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Research article

Removal of cobalt and copper from aqueous solutions with sulfonated fruit waste

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Abstract: In this study, orange peel waste was successfully sulfonated with SO_3-pyridine complex in 1-allyl-3-methylimidazolium chloride ionic liquid in various reaction conditions. ^1H NMR was used to verify the occurrence of the reaction and to select the most promising material for the adsorption experiments. The degree of substitution of the sulfonated orange peel waste used for cobalt and copper removal was found to be 0.82. It was prepared with the reaction temperature and time of 70 °C and 60 min respectively and with the SO_3-pyridine complex to-peel waste ratio of 5:1. The selected material combined with ultrafiltration removed 98% of copper and 91% of cobalt from single metal solutions and 93% of copper and 83% of cobalt from binary metal solution at pH 5 with adsorbent dosage of 12.5 mg/100 mL and initial metal concentration of 8 mg/L. Preliminary experiments were also performed with apple pomace which was sulfonated in the conditions found best for the orange peel waste. The prepared sulfonated apple pomace proved to be almost as effective in cobalt and copper removal as sulfonated orange peel waste, removing 82% of copper and 77% of cobalt from binary metal solution with 12.5 mg/100 mL dosage at pH 5 and an initial metal concentration of 8 mg/L.

Keywords: fruit waste; sulfonation; copper; cobalt; ultrafiltration; metal binding; biomass; SO_3-pyridine complex

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Abbreviations: OP: Orange peel waste; AP: Apple pomace; UF: Ultrafiltration

1. Introduction

Heavy metals are the most common contaminants found in water. They can cause severe health effects even at low concentrations due to their accumulation in living organisms, and severely interfere within the aquatic ecosystem. Toxic heavy metals can be present in water bodies due to natural causes or human actions, e.g., industrial activity and mining. Thus, effluents produced at the industry level must be treated before releasing wastewater to the natural water bodies [1,2].

There is a wide range of different methods for heavy metal removal [3]. Methods such as coagulation and chemical precipitation are simple and inexpensive but generate large volumes of sludge which needs to be disposed of or processed further. In addition, precipitation requires neutral to basic pH. Thus, it cannot be utilized in every case. Precipitation is also ineffective for low metal concentrations (1–100 mg/L) [4,5]. Ion exchange, in turn, is a fast and effective process and can be carried out as batch or continuous flow process, but fouling due to the organic matter can cause challenges in the process. Also, treating large volumes of water requires large ion exchange columns [4]. Adsorption is a simple method with fast kinetics and can be applied for a wide range of contaminants [3]. Carbon-based adsorbents like activated carbons are widely used for heavy metal removal due to their high surface area and uptake capacity but can be expensive. Also, uptake capacity of activated carbon adsorbents depends on the pore size distribution and functional groups on the surface [3,4].

Lignocellulosic biomass is an inexpensive and abundant raw material, which can be used for heavy metal removal [6] or modified via surface functional groups e.g., by sulfonation to enhance binding efficiency [7]. Sulfonation increases the amount of negatively charged binding sites on the surface of the biomass which improves binding of cationic species such as heavy metal ions from aqueous solutions [8]. However, lignocellulose is poorly soluble in water and common organic solvents. Therefore, sulfonation reactions have been carried out in solvents like dimethyl sulfoxide, pyridine or toluene, which have undesired properties like carcinogenicity [9].

Ionic liquids are considered as green alternatives for organic solvents. They are practically nonvolatile and nonflammable and have good thermal and chemical stability. They can also dissolve well organic and inorganic compounds, such as natural polymers [10]. Dissolving biomass in the reaction medium prior to the modification enhances reaction efficiency and even distribution of the attached groups [8,9]. Sulfonation with SO_3-pyridine complex has been studied previously e.g., with starch, cellulose and pectin and it has shown high reactivity but has not been used for more heterogeneous biomass waste materials such as fruit waste [9,11–13].

Fruit waste, such as orange peel waste (OP) and apple pomace (AP), is generated in large amounts globally every year. According to food and agricultural organization (FAO) the global production of orange and apple in 2020 was 75 and 86 million tons, respectively [14]. From produced orange approximately 50%–60% is lost as waste, mainly peels [15]. AP generated from apple processing (juicing etc.) is 20%–35% of the fresh apple weight [16]. The produced peels and pomace are mainly discarded as waste, which causes pollution of the environment and is a waste of resources. Fruit wastes contain typically significant amount of holocellulose, which is rich in hydroxyl groups [17]. Hence, fruit waste is a suitable raw material for sulfonation where SO_3-groups are attached to those hydroxyl groups. During work-up the sulfated product can be precipitated as sodium salt with cold ethanol [9,13,18]. Sulfonation reaction with SO_3-pyridine complex and formation of sodium salt is described in Figure 1.

