Groundwater for Sustainable Development 23 (2023) 101004

Contents lists available at ScienceDirect

Groundwater for Sustainable Development

journal homepage: www.elsevier.com/locate/gsd

Purifying water with plant-based sustainable solutions: Tannin coagulants and sorbents

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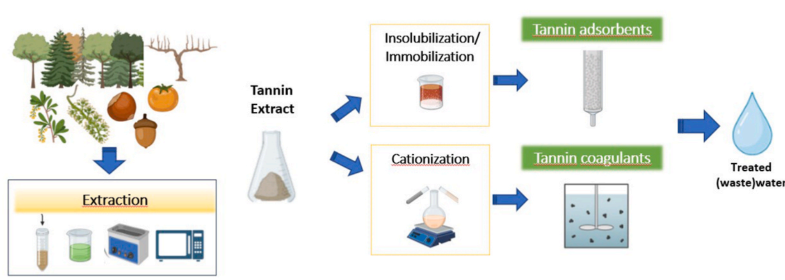
HIGHLIGHTS

- Tannin as a feedstock for coagulants and sorbents for water treatment.
- Overview of raw materials, synthesis, usage, and pollutant removal mechanism.
- Comparison of tannin coagulants and conventional/commercial coagulants.
- Discussion on potential applications of tannin sorbents.
- More work is needed to obtain valid assessments about cost-efficiency.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Coagulation
Adsorption
Synthesis
Water treatment
Pollutants

ABSTRACT

More and more efforts are being made to find efficient bio-based water and wastewater treatment products. Especially the use of tannin-based materials has become more prevalent in recent years due to the wide availability of sustainable tannin sources. This article provides an updated literature review on the potential for tannin use for coagulants and adsorbent synthesis and practical applicability in water purification. Tannin coagulants work well in many applications, especially in color, turbidity, and COD removal from industrial waters, and are often even better than conventional ones (e.g., metal salts). One of the most significant benefits of tannin coagulants is their small effect on the pH of the treated water. Also, tannin coagulants can work at a wide pH range, and sludge volume is typically smaller than with metal salts. However, it is worth noting that the performance varies widely among tannin coagulants. Tannin-derived resins and composites have been synthesized and evaluated as adsorbents for water purification. In general, tannin-derived adsorbents present good adsorption capacities for metals, antimony, cationic dyes, and uranium ions, owing to their chelating ability and negative surface charge in the pH conditions of interest and reducing power in the case of chromium(VI). With simple chemical modifications, tannin can be converted into effective sorbents for more challenging pollutants. More research is needed to test tannin materials on a larger scale and evaluate their overall benefits and cost-effectiveness.

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https://doi.org/10.1016/j.gsd.2023.101004
Received 19 June 2023; Received in revised form 21 July 2023; Accepted 21 August 2023
Available online 23 August 2023

1. Introduction

Coagulation-flocculation and adsorption are well-established operations in water and wastewater treatment plants. Coagulation-flocculation is an important process for removing colloidal and suspended particles from water. Adsorption is a simple and cost-effective method used at a tertiary treatment level to remove persistent pollutants, including organic micropollutants, metals, and toxic metalloids. Conventional coagulants/flocculants mostly used for water treatment include iron and aluminum-based salts, and synthetic organic polymers. Commercial adsorbents used in large-scale processes include activated carbon, activated alumina, and polymeric adsorbents. Among other possible disadvantages, most of these water treatment materials (e.g., chemical coagulants, coal activated carbons) are produced using non-renewable resources and through energy-intensive processes (e.g., pyrolysis and activation in activated carbon production), generating significant emissions to the environment (Vilen et al., 2022). In the context of stringent regulations, water scarcity, and the need to reduce dependence on primary mining, it is increasingly important to find cost-effective and green technologies to produce potable water and to remediate wastewater. Much work has been done to develop sustainable bio-based coagulants and adsorbents from renewable sources. Especially the use of tannin-based materials has become more prevalent in recent years due to the wide availability of tannin raw materials. Tannins are present in different parts of multiple vegetable species and are easily extracted with water, avoiding organic solvents. They present a high chelating capacity, abundant hydroxyl groups, and many ways of chemical modification (Arbenz and Averous 2015; Vera and Urbano 2021) which explain the increasing recognition of tannin as a raw material for sustainable green industries. The use of tannins as precursors of alternative coagulants/flocculants and adsorbents for water purification is a newly recognized field of application.

Black wattle (*Acacia mearnsii*) and quebracho (*Schinopsis lorentzii*) are the most used source of commercial tannins, also highly investigated as feedstock for coagulants and adsorbents production (Beltrán-Heredia et al., 2012; Sánchez-Martín et al., 2013). Tannin from other plant species such as grape stems, persimmon, spruce, eucalyptus and maritime pine bark, acacia catechu have been researched (Thakur and Choubey 2014; Bacelo et al., 2020; Bello et al. 2020, 2022; Giroletti et al., 2022; Liu et al., 2022; Tomasi et al., 2023) but there is still room for innovation. Evaluating other agro-food and agroforestry residues, as an effort to value locally available materials and reduce the production impact of coagulants/flocculants and adsorbents is essential. Tannins can be extracted by conventional solid-liquid procedures and advanced extraction methods, such as supercritical fluid extraction, pressurized liquid extraction, ultrasound-assisted and microwave-assisted extraction (Ibrahim et al., 2021). The best extraction method and operating conditions should be optimized on a case-specific basis to simultaneously provide good yields and extracts with high-condensed tannin content (Tomasi et al., 2023), minimizing energy and chemical requirements. Purification or isolation of tannin extracts is usually considered unnecessary for coagulants/adsorbents synthesis (Ibrahim et al., 2021), although smaller phenolic compounds, carbohydrates, and inorganics could be extracted along with tannins and affect coagulant ability.

Tannin coagulants provide a sustainable alternative to conventional coagulants. Cationization of tannin extracts can be done by simple Mannich reaction, where formaldehyde and amine react to form an iminium ion, which further reacts with the phenolic rings of the tannin. This results in water-soluble polymer with cationic nature (Graham et al., 2008).

Tannins are water-soluble compounds but can be easily rendered insoluble or immobilized, making them highly valuable as adsorbents. The most common way to insolubilize tannin is through polymerization with an aldehyde (also called gelification), which creates a cross-linked three-dimensional structure (Arbenz and Averous 2015). Auto-condensation of tannin and innovative immobilization procedures (grafting with chemical moieties and incorporation into composites) have generated adsorbents with enhanced chemical functionality and properties.

Comprehensive reviews have been published on tannin coagulants (Ibrahim et al., 2021; Das et al., 2022; Tomasi et al., 2022), addressing extraction, modification and purification performance, and on adsorbents (Santos et al., 2019; Sadegh et al., 2023). This article presents an up-to-date literature review, offering a comprehensive understanding of the recent advancements on tannins use in water purification, an area that has witnessed rapid progress in last years. Regarding tannin coagulants, the review aims explicitly to summarize findings comparing tannin coagulants with other coagulants. The adsorbents chapter discusses new synthesis routes, critically analyzes the challenges and gaps, and highlights the potential applications.

2. Tannin coagulants for water treatment

2.1. Preparation of tannin coagulants and coagulation mechanism

Most colloidal particles in water are anionic and their destabilization requires cationic coagulant. Cationic tannin coagulants are obtained by introducing amine groups into tannin structure. This can be done by simple Mannich reaction, where formaldehyde and amine react to form an iminium ion, which further reacts with the phenolic ring of the tannin structure and substitutes the hydrogen. Mannich modification of tannin, which have been reviewed recently (Ibrahim et al., 2021; Tomasi et al., 2022), has been done with different amines and by changing reaction conditions such as ratio of amine and formaldehyde, temperature, pH, and reaction time.

The amount of phenolic groups in the tannin structure affect reactivity and thereafter properties of the obtained coagulant. For example, a higher amount of phenolic groups in the quebracho tannin compared to spruce bark tannin resulted in much higher charge density of the quebracho coagulant (Bello et al., 2020). Charge densities of tannin coagulants have typically varied in the range of 0.8–3.8 meq/g (Fang 2007; Bello et al. 2020, 2022; Bello and Leiviskä 2022), which can be referred to as low to medium charge densities. Besides raw material, the tree harvesting season and extraction procedure may have significant effects on the amount of impurities in extracts/coagulants as well as on the charge densities of coagulants. Bello et al. (2022) obtained higher charge densities for spruce tannin coagulants, when they were produced from tannin extracted from winter spruce bark and having a preliminary cold-water extraction prior to the hot-water extraction. This extraction procedure reduced the amount of non-phenolic constituents (impurities) from the winter bark but not from the summer bark.

The main mechanisms for the destabilization of colloidal impurities are the charge neutralization and interparticle bridging mechanisms (Ibrahim et al., 2021). The charge density is pH-dependent due to amine protonation/deprotonation. Graham et al. (2008) showed that the optimal pH for the destabilization of kaolin suspension by a tannin coagulant was at pH 4 due to the charge neutralization mechanism. A higher dosage was needed at higher pH, however lower residual turbidity was obtained due to polymer precipitation and interaction with kaolin particles. Nevertheless, at pH 7, aluminum sulfate (AS) and polydiallyldimethylammonium chloride (polyDADMAC) achieved lower residual turbidity than tannin coagulant (TC).

2.2. Purification efficiency and dosage requirements

Table 1 compares tannin coagulants to other coagulants in water and wastewater treatment in terms of dosage requirements and purification efficiency. They are considered the most important factors in determining the superiority of coagulants, while the floc characteristics, flocculation time, and sludge properties are also critical parameters when considering the overall process. The wastewater quality has a major impact on what type of coagulant works best. The comparison of

Table 1
Summary of comparison of tannin coagulants to other coagulants in water and wastewater treatment.

