Journal of Cleaner Production xxx (2012) 1–8

Contents lists available at SciVerse ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Spent coffee grounds as a valuable source of phenolic compounds and bioenergy

Antonio Zuorro, Roberto Lavecchia*

Department of Chemical Engineering, Materials & Environment, "La Sapienza" University, Via Eudossiana 18, 00184 Rome, Italy

ARTICLE INFO

Article history:
Received 15 August 2011
Received in revised form
30 November 2011
Accepted 2 December 2011
Available online xxx

Keywords:
Biomass
Energy production
Phenolic compounds
Solvent extraction
Spent coffee grounds

ABSTRACT

Spent coffee grounds collected from coffee bars (SCG-1) or recovered from coffee capsules (SCG-2) were investigated as a potential source of phenolic compounds and energy. Preliminary characterization of these materials provided a total phenolic content of 17.75 mg GAE/g for SCG-1 and 21.56 mg GAE/g for SCG-2. A solvent-extraction procedure using aqueous ethanol as the solvent and operating under mild temperature conditions was developed and tested. A two-level factorial design was used to study the effects of temperature ($T = 30–50$ °C), extraction time ($E = 60–120$ min), liquid-to-solid ratio ($R = 20–40$ mL/g) and ethanol concentration in the aqueous mixture ($C = 30–70$ vol%) on the recovery of phenolic compounds. Under the best conditions, over 90% of the phenolic compounds contained in the starting waste materials were recovered. *T*, *R* and *C* were the most influential factors and all of them had a positive effect on the extraction efficiency.

The calorific values of the two coffee wastes were 23.72 MJ/kg (SCG-1) and 24.07 MJ/kg (SCG-2). They were only marginally affected by the extraction procedure, which supports the possibility of integrating the recovery of phenolic compounds with the use of the resulting solid residue to produce pellets or other agglomerates for heating purposes. A case study application aimed at evaluating the potential valorization of the spent coffee produced in the Province of Rome is also presented.

1. Introduction

Coffee is the most important agricultural commodity in the world and is second only to petroleum in global trade activity and value (Njoroge et al., 2005). According to the International Coffee Organization (ICO, 2009), about 120 million bags of coffee are produced annually worldwide, corresponding to over 7 million t of coffee beans per year. Of the several species in the genus Coffea (Rubiaceae), only *Coffea arabica* and *Coffea canephora* var. *robusta* are cultivated for commercial production. They are commonly referred to as Arabica and Robusta, with the former accounting for 70–75% of the total production (Wintgens, 2009). Arabica is grown at altitudes over 1000 m and is considered to be of superior quality because of the milder and more flavorful taste developed by the beans during roasting (Bertrand et al., 2003). The Robusta variety is mostly used by the instant coffee industry for producing soluble coffee extracts (Clarke and Vitzhum, 2001).

During the preparation of a coffee beverage or the manufacturing of instant coffee, raw coffee powder is contacted with hot water or steam under conditions favoring the release of aroma compounds and other coffee-bean constituents into the liquid. From these operations, a solid residue known as spent coffee grounds (SCG) is produced. SCG have no commercial value and are usually discarded as solid waste or, to a very limited extent, sent to compost facilities. In recent years, however, the increasing awareness of the need for waste reduction and environmental protection has stimulated the search for possible methods of using this waste.

Most research efforts have been devoted to the direct use of SCG rather than the recovery of potentially valuable components from it. In particular, some studies have highlighted the possibility of using SCG to remove basic dyes (Franca et al., 2009) or heavy metal ions (Tokimoto et al., 2005; Utomo and Hunter, 2006; Zuorro and Lavecchia, 2010) from contaminated waters. For metal ions, the order of adsorption capacity was Cd^{2+} gt; Zn^{2+} gt; Pb^{2+} gt; Cu^{2} and the effectiveness of metal removal was higher between pH values of 4 and 10 (Utomo and Hunter, 2006). These properties seem to be closely related to the presence of phenolic compounds with metal-chelating properties and to the protein content.

Another application exploiting the ability of SCG to bind metal ions is the use of Fe-treated SCG to increase Fe availability to plants in neutral to alkaline soils (Morikawa and Saigusa, 2008). According to the authors, the Fe-containing material can be prepared easily by adding appropriate amounts of a soluble ferric compound to SCG and composting the resulting material. In a reported example, dried

* Corresponding author. Tel.: +39 06 44585598; fax: +39 06 4827453.
E-mail address: roberto.lavecchia@uniroma1.it (R. Lavecchia).

0959-6526/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jclepro.2011.12.003

SCG and ferrous sulfate ($FeSO_4 \cdot 7H_2O$) were mixed in a ratio of 4:1 by weight and composted in plastic bags at 60 °C for 60 days.

Kondamudi et al. (2008) investigated the suitability of SCG for producing a biofuel product. The method consists of a preliminary extraction of oil from the spent material, followed by transesterification of triglycerides to fatty acid methyl esters. The biodiesel obtained by this procedure was approximately 51% saturated methyl esters and was stable for more than one month at ambient temperature.

The possibility of using SCG, alone or in combination with other coffee byproducts, as a substrate for the production of α-amylase by solid-state fermentation has also been assessed (Murthy et al., 2009). The authors used a strain of the fungal species *Neurospora crassa* isolated from coffee waste to carry out the fermentation process. All of the waste types examined were capable of inducing the production of α-amylase, with coffee pulp and a mixed waste made up of coffee pulp, husk, silverskin and SCG in equal proportions being the most effective. A steam pretreatment of the waste promoted waste digestibility, probably as a result of the degradation of hemicellulose and lignin induced by thermal effects (Hendriks and Zeeman, 2009).

