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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.

Table 1
Elemental analysis, atomic ratios and acidic groups of two exhausted coffee wastes (EC1 and EC2).

	EC 1	EC 2
Elemental composition (%)		
C	57.16	59.77
H	7.17	7.57
N	1.18	1.32
Atomic ratios		
H/C	1.51	1.52
O/C	0.45	0.39
C/N	56.51	52.83
(O + N)/C	0.47	0.41
Acidic groups (mmol g^{-1})		
all groups	1.69	1.27
strong carboxylic groups	0.56	0.36
weak groups	~0	~0
phenolic groups	1.13	0.95

2.8. Lipophilic extractives composition

Aliquots of the dichloromethane extracts (1–5 mL) were filtered through Anatop 10 membranes (pore dimensions 0.2 μm, Merck). The filtrate was evaporated under N_2 flow and dried under vacuum at room temperature. The residues were dissolved in 250 μL of pyridine per mg of dry mass and the compounds containing hydroxyl and carboxyl groups were trimethylsilylated into trimethylsilyl (TMS) ethers and esters, respectively, by adding 250 μL of bis(trimethylsily)-trifluoroacetamide. The reaction mixture was carried out for 30 min in an oven heated at 60 °C.

The final extracts were analyzed by GC performed with an Agilent 5973 MSD gas chromatograph coupled to a mass spectrometer. The separation was achieved using a DB5-MS column (30 m length, 0.25 mm I.D., 0.25 μm film thickness), injector temperature 320 °C, oven temperature program, 100 °C (5 min), rate of 8 °C/min up to 250 °C, rate of 2.5 °C/min up to 320 °C (20 min). The MS source was kept at 220 °C and the electron impact mass spectra (EIMS) taken at 70 eV of energy.

The compounds were identified as TMS derivatives by comparing their mass spectra with data from a GC–MS spectral library (Wiley, NIST), and their fragmentation profiles with published data (Eglinton and Hunneman, 1968; Kolattukudy and Agrawal, 1974). For semi-quantitative analysis, peak area integration with total area detected normalized to 100% was used to calculate the different components content, expressed as percentages.

All the experiments and GC-MS analysis were performed in duplicate and the average results are presented in this work.

2.9. Fourier transform infrared ray (FTIR) analysis

FTIR analysis was used to identify the functional groups on the EC samples surface. Spectra were recorded in KBr pellets using a Galaxy 5000 FTIR spectrometer (Mattson Instrument Co., Madison, WI). To prepare the pellets 2 mg of coffee samples was grinded for 1–2 min together with 200 mg of KBr (FT-IR grade, Acros Organics). The FTIR spectra were measured in the 3500 to 400 cm^{-1} range by co-addition of 32 scans with a resolution of 2 cm^{-1}.

3. Results and discussion

3.1. Elemental analysis

Elemental analysis of EC1 and EC2 samples and their atomic ratios are shown in Table 1. The percentage of the different elements (on average C: 58.5, H: 7.4, N: 1.3) is within the range of values reported in the literature for spent coffee (Bizzo, 2003). Compared to other materials used for composting, EC waste samples show a lower nitrogen content (<2%) and consequently a higher C/N ratio (Droussi et al., 2009; Preethu et al., 2007). The low value of nitrogen limits the use of this material as compost although it would be possible to add inorganic nitrogen (ammonium phosphate) or other organic sources of nitrogen such as green weeds, forest litter, or micronutrients to improve the quality of the compost (Preethu et al., 2007; Pazhanivelan et al., 2006).

Atomic ratios exhibited by both studied EC samples are similar with the exception of H/C elemental ratio. The slightly higher H/C ratio of EC2 indicates a higher aliphatic character of this sample as compared to that of EC. The polarity coefficient (O + N)/C is an important parameter inversely correlated with the aromatic character of the sample. The polarity coefficients found for both samples (on average 0.44) are closer to the polarity range of some commercial lignins (0.33–0.65) than to that of cellulose and chitin (0.84–1.94) (Rodríguez-Cruz et al., 2007; Wang and Xing, 2007; Xing et al., 1994). A negative correlation between this coefficient and the hydrophobic pollutants sorption was also reported (Rutherford et al., 1992; Xing et al., 1994). Lignins have predominantly aromatic carbons and their affinity for hydrophobic pollutants is much higher than that of chitins and celluloses (Wang and Xing, 2007).

