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Characterization of hemicellulosic fractions from spelt hull extracted by different methods

E. Escarnot[a,*], M. Aguedo[b], M. Paquot[b]

[a] Walloon Agricultural Research Centre, Department of Life Sciences, Breeding and Biodiversity Unit, Emile Marchal Building, Rue de Liroux, 4, 5030 Gembloux, Belgium
[b] University of Liège, Gembloux Agro-Bio Tech, Department of Industrial Biological Chemistry, Passage des Déportés, 2, 5030 Gembloux, Belgium

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ABSTRACT

Arabinoxylans (AXs) from spelt hull were extracted by three different alkaline methods and by two methods with several modalities and two organic acids. The first method enabled to extract 1.4% of the water-extractable AXs (WE-AXs) of the hull with molecular weight (MW) of 5400 g/mol and arabinose to xylose (A/X) ratio of 0.55. The two successive extractions with 2% alkaline peroxide hydrogen at 60 °C during 4 h enabled to extract 20.4% of the water-unextractable AXs (WU-AXs) of the hull. Those fractions had MWs of 6800–7800 g/mol and 227 700–274 600 g/mol and A/X ratios of 0.32 and 0.45. The second method with 2% alkaline peroxide hydrogen at 50 °C during 24 h enabled to extract 25.4% of the hemicelluloses of the hull. The two AX populations had MW of 9200–11 400 g/mol and 256 800–273 200 g/mol with an A/X ratio of 0.36. The third method with NaOH gave the highest yield, 41.9% after a 16 h extraction. A/X ratios (0.18) and MWs (two populations of 9300–9500 g/mol) were lower than those of the previous methods. Organic acids method offered insufficient yields and compounds of very low MW (1300–11 300 g/mol). Methods with alkaline peroxide hydrogen enabled to obtain high MWs and high A/X ratios with moderate yields while the NaOH method gave the highest yield efficiency with lower MWs and A/X ratios. Organic acids method did not bring any advantage neither on the yield nor on the MWs of the compounds.

1. Introduction

Spelt is a traditional cereal mainly grown in middle and Eastern Europe countries. It is an environmental-friendly crop well-known for its rusticity and its adaptation to low input cultivation. As a hulled cereal, spelt is mainly used for feeding however it is developing in "niche" markets for human food thanks to its image of "more natural, less over-bred" cereal (Schober, Bean, & Kuhn, 2006) and thanks to health peculiar properties. Spelt is recommended in the treatment of colitis ulcerosa, neurodermitis and other allergies and high blood cholesterol (Strechlow et al., 1991; Hertzka & Strechlow, 1988; Portman, 1991; all in Zielinski, Ceglinska, & Michalska, 2008). In this case, the hull is separated from the grain and returns generally for feeding with very low added value. Hull represents 21–32% of the harvest (Percival, 1921) and nowadays in Belgium in average 15 000–22 000 tons of hulls are produced per year (according to Direction générale de la Statistique et de l'Information économique, 2010).

To the best of our knowledge, composition of spelt hull is not reported in the literature, however it should not be far from the composition of the straw. Wheat straw contains 30–50% cellulose, 20–40% hemicellulose and 10–30% lignin. The main sugars from wheat straw are glucose (39.6%), xylose (24.3%), arabinose (2.1%) and galactose (0.2%) (Lequart, Nuzillard, Kurek, & Debeire, 1999).

Hemicelluloses are branched polymers of low molecular weight (MW), with general formulas $(C_5H_8O_4)_n$ and $(C_6H_{10}O_5)_n$, i.e. respectively pentosans and hexosans (Cai & Paszner, 1988). Wheat straw hemicelluloses are mainly composed of xylose, and to a lesser extent of arabinose, while glucose, galactose, mannose and rhamnose are minor sugars. The β-(1–4)-D-xylopyranose backbone is substituted at C-3 by α-L-arabinofuranose and at C-2 by α-D-glucuronic acid (mainly 4-O-methyl-D-glucuronic acid). Galactose and xylose residues are potentially linked to arabinofuranosyl branches (Sun, Lawther, & Banks, 1996). As well as glycol-proteins, pectins, waxes and ashes, the cell walls of wheat straw also contain small amounts of p-hydroxy-cinnamic acids (mainly ferulic and p-coumaric acids), esterified on arabinofuranosyl residues (Sun, Lawther, & Banks, 1995; Sun, Sun, & Zhang, 2001). All the cell wall

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Abbreviations: AE1, first alkali extract; AE1D, first alkali extract after dialysis; AE2, second alkali extract; AE2D, second alkali extract after dialysis; AX, arabinoxylan; A/X ratio, arabinose to xylose ratio; CRR, cellulose rich residue; F, filtrate; MW, molecular weight; P, precipitate; PWEM, purified water-extractable material; V, volume of ethanol for precipitation; R, residue; WE, water-extractable; WEM, water-extractable material; WU, water-unextractable; WUM, water-unextractable material.

* Corresponding author. Tel.: +32 81 62 03 36; fax: +32 81 62 03 49.
E-mail address: escarnot@cra.wallonie.be (E. Escarnot).

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constituents are closely bound, either by weak bonds such as hydrogen or Van der Waals bonds or by covalent bonds (Sun, Tomkinson, Wang, & Xioa, 2000). Xylans form hydrogen bonds with cellulose, covalent bonds with lignins, and ester linkages with acetyl units and p-hydroxycinnamic acids (Sun et al., 2000). The liberation of xylan from the cell wall of cereal straws is restricted by the presence of the lignin network and their ester or ether linkages (Xu, Liu, et al., 2006). The covalent bonds between cellulose and xylan are extremely resistant and cannot be broken even by treatment with acids (Taiz, 1984 in Heredia, Jimenez, & Guillen, 1995).

Hemicelluloses can be used to produce health food supplement. For instance, xylans from cereals contribute as dietary fibers upon some biochemical and physiological processes in human and animal organisms by lowering blood cholesterol and decreasing post-prandial glucose and insulin responses (Asp, Bjorck, & Nyman, 1993; Baghurst, Baghurst, & Record, 1996; Chesson, 1995). Besides, non-digestible arabino-xylo-oligosaccharides originating from arabinoxylans were described as prebiotics (Courtin, Swennen, Verjans, & Delcour, 2009). Polymeric hemicelluloses can be used to produce barrier films, hydrogels, paper additives (Persson, Ren, Joelsson, & Jönsson, 2009) and also adhesives, thickeners, stabilisers and emulsifiers (Doner & Hicks, 1997).

It is difficult to separate lignin from hemicelluloses and cellulose without modifying the hemicelluloses since the components of lignocellulose are tightly associated (Puls & Schuseil, 1993 in Lundqvist et al., 2002). The different ways to fractionate the hemicelluloses from lignocelluloses include physical methods such as steam treatment (Han, Deng, Zhang, Bicho, & Wu, 2010) and chemical methods such as the organosolv process (Paszner, Jeong, Quinde, & Awrdel-Karim, 1993). A traditional hypochlorite bleaching process as used in chemical pulp bleaching causes a serious environmental problem (Fang, Sun, Salisbury, Fowler, & Tomkinson, 1999). Gould (1984) demonstrated that approximately half of the lignin and most of the hemicelluloses present in wheat straw are solubilized when the material is treated at 25 °C in an alkaline solution of hydrogen peroxide. According to Sun et al. (2000), the macromolecular hemicelluloses are only solubilized and partially degraded with no monocarboxylic acid formed. Indeed, alkalis hydrolyse the ester linkages between plant polysaccharides and lignin, which increases the solubility of the hemicelluloses without reducing their MWs, provided the conditions are not too severe (Persson et al., 2009). Besides, hydrogen peroxide presents mild oxidation during the delignification process and environmental compatibility.

