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Review

Tannin-based coagulants: Current development and prospects on synthesis and uses

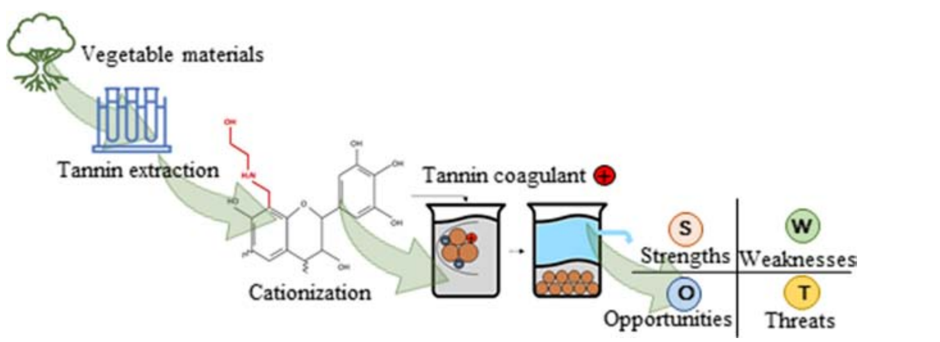
Isabella T. Tomasi, Cláudia A. Machado, Rui A.R. Boaventura, Cidália M.S. Botelho *, Sílvia C.R. Santos

LSRE-LCM - Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
ALiCE - Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

HIGHLIGHTS

- Tannin-based (TB) coagulants have been used successfully.
- TB coagulants are synthesized from wastes/by-products from fruits and plants sources.
- There is a need to find greener procedures for synthesis.
- Research is needed to turn the use more economically attractive.
- SWOT analysis on production and application of tannin coagulants

GRAPHICAL ABSTRACT



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ABSTRACT

Population growth, industrialization, urbanization, and agriculture lead to a decrease in the availability of clean water. Coagulation/flocculation is one of the most common operations in water, urban wastewater, and industrial effluents treatment systems. Usually, this process is achieved using conventional coagulants that have their performance affected by pH, are poorly biodegradable, produce a huge volume of sludge, and are associated with degenerative diseases. As a substitute for these chemicals, natural coagulants have been highly researched for the last ten/fifteen years, especially the tannin-based (TB) ones. This review paper highlights the advantages of using these greener products to treat different types of water, wastewater, and effluents, especially from dairy, cosmetics, laundries, textile, and other industries. TB coagulants can successfully remove turbidity, color, suspended solids, soluble organic (chemical/biochemical oxygen demand) and inorganic matter (total phosphate, and heavy metals), and microorganisms. TB coagulants are compatible with other treatment technologies and can be used as coagulant-aid to reduce the consumption of chemicals. TB coagulants can reduce operating costs of water treatment due to less alkalinity consumption, as pH adjustment is sometimes unnecessary, and the production of a smaller volume of biodegradable sludge. TB coagulants can be synthesized by valorizing wastes/by-products, from the bark of some specific trees and skins/pomace of different fruits and vegetables. The strengths, weaknesses, opportunities, and threats (SWOT) on TB coagulants are discussed. The progress of TB coagulants is promising, but some threats should be overcome, especially on tannin extraction and cationization. The market competition with conventional coagulants, the feasibility of application in real waters, and the reluctance of the industries to adapt to new technologies are other weaknesses to be surpassed.

* Corresponding author.
E-mail address: cbotelho@fe.up.pt (C.M.S. Botelho).

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Contents

Nomenclature

AB	Acid Black dye
Adv	adenovirus
AF	anionic flocculant
CF	cationic flocculant
CE	catechin equivalent
COD	chemical oxygen demand
CT	condensed tannins
CV	Crystal Violet dye
Cya	cyanidin equivalent
Cy3-glc	cyanidin-3-glycoside
$[C_2mim][Br]$	Ionic Liquid, 1-ethyl-3-methylimidazolium bromide
$[C_4mim][Br]$	Ionic Liquid, 1-butyl-3-methylimidazolium bromide
DB	Direct Blue dye
DEA	diethanolamine
DMA	dimethylamine hydrochloride
DOC	dissolved organic carbon
DR	Direct Red dye
EE	epicatechin equivalent
ETA	ethanolamine
FC	fecal coliforms
FS	fecal streptococcus
GAE	gallic acid equivalent
g-e	gram of extract, dry basis
g-s	gram of starting material (tannin source), dry basis
GT	gallotannins
HT	hydrolysable tannin
HTC	hydrolysable tannin content
MB	Methylene blue dye
MS	Mannich solution
PA	proanthocyanins
PAM	polyacrylamides
POME	palm oil mill effluent
QE	quercetin equivalent
QTE	purified Quebracho tannin equivalent
SN	Stiasny number
SWOT	Strengths, Weaknesses, Opportunities, and Threats
TA	total anthocyanins
TAE	tannic acid equivalent
TC	total coliforms
TCT	total condensed tannins
TDS	total dissolved solids
TFC	total flavonoids content
TOC	total organic carbon
TPC	total phenolic content
TS	total solids
TSS	total suspended solids
TTC	total tannins content
Turb	turbidity

1. Introduction

The demands for freshwater have been growing, but water resources are increasingly under stress due to excessive use, pollution, and climate changes (WWAP, 2017). Climate change is caused by human activities, such as the use of fossil fuels, agriculture, deforestation, and urban and industrial activities, and by natural drivers (Akmal et al., 2021). The impacts of climate change have been discussed in the literature (Waqas et al., 2021; Fahad et al., 2021a,b) and further challenge water availability. Water scarcity is expected to increase due to the global warming, intensity and frequency of precipitation (Waqas et al., 2021).

It is estimated that nearly 80% of wastewater is returned to waterways without adequate treatment (WWAP, 2017). Ensuring the availability and sustainable management of water and sanitation for all is one of the 17 Sustainable Development Goals adopted by United Nations Member States in the 2030 Agenda (UN, 2015). Promoting water treatment, recycling and reuse provides advantages related to the release of emerging pollutants, antibiotic resistant genes (Tzanakakis et al., 2020), and pathogens, especially nowadays, while the world is facing the SARS-CoV-2 pandemic (Lesimple et al., 2020). To conserve the availability of clean water sources, cost-effective and eco-friendly treatment technologies have been researched.

Coagulation/flocculation are essential operations in water and wastewater treatment plants and industrial effluents treatment systems. The coagulation process involves destabilizing the colloidal particles by using a coagulant, usually with the opposite chemical charge, added under rapid mixing. The coagulant agglomerates the colloidal particles, which subsequently form heavier and settleable flocs (flocculation) under gentle stirring, directly or through the use of a flocculant. The flocs are then separated from the liquid phase by sedimentation, filtration, or flotation.

Coagulation/Flocculation technology has been considered one of the simplest and cost-effective approaches to remove colloidal and suspended impurities from water (Ang and Mohammad, 2020). Coagulation/flocculation has found application on drinking-water production (Matilainen et al., 2010; Sillanpää et al., 2018; Ma et al., 2019; Lapointe et al., 2020), treatment of municipal wastewater (Schmitt et al., 2021) and on the remediation of effluents generated in numerous activities such as textile dyeing (Aleem et al., 2020; Dotto et al., 2019; Masmoudi et al., 2016), tanning (El-Khateeb et al., 2021), food processing (Amin et al., 2021), solid waste landfilling (Kamaruddin et al., 2017; Amor et al., 2015), agriculture and aquaculture (Teh et al., 2016). The technique has also been investigated on the removal of antibiotic resistance genes (Li et al., 2017; Yu et al., 2021) microplastics from water (Ma et al., 2019; Lapointe et al., 2020) and to harvest microalgae (Roselet et al., 2016). The technique can be used as primary or tertiary treatment (Duan et al., 2010; Kamali and Khodaparast, 2015), or even as a post-treatment (Bashir et al., 2019) process.

The conventional coagulants used in coagulation/flocculation include aluminum and iron salts (such as alum, ferric sulfate, ferric chloride), pre-hydrolyzed salts (e.g., PAC), and synthetic organic polymers (e.g., polyacrylamide) (Tchobanoglous et al., 2002). Metal-based coagulants produce a large volume of sludge, and their performance is strongly affected by pH, which increases operating costs. Al-coagulants, in particular, have been associated with neurodegenerative and Alzheimer's diseases (Wang et al., 2016). Synthetic polymers are expensive, poorly biodegradable, and monomer residues represent a health hazard (Siah Lee et al., 2014).

As an alternative to these conventional chemicals, some eco-friendly coagulants have been researched. Natural coagulants aim to comply with the goals of green technology and sustainable development (Oladoja, 2015). The most attractive advantages of these coagulants are related to their origin from renewable resources, biodegradability, non-toxic and non-corrosive properties, and expected interesting cost-effectiveness (Saleem and Bachmann, 2019). Natural coagulants can be obtained from bacteria, fungi, animals, and plants, produce a smaller volume of biodegradable sludge, and their performance is less affected by water pH (Mohd-Salleh et al., 2019).

The production of natural coagulants is a growing research topic, and plant-based ones are in a higher focus. Among the plants, *Moringa oleifera*, cactus, okra, and mango are the most investigated bio-coagulants/flocculants sources (Othmani et al., 2020). Tannin-based coagulants, in particular, are getting attention due to the successful removal of turbidity, color, suspended solids, chemical oxygen demand, total phosphate, algae, and heavy metals (Hameed et al., 2016, 2018). *Acacia mearnsii*, Quebracho, and *Castanea sativa* have been highly investigated to produce tannin-based coagulants (Beltrán-Heredia et al., 2011; Grenda et al., 2020; Šćiban et al., 2009). Tannins are abundant in nature, are easily chemically modified, and can play a crucial role in developing the bioeconomy of forest regions (Pagliaro et al., 2021). Tannins are excellent hydrogen donors and present an anionic nature due to the deprotonation of the abundant phenolic groups and delocalization of electrons within the aromatic ring (Yin, 2010). Due to tannin's anionic nature and because most of the colloidal particles present in water/wastewater have anionic characteristics, the preparation of tannin-based coagulants usually involves a modification process known as cationization.

Some of the tannin-derived coagulants have already been commercialized for water and effluents treatment. TANAC Company (Brazil) developed the *Tanfloc* line, composed of a diverse range of eco-friendly products, such as *Tanfloc SG* and *Tanfloc SL*, obtained from the extraction of *Acacia mearnsii* and modified by *Mannich* reaction (Sánchez-Martín et al., 2010a). Other companies produce tannin-derived coagulants from *A. mearnsii*, for example, SETA company (Brazil), which developed *Acquapol* and *Polyacqua* (flocculant) (SETA Company, 2020), and Servyeco (Spain), which has been commercializing *Ecotan* (Servyeco, 2020). Silvateam (Italy) produces *SilvaFLOC*, a tannin-derived coagulant from *Schinopsis balansae*, known as Quebracho (Sánchez-Martín et al., 2014). WaterChem Pte Ltd. (Singapore) introduced *Organo-Floc™*.

