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Improved efficiency of brewer's spent grain arabinoxylans by ultrasound-assisted extraction

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ABSTRACT

Arabinoxylan (AX) rich extracts from brewer's spent grain (BSG) were produced by the application of ultrasound-assisted extraction (UAE) and conventional alkaline extraction (AKE). UAE and AKE were optimised for the production of the highest yield of ethanol insoluble material using response surface methodology (RSM). The efficiency of UAE was established by the significant reduction of time (7 h to 25 min) and energy when compared to AKE, to recover similar amounts of AX (60%) from BSG, leading to the production of starch-free AX-rich extracts.

1. Introduction

Arabinoxylans (AX) are the main non-starch polysaccharide of cereal grains such as wheat, barley, oat, corn and rice. The AX are composed of β-D-(1 → 4)-linked-xylopyranosyl residues to which α-L-arabinofuranose units are linked as side chains, with some of them substituted with monomeric or dimeric ferulic acid residues (Fig. 1) [1]. Similar to other non-digestible carbohydrates, AX are of particular interest in the formulation of functional foods due to the health benefits associated with their consumption [2]. They have been classified as prebiotics because they (i) are not hydrolysed nor absorbed in the upper part of the gastrointestinal tract, (ii) maintain a good gastrointestinal environment and (iii) selectively stimulate the microflora that confer benefits upon the host wellbeing and health [3].

Brewer's spent grain (BSG) is the residue left after barley malting and separation of the wort (fermentation medium to produce beer) during the brewing process. BSG is the most abundant brewing by-product amounting to around 85% of total by-products generated by the brewing industry. Million of tonnes of BSG are produced annually across Europe and common applications are direct disposal in a landfill or use as an animal feed. BSG is a lignocellulosic material composed of AX (28%), cellulose (17%) and lignin (28%) [4,5]. As the germinated grain during brewing has already been submitted to a hot water extraction process, the BSG AX are mostly not extractable with water. Thus, chemical and/or enzymatic methods need to be used for their extraction. These include sequential extraction with mild and strong alkali solutions [6,7] and sequential extraction with alkali solution and a mixture of feruloyl esterases and glycoside hydrolases. This last extraction method allows for the recovery of phenolic acids and diferulate AX oligosaccharides [8]. Autohydrolysis of BSG, an environmentally friendly treatment carried out in a reactor with hot water or steam, promotes the recovery of several AX oligosaccharide (AXOS) mixtures [9]. More recently, a sequential extraction applying microwave superheated water and dilute alkali extraction of BSG AX was proposed, separating AX, AXOS, and feruloylated AXOS from the proteins and residual starch [10].

Ultrasound-assisted extraction (UAE) is a process that uses acoustic energy and solvents to extract target compounds from various plant matrices. The application of high-intensity ultrasound causes pressure fluctuations, which propagate through the material. These fluctuations give rise to microscopic bubbles that are highly unstable and collapse within a few milliseconds after their formation. In the wake of the collapse, high shear forces are applied to any material that is present in the vicinity of these cavitational bubbles. In addition to the mechanical shear forces, the temperature in the vicinity of the bubbles increases. The ultrasound pressure waves and resulting cavitation phenomena are able to break cell walls, promoting the release of the contents of the cell into the extraction medium [11,12].

UAE has already been used to obtain xylans from corn cobs [13,14], corn bran [15], wheat straw [16,17], buckwheat hulls [18], sugarcane bagasse [19], wheat bran [20] and almond shells

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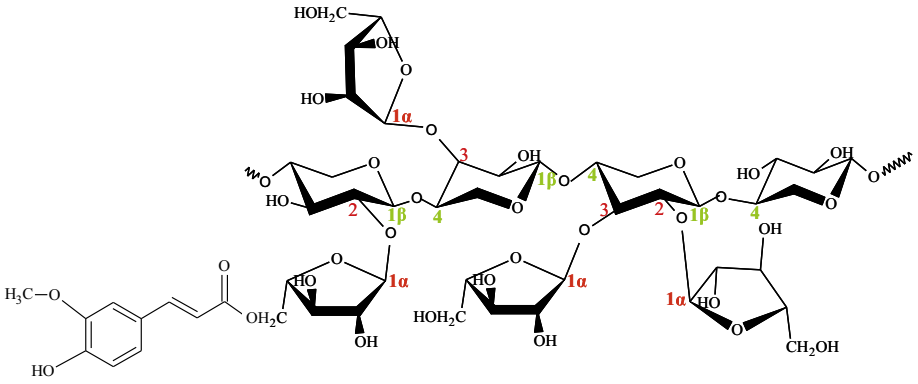

Fig. 1. Arabinoxylans structure.

