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Published in:
Industrial Crops and Products

DOI:
10.1016/j.indcrop.2023.117962

Published: 01/03/2024

Document Version
Publisher's PDF, also known as Version of record

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Please cite the original version:
Characterization of crude extracts from willow barks and their performance as proanthocyanidin-based coagulants in water treatment

Jinze Dou a,*,1, Adedayo Bello b,1, Jari Koivist o c, Kristoffer Meinander a, Tiina Leiviska b, Tapani Vuorinen a

a Department of Bioproducts and Biosystems, Aalto University, Espoo, Finland
b Chemical Process Engineering, University of Oulu, Oulu, Finland
c Department of Chemistry and Materials Science, Aalto University, Espoo, Finland

ARTICLE INFO
Keywords:
Colloids destabilization
Biocoagulant
Proanthocyanidins
Willow bark crude extracts
Surface water treatment

ABSTRACT
This work investigates the proanthocyanidin profile of willow bark crude extracts and these materials were cationized and preliminarily tested as biocoagulants for water treatment. The characteristics of crude extracts proanthocyanidin were investigated using size exclusion chromatography (SEC), nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS). XPS analysis indicates that the crude extracts contain significant amounts of sugars. Furthermore, SEC and liquid-state NMR spectroscopy showed that crude extract contains roughly 3–4 flavan-3-ol units with procyanidin (PC)/prodelphinidin (PD) ratio of roughly 3–5. Thus, the modified form of tannin (proanthocyanidin-enriched) coagulants obtained the higher cationic charge density. The coagulation experiments with kaolin-river water mixture suggested that all the selected willow hybrids’ tannin coagulants were effective in settling the particles down. This study indicates that the value of willow bark can be significantly improved by the usage of crude extracts for water treatment.

1. Introduction

The barks represent 10–15 wt% of wood logs (Chen et al., 2020) in the forest and pulp (paper) industry. Traditionally, the removal of bark has been the first step carried out in production of pulp, paper, and timber. Like the fast-growing hardwood tree willow, the million tons of bark has been primarily used for energy. Willow bark has received growing attention for its rich source of the extractives (Dou et al., 2018, 2016) and the sclerenchyma fiber bundles (Baker et al., 2022; Dou et al., 2022b, 2019). The sclerenchyma fiber bundles can be both chemically (Dou et al., 2021b) and biologically isolated (Dou et al., 2022b), and further applied as wound dressing material (Dou et al., 2023a). Although the small molecular weight (Mw) fractions of the crude extracts of willow bark have been the major focus (Agolet et al., 2012; Dou et al., 2018; Poblocka-Olech et al., 2007), few research has been conducted on the chemistry and use of the high Mw proanthocyanidins (represent more than 50% of its overall fraction) from the crude extracts of willow bark.

Condensed tannins (or proanthocyanidin), with the Mw of 500–3000 Da, are a natural macromolecular polymer present at the bark of many tree species (Bello et al., 2022; Bianchi et al., 2015; Kemppainen et al., 2014; Palma et al., 2003; Yazaki, 2015). Tannins are composed of three main structural groups, which are hydrolysable tannins, proanthocyanidins, and phlorotannins. Proanthocyanidins are polyphenol of flavan-3-ol units with C6-C3-C6 skeleton. Procyanidins (PCs) and prodelphinidins (PDs) represent the prominent form depending on its monomer units (Yazaki, 2015). In particular, spruce bark tannin fractions have been reported as a potential source of biocoagulant for industrial wastewater treatment (Bello et al., 2022).

