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NOTE

The broad spectrum of possibilities for spent coffee grounds valorisation

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Abstract Coffee is the world's second most traded commodity and the most renowned drink worldwide. The increasing production of coffee has been accompanied by a rise in consumption, and consequent increment in the amount of spent coffee grounds (SCGs) remaining as a solid residue from coffee brewing. In view of the high content of biodegradable compounds, if disposed, SCGs will certainly need to be biostabilized, although they should preferably be exploited in a biorefinery chain scheme. A wide range of alternative options is available for use in recycling SCGs as a valuable resource: food additives, pharmaceutical components, bio-sorbents, bio-fuels, and bio-products. The option of producing biogas from SCGs was tested and lab-scale bio-methane potential experiments were performed using different substrate to inoculum (*S/I*) ratios, namely 0.5, 1, and 2. A *S/I* ratio of 2 was found to be the optimal condition, resulting in a methane yield of 0.36 m^3CH_4/kgVS.

Keywords Spent coffee grounds (SCGs) · Biorefinery · Anaerobic digestion

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Introduction

Coffee is the world's second most traded commodity after oil and the most renowned drink worldwide. The International Coffee Organization [1] has published the latest data related to coffee production throughout the different nations of the world, with the top ten comprising: Guatemala 224,871 tons; Mexico 257,940 tons; Uganda 314,489 tons; Honduras 380,296 tons; India 385,786 tons; Ethiopia 423,287 tons; Indonesia 814,629 tons; Colombia 892,871 tons; Vietnam 1,818,811 tons; and Brazil 2,859,502 tons [1]. These production data all show an increase ranging from 10 to 12% in comparison with the yield obtained in 2015. However, in terms of exports, the ranking changes. According to the latest report [1], Brazil remains in the first place with 1,708,700 tons of coffee exported every year, followed by Vietnam (1,147,500 tons/year), Colombia (601,860 tons/year), India (300,360 tons/year), Indonesia (290,820 tons/year), Honduras (284,760 tons/year), Uganda (169,020 tons/year), Ethiopia (150,840 tons/year), Guatemala (145,920 tons/year), Peru (136,800 tons/year). Europe, USA, and Japan are the main coffee-importing countries with 3,140,400; 1,125,960 and 319,980 tons/year, respectively.

In line with the increasing production of coffee, consumption of the beverage, and consequently the amount of spent coffee grounds (SCGs) remaining as a solid residue from coffee brewing, are on an upwards trend. Murthy and Naidu [2] reported that for every ton of green coffee beans, 650 kg of residues remain as SCGs. As assessed by Obruca et al. [3] the composition of SCGs is made up of hemicellulose (30–40 ww%), lignin (25–33 ww%), oil (10–20 ww%), cellulose (8.6–13.3 ww%), proteins (6.7–13.6 ww%), and polyphenols (2.5 ww%). Approximately 5,817,500 tons of SCGs are generated worldwide every

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year as a municipal solid waste [4]. These residues are of no economic value [5] and are usually discarded without further valorisation. In view of the high content of biodegradable compounds, if disposed, SCGs will certainly require biostabilization, although they should preferably be exploited in a biorefinery chain scheme. On identifying a potentially profitable use for energy and goods produced from any waste source, investments should focus increasingly on alternative biorefinery options rather than on waste disposal. In the context of a biorefinery concept applicable to food waste in general [6], SCGs feature an incredibly wide range of potential applications. In some cases, due to the high fibre and polyphenol content of these residues, they are utilized in the food industry [7, 8] or the pharmaceutical sector [7, 9].

Worldwide, the major drivers of a bioenergy approach are represented by an enhanced supply of renewable energy and mitigation of climate change. New sources of sustainable and green energy are needed to reduce the disproportionate use of common fossil fuels or substitute for these. Over the last decade, numerous studies have been performed with the aim of valorising SCGs as a raw substrate for use in the production of ethanol [10, 11], biosorbents [12–16], biodiesel [2, 4, 17, 18], pyrolysis oil [19–22], and polyhydroxyalkanoates [3, 23–25] for bioplastic production.

Studies focused on investigating energy recovery from SCGs by means of anaerobic digestion (AD) were first set up in 1983 [26], although no in-depth assessments of optimal operating conditions were carried out.

The aim of this study is to provide an updated overview of the series of possibilities available to promote the exploitation of SCGs as a valuable resource for energy and product recovery. A comparison of the energy obtainable via different routes is provided. Moreover, the results of an original batch scale evaluation of the best AD conditions, in terms of substrate to inoculum (*S/I*) ratio, to enhance recovery of bio-methane from SCGs under mesophilic conditions are illustrated. The Authors tested different *S/I* ratios, namely 0.5, 1, and 2.

