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Synthesising tannin-based coagulants for water and wastewater application: A review

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ABSTRACT

Coagulation-flocculation has been applied widely in water and wastewater treatment. Tannin, a natural water-soluble polyphenol that is present in most vegetable cells, has been widely accepted and applied as a plant-based coagulant. The application of a tannin-based coagulant in water and wastewater treatment around the world has shown successful removal of pollutants including turbidity, colourants, suspended solids, chemical oxygen demand, algae, and heavy metals. The level of effectiveness of tannins as a coagulant is associated with their chemical structure and the degree of tannin modification, which are linked to the plant source from which they are extracted. This review summarises the characteristics of tannin, extraction techniques applicable to tannin, as well as factors affecting tannin modification during the synthesis process. Developments and prospective of tannin-based coagulants as application in various types of water and wastewater treatment are also being reviewed.

1. Introduction

Coagulation-flocculation has been applied in water and wastewater treatment for a very long time. This treatment technique is favourable due to its advantages of being low-cost, easy operation and effective in removing water pollutants. The effectiveness of coagulation depends very much on the type of coagulant being selected [1]. There are several types of coagulants to be chosen for water and wastewater treatment. Conventional chemical coagulants that are widely applied can be classified into three large groups which are synthetic cationic polymers (aminomethyl polyacrylamide, polydiallyldimethylammonium chloride (polyDADMAC) etc.), pre-hydrolysing metallic salts (polyferrous sulphate, polyaluminium chloride (PAC) etc.), and hydrolysing metallic salts (aluminium sulphate $Al_2(SO_4)_3$, ferric chloride ($FeCl_3$) etc.) [2]. The most common inorganic coagulants are iron and aluminium salts which are favourable due to their effectiveness in pollutant removal, mixing properties, user-friendly, handling and storage, as well as low cost [3]. However, their usage in water and wastewater treatment having a disturbing drawback including the generation of a high volume of sludge, the requirement for alkalinity and pH adjustment and the high concentration of residual metals in the treated water or sludge. There has been a remark on the possible link of the pathogenesis of Alzheimer's disease to the neurotoxicity of aluminium found in wastewater sludge [3].

Following the need to deal with the problems of chemical coagulants correlated with rising environmental concerns, significant interest has been shown by researchers in the development of environmentally friendly natural coagulants derived from animals or plants as a substitute. The usage of natural coagulants for applications in water and wastewater clarification has been noted for more than two millennia in China, Africa and India [4]. Similar to an inorganic coagulant, a natural coagulant acts by agglomerating colloidal particles in wastewater and producing a lesser amount of biodegradable sludge, which is safe and can be used as fertiliser. Apart from that, the adjustment of pH and alkalinity is not required [3]. These coagulants that are either natural polysaccharides, tannins or proteins can be anionic, cationic or non-ionic, and are generally referred to as polyelectrolytes [5,6]. Examples of natural anionic polymers are sulphated polysaccharides, modified lignin sulphonates and tannin [1], while chitosan [7] and cationic starches [8] are cationic polymers. Starch and cellulose derivatives are types of non-ionic natural polymers [3].

The usage of plant-based coagulants for water and wastewater treatment that have received great attention and frequently studied are *Moringa oleifera (M. oleifera)*, *Strychnos potatorum* (nirmali), tannin and cactus [9,10]. *M. oleifera* has been successfully applied to remove cyanobacteria from surface water [11] as well as turbidity and total

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coliforms from synthetic raw water [4]. *M. oleifera* has been applied by Oliveira et al. [12] in leachate treatment and has been found successful in removing turbidity, colour, biological oxygen demand (BOD) and chemical oxygen demand (COD). Beyene et al. [13] have shown that a combination of cactus powder with alum is effective in turbidity removal, while Sellami et al. [14] reported that cactus was more efficient in removing suspended solids (SS) and COD from industrial wastewater in comparison to polyacrylamide (PAM). High turbidity removal from highly turbid water was also observed when using *S. potatorum* or nirmali seed [15,16]. Tannin extracted from valonia oak [17,18], Silvafloc, a tannin-derived coagulant from *Schinopsis balansae* [19] and Tanfloc, a tannin-derived coagulant from *Acacia mearnsii* [20,21] have been applied to remove turbidity from water in wastewater treatment. Tanfloc usage has proven successful for the total decolourisation of synthetic textile wastewater [22] and also effective for heavy metal removal in surface water treatment [23].

Various studies have been reported concerning the use of condensed anionic tannin as a coagulant aid in sludge dewatering [24] and for particle removal [17,18]. Usage of cationic tannin polyelectrolyte in the water treatment field was later studied with the entering of commercial modified tannin coagulant in the market [23,25]. Synthesis of cationic tannin-based coagulant was later performed via Mannich reaction in the lab by few researchers [26–28], to look at factors affecting the coagulant effectiveness. Arbenz and Avérous [29] has provided an extensive review of different pathways for chemical modification of tannin of various tannin application. This review will summarise some of the synthesis works done in tannin coagulant modification since a very limited review has been done on it.

To date, the application of natural coagulants in water and wastewater treatment has been reviewed by many researchers, however with limited focus on tannin. Kumar et al. [30] discussed several types of natural coagulants that have been used in water and wastewater including microbial polysaccharides, starches, cellulose derivatives, chitosan, and others. Those natural coagulants were classified as either non-plant based or plant-based coagulants with tannin mentioned briefly under the latter category. Choy et al. [31] covered 21 types of plant-based coagulants but only mentioned tannin under the topic of barriers and prospects of commercialisation of natural coagulants in the near future. Freitas et al. [3] reviewed the utilisation of plant-based coagulants, including tannin, but only for textile wastewater treatment. The application of tannins in various industries was also reviewed by Singh and Kumar [32] and Pizzi [33], but not as a coagulant for wastewater treatment. Recently, a review of effective extraction methods of tannin from diverse sources and technological applications of tannin in various fields was published [34]. Sánchez-Martín et al. [35] had summarised the utilisation of commercial tannin-based coagulants in water treatment namely Tanfloc, Aquafloc and Silvafloc up to the year of 2012.

This review aims to summarise the findings on the synthesis and application of tannin-based coagulants, including their characteristics and extraction techniques. The chemical modification process involved in the cationisation of tannin coagulant along with factors governing the coagulant outcome is also reviewed. Moreover, the coagulation mechanism of tannin-based coagulants and the efficiency of tannin as the main coagulant when applied to various types of water and wastewater treatment over the past 20 years will also be discussed.

2. Tannins and its characteristics

Tannins are water-soluble phenolic compounds with molecular weights in the range of 500–3000 g/mol. Tannins are polyphenolic secondary metabolites of higher plants, which can be either galloyl esters, or they are polymeric and oligomeric proanthocyanidins possessing different inter-flavanyl coupling and substitution patterns [29,36]. It is the most plentiful compounds extracted following cellulose, hemicellulose, and lignin [37]. Tannins are available in every vegetable cell, mostly in the soft tissues of the plant such as bark, needles and sheets, however, only in small utilisable quantities from selected plants [18]. For example, high tannin content can be found in the wood of quebracho (*S. balansae*) and chestnut (*Castanea sativa*), in the sheets of gambier, or in the bark of pine (*Pinus radiata* and *Pinus nigra*), black mimosa (*A. mearnsii*) or oak (*Quercus spp*.) and others [29,33]. The tannin structure also varies depending on the location and origin of the plant [38]. Initially, *S. balansae* has been the main feedstock of tannin extract for many years in the past before *A. mearnsii* was industrially used [39]. Another potential plant with high condensed tannin content would be *Acacia mangium,* another species from the *Acacia* family which could be found abundantly in Asia. Its extract has been used as an adsorbent to remove heavy metal from wastewater [40], but the study on the usage as a coagulant is still limited.

Since there are several types of tannin and the fact that tannin extract is obtained from different plant sources, tannin chemical structures are complex and diverse. Hence, it is difficult to conclude the exact chemical structure of tannins [41,42]. The immediate biosynthetic precursors of the commercially-used condensed tannins could be 5-deoxyflavan-3,4-diols and catechins [43]. Tannins are generally classified under two groups of phenolic (polyphenols) compounds, namely, hydrolysable tannins and condensed tannins with each possessing its own chemical nature. Hydrolysable tannins are further subcategorised as gallotannins and ellagitannins. Hydrolysable tannins are a combination of phenols such as ellagic acid, gallic acid, digallic acid, and esters of sugars. The main uses of hydrolysable tannins are in the tanning industry and are less attractive when compared to condensed tannins due to their weak nucleophilicity and low availability with a relatively high price [29].

Condensed tannins, also known as proanthocyanidins, represent over 90% of the global production of commercial tannins [29]. Naturally occurring condensed tannins consist of polyphenolic bioflavonoids polymers of polyhydroxy flavan-3-ol units. Based on the reaction rate, some condensed tannins have a fast reaction like pecan and pine, while some have a slow reaction such as mimosa and quebracho. Often, both kinds of tannins co-occur in the same plant or plant tissue [17]. Algae, from the *Phaeophyceae* class, have been found as an organism capable of synthesising tannins called phlorotannins. The chemical classification of tannins can now be categorised as phlorotannins, complex tannins, condensed tannins, ellagitannins and gallotannins [34].

The natural existence of condensed tannins is greater as compared to hydrolysable tannins. Accordingly they represent the leading and more valuable source of commercial tannins [36]. Based on estimation in 2015, 1076.3 kilotons of tannin were required which is predicted to increase at a compounded annual growth rate of 5.8% from 2016 to 2025. The use of condensed tannins is anticipated to rise to 424.8 kilotons by 2025 in contrast to 242.9 kilotons in 2015 [32].

Tannins have been applied in the early years in the preservation of leather [44]. Vegetal tannins, which are bitter and astringent substances in plants, have been used as tanning agents, dyestuffs and drugs since earlier times [45]. Tannins have also been broadly applied in several industries. An extract from *A. mangium* tree bark (tannin-paraformaldehyde) was used as an adhesive in plywood manufacturing, replacing conventional phenol-formaldehyde adhesive [46]. Tannins from chestnut, mangrove, and quebracho act as reducing agents for the green synthesis of colloidal silver nanoparticles [47]. Water treated with tannin was found suitable for use as the reaction medium in the emulsion polymerisation of industrial styrene-butadiene rubber [45,48]. Tannin could also be used as a UV stabiliser by promoting the stabilisation of polyurethane foams against UV radiation [49]. In the food industry, chestnut tannin extract was either used alone or mixed with other polyphenols to act as an antioxidant, antimicrobial additive and for cutting down mycotoxins and nitrosamines in raw food materials for animals and humans [50]. In the medical field, tannin was used as a macroporous biomaterial for bone engineering applications since it can be prepared in such a way to resemble ceramics [51]. Tannins have also been used in the tissue engineering field to make antibacterial films where poly(vinyl alcohol)/cationic tannin films present antimicrobial, cytocompatibility and antioxidant activities [52]. Tannins were also often used in the water and wastewater industry for microalgae harvesting [53,54], sludge dewatering [24], as adsorbent [55–57] and as coagulant/flocculant [1,22,58].

Tannins being natural high molecular weight polysaccharides have been reported as efficient natural water clarifiers for all types of wastewater. For that reason, it is thought that tannins were the earliest commercialised natural coagulant instead of other plant sources. Apart from that, the availability of simple extraction methods that can be used for tannin extraction makes it preferable over other plant extracts which is advantageous from the research and development aspect. Furthermore, the use of tannin as a coagulant is favourable over the other natural coagulants as no further purification or isolation processes on the tannin extract would be required which could save both time and cost.

3. Tannin extraction

One of the main advantages of tannin is that it can be extracted in so many ways just like other plants either traditionally or using advanced techniques for better extraction yield. According to Arbenz and Avérous [29], tannin extract composition is greatly influenced by the plant preparation and extraction processes. Various extraction methods of tannins including solvent extraction, decoction, ultrasound, microwave, irradiated radiation, as well as topics about tannin extraction efficiency including collection, management and materials storage have been reviewed in detail by Cuong et al. [59]. Phenolic compounds can be extracted either from fresh, frozen or dried plants [29]. Generally, by applying the traditional method of extraction, plants are milled and homogenised after undergoing a drying treatment. Drying has a strong impact on the final composition of the tannin extracts. Under aerobic conditions, the free tannin content decreases strongly with the temperature, whereas under anaerobic conditions, there is a slight increase in the free tannin content. Applying freeze-drying methods may preserve the molar masses of the condensed tannins, whereby high levels of phenolic compounds could be extracted while maintaining the native structures [29].

Traditionally, the simplest extraction method to recover tannins from plants is the solid/liquid extraction by water or hot water or other types of solvents followed by filtration and concentrating the resultant extract by evaporation. In industry, water is the preferred solvent which allows the extraction of concentrations of tannins ranging from 29 to 887 mg/g of the dried extract [60]. In a study, barks of *Acacia caetchu* powder was thoroughly mixed with distilled water to extract the tannin [61]. In another study, tannin was extracted from spruce bark by boiling the bark in distilled water [62].

Extraction is also achieved using alkaline [63,64] or acid solutions to increase the yield. In a study, whole fava bean seeds powder was stirred in distilled water or sodium chloride (NaCl) solution to extract the tannin, followed by filtration [64]. Yang [65] performed tannin extraction of sea-buckthorn by soaking the leaves in methanol to obtain an extract and recovering the solvent by reduced pressure distillation. Chinese *coriaria* crude bark powder was subjected to an alkali solution and extracted at high temperatures [66]. Qiu [67] extracted tannin from ginkgo leaves where enzymolysis was carried out on the ginkgo leaf powder and later crude tannin was extracted and purified through a sodium carbonate solution and a sodium hydroxide (NaOH) solution. Cashew nut testa powder was extracted with 70% aqueous acetone. Acetone inhibits any tannin-protein interaction making acetone a better extractant than alcoholic solvents [68]. Soxhlet extraction was performed at elevated temperature with a water-ethanol mixture to obtain tannin from *Laura nobilis* leaves powder [69].

On the negative side, these conventional liquid extraction methods require high volumes of water or organic solvents and suffer long extraction times. Moreover, the usage of excessive solvents such as hexane and acetone generates residues that pose environmental and health threats [34]. To overcome these problems, various advanced methods have been established over the past few years which increase the tannin extraction yield and improve the extraction process. Tannins have been extracted using ultrasonic-assisted extraction (UAE) [70,71], microwave-assisted extraction (MAE) [72,73], pressurised water extraction (PWE) [74] and supercritical fluid extraction (SFE) [75,76]. The chemicals or solvents used in each extraction process depend on the plant parts or species having diverse physical properties such as solubility or polarity [29].

UAE was used to extract tannin from *Trapa* Sp. *pericarp* powder [70] and walnut green seedcases [77]. Tannin was extracted from pomegranate rind via UAE by using an organic extraction solvent containing acetone solution [78]. In another work, pomegranate leaves powder underwent tannin extraction by UAE using 70% acetone as the extracting solvent [79]. UAE was also applied in extracting tannin from wild persimmon leaves with ethanol and water used as extraction solvents [80].

