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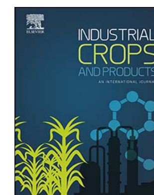

Recovery of phenols from autohydrolysis liquors of barley husks: Kinetic and equilibrium studies

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ABSTRACT

The liquid stream generated during the hydrolytic fractionation of barley husks, under conditions maximizing both the solubilisation of xylooligosaccharides and the lignin soluble fraction, was extracted with ethyl acetate to selectively separate the phenolic rich fraction. Further refining of this phenolic fraction is required to achieve a phenolic enriched product which leads to an integral valorisation of the raw material. The equilibrium and kinetics of sorption process onto Sepabeads SP-700 resins of the major components (gallic acid, 3,4-dihydroxybenzaldehyde, vanillic acid, syringic acid, vanillin and *p*-coumaric) was studied. The adsorption kinetics was found to follow a pseudo-second order model, and equilibrium could be modelled using Langmuir and Freundlich isotherms. The GC–MS analysis of the extracts desorbed by aqueous ethanol showed a final product concentrated in bioactive lignin derived phenolic and hydroxycinnamic acids.

1. Introduction

Autohydrolysis technology has been proposed for the efficient environmentally friendly fractionation of several biomass (Balboa et al., 2013; Conde et al., 2011a). The spent solid is enriched in cellulose and lignin hardly altered, while in the liquid phase a mixture of hemicelluloses oligomers, monomers and degradation products, lignin depolymerisation fractions and extractives are found. The success of a valorisation process besides its economic and practical viability depends on the commercial interest and marketing potential of the different products and by-products obtained (Conde et al., 2009).

Non-isothermal autohydrolysis of barley husks, a residue obtained during the cleaning stages in the barley malting, has been optimized to obtain i) xylooligomers with prebiotic properties, ii) monomeric sugars, which are potential carbon sources for bioconversion into biofuels and chemicals, and iii) an crude extract with up to 30% of the phenolic content and radical scavenging capacity comparable to synthetic antioxidants. The crude extract consists of derived lignin compounds (benzoic acid, gallic acid, 4-hydroxybenzaldehyde, coumaric acid, ferulic acid, vanillin, vanillic acid), products from sugar decomposition and compounds derived from the extractives which can be refined to obtain a product with enhanced antioxidant activity and phenolic concentration. A solvent fractionation followed by an adsorption-desorption process onto polymeric resins improved the phenolic content up to near 50% and the antioxidant activity equivalent to 1.64 g of Trolox (Conde et al., 2008).

Resins are widely used for the purification of solvent extracts from vegetal biomass with the aim of selectively recover target plant metabolites, suitable for specific food applications, or for the removal of undesired compounds (Conde et al., 2011b). The use of macroporous resins to phenolic fraction valorisation involve higher selectivity, easier desorption, lower solvent consumption, absence of chemical residues in the product, better mechanical strength and ability to reuse (Petrotos et al., 2016). Thus, the adsorption process is preferred because it is a low-cost separation technique, applicable for industrial scale processes, with high adsorption capacities, possible recovery of the adsorbed molecules and easy regeneration (Abdelkreem, 2013; Kammerer et al., 2011; Soto et al., 2011). Resins have been applied for the adsorption of phenolic compounds and hydroxytyrosol from olive oil mill wastewater (Agalias et al., 2007; Frascari et al., 2016; Petrotos et al., 2016, 2013), hydroxytyrosol and tyrosol from fermentation brine wastewater (Ferrer-Poloniom et al., 2016), spinacetin and patuletin from spinach leaves (Aehle et al., 2004), polyphenols from kiwifruit juice (Gao et al., 2013), limonin and naringin from orange juice (Ribeiro et al., 2002), hesperidin from orange peel (Di Mauro et al., 1999), anthocyanins from roselle (Chang et al., 2012), narirutin from a water-extract of *Citrus unshiu* peels (Kim et al., 2007), genistein and apigenin from extracts of pigeon pea roots (Liu et al., 2010), anthocyanins and hydroxycinnamates from orange juice (Scordino et al., 2005), chlorogenic acid and apigenin-7-*O*-glucoside from artichoke wastewaters (Conidi et al., 2015), catechin, epicatechin, epicatechin gallate, epigallocatechin gallate and caffeine from green tea (Jin et al., 2015; Monsanto et al.,

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2016), catechins and theaflavins from black tea (Monsanto et al., 2015). The study of plant extracts is complex due to the interactions of other plant constituents, which could has an impact on phenolic binding (Bretag et al., 2009; Kammerer et al., 2010). The use of commercial resins for detoxification of lignocellulosic acid hydrolysates has been reported (Mussatto and Roberto, 2004; Weil et al., 2002), but the recovery of the phenolic fraction has been less studied. da Costa Lopes et al. (2016) involve an integrate process of biomass fractionation focused on the extraction and separation of phenolic compounds from wheat straw using resin adsorption to recover phenolic fraction from IL samples.

The present work aims at studying the effectiveness of the non-ionic polymeric resin Sepabeads SP700 for the selective adsorption of phenolic compounds released during the autohydrolysis treatment of barley husks. The effects of adsorbent dose, initial adsorbate concentration and contact time have been studied. The pseudo-first order, pseudo-second order and Elovich model have been used to fit the kinetic data and the Freundlich and Langmuir adsorption isotherms have been used to model the equilibrium adsorption data. Mathematical modeling of the kinetics and isotherms of adsorption of barley husks phenols are necessary in order to obtain valuable information for extract purification and its feasible industrial application.

