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Removal of natural organic matter and trihalomethane minimization by coagulation/flocculation/filtration using a natural tannin

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ABSTRACT

Natural organic matter (NOM) is found in all surface, ground, and soil waters. The presence of NOM causes many problems in drinking water treatment processes. Minimization of the disinfection byproducts precursors or effective removal of NOM has emerged as a critical issue in the production of high quality drinking water from surface water. The objective of the present investigation is to explore the capacity of tannin to remove NOM in coagulation/flocculation/filtration/chlorination process from surface water in order to minimize total trihalomethanes (TTHM) formation. For the tests, raw water from Pirapó River Basin (Maringá, Paraná, Brazil) was used. Optimization of coagulation/flocculation tests was performed in jar test with dosage of Tanfloc 0.5% as coagulant ranging from 2.5 to 15 mg L^{-1}. The parameters analyzed were color, turbidity, compounds with absorption at UV-254 nm, dissolved organic carbon (DOC), and zeta potential. In view of the statistical analysis results, Tanfloc with dosage of 7.5 mg L^{-1} was chosen as coagulant for the follow-up tests of coagulation/flocculation/filtration/chlorination. The implementation of slow sand filtration after the sedimentation stage achieves almost 100% removal of turbidity. Besides, the combination of coagulation/flocculation/filtration/chlorination using this tannin improved NOM removal according to UV_{254nm} and DOC parameters, minimizing TTHM formation. The amount of TTHM in drinking water varied from 31.3 to 47.7 μg L^{-1}, while the amount of raw water TTHM was found to be 4.0 μg L^{-1}. Although these values lie below the ones stipulated by Ordinance no. 2914/2011 for TTHM limits, it is advisable to check periodically this parameter. In view of these results, this tannin can be recommended as a promising agent for surface water treatment.

Keywords: Natural tannin; Coagulation/flocculation/filtration; Trihalomethane; Natural organic matter; Water treatment

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1. Introduction

The loss of the intrinsic quality of freshwater sources renders necessary to use increasing amounts of chemicals for the removal of suspended and colloidal particles, in order to make them suitable for the characteristics of potability required by legislation. Iron and aluminum salts are widely used for this purpose in coagulation/flocculation process, since they are characterized by low cost and effectiveness in removing impurities of different natures [1,2]. However, recent studies have discussed several serious drawbacks of using the alum salts, namely Alzheimer's disease and other related problems associated with residual aluminum in treated waters [3–5].

Discharges of clarifiers and filter washes are major sources of waste pollutants in conventional water treatment plant (WTP). The filtration step is responsible for the retention of flocculent particles not removed in decanters, generating a considerable volume of liquid residues during backwash [6–8].

Other problem is when natural organic matter (NOM) that has not been completely removed in the treatment reacts with chlorine and forms disinfection byproducts (DBPs) [9]. DBPs have become a focus of attention in water treatment, since they have been reported to have adverse health effects [10,11]. More than 600 compounds of DBPs have been identified, among which trihalomethanes (THMs) and haloacetic acids are the most common ones [12].

Thus, minimization of the THMs' precursors or effective removal of NOM (both hydrophobic and hydrophilic organic compounds) prior to disinfection and distribution has emerged as a critical issue in the production of high quality drinking water from surface water [13].

Due to water quality problems and stricter regulations for drinking water treatment, there is a need for more efficient and still economical methods for the removal of NOM. Generally, the most common and economically feasible processes for the removal of NOM are considered to be coagulation/flocculation sedimentation and sand filtration [14]. Hence, the enhanced and/or optimized coagulation process has been suggested to be the best option for maximum control of NOM and DBP formation in conventional treatment processes [15,16].

The change of coagulant is one of the procedures adopted in order to reduce the environmental impacts of discharge from the decanters and backwash the filters, minimizing TTHM formation by the removal of NOM before disinfection [9,17]. The chemical coagulation has direct influence on the subsequent stages since the filter performance is related to the nature of the particles to be removed, which, in turn, depends on the type of coagulant used to destabilize these particles and promote their flocculation [8].

However, the coagulation performance of metal coagulants may not satisfy the increasing demand for NOM removal, and thus numerous researchers have focused on the use of natural coagulants in drinking water treatment [18,19,20,21].

