Using vegetable tannin and polyaluminium chloride as coagulants for dairy wastewater treatment: A comparative study

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ABSTRACT

The aim of this work was to compare the performance of tannin and polyaluminium chloride (PAC) in the coagulation process for dairy industry wastewater. The conditions of coagulation/flocculation with regards to the dosage, pH, velocity gradient and slow-mixing time were optimized and some parameters such as floc aggregation (K_A) and breakage (K_B) coefficients were computed. Additionally, it was carried out a thermogravimetric analysis of the obtained sludge for both coagulants. The results showed no statistical differences between the performance of the two coagulants based on chemical oxygen demand, colour, turbidity and total solids removal. Particularly, the PAC showed higher alkalinity consumption and increased the electrical conductivity of the clarified wastewater, while tannin showed good performance within a wider pH, ranging from 5.0 to 10.0. Moreover, although the greatest K_A values were observed for PAC usage, the tannin use presented higher resistance to floc breakage during the slow-mixing time. The obtained sludge from the experiments using tannin accounted for higher volatile solids and fixed carbon, and lower ash content when compared to PAC. In conclusion, tannin is a promising alternative for dairy wastewater treatment regarding its process performance and wastewater treatment residuals management.

1. Introduction

Coagulation is an essential process for surface water and industrial wastewater treatment [1]. It consists in a well-known process involving destabilization of colloids and other suspended substances so as to promote its aggregation as greater and weightier flocs [2,3]. Typically, inorganic coagulants derived from iron and aluminium salts as $Al_2(SO_4)_3$, $FeCl_3$, and Polyaluminium Chloride (PAC), are employed in the coagulation processes [1,2]. Among these, the pre-hydrolyzed ones like PAC present some advantages, over the non-hydrolyzed, such as lower alkalinity consumption, and the generation of a smaller sludge amounts [4,5].

Alternatively to those inorganic metal-based coagulants, researchers have been looking for new and natural plant-based coagulants which have shown some advantages like the production of biodegradable sludge, lower alkalinity consumption and renewable sources origin [1]. On this way, tannin based coagulant has been being an effective coagulant in the treatment of numerous types of water and wastewater, presenting comparable or better performance than inorganic coagulants [6–9].

The tannins are macromolecular polyphenols, extracted from different vegetable sources such as *Schinopsis balansae* Engler, *Castanea sativa* Miller and *Acacia mearnsii* De Wildemann. Due to the several natural sources extraction, tannin chemical structures are diverse, described as complex. Therefore, it is still a challenge to determine exactly the chemical structure of tannins [9]. Nevertheless, tannin is present in some plant barks and its presence is related to antimicrobial properties and thermal protection [10]. When naturally obtained, the vegetable tannin does not present cationic features, which is provided after a cationization procedure involving the Mannich reaction.

In this process, a quaternary nitrogen is added to tannin polyphenolic structure through a reaction with an aldehyde and an amine, producing a higher molecular weight compound [2]. Even though the cationization, which is essential for its application as a coagulant, the tannin preserves some original plant extract features like the water solubility. Moreover, tannin has an ampholytic behaviour caused by the presence of quaternary nitrogen and phenolic hydroxyls [9].

When tannin is extracted from *Acacia mearnsii,* the main monomeric units are gallocatechin and robinetinidol, but sometimes there are also catechin and fisetinidol units. Additionally, tannin from *Acacia mearnsii*

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is condensed tannin [11]. These condensed tannins are polymers of flavonol units linked each other by carbon-carbon bonds, differently from hydrolysable tannins, which presents polyester linkage among gallic or ellagic acids in structure [12]. The cationized tannin coagulant polymeric chain from *Acacia mearnsii* De Wildemann, traded by TANAC company (used in this work), has approximately 600,000 g.mol^{-1}, and 1000 to 2000 repeating of monomeric units, which means a moderate to high molecular weight [6].

Dairy effluent has a variable composition consisted of high biochemical oxygen demand (1400 to 3383 $mgO_2 L^{-1}$) and high concentrations of suspended solids (28 to 80,000 $mg L^{-1}$), and PAC is constantly applied for the coagulation process [13]. In addition, the concern on disposal of generated sludge from the coagulation-flocculation process has motivated the industry to find a way in managing those sludge appropriately [14]. Although, the application of tannin and PAC in water and wastewater treatment is deeply reported, to date, there are no published studies which have evaluated the use of tannin for dairy wastewater treatment. In this context, the performance of a tannin-based coagulant and PAC for treating a real dairy wastewater were comparatively evaluated.

2. Material and methods

2.1. Samples collection, storage and preservation

Raw effluent samples were collected directly from the equalization tank in a real dairy industry, described in a previous study [15]. Collections were performed once a week at alternate days and times, aiming to cover possible variances in raw wastewater features. After the collection, samples were stored in high-density polyethene bottles at maximum temperatures of 4 °C before been analyzed.

