Tannin-based Coagulants from Laboratory to Pilot Plant Scales for Coloured Wastewater Treatment

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Bark tannin extract from Acacia mearnsii (Mimosa ME) was modified at laboratory and pilot plant scales via the Mannich condensation reaction formaldehyde and dimethylamine hydrochloride. using Several conditions were varied during the modification procedure (heating rate, formaldehyde dosage, and Mannich solution activation time) to evaluate their influence on the shear viscosity and shelf life of the resulting products. It was possible to tune these properties with the reaction conditions. Modified condensed tannins with five distinct shear viscosities (30 cP to 430 cP) were selected to test the colour removal of anionic (Duasyn Direct Red and Acid Black 2) and cationic (Methylene Blue and Crystal Violet) dyes. The performance was monitored by ultraviolet spectroscopy. Colour removal was studied over different pH levels (1 to 14). Good decolouration results (85% to 96% reduction) were obtained with the simultaneous introduction of other additives to the process, which were bentonite and a cationic or anionic polyacrylamide, with minimal dosages of the latter additives. An improvement to decolouration performance with an increase in the biocoagulant viscosity was typically observed. However, for practical applications, modified condensed tannins with a lower viscosity may be preferred because they exhibited a longer shelf life and presented reasonable removal efficiencies.

Keywords: Biocoagulant; Coagulation/flocculation; Decolouration; Tannin; Scale-up

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INTRODUCTION

Tannins have been used in tanning processes for millennia (since *ca.* 1500 BC). They also have been widely applied in several industries (Haslam 1998), from uses in the medical field (anti-inflammatory, antidiarrheal, haemostatic, anti-hemorrhoidal, antiviral, and antibacterial properties) (Akiyama *et al.* 2001; Funatogawa *et al.* 2004; Lü *et al.* 2004; Ashok and Upadhyaya 2012), to the food industry (as antioxidant, and used to clarify beer, fruit juices, and wine) (Corder *et al.* 2006), and ink manufacturing (iron gallate ink). Furthermore, tannins are used in surface coatings, plastics (Grigsby *et al.* 2014), resins (Bisanda *et al.* 2003), manufacturing adhesives (Pizzi 1982, 2006; Hoong *et al.* 2011), and water purification (Sánchez-Martín *et al.* 2010a). In addition to their principal application in leather manufacturing and dying, they are often used as viscosity reducing agents in drilling muds for oil wells, as well as in water boilers to prevent scale formation (Khanbabaee and Van Ree 2001). Moreover, based on the chemical structure of tannins, the presence of phenolic groups with an anionic nature (deprotonation and formation of phenoxides stabilized by resonance) enables their use as natural coagulants for the treatment of drinking water, wastewater, and industrial effluents. The effectiveness of tannins as coagulants when used for the clarification of water strongly depends on the degree of modification and their chemical structure, which in turn is dependent on the plant from which it was extracted (Sánchez-Martín *et al.* 2010a).

Tannins are a secondary polyphenolic metabolite that are distributed widely in wood, bark, leaves, fruits, roots, and seeds, and for many different plants they protect against infections and insects (Haslam 1988). The complexity of their structure, properties, and chemistry are highly dependent on their origin, role in plant life, location, and surrounding vegetation. Additionally, tannins can be found in almost all plants and climates worldwide (Ashok and Upadhyaya 2012), which can explain their wide range of molecular structures and molar masses (below 1000 Da to 20000 Da). The most common commercial tannins are mainly obtained from Quebracho wood (*Schinopsis balansae* and *S. lorentzii*) (Long 1991), as well as from the bark of Mimosa (*Acacia mearnsii*), *Pinus*, and *Eucalyptus* species (Vázquez *et al.* 2008).

This study's main focus was on the bark tannin extract from *A. mearnsii* (Mimosa ME) from South Africa, where Mimosa bark is harvested from commercial plantations in a sustainable process. The condensed tannin extract, which has a 50% yield when obtained by water extraction, consists of polymeric flavonoid units (namely flavan-3-ol monomer) and proanthocyanidin oligomers.



Fig. 1. Flavan-3-ol monomers that constitute the Mimosa ME tannin extract: fisetinidol (A); robinetinidol (B); and gallocatechin (C) (Covington *et al.* 2005)

Condensed tannins from Mimosa ME essentially contain a proanthocyanidin polymer that encloses monomers, such as robinetinidin (70%, Fig. 1B), fisetinidin (25%, Fig. 1A), and gallocatechin (5%, Fig. 1C) (Covington *et al.* 2005). Typically, the monomers in tannin that create the proanthocyanidin polymer are linked by covalent C-C bonds between the C-4 of one flavanol unit and the C-8 or C-6 of another (Fig. 2) (Griffiths 1991; Pizzi 2006; Graham *et al.* 2008), which classifies it as a condensed tannin. Furthermore, the number average molecular weight of Mimosa ME is approximately 1270 g/mol and the weight average molecular weight is more than 2000 g/mol. The number average degree of polymerization has been determined to be in the range of 4.4 to 5.4 (Roux and Evelyn 1958).