In the present work, spelt hull AXs were extracted by four different methods described in the literature: the first comes from Maes and Delcour (2002) on wheat bran, the second from Sun et al. (2000) on wheat straw, the third from Sun, Fang, Rowlands, and Bolton (1998) on wheat straw and the fourth from Xu, Liu, et al. (2006) also on wheat straw. The two first methods use H_2O_2 at different temperatures and times of extraction and the first includes successive extractions. They were chosen because H_2O_2 is an environmental-friendly chemical and because they were described as providing a compromise between MW and yield of extraction. The third method was performed with NaOH and KOH and included a delignification with sodium chlorite. The fourth and last method relied on organic acids to obtain high yields and to evaluate the effects of such chemicals on hull. The characteristics of AXs and their extraction yields with the different methods were compared.

2. Materials and methods

2.1. Materials

Hulls came from the spelt variety Ressac harvested in August 2007. The spikelets were hulled at “Le Moulin de Hollange” in November 2007 and hulls were stored at 4 °C until they were micronised with jet milling (Alpine 100 AFG, Augsburg, Germany) with 6–7 bars of pressure and turbine at 3000 rpm. All reagents were of analytical grade. All enzymes were a kind gift from Novozymes (Bagsvaerd, Denmark).

2.2. Methods

2.2.1. Hull deproteinisation and destarching

Micronised hulls in 0.05 M phosphate buffer pH 6.5 (ratio 1:7, w/v) were heated under continuous stirring until 75 °C and α-amylase Termamyl 120L (Novozymes, Bagsvaerd, Denmark) was added (5 μL/g hull). The suspension was then heated to 90 °C and maintained 1 h. It was then cooled down to 50 °C and Fungamyl 800L (Novozymes) was added (0.4 μL/g hull). The suspension was kept 30 min at 50 °C. Three proteases were successively added: Neutrase® 50 μL/g hull, Alcalase® 50 μL/g hull and Flavourzyme 1000L® 2 μL/g hull (all three from Novozymes). The suspension was heated during 4 h at 55 °C under continuous stirring. In order to desactivate the enzymes, the suspension was then heated at 100 °C during 15 min. The mixture was vacuum-filtered through a 20 μm nylon filter. The residue, i.e. destarched and deproteinised spelt hull or water-unextractable material (WUM), was washed several times with distilled water and dried at 50 °C in a drying oven for 24 h. The filtrate containing WE-AX was kept for the first method of extraction.

2.2.2. First method of AX extraction: two successive extractions with H_2O_2

This method was adapted from Maes and Delcour (2002) and was previously described elsewhere (Escarnot, Aguedo, Agneessens, Wathelet, & Paquot, 2011).

2.2.3. Second method of AX extraction: one extraction with H_2O_2

This method was adapted from Sun et al. (2000), however the durations of the experiment and the volumes of precipitation with ethanol were different. A solution of 2% H_2O_2 was freshly prepared and the pH was adjusted to 11.5 with NaOH 4 M. The destarched deproteinised hulls were dissolved at a ratio 1:10 (w/v). The solutions were maintained at 50 °C during 4 h, 8 h, 16 h or 24 h under slow continuous stirring. The residue was recovered by vacuum filtration through a 20 μm nylon filter, washed with distilled water until the pH of the filtrate was stable. Consequently four filtrates (F) were obtained, F4, F8, F16 and F24 which pH was neutralized. For precipitation, each filtrate was then set to pH 5.5 with 10% HCl and 3 or 4 volumes of ethanol were added and left overnight at 4 °C. On the next day, they were centrifuged (10 000 × g, 30 min, 4 °C), the ethanol was removed and the precipitates were recovered, dried under air flux and then milled (Ika A11 basic). Eight different precipitates (P) were obtained according to the duration of the experiment and the volume of precipitation with ethanol (v): P4 3v, P4 4v, P8 3v, etc. Residues (R) (R4, R8, R16 and R24) were washed with distilled water, dried at 60 °C in a drying oven for 24 h and milled (Ika A11 basic).

2.2.4. Third method of AX extraction: successive NaOH and $NaClO_2$–KOH extractions

It was from Sun et al. (1998) however times of extraction were different. Destarched deproteinised hulls were dissolved in a fresh 3% NaOH solution at a ratio 1:27 (w/v). The solution was maintained at 45 °C for 2 h, 5 h or 16 h under continuous stirring. The suspension was vacuum filtered through a 20 μm nylon filter and the pH of the supernatant was neutralized. Three filtrates were obtained F2, F5 and F16, and for precipitation their pH were set to 5.5 with 20% HCl, 3 or 4 volumes of ethanol were added and left overnight at 4 °C. On the next day, they were centrifuged (10 000 × g, 30 min, 4 °C), the ethanol was removed and the precipitates were recovered, dried under air flux and milled (Ika A11 basic). Residues were washed with distilled water, with 70% ethanol, dried at 60 °C in a drying oven for 16 h and milled (Ika A11 basic).

A solution of 1.3% $NaClO_2$ was freshly prepared and the pH was adjusted to 4 with 10% acetic acid. The previous residues were dissolved in this solution at a ratio 1:50 (w/v) and maintained at 75 °C during 2 h. Again, residues were vacuum filtered through a 20 μm nylon filter, washed with distilled water, dried at 60 °C in a drying oven for 16 h and milled (Ika A11 basic).

Then this residue was dissolved in a 10% KOH solution at a ratio 1:25 (w/v). It was left 16 h at 25 °C under continuous stirring. The solution was vacuum filtered through a 20 μm nylon filter. Filtrates F2K, F5K and F16K were neutralized. For precipitation, the filtrate was set at pH 5.5 with 20% HCl and 3 or 4 volumes of ethanol was added. The precipitates (P2K 3v, P2K 4v, P5K 3v, etc.) were left overnight at 4 °C and were centrifuged the day after (10 000 × g, 30 min, 4 °C), then the ethanol was removed and the precipitates were recovered, dried under air flux and milled (Ika A11 basic). Residues (R2, R5, R16) were washed with distilled water, dried at 60 °C in a drying oven for 24 h and milled (Ika A11 basic).

2.2.5. *Fourth method of AX extraction: acidic extractions*

This method comprises several modalities of extraction with organic acids and is based on the work of Xu, Liu, et al. (2006). Micronised destarched deproteinised hull was dissolved in 5 fresh solutions at a ratio 1:20 (w/v) of acetic acid and distilled H_2O, with proportions of 65/35, 80/20 and 90/10 and in solutions of acetic acid, formic acid and distilled H_2O with proportions of 60/20/20 and 60/30/10. 0.1% HCl was added as a catalyst and the suspension was stirred during 4 h at 85 °C. It was then filtered on a glass filter of porosity 4 (10–16 μm). The filtrate was collected and 3 volumes of ethanol were added and left 12 h at room temperature. The residue was washed with distilled water and ethanol, dried at 60 °C in a drying oven for 24 h and milled (Ika A11 basic). The precipitates were recovered by centrifugation (10 000 × g, 30 min, 4 °C), washed with 70% ethanol, dried under air flux and then milled (Ika A11 basic).

2.3. *Analyses*

Granulometry was measured in triplicate by a Mastersizer 2000 (Malvern Instruments Ltd, Worcestershire, UK).

Protein content was determined (in duplicate) by the Kjeldahl method (Kjeltec 2300, Foss) and by multiplying the N content by 5.7.

For the ashes content, samples were put at 600 °C in a muffle furnace during 5 h and were then cooled in a dessicator.

The monosaccharide analysis was based on the method of Englyst and Cummings (1984), previously described in Escarnot et al. (2011). The hydrolysis was performed during 3 h at 100 °C with TFA 2 M for solids, with TFA 0.5 M for liquids from chemical extraction and with H_2SO_4 1 M for liquids from water extraction.