Tannins are considered polar compounds, while carbon dioxide which is the most used solvent in SFE is a non-polar molecule [34]. Thus, to enhance the solubility of tannins and the efficiency of their extraction, polar co-solvents are commonly used. Shao, Meng and Xie [75] carried out tannin extraction of *Scabiosa comosa* by supercritical carbon dioxide with 85% water-acetone solution as an entrainer. In another study, tannin from the waste bark of *Picea abies* was extracted using supercritical carbon dioxide and ethanol/water mixture [76].

Yao et al. [72] extracted tannin from *Filipendula palmate* by applying MAE and ultra-high pressure coupling technology. Ethanol was used as a solvent to carry out microwave pre-treatment before the ultra-high pressure extraction was carried out. Liu et al. [81] extracted tannin from *Shaniodendron subaequalum* leaves using alcohol aqueous solution via a MAE, followed by centrifugation and purifying the tannin solution through a macroporous resin. PWE was applied in the extraction of tannin from larch wood waste [74]. It was found that the addition of ethanol and increasing the flow rate resulted in an increment of the extraction yield. However, the tannin content does not increase proportionally with the yield. Table 1 below shows different types of extraction methods practiced to extract tannins in some literatures.

In a nutshell, there are no common extraction procedures since each plant sample has an effective extraction solvent and an optimised extraction condition. The composition of extracts and the extract yield depends on conditions such as the type of extraction solvent (polarities), the sample/solvent ratio, and the extraction temperature and time. A study by Fraga-Corral et al. [34] concluded that selecting a suitable extraction technique could maximise the final extraction recovery rate. It has been shown that modern tannin extraction methods offer parallel or better performance compared to conventional methods in terms of extract purity and the amount of tannin yield. Moreover, reduced extraction times and the amount of solvent needed lead to lower energy consumption which is good news for the environment. Unfortunately, in reality, the majority of the current industrial tannin production is still operated traditionally by solid–liquid extraction utilising high water and solvent volumes. Solid-liquid extraction has been the most common and widely used tannin extraction method for tannins from various plant sources due to its simplicity and low cost in application [60] while most of the equipment of modern extraction techniques for industrial-scale is expensive [59]. Although there have been efforts made recently to apply modern methods of tannin extraction, they usually stay at the laboratory scale [60]. Nevertheless, modern extraction techniques have an advantage in avoiding the degradation of tannins during the treatment, with UAE being potentially the most efficient approach since its relative cost is lower compared to other modern techniques [34].

4. Tannins modification

The anionic nature of tannin is indicated by the presence of the

Table 1
Different types of extraction methods practiced to extract tannins in some literatures.

Extraction methods	Raw material	Solvent	Extraction temperature (°C)	Extraction time	Post extraction process	Others	Ref
Solid/liquid extraction	*Acacia catechu* bark	Distilled water	Room temp	5 min	Filtration and centrifuging at 30 rpm for 5 min	–	[61]
	Picea abies spruce bark	Hot water	85	2 h	Decanting and centrifuging at 3000 rpm for 10 min	Stirring at 100 rpm	[62]
	Vicia faba L. seed	Distilled water or NaCl	Room temp	10 min	Filtration	–	[64]
	Cashew nut testa	Acetone	–	–	Evaporation	–	[68]
	Camellia sinensis L. tea leaves	Distilled water	70	5 min	Filtration and centrifuging at 10,000 rpm for 15 min	–	[82]
Soxhlet extraction	*Laura nobilis* leaves	Water - ethanol	–	–	Evaporation and dried at 50 °C	–	[69]
Supercritical fluid extraction	*Picea abies* spruce bark	Supercritical CO_2–ethanol	40	–	–	100 bar pressure	[76]
	Camellia sinensis L. tea leaves	Supercritical CO_2–ethanol	50	–	–	188 bar pressure, Ethanol flow rate 2.94 g/min	[83]
Pressurised water extraction	Larch wood	Deionized water with inert N_2 gas	100	30 min	Filtration and evaporation under reduced pressure until dryness at 40 °C	20 bar pressure	[74]
Ultrasound/ ultrasonic-assisted extraction	*Piper beetle* leaves	Ethanol	51.6	30 min	–	400 W power, Solute to solvent ratio 1:21.85 g/ml	[71]
	Cannabis sativa L. flowers, leaves and seed husks	Methanol	–	15 min	–	130 W power	[84]
Microwave-assisted extraction	*Ceratonia siliqua* kibbles	Ethanol	–	–	–	340 W power, Solute to solvent ratio 1:30 g/ml	[73]
	Myrtus communis leaves	Ethanol	–	–	–	500 W power, Solute to solvent ratio 1:32 g/ml	[85]

Note: (–) indicates that related information are not available in the respective literature.

phenolic groups since they are an excellent hydrogen donor. Fig. 1 depicts a schematic illustration of the basic tannin structure and probable molecular interactions that induce coagulation in an aqueous solution. Phenolic groups become deprotonated, forming phenoxide, and stabilised via resonance. This deprotonation occurs as a result of the delocalisation of electrons within the aromatic ring, which escalates the electron density of the oxygen atom [6]. This suggests that the availability of more phenolic groups in a tannin structure increases the efficiency of their coagulation capability.

Since condensed tannin is anionic and most colloids are anionic, condensed tannins are not applied directly as a coagulant to remove anionic contaminants in water or wastewater. The tannin extract will usually be subjected to a chemical modification to provide cationic features. The commercial tannin-based coagulant in the market has undergone a cationisation process. Commercial modified tannin containing both the phenolic groups and amine was studied in water treatment and the result revealed that the modified tannin exhibits a cationic nature since there is a single tertiary amine group per monomer. Moreover, it is also amphoteric in nature due to the presence of phenolic groups [86]. Diverse modifications interrelated with their chemical structure, can be performed with condensed tannins [29]. As a natural source, tannins have two main ways of being used in water and wastewater treatment. That is either by gelation or cationisation. Although gelation is commonly applied for the adsorption of cationic contaminants in water, tannin cationisation may drive a new type of coagulant which can remove anionic pollutants [87]. The main chemical modification can be classified into three main categories [29] as shown in Fig. 2.

Under each category, different reactions are directing to new building blocks, which are important for polymer synthesis. The heterocycle can be opened leading to readjustments of the chemical structure. In hydroxyl group reactivity, reactions can occur directly with the hydroxyl. Lastly, the reactivity of nucleophilic sites, formed by hydroxyl groups on the aromatic rings, directs to electrophilic aromatic substitutions. The presence of nucleophilic sites in the tannin structure is due to the phenol groups. Hydroxyl is an electron donor that can be strengthened under alkaline conditions forming a phenoxide ion. Typically, under strongly acidic conditions, the Mannich reaction (Fig. 3) involves the introduction of quaternary nitrogen to the tannin polyphenolic structure by undergoing a reaction with an amine and an

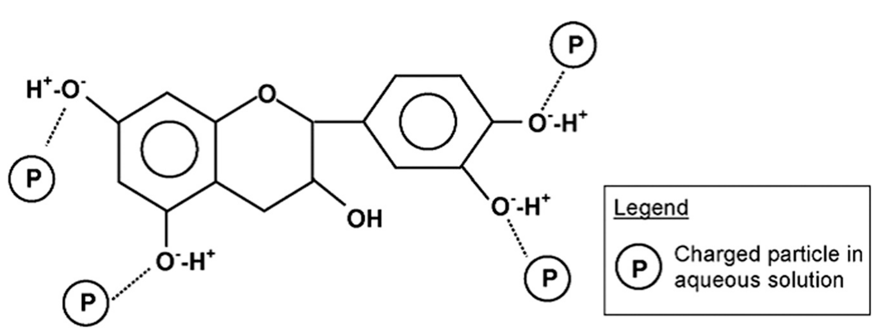

Fig. 1. Schematic illustration of primary tannin structure in aqueous solution and probable molecular interactions [6].

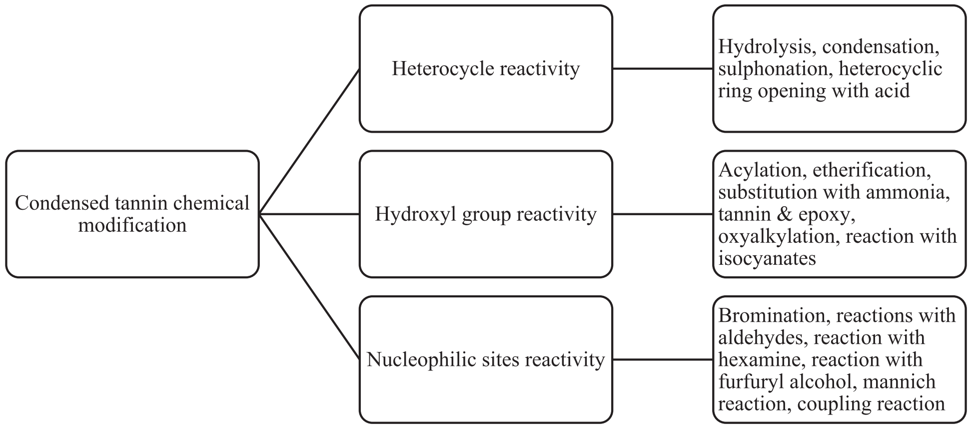

Fig. 2. Chemical modification of condensed tannins.

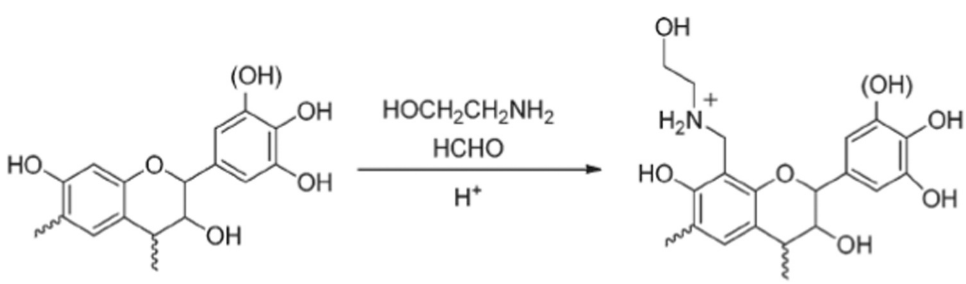

Fig. 3. The Mannich reaction with tannins [29].

aldehyde to produce a higher molecular weight compound [29].

In the initial step of the Mannich reaction, aldehyde and amine react to produce an iminium ion which is later added to any phenoxide ion (phenolic ring) of the tannins by substituting the hydrogen of the aromatic structure. Acidic conditions must be maintained after the aminomethylation step to create the protonation of the amine attached to the tannin [88]. The resulting tannin polymer possesses an amphoteric character by having both anionic phenols and cationic amines on the polymer, which are water-soluble [41,44]. The cationisation procedure follows a Mannich reaction path with some variations as has been established in several patents [89–91]. In this procedure, several characteristics can be tuned, such as stability and solubility at various pH levels. The appearance of new positively charged groups in the molecular structure can be advantageous in the coagulation systems because cationic molecules may destabilise anionic molecules once mixed in an aqueous media [28].

According to Quamme and Kemp [89], a stable tannin-based polymer is formed from a tannin, an aldehyde and an amino compound reacting under a slightly acidic condition with the molar ratio of the amino compound to the tannin repeating unit in the range of 1.5:1–3.0:1. The amino compound to be used could be ammonia or a primary or secondary amine or amide compound. However, primary amines are favourable being more reactive amines than secondary or tertiary amines. Aldehyde compound for the reaction includes organic chemical compounds that contain at least one aldehyde group such as glyoxylic acid, acetaldehyde, formaldehyde, glycolaldehyde or polyaldehydes such as paraformaldehyde and glyoxal. Aldehyde generating agents such as melamine-formaldehyde monomeric products and derivatives are also suitable to be used. The right ratio or proportion of tannin, aldehyde, and amine in the Mannich reaction ensures that tannin gelation will not occur which prevents dissolving the tannin in water [42].

Several studies have been performed by Beltran-Heredia et.al. [26, 39,92–94] on the synthesis of tannin-derived coagulants. One of the studies was to determine the likely combinations of two types of tannin extracts, *A. mearnsii* (Clarotan and Weibull black) and *S. balansae* (Quebracho Colorado) with three types of amine compounds (NH_4Cl, glycidyltrimethylammonium chloride, and diethanolamine) through a factorial design. Diethanolamine was determined as the best nitrogenous compound that can fix a cationic character to the tannin structure to produce coagulants for surface water clarification. Meanwhile, a combination of *A. mearnsii* tannin extract with either one of the amine compounds produced an efficient coagulant for the treatment of industrial wastewater effluent [26]. Subsequently, optimisation studies were performed on the synthesising reaction of *A. mearnsii* tannin extract with formaldehyde and NH_4Cl. Temperature and the tannin–NH_4Cl ratio (g of NH_4Cl/g of tannin extract) seem to influence the cationic coagulant performance and proven effective in the treatment of surfactant wastewater and dye-polluted wastewater. The NH_4Cl ratio was found to be more sensitive than temperature and no interaction was observed between these two parameters [92].

Further, optimisation was performed on the synthesis process of *A. mearnsii* tannin extract with diethanolamine and formaldehyde [93]. Variables studied included pH and temperature of the two stages of the Mannich reaction and also the reaction time. The optimum conditions for synthesising the coagulant was determined by looking at the removal percentages of dye (Alizarin violet 3R) and surfactant (sodium dodecylbenzene sulphonate). Subsequently, tannin modification of *S. balansae* extracts with diethanolamine and formaldehyde was studied [39,94]. An optimisation process was performed to search for the optimum operating range of reagent dosages, reaction time, and pH level. The coagulant produced was successfully tested on the removal of 9 types of dye and 8 types of detergent.

A two-step Mannich reaction was performed in synthesising *A. mearnsii* bark tannin coagulants using dimethylamine hydrochloric (DMA•HCl) and formaldehyde [28,95]. The reaction required overnight preparation of the Mannich solution (MS) with a DMA•HCl/ formaldehyde /water mass ratio of 1:1:1, which was followed by a modification procedure. An extra amount of formaldehyde was added during the cationisation to force the reaction of the tannin and iminium ion. Varying experimental conditions in the reaction, such as the heating rate, formaldehyde dosage, reaction time, and MS activation time, influence the shear viscosity and shelf life of the resulting biocoagulant. While maintaining the MS activation time, carrying out the work using the same heating rates and higher dosages of formaldehyde produced tannin coagulants with a remarkably higher shear viscosity compared to the work performed without any extra formaldehyde. Extending the MS activation time or applying a lower heating rate also produced coagulants with higher shear viscosities. If the MS activation time exceeded a certain threshold, tannin gelation may occur, resulting in unusable coagulant for wastewater treatment. In order to avoid fast tannin gelation, a higher formaldehyde/tannin ratio was required to operate over a lower MS activation time. Even though it was observed that the wastewater decolouration performance improved with an increase in biocoagulant viscosity, a lower viscosity may be preferred because such coagulants exhibited a longer shelf life and presented reasonable removal efficiencies [28].