Improving sustainability of wastewater treatment has been considered as a challenging topic in our urbanizing world. Coagulation-flocculation is a process which involves the addition of chemicals known as coagulants to destabilize colloidal impurities in polluted water (Lee et al., 2012; Teh et al., 2016). Most of the negatively charged colloidal impurities in water can be destabilized with cationic coagulants (Koohestanian et al., 2008). Tannin-based cationic coagulants offer sustainable and environmentally friendly alternatives for water treatment. Anionic polyphenol tannins can be cationized by Mannich reactions.

https://doi.org/10.1016/j.indcrop.2023.117962
Received 17 October 2023; Received in revised form 4 November 2023; Accepted 15 December 2023
Available online 5 January 2024
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modification. The Mannich reaction is known to replace hydrogen atom in the polyphenolic matrix of tannin structures with a positively charged iminium ion (Bello et al., 2022; Bello and Leiwicka, 2022). Many studies have reported the efficacy of Mannich-modified tannins in different domestic and industrial water treatment applications (Arismendi et al., 2018; Bello et al., 2023; Ibrahim et al., 2021; Sánchez-Martín et al., 2014). Castanea sativa, Schinopsis balansae, Acacia mearnsii and Picea abies are the woody sources of the most investigated tannin-based coagulant species (Ibrahim et al., 2021; Tomasi et al., 2022). However, the performances of these coagulants in water treatment have been observed to vary significantly among different tannin sources due to the distinctive chemical configurations of the tannin structures (Ibrahim et al., 2021). For example, in comparison of Schinopsis balansae (quebracho) and Picea abies (spruce) tannins, it was reported that cationization was less effective in spruce tannin due to lower amount of phenolic groups or phenolic constituent in the tannin extract (Bello et al., 2020). The application of cationized willow tannin as a water treatment coagulant has not been previously investigated. Most specifically, new information is obtained about the effects of chemical composition of hybrid differences on Mannich modification and coagulant’s performance in water treatment.

Although the adsorption experiments of the activated foams made of willow bark crude extracts has been shown promise for zinc and bisphenol A removal (Dou et al., 2023b), the aim of this study was to investigate the coagulation performance of a bio-coagulant from willow bark. In this study, we utilized a combination of size exclusion chromatography (SEC), X-ray photoelectron spectroscopy (XPS), and nuclear magnetic resonance (NMR) spectroscopy to elucidate both the morphological and chemical structure of the crude extracts, and to explore further its performance in usage as coagulants based on the charge density of its modified forms. In particular, the properties of biocoagulants were assessed for their performances in removing the turbidity and the organic matter from the kaolin/river water mixture.

2. Materials and methods

2.1. Materials and chemicals

Eight willow hybrids (Klara; Myrsinifolia; Schweinni; Winter; Lisa; Linnéa; Petra; and Erna) were harvested from multiple institutes and locations, including the Carbons Finland Oy (Kouvola, Finland), VTT Technical Research Center of Finland Ltd (Kyyjärvi, Finland), Lantmännen Lantbruk (Svalöv, Sweden). The detailed harvesting information and their pedigree tree have been reported previously (Dou et al., 2022a). The manually peeled and oven-dried (50 °C) willow bark was ground into 1 mm mesh size using the Wiley-mill. The crude extracts were recovered under the optimized extraction conditions (80 degrees with an extraction time of 20 min) using water as previously reported for willow bark (Dou et al., 2018). The crude water extracts were then lyophilized and kept in the desiccator for further experiments, as shown in Fig. 1. Arabinose, D2O, fructose, galactose, glucose, rhamnose, 1,3, 5-trioxane, and xylose were all analytical grade and supplied from Sigma-Aldrich, Finland. (+)-Catechin and (+)-gallocatechin were purchased from MedChemExpress, Finland. The ethanolamine used as an amine source in cationization was produced by Sigma Aldrich Chemicals (Germany) and HCl used for biocoagulant acidification was supplied by Merck KGaA (Germany). Formaldehyde (37% V/W) used as a cross-linking agent during biocoagulant synthesis was manufactured by VWR International (France). NaOH was supplied by VWR chemicals BDH (Czech Republic).