The use of SCG as a potential source of bioactive compounds, particularly polyphenols, is another promising but as yet little-explored approach, at least from a technological point of view (Esquivel and Jiménez, 2011). As evidenced in a recent review by Dai and Mumper (2010), plant polyphenols are receiving increasing attention from the scientific and medical communities due not only to their potent antioxidant properties but also to their ability to intervene at many stages of cancer development. Coffee beans and SCG contain large amounts of chlorogenic acid and its derivatives such as caffeoylquinic acids, feruloylquinic acids, p-coumaroylquinic acids and mixed diesters of caffeic and ferulic acids with quinic acid (Farah and Donangelo, 2006). These compounds, which are collectively referred to as chlorogenic acids, are powerful in-vitro antioxidants (Yen et al., 2005; Brezová et al., 2009) and are believed to provide many health benefits (Rawel and Kulling, 2007). Pharmacokinetic studies have demonstrated that about one-third of ingested chlorogenic acids are absorbed in the stomach and proximal duodenum, while the remaining are cleaved by the gut microflora into caffeic and quinic acids (Rechner et al., 2002; Stalmach et al., 2010). Interestingly, the latter compounds have recently been shown to possess neurotrophic and neuroprotective properties (Kim, 2007; Sul et al., 2009; Jeong et al., 2011), giving further support to the production of functional foods or dietary supplements containing coffee phenolics.

The present study was undertaken to evaluate the technical feasibility of recovering the phenolic compounds contained in SCG by an environmentally friendly and cost-effective extraction process. The process is based on the use of aqueous ethanol as the solvent and is conducted under mild temperature conditions to preserve the activity of the phenolic compounds. Another aim of this study was to assess the energy potential of SCG before and after the recovery of phenolics, to determine their suitability for producing pellets, briquettes or other agglomerates for heating purposes.

2. Materials and methods

2.1. Chemicals

Ethanol, hydrochloric acid and sodium carbonate were purchased from Carlo Erba (Milano, Italy). The Folin–Ciocalteu's phenol reagent and gallic acid (3,4,5-trihydroxybenzoic acid) were obtained from Sigma–Aldrich Co. (St. Louis, Mo, USA). All chemicals were analytical grade, with purities greater than 99%, and used without further purification. Aqueous solutions were prepared with distilled deionized water.

2.2. Spent coffee grounds

Two types of SCG were used. The first (SCG-1) was collected from coffee bars in the city of Rome, while the second (SCG-2) was recovered from spent coffee capsules. Coffee waste from coffee bars underwent preliminary hand-screening to remove materials other than coffee grounds and to thoroughly mix the waste. Coffee capsules were unloaded from an automatic espresso machine and opened with a knife to recover the spent coffee powder contained in the plastic packages.

To prevent microbial spoilage during storage, both types of SCG were dried in an electric forced-air food dehydrator (Stöckli, Switzerland) at 40 °C for 12–15 h. Dried SCG were then placed in glass containers and stored in the dark at room temperature until use.

Sawdust to be used in an admixture with SCG was obtained from a local carpenter's shop and utilized as received, without sieving.

2.3. Analytical measurements

Moisture content was measured by an electronic moisture analyzer (model MAC 50/1, Radwag, Poland) with an accuracy of ±0.0001 g.

Total phenolics were determined by the Folin–Ciocalteu method, according to the procedure described by Singleton et al. (1999) with some modifications. Briefly, 5 mL of 0.1 M HCl, 195 μL of Folin–Ciocalteu's reagent and 200 μL of the liquid to be assayed were poured into a graduated glass vial, followed by the addition of 20% (w/v) Na_2CO_3 solution to a final volume of 10 mL. The vial was vigorously hand-shaken and kept at room temperature in the dark for 1 h. Then, the absorbance at 525 nm was measured with a colorimeter (Hanna Instruments, Italy). The total phenolic content was expressed in gallic acid equivalents (mg of GAE/g sample) using a calibration curve of gallic acid.

Evaluation of the initial phenolic content of SCG was performed by a three-stage extraction procedure under conditions allowing for an almost complete recovery of phenolics. The extraction was conducted at 25 °C in magnetically stirred flasks containing 1 g of coffee waste and appropriate amounts of solvent (50% ethanol in water). In particular, solvent volumes of 100, 50 and 20 mL were used in the first, second and third stage, respectively. The contact time was set to 1 h in each stage. At the end of each extraction, the suspension was filtered, the solid recovered for re-extraction and the liquid assayed for phenolic content. The total amount of phenolics was determined as the sum of the values obtained in each stage.

The calorific value of spent coffee samples was measured by an automatic adiabatic bomb calorimeter (model C5000, IKA-Werke, Germany) controlled by C5040 CalWin software. Measurements were made in duplicate on a weighed amount of about 1 g.

2.4. Extraction procedure

The extraction experiments were carried out in batch mode. One g of SCG and an appropriate amount of the ethanol–water mixture were loaded into 50 or 100 mL screw-top Pyrex flasks. The flasks were placed in a water bath thermostated at ±0.1 °C and magnetically stirred. At the desired time, a sample of the liquid was taken, passed through a 45-μm nylon filter and assayed for phenolic content.

Experiments aimed at determining the amount of dry phenolic extract obtainable from SCG and its titer were carried out in a Pyrex glass extractor with a working volume of about 1 L. The extractor was provided with a thermostated water jacket and a mechanical stirrer (50-mm diameter, two-blade impeller operated at 300 rpm). In these runs, 30 g of SCG were contacted with 750 mL of the

Please cite this article in press as: Zuorro, A., Lavecchia, R., Spent coffee grounds as a valuable source of phenolic compounds and bioenergy, Journal of Cleaner Production (2012), doi:10.1016/j.jclepro.2011.12.003

Table 1
Factors and levels of the experimental design.

Factor	Units	Level		
		−1	0	+1
Temperature (T)	°C	30	40	50
Extraction time (E)	min	60	90	120
Liquid-to-solid ratio (R)	mL/g	20	30	40
Mixture composition (C)	vol%	30	50	70

ethanol–water mixture (50% ethanol in water) at 40 °C for about 6 h. The solvent was then withdrawn from the extractor and evaporated in a Rotavapor (model R-215, BÜCHI Labortechnik AG, Switzerland) equipped with a vacuum controller and a membrane pump. Finally, the solid residue was weighed, redissolved in ethanol and analyzed for phenolic content.

2.5. Influential factor analysis

In a previous study we found that temperature (T), extraction time (E), liquid-to-solid ratio (R) and ethanol concentration in the aqueous solvent (C) were the factors that most influenced the yield of phenolic extraction from SCG (Zuorro and Lavecchia, 2011). To quantitatively evaluate the contribution of these factors to the extraction efficiency, we used a full-factorial design with the above four factors (T, E, R and C) and two levels. Factor levels were chosen to cover a range of values of practical interest (Table 1).