In this context, natural coagulants (polymers), which can be derived from certain kinds of plants and animal life, are workable alternatives to synthetic coagulants. The advantages of these natural coagulants over the synthetic ones include safety to human health, biodegradability, low sludge volume, a wider effective dose range of coagulation/flocculation for various colloid suspensions (between 1 and 10 mg L^{-1}), and dispensable pH adjustment is not needed [3,7,8,22,23]. Furthermore, the polymers also exhibit the best effect on dissolved organic matter removal when compared to metal coagulants [24].

Tannins are mostly vegetal water-soluble polyphenolic compounds. Their molecular weight ranges between 500 and some thousands Daltons. Trees such as Schinopsis balansae (Quebracho), Castanea sativa (Chestnut), or Acacia mearnsii de Wild (Blackwattle) are traditional tannin sources [25].

Previous studies have been carried out on tannins coagulant activity in water treatment [26–28]. The main aim of the present investigation is to explore the capacity of tannin for removing NOM in coagulation/flocculation/filtration/chlorination process from surface water in order to minimize THMs formation.

2. Materials and methods

2.1. Coagulation/flocculation tests

For the tests, raw surface water was obtained from Pirapó River, in Maringá City (North of Paraná State —Brazil) with characteristics of low color/turbidity and constant pH.

The coagulant used for the tests was a tannin-based product called Tanfloc that is a trademark that belongs to TANAC (Montenegro, Brazil). This product, supplied as a solid, is modified by a physical–chemical process from Acacia mearnsii de Wild. This tree is very common in Brazil and it has a high concentration of tannins with considerable flocculant power [29].

According to TANAC specifications, Tanfloc is a vegetal water-extract tannin, mainly constituted of flavonoid structures with an average molecular weight of 1.7 kDa. More groups such as hydrocolloid gums and other soluble salts are included in Tanfloc formula. Chemical modification includes a quaternary nitrogen that gives Tanfloc a cationic character [30].

The standard solution was prepared as 0.5% w/v, adding 0.5 g of tannin extract to 100 mL of distilled water at room temperature. Some preliminary tests were undertaken to evaluate the optimal coagulant dosage. The dosage range investigated during the tests was 2.5–15 mg L^{-1} [28].

Experimental tests were conducted in jar test equipment Nova Ética—Model 218 LDB with six samples of raw water run simultaneously in beakers of 1 L capacity, using 500 mL of raw water for step optimization of coagulant.

Subsequently, the coagulant was added to jars, undergoing rapid mixing for 2.5 min at 120 rpm and slow stirring for 20 min at 20 rpm. Twenty minutes were allowed for the settling of the flocs [31]. The parameters apparent color, turbidity, compounds with absorption at UV-254 nm, dissolved organic carbon (DOC), and zeta potential of the supernatant sampled from 3 cm depth have been measured. Each experiment was performed in duplicate.

2.2. Filtration and disinfection tests

The filtration apparatus is composed of a rapidly descending column filtration in acrylic, diameter of 6.5 cm and height of 35 cm.

The relative thickness of sand and anthracite layers has direct influence on carrier length filtration. The higher the ratio of sand and anthracite volumes, the longer the time between consecutive washes. Good results have been obtained with a filter bed consisting of 60% (volume) of anthracite and 40% of sand. Thus, the filter bed with a total height of 15 cm was built with a sand layer (6 cm) with particle size between 0.421 and 2.00 mm and anthracite layer (9 cm) with a particle size between 0.71 and 2.40 mm supported by a screen, as recommended by Di Bernardo [32].

The double-layer filter (sand and anthracite) was filled with a weight of 297 g of sand and 246 g of anthracite. This mass of each component to be used in the filter in order to complete a total height (H) of 15 cm was determined by Eq. (1) [32].

$$m = (1 - \varepsilon)A \cdot L \cdot \rho \qquad (1)$$

in which L is the bed height of each component of the filter and A is the filter internal area, assuming ε the porosity of the bed equals to 0.42 for sand and 0.47 for anthracite, and densities ρ_{sand} and $\rho_{\text{anthracite}}$ equal to 2.65 and 2.67 g cm^{-3}, respectively [8].