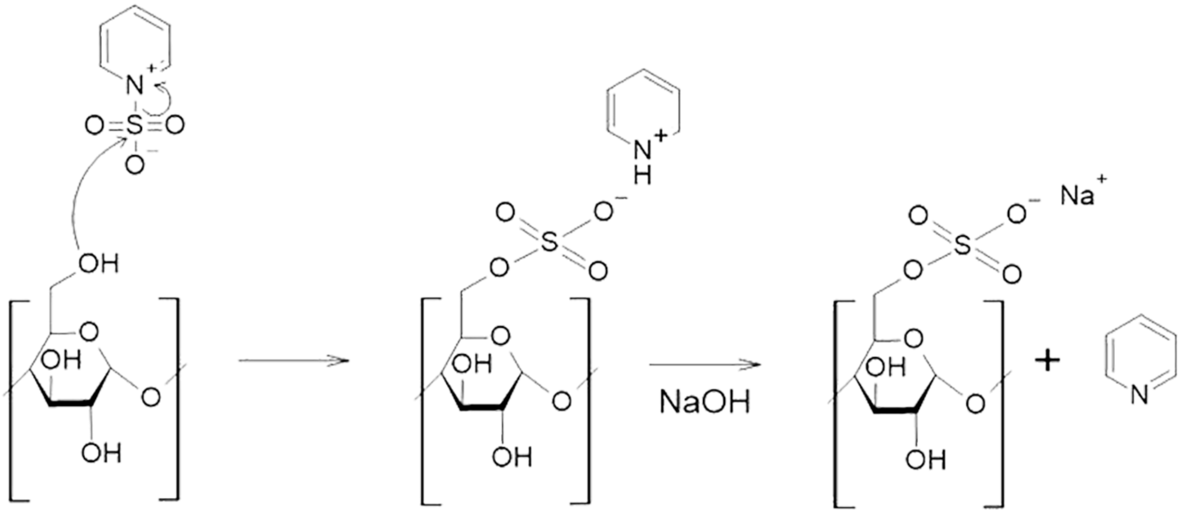

Figure 1. Sulfonation of anhydroglucose unit of holocellulose with SO_3-pyridine complex and formation of sodium salt.

In this study, OP and AP were sulfonated with SO_3-pyridine complex in ionic liquid, 1-allyl-3-methylimidazolium chloride [AMIM]Cl. The occurrence of the sulfonation reaction was verified with ^1H NMR analysis by monitoring a signal at 4.94 ppm. The intensity of the signal increased with increasing amount of SO_3-pyridine complex and reaction temperature. Therefore, the product which spectrum had the highest signal at 4.94 ppm was considered as the most promising material and was selected for the cobalt and copper removal experiments performed with sulfonated fruit waste enhanced ultrafiltration. Based on the ICP-OES analyses, both studied materials bound cobalt and copper well, both from a single metal solution and from a binary metal solution. To our knowledge, sulfonation of OP or AP or the use of similarly prepared sulfonation products has not been studied before.

2. Materials and methods

2.1. Materials

OP was obtained from Finnish grocery store (Prisma, Oulu, Finland) and AP from local juicing facility (Marjarannikko, Tupos, Finland). Materials were stored in a freezer. Before use, flavedo, i.e., the orange surface layer of the peel, was removed and only albedo was used in the study. OP and AP were dried until constant weight in the oven at 45 °C and then ground to a fine powder with a coffee grinder. The moisture content of OP (79.4%) and AP (82.3%) was determined by calculating mass loss during drying. Dried and ground biomasses were extracted by Soxhlet extraction for 4 h with acetone (anhydrous, BDH chemicals). After the extraction, powders were dried again at 45 °C until constant weight. Dried powders were stored in a desiccator. The mass% of extractives of OP (10.5%) and AP (15.6%) were determined gravimetrically by calculating mass loss due to extraction.

An estimate of the composition of dry OP and AP was obtained using known methods [19]. The ash content determination was made for unextracted OP and AP but for other determinations extracted biomass was used. All analyses were performed in duplicate.

