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Extraction and identification of polyphenols from spruce bark using HPLC-DAD-ESI-MS/MS

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MAIN CONCLUSION

The results indicated that Fe_3O_4-CA exhibits better efficiency than bare Fe_3O_4 and 1h of shaking was optimal (4h shaking degraded the original polyphenol composition, and 15 min was not efficient). MNPs show the potential in extracting viable polyphenol from bark (hot water extraction) followed by different modified Fe_3O_4 separation, and possibly continuous (cycling) processes.

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INTRODUCTION

Spruce is a widely used raw material in the pulp and paper industry where it contributes significantly to considerable amounts of biomass waste generated. As with most woody biomass used for pulp and paper, the removed bark from spruce ends up being a low-value by-product. In spruce, the bark constitutes 10-15% total weight of tree stems, is detrimental in the pulping process, as it has to be removed before processing. Once removed, the bark is generally used as an energy source. Extraction of commercially viable compounds from the bark before burning is an interesting value-added option. Bark is heterogenous both morphologically and chemically, as it contains cellulose, hemicelluloses, pectins, lignin and various extractives in different proportions. Spruce bark is a renewable source of biologically active compounds. More than 60 antioxidant compounds can be isolated from spruce bark including piceid astringin, quercetin and resveratrol [1]. These polyphenolic compounds showed anti-inflammatory, anti-microbial, anti-tumor, antioxidants and antiaging properties, and therefore, are potential ingredients for cosmetics, food and pharmaceuticals.

The present study describes the extraction of polyphenols from spruce bark using hot water extraction followed by the separation of polyphenols from the debarking water using magnetic beads through adsorption and desorption methodology. In the experimental section, the efficiency of magnetic iron oxide nanoparticles (MNPs - bare Fe_3O_4, modified Fe_3O_4), concentration and shaking time were tested.

MATERIALS & METHODS

Magnetic nanoparticles synthesis: MNPs were synthesized by coprecipitation from an aqueous solution of Fe^{2+} and Fe^{3+} salts in a two-step process. First, the pH was raised to 3 and after 30 min to pH 11 by using ammonia solution (25%). The synthesized particles were washed several times with water, collected by magnet and re-dispersed in water in a form of water-based suspension with a concentration of 10 g/L (bare Fe_3O_4). Additionally, citric acid (CA) was adsorbed on a bare Fe_3O_4 to modify their surface charge (Fe_3O_4-CA).

Bark polyphenol extraction: 500mg of samples (38 to 850 µm) were taken in 20mL of water and ultrasonicated at 80°C for 30min followed by filtration. Different concentrations (0.5, 2.5 g/L) of Fe_3O_4 and Fe_3O_4-CA were added into the filtrate at different shaking times (15min, 1h and 4h). Then, MNPs were collected by a magnet and debarking water was then separated and analyzed; 5mL of methanol was added to the collected MNPs shaked and the separated methanol was analyzed.