The filter medium was washed and oven dried before being weighed. A support layer with two sizes of gravel was properly placed aiming at supporting the double-layer filter (sand and anthracite) and preventing loss of these layers. For proper placement of the filter medium in the column, it is recommended that the column be partially filled with water. This procedure minimizes the presence of air bubbles in the filtering media [32].

For the tests, coagulated/flocculated water was filtered by applying a flow rate of 240 L m^{-2} h^{-1}, minimum rate to be used for rapid filtration using dual media [32], for a period of 40 min. In Fig. 1 is shown the experimental apparatus used in conventional filtration step.

The disinfection of filtered water was performed with sodium hypochlorite in 500-mL flasks wrapped in aluminum foil with the purpose of protecting against light and minimizing the degradation of chlorine. A concentration of 1.5 mg L^{-1} was applied, which is used by local water treatment station SANEPAR with contact times of 30 min, 1, 2, 4, and 8 h. To cease the reaction of residual chlorine and organic matter in each contact time, the samples were supplemented with free residual chlorine sequestrant (sodium thiosulfate solution ($Na_2S_2O_3$)).

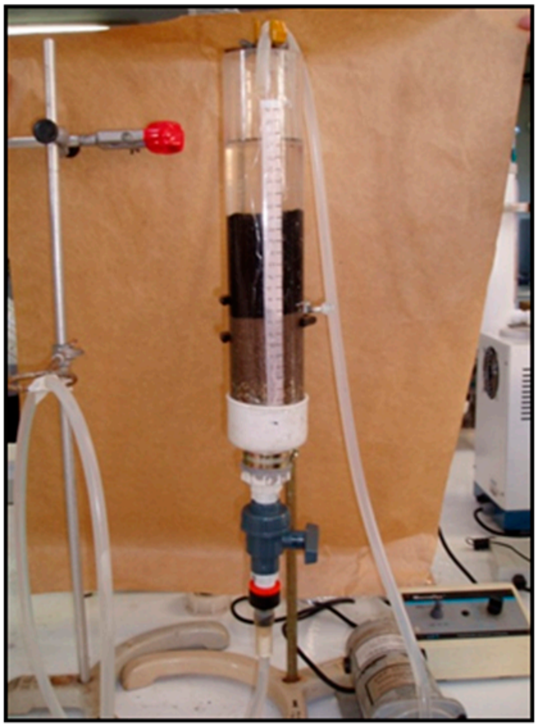

Fig. 1. Experimental apparatus used in conventional filtration step.

2.3. Analytical methods

2.3.1. Apparent color

Color was measured in spectrophotometer Hach DR/2000 model, program 120, wavelength 455 nm, by visual comparison with platinum–cobalt with results expressed in uH (Hazen unit) or mg Pt-Co L^{-1}, according to Standard Methods [33].

2.3.2. Turbidity

The nefelometric method is based in light intensity comparison by reference standard suspension. The turbidity measure was determined in Policontrol turbidimeter, AP2000 model, using formazin standard solutions with results expressed in nephelometric turbidity units (NTU), according to Standard Methods [33].

2.3.3. Compounds with absorption in UV-254 nm (UV_{254nm})

Absorbance measures were performed in spectrophotometer Hach DR 5000 model, at 254 nm wavelength, which identifies groups of aliphatic and aromatic organic compounds and humic substances, showing an alternative of NOM representation or THMs potential formation in water with results expressed in cm^{-1} (absorbance values must be divided by the cell length, 1 cm cell in this study) [34].

2.3.4. Dissolved organic carbon

The samples were filtered on Millipore cellulose ester membrane, with a mean pore diameter of 0.45 μm pore size, using a vacuum pump before the determination of COD.

The COD concentration was determined by sample combustion and infrared carbon dioxide detection (Method 5310-B) according to Standard Methods [33] using TOC Analyzer, Shimadzu mark, model 5000A with results expressed in mg L^{-1}.

2.3.5. Total trihalomethanes

For the total trihalomethanes (TTHM) determination in drinking water, the analyses were performed on a gas chromatograph coupled to "quadrupole" mass spectrometer (GC-MS) equipped with 70 eV electron impact ionization operating in total ion current mode 65–180 m/z, "Thermo-Finnigan" trademark, "Focus DSQ II" model, with automatic sampler "Triplus" model. The autosampler is equipped with a support tray for 54 sample vials and an oven with a capacity of six bottles for extraction "headspace".