The test variables were coded to vary between −1 and +1 using the following equations:

$$x_1 = \frac{T - 40}{10}$$
$$x_2 = \frac{E - 90}{30}$$
$$x_3 = \frac{R - 30}{10} \quad (1)$$
$$x_4 = \frac{C - 50}{20}$$

The midpoint of all factor values ($x_1 = x_2 = x_3 = x_4 = 0$) was used to estimate the experimental error and to check the adequacy of the model. The experiment was replicated four times, for a total of $2^4 + 4 = 20$ runs for each type of waste material (Table 2). Replicates were performed in a randomized order to minimize the effects of variability in the observed responses due to extraneous factors.

The analysis of results was carried out with Minitab® (Minitab, 2005).

3. Results and discussion

This study was made on two different types of SCG, namely, the waste collected from some coffee bars in the city of Rome (SCG-1) and the material recovered from spent coffee capsules (SCG-2). They were preliminary characterized to evaluate their phenolic content and calorific value. Subsequently they were submitted to a solvent-extraction procedure aimed at assessing the amount of phenolics that could be recovered from these materials and the influence of process variables on the extraction efficiency. Finally, the solid residue remaining after the extraction of phenolics was assayed for its calorific value, either alone or in combination with varying amounts of sawdust.

3.1. Characterization of SCG

The initial moisture content of SCG-1 and SCG-2 was 47.5 ± 4.6 and 48.6 ± 3.9 wt%, respectively. After the dehydration treatment, it was reduced to about 6 wt% (5.97 ± 0.49% for SCG-1 and 6.35 ± 0.79% for SCG-2).

Table 2
Experimental design layout. y is the experimental response, representing the yield of phenolic extraction (expressed as mg of GAE per g of dry matter) from SCG.

Std order	x_1	x_2	x_3	x_4	y (mg GAE/g)	
					SCG-1	SCG-2
1	−1	−1	−1	−1	9.23	12.03
2	+1	−1	−1	−1	12.62	14.15
3	−1	+1	−1	−1	10.08	11.70
4	+1	+1	−1	−1	12.38	14.00
5	−1	−1	+1	−1	10.77	12.94
6	+1	−1	+1	−1	14.17	17.45
7	−1	+1	+1	−1	11.93	13.89
8	+1	+1	+1	−1	15.21	18.14
9	−1	−1	−1	+1	10.39	13.07
10	+1	−1	−1	+1	13.52	15.51
11	−1	+1	−1	+1	13.62	13.94
12	+1	+1	−1	+1	13.57	15.66
13	−1	−1	+1	+1	13.85	17.31
14	+1	−1	+1	+1	15.95	19.49
15	−1	+1	+1	+1	13.32	16.41
16	+1	+1	+1	+1	17.09	19.98
17	0	0	0	0	15.27	18.20
18	0	0	0	0	15.14	18.53
19	0	0	0	0	15.35	18.77
20	0	0	0	0	15.88	18.61

The total phenolic content, expressed as mg of GAE per g of dry weight, was 17.75 ± 0.35 mg/g, for SCG-1, and 21.56 ± 0.52 mg/g for SCG-2. These values are in agreement with those from the few published studies on SCG (Ramalakshmi et al., 2009; Murthy and Naidu, 2010; Bravo et al., 2011). In addition, they are higher than those found for some other agroindustrial wastes. For example, about 14 mg GAE/g dry matter is reported for both grape pomace (Louli et al., 2004) and carrot peel waste (Chantaro et al., 2008). Similarly, a total phenolic content of 8.2 and 11.4 mg GAE/g dry matter was measured for kiwi and apple peel waste, respectively (Wijngaard et al., 2009). Therefore, based on total phenolic content, SCG may be an exploitable resource for natural antioxidant production. We also note that the phenolic content of the waste from spent capsules was about 20% higher than that from coffee bar waste. This could be because the capsules used in this study contained pure Arabica coffee, while blends of Arabica and Robusta beans are commonly used in coffee bars. Consistent with this, a recent study reported that the phenolic content of SCG from Arabica beans was 30% greater than that for the Robusta variety (Ramalakshmi et al., 2009).

The calorific values of the two types of coffee waste were 23.72 ± 0.76 MJ/kg (SCG-1) and 24.07 ± 0.37 MJ/kg (SCG-2). The

Please cite this article in press as: Zuorro, A., Lavecchia, R., Spent coffee grounds as a valuable source of phenolic compounds and bioenergy, Journal of Cleaner Production (2012), doi:10.1016/j.jclepro.2011.12.003

Table 3
Higher calorific value (*HCV*) of some agroindustrial wastes and wood materials. SCG-1 and SCG-2 denote spent coffee grounds from coffee bars and coffee capsules, respectively.

Biomass	*HCV* (MJ/kg)	Reference	Biomass	*HCV* (MJ/kg)	Reference
Cotton residue	18.30	Vamvuka and Kakaras, 2011	Birch wood	18.40	Thunman et al., 2001
Forest residue	21.70	Vamvuka and Kakaras, 2011	Danish pine wood	21.20	McKendry, 2002
Groundnut shell	18.65	Raveendran et al., 1996	Fir wood	21.00	McKendry, 2002
Mango leaves	19.17	Panwar et al., 2010	Oak wood	18.70	Ingram et al., 2008
Olive kernel	20.40	Vamvuka and Kakaras, 2011	Pine wood	21.90	Ingram et al., 2008
Palm kernel	18.67	Razuan et al., 2010	Poplar wood	18.50	McKendry, 2002
Palm stone	27.46	Razuan et al., 2010	Spruce wood	18.80	Thunman et al., 2001
Rice husks	15.29	Raveendran et al., 1996	Willow wood	20.00	McKendry, 2002
Rice straw	16.78	Raveendran et al., 1996	Oak bark	18.30	Ingram et al., 2008
Sunflower-seed hulls	20.00	Raclavska et al., 2011	Pine bark	18.30	Ingram et al., 2008
Vine shoots	18.30	Vamvuka and Kakaras, 2011	SCG-1	23.72	Present work
Wheat straw	17.51	Panwar et al., 2010	SCG-2	24.07	Present work

closeness of the two values indicates that the energy potential of these materials is not noticeably affected by the phenolic content, nor by the type of phenolic compounds. Table 3 presents caloric data from the literature for some forms of biomass, including different types of wood, wood bark and agricultural residue. The calorific value of SCG exceeds that of hardwoods by about 20% and is also higher than that of most agricultural residues.