The global coagulants and flocculants market has been growing, and tannin-derived coagulants have been capturing attention from scientists and companies. Motivated by the positive results on the use of plant-based coagulants in water treatment, this review paper aims to present and discuss the preparation (extraction and synthesis methods), application, performance, and sustainability of tannin-based coagulants derived from vegetable species.

2. Synthesis of tannin-based coagulants

2.1. Tannins

Tannins are polyphenolic compounds containing an extensive family of secondary metabolites, such as esters or glycosides, stored in vacuoles of vegetable cells (Fraga-Corral et al., 2020). They can be found in wood, the bark of trees, leaves, buds, stems, fruits, seeds, roots, and plant galls. They are polycyclic aromatics compounds with high molecular weight (Thakur and Choubey, 2014) ranging between 500 and 3000 g mol^{-1} and divided into three kinds: hydrolyzable, condensed, and complex tannins (Arbenz and Avérous, 2015). It has been suggested that a higher content of phenolic groups increases tannins coagulation ability (Ibrahim et al., 2021), and species with a higher condensed tannins content show a higher percentage of total polyphenols (Grasel et al., 2016).

2.2. Tannin extraction

The tannin presence in vegetable species depends on the geography, biological origin, species, populations, age, and specific location in the plant (Puech et al., 1999; Pizzi, 1980). Since tannins can be obtained from various plants, their chemical structures are complex and diverse, and a single extraction protocol may not be suitable for all cases and extraction purposes (Das et al., 2020).

There are several methods to extract bioactive compounds from vegetable sources, such as solid-liquid extraction (SLE), pressurized liquid extraction (PLE), supercritical fluid extraction (SFE), microwave-assisted extraction (MAE), and ultrasound-assisted extraction (UAE). The extraction principles, merits, and demerits have been reviewed by Ameer et al. (2017) and Zhang et al. (2018), and the extraction of tannins, in particular, has been covered by de Hoyos-Martínez et al. (2019). However, most of the literature is directed to the obtention of bioactive compounds for pharmaceutical and food industries. The present section presents a brief update of recent literature regarding tannins extraction and directing the data collected to coagulants production. The best extraction technique should be selected on a case-specific basis. The subsequent steps (air-drying, oven-drying, or freeze-drying), necessary to concentrate the extracts and avoid their degradation, should also be considered in the decision process, as the drying method has been considered the primary contributor to the environmental impact of tannin production (Ding et al., 2017). The work conducted by Bacelo et al. (2018) shows that a freeze-dried extract could present a 65% higher total phenols content (TPC) than an air-dried (evaporated) tannin extract, and also a higher content of formaldehyde condensable phenols. Bello et al. (2020) compared spruce bark tannins obtained by spray and freeze-drying and considered the former a more suitable method, considering that freeze-drying is a much slower operation and a prolonged pulverization might impair the product quality.

2.2.1. Solid-liquid extraction (SLE)

SLE includes the most conventional methods to extract polyphenols, such as Soxhlet extraction and maceration. Various organic solvents have been used over the years to extract tannins from a wide variety of plants, such as methanol, ethanol, and acetone (Pereira et al., 2003; Markom et al., 2007; Vijayalaxmi et al., 2015; Conde et al., 1996; Saad et al., 2012; Meregalli et al., 2020; Aspé and Fernández, 2011) considering the toxicity, flammability, and the management of resulting residues, scientific attention has been turned to greener SLE procedures involving water (or aqueous media) and ionic liquids (de Hoyos-Martínez et al., 2019).

The ionic liquids (Ils) are an alternative to the traditional organic solvents due to their thermal stability, negligible vapor pressure, and ability to dissolve many compounds present in plants. Ils are salts in the liquid state that consist of organic cations paired with organic or inorganic anions. Ćurko et al. (2017) employed eight different types of imidazolium-based Ils in flavonoids extraction from the grape skin. Results obtained with Br^- paired with C_2-C_{10} chains showed a remarkable impact of the alkyl chain length on the extraction of proanthocyanins, which has increased from ethyl to butyl, and drastically decreased from butyl to decyl. In general, extraction yields of total proanthocyanins were significantly enhanced when Ils concentrations increased. Some Ils were even able to extract higher concentrations of total proanthocyanins than methanol.

The SLE process is affected by the solvent nature, temperature, solid:liquid ratio (S/L), extraction time, stirring rate, and the number of extraction cycles. Regarding aqueous extractions, it is well established in the literature that alkaline conditions increase the extraction yields as avoid self-condensation of tannins, which are promoted at acidic media (de Hoyos-Martínez et al., 2019). NaOH, Na_2CO_3, and Na_2SO_3 have been added to water at levels up to 10% concentrations (w/w percentages, related to the starting material) to provide the required pH conditions. Several works show that extraction yields increase with salt concentrations (Bacelo et al., 2020; Seabra et al., 2018; Low et al., 2015). Antwi-Boasiako and Animapauh (2012), for instance, reported a 5-fold increase in the extraction yield obtained from *T. tetraptera* bark when NaOH 1% was added to water. NaOH seems to provide much higher extraction yields than Na_2SO_3, as observed in chestnut peels extraction (Aires et al., 2016). The increase of the extraction yield with increasing NaOH concentration has been explained by polysaccharides extraction (e.g., hemicelluloses) and partial lignin solubility in alkaline solutions, which appear in alkaline aqueous extracts (Seabra et al., 2018). The optimization of the amount of salt used in SLE is then necessary, as its excessive use decreases the selectivity of the operation and the quality of the tannin extracts (containing non-tannin compounds and the employed salts), leading also to a difficult pH neutralization of the aqueous extract (Bacelo et al., 2020). Indeed, the results obtained by Aires et al. (2016) showed that the highest amounts of condensable phenols (represented by the Stiasny Index) were in the extracts obtained at the lowest NaOH concentrations. Bacelo et al. (2020) reported a 17% lower phenolic content on *P. pinaster* bark extract obtained at 10% NaOH, compared to the one obtained at 2.5% solute dosage. Optimization of the extraction conditions should take both extraction yield and reactivity into consideration (Low et al., 2015).

In general, higher temperatures increase extraction yields in SLE (Low et al., 2015). In many procedures (particularly Soxhlet extractions), the temperature is set up at the solvent boiling point (de Hoyos-Martínez et al., 2019). However, regarding aqueous extractions, not consistently the best results are found at higher temperatures. Arina and Harisun (2019) studied tannins extraction from *Q. infectoria* (Manjakani) galls using water at 50, 75 and 100 °C. The highest tannin concentration was recorded at 75 °C, and is 27% above the value recorded at 50 °C, and close to the value observed at 100 °C. Bacelo et al. (2020) did not find a significant impact of temperature in the range 70–90 °C in tannins extraction from *P. pinaster* bark using NaOH 5% solution.

In SLE, S/L ranging from 1:20 to 1:6 has been usually applied. A lower S/L usually provides higher extraction yields since higher amounts of solvent are employed to solubilize the extracted compounds but require additional energy in the subsequent drying of the high amount of solvent in the extract. High solvent consumption is indeed one of the main disadvantages of SLE.

Considering the diffusional and mass transfer phenomena, at least up to the equilibrium state, higher contact times are expected to favor the extraction of compounds from a plant matrix. However, excessive exposure to heat, light, and oxygen can cause the oxidation of phenolics with consequences for the tannin content and properties of the extract. Aires et al. (2016) observed an increase in the extraction yields and Stiasny Number when water was used as a solvent, and extraction times varied from 30 min to 480 min. However, when Na_2SO_3 and NaOH solutions were used, very slight and no consistent variations were observed with the time. Marginal effects were also reported by Bacelo et al. (2020) and Low et al. (2015) when extraction time was raised from 60 to 90 min. Even so, the required time to maximize extraction efficiency by SLE is usually considerable (particularly for Soxhlet extraction), which has implications in the energy consumption and is another disadvantage of these extraction techniques.

Table 1 presents an overview of conditions and results from the literature on SLE of tannins from different vegetable sources and using different solvents. Results of extraction yield (η) and amount of tannin extracts, expressed per gram of tannin source or dried extract, were collected.

2.2.2. Pressurized Liquid Extraction (PLE)

Pressurized Liquid Extraction (PLE) is a technique that uses elevated pressures to maintain the solvent in the liquid state above its normal boiling point (Wianowska and Gil, 2019). The technique is an alternative to SLE and the Soxhlet apparatus, which operate under atmospheric pressure. In PLE, the elevated temperatures increase solubility and mass transfer rates between the solid and the liquid phases and decrease extractant viscosity, resulting in an enhanced wetting of the solid and higher solubility of the targeted compounds (Ameer et al., 2017). In addition, the breakage of

Table 1
Conditions and results reported in the literature for polyphenols extraction from different tannin sources by SLE.

Tannin source	Solvent	S/L	t (min)	T (°C)	η (%)	Tannin content	Ref.
Phyllanthus amarus aerial parts	H_2O	1:200	30	80–90	–	TPC: 42.78 mg/g-s	(Sousa et al., 2016)
Carob (*Ceratonia siliqua*) kibbles	EtOH 45%	1:30	120	–	–	TPC: 69.87 mg-GAE/g-s TTC: 4.22 mg-CE/g-s	(Huma et al., 2018)
Spent coffee grounds	H_2O + 5% NaOH	1: 8.2	30	100	21.02	SN: 29.69%	(Low et al., 2015)
Chestnut peels (*Castanea sativa*)	H_2O	4:1	480	85	7.55	SN: 30.80%	(Aires et al., 2016)
	H_2O + 1% Na_2SO_3	4:1	960	85	6.63	SN: 86.27% CT: 509 μg/g-s	
	H_2O + 1% NaOH	4:1	240	85	11.63	SN: 72.87% HT: 4971 μg/g-s	
Olive fruits (*Olea europaea L*)	MetOH 80%	1:24	282	50	–	TPC: 5.18 mg-GAE/g-s	(Deng et al., 2017)
Grape skin (*Vitis vinifera*)	[C2mim][Br] 2.5 M	1:25	240	RT	–	TA: 17.9 mg/g-s TCT: 129.9 mg/g-s	(Ćurko et al., 2017)
	[C4mim][Br] 2.5 M	1:25	240	RT	–	TA: 15.9 mg/g-s TCT: 137.0 mg/g-s	
Manjakani galls (*Quercus infectoria*)	H_2O	1:20	120	75	–	TC: 2233,82 mg-TAE/g-e	(Arina and Harisun, 2019)
Spruce bark (*Picea abies*)	H_2O	1:10	120	85	–	PA: 17.3 mg/g-e	(Bello et al., 2020)
Cacao (*Theobroma cacao* L.) pod husk	EtOH	1:30	150	RT	0.35	TPC: 23.2 mg-GAE/g-e	(Valadez-Carmona et al., 2018)
Sage (*Salvia officinalis* L.) herbal dust	MetOH	1:10	24 h	25	19.83	–	(Pavlić et al., 2016)

dipole-dipole, van der Waals, and hydrogen-bonding facilitates the diffusion of phenolic compounds to the outer surfaces of plant matrices (Ameer et al., 2017). More details on extraction principles and equipment available can be obtained from Wianowska and Gil (2019). In the case of using water as the solvent, PLE is named as PHWE (Pressurized Hot Water Extraction) or subcritical water extraction (SWE).