These results suggest that coffee waste due to their high aromatic character could be an effective sorbent for the removal of hydrophobic pollutants. The polarity coefficients of the studied EC samples found in this work are higher than those of the humic-acid-like compounds during composting of olive mill by-products (i.e. 0.19–0.34) (Droussi et al., 2009) and similar to those found for raw cork by-products (i.e. 0.33–0.61) (Olivella et al., 2013) that also showed high affinity for polycyclic aromatic hydrocarbons sorption (Olivella et al., 2011).

3.2. Acidic compounds

As seen in Table 1, the main acidic compounds of EC1 and EC2 are phenolic groups which are mostly located in lignin and extractives. The sum of phenolic and strong acidic groups is higher in EC1 than in EC2 and none of the tested samples show weak acidic compounds (i.e. carboxylic, lactonic and enolic). The amount of total acidic groups of exhausted coffee samples are in the range of values reported for mango pit husk (1.38 mmol g^{-1}) (Elizalde-González and Hernández-Montoya, 2007), slightly lower than those for *Quercus suber* cork samples (1.1–1.80 mmol g^{-1}) (Olivella et al., 2013) and much lower than those for mango pit/seed (3.15 mmol g^{-1}) (Elizalde-González and Hernández-Montoya, 2007).

3.3. Summative chemical composition

The results obtained for the summative chemical composition of the EC waste samples (EC1 and EC2) are shown in Table 2. As seen, the total content of extractives, including the compounds solubilized by the 1% NaOH treatment is very high and similar in both coffee samples. A large proportion of the extractives correspond to non-polar compounds that are soluble in dichloromethane. The content of lipids in EC is higher than oil content in maize seeds (3.75%) (Ali et al., 2010) and in cherry seeds (8.70%) (Duman et al., 2011), similar to the percentage of oil in *Parkia biglobbossa* (26.52%) and lower than that in *Jatropha curcas* seeds (47.25%) (Akintayo, 2004).

Polar compounds extracted by ethanol and water, which include especially phenolic and polyphenolic compounds (Miranda et al., 2013), correspond to a lower proportion of the extractives total content, and amount to 6.7% in EC1 and 4.3% in EC2.

As regards the extraction with 1% NaOH, it must be remarked that not only tannins and other polyphenols insoluble in water and

Table 2
Summative chemical composition (% oven dry mass) and monosaccharide composition (% of the total neutral monosaccharides detected by GC) of two exhausted coffee wastes (EC1 and EC2).

Composition	EC1 (%w/w)	EC2 (%w/w)
Total extractives	51.43	55.78
Dichloromethane	19.67	25.41
Ethanol	5.36	3.42
Water	1.30	0.89
NaOH 1%	25.10	26.06
Total lignin	26.51	19.84
Klason lignin	22.71	16.67
Soluble lignin	3.80	3.17
Polysaccharides[a]	22.00	24.13
Glucose	59.20	62.94
Mannose	40.80	37.06

[a] Polysaccharides include only the neutral monosaccharides.

ethanol are extracted but molecules of high molecular weight such as lignin and polysaccharides can be also found in the extract. In this case the more chemically labile moieties are either cleaved or solubilized in this alkaline medium especially when more drastic alkaline conditions (i.e. 100 °C) are used (Fradinho et al., 2002).

As it is shown in Table 2, the solubilization by 1% NaOH represents a significant proportion of the EC samples. The percentage of alkaline bark extract obtained from a maritime pine from Portugal using the same temperature but different time and NaOH concentration (2% NaOH, 0.5 h) was lower (11%) than those obtained in this study (Fradinho et al., 2002).

The high content in EC wastes of such extractives of phenolic character opens expectations for applications like the production of wood adhesives, biocides, pharmaceuticals or leather tanning (Atanassova et al., 2011; Fernandes et al., 2009; Mazimba et al., 2011; Pizzi, 1991). It is clear that for such specific applications the components in the alkaline extracted material should be deeply investigated.