Fig. 2. Typical flavan-3-ol skeleton in condensed tannins (Graham et al. 2008)

There have been some studies that used condensed anionic tannins as a coagulant for the removal of particles (Özacar and Şengil 2003) and some reports have described the use of cationic tannin-based coagulants in water treatment (Sánchez-Martín *et al.* 2010b). The cationization of tannins requires the addition of positively charged groups to the tannin matrix through chemical modification. In this procedure, several characteristics can be tuned, such as the solubility and stability at different pH levels. The appearance of new positively charged groups in the molecular structure can be advantageous in coagulation systems because cationic molecules may destabilize anionic molecules once mixed in an aqueous media. Destabilisation followed by settling may initiate separation and removal of many anionic substances (dyes, organic matter, and surfactants) (Beltrán-Heredia *et al.* 2010).

The modification of tannin molecules by the introduction of positively charged groups typically follows the Mannich reaction, where a protonated tertiary nitrogen becomes part of the tannin complex structure (Arbenz and Avérous 2015; Roman 2015). Many variations of this reaction have already been studied (Vasconcellos *et al.* 1993; Reed and Finck 1997; Curran *et al.* 1998; Hoong *et al.* 2011). Typically, a reaction with aldehyde and an amine allows for crosslinking between formaldehyde and the Mannich base, which results in a higher molecular weight of the obtained tannin-based polymers (Roux *et al.* 1975). The obtained products exhibit an ampholytic nature due to the presence of both cationic (tertiary ammonium) and anionic (ionized phenols) groups (Beltrán-Heredia *et al.* 2010).

The objective of this research is to produce natural-based treatment agents for water decolouration. Polymerization of tannin from Mimosa ME through a Mannich reaction with dimethylamine hydrochloride and formaldehyde was performed. Several conditions in the modification procedure were varied, namely the heating rate, formaldehyde dosage, and Mannich solution (MS) activation time, and their influence on the shear viscosity and shelf life of the resulting products was evaluated. The optimised procedure of tannin modification was implemented at a pilot plant scale. The resulting tannin-based coagulants were evaluated for their performance in the treatment of several model coloured waters. The effect of the viscosity of the obtained eco-coagulants and of the pH on the treatment of each model coloured effluent were investigated.

EXPERIMENTAL

Materials

A batch of South African *A. mearnsii* bark tannin extract (batch number 0208) was provided by Extract Dongen B.V., Netherlands (Dongen, Netherlands), and was used without any further treatment. The dimethylamine hydrochloride (DMA·HCl, powder, 99%) was purchased from Sigma-Aldrich (Steinheim, Germany). Formaldehyde (FA, aqueous solution of 37 wt%) was purchased from Acros Organics (Geel, Belgium). Model coloured effluents were prepared using Methylene Blue (Fluka Chemie AG, Buchs, Germany) Crystal Violet (Feldkirch Inc., Feldkirch, Austria), Duasyn Direct Red (Feldkirch Inc., Feldkirch, Austria), and Acid Black 2 (Carl Roth, Karlsruhe, Germany). The bentonite used in the coagulation tests was purchased from Riedel-de Haën (Steinheim, Germany). Polyacrylamides (PAM), distributed under the brand name SnowFlake (cationic (BHMW at 80% charge) and anionic (X0 at 30% charge)), were kindly provided by aquaTECH (Geneva, Switzerland). All of the other chemicals were purchased from Sigma-Aldrich (Steinheim, Germany).

Methods

Synthesis of the tannin-based coagulants: Mannich reaction

Tannin-based coagulants were synthesized *via* Mannich aminomethylation (Kukhareva *et al.* 2004) using as amine and aldehyde sources DMA·HCl and FA, respectively. The reaction mechanism is presented in Fig. 3. Water was used as the reaction medium. The two-step reaction required previous preparation of the Mannich reagent with a DMA·HCl/FA/water mass ratio of 1:1:1, which was followed by a 10-stage modification procedure (Fig. 4). The MS was left resting over night and was then added (Fig. 4; 4) to the tannin aqueous solution that was dissolved at 30 °C under agitation (Fig. 4; 1, 2, and 3). The cationization of the tannin was performed at 85 °C for 1 h (Fig. 4; 8). Additionally, an extra amount of FA solution was added (Fig. 4; 7) to force the reaction of the tannin and iminium ion.