For the chromatographic separation, a TR-5MS column 30 m × 0.25 mm × 0.25 μm with 5% Fenilpolisilfenileno siloxane was used. The mobile phase used in chromatography was helium gas with 99.999% purity obtained from White Martins.

The conditions used for gas chromatograph were: injection volume of 0.5 mL; injector and transfer line temperatures of 200℃; and split of 1/20. The conditions used for extraction "headspace" were: sample volume of 12 mL; temperature of 75℃; retention time of 20 min; and 4 g of KCl. The KCl is widely used for headspace analyses in order to diminish the solubility of organic compounds in an aqueous medium so as to facilitate their volatilization.

A calibration curve concentration × peak area of each trihalomethane was made for subsequent conversion of area readings in TTHM concentration, which corresponds to the sum of the THMs chloroform, bromodichloromethane, chlorodibromomethane, and bromoform. The standard solutions of THMs for calibration curve construction were purchased from Supelco at 2,000 μg mL^{-1} concentration of each compound. In the preparation of a stock solution (10 mg L^{-1}), the solvent used was a "Fischer" brand methanol with HPLC purity. As for the other dilutions used for the preparation of calibration curves (0, 20, 40, 60, and 80 μg L^{-1}), the solvent used was Milli-Q ultrapure water.

For the construction of calibration curve and quantification of THMs in the samples, the method of addition of the internal standard was used; in this case, the fluorobenzene with molecular weight of 96 and formula C_6H_5F, Sulpelco brand with 99% purity and concentration of 2,000 μg mL^{-1}, is used to measure the reference response relative to other compounds in the sample in μg L^{-1} according to Method 501.3 [35]. The acquisition and treatment of the data were performed using the Xcalibur, version 1.4 SR1 software.

The analytical curves, $Y = a + bC$, were constructed by plotting the area of the chromatographic peak, Y (ratio trihalomethane area and internal standard area) vs. the concentration, C, of the analyte (each trihalomethane). The experimental coefficients of the linear regression indicated a first-order correlation in all cases, as can be observed in Table 1.

The limits of detection (LOD) and quantitation (LOQ) were calculated considering $LOD = 3.3\,S/b$ and $LOQ = 10\,S/b$, where S is the estimated standard deviation of linear coefficient obtained through analytical equation $Y = a + bC$, and b is the angular coefficient from the same equation [36,37]. The obtained results are shown in Table 1.

Table 1
The analytical parameters obtained for the chromatographic and determination of THMs. Analytic column: TR-5MS (30 m × 0.25 mm × 0.25 μm). Mobile phase: helium gas

Trihalomethane	Retention time (min)	Analytical equation $Y = a + bC$ a (10^{-3})	b (10^{-3})	R	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)
Chloroform	2.06	33.58	11.16	0.9975	5.73	17.37
Bromodichloromethane	2.95	0.16	0.13	0.9972	6.07	18.40
Chlorodibromomethane	4.27	−4.46	5.79	0.9976	5.59	16.92
Bromoform	7.50	−5.11	3.72	0.9982	4.88	14.78

a = Linear coefficient; b = angular coefficient; C = concentration in $\mu g\,L^{-1}$; R = coefficient of correlation; LOD = limit of detection; LOQ = -limit of quantitation.

The LOD and LOQ obtained for the proposed method in $\mu g\,L^{-1}$ were, respectively: chloroform 5.73 and 17.37; bromodichloromethane 6.07 and 18.40; chlorodibromomethane 5.59 and 16.92; and bromoform 4.88 and 14.78.

2.3.6. Free residual chlorine

The free residual chlorine was measured using the colorimetric method at the wavelength of 515 nm, with the powder reagent DPD (N,N-diethyl-p-phenylenediamine), using a Hach spectrophotometer according to Standard Methods [33], with results expressed in $mg\,L^{-1}$.

2.3.7. Zeta potential

The zeta potential measurements were performed on colloidal suspensions using a Malvern Zetasizer instrument equipped with the zeta potential cell DTS1060 at 20°C. The way and the speed of the particle movements are directly proportional to the sign and the magnitude of their charge. The values are then translated into zeta potential by using the Helmholtz–Smoluchowski equation which links the zeta potential to the electrophoretic mobility. Each result was an average of three readings with results expressed in mV.