Water type	Tannin coagulant	Required dosage and removal efficiencies	Reference
Municipal wastewaters			
Raw municipal wastewater	Commercial TC (Acquapol C1 18, Acquachimica)	Dosage: – Total coliforms: AS ≈ TC > FAS ≈ FC > PAC *E. coli*: AS ≈ TC > FAS ≈ FC > PAC Adenovirus: AS > TC > FAS ≈ FC > PAC (pH of wastewater)	(Fabres et al., 2017)
Raw municipal wastewater	Commercial TC (Tanfloc, Tanac)	Dosage: TC ≈ PAC Turb.: TC > PAC BOD_5: TC ≈ PAC COD: TC ≈ PAC TSS: TC > PAC Tot-P: TC ≈ PAC (pH 7.2–7.9)	Hameed et al. (2016)
Treated municipal wastewater	Commercial TC (Tanfloc SG, Tanac)	Dosage: TC < AS Turb.: AS > TC Color: AS > TC TOC: AS > TC Culturable bacteria: AS ≈ TC ARGs: AS > TC (pH 6.6 (AS), pH 7.5 (TC))	(Grehs et al., 2019)
Secondary treated municipal wastewater	Commercial TC	Dosage: Starch < Chit < TC < PAC Turb.: Chit > TC > PAC ≈ Starch BOD_7: Starch > TC > PAC > Chit COD: Starch ≈ TC ≈ PAC > Chit SS: TC > Starch ≈ PAC > Chit PO_4–P: TC ≈ PAC > Starch > Chit Tot-P: TC ≈ PAC > Starch > Chit Tot-N: TC ≈ PAC ≈ Chit > Starch (pH 6.4–6.7)	(Cainglet et al., 2020)
Treated municipal wastewater	Commercial TC (Acquapol 893/11, Acquachimica)	Dosage: – Total coliforms: FC > TC > PAC > FAS > AS *E. coli*: FC ≈ TC > PAC > FAS > AS Adenovirus: FC > TC > PAC > FAS > AS (pH of wastewater)	(Fabres et al., 2017)
Industrial wastewaters			
Blast furnace gas wash water	Commercial TC (Grove)	Dosage: PAM < TC < FS Turb.: PAM ≈ TC > FS (pH 8.0–8.1)	(Kiventerä et al., 2016)
Humic peat extraction runoff	Commercial TC (Grove)	Dosage: Chit ≈ PD < FS < TC DOC: FS > PD > TC ≈ Chit Tot-P: FS > PD > Chit ≈ TC Tot-N: FS > Chit > PD > TC SS: Chit ≈ TC > FS > PD (pH 6.5)	(Heiderscheidt et al., 2016)
Synthetic textile solution (DB85, NaCl, $NaHCO_3$)	Commercial TC (Tanfloc SG, Tanac)	Dosage: FS < TC Color: FS ≈ TC (pH 4–8)	(Lopes et al., 2019)
Synthetic textile solution (DB85, NaCl, $NaHCO_3$, auxiliary dyeing chemicals)	Commercial TC (Tanfloc SG, Tanac)	Dosage: FS < TC Color: FS ≈ TC (pH 4 and 5) Dosage: TC < FS Color: TC > FS (pH ≥ 6)	(Lopes et al., 2019)
Synthetic textile solution (Reactive Blue 19, NaCl, auxiliary dyeing chemicals)	Commercial TC (Tanfloc SG, Tanac)	Dosage: RF < TC Color: RF > TC (pH 9)	(Machado et al., 2022)
Textile wastewater	Commercial TC (Polysep3000, AQUAREX-ARCIE)	Color: FC > TC > AS COD: AS > FC > TC (pH 8 (FC), pH 7 (AS), pH ≤ 10 (TC))	(Aboulhassan et al., 2005)
Swine slaughterhouse wastewater	Commercial TC (Tanfloc SG, Tanac)	Dosage: TC ≈ PAC Turb.: TC > PAC Color: TC ≈ PAC (pH 6.6)	(Bongiovani et al., 2018)
Cassava processing wastewater	Commercial TCs (Acquapol WW, Acquapol S5T, Acquachimica; Tanfloc SL, Tanfloc SG, Tanac)	Dosage: TCs < AS Turb.: TCs > AS Color: TCs > AS (pH 7.1)	(dos Santos et al., 2018)
Paint manufacturing wastewater	TC	Dosage: TC ≈ FC < AS COD: TC > FC > AS Color: TC > FC ≈ AS (optimal pH for coagulants)	(Aboulhassan et al., 2016)
Dairy wastewater	Commercial TC (Tanac)	Dosage: TC ≈ PAC Color: TC ≈ PAC Turb.: TC ≈ PAC	(Dela Justina et al., 2018)

(continued on next page)

Table 1 (*continued*)

Water type	Tannin coagulant	Required dosage and removal efficiencies	Reference
		COD: PAC ≈ TC TSS: TC ≈ PAC (pH 6.0–7.0)	
Plastic recycling wastewater	Commercial TC (Tanfloc, Tanac)	Dosage: MO < TC Turb.: MO > TC Color: MO > TC COD: MO > TC (pH 7.3)	(Ribeiro et al., 2023)
Tannery wastewater	TC	Dosage: TC ≈ AS Sulfide: TC > AS Turb.: AS > TC Color: AS > TC COD: AS > TC Tot.N: AS > TC	(Uez et al., 2023)
Other waters			
Kaolin suspension	Commercial TC (Tanac)	Dosage: PD < TC < AS Turb.: AS > PD > TC (pH 7)	(Graham et al., 2008)
Kaolin/river water	TCs (Spruce, Quebracho)	Dosage: TCs < FS Turb.: TC (Quebracho) ≈ FS > TC (Spruce) UV_{254}: FS > TCs (pH 7.5)	(Bello and Leiviskä 2022)
River water enriched with *Oocystis* algae	Commercial TCs (Acquapol C1, Acquachimica; Tanfloc, Tanac; Silvafloc, Silvateam)	Dosage: – Algae removal: TCs > cationic starch > AS (dosage of 10 mg/L) (pH 7.8)	(Barrado-Moreno et al., 2016)

TC – tannin coagulant; Chit – chitosan; PD – PolyDADMAC; FS – ferric sulfate; PAM – polyacrylamide; AS – aluminum sulfate, PAC – polyaluminum chloride; FAS – ferrous aluminum sulfate; FC – ferric chloride; PA – polyamine; Turb. – Turbidity; DB85 – Direct Blue 85 dye; RF – Rifloc 6548; MO – *Moringa oleifera*.

purification efficiency is not so straightforward when considering same time several different water quality parameters, and since the treatments are being made with or without pH adjustments depending on the situation. Nevertheless, many studies have shown that tannin coagulants work just as well as other coagulants and sometimes even better. Fig. 1 shows the specific parameters associated with various water types, in which tannin coagulants demonstrate remarkable removal efficacy. It is worth to note that several commercial tannin coagulants are available, such as Tanfloc and Acquapol.

2.2.1. *Turbidity, organic matter and nutrients removal*

Few studies have compared tannin coagulants to other coagulants in the treatment of municipal wastewaters. Grehs et al. (2019) showed that both AS and tannin coagulant removed well turbidity, color, total organic carbon (TOC), and culturable bacteria from municipal wastewater effluent. The main difference was that AS decreased the analyzed antibiotic resistance genes (ARG) content to a lower level than the TC, and that the TC-treated effluent showed bacterial reactivation after storage. Hameed et al. (2016) showed that the tannin coagulant achieved higher removal of turbidity than polyaluminum chloride (PAC, pH 7.9) in a raw municipal wastewater (dosage 35 mg/L for both coagulants). On the other hand, chemical oxygen demand (COD), biological oxygen demand (BOD), and total phosphorus (Tot-P) removals were not significantly different with studied coagulants. In a study by Fabres et al. (2017), several commercial tannin coagulants were tested for total coliform bacteria, *Escherichia coli*, and adenovirus removal from raw and treated municipal wastewaters. In raw wastewater, AS achieved the best removal rates, followed by the Acquapol C1 18 tannin coagulant. In treated wastewater, ferric chloride (FC) and Acquapol 893/11 tannin coagulant resulted in best performance. The study also showed that among tested tannin coagulants, significant differences in purification results were observed. This underlines the important fact that different tannin raw materials and modification conditions will affect the properties of the tannin coagulant, and the optimal tannin coagulant needs to be tested in the application. Cainglet et al. (2020) tested PAC, several polyDADMACs, and polyamines with different molecular weights (MW), chitosan, and starch- and tannin-based coagulants in the treatment of municipal wastewater collected from the secondary sedimentation stage. In general, tannin coagulant performed well, although some higher dosages were needed (except PAC, which needed an even higher dosage). High-MW polyamine achieved the best removal of suspended solids (SS), phosphate-phosphorus (PO_4–P), and BOD_7.

In surface water treatment, tannin coagulants have been investigated for the removal of algae, turbidity, and natural organic compounds. Barrado-Moreno et al. (2016) reported that tannin coagulants removed to a higher extent *Oocystis* algae from surface water than cationic starch (Optifloc, Kemira) and AS when coagulants were applied with constant dosage (10 mg/L). Acquapol C1 tannin coagulant was selected for further studies and also proved to have a stable efficiency at a pH range 5–9 with constant dosage. The good performance of Acquapol C1 tannin coagulant was also verified in pilot tests, in which algae removal reached 90% removal in the coagulation process (at neutral pH) and was further improved after sand filtration. Bello and Leiviskä (2022) observed that tannin coagulants provided lower residual turbidities with lower dosages (25 and 50 mg/L) in kaolin/river water (pH 7.5) when compared to ferric sulfate (FS). As the pH decreased with increasing FS

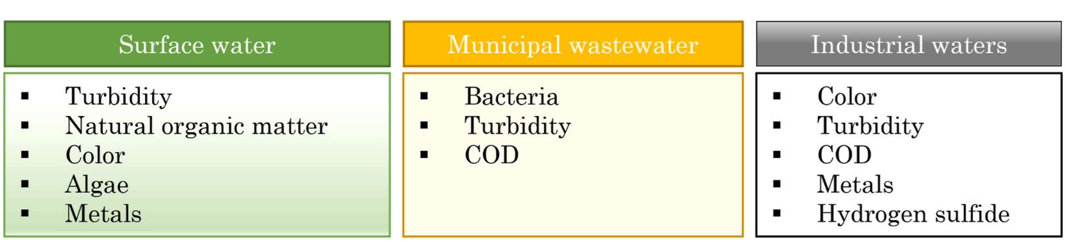

Fig. 1. Tannin coagulants applications: parameters typically well removed by TC.

dosage, very low residual turbidity was also observed with 125 mg/L FS and even lower UV_{254} values than with the tannin coagulants.