In some cases, the developed modification procedures applied for cationisation of tannin extracts were not suitable to be applied to certain tannin extracts. This could be linked to different types and sources of the tannin. In such cases, some adaptations in the developed procedure had to be applied. It was observed that by applying a cationisation procedure optimised for *A.mearnsii* bark tannin extracts as developed in the previous study [28] directly to *S. balansae* wood tannin failed to produce the expected product. Insoluble tannin powder was found at the bottom of the reactor [95]. *S. balansae* tannin was found to be mainly composed of fisetinidin while *A. mearnsii* tannin was predominantly composed of robinetinidin which was not mainly found in *S. balansae* tannins [96]. As a result of the source variety, adaptation to the developed procedure was made and as for *S. balansae* tannin, a complete dissolution of the tannin was achieved at a much higher temperature. In condensation/polymerisation reactions, the chain length and crosslinking between the Mannich base, tannin molecules and formaldehyde of the cationic tannin-based coagulants produced progress over time leading to a thickening of the product. The extent to which the condensation reaction lasted during storage was very much influenced by the final pH of the polymer in solution. It was shown that as the acidity increased the significant shear viscosity of the resulting product was reduced [95].

Arismendi et al. [88] performed a synthesis of tannin extracts from *A. mearnsii*, *S. balansae*, and *Castanea sativa* via the Mannich reaction with formaldehyde and several amine derivatives (ethanolamine, diethanolamine and NH_4Cl). Aminomethylation does not proceed efficiently in *C. sativa* extracts possibly because: (a) the carboxyl or ester groups that tend to inhibit or slow down the reaction of the iminium ion with tannin phenols by deactivating the electrophilic properties in the aromatic ring, and (b) limited active hydrogens in polyphenols for their replacement by iminium ions due to occupancy of the sites by hydrolysable tannins. In contrast, the high percentage of condensed tannins found in *A. mearnsii* and *S. balansae* provide ample active hydrogens for a possible substitution reaction and do not have electrophilic groups. This could be the reason why the bio-flocculants *S. balansae*-ethanolamine, *A. mearnsii*-ethanolamine, *A. mearnsii*-NH_4Cl, and *S. balansae*-diethanolamine demonstrated statistically significant results in removing true colour, total solids and turbidity from the wastewater samples. Chemical modifications with diethanolamine and ethanolamine were completed following the tannin extract-amine-formaldehyde sequence. Meanwhile, for chemical modifications with NH_4Cl, a preliminary reaction between formaldehyde and amine followed by the reaction with the tannin extract is more suitable. This sequence would ensure that the preformed substances such as imines, with important electrophilic properties, would create a high chance for nucleophilic substitution in the tannins, thus having greater reactivity to generate more amino alkylation. Moreover, the formation of by-products as a result of using primary and secondary amines could be avoided [88].

In expanding the application of tannins to work effectively as a coagulant, the tannin modification process mostly implies the addition of harmful substance such as formaldehyde that considered carcinogenic to humans (group 1) by the International Agency for Research on Cancer thus, it is hazardous to persons handling the solution [97]. Noticeably, formaldehyde is the only type of aldehyde compound being used in most modification works presented above and as summarised in Table 2, thus providing an opportunity for more research to look at possible safer alternatives to formaldehyde in the tannin modification process. Another non-enolizable aldehyde which could be considered is benzaldehyde, which is not categorised as carcinogenic [98]. Benzaldehyde had been used as an aldehyde component in the Mannich reaction by various researchers [99–102]. Recently, work had been done by Machado et al. [103] in producing formaldehyde-free tannin-based flocculants. The novel synthesis method produced remarkable results with 89.9% and 100% of colour and turbidity removal respectively. However, since formaldehyde is not applied to allow polymerisation, the flocculants produced have small polymeric structures thus higher dosage of the flocculants were required to allow interaction with effluents pollutants.

From works on the synthesis of tannin-based coagulants mentioned above, it can be concluded that the efficiency of tannin as a coagulant is related to the tannin modification process. The heating rate, formaldehyde dosage and activation time of the Mannich solution will determine the degree of viscosity of the tannin polymer but over a certain limit of activation time, it can cause gelation to occur which is undesirable. Some adaptation to the general modification procedure may be needed whenever necessary depending on the type and source of tannin, and also the type of amine selected. This will ensure the production of a tannin-based coagulant which is effective for water and wastewater treatment.

5. Tannin-based coagulant mechanism

The mechanism associated with tannin-based coagulants depends on coagulation parameters such as coagulant dosage and effluent pH, as well as the type of wastewater being treated and the source of the tannin. Generally, the aggregation of the particles during coagulation can take place by the following mechanisms: (a) sweep flocculation, (b) double-layer compression, (c) adsorption and interparticle bridging, and (d) adsorption and charge neutralisation [6,30]. In particular, the latter two mechanisms are closely related to polymeric plant-derived coagulants such as tannins owing to their long-chained structure which upsurges the availability of unoccupied sites.

The existence of background electrolytes in an aqueous medium can assist the coagulation effect of natural polymeric coagulants since electrostatic repulsion between the particles is less [6]. This is also supported by Verma et al. [2] that mentioned tannin has a high molecular weight and contains a long-chained structure, therefore tannin-based coagulants offer abundant adsorption sites. Adsorption and charge neutralisation occurs by the sorption of two oppositely charged ions, whereas interparticle bridging occurs when a polysaccharide chain of coagulants sorbs the particulates. According to Bolto and Gregory [105], for bridging flocculation to take place, there should be adequate unoccupied surfaces on a particle for the attachment of segments of polymer chains adsorbed on other particles. Another requirement is that the adsorbed amount must not be very high that could make the particle surfaces become so highly covered resulting in inadequate adsorption site availability and the particles become re-stabilised. However, if the adsorbed amount is too low, insufficient bridging contacts may be formed. This is why the optimum dosage of coagulant needs to be considered for bridging flocculation.

Tannin displays an amphoteric nature due to the presence of phenolic groups [10]. Its polymeric structure consists of amino groups, which are involved in the bridging mechanism accountable for the

Table 2
Summary of tannin modification synthesis compounds.

Tannin extract	Amine used in the modification	Aldehyde used in the modification	Remark	pH	Temperature (°C)	Reaction time	Ref
1. *Acacia mearnsii* (Clarotan) 2.5 g or	Ammonium chloride (NH_4Cl) 2.5 g	Formaldehyde (FA) 1.5 g	–	–	30	90 min	[26]
2. *Acacia mearnsii* (Weibull black) 2.5 g or	Glycidyltrimethylammonium chloride (GTMAC) 2.5 g	FA 0.6 g	–	–			
3. *Schinopsis balansae* (Quebracho colorado) 2.5 g	diethanolamine (DEA) 10.8 g	FA 1.5 g	–	–			
Acacia mearnsii 2.5 g	NH_4Cl	FA 5 ml	Mass ratio NH_4Cl: tannin 2:1	–	30	90 min	[92]
	GTMAC 2.5 g	FA 5 ml / 0.23 g	–	–	30	90 min	[87]
	NH_4Cl 5 g	FA 5 ml	–	–	30	–	[27]
	DEA 10.8 g	FA 1.5 g	–	6–6.8	32.3–32.9	60 min	[93]
Schinopsis balansae (Quebracho colorado) 2.5 g	DEA 15.64 ml	FA 8.5 ml	–	–	30	60 min	[94]
Schinopsis balansae (Quebracho colorado) 1 g	DEA 6.81 g	FA 2.78 g	–	–	30	60 min	[39]
Acacia tannic extract 8.66 g	NH_4Cl 3.8 g	FA 30 ml	–	–	65	2 h	[104]
Acacia mearnsii	dimethylamine hydrochloride (DMA-HCl)	FA	Mass ratio	–	85	45/ 60/ 90/ 120 min	[95]
			Water: DMA: FA 1:1:1				
Schinopsis balansae (Quebracho)						60/ 100/ 135 min	
			FA: tannin 0.02 or 0.04				
Acacia mearnsii	$NH_4(OH)$	None	Tannin: water 20 g:100 ml Molar ratio Tannin: $NH_4(OH)$ 1:1	1–2	20–25	4 h	[103]
	DMA-HCl	FA	Mass ratio Water: DMA: FA 1:1:1 FA: tannin 0.03 or 0.06	6	85	60 min	[28]
1. *Acacia mearnsii* 12.58 g or	Ethanolamine (ETA), 4.73 ml	FA 16.78 ml	Molar ratio	6.4–6.7	65–80	–	[88]
			Tannin: ETA: FA 1: 1.8:1.8				
2. *Schinopsis balansae* (red Quebracho) 12.58 g	DEA 7.62 ml		Molar ratio				
			Tannin: DEA: FA 1: 1.8:1.8				
Castanea sativa (Castanea) 8.66 g	NH_4Cl 3.8 g	FA 30 ml	Molar ratio	–	65–70	2 h	
			Tannin: NH_4Cl: FA 1: 1.8:1.8				
Picea abies 2.5 g	DEA 10.7 ml ETA 4.9 ml	FA 1.38 ml	–	6.5	85	3 h	[62]

Note: (–) indicates that related information are not available in the respective literature.

coagulation/flocculation of particles. The polymer chains that contain positively charged amino groups will neutralise the negatively charged colloids thus destabilising them. After no electrical forces are repelling them, the particles will then combine and interlock in the long polymer chains, forming dense flakes sufficient enough to form sediment [105].

According to Beltrán-Heredia et al. [92], decolouration using coagulation with modified tannin-based materials is usually called adsorption-like coagulation in the literature. Coagulation is a very complicated process to model because of the existence of many influential variables. Nevertheless, a theoretical proposal could be adopted based on the surfactant-polymer interaction models. These mathematical methods are called adsorption-like coagulation models as reported by Beltrán-Heredia and his team. Adsorption capacity, q is the parameter widely used in the adsorption processes. According to Beltrán-Heredia et al. [87], contaminant removal by coagulation and flocculation takes place in two stages. Initially, the destabilisation of colloids occurs through chemical interaction between the cationic coagulant molecules and the anionic contaminants. Then, flocs of the coagulant-contaminant begin to develop due to the sorption mechanism. This becomes the controlling stage, where the whole process can be simulated as an adsorption phenomenon [106].

They also added that although another hypothesis is feasible, the main adsorption (and coagulation) model is the one presented by Langmuir in the twentieth century which is still practical and applicable today. The likelihood of adsorption is proportional to the number of available sites, while the likelihood of desorption is relative to the number of occupied sites. Those probabilities could be linked to the strength of the interaction between the adsorbate and the adsorbent surface. The interaction between a tannin-based coagulant and dye can be modelled following the Langmuir hypothesis, resulting in very high maximum q levels of 1.21 mg/mg and 0.87 mg/mg for Palatine Fast Black WAN and Alizarin Violet 3R, respectively.

In a later study, Sánchez-Martín et al. [94] mentioned other adsorption-like coagulation models, i.e. Frumnkin-Fowler-Guggenheim, Freundlich as well as Gu and Zhu. These models are established on the adsorption capacity, q which is given by Eq. (1).

$$q = \frac{(C_0 - C_l)V}{W} \quad (1)$$

where:

C_0 is the initial pollutant concentration (mg/L),

C_l is the equilibrium pollutant concentration in bulk solution (mg/L),

V is the volume of the solution (L), and.

W is the coagulant mass (g) (calculated based on the tannin raw extract in the coagulant synthesis).

The Frumnkin–Fowler–Guggenheim model was proposed as a simple model which can be applied to describe the correlation between coagulant and contaminant molecules in dilute solutions [107]. The Freundlich model has been widely used in the adsorption process where q represents a power function of the equilibrium contaminant concentration C_l [108]. The Zhu and Gu model is proposed for polymer and suspended matter removal, with the assumption that the adsorbed layer is made of pollutant aggregates [109]. The experimental data from the study fits reasonably well with the three proposed equations, with $r^2 = 0.95$, $r^2 = 0.91$ and $r^2 = 0.93$ for Frumnkin–Fowler–Guggenheim, Freundlich and Gu and Zhu, respectively [94].

Plant-based coagulants may not engage the sweep coagulation method such as chemical coagulants as can be observed from the drop in treatment efficiency past the optimum coagulant dosages [110]. Most of the time, more than a single mechanism can be associated during the coagulation process. As observed by Graham et al. [25] in their study, as the pH increases from 4 to 7, the tannin-based polymer optimum dosage also increases while the polymer charge density reduces. This trend is consistent with a charge interaction/neutralisation mechanism between the negatively charged kaolin suspension and the polymer. However, as the optimum tannin-based polymer dose increases with pH, the magnitude of the flocculation index increases correspondingly thus designating a greater extent of floc formation. At pH 6 and 7 the coagulation mechanism may follow both charge destabilisation and adsorption/enmeshment. At pH 7, in particular, the behaviour is difficult to explain since at this pH region, a loss of polymer charge and solubility happens abruptly. This outcome could most likely be as a result of the combination of electrostatic charge interactions and physical phenomena such as polymer bridging and solid-phase enmeshment. Above pH 7, the magnitude of the tannin-based polymer charge density is so small thus the coagulation of kaolin is thought to be mainly by adsorption/enmeshment by the precipitated polymer (‘sweep’ coagulation). In contrast, it has been proposed by Nnaji et al. [68], that bridging is the principal mechanism of particle destabilisation and floc formation at a high pH.

Some researchers have looked at the usage of polymers as coagulant aid or flocculant in coagulation experiments using tannin as the main coagulant. PAM, PolyDADMAC, polyacrylic acid and polyamine are among the frequently used polymeric flocculants [1]. When a polymer is added to oppositely charged particles, the key driving force for adsorption could be an electrostatic attraction and the acclaimed mechanisms by which a polymer can encourage flocculation are charge neutralisation, bridging or electrostatic patch models. Charge neutralisation happens when the electric double layer repulsion between particles is lowered caused by the adsorption of highly charged polyelectrolytes on oppositely charged particles. Bridging takes place when fragments of similar polymer molecule are attached to more than one particle, thus linking the particles together [111]. Ibrahim and Yaser [1] confirmed that dual system of tannin based coagulant with anionic PAM is effective in colour removal of biologically treated landfill leachate. In a study by Grenda et al. [28], it was found that anionic and cationic PAM flocculants improved the decolourisation of synthetic dyes effluents which undergo coagulation process with modified *A. Mearnsii* bark tannin extract. In another study, the tannin-based coagulant from *A. mearnsii* was successfully applied in a dual system with cationic PAM flocculants for industrial wastewater treatment at the pilot plant scale [95]. Scanning Electron Microscopy (SEM) analysis is a useful approach to look at the morphological surface structure of tannin and effect of bridging after it has undergone coagulation process as shown in Figs. 4 and 5 as example of works done by Banch et al. [112] and Ibrahim and Yaser [1] respectively.

6. Application of tannin-based coagulants in water and wastewater treatment

Tannin usage as flocculants and corrosion inhibitors received attention back in the late 1960s and early 1970s and applied industrially. A tannin-based polyelectrolyte received attention as a coagulant to treat turbid water in 1964 by Rice et al. [113]. After practically vanishing from the market for a certain period, it started to regain favour both in research and industry due to interest in substituting toxic synthetic materials with bio-derived material [114].

There is an increasing tendency in tannin-based coagulant research as shown in Fig. 6. From the graph, it can be seen that researchers have started showing a growing interest in studying tannin as a coagulant in 2008. A rise in the number of studies in 2009 and 2011 was contributed mostly by studies from Beltran-Heredia and his team [23,27,87,92,115,116]. A drop of interest in 2015 might have been caused by researchers showing interest to study other types of natural or chemical coagulants, or other techniques for wastewater treatment. It could also be that researchers were interested in tannin applications other than as coagulants. As suggested by Vijayaraghavan et al. [10], the limited application of tannins as a natural coagulant for water treatment may be associated with contradictory reports on the effect of tannin on human health. Nonetheless, promising outcomes from the application of tannin in water and wastewater treatment have been observed within the past 10 years and showing an increasing trend in 2020.