2.4. Statistical procedures

To assess the optimal dosage of coagulant, a completely randomized design was used, divided into six dosages with two replications using STATISTICA 6.0 software. Analysis of variance, with Tukey's test was carried out to verify the significance of differences among the means. All statistical significance was considered when $p < 0.05$. The letters (*a*, *b*, *c*, etc.) identify statistically different significant groups, with larger letters representing the best dosages.

3. Results

The characterization of the raw water in terms of parameters related to the organic matter is shown in Table 2.

Due to the fact that most of the raw water from the treatment plant site was characterized as being of low color/turbidity, due to long periods of drought and difficult treatment, this kind of water, with these specific characteristics, was used in this study.

3.1. Optimum coagulants dosage

Jar test experiments were run with tannin dosages of 2.5; 5.0; 7.5; 10.0; 12.0; and 15.0 $mg\,L^{-1}$. Fig. 2 presents removals of turbidity, color, and UV_{254nm} and their residuals amounts and zeta potential of these trials with coagulant dosage.

Changes in the zeta potential values of colloid microflocs are generally used to evaluate the destabilization ability of coagulation reagents. In other words, it is a convenient way to optimize coagulant/flocculant dosage in water and wastewater treatment since

Table 2
Raw water characterization

Parameters	Mean values
Turbidity (NTU)	56.4 ± 5.6
Apparent color (uH)	262 ± 22.4
pH	7.5 ± 0.71
UV_{254nm} (cm^{-1})	0.230 ± 0.08
DOC ($mg\,L^{-1}$)	4.455 ± 0.77
TTHM ($\mu g\,L^{-1}$)	4.31 ± 0.49