The total lignin content was 26.5% and 19.8% in EC1 and EC2, respectively. While the soluble lignin content was similar in both samples, Klason lignin content was higher in the EC1 sample and EC2 showed a lower lignification of the cell wall. In the literature, 31.9 and 1.7% Klason lignin and soluble lignin, respectively, were reported for spent coffee grounds (Caetano et al., 2012); 39.4% total lignin for exhausted coffee residue (Tsai et al., 2012), and 38.6 and 39.4% total lignin for coffee pulp and coffee husk, respectively (Preethu et al., 2007).

It should be noted that in this work lignin determination was made on the alkali extracted material, which otherwise would increase the lignin values. In other materials, such as barks of different species, Klason lignin values are reported within the range 23.4–27.1% (Kofugita et al., 1999), for *Picea abies* and *Pinus sylvestris* barks as 26.8 and 32.9%, respectively (Miranda et al., 2012) for *Quercus suber* cork from 21 to 23% (Pereira, 2007) and 27% for *Quercus cerris* cork (Şen et al., 2010).

The polysaccharides were calculated based on the amount of total neutral sugar monomers released by total hydrolysis and resulted to be 22.0 and 24.1% in EC1 and EC2 samples (Table 2). The carbohydrate composition of EC waste is reduced to only two monomers: glucose (59.2 and 62.9% of total sugars) and mannose (40.8 and 37.1%) for EC1 and EC2 samples, respectively. Glucose is the building monomer of cellulose. As regards hemicelluloses, the results obtained in this study contrast with those reported in the bibliography that showed that galactose and arabinose were also present in the spent coffee grounds (Mussatto et al., 2011b; Simões et al., 2009). These two monomers were not present in the studied spent coffee samples and a possible explanation is that these monosaccharides, that are more easily hydrolysed, were dissolved in the alkali extraction.

Table 3
Elemental constituents of ashes of two exhausted coffee wastes (EC1 and EC2).

Elements	EC1 (g/kg)	EC2 (g/kg)
Ca	0.771	0.498
Mg	0.178	0.073
K	0.253	0.215
Na	0.329	0.627
Fe	0.326	0.147
Cu	0.046	0.039
Zn	0.012	0.010
Mn	0.033	0.029

3.4. Ashes and mineral composition

The ash contents of the studied EC samples were lower compared with the range of values reported for spent coffee (0.4–1.6%) (Caetano et al., 2012; Lago et al., 2001; Mussatto et al., 2011b). The low amount of ashes together with the high content of carbon and hydrogen make these EC samples suitable as energy source. The calorific values calculated following the method reported by Van Loo and Koppejan (2008) are relatively high, up to 26 MJ/kg dry weight basis. This value is similar to the reported values by Bizzo (2003) (i.e. 21.8–26.9 MJ/kg) and lower than the one reported by Caetano et al. (2012) (4629 MJ/kg) for spent coffee grounds. The calorific value found for EC in this study is also comparable to those reported for other agricultural by-products (Gravalos et al., 2010).

The concentration of major mineral elements (i.e. Ca, K, Mg and P) in the exhausted coffee ashes is presented in Table 3. Calcium and sodium are the most abundant elements in EC1 and EC2 samples. Significant differences of mineral compositions were found between the two spent coffee samples: EC1 contains higher concentration of Ca, Mg, and Fe and lower concentration of Na than EC2, and both samples exhibit similar concentration of K, Cu, Zn and Mn. The reported trends for the major constituents of spent coffee grounds are: K > P > Mg (Mussatto et al., 2011b) and K > Mg > P > Ca (Tsai et al., 2012), while Ca > Na > Fe > K is the trend found in the present study. Differences of spent coffee mineral composition must be attributed to the soil and the fertilizers used in the cultivation of coffee varieties (Hombunaka and Rowell, 2002; Laviola et al., 2007). This diversity should be taken into account when assessing the potential of the spent coffee wastes as feedstock.