Enol reacts with the iminium ion to form the modified tannin product



Fig. 3. Schematic of the Mannich reaction to modify the tannin



Fig. 4. The modification of the tannins using the Mannich reaction. The process steps were: 1- heating of the water, 2- addition of the tannin powder, 3- tannin dissolution, 4- addition of the MS, 5- heating, 6- activation of the MS, 7- FA addition, 8- cooking, 9- dilution; and 10- acidification

Mannich reaction at the laboratory scale

First, the MS was prepared in a conical flask, where 50 g of DMA·HCl were dissolved in 50 g of water (pH = 6). After full dissolution, 50 g of 37 wt% aqueous FA were added. The mixture was stirred with a magnetic stirrer for 20 min at 150 rpm. In a 2-L beaker that was covered with aluminium foil, 150 g of the Mimosa ME tannin powder were dissolved in 352.5 g of water under stirring for 1 h at 30 °C. Following this, 121.5 g of MS were added, the mixture was agitated for 5 min at 30 °C, and then it was heated to 85 °C. Two different heating rates, 0.9 °C/min and 1.8 °C/min, were evaluated. At 85 °C, 5 g of 37 wt% aqueous FA (FA/tannin ratio of 0.03) were injected. The influence of the MS activation time (period between reaching 85 °C and the addition of the extra FA) and of different FA/tannin ratios (0, 0.03, and 0.06) were studied. The reaction mixture was then maintained isothermally for 1 h at 85 °C. The solution was subsequently diluted with 300 g of water, followed by an acidification step with hydrochloric acid, which reduced the pH to 1.6. The total mass of the final product after dilution was 936 g. The shear viscosity of the solution was determined with a Brookfield Viscometer (LVDV-II+ Pro, Stoughton, USA) at 30 rpm and a temperature of 24.5 °C to 25.0 °C using the appropriate spindle (1 to 6 depending on the product viscosity).

Several experiments were performed by changing the heating rate, FA dosage, and MS activation time. The coagulants of the T_A series were prepared by using a heating rate of 0.9 °C/min and FA/tannin ratio of 0.06. The MS activation times were 15 min, 30 min, 45 min, 60 min, 90 min, and 120 min, which corresponded to the T_A1 , T_A2 , T_A3 , T_A4 , T_A5 , and T_A6 samples, respectively. The samples of the T_B series were prepared by repeating the method used to prepare T_A , but with a 0.03 FA/tannin ratio. The MS activation times of 60 min, 90 min, 120 min, 150 min, and 180 min corresponded to the T_B1 , T_B2 , T_B3 , T_B4 , and T_B5 samples, respectively. The modified tannins of the T_C series were obtained by using a FA/tannin ratio of 0.03 and a 1.8 °C/min heating rate, and the MS activation times of 90 min, 120 min, 150 min, and 180 min corresponded to the T_C1 , T_C2 , T_C3 , and T_C4 samples, respectively. A set of products (T_D) was obtained without the addition of extra FA and with a 0.9 °C/min heating rate, and the MS activation times of 120 min, 220 min, and 240 min corresponded to the T_D1 , T_D2 , T_D3 ,

 T_D4 , and T_D5 samples, respectively. The changes to the shear viscosity over time for the obtained products were monitored and the shelf life was evaluated.

Mannich reaction at the pilot plant scale

In a large container, 4.5 kg of DMA·HCl were dissolved in 4.5 kg of water (pH = 6). After full dissolution, 4.5 kg of 37 wt% aqueous FA solution were added. The MS mixture was stirred with a mechanical stirrer for 20 min at 200 rpm.

In a 75-L steel reactor (Hoppes INC, Springfield, USA), 12.0 kg of the Mimosa ME tannin powder were dissolved in 28.3 kg of water under stirring for 1 h at 30 °C. Following this, 9.7 kg of MS were added, the mixture was agitated for 20 min at 30 °C, and then it was heated to 85 °C. At this temperature, 1.2 kg of 37 wt% FA were added. The reaction mixture was then maintained isothermally for 1.5 h at 85 °C. The solution was subsequently diluted with 24.1 kg of water, followed by an acidification step at 45 °C with hydrochloric acid, which reduced the pH to 1.6. The heating profile of the reaction is presented in Fig. 5.



