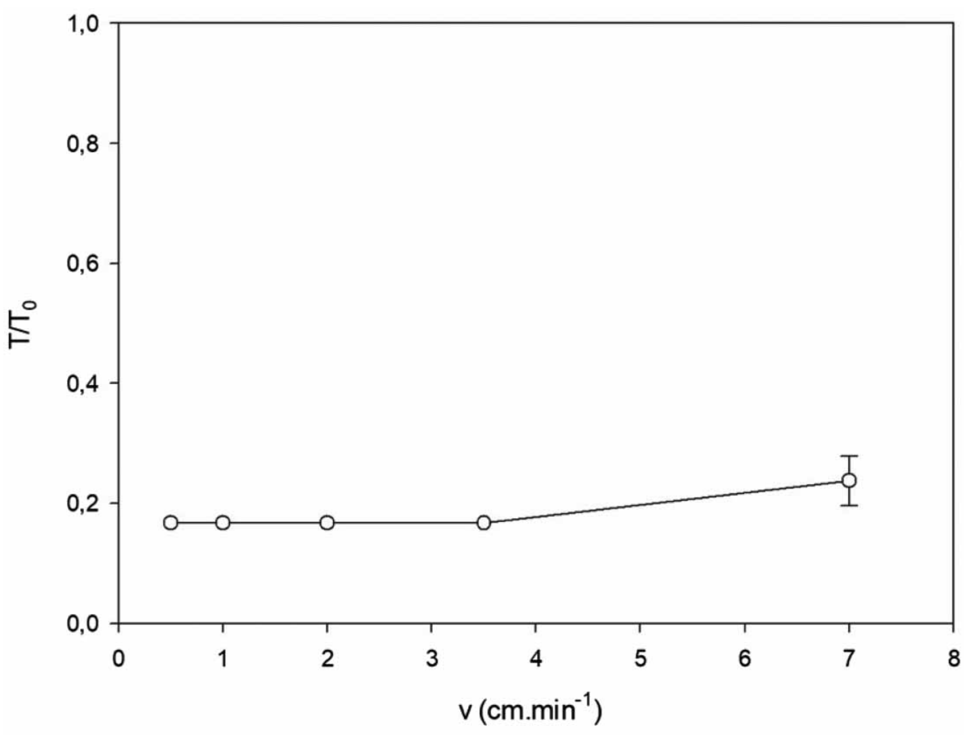


Figure 4 | Sedimentation curve expressed as residual turbidity (dimensionless) and settling velocity (cm·min^{-1}). Initial turbidity of 7 NTU. T is the turbidity at a velocity v, and T_0 is the initial turbidity.

Table 2 | Average concentration of metals in mg·kg^{-1} for the sludge

		Reference values for land application (mg·Kg^{-1})	
Metal	**Concentration (mg·kg^{-1})**	**USEPA 40 CFR Part 503 (US-EPA (1993))**	**CONAMA 498/2020 (Brasil 2020)**
Aluminum	1,371.62 ± 359.13	–	–
Beryllium	<0.17	–	–
Boron	18.45 ± 4.54	–	–
Calcium	38.00 ± 92.77	–	–
Cobalt	<1.37	–	–
Iron	1,142.23 ± 86.04	–	–
Lithium	<0.07	–	–
Magnesium	49.67 ± 7.29	–	–
Manganese	17.36 ± 5.17	–	–
Phosphorus	17.03 ± 49.74	–	–
Potassium	<86.86	–	–
Silicon	685.69 ± 47.56	–	–
Sodium	<65.94	–	–
Strontium	1.64 ± 0.77	–	–
Titanium	69.50 ± 4.16	–	–
Vanadium	3.43 ± 0.32	–	–
Barium	4.57 ± 1.35	–	1,300[a,b]
Cadmium	<2.4	39	39[a] and 85[b]
Chromium	<4.49	–	1,000[a] and 3,000[b]
Copper	<3.22	1,500	1,500[a] and 4,300[b]
Lead	<34.61	300	–
Molybdenum	<19.66	–	50[a] and 75[b]
Nickel	<7.05	420	420[a] and 420[b]
Zinc	6.69 ± 1.84	2,800	2,800[a] and 7,500[b]

The limit of detection was defined as 3 times of blank standard deviation.
[a]sludge class A (<10^3 *Escherichia coli* per gram of total solids).
[b]sludge class B (<10^6 *Escherichia coli* per gram of total solids).