In general, higher temperatures improve PHWE kinetics and yields. Kovačević et al. (2018), for instance, analyzed the extracts of *Stevia rebaudiana* leaves obtained by PHWE at 100, 130, and 160 °C, and reported greater extraction of most of the bioactive compounds at the highest temperature tested. However, the excessive temperature may also decrease the selectivity of the extraction and cause degradation of analytes and the occurrence of chemical reactions, such as the hydrolysis of polysaccharides and proteins, catalyzed by the higher abundance of H_3O^+ and OH^- ions (Plaza and Turner, 2015). Depending on the substrate and other conditions, suitable temperatures usually fall in the range of 100–180 °C (Pagano et al., 2021). Erşan et al. (2018), for instance, obtained extracts from Pistachio hulls at 6.9 MPa and temperatures ranging from 110 to 190 °C. Maximum yield was observed at 150 °C, remaining widely unchanged between 150 and 190 °C, and the amount of total extracted phenols slightly raised from 110 to 150 °C, but declined when temperature raised from 170 to 190 °C. Ravber et al. (2015) suggest that in the PHWE of larch wood bark, the effects of hydrothermal degradation reactions begin to take place at temperatures higher than 200 °C and water-insoluble compounds (e.g., hemicellulose, cellulose) depolymerize into soluble products transferred to the extract. Excessive extraction time can also negatively affect the extraction efficiency. Ravber et al. (2015) report that most of the extraction yield value obtained in semi-continuous PHWE of larch wood bark is attained in the first 40 min. However, the total phenols content decreased right after 20 min of extraction since other products are probably extracted or formed. To increase tannin concentration and obtain fewer non-tannin compounds (including sugars) in extracts, Ding et al. (2017) proposed a cold-water extraction before a sequence of PHWE steps and ultrafiltration after the extraction. The authors have also investigated the impact of successive hot water extractions using fresh water at each cycle. After two extraction steps, more than nearly 75% of the cumulative extraction yield and cumulative tannin yield (obtained in the four extraction steps) were recorded.

The main parameters influencing extraction efficiency are temperature, extraction time, solid-to-liquid ratio, flow rates, and modifiers/additives. Table 2 summarizes PLE conditions and results obtained from the literature for different vegetable species.

2.2.3. Supercritical fluid extraction (SFE)

The SFE uses fluids above critical pressures and temperatures, conditions in which they present properties of both liquids and gases (Pagano et al., 2021). Supercritical CO_2 is the most widely used solvent in SFE due to its non-toxic, non-flammable, and non-corrosive properties, availability and cost, and easily achievable critical point (31.1 °C; 7.38 MPa) (Talmaciu et al., 2016). However, considering that CO_2 is a non-polar compound, the addition of small amounts of a co-solvent is usually required to improve the extraction of polar compounds (de Hoyos-Martínez et al., 2019; Talmaciu et al., 2016). Water is not commonly used as a co-solvent due to the non-solubility in CO_2. Ethanol has been the co-solvent of choice (Talmaciu et al., 2016; Ferrentino et al., 2018) possibly because of its acceptance in the pharmaceutical and food industries (Valadez-Carmona et al., 2018). Among the factors affecting SFE, the co-solvent composition is the variable that most influences the extraction efficiency of phenolic compounds (Talmaciu et al., 2016; Ferrentino et al., 2018). Ferrentino et al. (2018) compared extraction results from apple pomace by SFE in the presence and absence of ethanol. Higher yields, total phenols content, and antioxidant activity were obtained with the use of the co-solvent. Extracts obtained with ethanol from freeze-dried pomace presented 37–45% higher phenolic contents than those obtained in the absence of co-solvent. Ethanol increases the polarity of CO_2 and enhances the solute solubility due to the hydroxyl group in its chemical structure and the possible establishment of hydrogen bonds with the matrix. The extraction yields and recovery of phenolic compounds can be improved if a previous extraction using only supercritical CO_2 is used to remove lipophilic compounds (Talmaciu et al., 2016).

Temperature, pressure, and time are other variables affecting SFE. The typical temperatures and pressures used in SFE are in the ranges of 40–90 °C and 10–65.5 MPa, respectively (de Hoyos-Martínez et al., 2019; Pagano et al., 2021). Several works report that temperature does not significantly affect the extraction yields in the referred range (Talmaciu et al., 2016; Ferrentino et al., 2018), although extracts obtained at 60 °C present higher TPC and TTC than those obtained at 40 °C. A minor effect of the extraction pressure (100–200 bar) was reported in the isolation of bioactive compounds from spruce bark waste (Talmaciu et al., 2016), but in the polyphenols extraction from cacao pod husk, higher pressures (100–300 bar) improved the extraction yields (Valadez-Carmona et al., 2018).

Ferrentino et al. (2018) compared SFE with conventional SLE techniques, such as Soxhlet extraction with ethanol and boiling water maceration. SFE provided much lower extraction yields, but higher recoveries of

Table 2
Conditions and results reported in the literature for polyphenols extraction from different tannin sources by PLE and PHWE.

Tannin source	Type	Solvent	Flow rate[c]	S/L	t (min)	T (°C) – P (bar)	η (%)	Tannin content	Ref.
Larch wood bark	Batch	H_2O	2	–	30	100–20	10.60	TPC: 60 mg-GAE/g-e	(Ravber et al., 2015)
	Semi-continuous PHWE	H_2O	2	–	90	150–20	≈ 24	TPC: 484 mg-GAE/g-e	
	Semi-continuous PHWE	H_2O	2	–	20	300–100	≈ 4	TPC: 900 mg-GAE/g-e	
Sage (*Salvia officinalis* L.) herbal dust	Batch	H_2O	–	1:10	15.8	201.5–30	–	TPC: 79.8 mg-GAE/g-s TFC: 49.3 mg-CE/g-s	(Pavlić et al., 2016)
		H_2O + 1.5% HCl	–	1:10	20	120–30	45.48	TPC: 41.7 mg-GAE/g-s TFC: 17.7 mg-CE/g-s	
Phyllanthus amarus aerial parts	–	H_2O	–	1:24	15	192.4–103-117	–	TPC: 52.97 mg/g-s	(Sousa et al., 2016)
Spruce (*Picea abies Karst.*) bark	PHWE[a]	H_2O	–	1:9	20	90–100	7.85	TPC: 489 mg-QTE/g-e	(Ding et al., 2017)
		H_2O	–	1:9	20	90–100	6.84	TPC: 558 mg-QTE/g-e	
Bertoni (*Stevia rebaudiana*) leaves	Static extraction[b]	H_2O	–	–	10	160–103.4	–	TPC: 8.54 mg-GAE/g-s CT: 1.84 mg-CE/g-s	(Kovačević et al., 2018)
Pistachio (*Pistacia vera L.*) hulls	Semi-continuous PHWE	H_2O	4	–	30	150–69	70.9	TPC: 39.5 mg/g-s TPC: 5.84 mg/g-e GT: 45.84 mg-GT/g-e GT: 32.5 mg/g-s	(Erşan et al., 2018)
Phyllanthus tenellus leaves	Static extraction	H_2O	–	1:20	20	121–1	21.05	–	(Pavlić et al., 2016)

[a] Preliminary cold water extraction, 3 steps of PHWE.
[b] 1 cycle.
[c] mL/min.

Table 3
Conditions and results reported in the literature for polyphenols extraction from different tannin sources by SFE.

Tannin source	Fluid	Co-solvent	t (min)	T (°C) – P (bar)	η (%)	Tannin content	Ref.
Tea (*Camellia sinensis L.*) leaves	CO_2 8 g/min	EtOH 2.94 g/min	60	50–188	–	TPC: 131.24 mg-GAE/L-e TTC: 499,9 mg-TAE/L-e	(Maran et al., 2015)
Apple pomace	CO_2 2 L/h	EtOH 5% w/w	60 (static) + 60 (dynamic)	45–300	6.68	TPC: 8.76 mg-GAE/g-e	(Ferrentino et al., 2018)
Merlot grape pomace	CO_2 2 mL/min	EtOH 0.4 mL/min	–	60–250	–	TPC: 0.570 mg-GAE/g-s	(Aresta et al., 2020)
Merlot grape skins			–	60–250	–	TPC: 0.603 mg-GAE/g-s	
Merlot grape Seeds			–	60–250	–	TPC: 0.336 mg-GAE/g-s	
Cacao (*Theobroma cacao* L.) pod husk	CO_2 6 L/min	EtOH 13.7%	–	60–299	0.52	TPC: 12.97 mg GAE/g-e	(Valadez-Carmona et al., 2018)
Brown skin onion bulbs (*Allium cepa* L.)	CO_2 10 mL/min	EtOH 85% v/v 0.5 mL/min	120	40–100	16	–	(Campone et al., 2018)
Spruce (*Picea abies*) bark	CO_2 250 mL/min	EtOH 70% v/v 1.2 mL/min	15	40–100	–	TPC: 679.26 mg-GAE/g-e TFC: 120.40 mg-QE/g-e TTC: 129.94 mg-TAE/g-e	(Talmaciu et al., 2016)
	CO_2 250 mL/min	EtOH 70% v/v 2.5 mL/min	–	40–100	30.46	TPC: 314.49 mg-GAE/g-e TFC: 100.67 mg-QE/g-e TTC: 26,38 mg-TAE/g-e	

phenolic compounds (TPC values 8.76 mg-GAE/g extracts, versus 4.13 and 2.37 mg-GAE/g extract for the Soxhlet and boiling water extractions).

Table 3 presents some data on SFE collected from the literature.

