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The chemical composition of exhausted coffee waste

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ABSTRACT

The chemical composition of exhausted coffee waste generated in a soluble coffee industry was investigated. The chemical characterization included elemental analysis, mineral composition and ash content, summative composition; acidic functional groups, lipophilic extractives, total polyphenols, condensed tannins determination and FTIR analysis. The spent coffee samples showed high carbon (>58%), low nitrogen (<2%), and low ash (<1%) contents and low polarity coefficient (O + N)/C (<0.5). The summative composition reveals that extractives are the main components of exhausted coffee wastes (54%). This percentage includes lipophilic fractions (24%), ethanol and water soluble compounds (5%), and compounds solubilized in 1% NaOH (26%). Lignin and polysaccharides were found in a similar proportion between 20 and 26%. The GC analysis of monosaccharide showed about 60% glucose and 40% mannose. The main components in the lipophilic extractives are free fatty acids (>60%) of which more than 30% was identified to be n-hexadecanoic acid. Total polyphenols and tannins represent <6% and <4% of the exhausted coffee wastes, respectively. Assignments of the bands of the obtained FTIR spectra confirm the presence of lipids, polysaccharides and chlorogenic acid. Exhausted coffee wastes showed characteristics for various potential applications such as biodiesel production, as a source of antioxidants and as a biosorbent of hydrophobic pollutants.

1. Introduction

Soluble coffee has seen a significant rise in its production and consumption during the last decades. For instance, in Spain, the Coffee Spanish Federation reported an increase of around 4% in coffee consumption between 2009 and 2010. In 2010, 18.5% of the 177.5 thousand tons of green coffee consumed in Spain were used to make soluble coffee (Federación Española del Café, 2013).

In the process of soluble coffee production, the solid residue that results from coffee extraction is pressed and dried. This residue represents approximately 50% of the input mass of coffee feedstock (Tsai et al., 2012). Thus, a large amount of residue is annually generated in the production of soluble coffee. This requires from the industries involved the development of a wastes management plan consistent with the existing national regulations. In most of the soluble coffee production industries, the waste is collected by specialized agencies which sell the residues for different purposes (i.e. composting, gardening, bioenergy production, mushroom growth, etc.).

The spent coffee waste contains large amounts of organic compounds (i.e. fatty acids, lignin, cellulose, hemicellulose, and other polysaccharides) that justify its valorization. Some researchers have investigated spent coffee waste as a bioresource for various valuable compounds. Thereby, coffee residue has been investigated for biodiesel production (Caetano et al., 2012), as source of sugars (Mussatto et al., 2011a), as precursor for production of activated carbon (Kante et al., 2012; Pappa et al., 2012; Reffas et al., 2010; Tsai et al., 2012), as compost (Preethu et al., 2007), and as sorbent for metal ions removal (Fiol et al., 2008; Oliveira et al., 2008).

Due to the heterogeneous nature of coffee waste, most of the authors investigating its possible valorization carried out a selective fractionation of the coffee waste to analyze and determine the content of specific components, such as lignin, cellulose (Caetano et al., 2012; Tsai et al., 2012); tannins and total polyphenols (Anesini et al., 2008; Zhang et al., 2010). Mussatto et al. (2011a) reported the content of sugars and ashes; and ashes mineral composition in spent coffee waste. Some of these authors used one of more analytical procedures reported in the literature for the fractionation of lignocellulosic materials (Pereira, 2007).

Nevertheless, up to our knowledge none of the above referred authors reported (1) the composition of the liquid extracts obtained in each of the sequential extractions, and (2) a complete and integrated chemical characterization of coffee waste.

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In this work, the chemical composition of two exhausted coffee wastes from a soluble coffee production industry has been investigated with an integrated approach. The chemical characterization includes elemental analysis, acidic functional groups determination, mineral composition and ash content, Fourier Transform-Infrared (FTIR) spectroscopy, summative chemical composition, as well as the analysis of total polyphenols, condensed tannins, and lipids in the different liquid extracts.

The data obtained in this work will be essential to assess the potential use of this waste material as a source of high-added value compounds suitable for different applications.

2. Materials and methods

2.1. Samples

Exhausted coffee (EC) samples were kindly supplied by a company dealing on soluble coffee production. Two samples (EC1 and EC2) of coffee solid residue obtained after coffee extraction were characterized. The samples were collected from production batches of Spring 2011 (EC1) and Autumn 2011 (EC2). The samples were washed with distilled water, dried and sieved for a particle size of 0.25–0.45 mm.

2.2. Elemental analysis

The elemental analysis (C, H, N and S) of coffee samples was determined using a PerkinElmer EA2400 series II Elemental Analyzer. Oxygen content was calculated by difference. N and S detection limits were 1.20% and 0.44%, respectively.