Table 3 | Average aluminum, iron, and manganese concentration in raw water and after treatment

Metal	Raw water (mg·L^{-1})[a]	Treated water (mg·L^{-1})[a]	Average Removal
Aluminum	0.044 ± 0.007	0.003 ± 0.002	93.76%
Iron	1.240 ± 0.038	0.033 ± 0.017	97.37%
Manganese	0.112 ± 0.07	0.003 ± 0.002	97.54%

[a]Statistics based on $n = 13$ tests.

do not limit the application of tannin-based coagulant sludge in the soil. The cadmium, chromium, copper, lead, molybdenum, and nickel concentrations were down from the limit of detection associated with the applied methodology.

The prominent presence of metals in the sludge was associated with aluminum (1,371.62 mg·kg^{-1}) and iron (91,142.23 mg·kg^{-1}), possibly stemming from the raw water. We confirmed this observation by analyzing these metals in the raw and treated water (Table 3).

The removal percentage for aluminum, iron, and manganese was above 93%, which means that these metals are removed by precipitation and/or adsorption and are present in the sludge. Other authors also observed metal ions removal using tannin-based coagulants (Lugo *et al.* 2020; Righetto *et al.* 2021).

Silicon also presented a critical concentration compared to other metals and should be associated with the turbidity composition. Other metals showed concentrations lower than 100 mg·Kg^{-1} or below the limit of detection.

Thermogravimetric analysis of the sludge

According to the thermogravimetric analyses, it was possible to identify the points at which weight loss occurs in the sludge as the temperature increases. This weight loss included moisture and volatile matter and determining residues containing carbon not degraded during the analyses (Cao *et al.* 2013).

Figure 5 shows the thermogravimetric analysis curve for the sludge treated with Tanfloc. Three degradation stages were observed. The first corresponded to the dehydration stage and drying between 25 and 200 °C for tannin. The most considerable weight loss rate peaked at 118 °C, and the weight loss percentage in this process was 14%. The second weight-loss stage is related to low molecular weight and semi-volatile compounds decomposing organic compounds (Magdziarz & Werle 2014). Tannin presented a peek at 265 °C, and this transformation occurred at a narrower range from 200 to 335 °C, totaling a 12% weight reduction at this stage. The last weight-loss step is related to the degradation of low-biodegradability compounds such as cellulose (for example) and the oxidation of ash and reduced organic compounds (Vasques Mendonça *et al.* 2015). A continuous weight loss occurred from 335 °C, totaling 38% in this last stage up to 800 °C. The total weight loss at the end of this analysis was 64%.

Regarding the weight loss due to drying and dehydration, the range in which this process occurred was more expansive than in the works usually reported in the literature. Some authors reported that this process occurs between 25 and 160 °C (Vasques Mendonça *et al.* 2015) or 180 °C (Magdziarz & Werle 2014). Duval & Avérous (2016) determined that the degradation peak of the tannin extract from *Accacia catechu* occurs at 481 °C, with the combustion of this compound occurring at the range of 400–500 °C. A larger amount of organic compounds in the sludge may generally be an attraction to its thermal value (dela Justina *et al.* 2018).

CONCLUSION

Overall, a commercial tannin-based coagulant was successfully applied in the coagulation and flocculation of high-range turbidity water. It was possible to observe that Tanfloc MTH is a good alternative for water clarification in the city of Lages/SC,