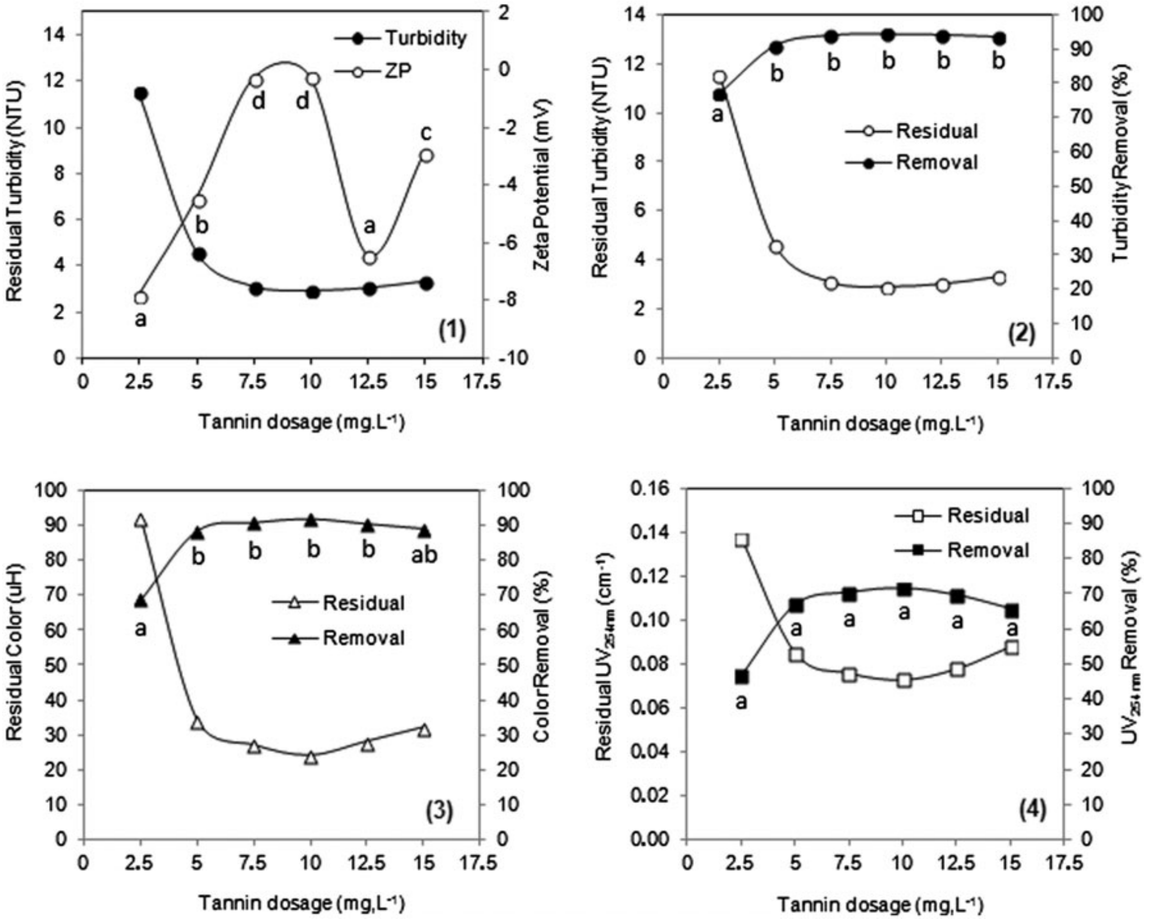

Fig. 2. Interaction graphics in qualitative optimizing (1) residual turbidity and zeta potential, (2) residual turbidity and turbidity removal, (3) residual color and color removal, and (4) residual UV_{254nm} and UV_{254nm} removal in coagulation/flocculation step using different tannin dosages. Letters (*a*, *b*, *c*, and *d*) in the graphics identify different statistically significant groups (Tukey's test, $p < 0.05$).

the key to effective particle removal is the reduction of their zeta potential [38,39].

In general, analyzing each parameter, higher removals of turbidity (>90%), color (>80%), and UV_{254nm} (>60%) were observed with dosages above 5.0 mg L^{-1}, obtaining residual amounts lower than 5.0 NTU for turbidity, 40 uH for color, and 0.090 cm^{-1} for UV_{254nm}, with turbidity and color within the current legislation. The analysis of zeta potential behavior, Fig. 2(1), showed that as the coagulant dosage increased, zeta potential increased significantly to values close to the point of zero charge (0 mV) and the residual turbidity decreased, presenting the best coagulation/flocculation performance at dosages of 7.5 and 10.0 mg L^{-1}. This fact suggested that charge neutralization may be the predominant mechanism for NOM removal by Tanfloc [40].

Tukey's test for multiple comparison show that there are differences between tannin dosages only for color, turbidity, and zeta potential. The efficacy of the coagulant was optimal in the range of 5.0–17.5 mg L^{-1} for color and turbidity. For zeta potential, the optimal dosages were 7.5 and 10.0 mg L^{-1}. According to Pallier et al. [41], when it is observed a more negative zeta potential of colloidal suspension, induced by the presence of organic matter, settleable flocs did not form. In this way, the coagulant dosage required for colloids destabilization and flocs formation is higher. The most efficient dosage is the one in which zeta potential of the colloidal suspension is slightly close to zero, reaching maximum turbidity removal.

According to Sanitation Company of Paraná State (SANEPAR), which uses polyaluminum chloride (PAC) as a coagulant, in order to obtain a long filter runs and a good quality filtrate, the turbidity level after coagulation/flocculation step has to lie below 5.0 NTU.

The residual parameters of turbidity, color, and UV_{254nm} showed that, using a dosage of 7.5 mg L^{-1}, the residual turbidity was below 5.0 NTU, which was considered the optimal dosage, with similar results obtained by Awad et al. [42] using PAC as coagulant with dosage of 10 mg L^{-1} and residual turbidity of 2.4 NTU from 61 NTU of raw water turbidity (96.1%). On the other hand, Yarahmadi et al. [43] also using PAC as coagulant and raw water with initial turbidity of 50 NTU, obtained turbidity removal of 4.5 NTU (89%) using a dosage of 20 mg L^{-1}.

Sánchez-Martín et al. [28] evaluated the coagulation/flocculation process comparing the coagulant Tanfloc with chemical coagulant aluminum sulfate for the MON removal of surface water. A very high efficiency in turbidity removal was satisfactory with reduced flocculant concentrations. Equal doses of alum have achieved a reduction of 82%, compared to 97% of turbidity removal that is achieved with the same dose of Tanfloc (10 mg L^{-1}).