Molecular weights were determined in triplicate by High Performance Size Exclusion Chromatography (HPSEC) on a Waters 2690-HPLC system (Waters Inc., Milford, MA, USA), equipped with a TSKgel GMPWxl column (300 mm × 7.8 mm) (Tosoh Co. Ltd., Tokyo, Japan) and coupled on-line with a single detector system: a Waters 2410 differential refraction index (RI) detector. Arabinoxylan solutions were filtered through a 0.45 μm membrane filter (Millipore Co., Milford, MA, USA) and 100 μL was injected in HPSEC. Elution was carried out at room temperature, at a flow rate of 0.7 mL/min with 50 mM sodium nitrate ($NaNO_3$) solution containing 0.05% sodium azide (NaN_3) as preservative. Dextrans of 1000, 5000, 12 000, 25 000, 50 000, 150 000, 270 000, 410 000, 610 000 g/mol (Fluka, Sigma–Aldrich, Buchs, Switzerland) were used to establish a calibration curve to calculate the MWs.

Table 1
Composition of the micronised hull (% dry matter) with standard deviation (SD %).

Component	% of micronised hull[a]		
Dry matter	92.7		
Proteins	7.0 ± 0.0		
Cellulose	30.2 ± 0.1		
Hemicellulose	35.5 ± 0.5		
Lignin	5.7 ± 0.1		
Arabinose	3.4 ± 0.0		
Xylose	18.1 ± 0.3		
Mannose	0.6 ± 0.0		
Glucose	18.9 ± 1.5		
Galactose	1.6 ± 0.0		
Ashes	6.1		
Starch	12.6 ± 0.6		
Total proteins + fibers + ashes + starch	97.1 ± 3.1		
	Distribution		
	d(0,1)	d(0,5)	d(0,9)
Particle size (μm)	12	109	686

[a] Granulometry.

3. Results

3.1. *Hull characterization*

Hull contained 12.6% starch coming from the dehulling, 5.7% of lignin, 30.2% of cellulose and 35.5% of hemicellulose (Table 1). The total composition of hull was close to what is reported in the literature for wheat straw (Lequart et al., 1999), however hull's contents are lower for lignin and cellulose and are higher for hemicellulose. Besides, the spelt hull is richer in non-starch polysaccharides than spelt bran. Indeed spelt bran contains 19% hemicelluloses, 2% lignin and 6% cellulose (Escarnot, Agneessens, Wathelet, & Paquot, 2010).

3.2. *Extraction by the first method: two successive extractions with H_2O_2*

The hull WE-AX fraction was poorly concentrated in AX: 12.3% and the A/X ratio was 0.55. The extraction yield (AX of the fraction/original AX of the hull) was low: 1.4%. WE-AX was composed of one population of 5.4 kDa (Table 2 and Fig. 1A).

Concerning WU-AX, EA1D (the first extraction fraction after dialysis) contained 28.6% AX with an A/X ratio of 0.45. Two AX populations were detected with MWs of 6800 and 230 000 g/mol. EA2D (the second extraction fraction after dialysis) contained 28.7% AX with an A/X ratio of 0.32. The decrease of A/X ratio between the first and the second alkali extraction was marked. Populations from this fraction had MWs of 7800 and 275 000 g/mol. WU-AX extraction yields were respectively 10.6 and 9.8% for each fraction.

3.3. *Extraction by the second method: one extraction with H_2O_2*

The composition of the liquid fractions obtained after 4 h and 8 h of extraction was similar (Table 3). AX content of the four filtrates varied between 7.3 and 10.1%. A/X ratios were 0.33 for the filtrates of 4 h and 8 h of reaction and 0.41 for the filtrates of 16 and 24 h of reaction. Short extractions resulted in a slightly higher AX content and less substituted AX. Ashes contents were very high for all filtrates: from 45 to 50% of the total material. Concerning the extraction efficiency (filtrate AX/hull AX), percentages were close for most of the filtrates, from 20.5 to 22.1% except for the filtrate from 16 h of reaction: 15.6%. MWs of the two main populations of AXs were similar for the four filtrates, i.e. 918–976 g/mol and 5100–6200 g/mol (Fig. 1B).

Concerning the precipitates, AX contents varied from 26.1 to 33.5% and A/X ratios from 0.25 to 0.42. The AX content did not

Table 2
Composition (% of dry matter) of the different fractions extracted with the first method, A/X ratios and yields of extraction.

Fraction	Hull	PWEM	WUM	AE1D	AE2D	CRR
Yield/hull	100.0	1.9	75.8	7.0	6.4	46.2
Yield/WUM	–	–	–	9.3	8.5	60.9
Ashes	6.1	6.8	6.4	7.6	6.3	9.9
Proteins	7.0 ± 0.0	18.5 ± 0.3	2.7 ± 0.1	7.6 ± 0.1	4.3 ± 0.1	0.5 ± 0.0
Total non-cellulosic sugars	42.6 ± 1.8	29.8 ± 3.4	25.1 ± 1.8	34.4 ± 0.6	33.8 ± 2.9	15.2 ± 0.8
Arabinose	3.4 ± 0.0	7.4 ± 0.6	3.6 ± 0.2	10.1 ± 0.1	7.9 ± 0.7	2.0 ± 0.1
Xylose	18.1 ± 0.3	9.0 ± 0.4	20.7 ± 1.3	22.4 ± 0.2	24.7 ± 2.1	13.1 ± 0.6
Mannose	0.6 ± 0.0	3.3 ± 0.3	0.0 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0
Glucose	18.9 ± 1.5	6.4 ± 1.3	0.2 ± 0.3	0.3 ± 0.1	0.2 ± 0.0	0.0 ± 0.0
Galactose	1.6 ± 0.0	3.5 ± 0.8	0.6 ± 0.0	1.5 ± 0.1	0.9 ± 0.1	0.1 ± 0.1
Starch	10.9 ± 0.6	0.1	0.1	–	–	–
Total	55.6 ± 2.4	55.1 ± 3.7	34.2 ± 1.9	49.6 ± 0.7	44.4 ± 3.0	25.6 ± 0.8
AX = 0.88(%ara + %xyl – 0.7%gal)	17.9	12.3	–	–	–	–
AX = 0.88(%ara + %xyl)	–	–	21.3	28.6	28.7	13.3
A/X (%ara – 0.7%gal)/%xyl	0.1	0.5	–	–	–	–
A/X	–	–	0.2	0.4	0.3	0.1
Yield[a] of extraction	–	1.4	–	10.6	9.8	32.6

[a] AX fraction/AX hull.