Fig. 5. The heating profile of the reaction of the tannins with MS and FA at the pilot scale. The modification steps were: 1- heating of the water, 2- addition of the tannin powder, 3- tannin dissolution, 4- addition of the MS, 5- heating, 6- activation of the MS, 7- FA addition, 8- cooking, 9- dilution; and 10- acidification

Characterisation of the raw material and modified tannins

To characterize the Mimosa ME tannin before and after modification, the Fourier transform infrared (FTIR) spectra were recorded with a Bruker Tensor 27 spectrometer (Karlsruhe, Germany) over the range of 400 cm⁻¹ to 4000 cm⁻¹ using 128 scans and a resolution of 4 cm⁻¹. The samples were analysed in KBr pellets. The elemental analyses of C, H, and N were performed using an EA 1108 CHNS-O element analyser from Fisons Instruments (Milano, Italy). The chemical 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene

was used as a standard. The elemental characterization of the unmodified tannin provided the following results: 52.71 wt% C, 5.75 wt% H, and 0.76 wt% N. Previously, gels of the modified tannins were oven-dried at $50 \text{ }^{\circ}\text{C}$.

Selected dyes and dye characterisation

In the present study, four dyes were selected for the preparation of model coloured effluents: Methylene Blue, Crystal Violet, Duasyn Direct Red, and Acid Black 2. Their characterization, including ultraviolet/visible spectra, pH, and conductivity of their aqueous solutions, can be found in Grenda *et al.* (2017).

Coagulation-flocculation experiments

The jar-test was applied to evaluate the flocculation performance of the modified tannins with different viscosities. A modified tannin solution at a 1% (w/w) concentration was prepared by dissolution in water under stirring at 500 rpm for 60 min. The model effluents were prepared by adding an adequate amount of dye to the water and stirring at 500 rpm. The dye concentration in the water was controlled by measuring the absorbance at 350 nm. Thus, depending on the dye type, different amounts were added to obtain an initial absorbance of approximately 0.250 at 350 nm. For the flocculation experiment, 200 mL of the dye solution was placed in a beaker, and the pH was adjusted to the target value by adding H₂SO₄ or NaOH, both at 10 wt%. A suitable amount of bentonite was added to the model effluent, followed by the dropwise addition of the tannin coagulant, and the suspension was mixed for 30 s. A cationic (BHMW with 80% charge) or anionic (X0 with 30% charge) PAM at a 0.1 wt% concentration was added after the biocoagulant. Supernatant samples of approximately 2 mL were collected at about 75% height from the bottom of the beaker, to determine the colour removal over time (1 min, 30 min, 1 h, 20 h, and 24 h). The decolouration was calculated based on the measurement of the absorbance of the supernatant at the optimised/universal wavelength of 350 nm according to Eq. 1,

$$Decolouration (\%) = \frac{A_0 - A_f}{A_0} * 100$$
(1)

where A_0 is the absorbance of the initial model wastewater at time zero, and A_f is the absorbance of the supernatant of the treated sample at a given time.

RESULTS AND DISCUSSION

This study may be divided into two sections: the synthesis of tannin-based coagulants at different scales and application of the obtained products in colour removal. The effects of the synthesis variables (heating rate, FA dosage, and MS activation time) on the biocoagulant shelf life and final application were studied. The influence of the pH on colour removal was also investigated. The results are presented in the following sections.

Synthesis and Characterisation of the Tannin-based Coagulants

First, the modification of tannin was studied at a laboratory scale using Mimosa ME tannin. Depending on the heating rate, MS activation time, and amount of FA that

were used in the reaction mixture, different shear viscosities of the final products were obtained (Fig. 6).

Decreasing the heating rate approximately 50% led to an increase in the viscosity of about 3- to 4-fold (T_B2 compared with T_C1 , or T_B3 compared with T_C2). During the process, the FA and Mannich base propagated crosslinking between the tannin (flavonoid) units through the methylene bridge at reactive positions on the tannin molecules (Pizzi 1992; Sánchez-Martín and Beltrán-Heredia 2012), which led to an increase in the molecular weight of the modified tannin, as was revealed by the higher viscosity of the final product. The trials performed with the same heating rates and higher dosages of FA (T_A and T_B) compared with the trial performed without any extra FA (T_D) yielded products with a remarkably higher shear viscosity when using the same MS activation time. Furthermore, applying a higher FA/tannin ratio required working at a lower MS activation time to prevent fast tannin gelation (over crosslinking). A longer MS activation time or lower heating rate (T_A and T_B) yielded products with higher shear viscosities. If the MS activation time is longer than a certain threshold, tannin gelation can occur, which renders the product useless as a coagulant for wastewater treatment. Thus, it was possible to control the viscosity and tune the reaction with the heating rate, FA/tannin ratio, and MS activation time.