Overall, the characterization of SCG suggests that these wastes, in addition to being a rich source of antioxidant compounds, are also an attractive fuel material.

3.2. Phenolic extraction and influential factor analysis

The experimental design of the present study was aimed at investigating the effects of temperature (T), extraction time (E), liquid-to-solid ratio (R) and the composition of the ethanol–water mixture (C) on the extraction yield (y) of phenolic compounds from SCG. y was calculated as the amount of phenolics extracted per unit weight of SCG, expressed as mg GAE/g dry matter. Inspection of the data revealed that (a) the extraction yields from SCG-2 were always higher than those from SCG-1; (b) the maximum yield was achieved under the same extraction conditions: $T = 50$ °C, $E = 2$ h, $R = 40$ mL/g and $C = 70\%$; and (c) these maximum yields (17.09 mg GAE/g for SCG-1 and 19.98 mg GAE/g for SCG-2) corresponded to of over 90% recovery of the phenolic compounds d in the starting materials (Table 2).

To evaluate the contribution of the four main factors (T, E, R, C) and their interactions to the extraction efficiency we used the following polynomial equation:

$$y = a_0 + \sum_{i=1}^{4} a_i x_i + \sum_{i=1}^{4}\sum_{j=i+1}^{4} a_{ij} x_i x_j + \sum_{i=1}^{4}\sum_{j=i+1}^{4}\sum_{k=j+2}^{4} a_{ijk} x_i x_j x_k + a_{1234} x_1 x_2 x_3 x_4 \quad (2)$$

where a_i are the coefficients associated with the four main effects, a_{ij} and a_{ijk} are those related to the binary and ternary interactions, a_{1234} is the quaternary interaction coefficient and the x's are the coded variables. The model described by the above equation contains 16 unknown coefficients, representing the contribution of each factor, alone or in combination with the others, to y. If we consider T, the extraction temperature, the value of $2{\cdot}a_1$ is the contribution of this factor to the extraction yield when T is varied over a dimensionless range of 2 (namely, from 30 to 50 °C). It should be noted that, because the independent variables were made dimensionless and normalized between −1 and +1, all of the coefficients can be compared directly with one another. Moreover, a positive (negative) value for a coefficient is indicative of a direct (inverse) association between the term containing that coefficient and the dependent variable.

The 16 coefficients were determined using the data from runs 1–16 in Table 2, resulting in the values reported in Table 4. To assess their statistical significance, we used the procedure described by Lewis et al. (1999). In particular, the standard deviation of the experimental response (σ_y) was first estimated using the central points of the factorial design (runs 17–20 in Table 2). We obtained $\sigma_y = 0.32$ mg GAE/g for SCG-1 and $\sigma_y = 0.24$ mg GAE/g for SCG-2. Then, we calculated the Student's t -values at the 95% confidence level for each coefficient. The following confidence intervals were derived: [−0.225, +0.225] for SCG-1 and [−0.167, +0.167] for SCG-2. As is known, if the value of a coefficient falls outside these intervals, the coefficient can be considered statistically significant.

Nine of the 16 coefficients are statistically significant at the confidence level considered (Table 4). In addition to the intercept, a_0, they include all four coefficients (three for SCG-2) associated with the main effects and four interaction coefficients (five for SCG-2). However, the main effects are of considerably higher magnitude (Fig. 1). For both materials, the most influential factors were the temperature, liquid-to-solid ratio and ethanol concentration in the extraction mixture. The positive sign of the associated coefficients indicates a positive effect on the extraction. The remaining factor, extraction time, seems to be much less relevant (or not at all, for SCG-2). This would suggest that most of the phenolic compounds contained in SCG are extracted within the first hour (the lower level for this factor in the design), so that a further increase in time has only limited effect on their recovery.

The observed enhancement of yields at higher ethanol concentration is in agreement with studies on the extraction of

Table 4
Values and t-statistics for the coefficients in Eq. (2). Values that are statistically significant at the 95% confidence level are represented in bold.

Coefficient	Effect	SCG -1		SCG-2	
		Value	t-value	Value	t-value
a_1	T	**1.333**	16.397	**1.443**	24.047
a_2	E	**0.419**	5.153	0.111	1.843
a_3	R	**1.055**	12.982	**1.597**	26.609
a_4	C	**0.932**	11.475	**1.067**	17.777
a_{12}	T–E	−0.170	2.092	0.037	0.614
a_{13}	T–R	**0.236**	2.907	**0.371**	6.176
a_{14}	T–C	−0.214	2.630	**−0.204**	3.406
a_{23}	E–R	−0.067	0.831	0.043	0.719
a_{24}	E–C	0.067	0.831	−0.034	0.573
a_{34}	R–C	0.084	1.031	**0.279**	4.655
a_{123}	T–R	**0.364**	4.476	0.104	1.739
a_{124}	T–E–C	−0.019	0.231	0.047	0.781
a_{134}	T–R–C	0.113	1.384	**−0.172**	2.864
a_{234}	E–R–C	**−0.266**	3.276	**−0.222**	3.697
a_{1234}	T–E–R–C	**0.243**	2.984	0.159	2.656

Please cite this article in press as: Zuorro, A., Lavecchia, R., Spent coffee grounds as a valuable source of phenolic compounds and bioenergy, Journal of Cleaner Production (2012), doi:10.1016/j.jclepro.2011.12.003

phenolics from other types of materials, such as peanut skins (Nepote et al., 2005), olive leaves (Mylonaki et al., 2008) and byproducts of kiwifruit juicing (Sun-Waterhouse et al., 2009). Such an effect is probably due to an on-average higher affinity of the phenolic compounds for ethanol than for water. Nevertheless, other mechanisms such as solvent-induced swelling of the solid matrix may also be involved (Obataya and Gril, 2005; Lavecchia and Zuorro, 2008).