Alternative biorefinery options for SCGs: state of the art

Innovative solutions for the recycling of SCGs within a circular economy approach are summarized in Fig. 1. The introduction of cutting-edge management solutions for these huge amounts of waste has contributed towards significantly reducing the amount of materials to be returned to the environment either as soil amendment or in a non-mobile form in artefacts (Back to Earth Alternatives, BEA).

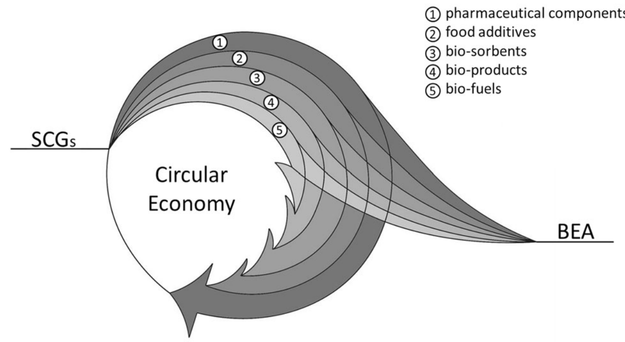

Fig. 1 Alternative biorefinery options for SCGs within the circular economy

Food and feed products

Spent coffee grounds constitute an excellent substrate for mushroom production, requiring no treatment prior to start-up of cultivation. Accordingly, several studies have cultivated a series of different types of edible fungi, including *L. edodes*, *Pleurotus* spp., and *Flammulina velutipes,* with a biological efficiency of up to 88.6% [2, 27, 28] signifying that each kg of dry SCGs used as a substrate resulted in the growth of nearly 0.9 kg of mushrooms.

Although featuring a high lignin content [3, 29, 30], SCGs have been investigated for potential use as animal feed. Claude [31] and Givens and Barber [32] demonstrated the suitability of SCGs as a source of nutrition for ruminants, pigs, chickens, and rabbits. However, the presence of polyphenols, caffeine and other substances in SCGs severely limits their application as animal feed [3].

SCGs represent an excellent source of bioactive, particularly phenolic compounds [33], known to exert beneficial effects on human health due to their antioxidant properties [7, 9]. Moreover, the high amount of total fibre contained in SCGs (80%) [2] has resulted in an increasing interest on the identification of alternative options for the reuse of this residue in the food industry. Bravo et al., demonstrated the feasibility of exploiting SCGs as a food ingredient or additive with potential preservation and functional properties [8]. Subsequent to coffee brewing, the remaining grounds are suitable for use as a source of natural antioxidants, nutraceuticals, and preservatives in food formulations [2]. López-Barrera et al. [7] reported how dietary fibres contained in SCGs are fermented by colon microbiota-producing short-chain fatty acids (SCFAs) capable of preventing inflammation. Further, due to their chemical composition, SCGs are a rich source of polysaccharides; indeed, several studies [30, 34–36] have been undertaken to assess the extraction yield of galactomannans and arabinogalactans known for their immunostimulatory properties.

SCGs may even be applied as a starter substrate in the production of distilled beverages. Sampaio et al. [10] produced liquor from SCGs, the organoleptic quality of which was considered acceptable for human consumption. This was achieved by three main steps, namely hydrothermal extraction, fermentation, and distillation. After being subjected to acid hydrolysis, SCGs hydrolysate may be used as a fermentation medium by *Saccharomyces cerevisiae* yeast and yield a 50.1 ww% ethanol production [11].

Bio-sorbents and energy storage

In addition to the exceptional properties associated with the use of SCGs as a mushroom-growing substrate, animal feed, and as food compounds, other effective reuse opportunities for SCGs have been investigated.

These studies have found that SCGs may be used as an inexpensive and easily available adsorbent for the removal of cationic dyes from aqueous solutions [12, 13]. Accordingly, SCGs can be applied efficiently in wastewater treatment units. Hirata et al. applied a microwave treatment to SCGs with the aim of obtaining carbonaceous materials to be used as adsorbates for the removal of basic dyes in wastewater [14]. Namane et al. [37] treated SCGs with $ZnCl_2$ to produce activated carbon. The newest form of biomass-based granular activated carbon was successfully prepared by entrapping granular activated carbon (GAC) powder derived from spent coffee grounds into calcium-alginate beads (SCG-GAC) [16]. Regeneration tests further confirmed that SCG-GAC has a promising reuse potential, showing a dye removal efficiency of more than 80% (expressed as percent ratio of removed dye concentrations to their initial concentrations) and an adsorption capacity up to 57 mg/g even after seven consecutive cycles [16].