2.2.4. Microwave-assisted extraction (MAE)

MAE combines traditional solvents for tannins extraction with fast heating in the microwave (de Hoyos-Martínez et al., 2019; Huma et al., 2018). The polar molecules, such as polyphenols, strongly absorb microwave energy due to their permanent dipole moment, resulting in a rapid rise of temperature and fast extraction (Ajila et al., 2011). The efficiency of MAE depends on the solvent, microwave power, time, temperature, and solvent to sample ratio. Compared to conventional techniques, MAE allows for a shorter extraction time, typically 1–20 min (de Hoyos-Martínez et al., 2019), and lower solvent consumption, being the high cost the main disadvantage (Dahmoune et al., 2015). Huma et al. (2018) report similar TPC, and condensed tannin contents in extracts of carob (*Ceratonia siliqua*) kibbles obtained by MAE and conventional extraction using 45% ethanol but in a lower extraction time in MAE (4.5 min, versus 2 h). Dahmoune et al. (2015) recorded a higher tannin content in extracts of *Myrtus communis* L. leaves obtained by MAE than by UAE and SLE.

Increasing concentrations of ethanol up to 40% led to higher TPC in extracts, but above 60%, a decline was recorded (Dahmoune et al., 2015). Quite similar observations were reported in MAE from carob kibbles (Huma et al., 2018). TPC and condensed tannins yields increased with an increase in ethanol concentrations up to 45–55% but started to decrease up to ≈90%. This was explained by protein denaturation at high ethanol concentrations, less solvent penetration into the plant matrix, and lower solubility of some extractable phenolics.

The rise in microwave power usually increases in amounts of polyphenols extracted (Dahmoune et al., 2015; Sharma et al., 2020), due to the better solvent penetration into the matrix and the faster energy transfer to the solvent and material. However, above certain levels of microwave irradiation, a decline in the extraction performance may be recorded due to the thermal degradation of phytochemicals (de Hoyos-Martínez et al., 2019), which has been reported above 540 W–600 W (Dahmoune et al., 2015; Sharma et al., 2020). The effect of microwave power is related to the temperature generated (not always reported or possible to be measured). Huma et al. (2018), for instance, reported no significant impact of microwave power in the range 170–900 W in MAE from carob kibbles, as all the experiments were exposed to boiling points of solvent mixtures, with minor temperature differences.

Sharma et al. (2020) studied the influence of pH (3.5–5.5), microwave power (360–720 W), and time (30–90 s) on the extraction of bioactive compounds from fruits of *Ficus racemosa* using water as solvent. The increase in pH generally favored tannin extraction, and within the combination of conditions tested, maximum tannins in the liquid extract (97.13 mg/100 mL) were found at pH 4.5, 540 W, and 110.45 s (S/L 1:15). Table 4 presents some results collected from the literature related to this extraction technique.

2.2.5. Ultrasound-assisted extraction (UAE)

The UAE technique uses ultrasonic energy (>20 kHz) to provide the formation, growth and collapse of cavitation bubbles inside a liquid phase, generating instantaneous high pressure and temperature (Pagano et al., 2021). Cavitation facilitates the disruption of plant cell walls and the leaching of compounds from the solid by increasing the mass transfer rate (Pagano et al., 2021). The solvent is mixed with the plant sample and sonicated for a certain time and at a specific temperature, employing continuous or pulsed ultrasound-assisted extractions. UAE has been studied for polyphenols extraction, with some examples presented in Table 5. It has been considered an economically viable method, requiring low extraction time and energy (de Hoyos-Martínez et al., 2019). In addition, some authors claim a superior performance of UAE compared to SLE in extraction yields, and tannins (Peanparkdee et al., 2018; Nisca et al., 2021). For instance, UAE provided an increase of 12% in anthocyanins extracted from red araçá peel and a 25% reduction in extraction time compared to maceration (Meregalli et al., 2020).

The extraction solvent significantly affects the UAE of polyphenols. Irakli et al. (2018) investigated different solvents (water; ethanol, methanol, and acetone aqueous solutions) to extract phenolics from olive leaves and reported that 50% v/v acetone extracted more ≈37% phenolics than water, whereas ethanol and methanol 50% v/v solutions presented intermediate efficiencies. Ethanol has been, however, the solvent of choice for UAE. Nonetheless, and in the pursuit of a greener procedure, the combined use of UAE with water (100%) has been considered, and extracts with high phenolic compounds and strong antioxidant activity were obtained from olive pomace (Goldsmith et al., 2018).

To take full advantage of UAE, extraction conditions should be optimized (ben Alaya et al., 2021). Optimization is usually based on response surface methodology and includes variables such as the solvent type and concentration, ultrasonic power, temperature, extraction time, and solid-to-liquid ratio. All these variables have a significant effect on polyphenols extraction efficiency (ben Alaya et al., 2021), but solvent concentration has presented the greatest influence (ben Alaya et al., 2021; Riciputi et al., 2018). Optimization studies have pointed to ethanol ideal concentrations in the range 40%–65% (Irakli et al., 2018; ben Alaya et al., 2021; Riciputi et al., 2018).

Ultrasonic power usually presents a positive relationship with TPC, but excessive levels may degrade the phenolic compounds. Powers ranging from 5 to 500 W have been investigated in UAE, and optimum values usually fall near 250 W (ben Alaya et al., 2021). Regarding temperature, Meregalli et al. (2020) studied the range 5–75 °C and reported the highest

Table 4
Conditions and results reported in the literature for polyphenols extraction from different tannin sources by MAE.

Tannin source	Solvent	S/L	Power (W)	T (°C)	t (min)	η (%)	Tannin content	Ref.
Myrtus communis L. leaves	EtOH 42% v/v	1:32	500	–	1.03	–	TPC: 162.49 mg-GAE/g-s TT[c]: 32.65 mg/g-s TF: 5.02 mg-QE/g-s	(Dahmoune et al., 2015)
Maritime pine (*P. pinaster*) bark	EtOH 80% v/v	1:10[a]	100	–	180	9.24	TPC: 28.30 mg-GAE/g-s TPC: 306.147 mg-GAE/g-e	(Chupin et al., 2015)
	EtOH 80% v/v	1:10[b]	100	–	180	13.16	TPC: 39,52 mg-GAE/g-s	
Beech (*Fagus sylvatica L.*) bark	MetOH 80% v/v	1:100	–	120	20	–	TPC: 58.08 mg-QE/g-s	(Hofmann et al., 2015)
	EtOH 80% v/v	1:100	–	120	20	–	TPC: 65.22 mg-QE/g-s	
	H_2O	1:100	–	120	10	–	TPC: 57.14 mg-QE/g-s	
Moroccan *A. mollissima* bark	MetOH 80%	1:20	150	–	5	–	TPC: 442 mg-GAE/g-s TCT: 19.09 mg-Cya/g-s HTC: 0.085 mg-TAE/g-s	(Naima et al., 2015)
	H_2O	1:20	150	–	5	–	TPC: 99 mg-GAE/g-s TCT: 47.64 mg-Cya/g-s HTC: 0.090 mg-TAE/g-s	
Apple tree (*Malus domestica*) wood residues	EtOH 60% (v/v)	1:200	–	100	20	–	TPC: 39.60 mg-GAE/g-s	(Moreira et al., 2017)
Carob (*Ceratonia siliqua*) kibbles	EtOH 45% (v/v)	1:30	340	–	4.5	–	TPC: 70.11 mg-GAE/g-s CT: 4.11 mg-CE/g-s	(Huma et al., 2018)
Apple (*Malus domestica*) skins	EtOH 68% (v/v)	1:10	–	150	90	–	TPC: 50.4 mg-GAE/g-s TFC: 13.9 mg-CE/g-s	(Casazza et al., 2020)
	H_20	1:10	–	150	60		TPC: 25.5 mg-GAE/g-s TFC: 2.4 mg-CE/g-s	

[a] Particle size < 1 mm.
[b] Particle size 0.05–0.1 mm.
[c] Determination according to polyvinyl polypyrrolidone (PVPP) method.

TA contents in red araçá peels extracts obtained at 40–65 °C. Applying the best solvent and extraction time conditions to UAE of olive leaves, Irakli et al. (2018) observed only a 9% increase in TPC when extraction temperature changed from 25 to 60 °C.

As stated above, the short extraction time is one of the main UAE advantages. Indeed, optimization studies indicated 7 and 10 min (Irakli et al., 2018) as optimal times for UAE of phenolic compounds from *Phyllanthus amarus* and olive leaves, respectively (Sousa et al., 2016; Irakli et al., 2018). However, other works refer to extraction times of 30–90 min as the recommended ones to maximize extraction efficiency (Meregalli et al., 2020; Riciputi et al., 2018), extraction times are closely related to the other variables, such as the ultrasonic power used in the extraction. Higher contact time provides a higher degree of plant cell rupturing, enhancing the extraction of phenolic compounds, but also involves the risk of degradation (Meregalli et al., 2020; Irakli et al., 2018).

2.3. Synthesis of tannin coagulants

As already explained, tannins present an anionic behavior in aqueous solutions, and most colloidal particles in water and wastewater present this same characteristic. For this reason, tannins extracts should be subjected to a chemical modification to provide them a cationic character, imparting or improving their coagulant activity and keeping their solubility, stability, and chelating activity. There are some works using tannins as coagulants without cationization (Thakur and Choubey, 2014; Kukić et al., 2015; Putra et al., 2020). However, most of the coagulants reported in the literature, and the commercialized ones, had undergone this process (Ibrahim et al., 2021).

Mannich reactions have been followed for turning anionic groups in tannins into cationic ones. Tannins undergo *Mannich* aminomethylation by reaction with an aldehyde and an amine (Roux et al., 1975), as shown in Fig. 1.

Two main ways to obtain *Mannich* bases are reported in the literature: one involving ammonium chloride and another involving other types of nitrogen compounds (a primary or secondary amine) (Subramaniapillai, 2013), which causes aminomethylation of the substrate and forms the *Mannich* base (Arismendi et al., 2018). The reaction is completed by adding a tiny volume of formaldehyde, as excessive doses drive to gelification, turning the product insoluble (Pizzi, 1994).

The *Mannich* reaction begins with the aldehyde (typically formaldehyde) and amine, generating an iminium ion (Fig. 2, Eq. (1)), which is later added to the phenolic ring of the tannin by substituting the hydrogen of the aromatic structure (Fig. 2, Eq. (2)). After the

Table 5
Conditions and results reported in the literature for polyphenols extraction from different tannin sources by UAE.