After having determined the statistically significant coefficients, simplified expressions can be derived for the yield of phenolic extraction from SCG by removing the non-significant terms from the full model (Eq. (2)). The equations for SCG-1 and SCG-2 are

$$y = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_{13}x_1x_3 + a_{123}x_1x_2x_3 + a_{234}x_2x_3x_4 + a_{1234}x_1x_2x_3x_4 \quad (3)$$

$$y = a_0 + a_1x_1 + a_3x_3 + a_4x_4 + a_{13}x_1x_3 + a_{14}x_1x_4 + a_{34}x_3x_4 + a_{134}x_1x_3x_4 + a_{234}x_2x_3x_4 \quad (4)$$

These models were tested for their ability to describe the experimental data and were assessed for their statistical significance. Very good agreement was found between the experimental and calculated yields (Fig. 2) with the average errors for SCG-1 and SCG-2 being 2.19% and 1.29%, respectively.

For each data point we calculated the model residuals, that is, the difference between experimental and calculated yields:

$$R_i = y_{i,\,\mathrm{exp}} - y_{i,\,\mathrm{calc}} \quad (5)$$

These residuals were then plotted against the corresponding normal-order statistics medians, which are defined as:

$$M_i = F^{-1}\left(\frac{i}{n+1}\right) \quad (6)$$

where F represents the standard normal cumulative distribution function. If the errors are normally distributed, data plotted as R_i against M_i would form an approximate straight line (Myers and Montgomery, 1995). In contrast, deviations from linearity would indicate that the model residuals do not follow a normal-probability distribution. A highly linear pattern was observed for both models (Fig. 3), with correlation coefficients higher than 0.97.

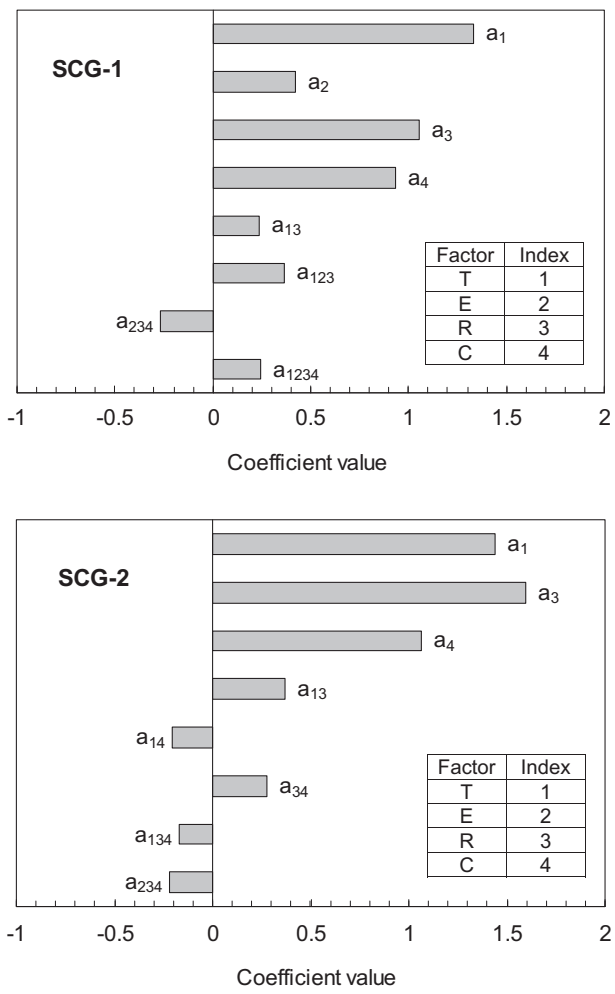

Fig. 1. Statistically significant (at the 95% confidence level) model coefficients for phenolic extraction from spent coffee grounds obtained from coffee bars (SCG-1) and coffee capsules (SCG-2).

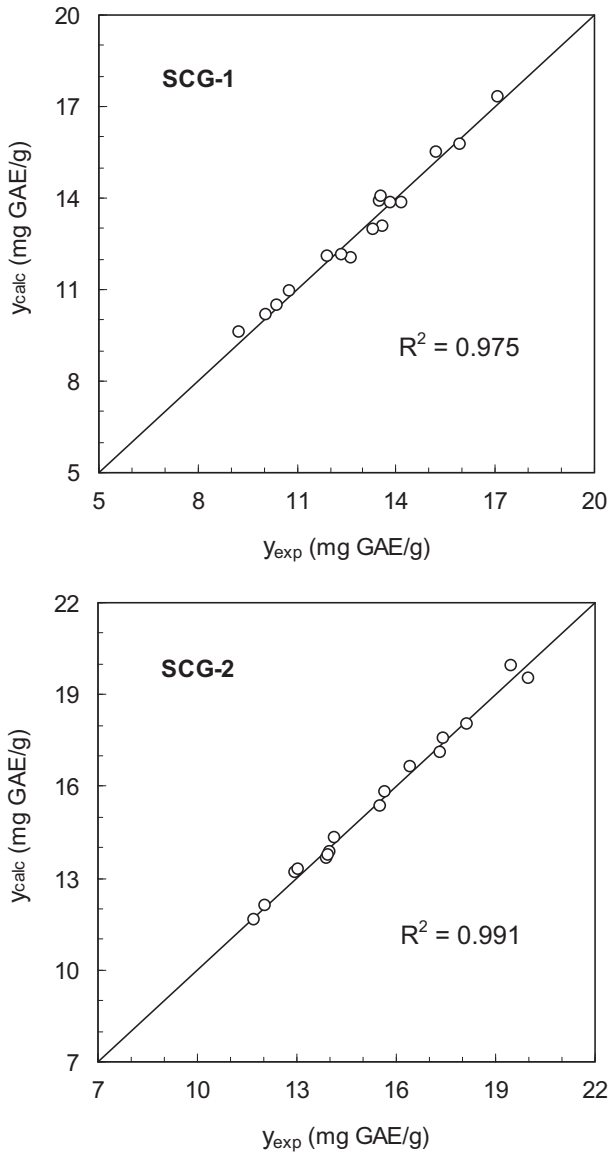

Fig. 2. Comparison between experimental and calculated (by Eqs. (3) and (4)) extraction yields for spent coffee grounds obtained from coffee bars (SCG-1) and coffee capsules (SCG-2).