Thomas et al. highlighted the potential of using SCGs in the production of electrode materials for cost effective energy storage systems. Supercapacitor electrodes prepared from coffee ground carbon displayed excellent stability with high charge–discharge rates [15].

Bioplastic

The relatively high acid value (caused by the presence of free fatty acids) exhibited by SCG oil, although complicating transesterification during biodiesel production [23] significantly stimulates the accumulation of polyhydroxyalkanoates (PHA) in the cytoplasm of microorganisms during batch scale experiments [3, 24]. Oil extraction from SCG by means of n-hexane [23] or supercritical carbon dioxide [24] yields up to 12% on a dry weight basis. The conversion rate of SCGs into PHA ranges between 8 and 20% (ww). Cruz et al. [24] succeeded in obtaining 97 kg of PHA from 1 ton of SCGs [24], while Obruca et al. [3] reached a yield of 14% (ww), both employing *Cupriavidus Necator* as PHA-cumulating bacteria. A limiting factor in the production of PHA from SCGs is represented by the presence of polyphenols [25], due to their inhibitory effect on the growth of some microorganisms.

Bio-fuels

SCGs have a high calorific power of approximately 24.9 MJ/kg (dw), thus representing an excellent substrate to be fed into industrial boilers [38]. A few industries have attempted to exploit SCGs for the generation of heating and electricity [22]; however, combustion of these wastes resulted in the generation of particulate matter and hazardous gases, particularly high nitrogen oxidants, thereby dramatically limiting the direct use of SCGs as solid fuels [39, 40].

Recent interest has focused on the use of SCGs in the production of liquid biofuels [22] such as bioethanol, biodiesel, and pyrolysis oil. A comparison of the amount of energy obtainable from SCGs via different routes is shown in Fig. 2.

The enzymatic rate of conversion of SCGs to fermentable sugars is around 85 dw% [41]. Pressure applied in the pretreatment step is fundamental in producing swelling and degradation of the SCG cell wall, which improves subsequent enzymatic hydrolysis and fermentation by increasing the surface area of SCGs, and making it more accessible to hydrolytic enzymes. Under optimal popping pretreatment conditions of 1.47 MPa and 18.3 mgCellulase/gSCGs, the ethanol concentration and yields (based on sugar content) obtained by means of enzymatic hydrolysis subsequent to simultaneous saccharification and fermentation were 15.3 g/L and 87.2%, respectively [41].

Conversely, the oil extracted from SCGs may be transesterified for use in biodiesel production [2, 4, 17, 18]. The conversion of oil into biodiesel is nearly complete, with Burton et al., reaching a biodiesel production yield of

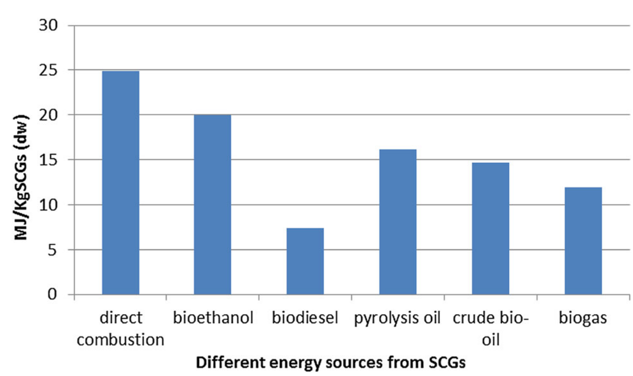

Fig. 2 Energy obtainable from SCGs via different routes

98.5% [17]. Nonetheless, the oil content of SCGs is quite low, ranging between 10 and 20% [4, 17, 18] depending on the coffee species (Arabica or Robusta), thus highlighting the scarce economic feasibility of extraction.

Accordingly, the practicability of using supercritical fluid extraction processes to obtain lipid fraction from SCGs has also been investigated [19, 42], together with a combination of ultrasonication [43] and conventional solvent extraction.

The conversion of SCGs into pyrolysis oil, however, produced a higher oil yield [20–22], ranging from 55 to 85% of wet mass depending on the moisture content of the feedstock. Reaction temperature and moisture content of the feedstock are the most important variables in fast pyrolysis of SCGs. Bok et al. obtained the highest yield of bio-crude oil (55%) at 550 °C [20], while Li et al. recorded maximum liquid yield of 66% at around 630 °C [21]. Unfortunately, SCGs feature a moisture content of between 50 and 60% mass fraction [18], therefore a pre-drying process should be applied prior to feeding SCGs into a pyrolysis system [22], with consequent negative economic consequences. A low temperature conversion pyrolysis process was also applied [44] to a sample of SCGs at 380 °C, although a lower pyrolysis oil yield, approximately 50% mass fraction [44], was achieved compared to regular pyrolysis process.