3.5. Total polyphenols and condensed tannins content

The content in total polyphenolic compounds and in condensed tannins was analyzed in the ethanol, water and 1% NaOH liquid extracts of EC1 and EC2. The results, expressed as percent of gallic acid equivalent (GAE), are presented in Table 4. The highest content in polyphenolic compounds in the ethanol and water liquid extracts was found in EC1. It must be pointed out that about 80%, 100% and 60% of the total polyphenolic compounds found in the EtOH, H_2O and 1% NaOH extracts, respectively, are condensed tannins. The

Table 4
Total polyphenols content and condensed tannins expressed in percentage of mass of gallic acid equivalents (GAE) in different extracts of two exhausted coffees (EC1 and EC2).

	EC1	EC2
Polyphenolic compounds (%GAE w/w)		
EtOH	1.23	0.75
H2O	0.34	0.17
NaOH	4.22	4.54
Condensed tannins (%GAE w/w)		
EtOH	0.97	0.61
H2O	0.34	0.17
NaOH	2.47	2.93

Table 5
Composition of dichloromethane extracts of two exhausted coffees (EC1 and EC2), in % of the chromatographic peak areas compounds detected by GC-MS.

Compound	EC1 (%)	EC2 (%)
Hydrocarbons	0.56	3.14
Tetracosane	0.42	1.76
Nonadecane	0.14	1.38
Saturated fatty acids	69.73	62.57
n-Hexadecanoic acid	48.93	37.97
n-Octadecanoic acid	10.41	9.92
n-Eicosanoic acid	4.48	5.51
9,10-dihidroxyoctadecanoic acid	0.15	2.49
2,3-dihidroxyhexadecanoic acid	4.84	4.66
n-Docosanoic acid	0.92	2.02
Unsaturated fatty acids	18.32	12.61
octa-9,12-dienoic acid	10.46	6.04
n-oleic acid	7.52	5.55
2-Butenedioic acid	0.34	1.02
Benzoic acids	1.09	1.27
1,4-Benzenedicarboxylic acid	1.09	1.27
Sterols	0.49	3.11
Stigmasterol	0.19	1.35
b-Sitosterol	0.30	1.76
Other compounds[a]	9.81	17.30

[a] Components that are present in the extract in a percentage lower than 1%.

condensed tannins are a source for tanning chemicals of hides or for wood adhesives (Vázquez et al., 1992).

Exhausted coffee shows a low tannin content as compared to other plants such as leaves of *K. candel* and *R. mangle* (106 mg/g and 219 mg/g, respectively) (Zhang et al., 2010). Polyphenols content found in the exhausted coffee samples is also low compared to green tea (14–21% GAE) (Anesini et al., 2008) but higher than that of the reported for peas (1.09 mg/g) (Chavan et al., 2001). The extraction yields of polyphenolic compounds found for the exhausted coffee samples in relation to the total extracted material open a path for further studies on EC waste valorization as natural source of antioxidants.

3.6. Lipophilic extractives

The results of the GC–MS analysis of dichloromethane liquid extracts are shown in Table 5. As seen, the extracted components include hydrocarbons, fatty acids, a benzoic acid and sterols. The predominant compounds in the lipidic fraction of exhausted coffee are fatty acids, which account for 88.1% and 75.2% in EC1 and EC2, respectively. The fatty acids are in the range from C_{16} to C_{22}, and the predominant component is n-hexadecanoic acid (C_{16}) followed by 9,12-octadienoic acid ($C_{18:2}$), n-octadecanoic acid (C_{18}) and oleic acid ($C_{18:1}$).

It is important to remark that the most common fatty acids in biodiesel are those of C_{16} and C_{18}. Therefore, the results found in this work for lipids composition are a starting point to evaluate the use of coffee waste for biodiesel production in the future. Caetano et al. (2012) evaluated the quality of biodiesel produced from spent coffee grounds and found that the oil parameters did not comply with the standard limits set by the European Standard NP EN 14214:2009.

Minor amounts of n-alkanes (<3%), benzoic acids (<1.5%) and sterols (<3%) were also identified in the EC samples. There is no bibliography on chemical composition of lipophilic extractives of spent coffee grounds. Martín et al. (2001) who studied the fatty acid profiles in the lipid fraction of green and roasted coffee beans of several coffee varieties reported that linoleic acid (9,12-octadienoic acid) and palmitic acid (n-hexadecanoic acid) were the most predominant components, followed by oleic ($C_{18:1}$) and stearic ($C_{18:0}$) acids. These results are in agreement with the trend found in the present study.