Please cite this article in press as: Zuorro, A., Lavecchia, R., Spent coffee grounds as a valuable source of phenolic compounds and bioenergy, Journal of Cleaner Production (2012), doi:10.1016/j.jclepro.2011.12.003

Based on these results, it can be concluded that the two simplified models are statistically significant. They can therefore be used for correlating yield data or for describing the influence of process conditions (temperature, extraction time, liquid-to-solid ratio and the composition of the ethanol–water mixture) on the yield of phenolic extraction from SCG.

Finally, from the experiments carried out in the mechanically-stirred extractor the following quantities were determined: (*a*) the amount of dry phenolic extract obtainable from SCG, and (*b*) the phenolic titer of the extract, expressed in terms of GAE. The first quantity was found to be approximately independent of the type of SCG and equal to about 140 mg of dry phenolic extract per g of SCG. The titer of such an extract was about 12% (by weight) for SCG-1 and about 14% for SCG-2. These results strongly support the possibility of using the proposed procedure to produce phenolic-rich extracts from SCG, especially since the above values were obtained under non-optimized conditions.

3.3. Energetic characterization of the residue of phenolic extraction

The calorific value (*HCV*) of the solid remaining after the extraction of phenolic compounds from SCG was determined to highlight possible changes to the unextracted materials during the removal of phenolics or the solvent-extraction procedure. Because of the high moisture content of SCG after being subjected to the extraction of phenolics (approximately 50–52 wt%), they were preliminary dehydrated as described in paragraph 2.2. The residual moisture was about 6 wt% and the measured calorific values were *HCV* (SCG-1) = 23.19 ± 0.45 MJ/kg and *HCV* (SCG-2) = 23.81 ± 0.29 MJ/kg. Because these values are very similar to those measured prior to extraction, it can be concluded that the heating potential of SCG is not reduced by the extraction procedure and is not dependent on the levels of phenolic compounds.

In experiments conducted on SCG-sawdust mixtures (from 100% sawdust to 100% SCG) *HCV* varied linearly with the SCG/sawdust ratio (*SSR*) and mixtures with SCG-2 exhibited a higher *HCV* (Fig. 4) In particular, the following relationships can be derived:

$$HCV(\mathrm{SCG}-1) = 16.45 + 0.0675\,SSR \quad (7)$$

$$HCV(\mathrm{SCG}-2) = 16.45 + 0.0740\,SSR \quad (8)$$

which can be used to estimate the *HCV* of mixtures obtained by combining SCG and sawdust in any proportion.

Because the low lignin content of SCG, the production of pellets or other agglomerates for fuel purposes would require appropriate binding agents. This could be avoided by adding sawdust or other lignin-bearing materials to SCG. In particular, considering the lignin content of sawdust, it can be said that the addition of 15–25% sawdust may be sufficient for this purpose (Tillman, 1991; Gani and Naruse, 2007). As shown in this study, such an addition would not substantially affect the heating potential of the final solid fuel composition and could be done simply and inexpensively.

3.4. Evaluation of the potential valorization of SCG in the Province of Rome

As a case study to illustrate the potential of the above described approach we considered the situation in the Province of Rome (4.2 million inhabitants). According to data from the Chamber of Commerce of Rome (CCR, 2011), the per-capita coffee consumption in the province territory is of 5.5 kg/year. It is estimated that about 60% of the total amount of coffee is used in bars, which leads to an annual production of 13,900 t of SCG. Assuming that 70–80% of this waste can be recovered through selective collection, it follows that over 10,000 t of SCG are available for the production of phenolic-

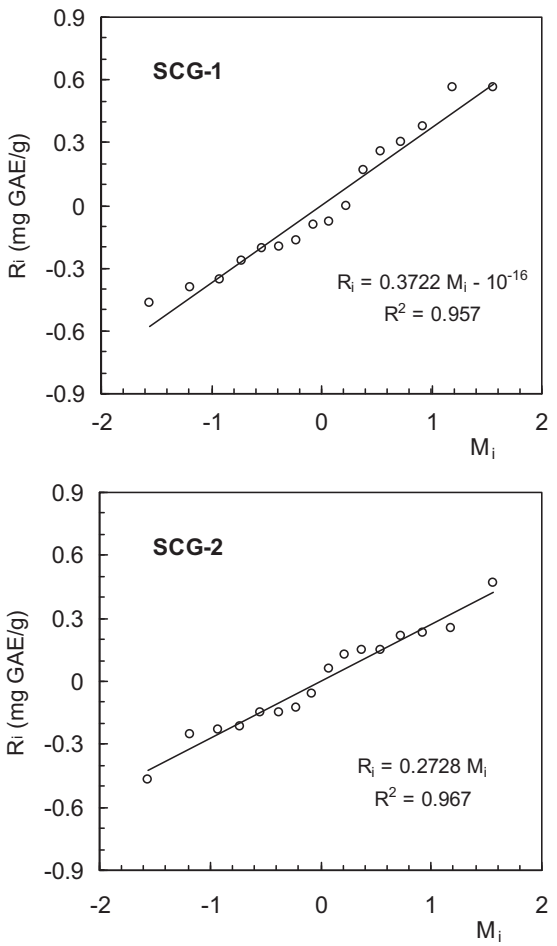

Fig. 3. Normal-probability plot showing the trend of ordered residuals (R_i) against normal-order statistics medians (M_i) for spent coffee grounds obtained from coffee bars (SCG-1) and coffee capsules (SCG-2).

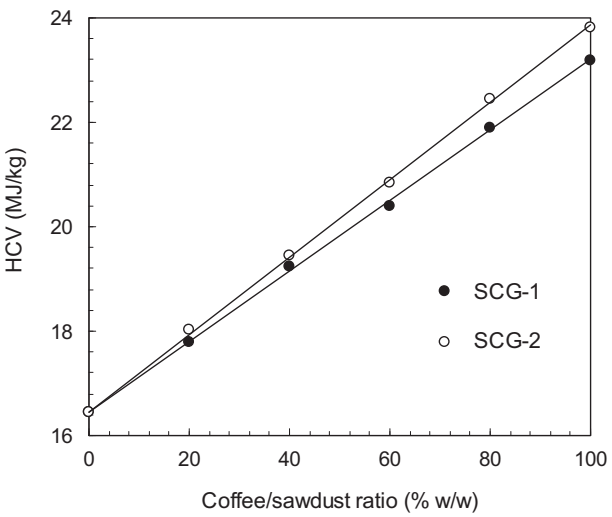

Fig. 4. Effect of the coffee-sawdust ratio on the higher calorific value (*HCV*) of the solid mixture for spent coffee grounds obtained from coffee bars (SCG-1) and coffee capsules (SCG-2).