RESULTS & DISCUSSION

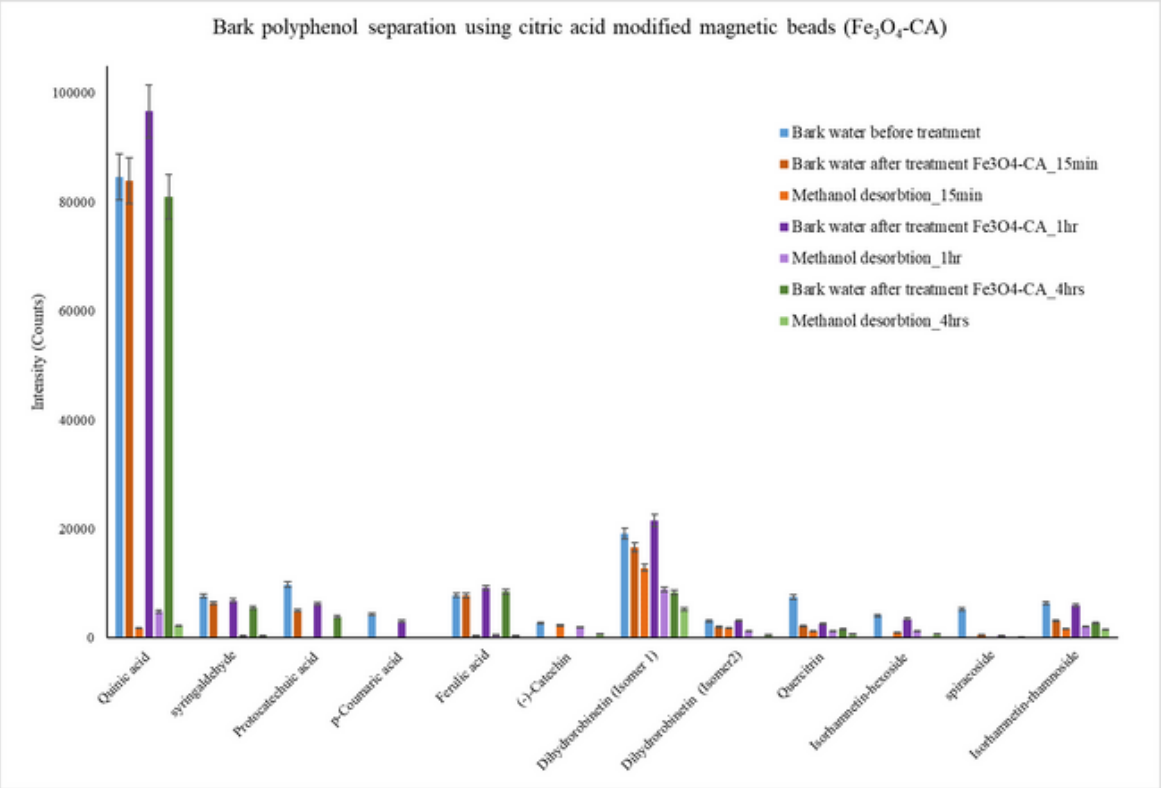

Figure1. Bark polyphenol separation using citric acid modified magnetic beads (Fe3O4-CA).

Identification and determination of phenolic compounds in the methanol fraction after desorption from the Fe_3O_4 and Fe_3O_4-CA were analyzed using LCMS-QTOF MS/MS. Based on the fragmentation pattern reported in the literature [2], quinic acid, syringaldehyde, p-coumaric acid, ferulic acid, dihydrorobinetin, isorhamnetin-hexoside, and spiraeoside were identified with Fe_3O_4.

The efficiency of Fe_3O_4 and Fe_3O_4-CA with different shaking time (15min, 1h, and 4h) was tested and the results for Fe_3O_4-CA (2.5 g/L) is presented in Fig.1, where individual polyphenol concentrations are shown for bark water before and after Fe_3O_4-CA treatment, and in methanol desorption samples. The results demonstrated that 15min shaking time is not sufficient to separate the polyphenols from the debarking water, whereas 4 h of shaking time degraded the polyphenols, as exhibited by the lower MS intensity counts. On the other hand, 1 h shaking time showed a better result compared to either 15 min or 4 h. Further experiments were also carried out with different Fe_3O_4-CA concentrations (0.5 and 2.5g/L) and the results indicated that an increase in Fe_3O_4-CA concentration enhances the extraction yield of polyphenols.

Therefore, the efficiency of bare Fe_3O_4 and Fe_3O_4-CA for polyphenols separation was compared at the higher concentration (2.5 g/L &1 h). Fe_3O_4-CA extract contains additional polyphenols such as catechin, quercitrin, and isorhamnetin-rhamnoside. No such compounds can be found with bare Fe_3O_4 extraction. However, comparing the methanol desorption results with the debarking water before and after magnetic nanoparticles (Fe_3O_4 and Fe_3O_4-CA), it is evident that only a small quantity of the polyphenols was removed. Therefore, the follow-up investigation will focus on either increasing the concentration of Fe_3O_4-CA, different modification methods for Fe_3O_4, or the possibility of several MNP extraction cycles.

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