Tannin source	Solvent	S/L	T (°C)	t (min)	Power/frequency	η (%)	Tannin content	Ref.
Phyllanthus amarus aerial parts	H_2O	1:40	25	7	301 W/cm^2	–	TPC: 27.23 mg-GAE/g-s	(Sousa et al., 2016)
Olive fruits (*Olea europaea L*)	MetOH 80%	1:22	47	30	240 W	–	TPC: 7.01 mg-GAE/g-s	(Deng et al., 2017)
Cannabis sativa L. flowers, leaves and seed husks	MetOH 80%	1:20		15	130 W	10.68	TPC: 312.452 mg-GAE/g-s TFC: 32.254 mg-QE/g-s	(Agarwal et al., 2018)
Olive pomace	H_2O	1:50	30	75	250 W	–	TPC: 19.71 mg-GAE/g-s	(Goldsmith et al., 2018)
Olive leaves	Acetone 50%	1:80	60	10	37 kHz	–	TPC: 37.44 mg-GAE/g-s	(Irakli et al., 2018)
Red araçá peel (*Psidium cattleianum* Sabine)	EtOH 90% pH 1.5 (HCl)	1:100		90	154 W–40 kHz	–	TA: 121.85 μg-Cy3-glc/g-s TPC: 589.49 μg-GAE/g-s	(Meregalli et al., 2020)
Riceberry bran	EtOH 65% v/v	1:20	51	40	43 KHz	46.58	TPC: 107.57 mg-GAE/g-s TA: ~87 μg-Cy3-glc/g-s	(Peanparkdee et al., 2018)
Chestnuts male flowers Male flowers (*Castanea sativa* Mill)	EtOH 51%	1:33	30	24	259 W	13	–	(ben Alaya et al., 2021)
Pinot noir grape pomace	EtOH 60%	1:30	70	20	300 W–37 kHz	–	TPC: 59.95 mg-GAE/g-s TTC: 79.93 mg-EE/g-s	(Zhao et al., 2021)

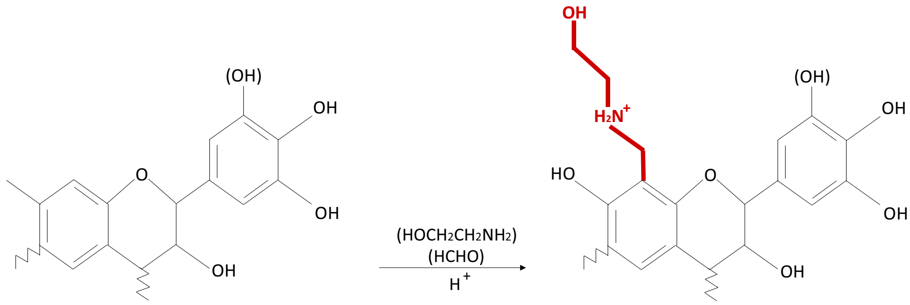

Fig. 1. The *Mannich* reaction with tannins (adapted from Arbenz and Avérous (2015)).

$$HCHO + HN\!< \longrightarrow \left[H_2C = \overset{+}{N}\!< \longleftrightarrow H_2\overset{+}{C} - N\!< \right] \quad (1)$$

$$\left[H_2C = \overset{+}{N} \longleftrightarrow H_2\overset{+}{C} - N\!< \right] + R - H \longrightarrow R - CH_2 - N\!< \quad (2)$$

Fig. 2. *Mannich* reaction: (1) iminium formation; (2) *Mannich* base formation (adapted from Beltrán-Heredia et al. (2012)).

aminomethylation step, acid conditions must be maintained to create the protonation of the amine attached to the tannin (Beltrán Heredia and Sánchez Martín, 2009; Sánchez-Martín et al., 2010b).

xAlthough the variations reported in the literature, procedures used to modify tannins commonly lie in two sequences of reactants addition (Fig. 3): (i) tannin-amine-formaldehyde sequence (procedure A), and (ii) previous reaction between the amine and formaldehyde (*Mannich* solution, MS) and later interaction with tannins (procedure B) (Arismendi et al., 2018). In addition to the coagulant ability (covered in the following chapters), properties such as the final viscosity and the charge density of the products are usually measured. Table 6 presents some conditions reported in the literature for the cationization of tannins from different sources. Diethanolamine (DEA), ethanolamine (ETA), and dimethylamine (DMA) are the most utilized amine sources, and formaldehyde (FA) completes the reaction. Infrared spectra of modified tannins demonstrate the formation of carbonyl and alkylammonium groups, which confirms that positively charged groups are added to the tannin backbone (Grenda et al., 2020; Bello et al., 2020; Grenda et al., 2018).

Grenda et al. (2018) employed a 10-step procedure to cationize *A. mearnsii* bark tannin extracts. The cationization took place for 1 h at 85 °C and the influence of MS activation time (15–240 min), FA/tannin ratio (0–0.06), and the heating rate (0.9 and 1.8 °C/min) on the shear viscosities (Table 6) of the resulting products was analyzed. The tannin coagulant viscosities (measured just after the production) increased when lower heating rates, higher FA/tannin ratios, and higher MS activation times were applied.

The effect of these variables on the shelf life was also studied. Cationic tannin-derived coagulants result from condensation reactions. The chain length and crosslinking between tannin molecules, formaldehyde, and *Mannich* base progress over time, leading to a thickening of the product during storage. Therefore, modified tannins with high viscosity, when freshly prepared, become more viscous with time, turning up to an insoluble gel and unfit as coagulants. In approximately two weeks, the authors observed that products with initial viscosities above 200 cP acquired a gel-type structure by aging very fast.

Decolorization results obtained in a tertiary system (bentonite, modified tannins, and polyacrylamides (PAM)) showed that tannin coagulants

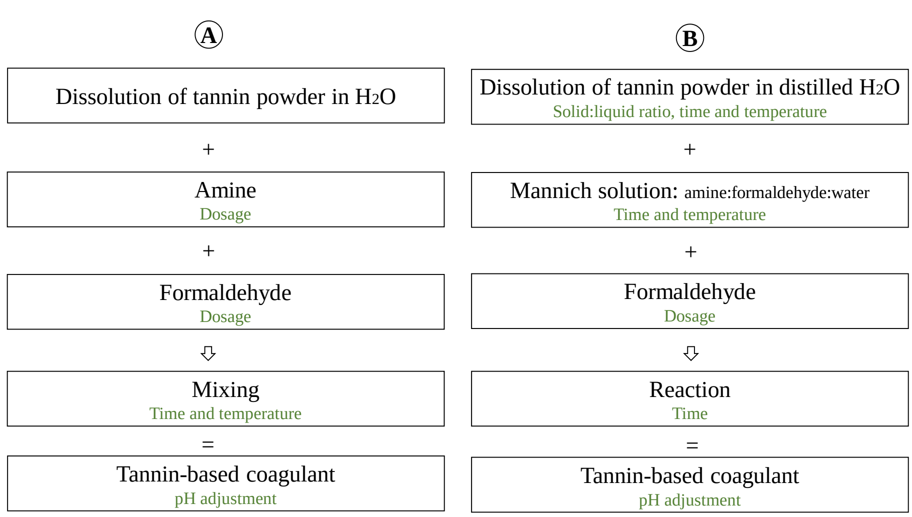

Fig. 3. Variations of *Mannich* reaction and the main studied factors.

Table 6
Mannich reaction conditions reported in literature for the cationization of tannins.

Extract	Amine	Aldehyde	Procedure	Properties[a]	Ref.
Spruce bark (*Picea abies*)	DEA	FA	A	0.83 meq/g[b]; 0.85 meq/g[c]	(Bello et al., 2020)
	ETA	FA	A	1.65 meq/g[b]; 1.88 meq/g[c]	(Bello et al., 2020)
Quebracho	DEA	FA	A	2.79 meq/g	(Bello et al., 2020)
	ETA	FA	A	3.84 meq/g	(Bello et al., 2020)
	DMA	FA	B	40 cP[b]	(Grenda et al., 2020)
	DEA or ETA	FA	A	–	(Arismendi et al., 2018)
	NH_4Cl	FA	B	–	(Arismendi et al., 2018)
	DEA	FA	A	–	(Sánchez-Martín et al., 2014)
Acacia mearnsii	DMA	FA	B	41cP[d]; 339cP[e]	(Grenda et al., 2020)
	DMA	FA	B	≈30–480 cP[f]	(Grenda et al., 2018)
	DEA or ETA	FA	A	–	(Arismendi et al., 2018)
	NH_4Cl	FA	B	–	(Arismendi et al., 2018)
	NH_4Cl	FA	B	–	(Lugo et al., 2020)
Castanea sativa	DEA or ETA	FA	A	–	(Arismendi et al., 2018)
	NH_4Cl	FA	B	–	(Arismendi et al., 2018)
L. gmelinni bark	DEA	FA	B	–	(Wang et al., 2013)

[a] Shear viscosity (cP) or charge density (meq/g).
[b] Freeze-dried extract.
[c] Spray-dried extract.
[d] Before acidification step.
[e] After acidification step.
[f] Range of values obtained for variable heating rate, FA/tannin ratios, and MS activation time.

with higher initial viscosity promoted higher color removal. However, reasonable color removal efficiencies were achieved even using low viscosity bio-coagulants (30 and 60 cP) (Grenda et al., 2018).

In further work (Grenda et al., 2020) the influence of final pH (1.6–3.4) on the shear viscosity of the coagulants was examined. The viscosity gradually decreased when the acidity increased, so the optimum final pH value was set as 1.6, which led to an initial viscosity of 49 cP. Viscosity values inferior to 50 cP guarantee a shelf life superior to 6 months (Grenda et al., 2020).

Bello et al. (2020) cationized spruce tannins extracted with hot water and pulverized through spray and freeze-drying through *Mannich* modification with formaldehyde and diethanolamine or ethanolamine. The resulting products presented charge densities in the range 0.83–1.88 meq·g^{-1}, lower than those recorded for an industrially extracted Quebracho tannin, modified under a similar procedure (2.79–3.84 meq·g^{-1}). The ethanolamine was a better amine source, generating coagulants with higher charge density, which has been demonstrated by Bello et al. (2020) and Fang (2007) to be important in reducing the coagulant dosage required in water treatment. Since the neutralization of the charges of the colloidal particles is one of the main coagulation mechanisms, the greater the difference between the colloidal and coagulant charges, the better the coagulant efficiency.

Acacia mearnsii, Quebracho, and *Castanea sativa* tannin extracts were chemically modified by *Mannich* reaction using different nitrogen compounds and formaldehyde (Arismendi et al., 2018). Procedure A, using ETA or DEA, and procedure B, using ammonium chloride, were compared. Although both modification methods generated effective bio-coagulants, procedure B was considered the most suitable because of the production of highly active electrophiles (Arismendi et al., 2018). Lugo et al. (2020) also implemented procedure B on *A. mearnsii* tannins cationization and proved that the generated products were very efficient in removing heavy metals from water.

Since formaldehyde is a toxic compound, Machado et al. (2020) explored an alternative cationization procedure using only ammonium hydroxide (free-formaldehyde process). A first screening was done, considering variables such as the order of the addition of reactants, reactant ratios, temperature, reaction times, and final pH adjustment, to select the conditions that may provide products with flocculant activity. Flocculants produced at a reaction time of 4.62 h and reactants ratio of 3:1 generated turbidity and color removals of 100% and 90%, respectively. Similar results were found for reactants ratio of 1:1 and reaction time of 4 h.

