



Recovering ferulic acid from wheat bran enzymatic hydrolysate by a novel and non-thermal process associating weak anion-exchange and electro dialysis



Stéphanie Dupoiron^{a,b,c}, Marie-Laure Lameloise^{a,*}, Magali Bedu^a, Richard Lewandowski^a, Claire Fargues^a, Florent Allais^{c,d}, Andreia R.S. Teixeira^{a,c}, Harivony Rakotoarivonina^b, Caroline Rémond^b

^a UMR Ingénierie Procédés Aliments, AgroParisTech, INRA, Université Paris-Saclay, 91300 Massy, France

^b UMR FARE, Chaire AFERE, Université de Reims Champagne-Ardenne, INRA, 51100 Reims, France

^c Chaire Agro-Biotechnologies Industrielles (ABI), AgroParisTech, 51110 Pomacle, France

^d UMR GMPA, AgroParisTech, INRA, Université Paris-Saclay, 78850 Grignon, France

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ABSTRACT

Agricultural by-products such as wheat bran and straw are rich in arabinoxylans. Composed of a main chain of β -(1,4) linked xylose ramified by arabinose and ferulic acid, these polymers are sources of valuable molecules, in particular ferulic acid and monomeric (xylose, arabinose and glucose) and oligomeric carbohydrates. Enzymatic hydrolysis using hemicellulasic cocktails obtained from *Thermobacillus xylanilyticus* provide an eco-friendly alternative to acid or alkaline deconstruction. In this article, downstream purification of the enzymatic hydrolysate of wheat bran with a weak anion-exchange resin (Amberlyst A21- Dow) in free-base form was studied and optimized to reach concentrated ferulate fractions in environment-friendly conditions. A demineralization step by homopolar electro dialysis prior to anion-exchange allowed most of the competing inorganic anions to be removed from the hydrolysate. The capacity of fixation of ferulic acid on the active sites of the resin was increased, as well as purity and concentration of the basic eluate, consequently. Ferulic acid could therefore be crystallized by adjusting the pH of the eluate. 83% was crystallized and purity (NMR) reached 90–95%. At last, 52% of ferulic acid released from wheat bran by the hemicellulasic cocktail was purified and recovered as a solid. Moreover, more than 50 BV (Bed Volume) of the hydrolysate could be recovered during the resin saturation step as rather pure carbohydrates under monomeric (xylose, arabinose and glucose) and oligomeric (xylobiose, xylotriose and xylotetraose) form.

1. Introduction

The biorefinery concept embraces a wide range of technologies that aims to produce biofuels, chemicals and materials from various biomass resources (e.g., wood, grasses, corn). Lignocellulosic biomass is a renewable feedstock abundant on earth and of interest for biorefinery. The enzymatic hydrolysis of agricultural by-products, such as wheat bran, rich in arabinoxylans, provides an eco-friendly alternative to acid and alkaline hydrolysis for the release of pentoses and phenolic acids such as ferulic acid, a high added value molecule [1]. Arabinoxylans are

composed of main chains of β -xylopyranosides (xyl) bound by β -(1,4) links that can be ramified by α -arabinofuranoside (ara). The ara can also be ramified by ferulic acid through an ester bond [2].

Recently, ferulic acid (4-hydroxy-3-methoxycinnamic acid), already known as a precursor of vanillin [3,4] has been used to synthesize bis- and tris-phenols [5] that not only exhibit potent antiradical and antioxidant properties [6,7] but also have been used for the preparation of bio-based polymers [8]. High purity crystallized ferulic acid is needed for the synthesis of these molecules.