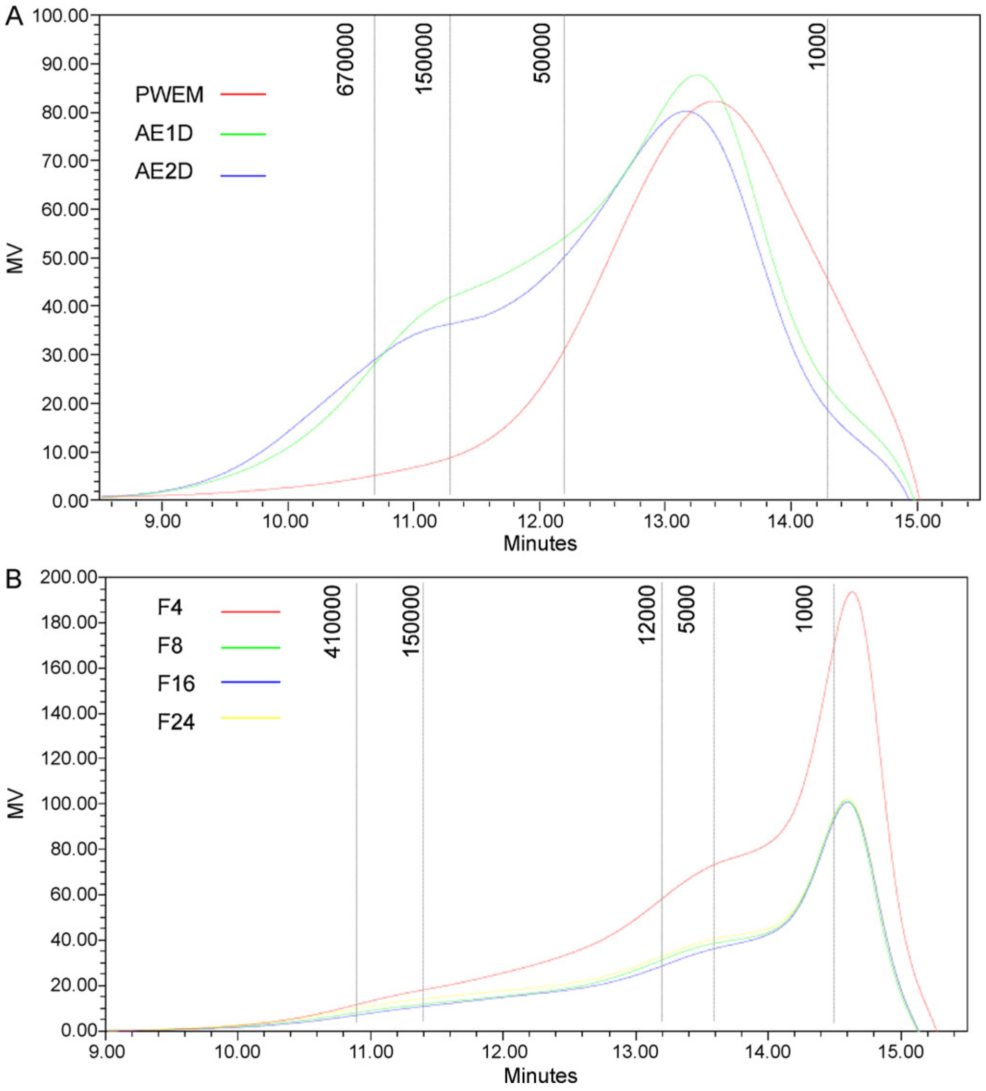


Fig. 1. HPSEC chromatographic profiles of (A) PWEM, AE1D and AE2D from the first method; (B) the four filtrates from the second method; (C) the eight precipitates from the second method; (D) the two precipitates from the third method; and (E) the five precipitates from the fourth method. Standard dextrans of MW values in g/mol are indicated in grey on the corresponding vertical lines.

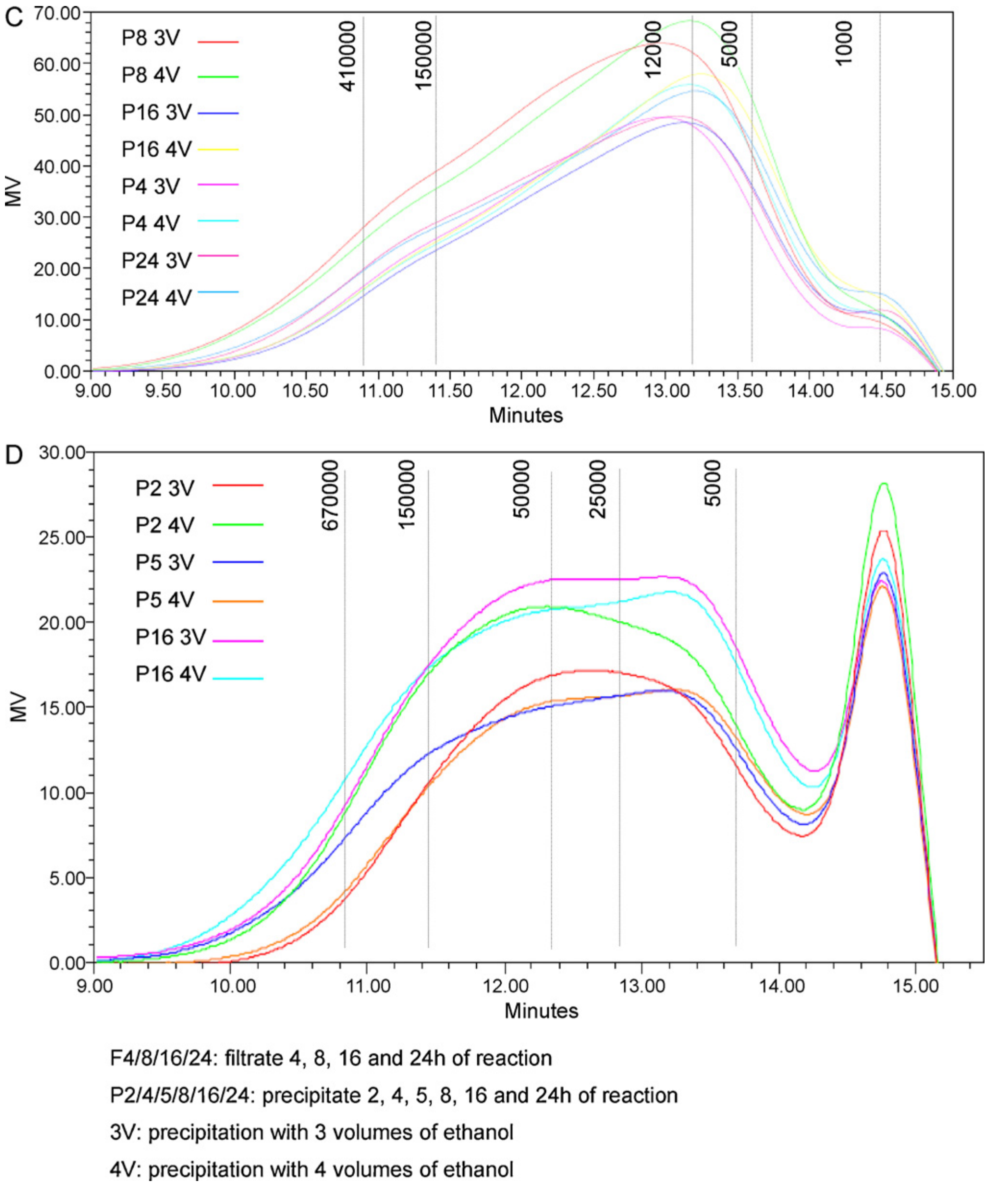


Fig. 1. (*Continued*)

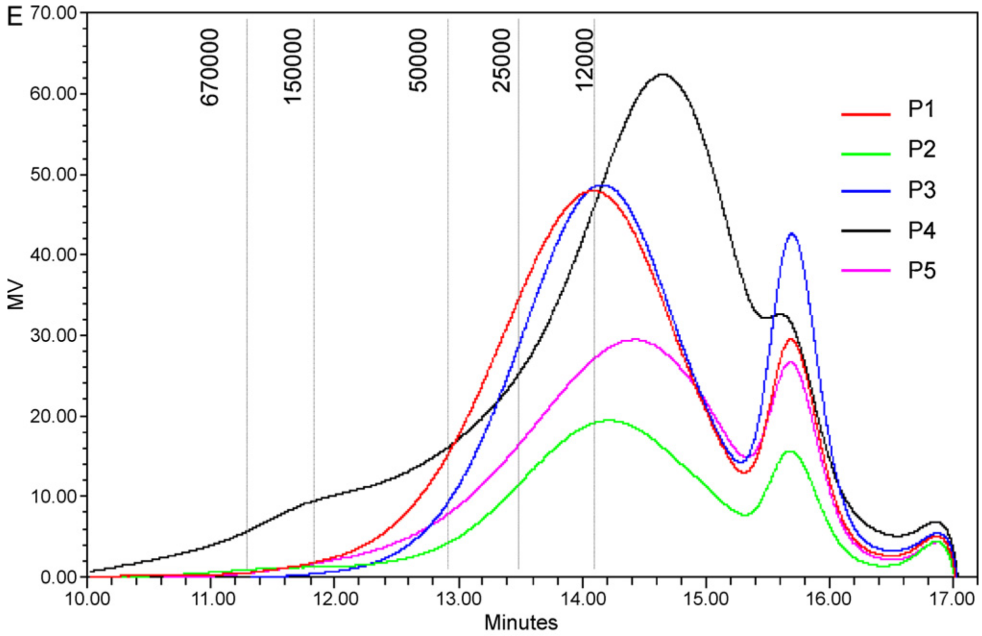
increase with the volume of ethanol nor the A/X ratio. The richest fractions in AX were obtained with an extraction time of 8 h and they also had the highest A/X ratios. AX populations were very broad; one low MW population could be distinguished and two other populations with higher MWs of 8800–14 000 g/mol and 257 000–367 000 g/mol (depending on the extraction time and the volume of ethanol) (Fig. 1C). Three volumes of ethanol gave higher MWs than 4 volumes. Whatever the volume of ethanol and the population, the highest MWs were obtained after 8 h of extraction. Ash content was again high however lower than in filtrates, from 17.5% to 41.3%.