Regardless of the challenges in the commercialisation of natural coagulants including regulatory approval, market awareness, support and recognition, local competition, and other problems [31], commercial natural coagulants have been used expansively in the wastewater and water treatment industries [117]. For example, the tannin derived from the barks of the *A. mearnsii* tree has been well commercialised as Tanfloc, Ecotan, Floccotan [3,31] and Acquapol [118], Organofloc derived from vegetal tannin [1], and Silvafloc from *S. balansae* [19], just to name a few.

Tannins are easier to apply in water treatment operations since no pH adjustment is required, simple modifications to the tannin extract are possible, and additional flocculants are not needed. Moreover, less sludge is produced and even so, that sludge is biodegradable. No leftover toxic or harmful residue is found in the treated effluent [94]. Tannin-based coagulant usage adheres to sustainability principles and does not affect the environmental equilibrium since it can be added in low dosages [119]. Most importantly, tannin-based coagulants have proven to be effective in the treatment of different types of wastewater. Table 3 summarised the application of tannin-based coagulants in various water and wastewater treatment for the past 20 years. The application of tannin as a primary coagulant is discussed thoroughly in the following section.

6.1. Domestic wastewater, river and surface water, and synthetic water

Several studies have been carried out by using raw tannin extracts as a coagulant without modification. The usage of tannin extract from fava bean seeds (*Vicia faba L.*) in synthetic turbid water was investigated by Kukić et al. [64]. The best turbidity removal was obtained by dosing 0.125 ml/L tannin in water with high initial turbidity. Singh and Choubey [61] investigated the feasibility of using widely distributed *A. catechu* tannin extract to purify surface water. At the optimal dosage of 3.0 ml/L, *A. catechu* powder could remove the turbidity of pond raw water by up to 91% and TDS by 57.3% at the optimal dosage of 4.0 ml/L.

Meanwhile, Heiderscheidt et al. [120] tested performance of modified tannin-based coagulants in comparison to ferric sulphate

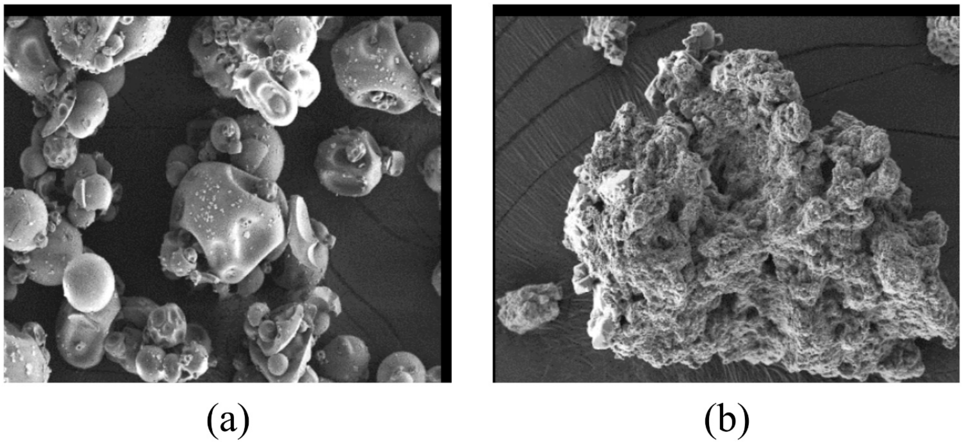

Fig. 4. Microscopic image of tannin (a) before and (b) after coagulation process [112].

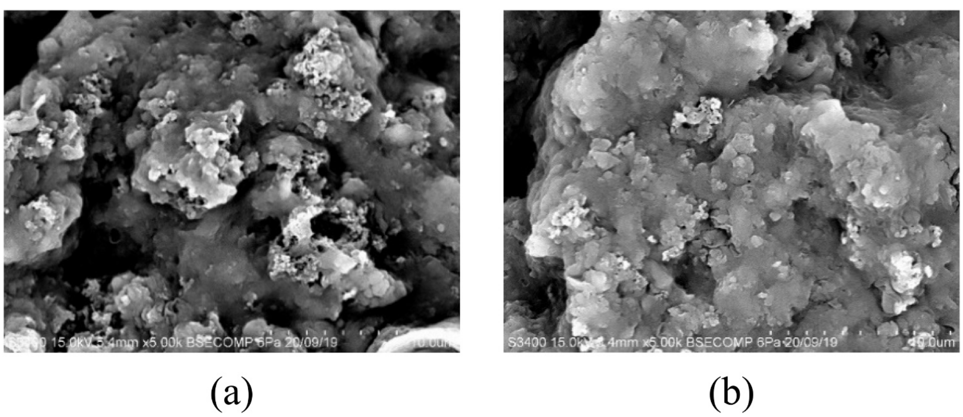

Fig. 5. Microscopic image of flocs after coagulation process with (a) tannin and (b) tannin with anionic PAM [1].

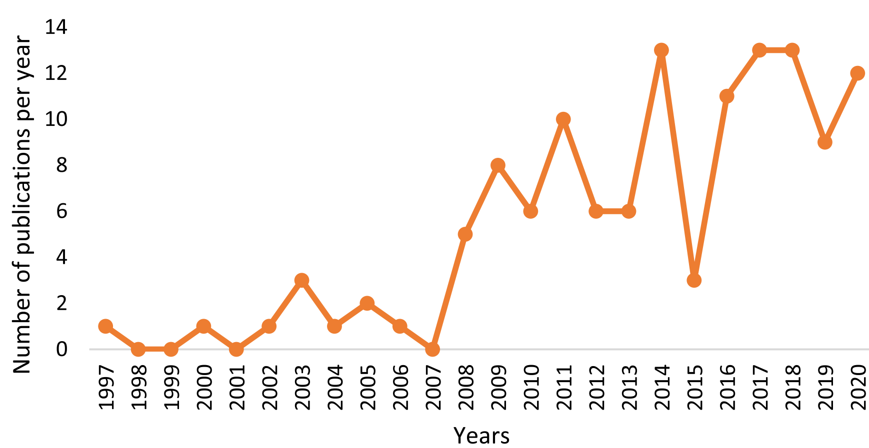

Fig. 6. Number of tannin-based coagulant publications per year indexed in Scopus.

($Fe_2(SO_4)_3$) in treating humic peat extraction runoff water. A considerably higher dosage (55–75%) of tannin coagulant was required to achieve the highest removal of SS (<58%), with flocs formed by a tannin-based coagulant presenting the best settling properties. Back in 2009, Graham et al. [121] studied the coagulation effectiveness of a new commercial tannin based polyelectrolyte on simulated and real coloured waters. The tannin coagulant was able to remove high levels of dissolved organic carbon (DOC) over a wide pH range (4–9) of simulated water. It was observed that the optimal dose increased proportionally with pH due to the loss of cationic charge and solubility. The performance of the tannin coagulant was as good as polyDADMAC and alum at optimum coagulant doses and a pH of 7. The tannin coagulant performance was comparable to polymeric $Fe_2(SO_4)_3$ in terms of turbidity and treated water colour removal from real coloured water, but not for residual DOC.

Tannin-based coagulants synthesised in a lab via the Mannich reaction were evaluated in wastewater samples from a contaminated river and synthetic wastewater to simulate toxic waters polluted with diazo dyes. Out of nine natural coagulants that were prepared by combining tannin extracts (*Acacia*, *Schinopsis*, and *Castanea*) and amines

Table 3
Summary of application of tannin-based coagulants in water and wastewater treatment.

Water/ wastewater sample	Source of tannin coagulant	Coagulant dosage	pH	Mixing rate (R – rapid, S – slow)	Mixing time (R – rapid, S – slow)	Settling time	Removal %	Ref
Domestic/sewage/ river/synthetic wastewater								
Synthetic raw water	Valonia –Turkish oak (raw tannin extract)	0.03 mg/L	11	R: 200 rpm S: 15 rpm	R: 1 min S: 15 min	15 min	Turbidity: 80.5%	[17]
Synthetic kaolin suspension	*A. Mearnsii* bark (modified tannin)	14 mg/L	9	R: 200 rpm S: 50 rpm	R: 30 s S: 30 min	30 min	Turbidity: ~70%	[25]
Surface water Guadiana River, Spain (1000 ml)	*S. balansae* (modified tannin- Silvafloc	20 mg/L	7	R: 100 rpm S: 30 rpm	R: 2 min S: 20 min	1 h	Turbidity: 90% Total coliforms: 70% Streptococcus: 99.9%	[19]
Surface water Budha Talab Pond, Raipur (1000 ml)	*A. catechu* bark (raw tannin extract)	3 ml/L	7.8	R: 150 rpm S: 30 rpm	R: 5 min S: 30 min	30 min	Turbidity: 91%	[61]
Synthetic turbid water (200 ml)	*Vicia faba* L. (fava bean) seed (raw tannin extract)	0.125 ml/L	7	R: 200 rpm S: 80 rpm	R: 1 min S: 30 min	30 min	Turbidity: 87%	[64]
Surface water Shatt Al-Arab River (50 ml)	*Laurus nobilis* leaves (modified lignin-tannin polymer)	0.2 g	3	R: 200 rpm S: 15 rpm	R: 1 min S: 15 min	15 min	Turbidity: 98%	[69]
Runoff water from peat extraction site, Vihanti, Finland (1000 ml)	Modified tannin	110 mg/L	4.5	R: 300 rpm S: 50 rpm	R: 10 s S: 15 min	30 min	DOC: 52% SS: 43%	[120]
Hostel municipal wastewater, Selangor, Malaysia (500 ml)	*A. Mearnsii* (modified tannin-Tanfloc)	35 mg/L	6–8	R: 200 rpm S: 100 rpm	R: 1 min S: 10 min	10 min	Turbidity: 90% SS: 63% BOD_5: 60% COD: 60%	[42]
Surface water Guadiana River, Spain (500 ml)	*A. Mearnsii* (modified tannin-Acquapol C1)	5 mg/L	7	S: 30 rpm	S: 30 min	15 min	Algae: 80%	[125]
Synthetic kaolin suspension (500 ml)	*A. Mearnsii* bark (modified tannin-Tanfloc)	2 mg/L	7	R: 200 rpm S: 60 rpm	R: 2 min S: 15 min	20 min	Turbidity: 91%	[21]
Raw domestic sewage Porto Alegre, Brazil (2000 ml)	*A. Mearnsii* bark (modified tannin-Acquapol C1 18)	1000 mg/L	–	R: 120 rpm S: 30 rpm	R: 1 min S: 5 min	40 min	Total coliforms: 99.66% E. coli: 99.61% Adenovirus: 96.22%	[118]
	A. Mearnsii bark (modified tannin-Acquapol C1 WW)						Total coliforms: 99.01% E. coli: 99.19% Adenovirus: 88.85%	
	A. Mearnsii bark (modified tannin-Acquapol 893/11)						Total coliforms: 96.69% E. coli: 100% Adenovirus: 98.85%	
Secondary treated urban wastewater, Northern Portugal (500 ml)	*A. Mearnsii* bark (modified tannin-Tanfloc SG)	50–80 mg/L	7.3	R: 100 rpm S: 40 rpm	R: 2 min S: 30 min	1 h	Turbidity: 89% Colour: 73.6%	[58]
Synthetic turbid water (200 ml)	*Persea* *Americana* seed (raw tannin extract)	0.02 g/ 200 ml	8	R: – S: –	R: 5 min S: 25 min	3 h	Turbidity: 87%	[138]
Dye/Textile wastewater								
Textile wastewater, Morocco	Vegetable tannin (modified tannin-Polysep3000)	100 mg/L	<10	R: 160 rpm S: 30 rpm	R: 5 min S: 20 min	1 h	Colour: 96% COD: 40–50%	[129]

(*continued on next page*)

Table 3 (*continued*)

Water/ wastewater sample	Source of tannin coagulant	Coagulant dosage	pH	Mixing rate (R – rapid, S – slow)	Mixing time (R – rapid, S – slow)	Settling time	Removal %	Ref
Stamping industry effluent, Florai, (500 ml)	Tannin extract	400 mg/L	7–7.5	R: 90 rpm S: 35 rpm	R: 2 min S: 20 min	30 min	COD: 94.8% Colour: 99.2% Turbidity: 99.7%	[128]
Synthetic dye effluent (100 ml)	*S. balansae* (lab modified tannin)	15 ml/L	7	R: 100 rpm S: 30 rpm	R: 2 min S: 30 min	–	Alizarin violet 3 R Dye: 70%	[94]
Industrial coloured effluent Geneva Switzerland (200 ml)	Acacia mearnsii bark extract (lab modified tannin)	200 mg/L (with cationic PAM as a coagulant aid)	7	R: – S: –	R: – S: –	1 h	Colour: 91% Turbidity: 92%	[95]
Synthetic coloured effluent containing Acid Black 2 (200 ml)	*A. Mearnsii* bark extract (lab modified tannin)	100 mg/L (with cationic PAM as a coagulant aid)	2.8	R: – S: –	R: – S: –	24 h	Colour: 83%	[28]
Synthetic coloured effluent containing Duasyn Direct Red (200 ml)		50 mg/L (with cationic PAM as a coagulant aid)	3.4				Colour: 89%	
Synthetic coloured effluent containing Methylene blue (200 ml)		50 mg/L (with anionic PAM as a coagulant aid)	2.9				Colour: 95%	
Synthetic coloured effluent containing Crystal violet (200 ml)		100 mg/L (with anionic PAM as a coagulant aid)	2.2				Colour: 93%	
Dyeing and laundry effluent Brazil (500 ml)	Modified tannin-Tanfloc	0.3 mg/L (with cationic PAM POLYCAP-32 as a coagulant aid)	7.5	R: 60 rpm	R: 20 min	–	Colour: 96% Turbidity: 79%	[139]
Synthetic textile effluent containing Direct Blue 85 (500 ml)	Acacia mearnsii bark (modified tannin-Tanfloc SG)	60 mg/L (with Magnafloc 155 as a coagulant aid)	5	R: 150 rpm S: 20 rpm	R: 3 min S: 15 min	15 min	Colour: 100% DOC: 27%	[22]
Industrial laundry wastewater, Parana, Brazil (1000 ml)	*A. Mearnsii* (Modified tannin- Tanfloc POP)	110 mg/L	6.4	R: 120 rpm S: 20 rpm	R: 2 min S: 2 min	10 min	Colour: 80.27% Turbidity: 86.5%	[140]
Landfill leachate								
Landfill leachate Sabah, Malaysia (200 ml)	Vegetable tannin (modified tannin-Organofloc)	100 mg/L (with PAM as a coagulant aid)	5	R: 57 rpm S: 57 rpm	R: 5 min S: 3 min	10 min	Colour: 81.8%	[1]
Landfill leachate Sepang, Malaysia (500 ml)	*A. Mearnsii* (Modified tannin)	0.73 g 1460 mg/L	6	R: 250 rpm S: 60 rpm	R: 15 min S: 30 min	30 min	COD: 53.5% TSS: 60.7% NH_3–N: 69.7% Colour: 91.4%	[112]
Agricultural effluent								
POME, Serting, Malaysia (500 ml)	Vegetable tannin (modified tannin - Organofloc)	5.05 mg/L	–	R: 75 rpm S: -	R: 22.5 min S: -	2 h	SS: 65.67% COD: 34.16%	[132]
Cleaning water of UF membrane (POME)	Vegetable tannin (modified tannin-Organofloc)	732.3 mg/L	7	R: 100 rpm S: 40 rpm	R: 2 min S: 30 min	1 h	Colour: 80.64% COD: 72.25%	[131]
Dengkil, Malaysia POME Dengkil, Selangor (500 ml)	*A. Mearnsii* bark (modified tannin-Tanfloc)	3 mg/L	5	R: 200 rpm S: 60 rpm	R: 2 min S: 15 min	20 min	Turbidity: 40%	[21]
Raw vinasse wastewater Parana, Brazil (200 ml)	*A. Mearnsii* (Modified tannin -Tanfloc SG)	250 ml//L	4.7	R: 100 rpm S: 50 rpm	R: 1 min S: 30 min	2 h	Colour: 85% Turbidity:95% COD: 45%	[134]
Pig slaughterhouse wastewater, Parana (500 ml)	*A. Mearnsii* (Modified tannin – Tanfloc SG)	57.5 mg/L	5.25	R: 200 rpm S: 15 rpm	R: 1 min S: 17.5 min	10 min	Colour: 72% Turbidity:95% COD: 55%	[141]
Synthetic dairy wastewater (2000 ml)	*Guazuma ulmifolia* (raw tannin extract)	775.8 mg/L	5.0	R: 200 rpm S: 30 rpm	R: 1 min S: 15 min	–	Turbidity: 95.8% BOD: 81.2% COD: 76% UV_{254}: 85.6%	[142]
Casava starch wastewater		640 mg/L	7	R: 120 rpm	R: 2 min	15 min	Colour: 51%	[133]