Other reagents used in the study were allyl chloride (99%, Sigma Aldrich), 1-methylimidazole (≥99%, Sigma Aldrich), ethyl acetate (≥99.7%, Honeywell), DMF (99.8%, Labscan), SO_3-pyridine complex (98%, Sigma Aldrich), ethanol (96%, BDH chemicals), NaOH (>95%, FF-Chemicals), NaCl (99.5%, Merck), cobalt chloride hexahydrate (≥98%, Riedel de Haën), copper sulphate pentahydrate (≥99%, Merck) and anhydrous sodium sulphate (≥99%, Sigma Aldrich). Elix water was used for preparation of aqueous solutions. Unless otherwise mentioned, all chemicals were used as received.

2.2. Preparation of 1-allyl-3-methylimidazolium chloride

[AMIM]Cl was prepared using a previously described method [20] from allyl chloride and 1-methylimidazole which was distilled prior to use. The molar ratio of allyl chloride and 1-methylimidazole was 1:1.3. The reaction was carried out in a round bottom flask under argon with continuous stirring. Allyl chloride was added slowly to cooled 1-methylimidazole while keeping temperature under 10 °C using ice/salt bath. After the addition, the reaction mixture was allowed to warm to room temperature prior to heating to 55 °C in an oil bath. The reaction was allowed to proceed for 12 hours while keeping the temperature constant. After the reaction, the crude [AMIM]Cl was purified by extracting it five times with ethyl acetate. Traces of water and ethyl acetate were removed by evaporation in a high vacuum. The dark brown colored and highly viscous [AMIM]Cl was stored under argon gas in desiccator.

2.3. Preparation of sulfonated fruit waste

Sulfonation was based on a method previously described by Kärkkäinen et al. [9]. OP (0.125 g) and [AMIM]Cl (2.5 g) were mixed in a microwave reactor tube (size 2–5 mL) equipped with a magnetic stirring bar. The mixture was heated in a microwave reactor (Biotage initiator) at 80 °C for 20 min. After the pretreatment 1 mL of DMF was added to the mixture to reduce the viscosity, and the mixture was transferred to a round bottom flask (25 mL) equipped with a magnetic stirring bar. The sulfonation reaction was started by mixing the SO_3-pyridine complex to the reaction mixture. The amount of the complex was such that the molar ratio of SO_3-pyridine complex to the anhydroglucose unit (AGU) was 1.5:1, 3.35:1 or 5:1. The reaction mixture was heated in an oil bath at 30, 50 or 70 °C for 60, 90 or 120 min. After the reaction, the mixture was allowed to cool to room temperature and 8 mL of water was added rapidly while stirring. NaOH (1 M) was added with molar ratio of 1.6:1 to SO_3-pyridine complex. The mixture was stirred for 5 min at room temperature. The crude product was precipitated by adding 50 mL of cold ethanol and allowing to set for 1 h. Light colored precipitate was filtrated with nylon membrane (Whatman 0.45 µm, 47 mm). The isolated crude product was purified from organic impurities by dissolving it in 15 mL of 2% NaCl and precipitating again with 50 mL of cold ethanol. The mixture was allowed to set for 30 min and filtrated again. Dissolving to NaCl, precipitation with cold ethanol, settling and filtration were repeated, and the product was dried at 45 °C until constant weight.

Sulfonated AP was prepared similarly at selected reaction conditions (reaction time 60 min, reaction temperature 70 °C, molar ratio of SO_3-pyridine complex to AGU 5:1).

2.4. Removal of salt from sulfonated fruit waste by ultrafiltration

The prepared sulfonated OP and AP were treated with ultrafiltration (Millipore Amican 8400) to remove the Na_2SO_4 salt. 1 g of OP or AP was mixed with 300 mL of water in an ultrafiltration cell, and the mixture was filtrated through regenerated cellulose membrane (Millipore Ultracel with 3 kDa cut-off weight). The pressure (3 kPa) was generated using nitrogen gas and kept constant during the filtration. Filtration was stopped when 200 mL was filtrated. Washing was carried out by adding 100 mL of water into the cell and filtration was continued until 100 mL was filtrated. The washing step was repeated five times. After the ultrafiltration, the remaining 100 mL was transferred from the cell to the round bottom flask and the filtration system was rinsed with 50 mL of water. Rinsing water was combined with the remaining 100 mL. Excess water was evaporated until the total volume was 10–30 mL. The product was precipitated with 5-fold amount of cold ethanol. The precipitated product was isolated by vacuum filtration using nylon membrane as described above and dried at 45 °C until constant weight.