Concerning the extraction efficiency, the yields varied from 17.9 to 20.6% for the majority of the fractions, the highest being obtained for the 24 h-extraction precipitate, with 3 volumes of ethanol (23.9%) and for the 24 h-precipitate with 4 volumes of ethanol (25.4%). This last contained 31.7% AX with an A/X ratio of 0.36 and with two main populations of 9200 and 273 000 g/mol. The precipitates from the 8 h-extraction had low ash content, high AX content, high A/X ratio and high MW, turning them the most interesting fractions.

Concerning the residues, their AX content varied from 20.7 to 24.9% and the AX chains were very lowly substituted, since A/X ratios varied from 0.18 to 0.21. Residues contained between 55.9 and 63.8% of the original total AX of the hull, indicating that only part of the AX was extracted.

3.4. Extraction by the third method: successive NaOH and NaClO$_2$–KOH extractions

NaOH-extraction filtrates contained between 7.2 and 8.2% of AX with A/X ratios between 0.14 and 0.20 (Table 4). The longest extraction time, 16 h, yielded the richest filtrate in AX with the highest A/X ratio. NaOH-extraction filtrates had much lower A/X ratios than H_2O_2-extraction filtrates even with the shortest extraction time (2 h) respectively 0.17 and 0.37. The KOH-extraction filtrates contained between 3.5 and 5% of AX with a very low A/X ratio around 0.11, whatever the extraction time. Concerning AX extraction yield, it varied between 45.6 and 49.6% for NaOH filtrates, and then between 25 and 37.5% for KOH filtrates; the highest corresponding to 5 h and 2 h of extraction.



P1: precipitate from 65% acetic acid and 35% H_2O

P2: precipitate from 80% acetic acid and 20% H_2O

P3: precipitate from 90% acetic acid and 10% H_2O

P4: precipitate from 60% acetic acid, 20% formic acid and 20% H_2O

P5: precipitate from 60% acetic acid, 30% formic acid and 10% H_2O

Fig. 1. (*Continued*).

For NaOH precipitates, AX content ranged from 26.7 to 33.3% and A/X ratios from 0.17 to 0.19. In the case of the 2 h-extraction, the use of 4 instead of 3 volumes of ethanol enabled to increase the extraction yield by 47% which was not observed for other durations. Here the precipitation of NaOH filtrates enabled to increase the A/X ratio of 0.04 which means that some xylose units were not recovered through precipitation.

Residues contained between 3.3 and 4.3% of AX, which were more substituted (A/X of 0.25) than the extracted AX. In other words, between 5.8 and 7.6% of the original AX remained in the hull, indicating a very efficient extraction.

All NaOH and KOH filtrates gave one peak on the HPSEC chromatogram corresponding to a small compound with MW around 880–900 g/mol (Fig. 1D). All chromatograms of NaOH precipitates had the same shape with three populations whatever the extraction duration: one of 1000 g/mol in average, the second of 8700–10 500 g/mol and the third of 99 000–188 000 g/mol (depending on the extraction time and the volume of ethanol).

Table 3
Composition of the different fractions extracted with the second method, A/X ratios and yields of extraction.

Fraction	Duration of extraction	Arabinose	Xylose	Mannose	Glucose	Galactose	Proteins	Ashes	AX[a]	A/X	Yield[b] of extraction
Hull	–	3.4 ± 0.0	18.1 ± 0.3	0.6 ± 0.0	18.9 ± 1.5	1.6 ± 0.0	7.0 ± 0.0	6.1	18.9	0.19	–
Filtrate	4 h	2.7 ± 0.0	8.7 ± 0.3	0.1 ± 0.0	0.6 ± 0.0	0.7 ± 0.0	4.8 ± 0.0	50.0	10.1	0.32	21.3
	8 h	2.8 ± 0.0	8.3 ± 0.5	0.1 ± 0.0	0.4 ± 0.0	0.5 ± 0.0	4.4 ± 0.2	45.6	9.8	0.34	22.1
	16 h	2.4 ± 0.1	5.8 ± 0.2	0.1 ± 0.0	0.4 ± 0.0	0.4 ± 0.0	5.1 ± 0.2	45.9	7.3	0.42	15.6
	24 h	2.9 ± 0.0	6.9 ± 0.1	0.0 ± 0.0	0.4 ± 0.0	0.5 ± 0.0	4.6 ± 0.3	49.4	8.6	0.41	20.5
Precipitate	4 h–3 v	9.9 ± 0.3	25.1 ± 0.4	0.4 ± 0.0	1.6 ± 0.1	2.9 ± 0.2	5.8 ± 0.0	31.1	30.7	0.39	19.0
	4 h–4 v	9.2 ± 0.5	23.1 ± 1.6	0.4 ± 0.1	1.5 ± 0.2	2.8 ± 0.4	6.3 ± 0.0	33.2	28.4	0.40	19.3
	8 h–3 v	11.3 ± 0.9	26.8 ± 1.9	0.5 ± 0.1	1.5 ± 0.1	3.3 ± 0.2	6.5 ± 0.1	17.5	33.5	0.42	18.1
	8 h–4 v	11.2 ± 1.0	26.1 ± 1.9	0.4 ± 0.0	1.3 ± 0.2	2.8 ± 0.3	6.6 ± 0.0	21.6	32.8	0.43	20.6
	16 h–3 v	8.4 ± 0.1	22.7 ± 0.6	0.1 ± 0.1	0.5 ± 0.0	1.3 ± 0.1	6.6 ± 0.1	41.4	27.3	0.37	17.9
	16 h–4 v	7.9 ± 0.4	21.7 ± 0.8	0.0 ± 0.0	0.5 ± 0.1	1.2 ± 0.1	6.8 ± 0.0	38.3	26.1	0.36	18.7
	24 h–3 v	10.2 ± 0.4	28.0 ± 1.1	0.0 ± 0.0	0.5 ± 0.0	1.5 ± 0.0	5.5 ± 0.0	33.8	33.7	0.37	23.9
	24 h–4 v	9.5 ± 0.1	26.5 ± 0.2	0.0 ± 0.0	0.6 ± 0.1	1.5 ± 0.1	5.9 ± 0.0	35.6	31.7	0.36	25.4
Residue	4 h	3.6 ± 0.1	19.8 ± 1.0	0.1 ± 0.1	0.9 ± 0.1	0.8 ± 0.0	0.7 ± 0.0	2.3	20.7	0.18	55.9
	8 h	4.9 ± 0.2	23.4 ± 2.2	0.0 ± 0.0	0.9 ± 0.2	1.0 ± 0.1	0.6 ± 0.0	2.3	24.9	0.21	63.8
	16 h	4.4 ± 0.3	21.0 ± 1.3	0.0 ± 0.0	0.9 ± 0.1	0.9 ± 0.1	0.7 ± 0.0	2.0	22.3	0.21	62.2
	24 h	4.3 ± 0.3	21.0 ± 2.5	0.0 ± 0.0	0.9 ± 0.1	0.8 ± 0.0	0.6 ± 0.0	2.1	22.3	0.21	59.1

v: volume of ethanol for precipitation.

[a] AX = 0.88(%ara + %xyl).

[b] AX fraction/AX hull.

Table 4
Composition of the different fractions extracted with the third method, A/X ratios and yields of extraction.