Many studies have compared tannin coagulants to other coagulants in the treatment of industrial wastewaters. In the treatment of cassava processing wastewater, several tannin coagulants (Acquapol WW and S5T, Tanfloc SL and SG) were tested at neutral pH and achieved better color and turbidity removal than AS (dos Santos et al., 2018). Among tannin coagulants, Acquapol S5T and Tanfloc SL resulted in the most efficient performance.

No significant difference was observed between tannin coagulant (*Acacia mearnsii*, Tanac) and PAC when used for dairy wastewater treatment at pH 6–7 (Dela Justina et al., 2018). The study, however, showed that the tannin coagulant had certain benefits over PAC, such as lower alkalinity consumption and lower impact on conductivity of treated water. Also, when the effect of pH was studied, tannin coagulant removed well turbidity and color in the pH range 5–10, but significantly lower efficiency was recorded at pH 4 (Dela Justina et al., 2018). PAC, on the other hand, worked well in a slightly narrower pH range (6–10).

In paint manufacturing wastewater, tannin coagulant removed the best COD and color compared to FC and AS (Aboulhassan et al., 2016). The coagulation pH did not significantly affect tannin coagulant efficiency on COD removal, while metal salts removed less COD at alkaline pH (Aboulhassan et al., 2016). In addition, in contrast to metal salts, tannin coagulant did not significantly affect the pH of the treated water, which would allow water to be led directly into the biological process.

In the case of synthetic textile effluents, tannin coagulant was more efficient than FS when the treatment was carried out at neutral or alkaline conditions (Lopes et al., 2019). However, lowering the pH of the effluent to 4 or 5, the required dosage of both tannin coagulant and FS was lower, and additionally FS provided decolorization at much lower dosages. In another study with synthetic textile effluent at pH 9, synthetic organic coagulant (Rifloc 6548) had better cost-efficiency and better color removal (81%) than tannin coagulant (42%) (Machado et al., 2022). In a study made with real textile wastewater (Aboulhassan et al., 2005), tannin coagulant achieved a high color removal (90.7%) and sufficient COD removal (50.2%), while the removal rates were higher for FC (color 97.6%, COD 57.4%). AS achieved the highest COD removal (87.2%) but the lowest color removal (71.4%).

Tannin coagulants have also been tested in combination with other coagulants. Grenda et al. (2020) showed that using tannin coagulant together with a small amount of cationic polyacrylamide (PAM) resulted in high turbidity and color removal from industrial effluent. High turbidity reduction from biologically treated industrial dyeing and laundry effluent was achieved by using both Tanfloc and cationic PAM (Costa et al., 2018). A combination of tannin coagulant (Organo-floc) and anionic PAM was successfully applied for biologically treated landfill leachate and resulted in high color removal at pH 5 (Ibrahim and Yaser 2019). Aboulhassan et al. (2006) found that the most suitable combination for the treatment of paint wastewaters would be FC, tannin coagulant and, anionic high-MW PAM when considering the sludge volume and purification results. In the treatment of turbid wastewater from plastic recycling industry, addition of magnetite nanoparticles improved the performance of tannin coagulant in terms of turbidity and color removal (Ribeiro et al., 2023). In case with *Moringa oleifera*, magnetite addition did not provide significant difference. In tannery wastewater, combining tannin coagulant with AS (in a 50:50 ratio) provided higher removal of hydrogen sulfide from wastewater (Uez et al., 2023).

2.2.2. Metal removal

Tannin coagulants have also proved to be effective in metal removal. Lugo et al. (2020) showed that copper, chromium, and mercury were most efficiently removed by *Acacia* tannin coagulant at alkaline pH from industrial wastewater (spiked with metals). This was due to higher degree of ionization of phenolic groups and stronger electrostatic attraction between metal ions and negatively charged surface of the tannin polymer. Commercial Tanfloc MTH proved to remove above 93% of aluminium, iron and manganese from turbid river water (de Oliveira et al., 2022). In the treatment of humic peat extraction runoff water, a tannin-based coagulant was able to remove 94% of iron, whereas the application of FS led to an increase in the metal level in the water (Heiderscheidt et al., 2016). Righetto et al. (2021) examined the effectiveness of coagulation as a pretreatment technique to remove metals and improve landfill leachate quality for subsequent nutrient recovery. Using a commercial tannin coagulant (derived from the bark of the *A. mearnsii* tree), they obtained high removal efficiencies for iron and titanium (>90%) and chromium (68%) at pH 7.3. Smaller percentages (33–52%) were found for aluminum, barium, vanadium, and manganese. It is important to highlight that metal removal may also be induced by pH adjustment to alkaline conditions, as precipitation of metal ions may occur quantitatively, depending on the pH, water characteristics, and the solubility product of the metal hydroxides. Arsenic contamination in groundwater is a major problem for which coagulation-flocculation and tannin coagulants could work, but are yet to be explored. According to the authors' best knowledge, only conventional chemical coagulants have been studied (Amiri et al., 2022).

2.3. Floc characteristics and sludge quality

Properties of the flocs generated by tannin coagulants and sludge amounts have been investigated in few studies and also compared to some conventional coagulants. Floc growth, size and resistance are being affected by the wastewater or suspension quality (pH and compounds). Sludge volume and amount are also important parameters due to high costs of sludge disposal.

Graham et al. (2008) found that tannin coagulant provided a higher coagulation rate and degree of floc growth in kaolin suspension at pH 9 compared to pH 7. Coagulation rate at pH 9 by the tannin coagulant was also higher than that for the polyDADMAC at pH 7, and the degree of floc growth was higher than that of AS at pH 7. Hameed et al. (2016) found that tannin coagulant produced bigger flocs with a faster settling rate than PAC in urban wastewater treatment. After 2 min settling time, Tanfloc had removed 70% of turbidity, while PAC removed only 30%. Sludge volume indexes were at a similar level for both coagulants up to 60 mg/L dosages. In dairy wastewater treatment, tannin coagulant presented higher resistance to floc breakage than PAC during slow-mixing time and at higher velocity gradients (Dela Justina et al., 2018), which is an advantage in turbulent flows.

In textile wastewater, the tannin coagulant produced a smaller sludge volume than FC and AS, but an intermediate sludge weight between FC and AS (Aboulhassan et al., 2005). In paint manufacturing wastewater, tannin coagulant produced less volume of decanted sludge than FC and AS (Aboulhassan et al., 2016). Similar results were found in tannery wastewater treatment, in which FS generated higher sludge volume without sufficient settling characteristics (sludge volumetric index above 100 mL/g), compared to the tannin coagulant (Aboulhassan et al., 2021). Sludge volume of municipal wastewater of the secondary sedimentation stage was decreased when tannin coagulant was applied (Cainglet et al., 2020). However, starch, chitosan, high-MW polyamine, and high-MW polyDADMAC achieved an even higher decrease in sludge volume. On the other hand, polyamine and polyDADMAC with lower MW as well as PAC did not have a decreasing effect on the volume of sludge produced.

The use of plant-based coagulants also allows for a safer disposal of the sludge, compared to conventional coagulants, and may be a route for nutrient recovery through the application of the generated sludge as fertilizer in agriculture, as proposed by Alnawajha et al. (2022) for aquaculture wastewater treatment.

Table 2
Maximum adsorption capacities (Q) reported in literature for tannin-derived adsorbents, and different organic and inorganic contaminants.

Adsorbate	Adsorbent	Q (mg/g)	Reference
Metal removal			
Cd(II)	Bayberry tannin polymer immobilized on cellulose	73.6 (298 K, pH 5)	(Zhou et al., 2019)
Cr(VI)	Black wattle tannin-gel	488 (298 K, pH 1)	(Rodrigues et al., 2015)
Cr(VI)	Black wattle tannin-immobilized nanocellulose	105 (pH 2)	(Xu et al., 2017)
Cr(VI)	Gelatin-chestnut biopolymer	80.6 (298 K, pH 4)	(Hassoune et al., 2018)
Cr(VI)	MnO_2-PEI-TA composite	790 (298 K, pH 2)	(Deng et al., 2021)
Cr(VI)	Biomaterial from chestnut tannin with proteins hydrolysate from wet blue chrome shavings (CT-PH)	40.16 (298 K, pH 3)	(Nechchadi et al., 2022)
Cr(VI)	Persimmon tannin functionalized waste paper	178.7 (298 K, pH 2)	(Liu et al., 2022)
Cu(II)	Tannin-PEI adsorbent	80 (298 K, pH 5)	(Jiang et al., 2020)
Cu(II)	Black wattle tannin-immobilized nanocellulose	52 (298 K, pH 6)	(Xu et al., 2017)
Cu(II)	Bayberry tannin polymer immobilized on cellulose	53.19 (298 K, pH 5)	(Zhou et al., 2019)
Cu(II)	MnO_2-PEI-TA composite	125 (298 K, pH 5.5)	(Deng et al., 2021)
Hg(II)	Tannic acid film covered magnetic microspheres	279 (303 K, pH 6.0)	(Luo et al., 2017)
Pb(II)	Silverwattle tannin resins	189 (pH 6)	(Okoli et al., 2018)
Pb(II)	Black wattle tannin-immobilized nanocellulose	53 (pH 6)	(Xu et al., 2017)
Pb(II)	Tannic acid film covered magnetic microspheres	1115 (303 K, pH 6)	(Luo et al., 2017)
Pb(II)	Tannin-based magnetic POP	252 (pH 5)	(Huang et al., 2019)
Pb(II)	Self-assembled metal-phenolic networks	356.1 (pH 5, 298 K)	(Qiu et al., 2022)
Zn(II)	Pinus tannin gel	65 (293 K, pH 7)	(Sánchez-Martín et al., 2011)
Radionuclides removal			
U(VI)	Polytannin (*A. nilotica* fruit) glutaraldehyde resin	104 (298 K, pH 3)	(Alhumaimess et al., 2019)
U(VI)	Persimmon tannin functionalized waste paper	242.3 (298 K, pH 6)	(Liu et al., 2022)
U(VI)	Tannin grafted bovine serum albumin nanospheres	488 (pH 5)	(Yu et al., 2018)
Toxic metalloids			
As(III)	Fe_3O_4@TA@UiO-66 microsphere	97.8 (RT)	(Qi et al., 2019)
As(V)	Iron-loaded pine bark tannin resin	0.7 (293 K, pH 3)	(Bacelo et al., 2020)
Sb(III)	Pine bark tannin resin	32.9 (298 K, pH 6)	(Bacelo et al., 2018)
Sb(V)	Pine bark tannin resin	47 (298 K, pH 2)	(Bacelo et al., 2022)
Sb(III)	Fe_3O_4@TA@UiO-66 microsphere	49.5 (RT)	(Qi et al., 2019)
Color removal			
MB	Pinus tannin gel	499 (293 K, pH 7)	(Sánchez-Martín et al., 2011)
MB	Tannin-immobilized cellulose microspheres	57.5 (303 K, pH 8)	(Pei et al., 2017b)
MB	Tannin-based magnetic POP	1696 (natural pH)	(Huang et al., 2019)
MB	Iron-polyphenol nanomaterial	187 (pH 7)	(Aktar and Ray 2022)
DY86	Oak gall tannin-immobilized HMS	436 (293 K, pH 2)	(Binaeian et al., 2016)
MO	APTES-functionalized tannin-rich grape biomass	314.6 (298 K, pH 6)	(Cavalcante et al., 2022)
AR1	Tannin-APTES adsorbent	217 (298 K, pH 2)	(Leite et al., 2017)
Pharmaceutical compounds			
CIP	Fe-modified bayberry tannin foam	112 (298 K)	(Hao et al., 2021)
DIC	Tannin from Indian almond leaf	71.9 (298 K)	(Sunsandee et al., 2020)