Decrease of salt in ultrafiltration cell was monitored by collecting samples during the ultrafiltration and analyzing them with ICP-OES.

2.5. Removal of heavy metals with sulfonated fruit waste enhanced ultrafiltration

Cobalt and copper solutions (8 and 6 mg/L, respectively) used in metal removal experiments were prepared from stock solutions (80 mg/L). Unmodified OP and AP were used as reference materials. In 100 mL of 8 mg/L cobalt solution, 25, 12.5 or 6 mg of modified or unmodified biomass was weighted. In 6 mg/L Cu-solution 6 mg of biomass was weighted. Experiments were carried out in pH 4 and 5. pH was adjusted with 0.1 M HCl. Contact time was 35 min due to the experimental setup even though the adsorption itself has been studied to be rapid [21]. Cobalt solution without any adsorbent was also filtrated to evaluate the effect of the membrane itself on the cobalt concentration. Samples were collected by ultrafiltrating 20 mL from the mixture. The membrane was washed between each experiment by rinsing with water and filtrating 20 mL of water through the membrane. All metal removal experiments were done in duplicate and results are reported as an average of those parallel experiments.

2.6. Analytical methods

[AMIM]Cl, sulfonated OP and unmodified and pretreated OP were characterized with ^{1}H NMR (Bruker Avance 400) in room temperature. [AMIM]Cl was dissolved in $CDCl_3$ and peel materials in D_2O. Spectra were processed with ACDLabs Spectrus Processor.

Thermo Elemental Flash 2000 CHNS/O Analyzer was used for the determination of the degree of substitution (DS). DS was calculated using Eq 1 [22]:

$$DS = (162.1 \times S\%)/(3207 - 102.2 \times S\%) \tag{1}$$

where S% is sulfur mass percentage of sulfonated and purified OP determined with elemental analysis. Standard error of the mean (SEM) was calculated using Eq 2 [23]:

$$SEM = \sqrt{((\sum(x_i - \bar{x})^2)/(n(n - 1)))} \tag{2}$$

where x_i is DS value based on single measurement of sulfur content, $\bar{x}$ is the mean value for DS based on three replicate measurements of sulfur content and n is number of measurements.

Samples collected from ultrafiltration and metal removal experiments were analyzed with ICP-OES (Agilent 5110) equipped with SPS 4 autosampler, concentric nebulizer and cyclonic spray chamber. Each sample was measured in triplicate at three different wavelengths. Selected wavelengths were 568.821, 588.995 and 589.592 nm; 238.892, 228.615 and 230.786 nm and 327.395, 324.745 and 213.598 nm for sodium, cobalt and copper, respectively. Automatic background correction was used, and argon gas was used in all gas flows. Measuring parameters were: vertical dual view, measuring time 5 s, plasma power 1.2 kW, stabilization time 25/20 s, pump speed 12 rpm, plasma gas flow rate 12 L/min, auxiliary gas flow rate 1 L/min, viewing height in radial measurements 8 mm.

3. Results and discussion

OP and AP were subjected to compositional analysis before use to get an estimate of their composition. The results of the analyses are presented in Table 1. The presented lignin amounts contain both the soluble and insoluble lignin. The determined polysaccharide (holocellulose + pectin) amounts (78% for OP, 56% for AP) were used as an approximation for the amount of anhydroglucose units of studied biomasses.

Table 1. Composition of dry OP and AP used in the study.

	OP, wt%	AP, wt%
Extractives	4	28
Ash	2	2
Lignin, total	16	14
Holocellulose	27	21
α-cellulose	11	12
Hemicellulose[a]	16	9
Other (mainly pectin)[b]	51	35

[a] calculated by subtracting α-cellulose from holocellulose; [b] calculated by subtracting extractives, ash, lignin and holocellulose from 100.

3.1. *Sulfonation of fruit wastes*

It was noted during the sulfonation reactions and the isolation of the product that reaction temperature and the amount of SO_3-pyridine complex had an evident impact on the reaction itself and on the obtained solid products. The viscosity of reaction mixture reduced with increasing reaction temperature and higher temperatures resulted in more efficient stirring. The homogeneity of the precipitated product increased with increasing SO_3-pyridine complex amount. With 5:1 molar ratio of the complex to anhydroglucose unit (AGU) the product was powder like and had a small particle size, while the molar ratio of 1.5:1 (complex:AGU) produced also larger flake like structures. With molar ratio of 3.25:1, the obtained product contained fine powder mixed with fiber like particles. When the product was dissolved to NaCl it was noted that the solubility increased with increasing amount of SO_3-pyridine complex and reaction temperature, which may indicate that the reactions performed in low temperatures produced products with uneven sulfate group distribution due to the inefficient stirring. In Richter's and Klemm's study cellulose sulfates were prepared homogeneously with several sulfating agents and all the products were completely water soluble [21,24]. Also, in the Qin et al. and Gericke et al., studies it was noted that cellulose sulfates with DS > 0.3–0.4 with even distribution of sulfate groups were soluble in water [11,12].