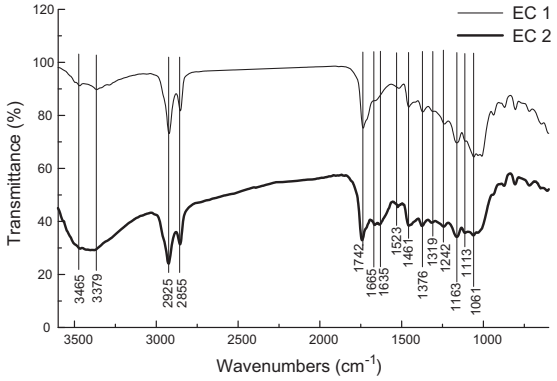

Fig. 1. FTIR spectra of two exhausted coffee wastes (EC1 and EC2).

3.7. FTIR analysis

The FTIR spectra obtained for the exhausted coffee samples are shown in Fig. 1. The broad band at about 3400 cm^{-1} included many vibration modes mainly attributed to —OH groups with a minor contribution of —NH functional groups (Kante et al., 2012). This band is more pronounced in EC2 than in EC1.

The presence of methyl and methylene groups is confirmed by the two sharp peaks at 2925 cm^{-1} and 2855 cm^{-1} attributed to asymmetric and symmetric stretching of C—H bonds in aliphatic chains. These peaks have been previously identified in roasted coffee and attributed to the presence of caffeine (Craig et al., 2012). The same peaks have been attributed to the presence of lipids in corn and corn flour (Cremer and Kaletunç, 2003). Given that the EC1 and EC2 samples are residues from coffee extraction in which most of the caffeine has been already extracted, these peaks can likely be attributed to lipids which are present in the coffee samples in a large amount. The sharp band at 1742 cm^{-1} is associated to the carbonyl vibration (C═O) in aliphatic esters (Lyman et al., 2003) or in triglycerides (Kemsley et al., 1995). Therefore, this band can be attributed to lipids. The low intensity bands at 1665 cm^{-1} and 1523 cm^{-1} are due to C═C vibration of lipids and fatty acids, and C═C vibration of aromatic rings from lignin moieties, respectively (Wang and Lim, 2012). The band at 1665 cm^{-1} can be also ascribed to the carbonyl stretching from lignin moieties (Herbert, 1971). The band at 1461 cm^{-1} corresponds to C-H bending of CH_3 groups. The bands of exhausted coffee spectrum at 1061, 1113, 1163, 1242, 1376 cm^{-1} could be attributed to chlorogenic acids which are a large family of esters formed by quinic acid and certain trans-cinnamic acids (Clifford et al., 2008). Axial C—O deformation of the quinic acid occurs in the range 1085–1050 cm^{-1}, O—H angular deformation occurs between 1420 and 1330 cm^{-1} and C—O—C ester bond absorbs in the 1300–1000 cm^{-1} range (Silverstein et al., 2005). The region 900–1400 cm^{-1} also exhibit several types of vibrations including C—H, C—O—C, C-N and P-O characteristic of polysaccharides (Haussard et al., 2003). FTIR spectroscopy cannot distinguish the bands corresponding to chlorogenic acids from those of polysaccharides, and a chromatographic analysis should be applied to detect the presence of chlorogenic acids. Chlorogenic acids are an important group of phenolic compounds which contribute to coffee flavor and are of potential biopharmacological importance for humans (Farah et al., 2006).

4. Conclusions

A complete chemical characterization of two samples of exhausted coffee was performed in this study. The high content of extractives (>50%) opens new expectations for industrial applications. The presence of high concentrations of n-hexadecanoic and

n-octadecanoic acids in the lipophilic extracts would justify further investigation on biodiesel production based on coffee wastes. The high ratio of polyphenolic compounds in relation to the total extracted material also envisages a potential source of antioxidants.

Furthermore, the low polarity coefficient values of exhausted coffee samples suggest their potential use as sorbent for hydrophobic pollutants.

As a final remark, the results of this research show the importance of characterizing abundant residues as an essential step to find out potential uses for their further valorization.

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