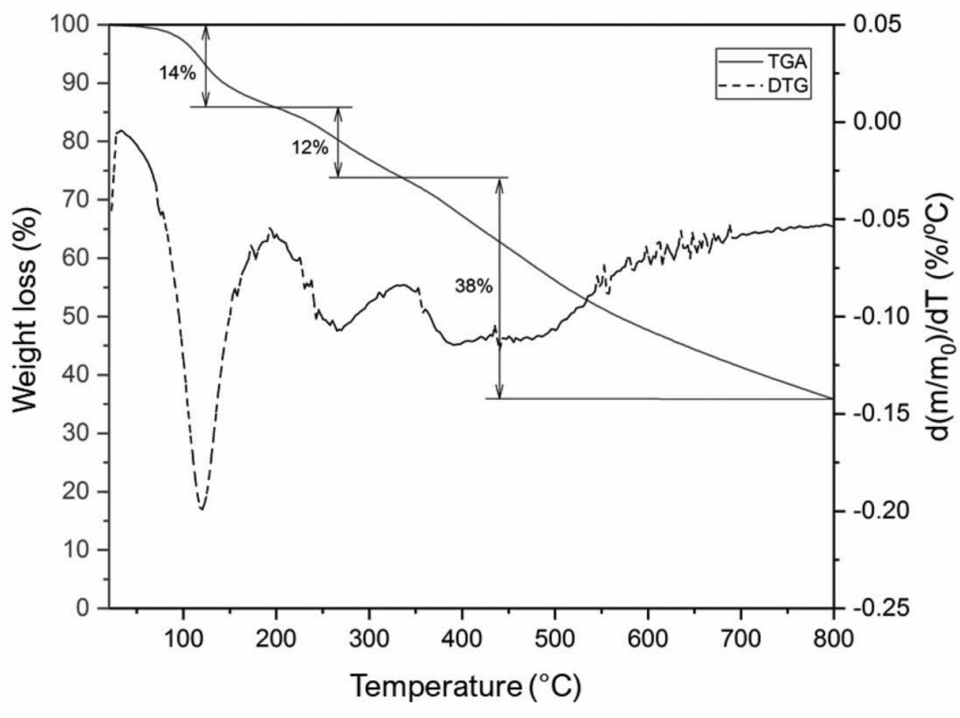


Figure 5 | Thermogravimetric analysis for the sludge obtained from treatment with tannin. m is the sample weight at a specific temperature, and m_0 is the initial weight.

Brazil, as the turbidity and apparent color in treated water were 0.94 ± 0.26 NTU and 3 ± 3 Pt-Co, respectively. Also, the operational stability in terms of water turbidity was not affected by the high coefficient of variation found for the turbidity in the raw water. Moreover, flocs are stable, and the turbidity removal at a settling velocity as high as 7 cm·min^{-1} was 76%. Aluminum and iron had the highest values regarding metals in the studied sludge, accounting for approximately 1,000 mg·Kg^{-1} in the dried sludge. The sludge contains as many as 50% on average of volatile solids. However, new tests must be performed to characterize the sludge for various dosages to evaluate the influence of water quality on the composition of such byproducts. Additionally, disinfection studies must be conducted to assess the potential for generating trihalomethanes in the treated water due to using tannin as the coagulant. These tests should also include pathogen credit removals due to the clarification process. Finally, studies involving economic issues must also be approached to complement the analysis performed.

ACKNOWLEDGEMENTS

The authors are grateful for the support from the Multiuser Center's infrastructure of the Center for Technological Sciences of the University of the State of Santa Catarina (CMU/CCT/UDESC) to Santa Catarina State Research and Innovation Support Foundation (FAPESC) (grant number 2019TR598), and the *Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – CAPES* – Brazil (PROAP and PROAP/AUXPE).

ADDITIONAL INFORMATION

The data supporting this study's findings are available from the corresponding author [ES], upon reasonable request. The corresponding author also declares that they are not affiliated with or involved with any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this paper.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

APHA/AWWA/WEF/Eaton A. D./American Public Health Association, American Water Works Association, Water Environment Federation 2005 *Standard Methods for the Examination of Water and Wastewater*, 21th edn., Vol. 21. American Public Health Association, (A. P. H. Association, Ed.), Washington, DC. https://doi.org/ISBN9780875532356.

Bacher, L. E., de Oliveira, C., Giacobbo, A., Benvenuti, T., Lacerda, A. B., Bernardes, A. M. & Rodrigues, M. A. S. 2017 Coupling coagulation using tannin-based product with electrodialysis reversal to water treatment: a case study. *Journal of Environmental Chemical Engineering* **5** (6), 6008–6015. https://doi.org/10.1016/J.JECE.2017.11.002.

Bello, A. & Leiviskä, T. 2022 Sustainable tannin-based coagulants synthesized through Mannich reaction using melamine as an amine source for water treatment applications. *Industrial Crops and Products* **176**, 114336. https://doi.org/10.1016/j.indcrop.2021.114336.

Bello, A., Virtanen, V., Salminen, J.-P. & Leiviskä, T. 2020 Aminomethylation of spruce tannins and their application as coagulants for water clarification. *Separation and Purification Technology*, 116765. https://doi.org/10.1016/J.SEPPUR.2020.116765.

Beltrán Heredia, J. & Sánchez Martín, J. 2009 Removing heavy metals from polluted surface water with a tannin-based flocculant agent. *Journal of Hazardous Materials* **165** (1–3), 1215–1218. Available from: http://www.sciencedirect.com/science/article/pii/S0304389408014726.