AR – Acid Red; CIP – ciprofloxacin; DIC – Dicloxacillin; DY – Direct Yellow; HMS – hexagonal mesoporous silicate; POP – porous organic polymers; RT – room temperature; TA – Tannin acid.

3. Tannin-derived adsorbents for water treatment

3.1. Tannin resins

Resins (or gels) result from the insolubilization of tannins through alkali- or acid-catalyzed polymerization with formaldehyde. This reaction primarily takes place at the nucleophilic centers on the A-ring (more reactive than B-ring sites), creating methylene bridges and forming a cross-linked three-dimensional structure (Arbenz and Averous 2015; Xiaojian and Guanben 2019). Formaldehyde effectively cross-links condensed tannins, enabling the development of sorbents from various sources such as pine bark, quebracho, cypress, and Weibull black tannin (Sánchez-Martín et al., 2011; Bacelo et al., 2020). Concerns regarding formaldehyde toxicity have motivated the use of alternative cross-linking agents, such as benzaldehyde (Okoli et al., 2018) and glutaraldehyde (Alhumaimess et al., 2019), though with lower reactivity. Autocondensation reactions are characteristic of polyflavonoid tannins (Xiaojian and Guanben 2019) and may be alternative routes for insolubilizing tannin molecules without aldehydes. In some instances, a catalyst is required as exemplified for persimmon tannin, converted into successful sorbents through boiling in concentrated sulfuric acid (Inoue et al., 2015). Studies conducted on wattle tannin-formaldehyde gelation show that tannin gels generated under acid conditions tend to develop higher pore volumes (Amaral-Labat et al., 2013; Braghiroli et al., 2019), whereas materials with smaller no appreciable pores are generated in alkaline conditions. The authors have also pointed out that shrinkage and porosity loss can occur in the drying process (Amaral-Labat et al., 2013). Indeed, most tannin resins evaluated as sorbents present minor surface areas (Sánchez-Martín et al., 2011; Okoli et al., 2018; Bacelo et al., 2020), despite showing good adsorptive properties, explained by the abundant phenolic hydroxyl groups prone to form stable chelates with metal ions (Koopmann et al., 2020). The ionization of these groups and stabilization by resonance generate a negative surface charge in practically the entire pH range, as indicated by isoelectric points measured at approximately pH 2 (Rodrigues et al., 2015; Sun et al., 2021; Bacelo et al., 2022). This feature enables electrostatic interactions with cationic adsorbates in a wide pH range, and explains the efficient uptake of various metals from water, such as Cd(II), Cu(II), Pb(II), Zn(II), and cationic organic species, such as methylene blue dye (MB). This is depicted in Table 2, which presents data collection on the maximum adsorption capacities reported for tannin sorbents (experimental or calculated values from valid equilibrium models). In addition to the electrostatic attraction, hydrogen bonds and van der Waals interactions explain significant uptake ability organic micropollutants such as dicloxacillin antibiotic (Sunsandee et al., 2020).

Removing radioactive elements from water, such as hexavalent uranium, is another potential use of tannins. Alhumaimess et al. (2019) synthesized a polytannin glutaraldehyde resin from *Acacia nilotica* fruit tannin, starting by reacting with formaldehyde followed by glutaraldehyde cross-linking. The material presented a rapid removal of U(VI) from water (60–90 min), efficient in the pH range of 3–6, and optimum adsorption at pH 6.

Tannin resins are also good sequestrants of metal(loid)s species that appear in water under anionic or neutral complexes, such as hexavalent chromium and antimony. In acidic and neutral conditions, Cr(VI) is present in water under the anionic species $HCrO_4^-$ and $Cr_2O_7^{2-}$ and therefore its uptake through electrostatic attraction is not possible. The outstanding adsorptive ability, exemplified for a black wattle tannin gel is explained by Cr(VI) adsorption by phenolic groups via chromate esterification, reduction of part of Cr(VI) to Cr(III) with the oxidation of phenolic hydroxyls in tannin; and Cr(III) uptake by electrostatic attraction (Rodrigues et al., 2015). A tannin resin polymerized from maritime pine bark extract showed great adsorption affinity for antimony, in particular for the most toxic species of Sb(III), which can be quantitatively removed from water in a wide pH range by complexation with adjacent hydroxyl groups on tannin sorbents (Bacelo et al., 2018).

In a different synthesis approach, a biobased phenolic resin was prepared through the polymerization of a blend of condensed tannin (black wattle commercial sample) and crude industrial Kraft black liquor (Moreira et al., 2022). The procedure involved several steps, starting with hydroxymethylation of the raw Kraft black liquor with formaldehyde, followed by mixing with tannin and sodium hydroxide mixture and ending with a thermal treatment at 170 °C. The biobased resin was able to provide 100% removal of metals from aqueous solution, being also quite effective in Diuron and methylene blue uptake but ineffective for methyl orange and atrazine. The authors concluded that more lipophilic compounds (highest distribution coefficient value) are more extensively removed.

3.2. Amine-functionalized tannin adsorbents

Amine functionalization based on hydrogen bonding between materials containing hydroxyl and amino groups has been highly investigated to generate tailored tannin resins. Introducing N-containing functions and replacing some hydroxyl groups create positively charged centers in the adsorbent surface. The pH range where the adsorbent assumes a positively charged surface is typically extended, and the adsorption performance is enhanced. The isoelectric points of tannin resins have been identified at a pH around 2, whereas a pH of 7.7 was obtained for a triethylamine-modified tannin gel (Shan et al., 2015). Different routes can be used to anchor N-ligands to tannins. Akter et al. (2016) prepared an amine-modified adsorbent by reacting a formaldehyde cross-linked tannin resin with ammonia. They confirmed a slightly higher performance of the resulting sorbent towards a cationic dye. Jiang et al. (2020) synthesized a composite using only tannin and polyethylenimine (PEI), a polymer with many repeating units containing amino groups. A first step in which hydrogen bonds formed between hydroxyl groups on tannin and amino groups on PEI was followed by continuous stirring and polymerization without the need of cross-linking agents. The synthetized adsorbent was effective in Cu(II) removal from water. The more interesting advantage of amino modification, however, is the removal of anionic adsorbates, which is usually more challenging. Binaeian et al. (2016) synthesized aminated hexagonal mesoporous silicate nanoparticles and further immobilized oak gall tannins using glutaraldehyde. The synthetized material showed a good adsorption capacity for the anionic dye Direct Yellow 86. Dye removals by aminated and non-aminated hexagonal mesoporous silicate nanoparticles, and oak gall tannin-immobilized adsorbent were compared. The improvement in dye uptake was attributed to the tannin incorporation, but amination has conferred the greatest improvement in the decolorization efficiency. Composites prepared by reacting tannins with APTES (3-aminopropyltriethoxysilane) at 75 °C using ammonia presented great adsorption capacities for the anionic dye Acid Red 1, especially at pH 2, under which the amino groups are protonated and able to interact electrostatically with the anionic dye (Leite et al., 2017). Cavalcante et al. (2022) grafted a tannin-rich grape residue with APTES in a single step 80 °C procedure. Although the smooth shift in the isoelectric point from 1.8 to 2.8, the functionalization generated enhanced chemical surface activity and a sorbent with remarkable adsorption capacity for methyl orange dye (Table 2). Although acidic conditions favored dye uptake due to an electrostatic attraction mechanism, pH 6 was considered a more realistic pH for adsorption assays.