3.2. Purification of fruit wastes by ultrafiltration

According to ICP-OES measurements approximately 40%–50% of the masses of the prepared sulfonated fruit wastes was Na_2SO_4 salt. The amount of salt was cut in half during the first three washes with ultrafiltration. During the last two washes the amount of salt was reduced by two-thirds. In total, sodium concentration was reduced from 1000 mg/L to under 10 mg/L by washing. According to ICP-OES results the amount of salt in the product was so low after purification that it was not considered in biomass dosage in heavy metal removal experiments.

3.3. ^{1}H NMR analysis of sulfonated OP

All sulfonated OP products as well as unmodified and pretreated OP were analyzed with ^{1}H NMR. ^{1}H NMR was used to confirm that sulfonation reaction had occurred and to evaluate the effect of the reaction conditions on the structure and DS of polysaccharides. Unmodified OP was poorly soluble in D_2O producing a poor-quality NMR spectrum (Supplementary). Therefore, the spectrum of pretreated OP (Figure 2a) was used as the reference spectrum for the spectra of sulfonated OPs. The pretreatment of OP in ionic liquid broke the structure of OP slightly resulting in better solubility of pretreated OP than unmodified OP.

Peak broadening and overlapping were observed due to the heterogeneous nature of the raw material, which caused challenges for the interpretation of the spectra. According to the literature the signal of nanocellulose H1 is observed at 4.4 ppm and the signal of anomeric H1 at 4.4–5.8 ppm while the signals of polysaccharides' H2 and H6 can usually be observed at 3.2–4.5 ppm. According to the literature β-anomeric H1 is observed more up field than α-anomeric H1 [25,26].

Signals of the sulfonated OP were broad and not clearly separated at 4–4.7 ppm (Figure 2b) which made interpretation of spectra challenging. However, a new signal was observed at 4.94 ppm which was concluded to prove that change in chemical environment of certain hydrogen had occurred due to the sulfonation (Figure 2b). The intensity of that signal increased with the increasing amount of SO_3-pyridine complex (Figure 2c). On the other hand, increasing the reaction time did not increase the intensity of the signal at 4.94 ppm. The studied signal was most likely caused by β-anomeric H1 of substituted product. Thus, it was concluded that stronger signal with corresponding shift indicated higher DS. Based on that conclusion the product from the reaction with following conditions: reaction time 60 min, reaction temperature 70 °C and the molar ratio of the SO_3-pyridine complex to AGU 5:1 was selected for the metal removal experiments. The product of the selected reaction had the most significant increase in signal intensity at 4.94 ppm. Increasing the amount of sulfating reagent to AGU has been reported by Kärkkäinen et al. and Gericke et al. to increase the DS of starch and cellulose, respectively [9,11].