Bondy, S. C. 2016 Low levels of aluminum can lead to behavioral and morphological changes associated with Alzheimer's disease and age-related neurodegeneration. *NeuroToxicology* **52**, 222–229. https://doi.org/10.1016/j.neuro.2015.12.002.

Bongiovani, M. C., Camacho, F. P., Coldebella, P. F., Valverde, K. C., Nishi, L. & Bergamasco, R. 2016 Removal of natural organic matter and trihalomethane minimization by coagulation/flocculation/filtration using a natural tannin. *Desalination and Water Treatment* **57** (12), 5406–5415. https://doi.org/10.1080/19443994.2015.1006260.

Brasil 2020 *Resolução CONAMA n° 498 de 19 de Agosto de 2020*. Brasília – DF. Available from: https://www.in.gov.br/en/web/dou/-/resolucao-n-498-de-19-de-agosto-de-2020-273467970.

BRASIL 2021 *Portaria GM/MS no 888, de 4 de maio de 2021., Pub. L. No. Diário Oficial da União: 07/05/2021 | Edição: 85 | Seção: 1 | Página: 127*. Ministério da Saúde/Gabinete do Ministro, Brasil, p. 29. Available from: https://www.in.gov.br/en/web/dou/-/portaria-gm/ms-n-888-de-4-de-maio-de-2021-318461562.

Camacho, F. P., Sousa, V. S., Bergamasco, R. & Ribau Teixeira, M. 2017 The use of Moringa oleifera as a natural coagulant in surface water treatment. *Chemical Engineering Journal* **313**, 226–237. https://doi.org/10.1016/j.cej.2016.12.031.

Cao, J., Li, L., Morishita, K., Xiao, X., Zhao, X. & Wei, X. 2013 Nitrogen transformations during fast pyrolysis of sewage sludge. *Fuel* **104**, 1–6. https://doi.org/10.1016/j.fuel.2010.08.015.

Crestini, C., Lange, H. & Bianchetti, G. 2016 Detailed chemical composition of condensed tannins via quantitative ^{31}P NMR and HSQC analyses: *Acacia catechu*, *Schinopsis balansae*, and *Acacia mearnsii*. *Journal of Natural Products* **79** (9), 2287–2295. https://doi.org/10.1021/acs.jnatprod.6b00380.

dela Justina, M., Rodrigues Bagnolin Muniz, B., Mattge Bröring, M., Costa, V. J. & Skoronski, E. 2018 Using vegetable tannin and polyaluminium chloride as coagulants for dairy wastewater treatment: a comparative study. *Journal of Water Process Engineering* **25**, 173–181. https://doi.org/10.1016/j.jwpe.2018.08.001.

Duval, A. & Avérous, L. 2016 Characterization and physicochemical properties of condensed tannins from *Acacia catechu*. *Journal of Agricultural and Food Chemistry* **64** (8), 1751–1760. https://doi.org/10.1021/acs.jafc.5b05671.

Hameed, Y. T., Idris, A., Hussain, S. A. & Abdullah, N. 2016 A tannin-based agent for coagulation and flocculation of municipal wastewater: chemical composition, performance assessment compared to polyaluminum chloride, and application in a pilot plant. *Journal of Environmental Management* **184**, 494–503. https://doi.org/10.1016/j.jenvman.2016.10.033.

Howe, J., Hand, D., Crittenden, J., Trussell, R. & Tchobanoglous, G. 2012 *Principles of Water Treatment*. Jhon Wiley & Sons, New Jersey.

Ibrahim, A., Yaser, A. Z. & Lamaming, J. 2021 Synthesising tannin-based coagulants for water and wastewater application: a review. *Journal of Environmental Chemical Engineering* **9** (1), 105007. https://doi.org/10.1016/j.jece.2020.105007.

Lertsutthiwong, P., Sutti, S. & Powtongsook, S. 2009 Optimization of chitosan flocculation for phytoplankton removal in shrimp culture ponds. *Aquacultural Engineering* **41** (3), 188–193. https://doi.org/10.1016/j.aquaeng.2009.07.006.

Lugo, L., Martín, A., Diaz, J., Pérez-Flórez, A. & Celis, C. 2020 Implementation of modified acacia tannin by Mannich reaction for removal of heavy metals (Cu, Cr and Hg). *Water* **12** (2), 352. https://doi.org/10.3390/w12020352.