3.3. Iron-tannin composites

Iron-based adsorptive media are usually suitable for pollutant removal from water, in particular for arsenic, radium, uranium, and antimony. Tannin resins or foams are also possible carriers of iron, owing to the high affinity of B-ring hydroxyl groups of the condensed tannins to transition metals and to the stability of complexes formed with iron(III) (Koopmann et al., 2020). Bacelo et al. (2020) prepared an iron-loaded tannin resin, starting with formaldehyde cross-linking of pine bark tannins, followed by partial oxidation with hot nitric acid and Fe(III) loading. The intermediate oxidation step was found important for the subsequent iron uptake, as some catechol hydroxyl groups oxidized to carbonyl groups, which have a higher affinity to iron ions. Hao et al. (2021) synthesized a foam from bayberry tannins using hexamethylenetetramine as a cross-linker. The resulting material preserved phenolic hydroxyls and was a porous supporting matrix for Fe(III) via coordination. Negative zeta potentials in almost the entire pH range were reported despite the iron modification, restraining the chances for electrostatic attraction with anionic adsorbates. Iron-tannin composites showed certain adsorption ability for arsenic(V), compared to unmodified tannin resins which presented negligible adsorption (Bacelo et al., 2020). Hao et al. (2021) reported successful removal of ciprofloxacin (an antibiotic) from water demonstrating that the metal was the main responsible for the observed efficiency. Qiu et al. (2022) prepared polyphenol-based adsorbents using tannic acid and ferric ions through simple cross-linking self-assembly reactions and indicated an excellent adsorption capacity for lead(II), assigned to the strong coordination between the metal and phenolic hydroxyl and ester groups, and specific adsorption on the newly formed hydrous ferric oxides.

3.4. Tannin composites using natural substrates

The use of natural polymers as substrates for tannin immobilization strengthens their functional performance, as they can be dispersed in a more suitable morphology for continuous processes and may provide high adsorption ability and efficient adsorption rate (Guan et al., 2023). The natural abundance and easy chemical modification of cellulose have motivated research on its use as a carrier to immobilize tannins. One of the main strategies to form covalent bonds for conjugating tannins and cellulose is using epichlorohydrin (ECH) as a crosslinker. Pei et al. synthetized tannin-immobilized cellulose microspheres and hydrogels via homogeneous reaction, using ECH and condensed tannins from *Areca catechu* fruits (Pei et al. 2017a,b; Pei et al. 2019). Zhou et al. (2019) proposed a tannin-phenolic polymer produced from bayberry tannins through paraformaldehyde cross-linking and cellulose immobilization by ECH. The authors argued that tannins insolubilization before immobilization on cellulose increases the effective phenolic hydroxyl content in the cellulose skeleton and enhances the adsorptive properties of the adsorbent. These cellulose-tannin composites showed a great potential to clean up waters from Cd(II), Cu(II), Pb(II), and cationic dye (Table 2), mainly due to the negatively charged surface and electrostatic-based adsorptive mechanism. The other approach to conjugate cellulose substrates with tannin derivatives is reported by Xu et al. (2017). A black wattle tannin-nanocellulose composite was prepared starting by oxidizing nanocrystalline cellulose using sodium periodate to get dialdehyde nanocellulose, which served as the matrix and cross-linker. Black wattle tannin did not leak out during the adsorption process, indicating tight immobilization onto nanocellulose by covalent bonding. In other work, dialdehyde waste paper was used as a cross-linking agent to immobilize persimmon tannin into a nanocomposite (Liu et al., 2022). The waste paper mainly comprises cellulose and hemicellulose and is easily oxidized, generating a mass of aldehyde that can be used to dismiss cross-linking agent usage. The persimmon tannin functionalized waste paper sorbent presented an isoelectric point of 4.18 and great potential to remediate U(VI) and Cr(VI) contaminated water, reaching adsorption capacities of 242 and 179 mg/g at pH 6 and 2 (Table 2), respectively. U(VI) uptake is mainly dependent on chelation, whereas the Cr(VI) adsorption might stem from a combination of electrostatic attraction and redox reaction. In another work, a cellulose nanofiber-based adsorbent was prepared by introducing persimmon tannin/MXenes-NH2 into dialdehyde cellulose nano-fibres. Characterization indicated plenty of functional groups (Ar-OH, $-NH_2$, Ti–OH), providing rich active sites for radionuclides uptake from water (Liu et al., 2023).

Immobilization of tannins on collagen and gelatin through covalent and non-covalent binding (hydrogen bonds and hydrophobic interactions) has also been reported in the literature (Guan et al., 2023). Meng et al. (2019) prepared a composite assembling gelatin, PVA (poly vinyl alcohol), and bayberry tannin by electrostatic spinning and crosslinking by glutaraldehyde. The results revealed that the tannin had been stably solidified on the composite, which showed great potential to adsorb uranium from simulated seawater. Hassoune et al. (2018) prepared biopolymers by precipitating gelatin extracted from untanned hide wastes with chestnut and quebracho tannins. Although the derived biopolymers seem to be less effective for Cr(VI) than tannin resins, the adsorption mechanism is referred to be the same. Moreover, the material cannot be used at strongly acidic and alkaline media, in which the composite is unstable.

Bayberry tannin can also be immobilized into other proteins, such as bovine serum albumin nanospheres (Yu et al., 2018). The developed sorbent efficiently removed uranyl ions from radioactive wastewater due to a chelating mechanism between UO_2^{2+} and the adjacent phenolic hydroxyls and chelating sites such as =–CO and $-NH_2$ on the serum albumin.

3.5. *Tannin-based nanoparticles and magnetic sorbents*

Nanoadsorbents synthesized from various materials are a promising approach for water purification. Their potential stems from the high adsorption capacities and rapid sorption kinetics, attributed to the large surface area, and can be enhanced through various engineered chemical modifications. Recently, several tannin-based nanostructured sorbents were investigated for water purification including oak gall tannin-immobilized hexagonal mesoporous silicate nanoparticles used for anionic dye removal (Binaeian et al., 2016), iron-polyphenol nanomaterial investigated, able to remove fluoride and cationic dye from water and whose synthesis process can be replicable in large quantities (Aktar and Ray 2022), and a black wattle tannin-nanocellulose composite successfully tested for metal adsorption (Xu et al., 2017). Persimmon tannin nanocomposites (Liu et al., 2022) and gelatin/PVA composite nanofiber band loaded with bayberry tannin (Meng et al., 2019) were proposed for uranium uptake. Despite the observed good performance of nanosorbents at the laboratory scale, their use on full-scale may be challenging due to their handling and safety concerns and difficult separation (Mudhoo and Sillanpää 2021). Magnetic nanosorbents have been the target of intense research, as they allow an easy solid-liquid separation provided by an external magnetic field. Tannin immobilization in magnetic particles, composed of an iron oxide core and a silica shell, has been proposed by several authors. Luo et al. (2017) prepared tannin acid film covered magnetic nanoparticles (Fe_3O_4@TA–Fe^{3+}). Great adsorption abilities were obtained for Pb(II) and Hg(II) (see Table 2). Huang et al. (2019) developed tannin-based magnetic porous organic polymers (POPs). As it can be seen from Table 2, the adsorbent presented remarkable and fast uptake of Pb(II) and MB pollutants from water due to the high surface area, abundant phenolic groups, and negatively charged surface at pH above 3. Considering that UiO derivatives are a promising methodology for As (III) and Sb(III) sequestering, a magnetic core-shell nanocomposite was designed, where polyphenol tannic acid acted as a modifier and bridge, connecting UiO-66 MOF (metal-organic framework) particles to the magnetic Fe_3O_4@TA (Qi et al., 2019). The removal mechanism was mainly attributed to complexation involving Zr–*O*–As and Zr–*O*–Sb bonds, but the abundant hydroxyl groups of tannin acid facilitated the uptake of the adsorbates.

3.6. *Application potential*

Different tannin-derived materials have been developed to remove of inorganic and organic contaminants from water, with potential for various applications, according to available literature (Fig. 2). It is, however, important to discuss several points related to the practical application. One of them is the possible interference of coexisting species in the solution. Most studies have been conducted using synthetic solutions (containing the adsorbate dissolved in water), but some others evaluate the adsorption performance under complex and real water matrices. No drastic interferences have been reported for lead uptake considering metal removal in water treatment or industrial effluent remediation. Luo et al. (2017) tested magnetic tannin composites for Pb (II) and Hg(II) removal in tap and lake water. Although a certain decrease in the adsorption capacity was obtained for Pb(II) (roughly a 30% decrease), compared to a simple aqueous solution, the adsorbent still presented an outstanding ability to sequester the metal (more than 750 mg/g). A negligible effect of the aqueous matrix was observed for mercury uptake. Qiu et al. (2022) indicated that most cations (Zn(II), Cd (II), Ca(II), Mn(II), and Mg(II)) exert little effect on Pb(II) adsorption by a polyphenol-based adsorbent, oppositely to Ni(II) and Cu(II) which can reduce the adsorption capacity of the material, but do not compromise sorbent efficiency. Aktar and Ray (2022) validated the fluoride uptake performance of an iron-polyphenol nanomaterial on groundwater samples collected in India. The adsorbent was able to reduce fluoride levels to recommended permissible limit (1.5 mg/L), by adjusting dosages between 2 and 3 g/L.

Bacelo et al. (2022) observed that the breakthrough in an adsorptive column containing pine bark tannin resin was reached faster and the sorbent usage efficiency decreased roughly to two-thirds when the column was fed with a simulated mine effluent, compared to a single metal solution. High sulfate levels characterize most mining-impacted waters, but the adsorbent's performance towards Sb(III) remained unaffected in the presence of this background ion. In contrast, high levels of calcium and magnesium ions moderately affect the antimonite uptake.

In organic micropollutants, dye removal from textile dyehouse effluents is another potential application (Table 2). Conventional treatment processes are not completely effective for textile effluent remediation, and a final refining treatment step of adsorption can be considered to achieve total decolorization. However, literature has been mostly focused on basic (cationic) dyes removal (e.g., MB), and few studies have been conducted using reactive dyes (widely applied to dye cotton and of particular challenging removal). In addition, complex aqueous matrices, typically characterizing textile effluents should be tested. Some potential of tannin sorbents is also expected for wastewater generated in pharmaceuticals production but with high specificity considering chemical properties of the adsorbates. Sunsandee et al. (2020) showed the performance of immobilized almond leaf tannins on dicloxacillin uptake, using a real effluent containing solvents, additives, and reactants.