2.3. Acidic groups on the EC surface determination

Acidic surface properties of the coffee samples were determined by the Boehm method (Psareva et al., 2005). Acidic groups can be selectively determined by neutralization with 0.1 M solutions of $NaHCO_3$, Na_2CO_3, and NaOH: strong-acid carboxyl groups are neutralized by $NaHCO_3$; weak-acid groups (i.e. carboxylic, lactonic and enolic) are neutralized by Na_2CO_3; NaOH consumes all those groups. Thus, the difference between NaOH and Na_2CO_3 consumption corresponds to the weakly acidic phenolic groups.

2.4. Chemical summative composition

The chemical summative analyses of EC included the determination of extractives soluble in solvents with different polarity, Klason and acid-soluble lignin, and monomeric composition of polysaccharides.

Extractives were obtained after successive extractions with dichloromethane (99.99% Fisher), ethanol (96% Aga) and water (Milli-Q) in a Soxtec extractor for 1.5 h with each solvent. The mass of extractives solubilized by each solvent was determined by the difference between the initial mass of dry coffee sample (2.2 g) and the mass of the solid residue obtained after extractions dried at 105 °C. Results are reported as a percentage of original samples mass.

The alkaline lixiviation with 1% NaOH of the extractive-free EC samples was performed in a stirred glass reactor with reflux using 1.0 g of material with a 1:50 solid:liquid ratio (g/mL), at 100 °C during 1 h.

Klason (TAPPI 13 m – 54) and acid-soluble (TAPPI UM 250) lignin, and carbohydrates content were determined after 1% NaOH extraction. Sulphuric acid (72%, 3.0 mL) was added to 0.35 g of extracted sample and the mixture was placed in a water bath at 30 °C for 1 h. After this time, the sample was diluted to a concentration of 3% H_2SO_4 and hydrolysed for 1 h at 120 °C. The sample was vacuum filtered through a crucible and washed with boiling purified water. Klason lignin was determined by the mass residue after drying at 105 °C. Acid-soluble lignin was determined on the combined filtrates by measuring the absorbance at 205 nm using a UV–vis spectrophotometer. Measurements of Klason and acid-soluble lignin were combined to give the total lignin content.

The polysaccharides were calculated based on the amount of the neutral sugar monomers released by total hydrolysis. The hydrolysed carbohydrates were derivatized as alditol acetates and separated by gas chromatography (GC) (HP5890A) equipped with a FID detector, using helium as carrier gas (1 mL/min) and a fused silica capillary column S2330 (30 m × 0.32 mm ID; 0.20 μm film thickness). The column program temperature was 225–250 °C, with 5 °C/min heating gradient, and the temperature of injector and detector was 250 °C. For quantitative analysis the GC was calibrated with pure reference compounds and inositol was used as internal standard in each run (method adapted from TAPPI 249 cm-00).

All determinations were made in duplicate aliquots.

2.5. Ash content and composition

Ash content was determined according to TAPPI Standard T 15os-58. 1 g dry EC was placed in an oven at 500 °C for 24 h. The ashes were extracted with three successive extractions with 3 M HCl (10 mL). Elemental composition was determined by Atomic Absorption Spectroscopy (Pye Unicam SP-9 equipped with a graphite furnace GF95).

2.6. Total polyphenol determination

The total polyphenol content (TPC) was determined in the liquid extracts after the extractions with ethanol, water and 1% NaOH. TPC was determined by spectrophotometry, using gallic acid as standard according to the Folin–Ciocalteu assay. The method was adapted from Pereira (1981). The calibration curve was obtained by preparing different concentrations of gallic acid within the range 0.1–0.6 mg L^{-1}. Briefly, a 100 μL aliquot of extracts, the gallic acid standard solutions (0.1–0.6 mg L^{-1}) and a blank (deionized water) were put in different tubes. Then, 4 mL of the Folin–Ciocalteu's phenol reagent diluted 1:10 were added to each tube, the tubes were shaken and allowed to react for 5 min. After this time, 4 mL of 7.5% Na_2CO_3 solution was added. After incubation of the mixture in a thermostatic bath for 15 min at 45 °C, the absorbance against a blank was determined spectrophotometrically at 765 nm (Hitachi U-2000 VIS/UV spectrophotometer). Total phenolic content was expressed as milligrams of gallic acid equivalents (GAE) per 100 g dry mass. All samples were analyzed in triplicate.

2.7. Condensed tannins determination

The total tannins content was determined in the same extract used for the total polyphenolic compounds determination. The method was also adapted from Pereira (1981). Condensed tannins were separated from the liquid extract by precipitation with a 0.04% methyl cellulose solution in deionized water. To precipitate the condensed tannins, 1 mL of extract was put into contact with 1 mL of 0.04% methyl cellulose, 0.8 mL of saturated sodium ammonium solution and 2.5 mL deionized water. After 20 minutes, the solution was filtered and total polyphenol content in the filtrates was determined by following the same procedure described in section 2.6. The difference between total polyphenols content and polyphenols determined after precipitation with methyl cellulose corresponds to the condensed tannins fraction. Samples were analyzed in triplicate.