Magdziarz, A. & Werle, S. 2014 Analysis of the combustion and pyrolysis of dried sewage sludge by TGA and MS. *Waste Management* **34** (1), 174–179. https://doi.org/10.1016/j.wasman.2013.10.033.

Messini, A., Buccioni, A., Minieri, S., Mannelli, F., Mugnai, L., Comparini, C., Venturi, M., Viti, C., Pezzati, A. & Rapaccini, S. 2017 Effect of chestnut tannin extract (Castanea sativa Miller) on the proliferation of Cladosporium cladosporioides on sheep cheese rind during the ripening. *International Dairy Journal* **66**, 6–12. https://doi.org/10.1016/j.idairyj.2016.10.012.

Okoro, B. U., Sharifi, S., Jesson, M. A. & Bridgeman, J. 2021 Natural organic matter (NOM) and turbidity removal by plant-based coagulants: a review. *Journal of Environmental Chemical Engineering* **9** (6), 106588. https://doi.org/10.1016/j.jece.2021.106588.

Rafaeli Neto, S. L., Becegato, V. A. & Cabral, J. B. P. 2013 Monitoramento da qualidade da água do rio Caveiras no planalto serrano de Santa Catarina com suporte de tecnologias de geomática. *Boletim Goiano de Geografia* **33** (1). https://doi.org/10.5216/bgg.v33i1.23629.

Rafaeli Neto, S. L., Padilha, V., Schina, B. Á., Schier, D. T., de Liz, M. S. M., Ricardo, G. d. S. & Magro, R. B. 2019 *Projeto Hidrolages. Meta 1 – Estudos e concepções: relatório das concepções hidrológicas*. Lages/SC.

Righetto, I., Al-Juboori, R. A., Kaljunen, J. U. & Mikola, A. 2021 Multipurpose treatment of landfill leachate using natural coagulants – pretreatment for nutrient recovery and removal of heavy metals and micropollutants. *Journal of Environmental Chemical Engineering* **9** (3), 105213. https://doi.org/10.1016/j.jece.2021.105213.

Saleem, M. & Bachmann, R. T. 2019 A contemporary review on plant-based coagulants for applications in water treatment. *Journal of Industrial and Engineering Chemistry* **72**, 281–297. https://doi.org/10.1016/j.jiec.2018.12.029.

Sánchez-Martín, J., González-Velasco, M. & Beltrán-Heredia, J. 2009 *Acacia mearnsii de Wild* tannin-based flocculant in surface water treatment. *Journal of Wood Chemistry and Technology* **29** (2), 119–135. https://doi.org/10.1080/02773810902796146.

Sánchez-Martín, J., Beltrán-Heredia, J. & Solera-Hernández, C. 2010a Surface water and wastewater treatment using a new tannin-based coagulant. pilot plant trials. *Journal of Environmental Management* **91** (10), 2051–2058. https://doi.org/10.1016/j.jenvman.2010.05.013.

Sánchez-Martín, J., González-Velasco, M. & Beltrán-Heredia, J. 2010b Surface water treatment with tannin-based coagulants from Quebracho (Schinopsis balansae). *Chemical Engineering Journal* **165** (3), 851–858. https://doi.org/10.1016/j.cej.2010.10.030.

Tomasi, I. T., Machado, C. A., Boaventura, R. A. R., Botelho, C. M. S. & Santos, S. C. R. 2022 Tannin-based coagulants: current development and prospects on synthesis and uses. *Science of The Total Environment* **822**, 153454. https://doi.org/10.1016/j.scitotenv.2022.153454.

Tse, I. C., Swetland, K., Weber-Shirk, M. L. & Lion, L. W. 2011 Method for quantitative analysis of flocculation performance. *Water Research* **45** (10), 3075–3084. https://doi.org/10.1016/j.watres.2011.03.021.

US-EPA 1993 *CFR 40 Part 503 - Standards for the use or Disposal of Sewage Sludge*. US-EPA, Washington, DC, USA, p. 62.

Vasques Mendonca, A. R., de Souza, G. U., Selene, M. A., Valle, J. A. B. & de Souza, A. A. U. 2015 Thermogravimetric analysis and kinetic study of pyrolysis and combustion of residual textile sludge. *Journal of Thermal Analysis and Calorimetry* **121** (2), 807–814. https://doi.org/10.1007/s10973-015-4551-y.

WHO 2017 *Guidelines for Drinking-Water Quality*, 4th edn. WHO, Geneva.

First received 29 June 2022; accepted in revised form 9 October 2022. Available online 18 October 2022