2. Materials and methods

2.1. Preparation of barley husk extract

Barley husks from a malting factory (*San Martín*, San Cibrao das Viñas, Ourense, Spain) were air-dried, milled, screened to pass 1 mm sieve, homogenized in a single lot, and stored in a dry dark place until use. The barley husks were processed by non-isothermal autohydrolysis using a liquid/solid ratio of 8 g water per gram of barley husks and up to achieve 226 °C. After cooling and filtering, the liquor stream obtained was liquid–liquid extracted twice with ethyl acetate at a liquor/ethyl acetate volume ratio of 1:3 (v:v) for 15 min. The ethyl-acetate phase was vacuum evaporated in rotaevaporator and the extract was washed with ethanol/water solutions and then freeze-dried. The final extract presented 32% d. w. phenolic content (Conde et al., 2008).

2.2. Adsorbent

The non-ionic polymeric resin Sepabeads SP700 (PS-DVB copolymers), kindly supplied by Resindion S.R.L. (Mitsubishi Chemical Corp.), has been selected on the basis of its adsorption capacity under different conditions (Conde et al., 2008). Physical properties as pore volume (2.2 mL/g), specific surface area (1200 m^2/g), mean particle size (450 μm), average pore radius (85 Å) and moisture content (65%) were provided by the manufacturer. The resin was activated by mixing with 2 BV (bed volume) of methanol, shaken for 1 min, and stirred (175 rpm, 25 °C) for 15 min. The resin was rinsed with 5 BV of deionized water before use. The moisture content of resin was determined by oven drying at 100 °C.

2.3. Batch adsorption studies

In order to characterize the resin effectiveness for phenolic compounds fractionation, the equilibrium time, the initial phenolic concentration and the effect of different resin/phenolic ratios were examined. Batch equilibrium adsorption tests were performed in 25 mL Erlenmeyer flasks containing 5 mL of the aqueous solutions of extract and weighed quantities of activated resin. The flaks were then shaken on an orbital shaker at 175 rpm at 25 °C for 20 min. All test were performed in two replicates. The concentrations of major phenolic compounds before and after adsorption were analyzed by HPLC. The phenol adsorption capacity q_t (mg/g) of resin were estimated by mass balance according to the following equation:

$$q_t = \frac{(C_0 - C_t)\,V}{W} \tag{1}$$

where q_t is the quantity (mg) of phenols adsorbed at time t onto a unit (g) of dry resin, C_0 and C_t are the concentrations of each phenolic compound in the extract solution (mg/L) at the initial stage and at t time, V is the volume of the solution added into the flask (L), and W is the weight of the dry resin (g).

The capacity of adsorption at equilibrium, q_e (mg/g resin); was calculated as indicated in equation (2):

$$q_e = \frac{(C_0 - C_e)\,V}{W} \tag{2}$$

where C_e is the equilibrium concentration of each phenolic compound in the extract solution (mg/L).

Adsorption kinetics tests were conducted by mixing 3 g (wet weight) of resin, with 5 mL of aqueous solutions of extract in flasks under the above conditions.

Adsorption isotherms at 25 °C were carried out by mixing a known amount of SP700 resin with 5 mL sample solutions at various initial concentrations in a constant temperature shaker.

2.4. Desorption and regeneration of activated resin

Static desorption was carried out under conditions previously optimized (Conde et al., 2008). The desorbed extract was freeze-dried and then dissolved in water for analyze by HPLC and GC–MS. The resin regeneration procedure consists on leaving the resin overnight in 1 M NaOH and further washing with deionized water.

2.5. Analytical methods

The total phenolic content was determined by the Singleton and Rossi (1965) method and data expressed as mg of GAE (Gallic Acid Equivalents) per liter.

2.5.1. HPLC

Quantification of individual phenolic compound was performed using an Agilent HPLC 1100 instrument equipped with a Supelcosil LC18 column and a DAD detector, operating with a flow rate of 1 mL/min. The injection volume was 20 μL. A non-linear gradient of solvent A (CH_3OH:H_2O:CH_3COOH, 10:89:1, v:v:v) and solvent B (CH_3OH:H_2O:CH_3COOH, 90:9:1, v:v:v) was used. Elution gradients were used as follows: 0 min, 100% A, 0% B; 30 min, 60% A, 40% B; 40 min, 60% A, 40% B; 42 min, 100% A, 0% B. Quantification was performed at the corresponding wavelengths of maximum adsorption (270 nm (gallic acid), 280 nm (3,4-dihydroxybenzaldehyde, syringic acid, vanillin, *p*-coumaric acid) and 254 nm (vanillic acid)), by comparison with previous calibration curves prepared using the respective reference compound.

Acid hydrolysis of crude extract was carried out by adding sulfuric acid to the samples to reach 4% (weight basis), and the solutions were kept for 30 min at 121 °C in stirred reactors to transform the glycosylated and esterified phenolics into their aglycons.

2.5.2. Conditioning of samples for GC–MS

About 0.25 mL of 3-octanol (10 ppm) was added as internal standard into 25 mL of a diluted extract solution (0.5 g extract/L). This mixture was extracted with 2.5 mL of dichloromethane (DCM) for 5 min at 600 rpm, the organic phase was removed and the aqueous phase was again extracted twice with 1.25 mL of DCM under the same conditions. The total organic phase was transferred to a graduate glass tube and concentrated with nitrogen stream up to a final volume of 0.5 mL.

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