2.2. Experimental flow

2.2.1. Mannich modification of willow tannins

The cationization of the willow tannins was performed by adapting the Mannich modification for spruce tannin, as described previously (Bello et al., 2020). After complete dissolution of willow bark tannins (2 g in 10 ml of Milli-Q (MQ) water), the solution was further raised to 70 °C under continuous stirring before introducing 37.2 mmol of ethanolamine (ETH). The solution’s pH decreased from 11 to 6 using 5 M HCl. The solution temperature was further increased to 80 °C. 14.9 mmol of formaldehyde was introduced to the solution at 90 min by a peristaltic pump. After that, the reaction was maintained at the temperature of 85 °C and continuously stirred for 180 min. The reaction was first quenched using 5 ml MQ water and an acidification step with 5 M HCl reduce its pH down to 1.5. The product was then standardized to 50 mg/ml using MQ water.

2.2.2. Model water and coagulation experiments

The pH of the Oulu river water (Oulu, Finland) was adjusted from 6.8 to 7.5 using 0.5 M NaOH. A model water used for the coagulation experiment was mimicked by mixing 3 g of fine kaolin clay (0.063–0.5 mm) into 10 liters of the river water. The spiking of the river water with kaolin was necessitated by its initial low turbidity (9.5 NTU).– (0.063

Fig. 1. Experimental flow of the crude extracts’ preparation, chemical characterization, and further coagulation performance determination for willow bark. a Physicochemical characterization. b Raw powdered crude extracts were modified and then used for water treatment; photographs show the before/after treatment of kaolin/river water mixture with the willow bark coagulants. Charge density has been measured after modification of the extract.
2000 flocculator, which simulates the coagulation with different doses of willow bark tannin coagulants. In a typical run of the coagulation experiment, the dosed model water (800 ml) was rapidly mixed at 150 rpm for 1 min and slowly mixed at 40 rpm for 20 min, and the sedimentation duration was maintained for 30 min. This was then proceeded further by carefully pipetting 200 ml of the supernatant of the test water at the point (approximately 3 cm from the surface) for the water quality analysis.

2.2.3. Water analyses in coagulation

The total surface charge (TSC) was determined using the Particle Charge Detector (Müteck PCD 05, Herrsching, Germany) by titrating 10 ml water samples with 0.0001 N cationic or anionic titrants (BTG, Sweden). A Metrohm 913 pH meter was implemented for pH measurement. The turbidity and dissolved organic carbon (DOC) measurements were characterized using a HACH 2100Q turbidimeter and Sievers 900 total organic carbon analyser, respectively. Ultra-violet (UV) absorbance was measured at the wavelength of 254 nm using a Shimadzu UV-1800 spectrophotometer. SUVA (specific ultraviolet absorbance) were further calculated by dividing the determined UV absorbance by the DOC according to Eq. (1).

\[
\text{SUVA} = \frac{1}{\text{mg/m}} = \frac{\text{UV}_{254} \text{(cm}^{-1} \text{)} \times 100 \text{cm/m}}{\text{DOC} \text{(mg/l)}}
\]  

(1)

2.3. Characterization

XPS measurements of the crude extracts were carried out with a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer using a monochromated Al Kα X-ray source (1486.7 eV) run at 100 W and its analysis area was 300 µm x 700 µm. A pass energy of 80 eV and a step size of 1.0 eV were applied for collection of the survey spectra, while a pass energy of 20 eV and a step size of 0.1 eV were used particularly for high-resolution spectra. Photoelectrons were collected at a 90° take-off angle under the ultra-high vacuum with a base pressure of the system typically below 1 x 10−9 Torr. Sampled spectra from three different surface spots is essential for obtaining the most representative results. All values given here are calculated averages. The detailed characterization of the SEC and liquid-state (1H, 13C and HSQC) NMR have been summarized in the supplementary material.

Charge densities of the Mannich-modified willow coagulants were determined with a Müteck smart PCD-05 (same equipment as in Section 2.2). Solutions used for the charge density measurements were prepared by diluting 0.1 ml of coagulants in 250 ml of MQ water, which produced solutions with a pH range of 4.3 to 4.5. Then, 10 ml of the diluted coagulant solutions were titrated to the endpoint with 0.001 N anionic titrant. The charge density for each coagulant was obtained from the mean of three titrated replicates. Charge densities were expressed as milliequivalents of positive charge per gram of willow bark tannin.