Fig. 6. Shear viscosity (at 25 °C) of the modified tannin products just after production as a function of the MS activation time

Tannin-based coagulants are products of condensation reactions. This implies that the chain length and crosslinking progress over time, which leads to a thickening of the product. It is important to determine the relationship between the studied reaction conditions and the length of time that the obtained product can be stored without becoming unfit for final application. The shelf life was measured by changes to the shear viscosity (at 25 °C) after 14 d, 30 d, and 90 d (Fig. 7) using samples selected from the T_A series (Fig. 6). It was possible to evaluate the influence of the MS activation time on the viscosity and shelf life by correlating Figs. 6 and 7. Samples T_A1 , T_A2 , and T_A3 , which had a starting shear viscosity below 50 cP, showed a small increase in the viscosity over time. Typically, if a tannin sample presents an initial viscosity above 200 cP, then the material acquires a gel-type structure very fast, as is normal for condensation reactions, which results in the insolubility of the product. From Fig. 7, it was inferred that products with initial viscosities higher than 100 cP had a shelf life much shorter when compared with those produced with a shear viscosity below 100 cP. When the initial shear viscosity was 182 cP (T_A5) and 480 cP (T_A6), the shelf life time was shorter than two weeks. Additionally, the product with an initial viscosity of 84 cP (T_A4) aged more slowly, even if the viscosity after 90 d increased to 960 cP, which was the maximum viscosity value before it becomes solid and unfit for final use.



Fig. 7. Changes in the shear viscosity of the modified tannin products obtained from the T_A test series monitored over time (0 d, 14 d, 30 d, and 90 d) as a function of the MS activation time (15 min to 120 min)

The tannins modified by the Mannich reaction, as well as the raw material (Mimosa ME tannin), were characterised by FTIR spectroscopy (Fig. 8). The spectrum of the Mimosa ME tannin showed bands at approximately 3370 cm⁻¹ and 2927 cm⁻¹, which were assigned to the O-H stretching of phenolic groups and asymmetric stretching of CH₂ groups, respectively. Within the 1650 cm⁻¹ to 1450 cm⁻¹ region, bands at 1617 cm⁻¹, 1508 cm⁻¹, and 1453 cm⁻¹ from -C=C stretching vibrations were evident in the tannin spectrum. Other bands were at 1341 cm⁻¹, 1312 cm⁻¹, 1234 cm⁻¹, 1203 cm⁻¹, 1158 cm⁻¹, 1113 cm⁻¹, 1069 cm⁻¹, and 1028 cm⁻¹. These bands indicated absorption caused by O-H deformation vibration, C-O stretching in =C-O-H and =C-O-C bonds (asymmetric and symmetric modes), CH₂ deformation vibration, and in-plane C-H deformation vibration. Finally, below 1000 cm⁻¹, several bands were also seen in the FTIR spectrum of the Mimosa ME tannin, which were mainly due to the out-of-plane C-H deformation vibrations. The FTIR spectrum was found to be similar to the one previously reported by Peña *et al.* (2009) for a tannin with the same origin.

After modification by the Mannich reaction, the FTIR spectrum (Fig. 8) was substantially different from that of the raw material. The bands were generally shifted, the relative intensities were changed, and new bands appeared in the spectra. In particular, a new band at 1716 cm^{-1} emerged, which was assigned to the C=O stretching of new carbonyl bonds that formed during the reaction. Another new band was also evident at 934 cm⁻¹, which arose from the C-N stretching in the alkylammonium groups that formed. The band formerly at 1453 cm⁻¹ (-C=C stretching) was shifted to higher

wavenumbers that were near 1470 cm⁻¹ in the modified tannin spectra, indicating that overlapping with the asymmetric bending of CH_3 groups occurred. These results confirmed the expected reaction of the Mimosa ME tannin with FA and amine, where positively charged groups were added to the tannin backbone (Peña *et al.* 2009).



Fig. 8. FTIR spectra of the raw tannin and modified tannin (T_B3)

The repeatability of the modification procedures was examined for the experiment that produced the T_A3 modified tannin. Three batches of the same product (T_A3 ' to T_A3 ''') were obtained by following the previously developed procedure. The final viscosities of the obtained biobased coagulants after dilution and acidification were in agreement with that of the previously developed T_A3 product (42 cP, 43 cP, and 44 cP).

The process for obtaining biocoagulants based on Mimosa ME bark tannin optimized at the laboratory scale using a 1-L reactor was brought to a pilot plant scale by using a 75-L reactor. The introduction of positively charged groups by the Mannich modification was performed using MS at 85 °C for 1.5 h. The full 10-step procedure (Fig. 4) resulted in a product with a shear viscosity of 38 cP measured at 24.8 °C and 30 rpm. Additionally, the visual inspection of the reaction mixture showed that it thickened during the modification process; the shear viscosity, which was measured during the production reaction in the reactor, also increased. It was possible to control the process to obtain a product with the desired shear viscosity below 40 cP and a shelf life above 90 d. Thus, the properties of the modified tannin produced at the laboratory scale were fully repeatable at a pilot plant scale.