Tannins' efficiency as coagulants depends on the tannin source and modification degree. The cationization procedure should be examined and optimized on a case-specific basis.

3. Application of tannin-based coagulants

3.1. Surface water treatment

Coagulation/flocculation is one of the conventional methods used in surface water treatment to produce drinking water. The literature presents several works, mostly conducted in batch mode, on using tannin-based coagulants in this field, particularly for the removal of microbiological agents, heavy metals, and turbidity. Table 7 summarizes the conditions and results obtained in batch and continuous mode.

A few studies found in the literature applied tannin materials or extracts as coagulants without further cationization. These include extracts of fava bean seeds (Kukić et al., 2015), avocado seeds (Putra et al., 2020), and *A. catechu* bark tannin extracts (Thakur and Choubey, 2014). Coagulant activity of avocado seeds and PAC was compared on the treatment of synthetic white clay-turbid water. The tannin coagulant demonstrated higher efficiency than PAC, removing approximately 81 and 92% of turbidity when used at 50 mg L^{-1} and 100 mg L^{-1}, respectively, while PAC removed only ≈70 and ≈81% at the same coagulant dosages (Putra et al., 2020). Chivatá et al. (2018) used liquid tannin extracts obtained with pure water and 10% of acetic acid of the episperm of avocado seeds and guava seeds to treat water from Bogotá River (Colombia). Turbidity removals ranging from 80 to 99% were achieved.

Bello et al. (2020) studied the potential of spruce bark (*P. abies*) tannin extracts as coagulants and compared them to industrially extracted Quebracho tannins. Both extracts were cationized by the *Mannich* reaction and applied to treating a water sample from Oulu River spiked with kaolin. Both coagulants allowed the particles to settle significantly, although Quebracho tannin coagulants showed a higher charge density and turbidity removal. The lower efficiency of *Picea abies* tannin coagulants (Table 7) was attributed to impurities and fewer phenolic groups in their structure. Even though the more stable residual turbidity and a total surface charge close to zero over a wide dosage range justify that spruce bark-derived coagulants should be considered effective products.

As indicated in Table 7, commercial tannin coagulants *Tanfloc*, *Silvafloc*, and *Acquapol* have been successfully used on surface water clarification, heavy metal removal, and pathogens elimination, providing, in some cases, a quite good disinfection level.

Silvafloc, for instance, used for river water clarification (Sánchez-Martín et al., 2010b), reduced up to 70% of total coliforms and provided 99.9% fecal streptococcus removal. The same study showed the superior efficiency of *Silvafloc*, compared to aluminum sulfate, due to its ability to destabilize the colloidal material and reorganize the flocks formed in raw water.

Table 7
Summary of the application of tannin-based coagulants for surface water treatment.

Water sample	Coagulant	pH	Coagulant dosage	Removal (%)	Ref.
Surface water, Guadiana River, Spain	*Tanfloc*	4–5	10 mg L^{-1}	Turb: 99 TC[a]: 80 FC[b]: 90 FS[c]: 99	(Beltrán Heredia and Sánchez Martín, 2009)
Surface water, Guadiana River, Spain	*Tanfloc*	7 8 9	150 mg L^{-1}	Cu^{2+}: 90 Zn^{2+}: 75 Ni^{2+}: 70	(Beltrán Heredia and Sánchez Martín, 2009)
Surface water, Guadiana River, Spain	*Silvafloc*	7	20 mg L^{-1}	Turb: 90 TC[a]: 70 Streptococcus: 99.9 Organic matter: 30	(Sánchez-Martín et al., 2010a)
Surface water, Budha Talab Pond, India	*A. catechu* bark (raw tannin extract)	7.8	3 mL/L 4 mL/L	Turb: 91 TDS: 57.3	(Thakur and Choubey, 2014)
Synthetic turbid water	*Vicia faba* L. seeds (raw tannin extract)	7	0.125 mL/L	Turb: 87	(Kukić et al., 2015)
Surface water, Guadiana River, Spain	*Acquapol C1*	7	5 mg L^{-1}	Algae: 80	(Barrado-Moreno et al., 2016)
Surface water, Salitre River, Colombia contaminated with diazo dyes	*A. mearnsii* (modified tannin)	8	1250 mg L^{-1}	Turb: 99 Color: 90 COD: 72 TS: 95	(Arismendi et al., 2018)
Surface water, Salitre River, Colombia contaminated with diazo dyes	*A. mearnsii* (modified tannin)[d]	–	10 mg L^{-1}	Turb: 90	(Arismendi et al., 2018)
Surface water, Oulu River, Finland, spiked with kaolin	*Picea abies* bark (modified tannin) Quebracho (modified tannin)	7.5	50 mg L^{-1} 50 mg L^{-1}	Turb: ~70 Turb: ~92	(Bello et al., 2020)
Raw water of the Municipal Water and Sewage Company, Brazil	TSG (raw tannin extract) TSL (raw tannin extract)	7	15 mg L^{-1}	Turb: 90 Color: 82.7 Turb: 92.3 Color: 85.6	(Schmitt et al., 2021)

[a] Total coliforms.
[b] Fecal coliforms.
[c] Fecal streptococcus.
[d] Continuous mode.

In another study, which examined algae removal from a river water sample, aluminum sulfate has shown the worst performance on chlorophyll reduction (50%), compared to *Acquapol C1*, *Optifloc*, *Tanfloc*, and *SilvaFLOC* (Barrado-Moreno et al., 2016). Experiments were also carried out in a pilot plant, with similar efficiency as in discontinuous jar-test experiments.

Recently, Schmitt et al. (2021) studied the efficiency of two tannin-based coagulants (TSG and TSL) in treating raw water from a drinking water treatment plant in Brazil. The results obtained (Table 7) with these coagulants were superior to those recorded for aluminum sulfate (15 mg·L^{-1}), which generated turbidity and color removals of 74.3 and 68.7%, respectively. Regarding settling properties, TSL coagulant generated visibly larger flocs and a higher sedimentation rate (0.24 cm/s) than the two other products.

The residual concentration of coagulant in the treated water is recognized as an important issue, particularly for conventional coagulants such as Al salts and organic synthetic polymers. Also, for tannin coagulants, this determination is important, although quite absent from the literature. Sánchez-Martín et al. (2010a) reported shallow polyphenol contents (0.4 mg L^{-1}) in water treated with *Silvafloc* after sedimentation.

3.2. Domestic/urban wastewater treatment

Table 8 summarizes the conditions and results on the application of tannin-based coagulants in wastewater treatment. As it can be seen, most of the research works are on the use of commercial coagulants and the efficiency evaluated on organic matter (COD, BOD_5), turbidity, suspended matter, and microbiological agents.

Table 8
Summary of the application of tannin-based coagulants for wastewater treatment.

Water sample	Coagulant	pH	Coagulant dosage	Removal (%)	Ref.
Raw urban wastewater	*Acquapol C1 18®*	7.5	1000 mg L^{-1}	TC: 99.66 *E. coli*: 99.61 Adv: 96.22	(Fabres et al., 2017)
Urban wastewater after secondary treatment	*Acquapol 893/11®*	7.5	1000 mg L^{-1}	TC: 96.69 *E. coli*: 100 Adv 98.85	(Fabres et al., 2017)
Raw wastewater (Hotel)	*Tanfloc*	6.6–7.9	35 mg L^{-1}	Turb: 75 TSS: 60 COD: 54 BOD_5: 60	(Hameed et al., 2018)
Urban wastewater after secondary sedimentation	*Tanfloc SG*	–	50–80 mg L^{-1}	Turb: 89 Color: 73.6 TOC: 35	(Grehs et al., 2019)
Municipal wastewater (University Hostel)	*Tanfloc*	7.78	35 mg L^{-1}	Turb: 90 TSS: 63 BOD_5 and COD: 60	(Hameed et al., 2016)

Two samples of urban wastewater were collected from the sewage treatment plant of Porto Alegre (Brazil), after preliminary treatment (raw sewage) and after secondary treatment by activated sludge (treated sewage). Several *Acquapol*® and conventional coagulants (PAC and other Al and Fe salts) were assessed to remove pathogenic microorganisms (Fabres et al., 2017). At a dosage of 1000 ppm, except for *Acquapol® 893/11* and *T832*, all the tannin coagulants removed more than 98% of total coliforms and *E. coli*, and 87% of adenovirus (Adv) from the raw sewage. At 100 ppm, however, removal efficiencies of adenovirus were around 50%, and most coagulants were completely ineffective on total coliforms reduction. Aluminum sulfate, aluminum ferrous sulfate, and ferrous chloride showed similar total coliforms removal (about 49%). Among the metal coagulants, aluminum sulfate presented the best performance (removal of 100% of total coliforms and *E. coli*, and 99.72% of Adv), which slightly surpassed the tannins coagulants. $FeCl_2$ (1000 ppm) provided the best performance among the tested coagulants for the treated sewage (100% of total coliforms and *E. coli*, and 99.06% of Adv), although closely followed by *Acquapol® 893/11* (1000 ppm), and *Acquapol® WW* (100 ppm). In general, the tannin-based products were more efficient than PAC and ferrous aluminum sulfate.

The current COVID-19 pandemic raised concerns regarding the presence and related impacts of SARS-CoV-2 in domestic wastewater. The infection through a pollution-to-human transmission mechanism seems to be of remote risk (Sangkham, 2021), but as precautionary measures, methods to treat wastewater containing SARS-CoV-2 can be researched. Lee et al. (2017) suggested that the optimal process for removing pathogens from water is a combination of the coagulation-sedimentation-ultrafiltration process using polyaluminum chloride as the coagulant (2.65 $mg{\cdot}L^{-1}$), while Sangkham (2021) stated that the process involving chemical coagulation in tertiary treatment can eliminate a huge number of pathogens from wastewater. Sherchan et al. (2020) and Kumar et al. (2021) confirmed that the adsorption-coagulation step was the most efficient for Covid-19 virus removal. Some recent research about SARS-CoV-2 mentions tannic acid as one of the principal Covid-19 inhibitors (Kanchibhotla et al., 2021; Coelho et al., 2020). Vilhelmova-Ilieva et al. (2020) state that tannins and polyphenols exhibit good antiviral properties. Hence, the use of tannin-based coagulants on removing SARS-CoV-2 virus from wastewater should be investigated in future work.