Fraction	Duration of extraction	Arabinose	Xylose	Mannose	Glucose	Galactose	Proteins	Ashes	AX[a]	A/X	Yield[b] of extraction
Hull	–	3.4 ± 0.0	18.1 ± 0.3	0.6 ± 0.0	18.9 ± 1.5	1.6 ± 0.0	7.0 ± 0.0	6.1	18.9	0.19	–
Filtrate NaOH	2 h	1.1 ± 0.1	7.1 ± 0.3	0.1 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	1.1 ± 0.0	79.9	7.2	0.15	45.6
	5 h	1.2 ± 0.0	8.1 ± 0.4	0.0 ± 0.0	0.5 ± 0.0	0.4 ± 0.0	1.3 ± 0.0	77.3	8.1	0.14	49.6
	16 h	1.6 ± 0.1	7.8 ± 1.4	0.1 ± 0.1	0.5 ± 0.0	0.5 ± 0.1	1.5 ± 0.0	73.5	8.2	0.20	48.1
Filtrate KOH	2 h	0.6 ± 0.0	5.8 ± 0.3	0.0 ± 0.0	0.3 ± 0.0	0.1 ± 0.1	0.1 ± 0.0	90.6	5.6	0.11	37.5
	5 h	0.6 ± 0.1	5.1 ± 0.3	0.0 ± 0.0	0.3 ± 0.0	0.1 ± 0.1	0.1 ± 0.0	91.7	5.0	0.11	33.2
	16 h	0.4 ± 0.0	3.6 ± 0.2	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	93.2	3.5	0.12	25.0
Precipitate NaOH	2 h–3 v	4.9 ± 0.2	25.5 ± 1.1	0.4 ± 0.1	1.9 ± 0.1	2.0 ± 0.1	3.0 ± 0.1	27.9	26.7	0.19	24.7
	2 h–4 v	6.0 ± 0.6	31.9 ± 1.0	0.4 ± 0.0	2.1 ± 0.1	2.3 ± 0.1	3.4 ± 0.0	30.0	33.3	0.19	36.3
	5 h–3 v	5.5 ± 0.1	32.4 ± 0.1	0.4 ± 0.1	2.0 ± 0.1	2.3 ± 0.1	2.9 ± 0.0	29.0	33.4	0.17	33.7
	5 h–4 v	6.0 ± 0.5	31.9 ± 2.4	0.4 ± 0.0	2.2 ± 0.2	2.5 ± 0.2	3.3 ± 0.0	27.4	33.3	0.19	33.1
	16 h–3 v	5.4 ± 0.4	29.7 ± 1.3	0.7 ± 0.4	2.0 ± 0.2	2.3 ± 0.2	3.2 ± 0.1	35.7	30.8	0.18	41.9
	16 h–4 v	5.5 ± 0.2	31.5 ± 0.1	0.8 ± 0.7	2.2 ± 0.2	2.4 ± 0.2	0.1 ± 0.0	30.7	32.6	0.17	39.5
Residue	2 h	0.9 ± 0.0	3.4 ± 0.2	0.0 ± 0.0	2.5 ± 0.2	0.5 ± 0.0	0.3 ± 0.0	13.6	3.8	0.25	6.6
	5 h	1.0 ± 0.1	3.9 ± 0.2	0.1 ± 0.2	2.9 ± 0.1	0.6 ± 0.1	0.3 ± 0.0	16.3	4.3	0.26	7.6
	16 h	0.8 ± 0.0	3.0 ± 0.1	0.1 ± 0.1	2.6 ± 0.3	0.5 ± 0.0	0.3 ± 0.1	13.2	3.3	0.25	5.8

v: volume of ethanol for precipitation.

[a] AX = 0.88(%ara + %xyl).

[b] AX fraction/AX hull.

The highest MWs (10 400 and 188 000 g/mol) were obtained with an extraction of 5 h and precipitation with 3 volumes of ethanol. The KOH precipitates had only one population with an average of 933 g/mol for all extraction times.

3.5. *Extraction by the fourth method: acidic extractions*

Concerning the filtrates, AX extraction yields increased with the concentration of acetic acid, respectively, 10.9, 24.7 and 39.1%. Formic acid increased the extraction yields to 48.5 and 64.2%. Concerning the precipitates, the maximum AX extraction yield was obtained with 90% acetic acid and 10% H_2O and it rose with the concentration of acetic acid, from 0.9 to 5.1% (Table 5). Extraction yields with acetic and formic acids were lower, 4.0 and 0.3%. A higher solubilization of hemicelluloses was observed with acetic and formic acids than with acetic acid alone however it was associated with the inability to recover the hemicelluloses through the precipitation with 3 volumes of ethanol.

In filtrates, xylose content increased with the concentration in acetic acid and formic acid. In precipitates, xylose content increased with the concentration in acetic acid and decreased with the one of formic acid. Glucose content varied between 4.0 and 9.2% in filtrates and decreased with the concentration of acetic and formic acids. In precipitates, glucose content decreased with the concentration of acetic acid but it increased drastically with the concentration of formic acid, 13.5%. The precipitation of filtrates extracted with the blend acetic acid/formic acid/H_2O, decreased the concentration of AX.

In precipitates, A/X ratios varied from 0.05 to 0.19 and in filtrates from 0.18 to 0.95. Precipitation of extracts from acetic acid provoked a loss of arabinose, while it was much less important from the blend formic and acetic acids. Indeed, A/X ratios of filtrates with acetic acid alone were high (0.28 and 0.95), they decreased with acetic acid concentration and were of 0.18–0.24 from the blend formic and acetic acids.

Extracted hemicelluloses had low MW and could be splitted into 3 populations, the first population had a MW of 9400–11 300 g/mol with acetic acid alone (depending on the amount of acetic acid) and 5300–7200 g/mol for formic and acetic acids (depending on the used proportions). The second and third populations had MWs of 1300–1500 g/mol and 280 g/mol respectively (Fig. 1E).

4. Discussion

With both methods of extraction using H_2O_2, the AX contents of the different extraction fractions were close (around 30%) and the extraction yields were similar. Concerning the liquid fractions of each experiment, the successive extractions of the first method enabled to get AX with higher MWs than those of the second method. In the second method, precipitation enabled to get higher MWs than those of the first method. A/X ratios were similar, depending on the time of extraction and the fraction considered. In the case of the filtrates, the longer the extraction time the higher the A/X ratio which means that more and more arabinose was released from the substrate. In the case of the precipitates, the contrary was observed: the longer the extraction time the lower the A/X ratio, indicating that part of the arabinose could not be precipitated as it might have been cut from the chain of xylan and might be under a monomeric or oligomeric form. The high yield and high MW of the AX can be explained by the use of alkaline peroxide processes which are efficient for delignification and removal of hemicelluloses (Fang et al., 1999; J.X. Sun, Sun, Sun, & Su, 2004).

The method with NaOH enabled to obtain higher extraction yields but less substituted AX and polysaccharides with lower MWs. The longest extraction with H_2O_2 (24 h) did not result in AX degradation, while a short extraction with NaOH was sufficient to provoke a disruption of the polymers and in a greater extent with $NaClO_2$–KOH, which yielded only compounds with low MW (1000 g/mol in average). The original amount of arabinose was not found in the filtrate, neither in the precipitate nor in the residue, consequently it seemed rapidly degraded by the treatment with $NaClO_2$–KOH, and precipitation managed to recover only a weak part of the arabinose in the hemicellulosic fraction. Alkali metal hydroxide can induce the intracrystalline swelling of cellulose and a widening of the lattice dimensions or even a crystal lattice conversion but no dissolution, and KOH causes less swelling than NaOH (Nevell & Zeronian, 1985 in Wertz, Bédué, Mercier, 2010). Furthermore, $NaClO_2$ causes oxidation of cellulose, randomly in the accessible regions of the fibers, and the degradation may occur simultaneously (Lewin & Epstein, 1962 in Wertz et al., 2010). It can be hypothesized that the changes in the configuration of the cellulose such as it could have happened in this experiment facilitated the liberation of hemicelluloses. This could also explain the higher yields than with the H_2O_2 methods, however degradation

Table 5
Composition of the different fractions extracted with the fourth method, A/X ratios and yields of extraction.