Table 1

<table>
<thead>
<tr>
<th>Willow hybrids</th>
<th>Charge density of biocogulant, meq/g ± STD (pH)</th>
<th>Molecular weight distribution of extract</th>
<th>Mn</th>
<th>Mw</th>
<th>mDP</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Freshly prepared</td>
<td>Two months after the preparation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1_12_04_Klara</td>
<td>1.979 ± 0.005 (4.5)</td>
<td>2.237 ± 0.029 (4.3)</td>
<td>935</td>
<td>1109</td>
<td>3.8</td>
<td>1.2</td>
</tr>
<tr>
<td>D3_10_17_Myrcifolia</td>
<td>2.045 ± 0.005 (4.3)</td>
<td>2.261 ± 0.024 (4.3)</td>
<td>764</td>
<td>1068</td>
<td>3.7</td>
<td>1.4</td>
</tr>
<tr>
<td>D4_10_17_Schweinii</td>
<td>2.416 ± 0.003 (4.3)</td>
<td>2.276 ± 0.025 (4.3)</td>
<td>837</td>
<td>1031</td>
<td>3.6</td>
<td>1.2</td>
</tr>
<tr>
<td>D7_12_04_Winter</td>
<td>2.348 ± 0.003 (4.3)</td>
<td>2.366 ± 0.025 (4.3)</td>
<td>908</td>
<td>1064</td>
<td>3.7</td>
<td>1.2</td>
</tr>
<tr>
<td>D9_02_06_Lina</td>
<td>2.173 ± 0.002 (4.5)</td>
<td>2.466 ± 0.018 (4.3)</td>
<td>792</td>
<td>967</td>
<td>3.6</td>
<td>1.2</td>
</tr>
<tr>
<td>D10_02_06_Linnéa</td>
<td>2.254 ± 0.004 (4.4)</td>
<td>2.480 ± 0.018 (4.4)</td>
<td>791</td>
<td>1045</td>
<td>3.6</td>
<td>1.3</td>
</tr>
<tr>
<td>D11_02_06_Petra</td>
<td>2.284 ± 0.006 (4.4)</td>
<td>2.743 ± 0.065 (4.3)</td>
<td>833</td>
<td>1049</td>
<td>3.6</td>
<td>1.3</td>
</tr>
<tr>
<td>D12_02_06_Erma</td>
<td>2.152 ± 0.003 (4.6)</td>
<td>2.402 ± 0.024 (4.3)</td>
<td>723</td>
<td>951</td>
<td>3.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Physicochemical indicators

The crude extracts represent 20 (w/w, %) of the studied willow hybrids (Dou et al., 2022a). Although benzyl mercaptan degradation method is considered as a more efficient protocol to calculate the mDP of proanthocyanidin, it has an obnoxious odor. The determined average degree of oligomerization ranged from 3–4 flavan-3-ol units based on the size exclusion chromatography (SEC) (Table 1 and Fig. S1), which is similar as the reported mDP from hybrid Klara using the ultra-performance liquid chromatography–tandem mass spectrometry (Dou et al., 2023b). The average molecular weight of all the crude extracts was approximately 1000 g/mol, indicating its richness of polymeric tannins.