(*continued on next page*)

Table 3 (*continued*)

Water/ wastewater sample	Source of tannin coagulant	Coagulant dosage	pH	Mixing rate (R – rapid, S – slow)	Mixing time (R – rapid, S – slow)	Settling time	Removal %	Ref
	A. Mearnsii husk (modified tannin-Acquapol WW)							
Toledo-PR (500 ml)								
				S: 20 rpm	S: 15 min		Turbidity: >86%	
	A. Mearnsii husk (modified tannin-Acquapol S5T)	320 mg/L					Colour: >77%	
							Turbidity: >86%	
	A. Mearnsii husk (modified tannin-Tanfloc SL)	480 mg/L					Colour: >77%	
							Turbidity: >86%	
	A. Mearnsii husk (modified tannin-Tanfloc SG)	320 mg/L					Colour: 60%	
							Turbidity: >86%	
Dairy wastewater (1500 ml)	*A. Mearnsii* (Modified tannin)	300 mg/L	8–9	R: 120 rpm	R: 90 s	1 h	Colour: >90%	[41]
				S: 45 rpm	S: 30 min		Turbidity: >95%	
Agricultural drainage ditch Ruukki, Finland (1000 ml)	*A. Mearnsii* (Modified tannin-Tanfloc HTG)	10 ml/L	6.9	R: 200 rpm	R: 20 s	15 min	Phosphorus: 95%	[8]
				S: 40 rpm	S: 5 min		Turbidity: 98%	
	A. Mearnsii (Modified tannin-Tanfloc HTH)						Phosphorus: 90%	
							Turbidity: 97%	
Agricultural manmade wetland Tarvaala, Finland (1000 ml)	*A. Mearnsii* (Modified tannin-Tanfloc HTG)	5 ml/L	6.6	R: 200 rpm	R: 20 s	15 min	Phosphorus: 70%	
				S: 40 rpm	S: 5 min		Turbidity: 82%	
Other industrial effluent								
Petrol station wastewater Parana, Brazil	*A. Mearnsii* (Modified tannin-Tanfloc)	500 mg/L	6.9	R: 100 rpm	R: 1 min	2 h	Turbidity: 90%	[136]
				S: 50 rpm	S: 30 min		COD: 73%	
Fibre-cement effluent, Emene, Nigeria (200 ml)	*Anacardium occidentale* (cashew) testa (raw tannin extract)	100 mg/L	12	R: 250 rpm	R: 2 min	30 min	TSS: 84%	[68]
				S: 40 rpm	S: 20 min			
Paint manufacturing wastewater	Modified tannin	600 mg/L	7	R: 150 rpm	R: 5 min	1 h	Colour: 99%	[135]
Casablanca, Morocco (1000 ml)				S: 30 rpm	S: 15 min		COD: 87%	

Note: (–) indicates that related information are not available in the respective literature.

(ethanolamine, diethanolamine, NH_4Cl), quebracho-diethanolamine and acacia-NH_4Cl were most successful in removing TS (12–99%), true colour (93–100%) and turbidity (34–99%) from the simulated wastewater. From the river sample, acacia-NH_4Cl managed to remove 90–95% TS, 98–99% turbidity, 62–72% COD and 77–90% colour. In the sample of simulated wastewater, acacia-NH_4Cl and the mixture of Quebracho-diethanolamine + acacia-NH_4Cl achieved the removal of turbidity (99%), colour (96%), COD (70.5%) and total solids (96.4%) [88].

Well-established commercial tannin-based coagulants such as Tanfloc, Silvafloc and Acquapol have been applied in many wastewater treatment studies over the past decades. A Tanfloc dosage lower than 10 mg/L was found to eliminate almost all suspended matter in a river water sample. The coagulant worked better in an acidic environment pH 4 to pH 5, however the effect of pH could be minimised by an accurate coagulant dosage. Process efficiency was observed to be influenced by high initial turbidity, but not temperature. The dosage would appear to affect turbidity removal much more than the duration of the coagulation and flocculation stages. The treated water was free of organic matter or tannin concentration residue. Microorganisms such as faecal streptococcus, faecal coliforms and total coliforms were also removed up to 99%, 90% and 80% respectively [115]. Heavy metal concentrations in surface water such as Cu^{2+}, Zn^{2+} and Ni^{2+} were successfully removed using Tanfloc up to 90%, 75% and 70% respectively under optimal Tanfloc and pH conditions. Higher Tanfloc dosage and higher pH values could enhance metal removal [23]. Tanfloc also has shown removal of BOD_5 and COD (around 50%) and high turbidity removal (almost 100%) from municipal wastewater which was comparable to the results for alum. The temperature was not an influencing factor in the coagulation process. It was determined that 30% of anionic surfactants were removed while polyphenol content did not increase significantly [122].

Tanfloc was used to remove sodium dodecylbenzene sulphonate (SDBS) from surfactant simulated wastewater where an increasing pH level was found to lead to a decrease of efficiency in SDBS removal. Meanwhile, an increase in the initial surfactant concentration led to an increase in the removal process efficiency [116]. In another study by Beltrán-Heredia et al. [123], Silvafloc was demonstrated as an efficient coagulant to remove SDBS. Applying Silvafloc doses of 300 mg/L at an optimum pH of 5.8, around 80% of SDBS was successfully removed. The pH has a negative influence on surfactant removal. Besides, Sánchez-Martín et al. [19] tested the Silvafloc for river water clarification and obtained a 90% turbidity removal in neutral pH with a 20 mg/L dose of the coagulant. The coagulant also decreased total coliforms and streptococcus by up to 70% and around 99.9% respectively. Low polyphenol content (about 0.4 mg/L) was observed in the treated water with organic matter removal of 30%. The coagulant dosage was found to have greater influence than the mixing period or stirring intensity. Silvafloc has been proven to be more efficient than $Al_2(SO_4)_3$ due to its net-forming ability. $Al_2(SO_4)_3$ may perform only as a coagulant, while the long molecules of Silvafloc can destabilise colloidal material and re-arrange the flocs in the raw water.

Tanfloc was used at a municipal wastewater treatment plant, treating a highly polluted river. Coagulation-flocculation was installed prior to an electrodialysis reversal process to get desalted water. Despite the complexity of the chemical structure of tannins, the ion-exchange membranes were found not permanently spoiled by the fouling caused by residual tannin-compounds [124]. Grehs et al. [58] found that $Al_2(SO_4)_3$ and Tanfloc SG reduced the colour and turbidity and decreased the bacterial load immediately after the coagulation treatment of a secondary treated urban wastewater. Tanfloc also indicated a challenging performance compared to PAC for reducing pollutant concentration in municipal wastewater (a university hostel) in terms of sludge characteristics, floc size, BOD_5, COD and turbidity removal [42].

Acquapol is another commercial tannin-based coagulant that has potential to be applied in raw and treated sewage (activated sludge) treatment. An investigation by Fabres et al. [118] showed that Acquapol C1 18 and WW (1000 ppm) provided good results among organic coagulants, removing up to 4 logs for virus and 7 logs for coliforms in raw sewage. In treated effluents, Acquapol 893/11 (1000 ppm) showed the best removal rates removing up to 4 logs for virus and 3 logs for coliforms. Acquapol C1, another tannin-based coagulant was also tested for algae removal in drinking water and found to be more efficient than $Al_2(SO_4)_3$. High levels of algae removal were observed at a lower coagulant dosage, and up to 80% algae were removed with 5 mg/L of coagulant at neutral pH and room temperature [125].

Tannins have also been used as a coagulant aid in some studies. Earlier in 2002, Ozacar and Şengil [17] found that tannins extracted from Valoria (Turkish oak) performed better as a coagulant aid rather than as the primary coagulant. Moreover, the amount of required alum (primary coagulant) was reduced considerably. At optimum conditions of using tannin as a coagulant, 63% and 80.5% turbidity removal were achieved for water with initial turbidity of 10 and 20 FTU, respectively. Tannin was also used as a coagulant aid for the treatment of wastewater containing ink with chitosan as the main coagulant. The highest colour removal was achieved at an optimum of pH 5 using approximately 20 mg/L and 70–100 mg/L concentration of chitosan (of highest molecular weight) and tannin respectively [126].

6.2. Textile and dye industry effluent

The textile industry contributes to worldwide water pollution due to the release of untreated dye-containing effluent into waterways, thus threatening the quality and aesthetics of water resources. It is challenging to treat effluent from the textile dyeing industries pertaining to colour inconsistency and the highly fluctuating composition. Coagulation has been effectively applied for removing colour from water-soluble dyes and also water-insoluble sulphur dispersed dyes [127]. In a work by Lopes et al. [22], dye house effluents treatment by coagulation-flocculation-sedimentation was carried out by comparing usage of a commercial tannin-based coagulant to common iron salt. Two simulated solutions of textile dyehouse effluents were prepared using Direct Blue 85 dye: E1, containing only dye and salts, and E2, with three supplementary dyeing chemicals. Optimisation of the treatment was done in batch mode in terms of pH and coagulant dosages, to get highest colour removal with acceptable flocs settling velocity. Optimum pH was found to be 4–5 for total decolourisation, at lowest coagulant dosages.

Modified condensed tannins with five distinct shear viscosities (30–430 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. Colour removal was studied over different pH levels (1−14). Good decolouration results (85–96% reduction) were obtained with the simultaneous introduction of other additives into the process, which was bentonite and a cationic or anionic polyacrylamide, with minimal dosages of the latter additives [28]. In another study, a tannin-based coagulant derived from *A. mearnsii* was applied in a dual system with cationic PAM flocculant for cosmetic and coloured microbeads industrial effluent treatment. Some 93% turbidity removal and 89% decolouration results were achieved with simultaneous minimal dosage (5 ppm) of a cationic, 40% charged PAM [95].

Osorio Moreira Couto et al. [128] performed an optimisation study to determine the coagulation, flocculation, and sedimentation time of a tannin-based coagulant in treating the stamping industry effluents. The removal efficiency of colour, turbidity, and COD were evaluated along with an economic analysis of the process. The tests were conducted using different mixing and sedimentation times. The percentages of removal using 400 mg/L tannin under optimised conditions were 94.8%, 99.2% and 99.7% of COD, colour and turbidity, respectively which were slightly higher when compared to treatment with 600 mg/L $Al_2(SO_4)_3$ resulting in 93.1%, 99.1% and 99.3% removal of COD, colour, and turbidity, respectively. The treatment of textile wastewater with modified tannin (Polysep3000) achieved 96% colour removal and 40–50% COD removal. Comparing with $Al_2(SO_4)_3$ and $FeCl_3$, Polysep3000 could produce lesser sludge [129].

Quebracho colorado tannin extract was also used effectively as a coagulant for removing dyes such as indigoid, anthraquinonic and azoic from effluent. The coagulation process was effective over a wide pH range, but the best was around neutrality. Stirring variables and temperature did not really affect the coagulation performance [94]. A tannin-based coagulant derived from *A. mearnsii* de Wild was tested for removing the anionic surfactant SDBS and anthraquinonic colourant Alizarin Violet 3R. The temperature was found to be negative-affecting while acidic pH could improve contaminant removal. Overall, the tannin coagulant worked effectively under a wide range of operating conditions for surfactant and dye removal from aqueous solutions [27].

The removal of a specific contaminant, sodium lauryl ether sulphate (SLES), from the laundry industry polluted waters was also studied [130]. Coagulation was performed with modified tannins namely, Acquapol C1, Acquapol S5T, Tanfloc and Silvafloc. The SLES removal rates were 62%, 65%, 36% and 61%, respectively for Tanfloc, Acquapol C1, Acquapol S5T and Silvafloc. These discrepancies may be related to the specific production process of each coagulant.

6.3. Agricultural effluent

Noticeably, limited studies were found on the application of tannin-based coagulants in the treatment of POME. In a study, coagulation was performed as a post-treatment of an ultrafiltration membrane after treating the POME. The applicability of a commercial tannin-based coagulant, Organofloc as a primary coagulant was evaluated. The study revealed that Organofloc was usable as an alternative coagulant in water and wastewater treatment processes as some of its abilities surpass the performance of alum with COD removal at 72.25% and colour removal at 80.64%, with no risk recorded from its application [131]. In another work, Organofloc was also used as a coagulant with the aid of flocculant for treatment of POME collected from Felda Serting Hilir, Negeri Sembilan. Organofloc showed comparable performance to alum in treating anaerobic POME [132]. In a study, the highest turbidity removal efficiency in treating POME was reported to be 44.6% with 3 mg/L of optimal Tanfloc doses at pH 5. FTIR measurement shows that carbonyl, nitrogen and methyl groups could play the main role in increasing the performance of the coagulation capacity of Tanfloc in turbidity removal of wastewater [21].

dos Santos et al. [133] investigated the performance of several coagulants in terms of turbidity and colour removal of cassava starch industry wastewater. Tannin-based commercial coagulants including Tanfloc SL, Tanfloc SG, Acquapol WW and Acquapol S5T, as well as $Al_2(SO_4)_3$ were applied at different concentrations at the natural pH of the wastewater. Tannin-based coagulants showed better performance than $Al_2(SO_4)_3$ in terms of colour and turbidity removal. In one study, coagulation was applied as a pretreatment to treat Vanesse wastewater prior to photocatalysis treatment. Usage of Tanfloc SG as a coagulant significantly reduced turbidity, colour and COD at 95%, 85% and 45% respectively [134].