Decolouration Studies (Dye Removal)

Decolouration using coagulation with modified tannin-based materials is usually called adsorption-like coagulation in the literature (Sánchez-Martín *et al.* 2010b; Beltrán-Heredia *et al.* 2011a, 2011b, 2011c; Sánchez-Martín *et al.* 2014). In this work, the pollutant (dye) was removed using a tertiary system with bentonite, a tannin-based coagulant, and a synthetic flocculant. The addition of the inorganic complexing agent with the modified tannin product destabilizes the colloids in the aqueous medium because

of the chemical interaction between the negatively charged dye and cationic biocoagulant molecules. This creates a dye-bentonite-coagulant complex, while flocs begin to grow slowly through sorption mechanisms. Moreover, introduction into the system of the third component (flocculant) results in noticeable improvements to the efficiency of the colour removal because of an increase in the flocs size, which improves their settling.

Performance of the modified tannins with different viscosities

The modified tannin-based coagulants obtained from the T_B trials (with different viscosities and produced at a laboratory scale, see Table 1) were evaluated for their ability to remove colour from four different model effluents. Commercial dyes (Methylene Blue, Crystal Violet, Duasyn Direct Red, and Acid Black 2) dissolved in water were used as the model effluents. The modified tannins were evaluated in the presence of an inorganic complexing agent (bentonite) and synthetic flocculant as a tertiary clarification system. The tannin coagulants alone were ineffective at colour removal, which is generally the case when using low molecular weight coagulants. Additionally, bentonite alone, without any biocoagulant or flocculant, only slightly removed the colour, through adsorption of dyes on the surface of the particles. However, the treated water would still be highly coloured or even turbid.

Identification	Time (min)ª	Viscosity (cP) ^b	pH of Final Product			
T _B 1	60	31	1.6			
T _B 2	90	61	1.6			
T _B 3	120	137	1.6			
T _B 4	150	204	1.6			
T _B 5	180	432	1.6			
^a Refers to the MS activation time at 85 °C; ^b viscosity of the modified tannin measured just after production at 24.5 °C to 25.0 °C and 30 rpm using the appropriate spindle						

Table 1. Characteristics of the Modified Tannins Tested as Coagulants in Colour

 Removal

During the tests it was observed that changing the pH could promote the process and lead to an improved colour removal. The goal was to eliminate colour and turbidity. The performance on the colour removal was evaluated after 1 min, 30 min, 1 h, 20 h, and 24 h. For each tested dye, the optimal procedure (further described below) had to be tuned (pH, bentonite, tannin, and polyacrylamide concentration) for maximum removal (Table 2). For the negatively charged dyes (Acid Black 2 and Duasyn Direct Red), a cationic PAM was used to complement the action of the modified tannin coagulant, while an anionic PAM was added for the positively charged dyes (Methylene Blue and Crystal Violet).

	Identification	Initial Absorbance at 350 nm	рНª	Bentonite (wt%)	Tannin (ppm)	PAM (ppm) (Type)	
Ι	Methylene Blue	0.410	2.9	0.3	50	7.5 (Anionic)	
II	Crystal Violet	0.420	2.2	1.4	100	10 (Anionic)	
III	Duasyn Direct Red	0.360	3.4	0.3	50	10 (Cationic)	
IV	Acid Black 2	0.419	2.8	0.4	100	10 (Cationic)	
^a Refers to the pH of the model effluent after adjustment							

Table 2. Colour Remova	Conditions for All	of the Model	Coloured Waters
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For Acid Black 2, a pH of 2.8, 0.4% bentonite, 100 ppm of the tannin-based coagulant, and 10 ppm of the commercial cationic flocculant were the conditions needed to obtain high colour removal (Fig. 9). The results are summarised in Fig. 10. The best decolouration results of up to 83% removal after 24 h (74% removal after 30 min) were obtained with the T_B5 biocoagulant, which had the highest shear viscosity (432 cP). Moreover, the lowest decolouration after 30 min (57% removal, and 72% removal after 24 h) was achieved while using the T_B1 modified tannin, which had the lowest viscosity (31 cP). This must have been due to a lower degree of substitution and/or lower molecular weight. Additionally, 66% removal after only 1 min was observed when using the modified tannins with a shear viscosity of 204 cP (T_B4) and 432 cP (T_B5).