Fraction	Experiment number	Rhamnose	Arabinose	Xylose	Mannose	Glucose	Galactose	AX[a]	A/X	Yield[b] of extraction
Hull		0.1 ± 0.1	3.4 ± 0.0	18.1 ± 0.3	0.6 ± 0.0	18.9 ± 1.5	1.6 ± 0.0	18.9	0.19	–
Precipitate	1	0.3 ± 0.0	2.8 ± 0.0	24.6 ± 0.6	1.6 ± 0.0	4.7 ± 0.1	4.1 ± 0.0	24.1	0.11	0.9
	2	0.0 ± 0.0	2.5 ± 0.1	28.5 ± 1.0	0.8 ± 0.0	3.0 ± 0.1	2.3 ± 0.1	27.3	0.09	1.5
	3	0.0 ± 0.0	2.3 ± 0.1	42.2 ± 1.7	0.4 ± 0.0	1.5 ± 0.1	1.2 ± 0.1	39.2	0.05	5.1
	4	0.0 ± 0.0	3.1 ± 0.1	35.8 ± 1.6	0.5 ± 0.0	3.3 ± 0.1	2.4 ± 0.0	34.2	0.09	4.0
	5	0.0 ± 0.0	1.8 ± 0.0	9.4 ± 0.3	0.7 ± 0.0	13.5 ± 0.4	2.6 ± 0.1	9.9	0.19	0.3
Residue	1	0.0 ± 0.0	2.4 ± 0.1	22.1 ± 0.5	0.0 ± 0.0	1.1 ± 0.1	1.1 ± 0.0	21.6	0.11	73.6
	2	0.0 ± 0.0	1.8 ± 0.1	19.3 ± 0.5	0.0 ± 0.0	1.0 ± 0.1	0.9 ± 0.0	18.6	0.09	61.8
	3	0.0 ± 0.0	1.4 ± 0.0	17.5 ± 0.5	0.1 ± 0.1	1.2 ± 0.0	0.8 ± 0.0	16.6	0.08	51.6
	4	0.0 ± 0.0	1.1 ± 0.0	13.8 ± 0.5	0.1 ± 0.1	1.4 ± 0.1	0.6 ± 0.0	13.1	0.08	34.6
	5	0.0 ± 0.0	0.5 ± 0.0	7.2 ± 0.2	0.0 ± 0.0	1.3 ± 0.0	0.3 ± 0.0	6.8	0.07	15.1
Filtrate	1	0.0 ± 0.0	11.5 ± 0.0	12.1 ± 0.2	0.6 ± 0.0	9.2 ± 0.4	3.2 ± 0.0	20.7	0.95	10.9
	2	0.0 ± 0.0	11.6 ± 0.0	26.2 ± 0.2	0.3 ± 0.2	6.1 ± 0.1	3.6 ± 0.1	33.2	0.44	24.7
	3	0.0 ± 0.0	8.2 ± 0.2	29.2 ± 0.7	0.6 ± 0.1	4.0 ± 0.2	3.2 ± 0.1	32.9	0.28	39.1
	4	1.2 ± 0.2	9.2 ± 0.2	38.3 ± 0.9	0.5 ± 0.3	7.5 ± 0.4	3.3 ± 0.2	41.8	0.24	48.5
	5	1.7 ± 0.1	7.4 ± 0.2	41.2 ± 0.8	0.5 ± 0.2	4.0 ± 0.2	2.8 ± 0.1	42.8	0.18	64.2
Residue	1	0.0 ± 0.0	2.3 ± 0.1	21.8 ± 0.8	0.2 ± 0.0	1.3 ± 0.1	1.2 ± 0.1	21.2	0.10	71.5
	2	0.0 ± 0.0	1.5 ± 0.1	18.9 ± 0.7	0.1 ± 0.1	1.3 ± 0.0	0.9 ± 0.0	18.0	0.08	55.4
	3	0.0 ± 0.0	0.7 ± 0.0	10.2 ± 0.1	0.0 ± 0.0	1.4 ± 0.0	0.4 ± 0.0	9.5	0.07	24.4
	4	0.0 ± 0.0	1.2 ± 0.1	13.8 ± 0.2	0.1 ± 0.1	1.4 ± 0.0	0.7 ± 0.0	13.2	0.09	34.7
	5	0.0 ± 0.0	0.5 ± 0.0	7.3 ± 0.0	0.0 ± 0.0	1.4 ± 0.0	0.3 ± 0.0	6.9	0.07	15.1

1: 65% acetic acid and 35% H_2O; 2: 80% acetic acid and 20% H_2O; 3: 90% acetic acid and 10% H_2O; 4: 60% acetic acid, 20% formic acid and 20% H_2O; 5: 60% acetic acid, 30% formic acid and 10% H_2O.

[a] AX = 0.88(%ara + %xyl).

[b] AX fraction/AX hull.

of hemicelluloses occurred. It should be mentioned that in spite of the environmental concern, chlorite was experimented to resolve the problem of coloration due to lignin (5–10%) and to phenolic compounds (Shin, Guebitz, & Cavaco-Paulo, 2001).

The organic acids used in the fourth method, associated with a temperature much higher than that of the other methods, lead to a considerable degradation of the polymers. Concerning filtrates, higher yields than with all other methods were obtained when formic acid was used. For similar yields, A/X ratios were higher with acetic acid showing that arabinose would be less degraded than with other chemicals (NaOH, $NaClO_2$, KOH and formic acid). Concerning the precipitates, as explained before, precipitation was impeded by the small size of the molecules. As reported by Wertz et al. (2010), formic acid in aqueous solution of suitable concentration can cause intercrystalline and intracrystalline swelling and dissolution of cellulose. Moreover, in wheat straw, the linkages between lignin and hemicelluloses and cellulose are relatively strong and can only be cleaved in acidic media (X.F. Sun, Sun, Fowler, & Baird, 2004). Such a cleavage could have happened in this experiment, liberating the hemicellulose with a high yield. The degradation of hemicelluloses led to oligomers with very low MW, this has also been observed on commercial straw pulping where inorganic agents achieve high cellulose extraction at the expense of the hemicellulosic fraction which undergoes hydrolysis and degradation (X.F. Sun, et al., 2004).

The advantage of the first method was the splitting into WE- and WU-AX, the short extraction time (maximum 8 h) and the preservation of high MWs while the other H_2O_2 methods required 24 h. Concerning yields of AX recovery, the methods with NaOH and $NaClO_2$–KOH were the most efficient. Organic and inorganic acids caused too much degradation to enable a good recovery of the hemicelluloses. It should be highlighted that fractions coming from the last two methods without dialysis had high ash contents, thus a demineralisation would be necessary in order to get a higher AX purity.

The quantity and quality of AXs obtained here from spelt hull can be compared to the literature data on fractions obtained from other cereal sources such as wheat straw, wheat bran, spelt bran and different hull and husk (Table 6). Sun et al. (2000) managed to extract from 77 to 91% of the hemicelluloses from wheat straw while with the same method here, AX extraction yields from hull varied from 17.9 to 25.4%; such a discrepancy may be due to different ligno-cellulosic structures, and different amounts of minor sugars (glucose, rhamnose, mannose, galactose). However MWs ranged from 24 000 g/mol to 31 000 g/mol for straw while MWs of hull AX were higher, from 8700 to 370 000 g/mol. In Sun et al.'s study (1998), the fraction extracted with NaOH represented from 32.7 to 41.5% of the dewaxed wheat straw after 2–15 h of reaction, while it was here between 24.0 and 29.2% for the destarched hull. Also, the final straw residue (after NaOH and $NaClO_2$–KOH extractions) represented 38.0–39.9% of the dewaxed straw while it made up here 40.6–43.3% of the destarched hull (not dewaxed). MWs of the compounds extracted with NaOH from straw ranged from 26 000 to 32 000 g/mol and those obtained from $NaClO_2$–KOH extraction from 60 000 to 62 000 g/mol. This was very different from the profile of the populations of hull which respectively ranged from 8700 to 188 000 g/mol with NaOH extraction and 930 g/mol with $NaClO_2$–KOH extraction. In the case of straw, the extraction with $NaClO_2$–KOH resulted in higher MWs than with NaOH, i.e. the contrary of what happened with hull. Xu, Liu, et al. (2006) dissolved 42.4–76.5% of the hemicelluloses from wheat straw with organic acids, with MWs between 10 000 and 16 100 g/mol. These figures are far from those obtained for spelt hull in the same conditions, with the highest yield of 5.1% and MW of 10 300 g/mol. Whatever the conditions, organic acids led to very divergent results between wheat straw and spelt hull (Table 6).

