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Hydrothermal extraction, separation and purification of hemicelluloses from residual biomass

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PURPOSE OF THE ABSTRACT

Introduction

The abundance of hemicellulose in residual biomass has made it an interesting material due to its good properties as biodegradability, biocompatibility and bioactivity. Its industrial applications are different depending on their molecular weight (MW): monomerics are used as sugars, chemicals and energy; oligomerics as feed and pharmaceutical additives; and polymerics in food packaging, hydrogels, and thermoplastics.

Methodology

Spent coffee and dry leaves were selected as residual biomass in this work.

Autohydrolysis at 140ºC was carried out in a flow-through pilot reactor of 2 L volume with a constant water flow rate of 10 L·h-1.

Autohydrolysis liquors were first pre-filtered (10 µm) and then multi-step ultrafiltration (UF) was carried out with 3 Pellicon XL Biomax polymeric membranes (Millipore, Bedford, MA) in cascade, with molecular weight cut-offs of 30, 10 and 5 kDa, and a filtration area of 50 cm2. To purify the retained hemicelluloses, the retentates were subjected to a discontinuous diafiltration (DF) process with both Milli-Q water and water from DF of previous membranes in the cascade. Transmembrane pressure (TMP) was maintained in the range 1.5-2 bar, feed volume reduction was 80% and feed flow was in the range 0.8-1 ml·min-1cm-2.

Composition analysis was done by High Performance Liquid Chromatography (HPLC). Molecular size characterization was carried out by Size Exclusion Chromatography (HPLC-SEC) using a GPC column.

Results

1. Yield of extraction

Extraction yield was determined by dividing the mass of hemicelluloses extracted by the total amount of carbohydrates in the raw material. The accumulated yield evolved linearly over time in both biomasses reaching a maximum of 40.0% (w/w) in dry leaves and 8.2% (w/w) in spent coffee. This difference may be due to: (1) the spent coffee oil, not completely removed before autohydrolysis; (2) spent coffee would require a higher temperature than the one used in the brewing process of coffee; and (3), the particular morphology of dry leaves, with the cell wall very exposed which facilitates the penetration of water into the structure.

2. MW distribution of hemicelluloses extracted

Fig. 1 shows that hemicellulose global concentration at the outlet of the reactor was decreasing with time for both spent coffee and dry leaves. In the case of spent coffee, after 40 min the concentration of high molecular weight hemicelluloses was strongly decreased, especially the >30 kDa group which was completely lost. In the case of dry leaves, the decrease in hemicellulose global concentration with time was lower than in the spent coffee extract. After 40 min, high molecular weight hemicelluloses from dry leaves continued to be extracted without appreciable autohydrolysis.

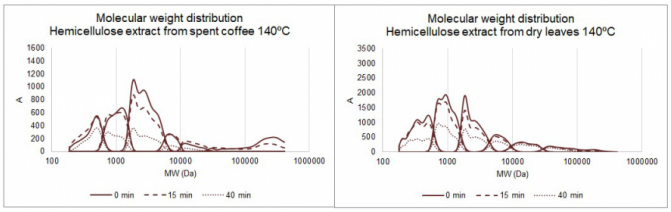
3. Separation and purification of hemicelluloses by UF/DF

Purity, defined as hemicellulose concentration over total HPLC detected compounds, was considerably improved after DF (Fig. 2). The purities of the three DF products in spent coffee were 96.64, 94.20 and 83.71 % (w/w), while for dry leaves they were 85.82, 80.85 and 80.42 % (w/w). DF caused also an enrichment in hemicelluloses of higher molecular weight, as it can be seen in the values of MW of the products before and after applying diafiltration. Certain hemicelluloses in dry leaves were clearly recovered after DF in the 10 kDa membrane, which was thanks to the reuse of the DF water from the 30 kDa membrane.

4. MW of the UF/DF products

The UF/DF experiments allowed obtaining products with different molecular weight distribution. From spent coffee, Ret-30kDa-DF contained mainly hemicelluloses >30 kDa (27.9% w/w). The other 2 retentates were majority in oligomers (40.2 and 53.1%, w/w). In the case of dry leaves, Ret-30 kDa-DF was composed mainly for hemicelluloses 1.6-5 kDa (25.2 % w/w) meanwhile, Ret-10 kDa-DF and Ret-5 kDa-DF were predominant in oligomers (35.0 and 40.5 %w/w).

FIGURES



	Spent coffee				Dry leaves			
	Hemicelluloses (ppm)	Byproducts (ppm)	Purity (% w/w)	MW (Da)	Hemicelluloses (ppm)	Byproducts (ppm)	Purity (% w/w)	MW (Da)
Feed	358.06	117.97	75.22	12762.55	349.6	423.75	45.21	3497.93
Ret-30 kDa	457.37	225.67	66.96	34657.34	810.14	422.46	65.73	17496.43
Ret-30 kDa DF	382.71	13.29	96.64	49063.09	709.76	117.31	85.82	22671.83
Ret-10 kDa	390.24	57.51	87.16	2029.34	45.7	115.79	28.30	1560.28
Ret-10 kDa DF	341.72	21.04	94.20	4157.84	209.78	49.68	80.85	5342.53
Ret-5 kDa	368.09	107.5	77.40	1563.94	324.89	273.79	54.27	1547.81
Ret-5 kDa DF	256.67	49.94	83.71	1641.09	254.49	61.96	80.42	1517.38
Perm-5 kDa	323.51	60.25	84.30	1941.13	262.73	520.32	33.55	1402.08
Mass balance error (%)	2.40%	16.13%			1.19%	4.55%		

FIGURE 1

Molecular weight distribution of hemicelluloses extracted

MW: weight-average molecular weight

FIGURE 2

Separation and purification of hemicelluloses by UF/DF

Feed: feed of the UF/DF system

Ret-30 kDa: retentate of 30 kDa membrane

Ret-30 kDa-DF: Ret-30 kDa after DF

Ret-10 kDa membrane: retentate of 10 kDa membrane

Ret-10 kDa-DF: Ret-10 kDa after DF

Ret-5 kDa membrane: retentate of 5 kDa membrane

Ret-5 kDa-DF:

KEYWORDS

hemicelluloses | residual biomass | autohydrolysis | ultrafiltration/diafiltration

BIBLIOGRAPHY