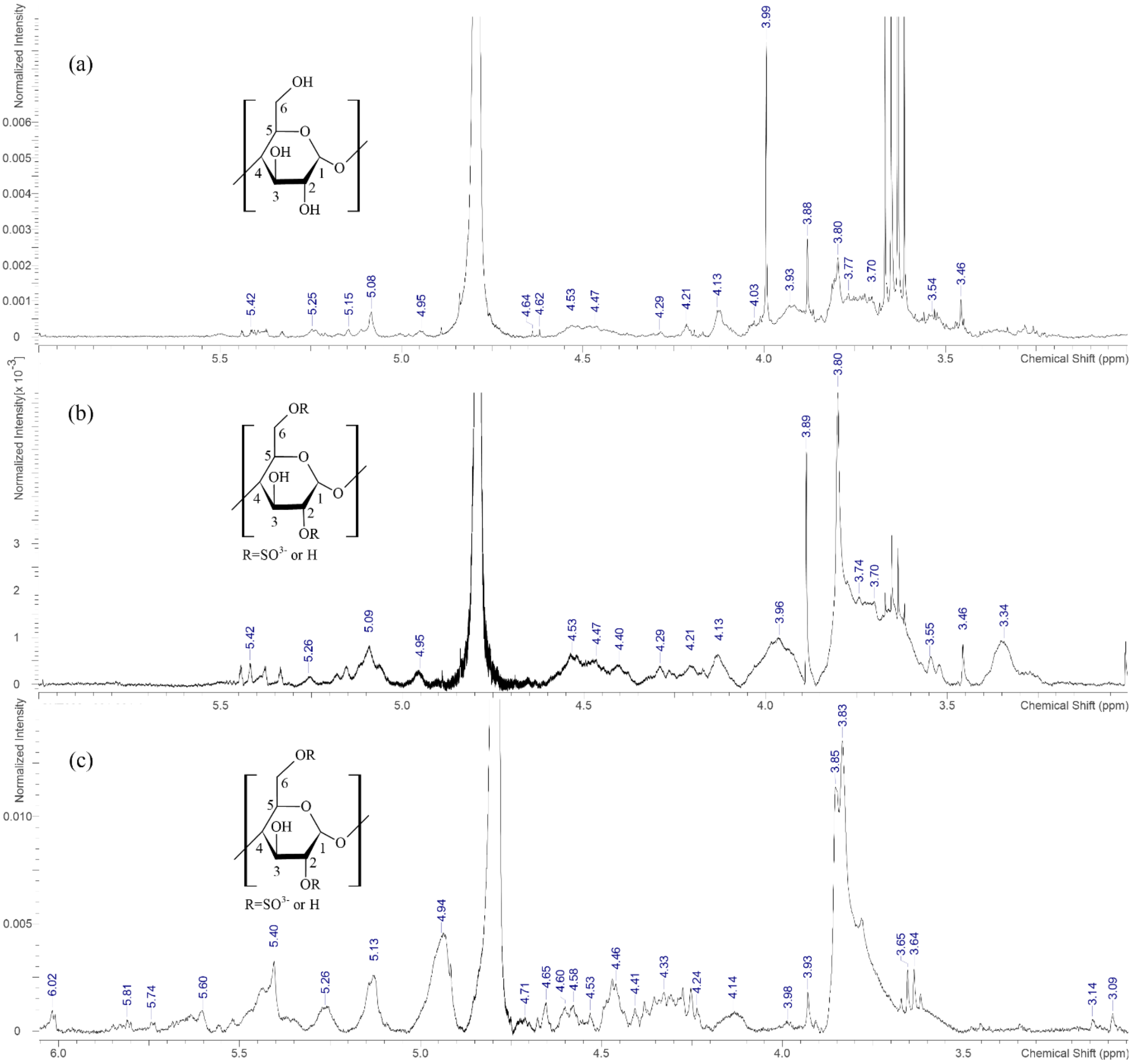

Figure 2. ^{1}H NMR spectra of (a) OP pretreated in ionic liquid, (b) sulfonated OP (reagent to AGU 1.5:1, 60 min, 70 °C), (c) sulfonated OP (reagent to AGU 5:1, 60 min, 70 °C).

Reference spectrum for sulfonated OP could not be found in the literature. However, signals corresponding to cellulose and cellulose sulfates were described by Kowsaka et al. [27]. According to their data, the substitution had occurred to the OH group at C2 position [25] even though the OH group at the primary C6 has been reported to be the most reactive site at least in starch [9]. C2 has been reported to be the second most reactive site in starch [9]. According to Kowsaka et al., the signal of H1 of C2 and C6 monosubstituted cellulose sulfate should be observed at 4.93 and 4.53 ppm, respectively. H1 of 2,6-disubstitued cellulose sulfate was also proposed to be observed at 4.93 ppm. Unsubstituted cellulose H1 was observed at 4.57 ppm [27]. Also, sulfonation agent has been reported to influence the substitution site. When trimethylsilyl cellulose was sulfonated with SO_3-pyridine complex, substitution occurred at C2 and C6 positions without clear preference on either site while SO_3-DMF preferred C6 position [24]. It must be acknowledged that in addition to cellulose, OP also contains hemicellulose and pectin which may have effect on the reactivity of different sites, and which can also undergo sulfonation making the interpretation of the NMR spectra more complex. Based on the ^{1}H NMR data, it was concluded that the sulfonation reaction had been successful when the reaction conditions were sufficient, i.e., the molar ratio of the SO_3-pyridine complex to AGU 3.25–5:1, temperature 50–70 °C and reaction time 60–90 min (^{1}H NMR spectra shown in Supplementary).

