ADVANCES IN RECOVERY OF HIGH-ADDED VALUE COMPOUNDS FROM ACID SULPHITE PULP PRODUCTION STREAMS

Dmitry D. Evtyugin,[1] António Prates,[2] Dmitry V. Evtuguin[1*]

[1] CICECO-Aveiro Institute of Materials, Department of Chemistry,
University of Aveiro, 3810-193 Aveiro, Portugal
[2] CAIMA S.A., 2250-058 Constância, Portugal
*Dmitrye@ua.pt

ABSTRACT

Acid sulphite pulping of *Eucalyptus globulus* wood provides high quality dissolving pulps widely used for production of rayon fibers and as a raw material for cellulose derivatives. Recent analyses of industrials streams (e.g., pulping liquor and bleaching effluents) from acid sulphite process revealed that they contain noticeable amounts of valuable biologically active substances, such as ellagic acid (EA) and β-sitosterol (BS). EA and BS have multiple applications in food and pharmaceutical industries, biomedicine, cosmeceutics and various technical areas. Lack of high purity large-scale production of ellagic acid and -sitosterol hampers their entry into the market. This study aimed to develop a competitive and industrially viable approach for the isolation of high purity ellagic acid and β-sitosterol from acid sulphite pulping streams. EA was found in highest concentration in the spent pulping liquor and in the alkaline extract from sulphite pulp purification step. EA was recovered from sulphite pulping streams via selective crystallization from acidified sulphite spent liquor under optimized conditions (temperature and time of holding in a container of appropriate surface-to-volume ratio) without using any organic solvents. The obtained crystals (yield of 0.25 to 0.44 g/L) were washed with acidified water to reduce contaminants and increased EA purity from *ca*. 55-70% (w/w) to *ca*. 85-95% (w/w). The obtained EA was exhaustively characterized by liquid and solid-state carbon nuclear magnetic resonance spectroscopy, mass spectrometry and wide-angle X-ray scattering. The purity and the content ofregulated metals in food and cosmetic applications, primarily As (< 0.8 mg/kg), Pb (<10 mg/kg), Cd (<0.03 mg/kg) and Hg (<0.05 mg/kg) were within acceptable levels. BS and its derivatives were detected in highest concentrations in the alkaline extract from sulphite pulp purification step. BS was recovered by two-step acidification at pH 5 and pH 3 under pre-selected conditions, followed by fractionation of the formed precipitate with water-miscible organic solvents, having obtained best results (>90% of BS purity; yield of 70-210 mg/L) with methanol fractionation followed by BS crystallization induced via water addition (*ca*. 10% vol.). When ethanol was used instead, BS was detected in minor quantities in the isolate, being fatty acid sterol esters and fatty acid glycerides the major constituents. It should be highlighted that after the isolation of EA and BS from industrial streams, the latter can be reintroduced into the conventional industrial process for energy and reagent recovery, thus creating no additional environmental impact. Both isolation methods are adaptable to large-scale industrial production of EA and BS. Considering an optimized process with presented yields, the eventual profits from EA and BS production, within existing market prices, can exceed the revenue from dissolving pulp production.

Keywords: Acid sulphite pulp, *Eucalyptus globulus*, Ellagic acid, β-sitosterol,