Sánchez-Martín et al. [44] carried out experiments of surface water clarification with four coagulant agents: three natural ones (*Moringa oleifera*, Silvafloc and Tanfloc) and a traditional inorganic salt which is commonly used in coagulation procedure in drinking water treatment plant, aluminum sulfate, and observed that natural coagulants presented higher performance in turbidity removal with dosages of 15 mg L^{-1}.

Beltrán-Heredia et al. [25] also studied the optimization of a new tannin-based coagulant using Acacia mearnsii de Wild tannin extract and observed that low levels of the coagulant are able to remove most of the natural turbidity present in the samples. The total removal of these suspended colloidal materials is achieved with 12.5–25 mg L^{-1}.

The fact that these natural coagulants were more efficient than aluminum sulfate is due to their net-forming ability: while alum seems to act just as a coagulant, the long molecules of natural coagulants (either polyelectrolyte, in the case of *Moringa*, or tannin Mannich base, in the case of Tanfloc and Silvafloc) are able to destabilize colloidal material in the raw water [26] and rearrange a flocculant action [45,46].

In view of these results, tannin with 7.5 mg L^{-1} dosage was chosen as coagulant for the follow-up tests of coagulation/flocculation/filtration/chlorination.

3.2. Coagulation/flocculation /filtration/process with optimal dosage

With the optimal dosage of the coagulant Tanfloc determined in the previous step, it was performed coagulation/flocculation with subsequent conventional filtration with the purpose of comparing the removal efficiency of NOM and minimization of thihalomethanes formation. Residues and removals of the parameters color, turbidity, UV_{254nm}, and DOC of these tests are shown in Table 3.

Table 3
Results of coagulation/flocculation/filtration with tannin optimal dosage

Parameters	Residual	Removal (%)
Turbidity (NTU)	0.46 ± 0.04	99 ± 0.71
Apparent color (uH)	2.62 ± 0.18	99 ± 0.71
UV_{254nm} (cm^{-1})	0.023 ± 0.003	90 ± 2.83
DOC (mg L^{-1})	1.916 ± 0.037	57 ± 2.79

These results show that turbidity and apparent color meet the Brazilian Legislation (Ordinance no. 2914/2011) after the filtration, with turbidity below 0.5 NTU, and color below 15 uH [47]. Furthermore, it could be observed that the removal of organic matter, measured mainly by COD parameter, was very small when compared to the parameters color, turbidity, and UV_{254nm}. This means that the major organic constituent present in these waters are consist of fulvic acids, which are known to be difficult to remove [48].

The removal efficiencies and residual color and turbidity using the tannin coagulant combined with filtration are close to those obtained by Zouboulis et al. [49] when using aluminum sulfate as primary coagulant with residual turbidity in the range 0.1–1.0 NTU with different dosages, not that Tanfloc can be considered a coagulant with promising potential for the use in treatment plants, since large and heavy flocs with easy settling were observed, in addition to generating biodegradable sludge [30].

When compared with the results obtained by Garcia-Villanova et al. [50], the value found for UV_{254nm} parameter (0.023) is close to that found in this study.

3.3. Post-chlorination and THM formation

After chlorination process of filtrated water, it was measured the TTHM formation and residual chlorine in treated water, which is presented in Fig. 3.

According to Ordinance no. 2914/2011 [47], it is mandatory to maintain at least 0.2 mg L^{-1} of free residual chlorine through the entire length of the distribution system (reservoir and network), as can be observed after contact time of 8 h in Fig. 3. However, it can be observed that the amount of TTHM increased with increasing contact time, with values in accordance with Ordinance no. 2914/2011 (100 μL^{-1}) [47].