[21]. The advantages reported are the substantial shortening of extraction time, solvent consumption, and extraction temperature, resulting in higher yields and purity of polysaccharides with no significant structural changes and no negative effects in their functional properties. However, high intensity ultrasound can break down polymers, which may negatively affect polysaccharides [22].

Due to the high demand of AX owing to their potential health benefits as dietary fibre and as prebiotics, in addition to the abundant availability of BSG as a source of AX, this work aims at examining the efficiency of ultrasound-assisted extraction in the production of AX-rich extracts in comparison to typical alkaline extraction procedures.

2. Material and methods

2.1. Chemicals

All chemicals were purchased from Sigma–Aldrich (Wicklow, Ireland) except for sulphuric acid, acetone, dichloromethane and ethanol, which were purchased from Fisher scientific (Ballycoolin, Ireland).

2.2. Brewer's spent grain (BSG)

BSG was obtained from the micro distillery plant located at University College Cork, Cork (Ireland). The dried BSG was coarsely ground to 250 μm particle size and stored in polyethylene bags at −20 °C until further use.

2.3. Ultrasound-assisted extraction (UAE)

2.3.1. Ultrasound pre-washing treatment with water

Suspensions of BSG (2 g) and distilled water (50 mL) were processed at a constant frequency of 20 kHz using a 750 W ultrasonic processor (VC 750, Sonics and Materials Inc., Newtown, USA) using a 13 mm diameter solid probe. Different amplitudes (8%, 25%, 50%, 75%, 92% and 100%) combined with different times (3.3, 5, 7.5, 10 and 11.7 min) were applied with pulse durations of 5 s on and 5 s off. The ultrasound probe was submerged up to 25 mm in the sample. The residue was separated from the supernatant by centrifugation at 14,400 rpm for 20 min, and then resuspended in distilled water (50 mL) and autoclaved at 120 °C for different times (4.8, 15, 30, 45 and 55 min).

2.3.2. Ultrasound alkaline extraction

The autoclaved residue was suspended in an alkali solution (0.3, 1, 2, 3 and 3.7 M) and submitted to ultrasound treatment by combining different amplitudes (8%, 25%, 50%, 75%, 92% and 100%) and times (3.3, 5, 7.5, 10 and 11.7 min) with pulse durations of 5 s on and 5 s off. The suspensions were then neutralised with HCl until pH 6–7 was reached and subsequently centrifuged. The supernatants were precipitated with 5 volumes of ethanol (96%) and the alcohol insoluble material was recovered as a powder; after centrifugation at 14,400 rpm for 10 min, solubilisation in distilled water, dialysis using a cellulose acetate membrane of 12 kDa cut off (Sigma, D9652) and freeze-drying. The scheme for the isolation of the polysaccharide fractions is shown in Fig. 2.

The ultrasonic intensity (UI) was determined using the following formula:

$$\mathrm{UI} = 4P/\pi D^2 \tag{1}$$

where P is the ultrasonic power (W) and D is the probe diameter (cm). Ultrasonic power was calculated using the following formula:

$$P = mC_p(dT/dt)_{t=0}\pi D^2 \tag{2}$$

where m is the mass (g), C_p is the specific heat (H_2O – 4.187 J g^{-1}° C^{-1}; 2 M KOH – 0.93 J g^{-1}°C^{-1}) and (dT/dt) is the change in temperature over time (°C s^{-1}).

2.4. Alkaline extraction (AKE)

BSG samples were also extracted using different concentrations (1, 2, 3, 4 and 5 M) of KOH solutions with 20 mM $NaBH_4$, in an incubator (Innova 42, Mason technology, Dublin, Ireland) over different times (1, 4, 7, 10 and 13 h) and temperatures (25, 35, 45, 55 and 65 °C). After each alkaline extraction the same steps described after ultrasound treatment using alkali solution (Section 2.3.2) were followed.

2.5. Sugar analysis

Neutral sugars were released by Saeman hydrolysis and analysed as their alditol acetates by gas chromatography [23,24] using a FISONS 8340 chromatograph with a split injector (split ratio 1:60) and a FID detector. A DB-225 column (Agilent J&W, USA; 30 m × 0.25 mm × 0.15 μm) was used. The injector and detector temperatures were 220 and 230 °C, respectively. The oven temperature program started at 200–220 °C at a rate of 40 °C per min and was held at 220 °C for 15 min, then increased up to 230 °C with a rate of 20 °C per min and was held at 230 °C for 1 min. The flow rate of the carrier gas (H_2) was set at 1 mL/min at 200 °C. Uronic acids (UA) were determined colorimetrically according to Coimbra et al. [23]. The hydrolysis of all samples was done in duplicate and each sample was injected twice.