Please cite this article in press as: Zuorro, A., Lavecchia, R., Spent coffee grounds as a valuable source of phenolic compounds and bioenergy, Journal of Cleaner Production (2012), doi:10.1016/j.jclepro.2011.12.003

rich extracts and bioenergy. According to the findings of this study, if all this waste were to be used for the recovery of polyphenols, 1400 t of phenolic extract (12–14% GAE) could be produced. The resulting solid residue (9600 tons) additioned with 20% sawdust would lead to over 11,000 t of pellets with a heating value of about 22 MJ/kg.

Although a detailed cost-benefit analysis is needed to assess the economic feasibility of the proposed approach, the above reported figures are of great significance. Next steps to be undertaken include construction and operation of a pilot-scale plant for the production of phenolic extracts, optimization of the whole system and engineering-and-cost analysis at larger scales.

In addition to economic benefits, this type of use for SCG would also lower their environmental impact because of the saved landfill space. Assuming an average moisture content of 50 wt% and an apparent density of 820 kg/m^3 for this waste, the saved volume would be of over 18,000 m^3 per year.

4. Conclusions

This study demonstrates that phenolic-rich extracts can be obtained from SCG by using an environmentally friendly and simple solvent-extraction procedure. The proposed method allowed for over 90% recovery of phenolic compounds from the starting material, which could be further improved by subsequent optimization based, for instance, on response surface methods or random search procedures. In this regard, the influential factor analysis we performed provides useful suggestions for future process-development strategies.

Another point emerging from our research is the very high calorific value of SCG, even after the recovery of phenolic compounds. This result strongly supports the possibility of exploiting the remaining solid residue for heating purposes, that is, for turning a waste material into a sustainable and renewable energy resource (Mizsey and Racz, 2010; Gold and Seuring, 2011). The integration of phenolic recovery with the production of an SCG-containing solid fuel could not only lead to a new natural product with high antioxidant properties but also could contribute to environmental protection and energy efficiency.

References

Bertrand, B., Guyot, B., Anthony, P., Lashermes, P., 2003. Impact of the *Coffea canephora* gene introgression on beverage quality of *C. arabica*. Theor. Appl. Genet. 107, 387–395.

Bravo, J., Monente, C., Juániz, I., Paz De Peña, M., 2011. Influence of extraction process on antioxidant capacity of spent coffee. Food Res. Int.. doi:10.1016/j.foodres 2011.04.026.

Brezová, V., Šlebodová, A., Staško, A., 2009. Coffee as a source of antioxidants: an EPR study. Food Chem. 114, 859–868.

CCR, 2011. Chamber of Commerce of Rome, 2011. Personal communication.

Chantaro, P., Devahastin, S., Chiewchan, N., 2008. Production of antioxidant high dietary fiber powder from carrot peels. LWT-Food Sci. Technol. 41, 1987–1994.

Clarke, R., Vitzhum, O.G., 2001. Coffee: Recent Developments. Blackwell Science Ltd., Oxford, UK.

Dai, J., Mumper, R.J., 2010. Plant phenolics: extraction, analysis and their antioxidant and anticancer properties. Molecules 15, 7313–7352.

Esquivel, P., Jiménez, V.M., 2011. Functional properties of coffee and coffee by-products. Food Res. Int.. doi:10.1016/j.foodres 2011.05.028.

Farah, A., Donangelo, C.M., 2006. Phenolic compounds in coffee. Braz. J. Plant Physiol. 18, 23–36.

Franca, S.F., Oliveira, L.S., Ferreira, M.E., 2009. Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds. Desalination 249, 267–272.

Gani, A., Naruse, I., 2007. Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass. Renew. Energy 32, 649–661.

Gold, S., Seuring, S., 2011. Supply chain and logistics issues of bio-energy production. J. Clean. Prod. 19, 32–42.

Hendriks, A.T.W.M., Zeeman, G., 2009. Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresour. Technol. 100, 10–18.

ICO, International Coffee Organization, 2009. Total Coffee Production of Exporting Countries, London (UK), www.ico.org/trade_statistics.asp, (accessed 05.08.11.).

Ingram, L., Mohan, D., Steele, P., Strobel, D., Mitchell, B., Mohammad, J., Cantrell, K., Pittman, C.U., 2008. Pyrolysis of wood and bark in an Auger reactor: physical properties and chemical analysis of the produced bio-oils. Energy Fuels 22, 614–625.

Jeong, C.H., Jeong, H.R., Choi, G.N., Kim, D.O., Lee, U., Heo, H.J., 2011. Neuroprotective and anti-oxidant effects of caffeic acid isolated from *Erigeron annuus* leaf. Chin. Med. 24, 6–25.

Kim, S.Y., 2007. Neuroprotective and neurotrophic agents. In: Suk, K. (Ed.), Research Focus on Natural Products and the Body's Immune and Inflammatory Systems. Nova Science Publishers, New York, pp. 23–39.

Kondamudi, N., Mohapatra, S., Misra, M., 2008. Spent coffee grounds as a versatile source of green energy. J. Agric. Food Chem. 56, 11757–11760.

Lavecchia, R., Zuorro, A., 2008. Improved lycopene extraction from tomato peels by cell-wall degrading enzymes. Eur. Food Res. Technol. 228, 153–158.

Lewis, G.A., Mathieu, D., Phan-Tan-Luu, T., 1999. Pharmaceutical Experimental Design. Marcel Dekker, New York, USA.

Louli, V., Ragoussis, N., Magoulas, K., 2004. Recovery of phenolic antioxidants from wine industry by-products. Bioresour. Technol. 92, 201–208.

McKendry, P., 2002. Energy production from biomass (part 1): overview of biomass. Bioresour. Technol. 83, 37–46.

Minitab, 2005. Minitab Reference Manual (Version 15.1.0.0). Minitab Incorporated, State College, PA, USA.

Mizsey, P., Racz, L., 2010. Cleaner production alternatives: biomass utilization options. J. Clean. Prod. 18, 767–770.