Hameed et al. (2016) studied the applicability of *Tanfloc* in a pilot plant treating wastewater generated in a university hostel. Results indicated that *Tanfloc* competes with PAC in terms of turbidity, BOD_5, COD, and TSS removal, but PAC showed superior results in terms of total phosphate removal. For instance, at the optimum dose of 35 mg L^{-1}, both coagulants showed high turbidity removals in jar tests (90–95% for *Tanfloc* and 86–87% for PAC). *Tanfloc* also showed a distinct performance in terms of floc size, compared to PAC, with bigger flocs and faster sedimentation. This was explained by the cationic nature of *Tanfloc* measured by zeta potential, which suggests a relationship between the charge neutralization and another flocculation mechanism. Moreover, sludge production was comparable to PAC up to 60 mg L^{-1} doses.

The presence of antibiotic resistant-bacteria and antibiotic resistance genes in treated wastewater may represent a threat to the environment and public health (Grehs et al., 2019). *Tanfloc SG* and aluminum sulfate were compared on the removal of antibiotic-resistance microorganisms and genes from a secondary treated urban wastewater (Grehs et al., 2019). The performance of both coagulants was similar, being able to reduce almost 100% of the bacterial load, but storage of tannin-treated wastewater led to the reactivation of antibiotic-resistant bacteria and antibiotic resistance genes content. The coagulants have also demonstrated remarkable results in turbidity and organic carbon removal, although aluminum sulfate was on average more efficient than tannin; higher doses of aluminum sulfate (about 4 times higher than tannin) were however used.

3.3. Remediation of industrial effluents

The performance of tannin-based coagulants has been assessed in the treatment of a wide variety of industrial effluents, namely on removing color, turbidity, and metal ions, as summarized in Table 9.

Heiderscheidt et al. (2016) tested the performance of a modified tannin-based coagulant (commercial name *Tan2*) on the treatment of runoff water from extraction peat sites and compared it to ferric sulfate. A significantly higher dosage of tannin coagulant (55–125% higher) was needed to achieve a proper removal of color and turbidity, but the flocks formed had the best sedimentation properties for settling times higher than 4 min (pH 6.5) or 6 min (pH 4.5). The influence of pH was studied in the range 4.5–6.5, as the typical real values of peat extraction runoff water are in the range pH 4.5–7.0. Under more acid conditions, a lower coagulant dosage was needed to remove color and turbidity. The addition of ferric sulfate considerably lowered the water pH, while the tannin coagulant impact on water pH was much less significant. In terms of DOC removal at pH 4.5, ferric sulfate (70 mg L^{-1}) achieved better results (76%) than the tannin-based coagulant (110 mg L^{-1}, 52%). However, high residual iron and sulfate concentrations were found in the purified water. Nevertheless, due to the high dosage required and the increase in the residual nitrogen concentration observed in water samples treated with tannin coagulant, this natural coagulant was not considered by the authors as suitable for the application under study. Thus, the use of ferric sulfate together with the tannin coagulant could be explored.

Effluent from a cosmetic industry was treated by *A. mearnsii*, and Quebracho modified tannins. However, a dual system combining bio-coagulant and a small amount of cationic PAM was required to improve turbidity removals to 93% (Table 8) (Grenda et al., 2020).

Coagulation/flocculation processes through tannin-derived coagulants have been highly studied on landfill leachate treatment, particularly using *A. mearnsii* modified tannins. Results (Table 8) show high removal efficiencies of heavy metals and considerable reduction of organic matter. One of the largest landfills in northern Europe, which receives wastes from approximately 1 million people, has its wastewater treated by tannin-based coagulant. *A. mearnsii* modified tannin (11.1 mL/ L) (HTH coagulant in liquid form, density of 1.04 $g.L^{-1}$, according to HAARLA OYED) at pH 7.3 was able to reduce more than 90% of Fe and Ti, almost 70% of Cr, and 52% of Al from the leachate (Righetto et al., 2021). Lugo et al. (2020) reported a higher Cr removal, 87%, at a pH of 10. The improvement in Cr removal, when compared to Righetto et al. (2021) work, can be explained by the increase of pH value, which increases the degree of ionization of the phenolic hydroxyl groups present in the tannin structure (Xu et al., 2017). Banch et al. (2019) used *Acacia* modified tannins as coagulant agents for a stabilized landfill leachate. At pH 6 (optimum condition for COD, NH_3-N, and suspended solids removal), the result for Fe removal was very similar to the one reported by Righetto et al. (2021), but Cr reduction was even superior, about 90%. Even after the biological treatment, leachate from landfills remains very dark, and some post-treatments are still necessary. Coagulation-flocculation employing *Organo-floc*™ was applied as a post-treatment in a Malaysian landfill. The results revealed that the increment of the coagulant dosage and the reduction of pH values enhanced color removal. At optimum conditions (100 mg L^{-1} and pH 3.6), approximately 80% of the leachate color was removed (Ibrahim and Yaser, 2019).

The coagulation process is widely employed as primary treatment in industrial laundries wastewaters. Huang et al. (2019) used *Tanfloc POP* to remove color and turbidity from an industrial laundry raw effluent. Coagulation experiments were performed to determine the best coagulant dosage at pH 7.5 and 30 °C. The results demonstrated that with 140 mg L^{-1} it was possible to remove about 80% of color and turbidity. However, the increase in coagulant dosage promoted a greater removal range (up to 90%). Nascimento et al. (2019) used the same coagulant and reached greater values of turbidity removal (94%), in a bit more acid medium (pH 6.3) with a lower coagulant dosage (120 mg L^{-1}). The acidification of the sample did not influence the efficiency of the coagulant, but in another work (Costa et al., 2018) the increase in pH is reported to impair turbidity removal.

Textile industry presents an elevated water consumption and generates high volumes of wastewater containing dyes, additives, and salts. These effluents present high turbidity, color, COD, and suspended solids. The pH may vary from 2 to 12 (Dotto et al., 2019), but it is frequently alkaline,

Table 9
Summary of the application of tannin-based coagulants for industrial effluents treatment.

Water sample	Coagulant	pH	Coagulant dosage	Removal (%)	Ref.
Humic peat extraction runoff water	*Tan2*	4.5	110 mg·L^{-1}	Tot-P: 71 DOC: 52 Fe: 94 TSS: 43	(Heiderscheidt et al., 2016)
		6.5	170 mg·L^{-1}	Tot-P: 76 DOC: 57 Fe: 98 TSS:21	
Cosmetic effluent	*A. mearnsii* modified tannin	Neutral	200 ppm	Turb: 68 Color: 82	(Grenda et al., 2020)
Cosmetic effluent	Quebracho modified tannin	Neutral	200 ppm	Turb: 61 Color: 80	(Grenda et al., 2020)
Cosmetic effluent	*A. mearnsii* modified tannin + 5 ppm of PAM (40% charge)	Neutral	200 ppm	Turb: 92 Color: 91	(Grenda et al., 2020)
Cosmetic effluent	*A. mearnsii* modified tannin + 5 ppm of PAM (80% charge)	Neutral	200 ppm	Turb: 45 Color: 73	(Grenda et al., 2020)
Landfill leachate	*A. mearnsii* modified tannin	7.3	11.1 mL·L^{-1}	Fe: 92 Ti: 91 Cr: 68 Al: 52	(Righetto et al., 2021)
Landfill leachate	*A. mearnsii* modified tannin	10	375 ppm	Turb: 94 Cu: 60 Cr: 87 Hg: 50–80 COD: 88 TSS: 86	(Lugo et al., 2020)
Landfill leachate	*A. mearnsii* modified tannin	6	1460 mg·L^{-1}	Color: 91.39 Cu: 94.15 Cr: 89.94 COD: 53.50 TSS: 60.26	(Banch et al., 2019)
Landfill leachate	*Organo-floc™*	3.6	100 mg·L^{-1}	Color: 78	(Ibrahim and Yaser, 2019)
Industrial laundry effluent	*Tanfloc POP*	7.5	140 mg·L^{-1}	Turb: 83.64 Color: 79.68	(Huang et al., 2019)
Industrial laundry effluent	*Tanfloc POP*	6.3	120 mg·L^{-1}	Turb: 94.34 Color: 91.09	(Nascimento et al., 2019)
Simulated textile effluent (MB)	*A. mearnsii* + 10 ppm of CF + 0.3% bentonite (wt%)	2.9	100 ppm	Color: 95[a]–76[b]	(Grenda et al., 2018)
Simulated textile effluent (CV)	*A. mearnsii* + 10 ppm of AF + 1.4% bentonite (wt%)	2.2	100 ppm	Color: 93[c]–72[d]	(Grenda et al., 2018)
Simulated textile effluent (DR)	*A. mearnsii* + 10 ppm of CF + 0.3% bentonite (wt%)	3.4	50 ppm	Color: 89[a]–76[b]	(Grenda et al., 2018)
Simulated textile effluent (AB 2)	*A. mearnsii* + 10 ppm of CF + 0.4% bentonite (wt%)	2.8	100 ppm	Color: 83[a]–74%[b]	(Grenda et al., 2018)
Simulated textile effluent (DB 85) – E1[e]	*Tanfloc SG*	4	80 mg·L^{-1}	DOC: 33 Color: 100	(Lopes et al., 2019)
Simulated textile effluent (DB 85) – E2[f]	*Tanfloc SG*	6	70 mg·L^{-1}	DOC: 14 Color: 100	
Simulated textile effluent (DB 85) – E2[f]	*Tanfloc SG*[h]	4	180 mg·L^{-1}	DOC: 22 Color: 100	
Palm oil refinery effluent	Commercial coagulant (*A. mearnsii* modified tannin)	6	200 mg·L^{-1}	Turb: 93 BOD: 98 COD: 89 TSS: 90	(Yasin et al., 2020)
Palm oil mill effluent	*Tanfloc*	5	3 mg·L^{-1}	Turb: 40	(Abdullah and Abidin, 2018)
Palm oil mill effluent	*Organo-floc™*	–	3 mg·L^{-1}	COD: 34.16 TSS: 65.67	(Tajuddin, 2015)
Synthetic dairy wastewater	*Tanfloc POP*	5	50 mg·L^{-1}	Turb: 95 COD: 66	(Muniz et al., 2021)
Synthetic dairy wastewater	*Guazuma ulmifolia* tannins	5	775.8 mg·L^{-1}	Turb: 95.8 COD: 76 BOD: 81.2	(Muniz et al., 2020)
Raw dairy wastewater	Commercial coagulant (*A. mearnsii* modified tannin)	5–10	300 mg·L^{-1}	Turb: >90 Color: >85	(Justina et al., 2018)
Synthetic dairy wastewater	*Tanfloc SG*	7.2	300 mg·L^{-1}	Turb: 100 Color: 99.92 TOC: 70.02	(Oldoni, 2020)
Treated dairy wastewater[g]	*Tanfloc SH*	5	20 mg·L^{-1}	Turb: 93	(Wolf et al., 2015)
	Tanfloc SG	6	20 mg·L^{-1}	Turb: 93	
Raw cassava processing wastewater	*Acquapol® WW*	7.1	320 mg·L^{-1}	Turb: 85 Color: 51	(dos Santos et al., 2018)
	Acquapol® S5T	7.1	320 mg·L^{-1}	Turb: 89 Color:81	(dos Santos et al., 2018)
	Tanfloc SL	7.1	320 mg·L^{-1}	Turb: 90 Color: 78	(dos Santos et al., 2018)
	Tanfloc SG	7.1	320 mg·L^{-1}	Turb: 89 Color: 65	(dos Santos et al., 2018)

especially in cotton dyeing. Coagulation/flocculation has been used for many years in the textile industry and considering the huge volumes of water to be treated, it is highly desirable to apply greener and cost-effective coagulants. Grenda et al. (2018) used a combination of bentonite, *A. mearnsii* modified tannin, and a synthetic flocculant to remove four different dyes with different fibers applications and types from textile wastewater samples. Color removal efficiencies varied between 54 and 95% (Table 8), depending on the dye and settling times, which are also quite considerable.