Charge densities have been widely acknowledged to be a vital indicator in evaluating the performance of tannin-based coagulants (Bello et al., 2020). Table 1 shows the charge densities of the willow tannin coagulants. For this study, the measurement of charge densities was arranged immediately after Mannich modification (freshly prepared values) and two months after coagulation to evaluate the stability of the product. A comparison of the charge densities obtained from the coagulants immediately after modification and after the two-month storage period revealed that the cationization process progressed in most samples (except D4 hybrid Schweinii during storage resulting in products with higher charge densities. This indicates that the adopted 180 min (from the modification of spruce tannin) (Bello et al., 2022) was not sufficient for the complete cationization of the willow tannin. It is well-known that the mechanism behind the cationization of tannin polymers involves the crosslinking between flavonoid units and the iminium ions (Arismendi et al., 2018; Beltrán-Heredia et al., 2010). This crosslinking progresses over time, and different re-action times have been reported for tannins from various sources (Ibrahim et al., 2021; Tomasi et al., 2022). Thus, more experiment is required to establish the specific reaction time for the cationization of willow tannin with ethanolamine. Nonetheless, it could be deduced from the measurements at the different timing intervals that the willow hybrids produced coagulants of medium-range charge densities. Charge densities of similar range have been reported for spruce (2.44 ± 0.58 meq/g) and quebracho (3.84 ± 0.41 meq/g) tannin coagulants produced with the same amine and modification conditions (Bello et al., 2022, 2020). A detailed breakdown of the results showed that during the measurements of the coagulants immediately after cationization, willow hybrid Schweinii coagulant possessed the highest charge density (2.42 meq/g), followed by the willow hybrid Winter (2.35 meq/g). The reason for the rapid cationization of the willow hybrids Schweinii and Winter could not be determined at this study. On the other hand, the charge density analysis performed after two months of storage revealed that hybrids Petra and Linnéa possessed superior cationic properties. The high charge density achieved by hybrids Petra and Linnéa was probably due to a relatively higher proanthocyanidin (catechin) to sugar content in the tannin extracts (Table S2). Previous studies have
established a positive correlation between higher proanthocyanidin content and charge density, whereas the presence of sugars has been reported to be detrimental to the Mannich modification of tannin coagulants (Bello et al., 2022, 2020).

### 3.2. Chemical indicators

High-resolution X-ray photoelectron spectroscopy provided chemical information on the composition of the top 10 nm atomic surface of the crude extracts (Fig. 2 and Table 2). All spectra were charge-corrected with respect to the C-C bonding position at 284.8 eV. The C 1 s spectra were fitted with four Gaussian components, with peak positions at 284.8 eV (C-C), 286.5 eV (C-O), 287.8 eV (C=O or O-C=O), and 288.9 eV (O-C=O), respectively. No clear evidence of large amounts of aromatic carbon was observed in the spectra, which is in line with the determined relative number of aromatics as shown in Table 2. Aromatic carbon appears with a C-C component at a slightly lower binding energy, coupled with a satellite at about 6 eV higher binding energy. Carbon bound to a single oxygen C-O was the most abundant component for all hybrids, which is to be expected for materials with a relatively large sugar content, as 83% of carbon in polysaccharides is bonded to a single oxygen. The only exception to this was hybrid Schweinni, with 58.6% aliphatic C-C carbon, which, however, corresponds well with its sugar content, which is lowest among the studied hybrids in Table 2. The largest relative variation between the high sugar level samples was seen in the amount of carbonyl groups. For example, the largest amount of C=O % (14.6%) is in line with the highest sugar content (332.7 mg/g, detected by GC-FID, Table S2) among the studied hybrids. Trace amounts of silicon could also be seen in most samples (Table S3), with relatively larger amounts present in the crude extracts of willow hybrid Schweinni. The Si 2p spectra could be fitted with a single Gaussian component at approximately 102.3 eV, which most likely corresponds to silicon in organosilicon compounds.

The HSQC spectrum (Fig. 3) demonstrates the fingerprints of PC- and PD-units based on references (Crestini et al., 2016; Fryganas et al., 2018; Zeller, 2019) and model compounds of catechin and gallocatechin. The correlated protonated PC-units are at chemical shifts of δC/δH 115.0/6.9 (B ring-2), 115.5/6.7 (B ring-5) and 119.1/6.6 (B ring-6). Additionally, the characteristic peaks of the C/H-2,6′ (δC/δH, 106–109/6.5–6.7 ppm) of the protonated prodelphinidin (PD) units are differentiated using the green triangle symbol at Fig. 3. Both PC- and PD-units were identified from the crude extracts. 1,3,5-Trioxane is used as the internal standard to calculate the relative contents of PC- and PD-units using 1H NMR. The estimated integral for PC-units (H2 of catechin) and PD-units (H2/6 of gallocatechin) is between 3 to 5 among all the studied willow hybrids. Overall, the XPS, HSQC, and molecular weight distribution of the crude extracts suggest that the chemical functionalities of the crude extracts from studied willow hybrids are rich in proanthocyanidins with PC-units. Charge density has been reported for dictating the performance of the organic polymers such as tannin coagulants for spruce bark (Bello et al., 2022). Coagulants with higher charge density are mostly preferred during tannin-based coagulant modification, and this is due to the importance of charge neutralization required in most water treatment. Four hybrids (D4 Schweinni, D7 Winter, D10 Linnéa, and D11 Petra) were selected for further coagulation studies owning to their high charge density from their modified forms.