Turunen et al. [8] tested the performance of biopolymer coagulants in polluted agricultural water. In more polluted water, chitosan and tannin coagulants performed better than starch coagulants at 5–10 ml/L dosage. Meanwhile, in less polluted water, a tannin coagulant was found efficient at the doses of 5–8 ml/L, reducing 22%, 82% and 70% of total phosphorus, TOC, turbidity and phosphorus respectively. Good removal of phosphorus and turbidity indicated that biopolymer coagulants were applicable for the treatment of polluted agricultural water where the resultant biodegradable biopolymer sludge could be readily used as a phosphorus fertiliser.

Dela et al. [41] studied the efficiency of tannin and PAC coagulant for the dairy industry wastewater treatment. No statistical difference was observed between the performance of the two coagulants based on TS, turbidity, colour and COD removal. PAC increased the electrical conductivity and consumed higher alkalinity of the clarified wastewater. Tannin performed better within a pH range of 5–10. Even though the highest K_A values were seen from PAC usage, higher resistance to floc breakage during the slow-mixing time was observed from tannin usage.

6.4. Landfill leachate

Landfill leachate contains organic and inorganic contaminants, including heavy metals, and ammonia-nitrogen (NH_3-N) [127]. To date, very few studies were reported on the application of tannin in the treatment of landfill leachate. One study was carried out using a tannin-based coagulant to treat stabilised landfill leachate. A central composite design (CCD) programme was used to perform optimisation of the effect of pH and tannin dosage on TSS, colour, COD and NH_3-N. The highest removal for TSS, colour, COD and NH_3-N was achieved with an optimum tannin dosage of 0.73 g at pH 6 [112]. For the first time, Ibrahim and Yaser [1] used Organofloc as a primary coagulant for the decolourisation of biologically treated landfill leachate with the aid of a polymer as a flocculant. At the optimum leachate pH of 5, coagulation was performed using Organofloc with 3 min of flocculation time and a sedimentation time of 10 min resulting in the highest colour removal (81.8%) at a coagulant dosage of 100 mg/L, with 1 mg/L anionic polyacrylamide (APAM) added. A coagulation-flocculation system consisting of Organofloc as a tannin-based coagulant combined with APAM as a flocculant has indicated promising results in the decolourisation of BTLL.

6.5. Other industries

Findings from the study of Aboulhassan et al. [135] indicated that a tannin-based coagulant was more effective than $FeCl_3$ and $Al_2(SO_4)_3$ for the treatment of COD and colour in paint manufacturing wastewater. No pH adjustment was needed and coagulation using the tannin-based coagulant obtained removal of more than 87% COD and 99% colour while producing a lower volume of decanted sludge when compared to metal salts coagulant.

The application of tannin extract from cashew nut testa as a coagulant for the removal of suspended solids in the effluent from a fibre-cement industry was also investigated. Some 84% of TSS was removed with 100 mg/L tannin-based coagulant dosage at an optimum effluent pH of 12.

The combined process of coagulation/ flocculation with heterogeneous photocatalysis processes for the treatment of petrol station wastewater was carried out by Ferrari-Lima et al. [136] which reported that coagulation with Tanfloc managed to reduce COD from 1363 mg/L (untreated) to 362 mg/L. In another study, tannin and cationic hemicellulose (CH) were used as cationic flocculants, and cellulose acetate sulphate (CAS) was used as an anionic flocculants for the treatment of biodiesel wastewater (industrial wastewater (EFID) and laboratory wastewater (EFLB) from biodiesel). PAM was used as a reference anionic flocculant for result effectiveness analysis obtained with CAS. For EFLB, the dual-flocculation application condition of 25% tannin and 75% CH showed turbidity removal of 89.1% for CAS additions and 89.5% for PAM additions. Meanwhile, for EFID, turbidity removal of 67% for CAS additions and 41% for PAM additions were observed. It could be concluded from the dual-flocculation performance that tannin and cationic hemicellulose may be used for treating biodiesel wastewater [137].

7. Final considerations

Quite frequently, treated wastewater discharged from coagulation-flocculation with tannin and sedimentation process will still need to be further treated to ensure that all pollutants in the wastewater have met the environmental regulations before allowed to be released into water bodies. Removal of colour from simulated textile wastewater and SDBS from simulated laundry wastewater showed improvement after sand filtration which followed after the coagulation process with tannin coagulant [27]. In another study, electrodialysis reversal was applied as tertiary treatment, after heavily polluted river water was subjected to prior treatments applying a tannin-based product as a coagulant and sand filtration [124]. Photocatalytic treatment was applied to further treat the effluent coming from the coagulation process using Tanfloc as a coagulant which resulted in significant reductions of COD, absorbance and elimination of toxicity [134,136]. Nascimento et al. [140] observed that coagulation-flocculation and the sedimentation steps utilising tannin-based coagulant and further treatment by ultrafiltration and microfiltration significantly improved the quality parameters of the treated laundry wastewater. There is a possibility to skip the sedimentation process and perform a filtration study using different types of filtration media as post-treatment to further improve wastewater discharge quality following coagulation with tannin.

Sludge produced from the coagulation process using natural coagulant is claimed as biodegradable and safe for use as fertiliser, and land application of biosolids which includes composting [143], has proven a cost-effective method of waste disposal by beneficially recycling organic matter and nutrients and improving soil quality. Nevertheless, application of the sludge may also pose a potential risk to the environment and human health. The risks could be related to the presence of heavy metals and organic contaminants in sludge composition related to the specific raw material of the industry that may gather in soil layers and travel up the food chain [41]. Furthermore, the presence of pathogenic microorganisms have to be considered for both industrial and sanitary sludges [144,145]. Due to this concern, it is very useful to perform the phytotoxicity evaluation of generated sludge as well as the treated wastewater to determine the suitability for agricultural purpose and safe discharge to the environment. Dela Justina and Skoronski [146] has conducted a study on sludge generated from dairy wastewater treatment process applying tannin coagulant, as a soil amender. As a result, the studied sludge is a non-hazardous waste and groundwater showed concentrations above the limits required by the international criteria for drinking water established by the World Health Organization and US-EPA.

Still, there is also the possibility of thermal or biological degradation of generated sludge due to the organic composition of tannin [128]. This was supported by results of solubilisation test by Dela Justina and Skoronski [146], where phenols concentration was detected exceeding the US-EPA allowed limit which can be related to phenol generation by tannin thermal degradation as suggested by Xia et al. [147] and Tondi et al. [148]. The existence of phenols in solubilised extract could be associated to the heating process of the sludge prior to carrying out the solubilisation test. Due to thermal degradation, tannin, which is a polyphenol present in the sample, could have been released and reacted with the reagents for phenol determination [146]. Bio-flocculants made from tannins, used in wastewater treatment in the study by Arismendi et al. [88] showed low levels of mutagenicity and toxicity. In all the literature analysed and consulted in this research, until now limited studies are evaluating the phytotoxicity of generated sludge or treated wastewater coming from the coagulation-flocculation process applying tannins as a coagulant. In conclusion, although tannin-based coagulants produce sludge with the potential for agronomic applications, some limits have to be considered to ensure it is safe for the environment.

The growing interest in the application of natural coagulants in water and wastewater treatment as a substitute for inorganic chemical coagulants has encouraged the research and development of a tannin-based coagulant, which is available commercially, or could be extracted and synthesised in a lab. Tannin is preferred over other natural polymers as it requires a simple extraction method without further purification and isolation. There are still abundant opportunities to look for more types of plant with high-condensed tannin content apart from the common *A. mearnsii*, and *S. balansae*. The potential of local Sabah's plant varieties such as *Acacia mangium* as a source of tannin, as well as *Mangifera pajang* (bambangan) and *Artocarpus odoratissismus* (tarap) which may be used as a coagulant is still lacking in research. Nonetheless, local agricultural waste could also be utilised as potential source of tannin [149].

High purity tannin and extract yield could be obtained through the right extraction technique. Moreover, the chemical modification process for cationisation of the tannin-based coagulant is achievable following the Mannich reaction path which is well established. By understanding the factors affecting the modification of tannin extracts during the synthesis process, a modified tannin coagulant can be produced that can improve the coagulation process.

During the synthesis of modified tannin-based coagulant and also during the coagulation process, usually traditional experimental method was applied to look at one factor at a time approach which is difficult to establish relationships among all the experimental input factors and the output responses. Conversely, by using design of experiments based on a mathematical and statistical method for modelling and analysing a process in which the response of interest is affected by various variables such as response surface methodology (RSM), will be a convenient alternative to observe an optimum value of the working parameters as well as interaction among them as had been done in most tannin coagulant modification works [93,103] and coagulation process [112,131]. The effect of experimental parameters on selected response could be presented pictorially as shown in Fig. 7.

An opportunity is available to look for safer substitutes to formaldehyde which has been preferred for use in published tannin modification work to date, or even better to produce formaldehyde-free coagulant. Tannin-based coagulant has been reported to work efficiently for various types of wastewater. A tannin-based coagulant with the right tannin source and coagulation parameter has shown to be effective in the removal of turbidity, algae, dye constituents, colour and COD in water and wastewater. Even though tannin-based coagulants have been applied to various types of wastewater, the applications were mostly for river and surface water, and the textile/dye industry. More research opportunities are available for studies into the tannin coagulant to be applied in treating other types of wastewater such as landfill leachate and POME.

To determine the suitability of a coagulant in a wastewater treatment plant, cost should also be one of the factor to be considered. Lower coagulant dosage will require lesser cost of operation for a wastewater treatment plant. In a study by Osorio Moreira Couto et al. [128], although the price of tannin coagulant is pricey than $Al_2(SO_4)_3$, lower dosage of tannin required enables a saving of up to 15% of the treatment cost as compared to using $Al_2(SO_4)_3$. However, comparing to lower price of PAC coagulant, usage of tannin coagulant at optimum dosage does not seem economically feasible [150]. Therefore, for this situation, decision whether tannin coagulant would be appropriate to be applied in water and wastewater treatment could be justified by considering other factors such as its performance in pollutant removal, amount of sludge generated, and dependency on operating conditions.

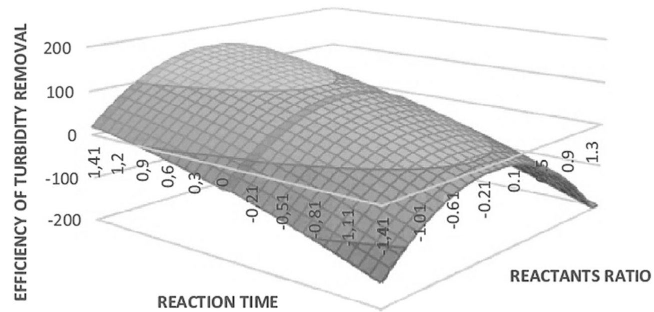

Fig. 7. Response surface plots for effect of reaction time and reactants ratio on turbidity removal [103].

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.

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References

[1] A. Ibrahim, A.Z. Yaser, Colour removal from biologically treated landfill leachate with tannin-based coagulant, J. Environ. Chem. Eng. 7 (2019), 103483.
[2] A.K. Verma, R.R. Dash, P. Bhunia, A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters, J. Environ. Manag. 93 (2012) 154–168.
[3] T.K.F.S. Freitas, C.A. Almeida, D.D. Manholer, H.C.L. Geraldino, M.T.F. de Souza, J.C. Garcia, Review of utilization plant-based coagulants as alternatives to textile wastewater treatment, in: S.S. Muthu (Ed.), Detox Fashion: Waste Water Treatment, Springer Singapore, Singapore, 2018, pp. 27–79.
[4] M. Asrafuzzaman, A.N.M. Fakhruddin, A. Hossain, Reduction of turbidity of water using locally available natural coagulants, ISRN Microbiol. 2011 (2011) 1–6.
[5] W.B. Kpan, M.W. Koné, B. Bonfoh, K. Kamanzi, Evaluation of eighteen west african plants for water purification, potential use for rural water treatment, J. Water Chem. Technol. 39 (2017) 310–316.
[6] C.Y. Yin, Emerging usage of plant-based coagulants for water and wastewater treatment, Process Biochem. 45 (2010) 1437–1444.
[7] F. Renault, B. Sancey, J. Charles, N. Morin-Crini, P.-M. Badot, P. Winterton, G. Crini, Chitosan flocculation of cardboard-mill secondary biological wastewater, Chem. Eng. J. 155 (2009) 775–783.
[8] J. Turunen, A. Karppinen, R. Ihme, Effectiveness of biopolymer coagulants in agricultural wastewater treatment at two contrasting levels of pollution, SN Appl. Sci. 1 (2019) 210.
[9] N. Chaibakhsh, N. Ahmadi, M.A. Zanjanchi, Use of Plantago major L. as a natural coagulant for optimized decolorization of dye-containing wastewater, Ind. Crop. Prod. 61 (2014) 169–175.
[10] G. Vijayaraghavan, T. Sivakumar, V. Adichakkravarthy, Application of plant based coagulants for waste water treatment, Int. J. Adv. Eng. Res. Stud. 1 (2011) 88–92.
[11] F.P. Camacho, V.S. Sousa, R. Bergamasco, M. Ribau Teixeira, The use of Moringa oleifera as a natural coagulant in surface water treatment, Chem. Eng. J. 313 (2017) 226–237.
[12] Z.L. Oliveira, M.R.C.C. Lyra, A.C.F. Arruda, A.M.R.B. Silva, J.F. Nascimento, S.R. M. Ferreira, Efficiency in the treatment of landfill leachate using natural coagulants from the seeds of Moringa oleifera Lam and Abelmoschus esculentus (L.) moench (Okra), Electron. J. Geotech. Eng. 21 (2016) 9735–9752.
[13] H.D. Beyene, T.D. Hailegebrial, W.B. Dirersa, Investigation of coagulation activity of cactus powder in water treatment, J. Appl. Chem. 2016 (2016) 1–9.
[14] M. Sellami, Z. Zarai, M. Khadhraoui, N. Jdidi, R. Leduc, F.B. Rebah, Cactus juice as bioflocculant in the coagulation-flocculation process for industrial wastewater treatment: a comparative study with polyacrylamide, Water Sci. Technol. 70 (2014) 1175–1181.
[15] C. Nirmala Rani, R. Talikoti, Adsorption isotherm studies of the simultaneous removal of turbidity and hardness by natural coagulants, Water Pract. Technol. 8 (2013) 495–502.
[16] G. Muthuraman, S. Sasikala, Removal of turbidity from drinking water using natural coagulants, J. Ind. Eng. Chem. 20 (2014) 1727–1731.