In most published studies, ferulic acid extracted from lignocellulosic

Abbreviations: A252, Amberlite A252; A21, Amberlyst A21; ara, arabinose; BV, bed volume; CE, capillary electrophoresis; DM, dry matter; DWB, destarched wheat bran; FB, free-base; glc, glucose; g_R, gram of resin (wet); L_H, liter of hydrolysate; L_R, liter of resin (wet); XOs, xylo-oligosaccharides; xyl, xylose; X2, X3, X4, xylobiose, xylotriose, xylotetraose; X3AF_e, X4AF_e, O- β -D-xylopyranosyl-[1,4]-O-[5-O-(feruloyl)- α -L-arabinofuranosyl-[1,3]-O- β -D-xylopyranosyl-[1,4]-O- β -D-xylopyranose and O- β -D-xylopyranosyl-[1,4]-O-[5-O-(feruloyl)- α -L-arabinofuranosyl-[1,3]-O- β -D-xylopyranosyl-[1,4]-O- β -D-xylopyranose; WB, wheat bran; TLC, thin layer chromatography

* Corresponding author.

E-mail address: Marie-laure.lameloise@agroparistech.fr (M.-L. Lameloise).

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biomass is recovered or purified by adsorption on polymeric adsorbents of XAD type or activated charcoal [9–11]. These hydrophobic materials fix the protonated ferulic acid and exclude polar compounds such as carbohydrates, inorganic ions and glucuronic acid. However, they were shown to fix feruloylated arabino-xylo-oligosides likely present in enzymatic hydrolysates [10] and other undetermined impurities (colored matter). These compounds are released with ferulic acid when regenerating the solid phase with ethanol, impeding recovery of pure crystallized acid.

With two acid functions: carboxylic acid $pK_{a1} = 4.6$ and phenol $pK_{a2} = 8.9$ [12], ferulic acid could interact with functionalized anion-exchange resin. Fixation of phenol by anion-exchange resin through phenolate ion at basic pH is considered as promising for the treatment of effluents [13–15]. It is generally admitted that fixation occurs on the active ionic sites of the resin, either by adsorption or by ion-exchange according to the pH. Regarding other phenolic compounds and especially ferulic acid, there are quite no studies published on their fixation by anion-exchange except Di Gioia et al. [4] who used an anion-exchange resin in Cl^- form and Ou et al. [11] who used a strong anion-exchange resin to complete ferulic acid purification after adsorption on active charcoal.

In contrast, literature on the purification of carboxylic acids by ion-exchange is abundant, driven by the intensive current development of the production of organic acids (e.g., lactic, malic, citric) by fermentation [13,16]. Strong and weak anionic resins and various ionic forms have been compared [17,18]. In a context of sustainable processing, weak resins are particularly attractive because they display high capacities and can be regenerated with a minimal amount of reactant, close to the stoichiometry [17–19]. The chloride form is well suited to address the treatment of neutral loads where the weak organic acid is fully dissociated; the acid is recovered during the elution phase by HCl. This strategy is not appropriate for ferulic acid that is hardly soluble. Use of HCl in ethanol/water has been proposed to address this problem [4,11]. Weak resin in the free base form (FB) is another alternative. It needs acidic pH ($< pK_a$) to be performed and the reaction is generally considered as acid-base neutralization or ion-pairing rather than true ion-exchange [20]. Regeneration by a strong base allows the acid to be released as a highly concentrated salt, considering the preference of weak-anion exchange resins for the FB form.

Preliminary column experiments with a 0.44 g/L solution of ferulic acid (natural pH 3.2, therefore the neutral form was largely predominant) and a weak Amberlyst A21 resin (Dow) in FB form showed a stiff breakthrough at 360 BV (Bed Volume), demonstrating a high affinity and a high capacity of the resin for ferulic acid, namely 1 eq/L_R at equilibrium, consistent with supplier data [21]. Ferulate was desorbed with 10 BV of NaOH 1 M and reached 23 g/L in the eluate. Similar experiment with ferulate solution at pH 6.0 revealed a severe capacity decrease (0.16 eq/L_R at equilibrium). These preliminary results confirmed the mechanism of fixation between the carboxylic group and the tertiary amine and the necessity of performing fixation at acidic pH ≤ 3.0 . However, deceiving value of capacity was observed when a destarched wheat bran hydrolysate obtained by hemicellulase cocktails from *Thermobacillus xylanilyticus* at pH 5.0 and further acidified with HCl, was processed [21]. This was attributed to the presence of competing anions such as chlorides, sulfates or phosphates, present in the hydrolysates (due to raw material and enzymatic cocktails) and added in a large amount by acidification.