### 3.3. Coagulation performance

According to the earlier studies, tannin polymers with superior cationic properties are more suitable for destabilizing impurities in the effluents with positive charged demands (Bello et al., 2022; Fang, 2007). Thus, hybrids Schweinni, Winter, Linnéa, and Petra were chosen for the coagulation studies based on their high charge densities during measurement at different timing intervals (freshly prepared and two months after the preparation). Fig. 4 displays the dosage curves for residual turbidity, TSC, UV254, and the SUVA value of the treated model water. Fig. 4a shows that all tested tannin coagulants were able to impressively reduce the residual turbidity (>90%) of the treated model water with a relatively low coagulant dosage (roughly 20 mg/l). The figure also depicts that hybrids Schweinni and Linnéa tannin coagulants possessed a wider optimal dosage range than hybrids Winter and Petra. However, all coagulants witnessed an increase in residual turbidity, also known as

Fig. 2. XPS survey and C 1 s spectra of selected willow hybrids for coagulation studies. The spectrum of pure cellulose is included as a reference. a D4.10.17_Schweinni, b D7.12.04_Winter, c D10.02.06_Linnéa, d D11.02.06_Petra.
charge reversal effects. Charge reversal is a phenomenon peculiar when charge neutralization is the main coagulation mechanism, and the excess coagulant dosage is applied (Bratby, 2016). This portrays the importance of the cationic charge of the tannin coagulants in the destabilization of colloids in the water of interest. Fig. 4b shows TSC as a function of dosage for the tested tannin coagulants. The dosage curve revealed that the total surface charge of the treated water samples by all coagulants became less negative as the increase of coagulant dosage. Once turbidity reached a minimum level (~20 mg/l), TSC values were still negative, indicating the presence of some anionic compounds of model water. Between 40 to 60 mg/l dosages, TSC was close to zero and then clearly positive when tannin coagulants were overdosed.

As seen in Fig. 4c, UV254 absorbance slightly decreased around the optimal dosage for turbidity reduction (~20 mg/l) but increased along with the adding of the excess coagulant. A critical elucidation of the plot showed a 20% reduction in the UV254 absorbance at the optimal dosage, while the increase at higher dosages (>50 mg/l) indicates the loading of organic compounds by the coagulants (Korshin et al., 2009). DOC also

Table 2
Chemical characteristics of the crude extracts using 1H NMR, GC-FID, and XPS. The reported aromatic and sugars are summarized based on the overall identified ones (Dou et al., 2022a). XPS results from the C 1 s region show the relative amounts of the different components of carbon (as atomic %), as compared to the total amount of carbon in the samples. For detailed elemental composition of crude extracts, see Table S3.