[17] M. Ozacar, İ. Şengil, The use of tannins from Turkish acorns (valonia) in water treatment as a coagulant and coagulant aid, Turk. J. Eng. Environ. Sci. 26 (2002) 255–263.
[18] M. Özacar, İ.A. Şengil, Evaluation of tannin biopolymer as a coagulant aid for coagulation of colloidal particles, Colloids Surf. Physicochem. Eng. Asp. 229 (2003) 85–96.
[19] J. Sánchez-Martín, M. González-Velasco, J. Beltrán-Heredia, Surface water treatment with tannin-based coagulants from Quebracho (Schinopsis balansae), Chem. Eng. J. 165 (2010) 851–858.
[20] Y.T. Hameed, A. Idris, S.A. Hussain, N. Abdullah, H.C. Man, F. Suja, A tannin–based agent for coagulation and flocculation of municipal wastewater as a pretreatment for biofilm process, J. Clean. Prod. 182 (2018) 198–205.
[21] Z. Abidin, M. Issa, Coagulation treatment of palm oil mill effluent using plant-based tannin, Pollut. Res. 37 (2018) 788–793.
[22] E.C. Lopes, S.C.R. Santos, A.M.A. Pintor, R.A.R. Boaventura, C.M.S. Botelho, Evaluation of a tannin-based coagulant on the decolorization of synthetic effluents, J. Environ. Chem. Eng. 7 (2019), 103125.
[23] J. Beltrán Heredia, J. Sánchez Martín, Removing heavy metals from polluted surface water with a tannin-based flocculant agent, J. Hazard. Mater. 165 (2009) 1215–1218.
[24] M. Özacar, ı.A. Şengıl, Effectiveness of tannins obtained from valonia as a coagulant aid for dewatering of sludge, Water Res 34 (2000) 1407–1412.
[25] N. Graham, F. Gang, G. Fowler, M. Watts, Characterisation and coagulation performance of a tannin-based cationic polymer: a preliminary assessment, Colloids Surf. Physicochem. Eng. Asp. 327 (2008) 9–16.
[26] J. Beltrán-Heredia, J. Sánchez-Martín, M.C. Gómez-Muñoz, New coagulant agents from tannin extracts: preliminary optimisation studies, Chem. Eng. J. 162 (2010) 1019–1025.
[27] J. Sánchez-Martín, J. Beltrán-Heredia, M.A. Dávila-Acedo, Optimum coagulant from Acacia mearnsii de wild for wastewater treatment, Chem. Eng. Technol. 34 (2011) 2069–2076.
[28] K. Grenda, J. Arnold, D. Hunkeler, J.A.F. Gamelas, M.G. Rasteiro, Tannin-based coagulants from laboratory to pilot plant scales for coloured wastewater treatment, Bioresources 13 (2018) 2727–2747.
[29] A. Arbenz, L. Avérous, Chemical modification of tannins to elaborate aromatic biobased macromolecular architectures, Green. Chem. 17 (2015) 2626–2646.
[30] V. Kumar, N. Othman, S. Asharuddin, Applications of natural coagulants to treat wastewater – a review, MATEC Web Conf. 103 (2017), 06016.
[31] S.Y. Choy, K.M.N. Prasad, T.Y. Wu, M.E. Raghunandan, R.N. Ramanan, Utilization of plant-based natural coagulants as future alternatives towards sustainable water clarification, J. Environ. Sci. 26 (2014) 2178–2189.
[32] A. Singh, S. Kumar, Applications of tannins in industry, in: A. Aires (Ed.), Tannins: Structural Properties, Biological Properties and Current Knowledge, IntechOpen, 2019.
[33] A. Pizzi, Chapter 8 – Tannins: major sources, properties and applications, in: M. N. Belgacem, A. Gandini (Eds.), Monomers, Polymers and Composites from Renewable Resources, Elsevier, Amsterdam, 2008, pp. 179–199.
[34] M. Fraga-Corral, P. García-Oliveira, A.G. Pereira, C. Lourenço-Lopes, C. Jimenez-Lopez, M.A. Prieto, J. Simal-Gandara, Technological application of tannin-based extracts, Molecules 25 (2020) 614.
[35] J. Sánchez-Martín, J. Beltrán-Heredia, A. Pizarro-Rebollo, Cationic tannins: new and effective coagulant/flocculant agents, Handb. Wastewater Treat.: Biol. Methods, Technol. Environ. Impact (2013) 221–247.
[36] K. Khanbabaee, T. van Ree, Tannins: classification and definition, Nat. Prod. Rep. 18 (2001) 641–649.
[37] A. Arbenz, L. Avérous, Tannins: a resource to elaborate aromatic and biobased polymers, in: S. Kalia, L. Avérous (Eds.), Biodegradable and Biobased Polymers for Environmental and Biomedical Applications, Scrivener Publishing, 2016, pp. 97–148.
[38] K. Grenda, Modification of Natural Polymers and Natural By-products for Coagulation and Flocculation Pruposes, in: Faculty of Sciences and Technology, University of Coimbra, 2018.
[39] J. Sánchez-Martín, J. Beltrán-Heredia, B. Coco-Rivero, New lab-made coagulant based on Schinopsis balansae tannin extract: synthesis optimization and preliminary tests on refractory water pollutants, Appl. Water Sci. 4 (2014) 261–271.
[40] M.P. Laksmi, D.A. Nurani, D.U.C. Rahayu, Polymerization of the tannin extract from the leave of Acacia mangium and its application as an adsorbent for the removal of lead, J. Phys.: Conf. Ser. 1442 (2020), 012058.
[41] M. Dela Justina, B. Rodrigues Bagnolin Muniz, M. Mattge Bröring, V.J. Costa, E. Skoronski, Using vegetable tannin and polyaluminium chloride as coagulants for dairy wastewater treatment: a comparative study, J. Water Process Eng. 25 (2018) 173–181.
[42] Y.T. Hameed, A. Idris, S.A. Hussain, N. Abdullah, A tannin-based agent for coagulation and flocculation of municipal wastewater: Chemical composition, performance assessment compared to Polyaluminum chloride, and application in a pilot plant, J. Environ. Manag. 184 (2016) 494–503.
[43] D.G. Roux, Recent advances in the chemistry and chemical utilization of the natural condensed tannins, Phytochemistry 11 (1972) 1219–1230.
[44] D.G. Roux, D. Ferreira, H.K. Hundt, E. Malan, Structure, stereochemistry, and reactivity of natural condensed tannins as basis for their extended industrial application, Appl. Polym. Symp. (1975) 335–353.
[45] I.Md Oliveira, V. Cruz, L.L.Y. Visconte, É.B.A.V. Pacheco, M. Dezotti, Tannin treated water for use in the emulsion polymerization of SBR, Polímeros 23 (2013) 326–330.
[46] Y.B. Hoong, M.T. Paridah, Y.F. Loh, H. Jalaluddin, L.A. Chuah, A new source of natural adhesive: Acacia mangium bark extracts co-polymerized with phenol-formaldehyde (PF) for bonding Mempisang (Annonaceae spp.) veneers, Int. J. Adhes. Adhes. 31 (2011) 164–167.
[47] P.B. Raja, A.A. Rahim, A.K. Qureshi, K. Awang, Green synthesis of silver nanoparticles using tannins, Mater. Sci. 32 (2014) 408–413.
[48] I.M. de Oliveira, L.L.Y. Visconte, V. Cruz, M. Dezotti, Tannin-treated water for use in the emulsion polymerization of SBR: effect of ageing on mechanical properties, Int. J. Polym. Mater. 56 (2007) 939–944.
[49] M. Oliviero, M. Stanzione, M. D'Auria, L. Sorrentino, S. Iannace, L. Verdolotti, Vegetable tannin as a sustainable UV stabilizer for polyurethane foams, Polymers 11 (2019) 480.
[50] E. Bargiacchi, P. Bellotti, P. Pinelli, G. Costa, S. Miele, A. Romani, P. Zambelli, A. Scardigli, Use of chestnut tannins extract as anti-oxidant, anti-microbial additive and to reduce nitrosamines and mycotoxins, LT 2904910T, 2019.
[51] S. Abdalla, A. Pizzi, F.S. Bahabri, Macro porous tannin spray-dried powder scaffolds with stem cells for bone engineering, Mater. Chem. Phys. 239 (2020), 121980.
[52] J.A. da Cruz, A.B. da Silva, B.B.S. Ramin, P.R. Souza, K.C. Popat, R.S. Zola, M. J. Kipper, A.F. Martins, Poly(vinyl alcohol)/cationic tannin blend films with antioxidant and antimicrobial activities, Mater. Sci. Eng.: C. 107 (2020), 110357.
[53] F. Roselet, J. Burkert, P.C. Abreu, Flocculation of Nannochloropsis oculata using a tannin-based polymer: Bench scale optimization and pilot scale reproducibility, Biomass & Bioenergy 87 (2016) 55–60.
[54] F. Roselet, D. Vandamme, M. Roselet, K. Muylaert, P.C. Abreu, Effects of pH, salinity, biomass concentration, and algal organic matter on flocculant efficiency of synthetic versus natural polymers for harvesting microalgae biomass, Bioenergy Res. 10 (2017) 427–437.
[55] Z. Wang, M. Gao, X. Li, J. Ning, Z. Zhou, G. Li, Efficient adsorption of methylene blue from aqueous solution by graphene oxide modified persimmon tannins, Mater. Sci. Eng. C 108 (2020), 110196.
[56] M. Gao, Z. Wang, C. Yang, J. Ning, Z. Zhou, G. Li, Novel magnetic graphene oxide decorated with persimmon tannins for efficient adsorption of malachite green from aqueous solutions, Colloids Surf. Physicochem. Eng. Asp. 566 (2019) 48–57.
[57] S. Zhang, Y. Ji, F. Ao, Y. Wang, J. Zhao, S. Chen, Selective adsorption of Au (III) from aqueous solution using 2,5–Dimercapto-1,3,4–thiadiazole modified persimmon tannin, J. Braz. Chem. Soc. 29 (2018) 1487–1498.
[58] B.W.N. Grehs, A.R. Lopes, N.F.F. Moreira, T. Fernandes, M.A.O. Linton, A.M. T. Silva, C.M. Manaia, E. Carissimi, O.C. Nunes, Removal of microorganisms and antibiotic resistance genes from treated urban wastewater: a comparison between aluminium sulphate and tannin coagulants, Water Res. 166 (2019), 115056.
[59] D. Cuong, N. Hoan, D. Dong, L. Thuy, N. Thanh, H. Ha, D. Tuyen, D. Chinh, Tannins: extraction from plants, in: A. Aires (Ed.), Tannins: Structural Properties, Biological Properties and Current Knowledge, IntechOpen, 2019.
[60] P.L. de Hoyos-Martínez, J. Merle, J. Labidi, F. Charrier, El Bouhtoury, Tannins extraction: a key point for their valorization and cleaner production, J. Clean. Prod. 206 (2019) 1138–1155.
[61] S. Singh, S. Choubey, Use of tannin based natural coagulants for water treatment: an alternative to inorganic chemicals, Int. J. Chemtech Res. 6 (2014) 974–4290.
[62] A. Bello, V. Virtanen, J.-P. Salminen, T. Leiviskä, Aminomethylation of spruce tannins and their application as coagulants for water clarification, Sep. Purif. Technol. 242 (2020), 116765.
[63] A.D. Bacardit, L.O. Olle, S.C. Sorolla, C.S. Casas, Process for obtaining a tannin extract isolated from grapes, tannin extract obtained and uses thereof, C. Patent 109952110, 2019.
[64] D.V. Kukić, M.B. Šćiban, J.M. Prodanović, A.N. Tepić, M.A. Vasić, Extracts of fava bean (Vicia faba L.) seeds as natural coagulants, Ecol. Eng. 84 (2015) 229–232.
[65] Z. Yang, Preparation method and applications of tannin extract of Sea-buckthorn, C. Patent 109694394, 2019.
[66] Y. Ma, L. Guo, T. Qiang, K.A.I. Du, T. Dai, Extraction method of Chinese Coriaria bark tannin and extract of Chinese Coriaria bark tannin, C. Patent 109867703, 2019.
[67] H. Qiu, Method for extracting and purifying tannin in Ginkgo leaves, C. Patent 107602627, 2018.
[68] N.J.N. Nnaji, J.U. Ani, L.E. Aneke, O.D. Onukwuli, U.C. Okoro, J.I. Ume, Modelling the coag-flocculation kinetics of cashew nut testa tannins in an industrial effluent, J. Ind. Eng. Chem. 20 (2014) 1930–1935.
[69] H.T. Abdulsahib, A.H. Taobi, S.S. Hashim, A novel coagulant based on lignin and tannin for bentonite removal from rawwater, Int. J. Adv. Res. 3 (2015) 426–442.
[70] X. Liang, Y.A.N. Jiang, Mechanochemical extraction method for preparing hydrolysable-tannin crude extract from Trapa Sp. Pericarps, C. Patent 110003290, 2019.
[71] A. Ali, X.Y. Lim, C.H. Chong, S.H. Mah, B.L. Chua, Optimization of ultrasound-assisted extraction of natural antioxidants from Piper betle using response surface methodology, LWT 89 (2018) 681–688.
[72] D. Yao, D. Zhan, B.O. Wang, Y. Li, L.I. Wan, Novel method for extracting tannin from Filipendula Palmata, C. Patent 109912667, 2019.
[73] Z.-E. Huma, V. Jayasena, S.M. Nasar-Abbas, M. Imran, M.K. Khan, Process optimization of polyphenol extraction from carob (Ceratonia siliqua) kibbles using microwave-assisted technique, J. Food Process. Preserv. 42 (2018), e13450.
[74] M. Ravber, Ž. Knez, M. Škerget, Isolation of phenolic compounds from larch wood waste using pressurized hot water: extraction, analysis and economic evaluation, Cellulose 22 (2015) 3359–3375.
[75] A. Shao, X. Meng, H. Xie, Scabiosa Comosa tannin extraction method, C. Patent 109966326, 2019.