Packed beds are the most used adsorbers in full-scale adsorption. Small particles are not amenable to adsorption columns due to the pressure drop, and a few studies address coarser particles or fixed bed column studies. Bacelo et al. (2022) employed a tannin resin in a packed

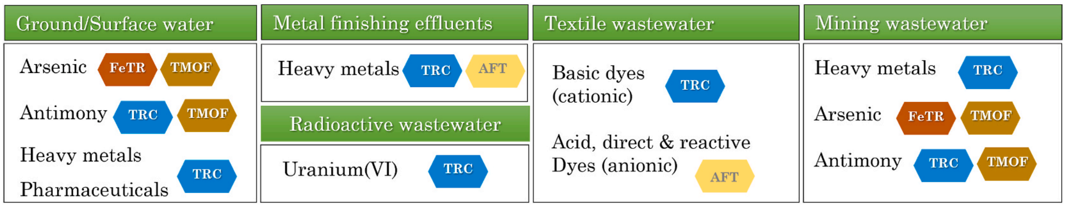

Fig. 2. Potential applications of tannin-derived adsorbents: TRC – Tannin resins and composites; FeTR – Iron-loaded materials; AFT – Amine-functionalized materials; TMOF – Tannin-MOF composites.

bed for Sb(III) uptake and the adsorptive capacity obtained was practically the same as the one found in batch mode. The authors indicate an adsorbent usage rate as low as 0.11 kg/m^3 to treat efficiently (90% removal) 1 mg-Sb/L aqueous solution, that could represent an Sb-contaminated groundwater. Qiu et al. (2022) reported that the metal-phenolic network they produced can produce 9500 and 7860 bed volumes of clean water, with Pb(II) levels below 1 mg/L, when fed with synthetic polluted and simulated electroplating wastewater. As an alternative to column processes and to the need for coarser particles, magnetic tannin particles can be applied in stirred adsorbents, offering feasible solid-liquid separation.

The regeneration of the adsorbents is also a critical factor for the cost-effectiveness of the process. Desorption, regeneration and reuse of tannin-derived adsorbents on uptake of cationic dye and metals (Pb and Cu ions) have been reported with practically no loss of adsorption efficiency (<10%) for 4–5 adsorption/desorption cycles. The eluents used are acid solutions (Xu et al., 2017; Huang et al., 2019; Jiang et al., 2020), and the desorption provided is probably due to the reversal of the electrostatic attraction mechanism. In contrast, tannin sorbents saturated with antimony or chromium(VI) presented a challenging regeneration, using alkaline and acid solutions, respectively (Xu et al., 2017; Bacelo et al. 2018, 2022). Despite the chromium can be desorbed with nitric acid solution, a poor adsorption performance after regeneration was found, attributed to an adsorption mechanism based on redox reaction. Fig. 3 summarizes the author's perspective on the strengths, weaknesses, opportunities, and threats related to this matter.

4. Conclusions

The market needs for water treatment chemicals produced from renewable resources is evident. Tannin's role in the future production of natural-based coagulants and adsorbents for water purification is increasingly recognized. Tannin coagulants have demonstrated remarkable efficacy across various applications, often surpassing the performance of conventional coagulants. A key advantage of tannin coagulants is their minimal impact on the pH of treated water. This characteristic proves particularly beneficial when it is necessary to maintain a specific pH level for subsequent processes. Also, many studies have concluded that tannin coagulants can work at a wide pH range (although the required dosage can vary), and sludge volume is smaller than with metal salts. However, more research is needed on different types of wastewater at a larger scale and to compare tannin coagulants with other bio-based coagulants. It is worth noting that the performance of tannin coagulants also varies widely among tannin coagulants since

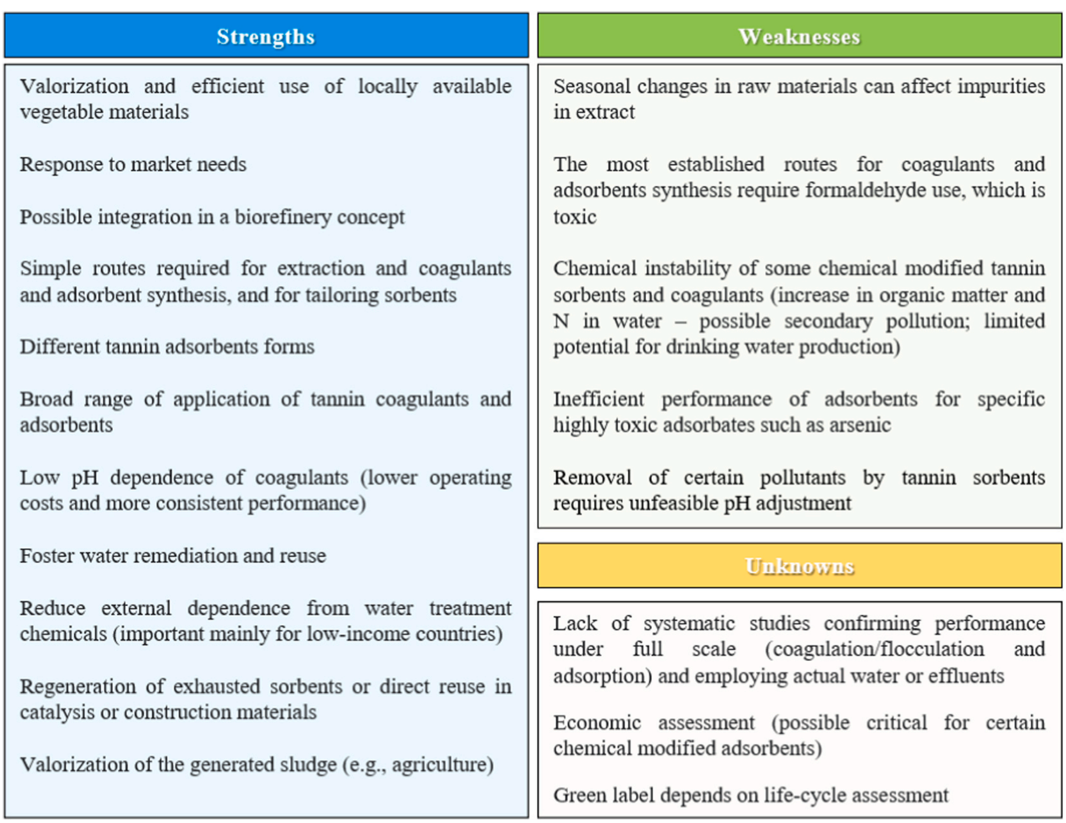

Fig. 3. Strengths, weaknesses, opportunities and threats of tannin coagulants/flocculants and adsorbents usage for water purification: authors perspective.

tannin raw material, modification conditions, and impurities affect the characteristics of tannin coagulants. In addition, tannin coagulant synthesis should continue to be investigated to go further on greener procedures and avoid organic matter or nitrogen leaching from tannin coagulants, which limits the application for drinking water treatment purposes. The tannin coagulant costs have been highlighted as still uncompetitive.

Various tannin-derived adsorbents have been synthesized for pollutant uptake from water. Strengths of tannin adsorbents lie in the use of locally available natural materials as precursors, synthesis processes with low chemicals and energy requirements, the possibility to prepare adsorbents in different particle sizes or to magnetize them, excellent and fast uptake of a broad range of metals, radionuclides, and organic compounds. Weaknesses are identified in the limited ability to uptake certain adsorbates, such as arsenic and anionic dyes, requiring amine-functionalization or MOF composites, involving additional processing and higher synthesis costs. More research is needed to validate the identified application fields.

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.

Data availability

No data was used for the research described in the article.

Acknowledgements

The work was conducted as part of the Supporting Environmental, Economic and Social Impacts of Mining Activity (KO1030 SEESIMA) research project and received financial support from the Kolarctic CBC (Cross-Border Collaboration), the European Union, Russia, Norway, Finland, and Sweden. Its contents are the sole responsibility of the authors at the University of Oulu, and do not necessarily reflect the views of the European Union or the participating countries. This work was financially supported by LA/P/0045/2020 (ALiCE), UIDB/50020/2020 and UIDP/50020/2020 (LSRE-LCM), funded by national funds through FCT/MCTES (PIDDAC). S. Santos acknowledges postdoctoral scholarship (SFRH/BPD/117387/2016) awarded by FCT.

References

Aboulhassan, M.A., Harif, S., Souabi, S., Yaacoubi, A., 2021. Efficient and sustainable treatment of industrial wastewater using a tannin-based polymer. Int. J. Sustain. Eng. 14 (6), 1943–1949.

Aboulhassan, M.A., Souabi, S., Yaacoubi, A., Baudu, M., 2005. Treatment of textile wastewater using a natural flocculant. Environ. Technol. 26 (6), 705–711.

Aboulhassan, M.A., Souabi, S., Yaacoubi, A., Baudu, M., 2006. Improvement of paint effluents coagulation using natural and synthetic coagulant aids. J. Hazard Mater. 138 (1), 40–45.

Aboulhassan, M.A., Souabi, S., Yaacoubi, A., Baudu, M., 2016. Coagulation efficacy of a tannin coagulant agent compared to metal salts for paint manufacturing wastewater treatment. Desalination Water Treat. 57 (41), 19199–19205.

Aktar, J., Ray, M., 2022. Iron-polyphenol nanomaterial removes fluoride and methylene blue dye from water and promotes plant growth. J. Environ. Chem. Eng. 10 (3).

Akter, N., Hossain, M.A., Hassan, M.J., Amin, M.K., Elias, M., Rahman, M.M., Asiri, A.M., Siddiquey, I.A., Hasnat, M.A., 2016. Amine modified tannin gel for adsorptive removal of Brilliant Green dye. J. Environ. Chem. Eng. 4 (1), 1231–1241.

Alhumaimess, M.S., Alsohaimi, I.H., Alqadami, A.A., Khan, M.A., Kamel, M.M., Aldosari, O., Siddiqui, M.R., Hamedelniel, A.E., 2019. Recyclable glutaraldehyde cross-linked polymeric tannin to sequester hexavalent uranium from aqueous solution. J. Mol. Liq. 281, 29–38.