To reduce this competition and favor the fixation of ferulic acid on the anion-exchange resin to the detriment of the other anions, it is proposed in this study: (i) to acidify the hydrolysate with a strong H⁺ cation-exchange resin so as to avoid the addition of supplementary inorganic anions such as chlorides or sulfates, and (ii) to reduce the concentration of inorganic ions by electrodialysis. It is expected that these upstream operations will notably increase the capacity and the selectivity of the anion-exchange resin for ferulic acid, and consequently the concentration and the purity of the eluate, allowing further precipitation of ferulic acid via a change of pH.

Table 1
Characteristics of the resins used.

Resins	Type	Matrix	Functional groups	Form as shipped	Capacity (eq/L _R)
Amberlyst A21	WA	PS-DVB	-NR ₂	FB	> 1.3
Amberlite A252	SC	PS-DVB	-SO ₃ ⁻	Na ⁺	> 1.8

WA: weak anionic resin; SC: strong cationic resin; PS-DVB: Polystyrene-divinylbenzene; FB: free base form.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

NaOH and HCl (1M) were purchased from Carlo Erba (Val-de-Reuil, France). Monosaccharides, anions and ferulic acid standards were purchased from Sigma-Aldrich (Saint Louis, USA). Tetradecyltrimethylammonium hydroxide (OFM-OH) was purchased from Waters (Guyancourt, France). All other chemicals or reagents were at least of analytical grade and supplied by Sigma-Aldrich unless specified otherwise.

2.1.2. Resins

The main characteristics of the different resins used in the study are summed up in Table 1. Cation exchange resin Amberlite A252 (Na⁺ form) was kindly provided by Dow (Chaunay, France). It is a strong polystyrene resin with sulfonate as functional group. It was rinsed in successive baths of demineralized water, then conditioned in H⁺ form by an excess of HCl 1 M bath for 1 h, then rinsed by demineralized water until the pH was neutral. Acidification of the hydrolysates was run in batch mode.

Anion exchange Amberlyst A21 resin was purchased from Sigma-Aldrich (Saint Louis, USA): it is a weak polystyrene resin, with tertiary amines -NR₂ representing more than 85% of the functional groups. The apparent density of the resin was 273 g per liter of dry resin as measured by Fargues et al. [20]. It was rinsed in successive baths of demineralized water then poured into a glass column (Omnifit 25 cm × 0.78 cm i.d.) from Sigma-Aldrich (Saint Louis, USA) so as to get a BV of about 10 mL. It was conditioned in FB form by percolating 5 BV of NaOH 1 M at 5 BV/h and then rinsed with 5 BV of demineralized water until pH reach neutrality at the same flow. The flow was adjusted with a peristaltic pump (Minipuls 3, Gilson, Villiers-le-Bel, France) and the fractions were collected with a Gilson collector. New samples of resin were used for each new experiment.

2.1.3. Electrodialysis membranes and pilot

The electrodialysis pilot used was a TS-2-10 from Eurodia (Pertuis, France). It contained 7 cells each representing 0.02 m² effective membrane area (total effective area: 0.14 m²). Cation- and anion-exchange membranes were arranged alternately so that the repeating unit (cell) contained two compartments. Diluate compartments received the hydrolysate and concentrate compartments a 5 g/L NaCl solution. A Na₂SO₄ solution (conductivity 20 mS/cm) was circulated through the electrode compartments. To maintain temperature constant a plate heat exchanger was interposed on the electrolyte circuit and fed from a water bath at 35 °C. NEOSEPTA cation- and anion-exchange membranes (CMX and AMX, respectively) were purchased from Tokuyama Soda. Their characteristics are reported in Table 2.

2.1.4. Model solutions

Due to restricted availability of enzymatic hydrolysates, the best operating conditions for electrodialysis were first determined on a model solution containing ferulic acid (0.1 g/L), xylose (9 g/L), arabinose (0.2 g/L), NaCl (0.5 g/L), CaSO₄ (0.17 g/L), MgCl₂ (0.84 g/L),

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