<table>
<thead>
<tr>
<th>Tannin Sample</th>
<th>Total proanthocyanidins mg/g</th>
<th>GC-FID mg/g</th>
<th>XPS (C 1 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Catechin-based PC</td>
<td>Gallocatechin-based PD</td>
<td>PC+PD</td>
</tr>
<tr>
<td>D1_12_04_Klara</td>
<td>209</td>
<td>45</td>
<td>253</td>
</tr>
<tr>
<td>D3_10_17_Myrsinifolia</td>
<td>53</td>
<td>12</td>
<td>65</td>
</tr>
<tr>
<td>D4_10_17_Schweini</td>
<td>186</td>
<td>44</td>
<td>230</td>
</tr>
<tr>
<td>D7_12_04_Winter</td>
<td>189</td>
<td>60</td>
<td>249</td>
</tr>
<tr>
<td>D9_02_06_Lisa</td>
<td>274</td>
<td>72</td>
<td>347</td>
</tr>
<tr>
<td>D10_02_06_Linnea</td>
<td>277</td>
<td>80</td>
<td>357</td>
</tr>
<tr>
<td>D11_02_06_Petra</td>
<td>185</td>
<td>64</td>
<td>250</td>
</tr>
<tr>
<td>D12_02_06_Ferna</td>
<td>356</td>
<td>105</td>
<td>461</td>
</tr>
</tbody>
</table>
increased in the treated water samples as the dosage increased but plateaued at approximately 50 mg/l for the tested willow coagulants (Fig. S12). UV$_{254}$ absorbance and DOC provide the information about the dissolved organic matter in water samples (Bratby, 2016). Previous studies have reported similar low effectiveness of tannin-based coagulants in the reduction of dissolved organic matter (Bello et al., 2020; Fang, 2007). However, it is essential to note that the performance of tannin coagulants has been reported to vary distinctively based on the characteristics of the effluent of interest (Bello and Leiviskä, 2022). The trends for dosage curves in Fig. 4d show that all tested coagulants produced similar SUVA value pattern. The results show that the raw water possessed an initial SUVA value of 3.3 l/mg-m, which indicates the presence of the aquatic humics and possibly a mixture of the organic matter fractions (Parsons et al., 2004). The reduction in the SUVA value to less than 2 l/mg-m at the optimal dosage for residual turbidity range implies that the water samples were composed mainly of non-humic and hydrophilic organic matter constituents after treatment (Edzwald and Van Benschoten, 1990). This trend was in close agreement with previous studies when tannin coagulants were used to treat river waters spiked with kaolin clay (Bello et al., 2020; Fang, 2007). High SUVA values at the extreme coagulants’ dosages were due to the increased UV$_{254}$ absorbance. Also, it is important to mention that the pH of the treated water was not significantly affected by the application of the tannin coagulants at the optimal dosage for turbidity reduction, as it reduced only to about 6.5 from an initial pH of 7.5 (Fig. S13). The low effect on the pH of the treated water samples showcases one of the main advantages of tannin coagulants over conventional metal salts.

Al and Fe salts are the most traditionally used coagulants, and several studies have highlighted in detail the detrimental effects of these chemical coagulants on human health and the environment (Flaten, 2001; Haarhoff and Cleasby, 1988; Yin, 2010). Thus, a viable replacement for chemical coagulants is of great interest and has been largely reported. This study demonstrates that willow tannin coagulant could replace conventional chemical coagulants in treating some effluents with positive charge demand. Willow production in southern Sweden is reported up to be as high as 30 tons/hectare and an average annual production of 17,000 ha (Rosenqvist et al., 2000) has been reported in the entire Sweden from 1991 to 1996, indicating approximately 0.1 million tons of produced willow bark is used solely for energy historically. The coagulation experiments with kaolin-river water mixture suggested that all the selected four willow hybrids’ tannin coagulants were effective in settling the particles down from river water. The upgradeable utilization of crude extracts as biocoagulants could substantially increase the value of willow bark. If both the high/ small Mw extractive fractions can be utilized together with the fiber from the willow bark, the value of willow bark is likely to be comparable to that of willow wood. This finding opens many prospects for the forest industry to rethink the usage of bark in a wiser way to gain greater revenue potential and to reduce its carbon footprint.

4. Conclusion

The viability of tannin-based coagulants to replace chemical coagulants in some water treatment applications has gathered continual attention from various stakeholders in various quarters. This is because it provides an upgrading usage of crude tannin extracts and promotes a more sustainable path for the treatment of water. Our study has shown that tannins from bark of different willow hybrids can be cationized through the Mannich reaction to produce effective tannin-based coagulants. The chemistry of the willow proanthocyanidin has been
Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2023.117962.

References