Alnawajha, M.M., Kurniawan, S.B., Imron, M.F., Abdullah, S.R.S., Hasan, H.A., Othman, A.R., 2022. Plant-based coagulants/flocculants: characteristics, mechanisms, and possible utilization in treating aquaculture effluent and benefiting from the recovered nutrients. Environ. Sci. Pollut. Control Ser. 29 (39), 58430–58453.

Amaral-Labat, G., Szczurek, A., Fierro, V., Pizzi, A., Celzard, A., 2013. Systematic studies of tannin-formaldehyde aerogels: preparation and properties. Sci. Technol. Adv. Mater. 14 (1).

Amiri, S., Vatanpour, V., He, T., 2022. Optimization of coagulation-flocculation process in efficient arsenic removal from highly contaminated groundwater by response surface methodology. Molecules 27 (22), 7953.

Arbenz, A., Averous, L., 2015. Chemical modification of tannins to elaborate aromatic biobased macromolecular architectures. Green Chem. 17 (5), 2626–2646.

Bacelo, H., Santos, S.C.R., Botelho, C.M.S., 2020. Removal of arsenic from water by an iron-loaded resin prepared from Pinus pinaster bark tannins. Euro-Mediterranean Journal for Environmental Integration 5 (3).

Bacelo, H., Santos, S.C.R., Ribeiro, A., Boaventura, R.A.R., Botelho, C.M.S., 2022. Antimony removal from water by pine bark tannin resin: batch and fixed-bed adsorption. J. Environ. Manag. 302.

Bacelo, H., Vieira, B.R.C., Santos, S.C.R., Boaventura, R.A.R., Botelho, C.M.S., 2018. Recovery and valorization of tannins from a forest waste as an adsorbent for antimony uptake. J. Clean. Prod. 198, 1324–1335.

Barrado-Moreno, M.M., Beltran-Heredia, J., Martin-Gallardo, J., 2016. Removal of Oocystis algae from freshwater by means of tannin-based coagulant. J. Appl. Phycol. 28 (3), 1589–1595.

Bello, A., Bergmann, U., Vepsalainen, J., Leiviska, T., 2022. Effects of tree harvesting time and tannin cold/hot-water extraction procedures on the performance of spruce tannin biocoagulant for water treatment. Chem. Eng. J. 449.

Bello, A., Leiviskä, T., 2022. Sustainable tannin-based coagulants synthesized through Mannich reaction using melamine as an amine source for water treatment applications. Ind. Crop. Prod. 176, 114336.

Bello, A., Virtanen, V., Salminen, J.P., Leiviska, T., 2020. Aminomethylation of spruce tannins and their application as coagulants for water clarification. Separ. Purif. Technol. 242.

Beltrán-Heredia, J., Sánchez-Martín, J., Gómez-Muñoz, C., 2012. Performance and characterization of a new tannin-based coagulant. Appl. Water Sci. 2 (3), 199–208.

Binaeian, E., Seghatoleslami, N., Chaichi, M.J., 2016. Synthesis of oak gall tannin-immobilized hexagonal mesoporous silicate (OGT-HMS) as a new super adsorbent for the removal of anionic dye from aqueous solution. Desalination Water Treat. 57 (18), 8420–8436.

Bongiovani, M.C., Werberich, T., Schneider, R.M., do Amaral, A.G., 2018. PAC and tannin as coagulants in swine slaughterhouse wastewater treatment. Wastes - Solut., Treat. Opportun. 57–62.

Braghiroli, F.L., Amaral-Labat, G., Boss, A.F.N., Lacoste, C., Pizzi, A., 2019. Tannin gels and their carbon derivatives: a review. Biomolecules 9 (10).

Cainglet, A., Tesfamariam, A., Heiderscheidt, E., 2020. Organic polyelectrolytes as the sole precipitation agent in municipal wastewater treatment. J. Environ. Manag. 271.

Cavalcante, E.H.M., Candido, I.C.M., de Oliveira, H.P., Silveira, K.B., Alvares, T.V.D., Lima, E.C., Thyrel, M., Larsson, S.H., dos Reis, G.S., 2022. 3-Aminopropyl-triethoxysilane-Functionalized tannin-rich grape biomass for the adsorption of methyl orange dye: synthesis, characterization, and the adsorption mechanism. ACS Omega 7 (22), 18997–19009.

Costa, A.F.S., Albuquerque, C.D.C., Salgueiro, A.A., Sarubbo, L.A., 2018. Color removal from industrial dyeing and laundry effluent by microbial consortium and coagulant agents. Process Saf. Environ. Protect. 118, 203–210.

Das, N., Shende, A.P., Mandal, S.K., Ojha, N., 2022. Biologia Futura: treatment of wastewater and water using tannin-based coagulants. Biol. Futur. 73 (3), 279–289.

de Oliveira, C., Trevisan, V., Skoronski, E., 2022. Application of tannin-based coagulant for high-range turbidity surface water clarification. J. Water, Sanit. Hyg. Dev. 12 (11), 803–815.

Dela Justina, M., Muniz, B.R.B., Broring, M.M., Costa, V.J., Skoronski, E., 2018. Using vegetable tannin and polyaluminium chloride as coagulants for dairy wastewater treatment: a comparative study. J. Water Proc. Eng. 25, 173–181.

Deng, X.Y., Wang, L.X., Xiu, Q.H., Wang, Y., Han, H., Dai, D.M., Xu, Y.J., Gao, H.T., Liu, X., 2021. Adsorption performance and physicochemical mechanism of MnO2-polyethylenimine-tannic acid composites for the removal of Cu(II) and Cr(VI) from aqueous solution. Front. Chem. Sci. Eng. 15 (3), 538–551.

dos Santos, J.D., Veit, M.T., Juchen, P.T., Goncalves, G.D., Palacio, S.M., Fagundes-Klen, M., 2018. Use of different coagulants for cassava processing wastewater treatment. J. Environ. Chem. Eng. 6 (2), 1821–1827.

Fabres, R.B., da Luz, R.B., Soliman, M.C., Staggemeier, R., Fleck, J.D., do Nascimento, C. A., do Nascimento, F.T., Spilki, F.R., 2017. 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 (8), 2195–2202.

Fang, G., 2007. Evaluation and Performance of a Tannin-Based Polymer as a Coagulant in Water Treatment. Imperial College London.

Giroletti, C.L., dos Santos Menezes, J.C.S., Santos Klienchen Dalari, B.L., Lobo-Recio, M. A., Nagel Hassemer, M.E., 2022. New tannin-based coagulant from grape stems: synthesis, characterization and coagulation tests. Environ. Eng.amp.; Manag. J. 21 (1), 145–152.

Graham, N., Gang, F., Fowler, G., Watts, M., 2008. Characterisation and coagulation performance of a tannin-based cationic polymer: a preliminary assessment. Colloids Surf. A Physicochem. Eng. Asp. 327 (1–3), 9–16.

Grehs, B.W.N., Lopes, A.R., Moreira, N.F.F., Fernandes, T., Linton, M.A.O., Silva, A.M.T., Manaia, C.M., Carissimi, E., Nunes, O.C., 2019. Removal of microorganisms and antibiotic resistance genes from treated urban wastewater: a comparison between aluminium sulphate and tannin coagulants. Water Res. 166.

Grenda, K., Arnold, J., Gamelas, J.A.F., Rasteiro, M.G., 2020. Up-scaling of tannin-based coagulants for wastewater treatment: performance in a water treatment plant. Environ. Sci. Pollut. Control Ser. 27 (2), 1202–1213.

Guan, X.Y., Zhang, B.Y., Wang, Z.Q., Han, Q.X., An, M., Ueda, M., Ito, Y., 2023. Natural polyphenol tannin-immobilized composites: rational design and versatile applications. J. Mater. Chem. B 11 (21), 4619–4660.

Hameed, Y.T., Idris, A., Hussain, S.A., Abdullah, N., 2016. 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, 494–503.

Hao, B.C., Wang, F., Huang, H., Wu, Y.L., Jia, S.H., Liao, Y., Mao, H., 2021. Tannin foam immobilized with ferric ions for efficient removal of ciprofloxacin at low concentrations. J. Hazard Mater. 414.

Hassoune, J., Tahiri, S., El Krati, M., Cervera, M.L., de la Guardia, M., 2018. Removal of hexavalent chromium from aqueous solutions using biopolymers. J. Environ. Eng. 144 (8).

Heiderscheidt, E., Leiviska, T., Klove, B., 2016. Coagulation of humic waters for diffused pollution control and the influence of coagulant type on DOC fractions removed. J. Environ. Manag. 181, 883–893.

Huang, L., Shuai, Q., Hu, S., 2019. Tannin-based magnetic porous organic polymers as robust scavengers for methylene blue and lead ions. J. Clean. Prod. 215, 280–289.

Ibrahim, A., Yaser, A., 2019. Colour removal from biologically treated landfill leachate with tannin-based coagulant. J. Environ. Chem. Eng. 7 (6).

Ibrahim, A., Yaser, A., Lamaming, J., 2021. Synthesising tannin-based coagulants for water and wastewater application: a review. J. Environ. Chem. Eng. 9 (1).

Inoue, K., Gurung, M., Xiong, Y., Kawakita, H., Ohto, K., Alam, S., 2015. Hydrometallurgical recovery of precious metals and removal of hazardous metals using persimmon tannin and persimmon wastes. Metals 5 (4), 1921–1956.

Jiang, W.Y., Xing, Y.H., Wang, T.S., Liao, J., He, J., Chen, W., Wang, J., Mo, L.X., 2020. Green synthesis of tannin-polyethylenimine adsorbent for removal of Cu(II) from aqueous solution. J. Chem. Eng. Data 65 (11), 5593–5605.

Kiventerä, J., Leiviskä, T., Keski-Ruismäki, K., Tanskanen, J., 2016. Characteristics and settling behaviour of particles from blast furnace flue gas washing. J. Environ. Manag. 172, 162–170.

Koopmann, A.K., Schuster, C., Torres-Rodriguez, J., Kain, S., Pertl-Obermeyer, H., Petutschnigg, A., Husing, N., 2020. Tannin-based hybrid materials and their applications: a review. Molecules 25 (21).