Fig. 9. Acid Black 2 colour removal: on the left, sample without treatment and on the right, sample after 24 h decolouration using the procedure IV from Table 2, with the modified tannin T_B4 .



Fig. 10. Acid Black 2 colour removal over time (1 min, 30 min, 1 h, 20 h, and 24 h) using the modified tannins with different viscosities

Figure 11 reports the colour removal results of Duasyn Direct Red (pH = 3.4) with 0.3% bentonite, 50 ppm of the biocoagulant, and 10 ppm of the cationic PAM. The T_B5 modified tannin was again the most effective in decolouration of this dye, and it achieved an efficiency of 76% after 1 min of treatment, as well as up to 89% dye removal after 24 h of settling. Using T_B1, 60% of the dye was removed during the first minute. For T_B2, T_B3, and T_B4, the dye removal was similar for the three coagulants during the monitored settling time: 71% to 74% removal after 1 min and 85% to 86% removal after 24 h. In general, the trends detected were very similar to the ones observed for the Acid Black 2 dye.

The modified tannins with different viscosities (T_B1 to T_B5) were also tested for Methylene Blue removal (Fig. 12). Adjusting the pH of the model effluent to 2.9, with the subsequent addition of bentonite (0.3%), modified tannin (50 ppm), and commercial synthetic anionic flocculant (7.5 ppm), allowed for good purification after the first minute of treatment. After 30 min of settling, the lowest colour removal (54% removal after 1 min and 67% removal after 30 min) was obtained while using T_B1 (lowest viscosity). For T_B2 , 65% colour removal was achieved, and for T_B3 , T_B4 , and T_B5 , 70% to 72% of the dye was removed during the first minute of the process. Nevertheless, for all of the tested tannins (T_B1 to T_B5), the decolouration became similar after 1 h of treatment: 79% to 84% removal. The same trend (90% to 95% removal) was observed after 20 h and 24 h of settling of the model coloured water.



Fig. 11. Duasyn Direct Red colour removal over time (1 min, 30 min, 1 h, 20 h, and 24 h) using the modified tannins with different viscosities



Fig. 12. Methylene Blue colour removal over time (1 min, 30 min, 1 h, 20 h, and 24 h) using the modified tannins with different viscosities

For the Crystal Violet model dye effluent, the best decolouration after 24 h of treatment (> 90% colour removal) was obtained with a pH of 2.2, the addition of 1.4% bentonite, 100 ppm of the tannin coagulant, and 10 ppm of the commercial anionic PAM, when using the T_B4 modified tannin with a shear viscosity of 204 cP (Fig. 13). The T_B2 , T_B3 , and T_B5 modified tannins showed similar performances after 24 h. During the first minute of settling, T_B4 and T_B3 (137 cP) were able to remove an equal amount of dye (70% removal). The first minute of treatment with T_B5 led to 75% colour removal. The lowest, but still relatively high, removal of 61% of the dye was achieved while using the modified tannin with the lowest shear viscosity (T_B1), while T_B2 provided moderate results (66%). The main difference between the different tannins was observed after 30 min of treatment. The colour removal efficiency increased with the viscosity of the tannin-based coagulant. After 1 h of settling, the performance of the T_B2 , T_B3 , T_B4 , and T_B5 tannins was similar (77% to 82% removal), as well as after 24 h.



Fig. 13. Crystal Violet colour removal over time (1 min, 30 min, 1 h, 20 h, and 24 h) using the modified tannins with different viscosities

In general, the viscosity of the modified tannins had a strong impact on the dye removal results. Especially for short removal times, higher viscosities led to higher removal efficiencies, which must have been due to higher degrees of modification and/or molecular weights. For longer settling times, the performance levelled-off and similar decolouration outcomes were obtained among the tested tannin-based coagulants.

pH influence on the colour removal

Previous studies have shown how important the pH is in decolouration processes (Sánchez-Martín *et al.* 2010c). Changes in the pH affect the process through the dissociation of functional groups (phenolic, carboxylic, *etc.*) from the surface active sites. Taking this fact into consideration, several assays with the selected four dyes were performed by varying the pH between 1 and 14, while keeping the other conditions tuned for each dye (Table 2) and using the T_B2 modified tannin in these tests. Figures 14 to 17 show the experimental results, expressed as the percentage of dye removal *versus* pH, for all of the tested dyes. It is very important to point out in the following figures that at certain pH values poor or no colour removal were achieved in the tertiary system. Thus, the negative values of colour removal did not necessarily represent an increase in colour, but probably an increase in the turbidity based on the low settling abilities of the added bentonite at the studied pH values.