Morikawa, C.K., Saigusa, M., 2008. Recycling coffee and tea wastes to increase plant available Fe in alkaline soils. Plant Soil 304, 249–255.

Murthy, P.S., Naidu, M.M., 2010. Recovery of phenolic antioxidants and functional compounds from coffee industry by-products. Food Bioprocess Technol.. doi:10.1007/s11947-010-0363-z.

Murthy, P.S., Naidu, M.M., Srinivas, P., 2009. Production of α-amylase under solid-state fermentation utilizing coffee waste. J. Chem. Technol. Biotechnol. 84, 1246–1249.

Myers, R.H., Montgomery, D.C., 1995. Response Surface Methodology. Process and Product Optimization Using Designed Experiments. John Wiley & Sons Inc, New York, USA.

Mylonaki, S., Kiassos, E., Makris, D.P., Kefalas, P., 2008. Optimisation of the extraction of olive (*Olea europaea*) leaf phenolics using water/ethanol-based solvent. Anal. Bioanal. Chem. 392, 977–985.

Nepote, V., Grosso, N., Guzman, C., 2005. Optimization of extraction of phenolic antioxidants from peanut skins. J. Sci. Food Agric. 85, 33–38.

Njoroge, J.M., Agwanda, C.O., Kingori, P.N., Karanja, A.M., Gathaara, M.P.H., 2005. Coffee. In: Chopra, V.L., Peter, K.V. (Eds.), Handbook of Industrial Crops. The Haworth Press, New York, USA, pp. 295–333.

Obataya, E., Gril, J., 2005. Swelling of acetylated wood I. Swelling in organic liquids. J. Wood Sci. 51, 124–129.

Panwar, V., Prasad, B., Wasewar, K.L., 2010. Biomass residue briquetting and characterization. J. Energy Eng.-ASCE 137, 108–114.

Raclavska, H., Juchelkova, D., Roubicek, V., Matysek, D., 2011. Energy utilisation of biowaste – sunflower-seed hulls for co-firing with coal. Fuel Process. Technol. 92, 13–20.

Ramalakshmi, K., Jagan Mohan Rao, L., Takano-Ishikawa, Y., Goto, M., 2009. Bioactivities of low-grade green coffee and spent coffee in different in vitro model systems. Food Chem. 115, 79–85.

Raveendran, K., Ganesh, A., Khilar, K.C., 1996. Pyrolysis characteristics of biomass and biomass components. Fuel 75, 987–998.

Rawel, H.M., Kulling, S.E., 2007. Nutritional contribution of coffee, cacao and tea phenolics to human health. J. Verbr. Lebensm. 2, 399–406.

Razuan, R., Chen, Q., Zhang, X., Sharifi, V., Swithenbank, J., 2010. Pyrolysis and combustion of oil palm stone and palm kernel cake in fixed-bed reactors. Bioresour. Technol. 101, 4622–4629.

Rechner, A.R., Kuhnel, G., Bremner, P., Hubbard, G.P., Moore, K.P., Rice-Evans, C.A., 2002. The metabolic fate of dietary polyphenols in humans. Free Radic. Biol. Med. 33, 220–235.

Singleton, V.L., Orthofer, R., Lamuela-Raventos, R.M., 1999. Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. Meth. Enzymol. 299, 152–178.

Stalmach, A., Steiling, H., Williamson, G., Crozier, A., 2010. Bioavailability of chlorogenic acids following acute ingestion of coffee by humans with an ileostomy. Arch. Biochem. Biophys. 501, 98–105.

Sul, D.G., Kim, H.S., Lee, D.H., Joo, S.S., Hwang, K.W., Park, S.Y., 2009. Protective effect of caffeic acid against beta-amyloid-induced neurotoxicity by the inhibition of calcium influx and tau phosphorylation. Life Sci. 84, 257–262.

Sun-Waterhouse, D., Wen, I., Wibisono, R., Melton, L.D., Wadhwa, S., 2009. Evaluation of the extraction efficiency for polyphenol extracts from by-products of green kiwifruit juicing. Int. J. Food Sci. Technol. 44, 2644–2652.

Thunman, H., Niklasson, F., Johnsson, F., Leckner, B., 2001. Composition of volatile gases and thermochemical properties of wood for modeling of fixed or fluidized beds. Energy Fuels 15, 1488–1497.

Tillman, D.A., 1991. The Combustion of Solid Fuels and Wastes. Academic Press, New York, USA.

Tokimoto, T., Kawasaki, N., Nakamura, T., Akutagawa, J., Tanada, S., 2005. Removal of lead ions in drinking water by coffee grounds as vegetable biomass. J. Colloid Interface Sci. 281, 56–61.

Please cite this article in press as: Zuorro, A., Lavecchia, R., Spent coffee grounds as a valuable source of phenolic compounds and bioenergy, Journal of Cleaner Production (2012), doi:10.1016/j.jclepro.2011.12.003

Utomo, H.D., Hunter, K.A., 2006. Adsorption of divalent copper, zinc, cadmium and lead ions from aqueous solution by waste tea and coffee adsorbents. Environ. Technol. 27, 25–32.
Vamvuka, D., Kakaras, E., 2011. Ash properties and environmental impact of various biomass and coal fuels and their blends. Fuel Process. Technol. 92, 570–581.
Wijngaard, H.H., Rößle, C., Brunton, N., 2009. A survey of Irish fruit and vegetable waste and by-products as a source of polyphenolic antioxidants. Food Chem. 116, 202–207.
Wintgens, J.N., 2009. Coffee: Growing, Processing, Sustainable Production, second ed. Wiley-VCH, Weinheim.
Yen, W.J., Wang, B.S., Chang, L.W., Duh, P.D., 2005. Antioxidant properties of roasted coffee residue. J. Agric. Food Chem. 53, 2658–2663.
Zuorro, A., Lavecchia, R., 2010. Adsorption of Pb(II) on spent leaves of green and black tea. Am. J. Appl. Sci. 7, 153–159.
Zuorro, A., Lavecchia, R., 2011. Polyphenols and energy recovery from spent coffee grounds. Chem. Eng. Trans. 25, 285–290.

Please cite this article in press as: Zuorro, A., Lavecchia, R., Spent coffee grounds as a valuable source of phenolic compounds and bioenergy, Journal of Cleaner Production (2012), doi:10.1016/j.jclepro.2011.12.003