Leite, A.J.B., Lima, E.C., dos Reis, G.S., Thue, P.S., Saucier, C., Rodembusch, F.S., Dias, S. L.P., Umpierres, C.S., Dotto, G.L., 2017. Hybrid adsorbents of tannin and APTES (3-aminopropyltriethoxysilane) and their application for the highly efficient removal of acid red 1 dye from aqueous solutions. J. Environ. Chem. Eng. 5 (5), 4307–4318.

Liu, F., Hua, S., Wang, C., Hu, B., 2022. Insight into the performance and mechanism of persimmon tannin functionalized waste paper for U(VI) and Cr(VI) removal. Chemosphere 287, 132199.

Liu, F., Hua, S., Xia, F., Hu, B., 2023. Efficient extraction of radionuclides with MXenes/persimmon tannin functionalized cellulose nanofibers: performance and mechanism. Appl. Surf. Sci. 609, 155254.

Lopes, E.C., Santos, S.C.R., Pintor, A.M.A., Boaventura, R.A.R., Botelho, C.M.S., 2019. Evaluation of a tannin-based coagulant on the decolorization of synthetic effluents. J. Environ. Chem. Eng. 7 (3).

Lugo, L., Martin, A., Diaz, J., Perez-Florez, A., Celis, C., 2020. Implementation of modified Acacia tannin by Mannich reaction for removal of heavy metals (Cu, Cr and Hg). Water 12 (2).

Luo, H., Zhang, S., Li, X., Liu, X., Xu, Q., Liu, J., Wang, Z., 2017. Tannic acid modified Fe_3O_4 core–shell nanoparticles for adsorption of Pb^{2+} and Hg^{2+}. J. Taiwan Inst. Chem. Eng. 72, 163–170.

Machado, C., Botelho, C., Santos, S., 2022. Decolorization of a simulated reactive textile dyeing effluent using a plant-derived coagulant. U.Porto. J. Eng. 8 (4), 13–25.

Meng, J., Lin, X., Zhou, J., Zhang, R., Chen, Y., Long, X., Shang, R., Luo, X., 2019. Preparation of tannin-immobilized gelatin/PVA nanofiber band for extraction of uranium (VI) from simulated seawater. Ecotoxicol. Environ. Saf. 170, 9–17.

Moreira, W.M., Viotti, P.V., de Moura, A.A., Gimenes, M.L., Vieira, M.G.A., 2022. Synthesis of a biobased resin and its screening as an alternative adsorbent for organic and inorganic micropollutant removal. Environ. Sci. Pollut. Control Ser. 29 (53), 79935–79953.

Mudhoo, A., Sillanpää, M., 2021. Magnetic nanoadsorbents for micropollutant removal in real water treatment: a review. Environ. Chem. Lett. 19 (6), 4393–4413.

Nechchadi, B., Gallart-Mateu, D., Krati, M.E., de la Guardia, M., Tahiri, S., 2022. Removal of hexavalent chromium from water using a biomaterial synthesized from tannins and chrome shaving proteins hydrolysate. Water Air Soil Pollut. 233 (12).

Okoli, B.J., Shilowa, P.M., Anyanwu, G.O., Modise, J.S., 2018. Removal of Pb^{2+} from water by synthesized tannin resins from invasive South African trees. Water 10 (5).

Pei, Y., Chu, S., Chen, Y., Li, Z.D., Zhao, J., Liu, S.Q., Wu, X.J., Liu, J., Zheng, X.J., Tang, K.Y., 2017a. Tannin-immobilized cellulose hydrogel fabricated by a homogeneous reaction as a potential adsorbent for removing cationic organic dye from aqueous solution. Int. J. Biol. Macromol. 103, 254–260.

Pei, Y., Wu, X.J., Xu, G.Q., Sun, Z.J., Zheng, X.J., Liu, J., Tang, K.Y., 2017b. Tannin-immobilized cellulose microspheres as effective adsorbents for removing cationic dye (Methylene Blue) from aqueous solution. J. Chem. Technol. Biotechnol. 92 (6), 1276–1284.

Pei, Y., Xu, G.Q., Wu, X., Tang, K.Y., Wang, G.Z., 2019. Removing Pb(II) ions from aqueous solution by a promising absorbent of tannin-immobilized cellulose microspheres. Polymers 11 (3).

Qi, P., Luo, R., Pichler, T., Zeng, J., Wang, Y., Fan, Y., Sui, K., 2019. Development of a magnetic core-shell Fe_3O_4@TA@UiO-66 microsphere for removal of arsenic(III) and antimony(III) from aqueous solution. J. Hazard Mater. 378, 120721.

Qiu, H., Ni, W., Yang, L., Zhang, Q., 2022. Remarkable ability of Pb(II) capture from water by self-assembled metal-phenolic networks prepared with tannic acid and ferric ions. Chem. Eng. J. 450, 138161.

Ribeiro, T., Janz, F.J.L., Vizibelli, D., Borges, J.C.A., Borssoi, J.A., Fukumoto, A.A.F., Bergamasco, R., Yamaguchi, N.U., Pereira, E.R., 2023. Magnetic natural coagulants for plastic recycling industry wastewater treatability. Water 15 (7).

Righetto, I., Al-Juboori, R.A., Kaljunen, J.U., Mikola, A., 2021. Multipurpose treatment of landfill leachate using natural coagulants - pretreatment for nutrient recovery and removal of heavy metals and micropollutants. J. Environ. Chem. Eng. 9 (3).

Rodrigues, L.A., Sakane, K.K., Simonetti, E.A.N., Thim, G.P., 2015. Cr total removal in aqueous solution by PHENOTAN AP based tannin gel (TFC). J. Environ. Chem. Eng. 3 (2), 725–733.

Sadegh, N., Haddadi, H., Sadegh, F., Asfaram, A., 2023. Recent advances and perspectives of tannin-based adsorbents for wastewater pollutants elimination: a review. Environ. Nanotechnol. Monit. Manag. 19, 100763.

Sánchez-Martín, J., Beltrán-Heredia, J., Delgado-Regaña, A., Rodríguez-González, M.A., Rubio-Alonso, F., 2013. Optimization of tannin rigid foam as adsorbents for wastewater treatment. Ind. Crop. Prod. 49, 507–514.

Sánchez-Martín, J., Beltrán-Heredia, J., Gibello-Pérez, P., 2011. Adsorbent biopolymers from tannin extracts for water treatment. Chem. Eng. J. 168 (3), 1241–1247.

Santos, S.C.R., Bacelo, H.A.M., Boaventura, R.A.R., Botelho, C.M.S., 2019. Tannin-adsorbents for water decontamination and for the recovery of critical metals: current state and future perspectives. Biotechnol. J. 14 (12).

Shan, W., Ren, F., Zhang, Q., Wan, L., Xing, Z., Lou, Z., Xiong, Y., 2015. Enhanced adsorption capacity and selectivity towards molybdenum in wastewater by a persimmon tannin waste based new adsorbent. J. Chem. Technol. Biotechnol. 90 (5), 888–895.

Sun, X.B., Zhang, J.Y., You, Y.H., 2021. Enhancement of Cu(II) removal by carbon disulfide modified black wattle tannin gel. Colloids Surf. A Physicochem. Eng. Asp. 608.

Sunsandee, N., Ramakul, P., Phatanasri, S., Pancharoen, U., 2020. Biosorption of dicloxacillin from pharmaceutical waste water using tannin from Indian almond leaf: kinetic and equilibrium studies. Biotechnol. Rep. (Amst) 27, e00488.

Thakur, S.S., Choubey, S., 2014. Use of Tannin based natural coagulants for water treatment: an alternative to inorganic chemicals. Int. J. ChemTech Res. 6 (7), 3628–3634.

Tomasi, I.T., Machado, C.A., Boaventura, R.A.R., Botelho, C.M.S., Santos, S.C.R., 2022. Tannin-based Coagulants: Current Development and Prospects on Synthesis and Uses, vol. 822. Science of the Total Environment.

Tomasi, I.T., Santos, S.C.R., Boaventura, R.A.R., Botelho, C.M.S., 2023. Microwave-assisted extraction of polyphenols from Eucalyptus bark-A first step for a green production of tannin-based coagulants. Water 15 (2).

Uez, D.E., Hansen, E., Osório, D.M., de Aquim, P.M., 2023. Reducing the pollution load of tannery wastewater and the atmospheric emission of hydrogen sulfide using modified tannin. Water Sci. Technol. 87 (6), 1542–1551.

Vera, M., Urbano, B.F., 2021. Tannin polymerization: an overview. Polym. Chem. 12 (30), 4272–4290.

Vilen, A., Laurell, P., Vahala, R., 2022. Comparative life cycle assessment of activated carbon production from various raw materials br. J. Environ. Manag. 324.

Xiaojian, Z., Guanben, D., 2019. In: Alfredo, A., Rijeka (Eds.), Applications of Tannin Resin Adhesives in the Wood Industry. Tannins. IntechOpen. Ch. 6.

Xu, Q.H., Wang, Y.L., Jin, L.Q., Wang, Y., Qin, M.H., 2017. Adsorption of Cu (II), Pb (II) and Cr (VI) from aqueous solutions using black wattle tannin-immobilized nanocellulose. J. Hazard Mater. 339, 91–99.

Yu, J., Luo, X.G., Liu, B., Zhou, J., Feng, J., Zhu, W.K., Wang, S.L., Zhang, Y.D., Lin, X.Y., Chen, P., 2018. Bayberry tannin immobilized bovine serum albumin nanospheres: characterization, irradiation stability and selective removal of uranyl ions from radioactive wastewater. J. Mater. Chem. A 6 (31), 15359–15370.

Zhou, P., Yuan, H., Ou, L.J., Peng, Z.Y., 2019. Removal of Cd(II) and Cu(II) ions from aqueous solutions using tannin-phenolic polymer immobilized on cellulose. J. Macromol. Sci., Pure Appl. Chem. 56 (7), 717–722.