The pH was one of the most important variables for colour removal of Acid Black 2, as is shown in Fig. 14. Increasing the pH from 3 to 5 led to dramatic decreases in the decolouration efficiency. However, the dye removal percentage increased when the pH increased from 5 to 12. The highest colour removal (84% to 90% after 24 h) was obtained at very acidic (pH 1 to 3) conditions. However, in very basic conditions (pH 12 and 13), it was also possible to remove up to 80% of the dye.



Fig. 14. pH influence on the removal of Acid Black 2 using the TB2 modified tannin

For Duasyn Direct Red (Fig. 15), the removal of the dye typically increased with a decrease in the pH. The highest efficiency (83% to 88% removal) was obtained for dye solutions with pH values of 2 to 4. A highly basic effluent (pH of 11 and higher) decreased the performance of the tested tertiary system, and led to highly turbid suspensions after 24 h of settling. It is very important to mention that less protons are expected to adsorb onto the surface of bentonite as the solution pH increases, resulting in an increase in its negative surface potential (Kim 2003). Thus, when applied for the treatment of the already negatively charged dye (Duasyn Direct Red), the dye molecules failed to adsorb onto the surface of the bentonite. As was mentioned previously, the addition of bentonite, modified tannin, and cationic synthetic flocculant was shown to work well in acidic conditions and removed 60% of the dye after the first minute of treatment.

For Methylene Blue (positively charged dye), increasing the pH from 2 to 6 led to a moderate loss in the colour removal efficiency (Fig. 16), which was more pronounced for shorter contact times (≤ 1 h). As the basicity of the effluent increases, it was expected that the cationic dye removal would increase because of the increase in the negative surface charge of the bentonite (Kim 2003). However, Methylene Blue was easily removed not only under basic conditions, but also with acidic pH values after 24 h, even if some loss of efficiency was observed within the pH range of 4 to 6. This loss could be caused by the neutral or slightly positive charge of the adsorbent (bentonite) (Kim 2003), which for these conditions may not be the most appropriate additive for the initial destabilisation of the low positively charged dye molecules in the solution. The addition of the positively charged modified tannin followed by the negatively charged flocculant helped with colour removal.



Fig. 15. pH influence on the removal of Duasyn Direct Red dye using the T_B2 modified tannin



Fig. 16. pH influence on the removal of Methylene Blue dye using the TB2 modified tannin

As for Crystal Violet (positively charged dye), there was not a great variation (from 60% to 82% removal) in the colour removal efficiency over the pH range of 1 to 12 after 24 h of settling (Fig. 17); although some loss of efficiency was observed in the pH range of 2 to 5. This latter trend was confirmed for the shorter contact times, especially for 1 min of settling. At the very basic pH values (pH > 11), the interaction between the dye molecules and negatively charged bentonite surface was so strong that the addition of the positive biocoagulant and anionic flocculant did not increase the colour removal. It is recommended to use a lower amount of bentonite or a higher amount of tannin-based coagulant for such basic pH values.



Fig. 17. pH influence on the removal of Crystal Violet dye using the T_B2 modified tannin

CONCLUSIONS

- 1. Tannin-based biocoagulants were synthesized from the tannin extract of *A. mearnsii* bark *via* the Mannich condensation reaction with FA and DMA·HCl under different experimental conditions. The heating rate, FA dosage, and MS activation time were varied, and their influence on the shear viscosity and shelf life of the resulting products was evaluated. It was possible to control the product viscosity and tune the reaction with these variables.
- 2. The optimised lab procedure of tannin modification was successfully implemented at a pilot plant scale. However, bringing the optimized procedure from the laboratory scale to the pilot plant scale required some adjustments to obtain a product with the desired properties (viscosity and shelf life).
- 3. Modified tannins (produced at the laboratory scale) with five distinct shear viscosities, were evaluated for the colour removal of cationic (Methylene Blue and Crystal Violet) and anionic (Acid Black 2 and Duasyn Direct Red) dyes. A tertiary system employing bentonite, a PAM, and the biocoagulant was used. It was evident that the decolouration performance improved with an increase in the viscosity of the biocoagulant. However, the progress of the condensation reactions in the modified tannin over time after its preparation, led to a continuous thickening of the product that shortened its shelf life. It can still be stated that reasonable removal efficiencies were achieved for all of the dyes tested, even using the modified tannins with lower viscosities (30 cP to 60 cP).
- 4. The influence of the pH on the performance of a modified tannin during dyes removal was also studied. The results showed that the performance was dependent upon the pH. Some of the dyes were more sensitive to this parameter than others, specifically Acid Black 2 and Duasyn Direct Red.

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