Lopes et al. (2019) compared the performance of *Tanfloc SG* and iron sulfate in the decolorization of synthetic textile dyeing wastewater. Two effluents were used: E1 was prepared by dissolving *Sirius Blue K-CFN* dye (DB 85), sodium chloride, and sodium bicarbonate; E2, containing industrial additives typically used in direct dyeing of cotton (a wetting, a lubricant, and a sequestering agent), beyond the cited dye and salts. Both coagulants were able to remove 100% of color in diverse pH ranges and coagulant dosages. At pH 4, the tannin-coagulant dosage required to find total decolorization and easily settleable flocs was found to be 3-times higher than that of iron sulfate. However, at pH 8 (close to the effluents pH), the tannin-coagulant was much more efficient than the iron coagulant: total decolorization was achieved using 180 mg L^{-1} of tannin-coagulant, while dosages up to 240 mg L^{-1} of iron sulfate were unable to provide more than 20% of decolorization and settleable flocs. In the same study, continuous mode experiments confirmed the good performance levels observed in jar tests for *Tanfloc SG*. Tannin-based coagulants, cationized by *Mannich* reaction, were tested in water samples from a river contaminated with diazo dyes (Arismendi et al., 2018). Coagulants were prepared with different sources of tannins (*Acacia mearnsii*, *Schinopsis balansae* and, *Castanea sativa*) and amines (ethanolamine, diethanolamine, and NH_4Cl). The combination of *Acacia* tannins with NH_4Cl led to the best results in terms of removal of total solids (95%), turbidity (99%), COD (72%), and color (90%). Due to the high tannin removal rates of *Acacia* and Quebracho, these plants appear to be the best candidates for a pilot-scale investigation and, later, to be used as primary treatment in a wastewater treatment plant. When compared to aluminum sulfate, widely used in wastewater treatment plants, tannin-based coagulants presented lower levels of mutagenicity and toxicity, as well as the ability to stabilize pH.

Effluents generated in crude palm oil refineries (POME) present high levels of turbidity, suspended solids, COD, and BOD_5. POME was submitted to a coagulation process using a commercial tannin-based coagulant obtained from *A. mearnsii* bark. At a 200 mg L^{-1} coagulant dosage and optimum pH 6, the tannin-based coagulant removed more than 89% of BOD, COD, turbidity, and suspended solids (Yasin et al., 2020). Other authors (Abdullah and Abidin, 2018; Tajuddin, 2015) applied *Tanfloc* and *Organofloc* as coagulants for POME treatment. More limited efficiencies were observed (see Table 8), but the applied dosages were much lower than the previous ones.

Tannin-based coagulants have been highly evaluated in the treatment of dairy industry wastewaters. Synthetic effluents have been mainly used due to the great variability in these effluents' properties. However, studies are advancing quickly since the obtained results are very positive. Muniz et al. (2020) and Muniz et al. (2021) determined the optimum conditions to use *Tanfloc POP* and tannins extracted from *G. ulmifolia* bark as coagulants for synthetic dairy wastewater. At a pH of 5 (optimum pH conditions), these coagulants provided high turbidity (above 90%) and organic matter removals (above 66% in terms of COD), although with quite different dosages (see Table 8). Wolf et al. (2015) evaluated coagulation using *Tanfloc SG* and *Tanfloc SH* as a post-treatment operation (after stabilization lagoons) for the clarification of effluent from a dairy industry. At optimum conditions, both coagulants generated wastewaters with the required standards for reuse in the pasture irrigation to feed the animals, closing the cycle. Dela Justina et al. (2018) compared coagulant activities of *A. mearnsii* modified tannins and PAC on the treatment of a raw effluent from a dairy industry. They reported no statistical differences between the performance of the two coagulants, considering COD, color, turbidity, and TSS removal. Tannin coagulant, however, had an average alkalinity consumption of only 24% of that achieved by PAC and presented a wider pH range of application, which indicates fewer pH corrections and lower process cost. Tannin coagulant has better performance at lower concentrations (100–300 mg L^{-1}) than PAC (400–600 mg L^{-1}). Oldoni (2020) also reports that greater efficiencies in color and turbidity removal are achieved for lower tannin dosages (300 mg L^{-1}) than for PAC, aluminum sulfate, and ferric chloride at much higher dosages (1300, 1100, and 1150 mg L^{-1}, respectively). However, it is worth noting that direct comparisons of very different coagulant dosages should be taken with caution as, in essence, the relevant comparison should be made in terms of price. *Tanfloc* prices are around 0.43–1.49 €/kg (Nunes and Yokoyama, 2016; Ramalho, 2013) while conventional coagulants such as aluminum sulfate (0,14 €/kg) (Niu et al., 2020), and aluminum polychloride (0.13–0.33 €/kg) (Gonjy Filter Industry Co., LTD, n.d.) present lower values.

Different tannin commercial coagulants were tested on cassava processing wastewater treatment (Table 8) (dos Santos et al., 2018). All the analyzed tannin coagulants presented greater efficiency of color and turbidity removals, compared to the chemical inorganic coagulant $Al_2(SO_4)_3$, which presented color and turbidity removals of 49 and 56%, respectively, at 640 mg·L^{-1} dosage.

4. Final remarks

By way of conclusion, Table 10 presents a SWOT analysis, resulting from this literature review. This critical analysis compiles the strengths, weaknesses, opportunities, and threats identified on TB coagulants production (tannins extraction and chemical modification) and application. It allows to understand the development of TB coagulant production to the present day and to know future opportunities and research needs.

CRediT authorship contribution statement

Isabella T. Tomasi: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. **Cláudia A. Machado:** Investigation, Methodology. **Rui A.R. Boaventura:** Funding acquisition, Project administration, Resources, Writing – review & editing, Supervision. **Cidália M.S. Botelho:** Funding acquisition, Project administration, Resources, Writing – review & editing, Supervision. **Sílvia C.R. Santos:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Visualization, Validation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Notes to Table 9:

[a] 24 h settling, TB_5 coagulant (viscosity of 432 cP and pH 1.6)1.
[b] 30 min settling, TB_5 coagulant (viscosity of 432 cP and pH 1.6).
[c] 24 h settling, TB_4 coagulant (viscosity of 204 cP and pH 1.6).
[d] 1 min settling, TB_4 coagulant (viscosity of 204 cP and pH 1.6).
[e] E1: dye + NaCl $NaHCO_3$.
[f] dye + NaCl $NaHCO_3$ + wetting, lubricant, and sequestering agents.
[g] Coagulation operation as a post-treatment aiming effluent reuse.
[h] Continuous mode.

Table 10
SWOT analysis of tannin-based coagulants.

S – Strengths	W – Weakness
• Toxicity free. • Generates about 5 times less sludge than a conventional coagulant (Ndabigengesere et al., 1995) – lower transportation cost. • Lower sludge treatment cost. • Coagulant precursors' (tannins) are of simple extraction (Das et al., 2020) from natural materials (no need of primary mining). • Sludge with higher nutritional value (Choy et al., 2014). • Promising results obtained in different application fields (drinking water production, wastewater treatment, industrial effluents remediation). • Biodegradable sludge. • Provide minimal change in effluent final pH (lower alkalinity consumption (Choy et al., 2014)) – pH/alkalinity correction needs are minimized. • Efficient in a wide pH range. • Expected to be produced at a lower cost than organic synthetic polymers (Oladoja, 2015). • Not corrosive, causing no pipe erosion (Swati and Govidan, 2005). • Companies that use tannin-based coagulants could promote themselves as environmentally friendly. • Promote human health. • Protect aquatic ecosystems.	• Organic solvents may be used for tannin extraction. • Cationization methods require formaldehyde use (toxic compound). • Most of the research is still limited to lab-scale, synthetic effluents, and batch-mode. • Limited knowledge about harmful effects of natural coagulants. • Limited knowledge about the compatibility of tannin-derived coagulants and other treatment operations. • Although residual tannin polymers are believed to not present adverse effects on aquatic life, ecotoxicity studies in treated water are needed. • An increase in the residual nitrogen concentration in water treated with tannin coagulant may be observed (Heiderscheidt et al., 2016). • Possible increase in DOC in treated water due to residual presence of tannin coagulant, especially for higher coagulant dosages (Lopes et al., 2019).
O – Opportunities	**T – Threats**
• Development of greener cationization (e.g. formaldehyde free) and extraction methods. • Make efficient use of natural materials, residues, and by-products. • Low variety of tannin-based coagulants in the market (e.g., commercialize tannin-based coagulants that do not derivate from *A. mearnsii* and Quebracho trees, but from locally available materials). • Governments support stimulating the consumption of eco-friendly products. • By valuing the local products, the chemical dependence of developing countries could be reduced. • A combination of coagulation--sedimentation-ultrafiltration process can enhance the removal of viruses from wastewater (Lee et al., 2017), and chemical coagulation in the tertiary treatment can eliminate a huge number of pathogens from the wastewater (Sangkham, 2021). Tannin-derived coagulants should be tested in water treatment systems to evaluate the removal of SARS-CoV-2. • Opportunity to be used in wastewater and drinking water treatment in developing countries - lots of indigenous plants are tannin sources. • Opportunity to be used as coagulant aid (Hameed et al., 2018; Grenda et al., 2018; Özacar, 2000; Özacar and Şengil, 2003) and associated with other technologies of treatment (Bacher et al., 2017).	• Required dosages of tannin-based coagulants may make them more expensive than conventional coagulants. • Market competition with chemical coagulants. • Lack of confidence of investors. • Usability in real treatment plants. • The reluctance of industries to adapt to new technologies.

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