Hoije, Grondahl, Tommeraas, and Gatenholm (2005) extracted hemicelluloses from barley husks and obtained fractions with 50–83% of AX. This high purity was facilitated by the chlorite which removed proteins and starch. Extraction yields ranged from 25.1 to 57% and MWs from 35 000 to 45 000 g/mol. Yields were lower for the spelt hull extraction even with NaOH (41.9% for 16 h) but MWs were higher, from 9400 to 178 000 g/mol. Another example comes from Hromadkova and Ebringerova, 2003 who extracted hemicel-

Table 6
Synthesis of the results from the present work and literature data on hemicelluloses and AXs extraction from hull, straw and husk.

Reference	Material	Extraction yield (AX%)	MW of AX (g/mol)	Method
Results from present work	Spelt hull	41.9%	9300 and 177 000	NaOH; 16 h; 45 °C
		20.4%	6800–7800 and 230 000–275 000	H_2O_2 2%; pH 11.5; 4 h twice; 60 °C
		25.4%	9200 and 273 000	H_2O_2 2%; pH 11.5; 24 h; 50 °C
		5.1%	283; 1300 and 10 300	90% acetic acid–10% H_2O; 4 h; 85 °C
		4.0%	288; 1500 and 5300	60% formic/20% acetic acid/20% H_2O; 4 h; 85 °C
Hromadkova and Ebringerova, 2003	Buckwheat hull	16.5%	61 and 3600	NaOH 5%; 60 °C; 10 min
Hoije et al., 2005	Barley husk	57%	39 100	HCl 0.05 M; 16 h then acetic acid with $NaClO_2$; 2 h; 75 °C then NaOH 1 M + 0.5% $NaBH_4$; 16 h
Roos et al., 2009	Barley husk	9%	52 000	Microwave irradiation 5 min; 200 °C; NaOH 0.5%; pH 12.3 + steam
	Barley husk	50%	13 000	Microwave irradiation 5 min; 210 °C; pH 6.5 + steam
Jin et al., 2009	Barley straw	94.6%	14 600–28 840	Neutral dioxane 90%; 4 h; 80 °C then acidic dioxane 80%; 4 h; 70 °C then DMSO; 4 h; 80 °C then KOH 8%; 4 h; 50 °C
Sun et al., 1998	Wheat straw	32.7–41.5%	27 740–31 810	NaOH 3%; 45 °C; 2–15 h
		4.5–9.8%	60 200–62 260	KOH 10%; 25 °C; 16 h
Sun et al., 2000	Wheat straw	91%	28 800	H_2O_2 2%; 50 °C; 16 h; pH 11.5
		90.0%	30 700	H_2O_2 2%; 50 °C; 12 h; pH 11.5
Persson et al., 2009	Wheat straw	47%	10 000	Steam pretreatment in alkaline environment NaOH 5%; 30 min; 190 °C; pH 11.1
		40%	20 000	Steam pretreatment in alkaline environment NaOH 2%; 30 min; 190 °C; pH 8.8
Thomsen, Thygesen, & Thomsen, 2008	Wheat straw	83%	–	Hydrothermic treatment: 80 °C p re-soaking then 170–180 °C for hemicelluloses and 19 5 °C for cellulose
Sun, Wang, Sun, & Sun, 2002	Wheat straw	53.4%	32 520	Methanol 60% and 0.5 M NaOH; 60 °C; 2.5 h; without sonication + HA 2% and tetraacetylethylenediamine 0.2%; pH 11.8; 12 h; 48 °C
		44.5–50.8%	28 400–31 160	Methanol 60% and 0.5 M NaOH; 60 °C; 2.5 h; with 5–35 min sonication + H_2O_2 2% and tetraacetylethylenediamine 0.2%; pH 11.8; 12 h; 48 °C
Sun et al., 2005	Wheat straw	32.3–37.5%	42 710 and 44 080	Aqueous alcohol pre-treated wheat straw; 4 h; 85 °C then H_2O_2 1.8%; cyanamide 0.18%; 4 h; 50 °C; pH 10
		19.6–45%	12 980–15 950	organic acid pre-treated straw; 4 h; 85 °C then H_2O_2, 1.8%; cyanamide 0.18%; 4 h; 50 °C; pH 10
		45%	15 950	organic acid pre-treated straw; 4 h; 85 °C then H_2O_2, 1.8%; cyanamide 0.18%; 4 h; 50 °C; pH 10
Xu, Liu, et al., 2006	Wheat straw	42.4–70%	8500–16 100	Acetic acid–H_2O; 4 h; 85 °C
		65.1–76.5%	10 000–12 100	Formic acid–acetic acid–H_2O; 4 h; 85 °C

luloses from buckwheat hulls with maximum yield of 16.5% and MWs of 61 and 3600 g/mol respectively. It should be highlighted that Roos, Persson, Krawczyk, Zacchi, and Stalbrand (2009) also worked on barley husks and managed to extract hemicelluloses of 40 000 g/mol with a yield of 8.6%, interestingly without chemicals (water, heat treatment, microwave irradiation).

Different applications for the obtained hemicellulosic fractions could be considered, depending on their MWs. High MW xylans may be used as adhesives and emulsifiers (Doner & Hicks, 1997). Xylans from cereal straw can also be used as gel-forming or thermoplastic materials, as fillers for polypropylene, as a component for paint formulation and as a coating for cellulosic fibers (Xu, Sun, Liu, & Sun, 2006). Endoxylanases can yield arabino-xylo-oligosaccharides from AX, which present interesting properties as prebiotics (Courtin et al., 2009). Monomeric xylose can be further fermented into ethanol (Hahn-Hägerdal, Kahrumaa, Fonseca, Spencer-Martins, & Gorwa-Grauslund, 2007) or transformed into xylitol (Granström, Izumori, & Leisola, 2007) which has many industrial applications for instance in medical fields (Xu, Sun, et al., 2006).

5. Conclusion

The MW of the AXs extracted from spelt hull varied a lot depending on the conditions of extraction. The most efficient extraction of AXs from spelt hull was obtained with the method using NaOH and $NaClO_2$–KOH during 16 h and precipitation with 3 volumes of ethanol, which yielded 41.9% of the total AX. The AX fraction obtained through these conditions had an A/X ratio of 0.17 and two main populations with MWs of 9300 and 177 000 g/mol. However, this method also led to the highest degradation of the polysaccharides. In order to obtain higher MWs, the method with 2% H_2O_2 at 50 °C during 8 h and 3 volumes of ethanol was the most adapted: it produced a fraction with two main AX populations of 14 000 and 367 000 g/mol with an extraction yield of 18.1%.

The tested methods offered diverse results with regard to the extraction yields, the MWs, the A/X ratios; therefore it may be possible to select the most adapted method for a chosen result. It may also be possible to further adapt and/or combine the methods. At this point, physical methods should also be explored and eventually combine with the chemical ones. Some perspectives of this work consist in focusing on the techno-functional properties of the hemicellulose extracts in order to define potential applications.

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