2.2. Evaluation of coagulants dosage effects

The coagulant solutions used for performing the experiments were prepared by diluting commercial PAC (Buschle & Lepper, 18% w/w concentration) and a tannin based coagulant extracted from *Acacia mearnsii* (TANAC, 25% w/w concentration). The concentrations of commercial solutions were provided by the manufacturers.

The evaluation of dosage effects in coagulation and flocculation performances was performed by the application of six different dosages, for both PAC and Tannin based coagulants. The dosages were 100, 200, 300, 400, 500 and 600 $mg L^{-1}$ in aliquots of 1.5 L of raw effluent. The mixing parameters used in jar test were as follow: 90 s at 120 RPM for the rapid-mixing, 30 min at 45 RPM for slow-mixing and 60 min for settling. After the coagulant addition, pH was adjusted to 6.0–7.0 by adding NaOH or HCl solutions. All the experiments were carried out at room temperature.

As soon as the cycle was accomplished, samples were collected from the upper clarified effluent for analyzing the following parameters: chemical oxygen demand (COD), colour, turbidity, total solids (TS), alkalinity, and electrical conductivity. The experiments were performed in four replicates to assess the colour and turbidity removal, alkalinity consumption and effect in wastewater electrical conductivity. For COD and TS removal experiments, the tests were carried out in triplicate.

For the colour, turbidity, COD and TS removal investigation, the experimental design followed a 2 × 6 factorial experiment, consisted by one factor with two levels (type of coagulant) and another with six levels (concentration of coagulant). When it comes to the alkalinity consumption and the effect in the wastewater electrical conductivity, a linear regression analysis was fitted aiming to observe the trends associated with the coagulant dosage.

2.3. Effects and optimization of pH

In order to assess the pH influence in the coagulation/flocculation

process, the coagulant concentration was fixed. This concentration was applied to aliquots of 1.5 L of raw effluent with different pH from 4.0 to 10.0 adjusted by the addition of NaOH or HCl solutions. The coagulation/flocculation performance was expressed in terms of the percentage of colour and turbidity removal. The experimental design followed a 2 × 7 factorial, with two levels according to the nature of the coagulant and seven level for the pH. The experiments were conducted in triplicate.

2.4. Flocculation kinetic

Once determined the optimal values for concentration and pH for coagulation/flocculation process, it was studied the best conditions for the velocity gradient and flocculation time. Firstly, it was evaluated the behaviour of flocculation performance for each coagulant over time, under different velocity gradients. The aggregation (K_A) and breakage (K_B) coefficients, obtained from the experimental data, were also calculated.

The study of flocculation kinetic was carried out by monitoring the turbidity removal as a function of slow-mixing time under six different velocity gradients, as follows: 25, 40, 55, 70, 85, and 100 s^{-1}. Velocity gradients were adjusted based on a calibration curve provided by the jar test manufacturer. This curve shows a relationship between the frequency of the stirrer and the respective velocity gradient. After sedimentation time (2 h), it was measured the residual turbidity. The data obtained for each velocity gradient was plotted in an N/N$_0$ *versus* slow-mixing time graphic, and to each velocity gradient, it was fitted curves using the software Origin® 8 [16]. Aggregation and breakage coefficients were calculated based on the following kinetic equation for flocculation (Eq. (1)):

$$\frac{dN}{dt} = -K_A NG + K_B N_0 G^2 \tag{1}$$

Where:

N_0: initial concentration of primary particles in wastewater (m^{-3});

N: remaining concentration of primary particles after sedimentation at a gift slow mixture time (m^{-3});

K_A: aggregation coefficient (dimensionless);

K_B: breakage coefficient (s);

G: velocity gradient.

The concentration of primary particles can be related to wastewater turbidity. For this reason, it was used this parameter in the calculus to obtain the aggregation and breakage coefficients. Using a classical approach, the integration of Eq. (1) to initial time = 0 and final time of slow-mixing = t, and considering N_0 = initial turbidity and N = final turbidity after sedimentation time for a specific velocity gradient, leads to Eq. (2):

$$\frac{N_0}{N} = \left[\left(\frac{K_B}{K_A} G \right) + \left(1 - \frac{K_B}{K_A} G \right) x\, e^{-K_A GT} \right]^{-1} \tag{2}$$

Where:

T: time of slow mixture.

For that slow-mixing time which has presented the best efficiency in the turbidity removal, we applied the relation represented in the Eq. (3). This relation considers that at the point where the tangent to the curve becomes horizontal, it is achieved an equilibrium condition. It is equivalent to match dN/dt, Eq. (1), to zero.

$$\frac{K_B}{K_A} = \frac{1}{G \frac{N_0}{N}} \tag{3}$$

Once calculated the values for the relation showed in Eq. (3), the rearrangement of Eq. (2) can provide the value of K_A, just as shown in Eq. (4). Therefore, taking successive points along the fitted curves for each velocity gradient (specifically at the times in which we collected the aliquots during slow mixture time) we could calculate mean K_A for