[76] A.I. Talmaciu, M. Ravber, I. Volf, Ž. Knez, V.I. Popa, Isolation of bioactive compounds from spruce bark waste using sub- and supercritical fluids, J. Supercrit. Fluids 117 (2016) 243–251.
[77] Y. Xu, Processing technology for extracting tannin from walnut green seedcase, C. Patent 108976266, 2018.
[78] H. Zhang, Method for extracting tannin extract from pomegranate rind, C. Patent 107488413, 2017.
[79] D. Jiang, W.E.I. Wang, X. Liao, Preparation method of pomegranate leaf tannin, C. Patent 103372036, 2013.
[80] Y.U. Xianchun, S.U.N. Delin, L.I. Xiangsu, Method for extracting wild persimmon leaf tannin by ultrasonic wave auxiliary semi-bionic method, C. Patent 102344470, 2012.
[81] M. Liu, H. Li, B.I.N. Zhu, G. Sun, Y. Tang, Method for extracting tannin from Shaniodendron Subaequalum, C. Patent 107266508, 2017.
[82] J. Khasnabis, C. Rai, A. Roy, Determination of tannin content by titrimetric method from different types of tea, J. Chem. Pharm. Res. 7 (2015) 238–241.
[83] J.P. Maran, S. Manikandan, B. Priya, P. Gurumoorthi, Box-Behnken design based multi-response analysis and optimization of supercritical carbon dioxide extraction of bioactive flavonoid compounds from tea (Camellia sinensis L.) leaves, J. Food Sci. Technol. 52 (2015) 92–104.
[84] C. Agarwal, K. Máthé, T. Hofmann, L. Csóka, Ultrasound-assisted extraction of cannabinoids from Cannabis sativa L. optimized by response surface methodology, J. Food Sci. 83 (2018) 700–710.
[85] F. Dahmoune, B. Nayak, K. Moussi, H. Remini, K. Madani, Optimization of microwave-assisted extraction of polyphenols from Myrtus communis L. leaves, Food Chem. 166 (2015) 585–595.
[86] N.A. Oladoja, E.I. Unuabonah, O.S. Amuda, O.M. Kolawole, Mechanistic insight into the coagulation efficiency of polysaccharide-based coagulants, in: Polysaccharides as a Green and Sustainable Resources for Water and Wastewater Treatment, Springer International Publishing, 2017, pp. 13–35.
[87] J. Beltrán-Heredia, J. Sánchez-Martín, M.T. Rodríguez-Sánchez, Textile wastewater purification through natural coagulants, Appl. Water Sci. 1 (2011) 25–33.
[88] W.A. Arismendi, A.E. Ortiz-Ardila, C.V. Delgado, L. Lugo, L.G. Sequeda-Castañeda, C.A. Celis-Zambrano, Modified tannins and their application in wastewater treatment, Water Sci. Technol. 78 (2018) 1115–1128.
[89] J.E. Quamme, A.H. Kemp, Stable tannin based polymer compound, U. Patent 4558080, 1985.
[90] P.E. Reed, M.R. Finck, Modified tannin mannich polymers, U. Patent 5659002, 1997.
[91] D.B. Mitchell, R.L. Minnis, T.P. Curran, S.M. Deboo, J.A. Kelly, R. Patwardhan, T. E.N. Tai Wun, Treatment of aqueous systems using a chemically modified tannin, U. Patent 5843337, 1998.
[92] J. Beltrán-Heredia, J. Sánchez-Martín, M.A. Dávila-Acedo, Optimization of the synthesis of a new coagulant from a tannin extract, J. Hazard. Mater. 186 (2011) 1704–1712.
[93] J. Beltrán-Heredia, J. Sánchez-Martín, L. Martín-García, Multiparameter quantitative optimization in the synthesis of a novel coagulant derived from tannin extracts for water treatment, Water Air Soil Pollut. 223 (2012) 2277–2286.
[94] J. Sánchez-Martín, J. Beltrán-Heredia, B. Coco-Rivero, Chapter 15 – Quebracho colorado: a new source for water coagulant—performance on dye removal, in: M. Fanun (Ed.), The Role of Colloidal Systems in Environmental Protection, Elsevier, Amsterdam, 2014, pp. 347–362.
[95] K. Grenda, J. Arnold, J.A.F. Gamelas, M.G. Rasteiro, Up-scaling of tannin-based coagulants for wastewater treatment: performance in a water treatment plant, Environ. Sci. Pollut. R. (2018).
[96] H. Pasch, A. Pizzi, K. Rode, MALDI–TOF mass spectrometry of polyflavonoid tannins, Polymer 42 (2001) 7531–7539.
[97] C.B. Moelans, N. ter Hoeve, J.-W. van Ginkel, F.J. ten Kate, P.J. van Diest, Formaldehyde substitute fixatives: analysis of macroscopy, morphologic analysis, and immunohistochemical analysis, Am. J. Clin. Pathol. 136 (2011) 548–556.
[98] A. Andersen, Final report on the safety assessment of benzaldehyde, Int. J. Toxicol. 25 (Suppl 1) (2006) 11–27.
[99] D.M. Nagrik, D.M. Ambhore, D.M. Gawande, One-pot preparation of β–amino carbonyl compounds by mannich reaction using MgO/ZrO_2 as effective and reusable catalyst, Int. J. Chem. 2 (2010).
[100] S.B. Han, J.Y. Wei, X.C. Peng, R. Liu, S.S. Gong, Q. Sun, $Hf(OTf)_4$ as a highly potent catalyst for the synthesis of mannich bases under solvent-free conditions, Molecules 25 (2020) 388.
[101] S. Sardar, C. Wilfred, J.-M. Lévêque, One-pot mannich base synthesis using task specific protic ionic liquids, Malays. J. Anal. Sci. 21 (2017) 1203–1209.
[102] H. Eshghi, A. Alipour, S. Damavandi, Highly efficient $Fe(HSO_4)_3$-catalyzed one-pot mannich-type reactions: three component synthesis of β-amino carbonyl compounds, Synth. React. Inorg. Metalorg. Nanometal Chem. 41 (2011) 266–271.
[103] G. Machado, C.A.B. dos Santos, J. Gomes, D. Faria, F. Santos, R. Lourega, Chemical modification of tannins from Acacia mearnsii to produce formaldehyde free flocculant, Sci. Total Environ. 745 (2020), 140875.
[104] L. Lugo, A. Martín, J. Diaz, A. Pérez-Flórez, C. Celis, Implementation of modified acacia tannin by mannich reaction for removal of heavy metals (Cu, Cr and Hg), Water 12 (2020) 352.
[105] B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, Water Res. 41 (2007) 2301–2324.
[106] S. Miller, E. Fugate, V. Oyanedel-Craver, J. Smith, J. Zimmerman, Toward understanding the efficacy and mechanism of Opuntia spp. as a natural coagulant for potential application in water treatment, Environ. Sci. Technol. 42 (2008) 4274–4279.
[107] R.H. Fowler, Statistical thermodynamics, CUP Arch. (1939).
[108] H. Freundlich, Über die adsorption in lösungen, Z. Phys. Chem. 57 (1907) 385–470.
[109] B.-Y. Zhu, T. Gu, Surfactant adsorption at solid-liquid interfaces, Adv. Colloid Interface Sci. 37 (1991) 1–32.
[110] W. Subramonian, T.Y. Wu, S.-P. Chai, A comprehensive study on coagulant performance and floc characterization of natural Cassia obtusifolia seed gum in treatment of raw pulp and paper mill effluent, Ind. Crop. Prod. 61 (2014) 317–324.
[111] Y. Zhou, G.V. Franks, Flocculation mechanism induced by cationic polymers investigated by light scattering, Langmuir 22 (2006) 6775–6786.
[112] T.J.H. Banch, M.M. Hanafiah, A.F.M. Alkarkhi, S.S.A. Amr, Factorial design and optimization of landfill leachate treatment using tannin-based natural coagulant, Polymers 11 (2019) 1349.
[113] D.M. Rice, G.J. Stander, J.H. Denysschen, Evaluation of a Tannin-Base Polyelectrolyte as a Coagulant for Turbid Waters, National Institute For Water Research, Council for Scientific and Industrial Research, 1964.
[114] A. Pizzi, Tannins: prospectives and actual industrial applications, Biomolecules 9 (2019) 344.
[115] J. Sánchez-Martín, M. González-Velasco, J. Beltrán-Heredia, Acacia mearnsii de wild tannin-based flocculant in surface water treatment, J. Wood Chem. Technol. 29 (2009) 119–135.
[116] J. Beltrán-Heredia, J. Sánchez-Martín, C. Solera-Hernández, Removal of sodium dodecyl benzene sulfonate from water by means of a new tannin-based coagulant: optimisation studies through design of experiments, Chem. Eng. J. 153 (2009) 56–61.
[117] J. Bratby, Coagulation and Flocculation in Water and Wastewater Treatment, IWA Publishing, 2016.
[118] R.B. Fabres, R.B. da Luz, M.C. Soliman, R. Staggemeier, J.D. Fleck, C. Ad Nascimento, F.Td Nascimento, F.R. Spilki, Evaluation of virus recovery methods and efficiency of tannin-derived coagulants in removing total coliforms, *E. coli* and enteric viruses in effluents of a domestic sewage treatment plant, Water Sci. Technol. 76 (2017) 2195–2202.
[119] Y. Nakamoto, T. Tsunoda, K. Ono, N. Kaeyama, Y. Yazaki, H. Jiang, F. Lawson, T. Uhlherr Peter Heinz, Method for the production of tannin and its use, U. Patent 2004/0219234, 2004.
[120] E. Heiderscheidt, T. Leiviskä, B. Kløve, Coagulation of humic waters for diffused pollution control and the influence of coagulant type on DOC fractions removed, J. Environ. Manag. 181 (2016) 883–893.
[121] N. Graham, G. Fang, G. Fowler, M. Watts, R. Camm, Evaluation of a tannin-based cationic polymer as a coagulant for coloured humic water, J. Water Supply Res. T. 58 (2009) 75–84.
[122] J. Beltrán-Heredia, J. Sánchez-Martín, Municipal wastewater treatment by modified tannin flocculant agent, Desalination 249 (2009) 353–358.
[123] J. Beltrán-Heredia, J. Sánchez-Martín, G. Frutos-Blanco, Schinopsis balansae tannin-based flocculant in removing sodium dodecyl benzene sulfonate, Sep. Purif. Technol. 67 (2009) 295–303.
[124] L.E. Bacher, C. de Oliveira, A. Giacobbo, T. Benvenuti, A.B. Lacerda, A. M. Bernardes, M.A.S. Rodrigues, Coupling coagulation using tannin-based product with electrodialysis reversal to water treatment: a case study, J. Environ. Chem. Eng. 5 (2017) 6008–6015.
[125] M.M. Barrado-Moreno, J. Beltrán-Heredia, J. Martín-Gallardo, Removal of Oocystis algae from freshwater by means of tannin-based coagulant, J. Appl. Phycol. 28 (2016) 1589–1595.
[126] J. Roussy, P. Chastellan, M. Vooren, E. Guibal, Treatment of ink-containing wastewater by coagulation/flocculation using biopolymers, Water SA 31 (2007).
[127] C.Y. Teh, P.M. Budiman, K.P.Y. Shak, T.Y. Wu, Recent advancement of coagulation–flocculation and its application in wastewater treatment, Ind. Eng. Chem. Res. 55 (2016) 4363–4389.
[128] J. Osorio Moreira Couto, B. Maria Angélica Simões Dornelas, P. Nehemias Curvelo, Study on coagulation and flocculation for treating effluents of textile industry, Acta Sci. Technol. 35 (2012).
[129] M. Aboulhassan, S. Souabi, A. Yaacoubi, M. Baudu, Treatment of textile wastewater using a natural flocculant, Environ. Technol. 26 (2005) 705–712.
[130] J. Beltrán-Heredia, J. Sánchez-Martín, M. Barrado-Moreno, Long-chain anionic surfactants in aqueous solution: removal by Moringa oleifera coagulant, Chem. Eng. J. 180 (2012) 128–136.
[131] M.A. Ahmad, A.W. Mohammad, T.C.S. Yaw, L.C. Abdullah, Effects of organo-floc as natural coagulant on posttreatment of ultrafiltration membrane, Pollut. Res. 35 (2016) 415–421.
[132] H.A. Tajuddin, L.C. Abdullah, A. Idris, T.S.Y. Choong, Effluent quality of anaerobic palm oil mill effluent (POME) wastewater using organic coagulant, Int. J. Sci. R. 4 (2015) 11.
[133] J.D. dos Santos, M.T. Veit, P.T. Juchen, G. da Cunha Gonçalves, S.M. Palácio, M. Fagundes-Klen, Use of different coagulants for cassava processing wastewater treatment, J. Environ. Chem. Eng. 6 (2018) 1821–1827.
[134] S. Renata Padilha de, G. Franciélle, S. Veronice Sluzarski, F.-M. Nádia Regina Camargo, G. Marcelino Luiz, Vinasse treatment using a vegetable-tannin coagulant and photocatalysis, Acta Sci. Technol. 35 (2012).
[135] M.A. Aboulhassan, S. Souabi, A. Yaacoubi, M. Baudu, Coagulation efficacy of a tannin coagulant agent compared to metal salts for paint manufacturing wastewater treatment, Desalin. Water Treat. 57 (2016) 19199–19205.
[136] A.M. Ferrari-Lima, R.G. Marques, N.R.C. Fernandes-Machado, M.L. Gimenes, Photodegradation of petrol station wastewater after coagulation/flocculation with tannin-based coagulant, Catal. Today 209 (2013) 79–83.

[137] E. Ribeiro, G. Filho, N. Rozeno, J. Nogueira, M. Resende, J. Junior, J. Vieira, S. Canobre, F. Amaral, Polymeric polyelectrolytes obtained from renewable sources for biodiesel wastewater treatment by dual-flocculation, Express Polym. Lett. 11 (2017) 504–517.
[138] R.S. Putra, R.Y. Amri, M. Ayu, Turbidity removal of synthetic wastewater using biocoagulants based on protein and tannin, AIP Conf. Proc. 2242 (2020), 040028.
[139] A.F.S. Costa, C.D.C. Albuquerque, A.A. Salgueiro, L.A. Sarubbo, Color removal from industrial dyeing and laundry effluent by microbial consortium and coagulant agents, Process Saf. Environ. Prot. 118 (2018) 203–210.
[140] C.O. Nascimento, M.T. Veit, S.M. Palácio, G.C. Gonçalves, M.R. Fagundes-Klen, Combined Application of coagulation/flocculation/sedimentation and membrane separation for the treatment of laundry wastewater, Int. J. Chem. Eng. 2019 (2019) 1–13.
[141] R. Bortolatto, D.C. Lenhard, A.K. Genena, Treatment of low COD wastewater from slaughterhouse with natural coagulant based on tannins, in: XXV Food Science and Technology Brazilian Congress (CBCTA) and the 10th CIGR Section IV International Technical Symposium, Centro de Eventos da FAURGS, Brazil, 2016.
[142] G.L. Muniz, T.C.Fd Silva, A.C. Borges, Assessment and optimization of the use of a novel natural coagulant (Guazuma ulmifolia) for dairy wastewater treatment, Sci. Total Environ. 744 (2020), 140864.
[143] A.Y. Zahrim, T. Asis, M.A. Hashim, T.M.T.M.A. Al-Mizi, P. Ravindra, A review on the empty fruit bunch composting: life cycle analysis and the effect of amendment (s), in: P. Ravindra (Ed.), Advances in Bioprocess Technology, Springer International Publishing, Cham, 2015, pp. 3–15.
[144] Q. Lu, Z.L. He, P.J. Stoffella, Land application of biosolids in the USA: a review, Appl. Environ. Soil Sci. 2012 (2012) 1–11.
[145] M. Dela Justina, M.V. Alves, E. Skoronski, Applying different doses of tannin coagulated dairy sludge in soil: Influences on selected pollutants leaching and chemical agronomic attributes, Agric. Water Manag. 209 (2018) 11–19.
[146] M. Dela Justina, E. Skoronski, Environmental and agronomical aspects of sludge produced from tannin-based coagulants in dairy industry wastewater treatment, Waste Biomass Valoriz. 11 (2020) 1385–1392.
[147] Z. Xia, A. Singh, W. Kiratitanavit, R. Mosurkal, J. Kumar, R. Nagarajan, Unraveling the mechanism of thermal and thermo-oxidative degradation of tannic acid, Thermochim. Acta 605 (2015) 77–85.
[148] G. Tondi, A. Pizzi, E. Masson, A. Celzard, Analysis of gases emitted during carbonization degradation of polyflavonoid tannin/furanic rigid foams, Polym. Degrad. Stab. 93 (2008) 1539–1543.
[149] I. Azreen, Y. Lija, A.Y. Zahrim, Ammonia nitrogen removal from aqueous solution by local agricultural wastes, IOP Conf. Ser. Mater. Sci. Eng. 206 (2017), 012077.
[150] A. Kaji, M. Taheriyoun, A. Taebi, M. Nazari-Sharabian, Comparison and optimization of the performance of natural-based non-conventional coagulants in a water treatment plant, Aqua (2019), https://doi.org/10.2166/aqua.2019.075.