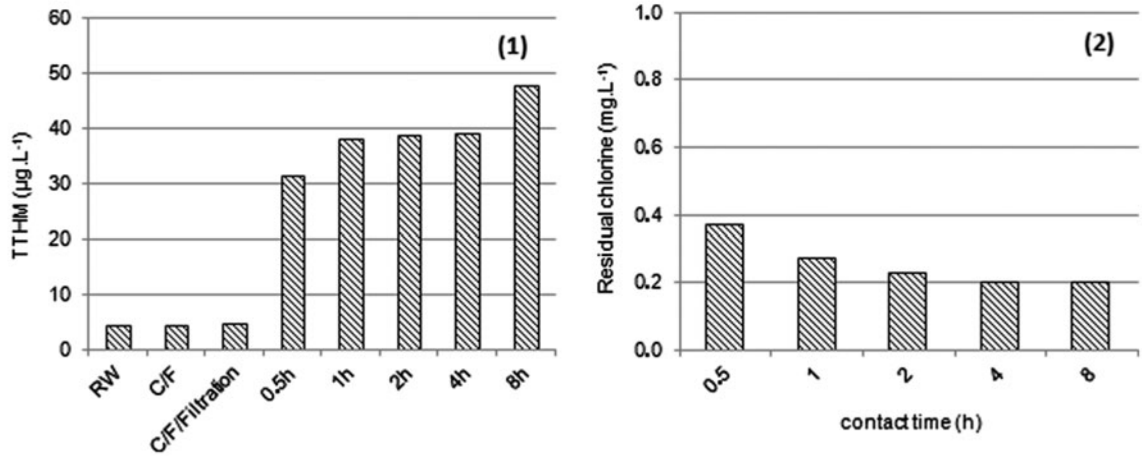

Fig. 3. (1) TTHM and (2) residual chlorine for coagulation/flocculation/filtration process before (RW—raw water; C/F—coagulation/flocculation; C/F/Filtration—coagulation/flocculation/filtration) and after chlorination at contact times of 0.5, 1.0, 2.0, 4.0, and 8.0 h.

Andreola et al. [51] evaluated the formation of THMs in the water treatment station of Maringá/Brazil SANEPAR, through the distribution network and completion of the process in household containers, and related the amount of THMs formed to the quantities of organic matter throughout the process. From the results, it was possible to observe that the formation of THMs in water treatment station occurs progressively over the sampling points, and in the raw water, as there is no chlorine in contact, there is no formation of THMs. The values of residual chlorine (>0.76 $\mathrm{mg\,L^{-1}}$) and TTHM (>50 $\mu\mathrm{g\,L^{-1}}$) output of treated water after contact tanks were in accordance with those established by Ordinance no. 2914/2011 [47], whose TTHM is higher than the one obtained in this study.

There have been earlier studies of Tanfloc's coagulant activity in coagulation/flocculation process [23,26,27]; therefore, there isn't complete water treatment (coagulation/flocculation/filtration/chlorination) with this tannin, especially when analyzing THMs formation.

Otherwise, the use of tannin in coagulation/flocculation process may present the advantage of improving the filter capacity, increasing its lifespan, accompanied by an improvement in the water quality [22], and in NOM removal, minimizing TTHM formation using a natural product which produces low amount of biodegradable sludge [30].

4. Conclusions

This study is concerned about THMs precursor by enhanced coagulation, which was applied in raw water, using a natural coagulant.

The tannin (Tanfloc) has been observed as a quite effective coagulant/flocculant agent for NOM removal in surface water treatment tested. The results of jar test, which was conducted for determining the optimum coagulation conditions, indicated that maximum color (>80%), turbidity (>90%), and $\mathrm{UV_{254nm}}$ (>60%) removals were achieved with 7.5 $\mathrm{mg\,L^{-1}}$ Tanfloc, showing zeta potential close to the point of zero charge (0 mV). This dosage was chosen for the follow-up tests of coagulation/flocculation/filtration/chlorination.

The implementation of slow sand filtration after the sedimentation stage achieves almost 100% removal of turbidity. Besides, the combination of coagulation/flocculation/filtration/chlorination with this tannin improved NOM removal according to $\mathrm{UV_{254nm}}$ and DOC parameters, minimizing TTHM formation. The amount of TTHM in drinking water varied from 31.3 to 47.7 $\mu\mathrm{g\,L^{-1}}$, while the amount of raw water TTHM was found to be 4.0 $\mu\mathrm{g\,L^{-1}}$. Although these values lie below the ones stipulated by Ordinance no. 2914/2011 TTHM limits, THMs should be periodically monitored in drinking water distribution systems to make sure that water supply is safe. In view of these results, this tannin can be recommended as a promising agent for surface water treatment.

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