3.4. Degree of substitution of sulfonated OP

The product that was used in metal removal experiments was selected based on the ^{1}H NMR spectra (60 min, 70 °C, 5:1 for molar ratio of SO_3-pyridine complex to AGU). The DS of the selected product was determined afterwards with elemental analysis due to the complexity of the obtained NMR spectrum. According to elemental analysis, the product, which was purified from sulfate salt by ultrafiltration prior analysis, contained 0.23%, 48.18%, 20.51%, 3.03% and 10.68% of nitrogen, oxygen, carbon, hydrogen and sulfur, respectively. The calculated DS was 0.82 (SEM ± 0.087). With the used method, i.e., ionic liquid as the reaction medium and SO_3-pyridine complex as the reagent, similar DS values have been reported for barley starch and cellulose [9,11].

3.5. Removal of heavy metals with sulfonated fruit waste enhanced ultrafiltration

Metal removal was first studied with cobalt. The initial cobalt concentration was 8 mg/L, and the amount of sulfonated OP was varied (6, 12.5 or 25 mg). The pH of the metal solution was adjusted to 4 or 5 due to the precipitation of metal in neutral to alkaline pH. In pH 4 a slight but not significant decrease in binding of cobalt was observed compared to pH 5 due to the higher H^+ content in more acidic media. Thus, binding was not particularly sensitive to pH change from 5 to 4. This was also observed in the study of Dong et al. [21] They modeled the effect of pH on metal removal efficiency and found that in pH below 4 the efficiency decreased significantly due to increasing H^+ content in solutions [21].

Unmodified OP was used as a reference material to confirm that binding improved with sulfonation. In addition, cobalt solution was ultrafiltrated without any biomass to study the effect of the ultrafiltration itself. According to ICP-OES measurements, the effect of ultrafiltration or unmodified OP in binding was minor compared to the sulfonated OP. Ultrafiltration alone removed 0–11% and unmodified OP with ultrafiltration removed 2%–15% of cobalt. Sulfonated OP in turn bound over 89% of cobalt in pH 5 and 4 with 12.5 and 25 mg/100 mL dosage. Since lower dosage (12.5 mg) did not decrease the removal-% significantly, it was concluded that using dosage <25 mg makes the process more cost-effective. When sulfonated OP dosage was reduced to 6 mg/100 mL, over 60% of cobalt was still bound. The results of the cobalt removal experiments are presented in Table 2.

Table 2. Cobalt removal from initial concentration of 8 mg/L with modified or unmodified OP.

Binding method	pH	m_{peel} (mg)	Co removal-%[a]
Ultrafiltration	5	0	11
	4	0	0
Unmodified OP + UF	5	6	6
	5	12.5	2
	5	25	15
Sulfonated OP + UF	5	6	63
	5	12.5	91
	5	25	98
Sulfonated OP + UF	4	6	56
	4	12.5	89
	4	25	95

[a] SD ± 4%.

Because removal of cobalt was effective with relatively low biomass dosage, the removal of another metal, i.e., copper, was also studied. The initial copper solution concentrations of 6 and 8 mg/L were used to evaluate the effect of the initial metal concentration on the removal. The studied sulfonated OP dosages were 12.5 and 6 mg/100 mL, since it was noted earlier that <25 mg is enough for efficient metal removal. Copper removal followed a similar trend than cobalt removal. The change of pH from 5 to 4 did not have a significant effect on binding. It was observed that copper removal-% was even higher compared to cobalt removal-% despite it was noted in Dong et al., study that copper removal was poorest compared to Fe and Pb from single metal solution as well as from ternary solution [21]. In addition, Lappalainen et. al., noted that copper bound to sulfated starch was unstable compared to other studied metals (Fe, Zn, Ni) [28]. The difference between copper and cobalt binding was more notable with 6 mg than 12.5 mg dosage. With 6 mg dosage of sulfonated OP, 27% more copper was bound compared to cobalt and, with 12.5 mg dosage, the difference was 7%. It was noted that binding was slightly more efficient with higher initial metal concentration. It has been studied that higher metal concentration increases the interactions between metal ions and adsorbent increasing the adsorption capacity. However, Sirviö et al. found that the highest metal removal was achieved with low concentrations [29]. Similar behavior was observed also in the study of Dong et al., where binding of metals with sulfonated cellulose decreased with increasing metal concentration [21]. The decrease of heavy metal removal with increasing metal concentration may be due to the lack of free adsorption sites. In Dong et al., study DS of cellulose sulfate was 0.56 which is lower compared to 0.82 determined in this study for sulfonated OP. Adsorbent dose was considerably higher (50 mg) in most experiments performed by Dong et al. when considering the volume and the metal content of the solution to be treated (volume 25 mL, metal concentration 25–200 mg/L) [21]. Results of copper binding are presented in Table 3.