For the above reasons, the emerging technology of hydrothermal liquefaction (HTL) has also been applied to SCGs with the aim of producing bio-oil. Optimal liquefaction conditions were assessed as 275 °C, retention time of 10 min and water/feedstock mass ratio of 20:1 [22]. The highest crude bio-oil yield of 47.3% mass fraction was achieved with a higher heating value of 31.0 MJ/kg (much higher than that of SCGs, which was only 24.9 MJ/kg) and a consequent energy recovery percentage of 72.6% [22].

Another innovative approach is represented by biogas production [45]. The biogas obtained could be used for numerous purposes, including the roasting of coffee grounds, thus closing the loop of the coffee production unit.

To date, very few studies have been conducted to investigate potential bio-methane production from SCGs.

Lane [26] evaluated methane production using SCGs alone, reporting a biogas yield of 0.54 m^3/kgVS (56–63% methane) [26].

Bio-methane potential testing on SCGs

On the scenario of the diverse bio-refinery approaches currently available, the promising option of biogas production has not yet been investigated in depth. The authors therefore decided to assess the potential for bio-methane production of SCGs using different substrate to inoculum (*S/I*) ratios to clarify optimal conditions for anaerobic digestion (AD) and the feasibility of applying the AD process to this specific kind of waste when processed alone.

Materials

SCGs were collected after the brewing of coffee using a moka coffee pot from the Environmental Engineering Laboratory of Padova University. SCGs were tested for TS and VS content [46], which were found to be 37 and 36.5 ww%, respectively. VS/TS ratio was 0.99. Elemental analysis (C, H, N, and S) was determined using an elemental analyzer (Vario MACRO CNS, Hanau, Germany). Oxygen content was calculated by difference. SCGs were also analysed in terms of hemicellulose, cellulose, and lignin content following the crude fibre procedure of AOCS [47]. Final analyses are illustrated in Table 1.

Granular sludge (5.2 gVS/L) from a full-scale upflow anaerobic sludge blanket (UASB) digester of a brewery factory located in Padova, Italy was used as inoculum.

Method

Lab scale tests were performed to evaluate the Biochemical Methane Potential (BMP) of SCG following anaerobic digestion. Tests were carried out in 1-Litre batch reactors under mesophilic conditions (35 ± 1 °C) (see Fig. 3a). In each reactor substrate concentration was kept constant at 10 gVS/L while the amount of inoculum was changed according to the desired *S/I* ratio. After water addition, the total liquid volume in the reactors was 500 mL each. Reactors were hermetically closed by means of a silicon plug enabling sampling of the gas and liquid produced

Table 1 Chemical characteristics and final analysis of SCGs used in this study

Parameter	Spent coffee grounds
TS (ww%)	37
VS (ww%)	36.5
pH	6.3
C (dw%)	58.8
H (dw%)	8.9
O (dw%)	28.7
N (dw%)	3.4
S (dw%)	0.2
Fibre composition	
Cellulose (dw%)	24.3
Hemicellulose (dw%)	24.8
Lignin (dw%)	13.5

Fig. 3 Lab tests experimental equipment. Mesophilic water bath containing the BMP bottles (**a**) and manual measurement of the biogas produces through water displacement (**b**)

during fermentation. The three different investigated ratios between the volatile solids of the substrate to be degraded and volatile solids of the inoculum biomass (*S/I*) were 0.5, 1, and 2 gVS/gVS. After preparation, the reactors were flushed with N_2 gas for 3 min and incubated under static conditions in a thermostatic chamber. Blank tests using the inoculum alone were also prepared to measure the quantity of methane produced only by the biomass. All tests were performed in triplicate.

The biogas volume produced during BMP tests was measured by means of the water displacement method (see Fig. 3b). The produced gas composition in terms of CH_4 and CO_2 was analysed using a portable gas analyzer (LFG 20-ADC, Gas Analysis Ltd). Methane volumes produced in the time interval between each measurement [$t-(t-1)$] during BMP tests, were calculated using a model, taking into consideration the gas concentration at time t and time $t-1$, together with the total volume of biogas produced at time t, the concentration of the specific gas at times t and $t-1$, and the volume of the head space of reactors [48]. The following equation was applied:

$$V_{C,t} = C_{C,t} \times V_{G,t} + V_H \times \left(C_{C,t-}C_{C,t-1}\right),$$

where $V_{C,t}$ is the volume of methane produced in the interval between t and $t-1$; $C_{C,t}$, $C_{C,t-1}$ are the methane concentrations measured at times t and $t-1$; $V_{G,t}$ is the volume of biogas produced between time t and $t-1$; V_H is the volume of the headspace of reactors.