Table 3. Copper removal from initial concentration of 6 or 8 mg/L with modified OP or AP.

Binding method	pH	m_{peel} (mg)	$Cu_{initial}$ (mg/L)	Cu removal-%[a]
Sulfonated OP + UF	5	12.5	8	98
	5	6	6	74
	5	6	8	89
	4	12.5	8	97
	4	6	6	64
Sulfonated AP + UF	5	12.5	8	97
	5	6	6	89
	5	6	8	87
	4	12.5	8	98
	4	6	6	85

[a]SD ±6%.

Due to the effective binding of both cobalt and copper with sulfonated OP, a preliminary binding experiment was performed with another fruit waste, AP. AP was sulfonated in the same conditions which were previously found best for OP (molar ratio of SO_3-pyridine complex to AGU 1.5:1, reaction time 60 min, reaction temperature 70 °C). Sulfonated AP was tested for copper removal first. No notable difference was observed between sulfonated OP and AP when initial metal concentration was 8 mg/L. However, sulfonated AP bound 15% and 21% more copper than sulfonated OP in pH 5 and 4, respectively, when initial metal concentration was 6 mg/L (Table 3).

The results achieved with metal removal from single metal solution with sulfonated fruit wastes were promising, and therefore the binding was also studied from binary solution. The initial concentration of both metals was 8 mg/L. Since the total concentration of metals doubled compared to single metal solutions, the dose of OP and AP was increased to 12.5 mg. It was noted in single metal experiments that <25 mg dosage was clearly enough. On the other hand, 6 mg proved to be a slight underestimate for effective metal removal in part of the experiments (Tables 2 and 3). From binary metal solution copper bound more effectively than cobalt (Table 4). Also, sulfonated OP seemed to bind both metals somewhat better in both pH conditions than sulfonated AP. Despite the more efficient removal of copper, the removal-% of both metals was 70%–82% in pH 4 and 77%–93% in pH 5.

Table 4. Copper and cobalt removal from binary metal solution (8 mg/L) with 12.5 mg of modified OP or AP.

Binding method	pH	Co removal-%[a]	Cu removal-%[a]
Sulfonated OP + UF	5	83	93
	4	73	82
Sulfonated AP + UF	5	77	82
	4	70	73

[a]SD ±4%.

4. Conclusions

Sulfonation with SO_3-pyridine complex in ionic liquid was observed to be an effective way to attach SO_3-groups on the surface of powdered OP. Based on the ^1H NMR analysis the best reaction conditions for the sulfonation reaction were 60 min for reaction temperature, 70 °C for reaction time and 5:1 for SO_3-pyridine complex to AGU. The DS of the product prepared in those conditions was 0.82.

The prepared sulfonated OP with DS of 0.82, combined with ultrafiltration, was effective in removal of cobalt and copper from single metal as well as from binary metal solutions with a relatively small dosage. From the single metal solution 91% of cobalt and 98% of copper was removed when pH of the solution was 5, the initial metal concentration 8 mg/L and the dosage of the adsorbent 12.5 mg/100 mL. From binary metal solution (pH 5, 8 mg/L/metal) the removal-% were 93% and 83% for copper and cobalt, respectively, when the adsorbent dosage was 12.5 mg/100 mL.

The successful experiments performed with OP were repeated with AP. Based on the preliminary results the sulfonated AP proved to be almost as effective in cobalt and copper removal as sulfonated OP. From binary metal solution (pH 5, 8 mg/L/metal) the removal-% were 82% and 77% for copper and cobalt, respectively, when the adsorbent dosage was 12.5 mg/100 mL.

The analysis of the prepared sulfonated fruit waste proved to be challenging due to the heterogeneity of the material. Therefore, an effective and accurate method for DS determination of sulfonated fruit wastes with NMR should be studied further. Further characterization of sulfonated fruit waste is needed also for evaluating the stability of the material in different conditions (thermal, chemical). In addition, regeneration of sulfonated fruit waste should be included in future studies.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

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Conflict of interest

The authors declare no conflict of interest.

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