Data on methane production are expressed at a temperature of 0 °C and pressure of 1 atm (Normal conditions).

Results and discussion

Biogas production reached a plateau after approximately 20 days.

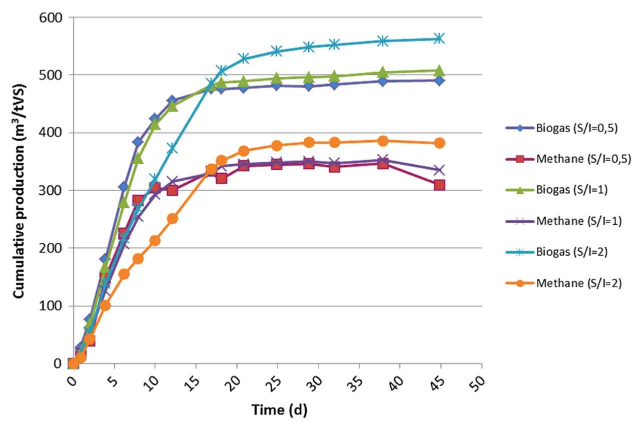

Fig. 4 Comparison between the three cumulative biogas and methane productions with *S/I* ratios of 0.5, 1, and 2

No differences were detected between biogas and methane productions using the ratios $S/I = 0.5$ and $S/I = 1$ (Fig. 4).

Compared to the methane yield reached at a *S/I* ratio of 0.5, a 23% increase was obtained using a substrate to inoculum ratio of 2. Maximum productions of biogas and methane obtained were 0.56 and 0.36 m^3/kgVS, respectively, considering the sole volatile solids of the substrate. These results are in agreement with the outputs published by Lane [26]. A 64% concentration of methane within biogas highlights the good quality of the latter. AD efficiency was also evaluated in terms of VS reduction. An increased biostability of the digestate was noticed when setting the *S/I* ratio at 2 in correspondence of which VS degradation (32.6 ± 1.0%) was 8 and 10% higher than the ones obtained in the other tests with *S/I* of 0.5 and 1, respectively, which is in agreement with the highest biogas production at this condition ($S/I = 2$).

Therefore, when dealing with SCGs, a *S/I* of 2 improved the performances of the AD treatment both in terms of energy recovery and final by-product biostability. Digestate could be promptly turned into a safe soil amending material without long and energy consuming treatment. Being hemicellulose and lignin, components of SCGs, resistant to enzymatic hydrolysis [49], a substrate pretreatment can be effective in enhancing the already high methane production yield.

Conclusions

Despite the potential options available for the exploiting of SCGs as a valuable resource in the form of food additives, pharmaceutical components, bio-sorbents, bio-products, and bio-fuels, to date scarce emphasis has been placed on these alternatives.

On the scenario of the diverse biorefinery approach currently available, the authors chose to assess the potential for bio-methane production of SCGs using different *S/I* ratios to clarify optimal conditions for anaerobic digestion, which remain to be fully investigated.

The highest bio-methane potential (0.36 m^3CH_4/kgVS) was obtained with a *S/I* ratio of 2, a remarkable yield compared to those obtained for other digested substrates, and which may justify the source segregation of SCGs when produced. The construction of a small-scale anaerobic biodigestor may constitute an innovative means of raising awareness into food waste management issues and the need for new sources of energy. If small-scale AD reactors were installed on the site of large cafes or restaurants, the energy recovered could be utilized by customers to charge their mobiles or supply power for lighting, TVs, or radios. This would undoubtedly favourably impress and attract the attention of the public, potentially acting as an effective campaign to promote renewable energies within the biorefinery concept.

References

1. International Coffee Organization (2016) Trade statistics tables. http://www.ico.org/trade_statistics.asp (2016). Accessed 24 Oct 2016
2. Murthy PS, Madhava Naidu M (2012) Sustainable management of coffee industry by-products and value addition—A review. Resour Conserv Recy 66:45–58. doi:10.1016/j.resconrec.2012.06.005
3. Obruca S, Benesova P, Kucera D, Petrik S, Marova I (2015) Biotechnological conversion of spent coffee grounds into polyhydroxyalkanoates and carotenoids. New Biotechnol 32(6):569–574. doi:10.1016/j.nbt.2015.02.008
4. Park J, Kim B, Lee JW (2016) In-situ transesterification of wet spent coffee grounds for sustainable biodiesel production. Bioresour Technol 221:55–60. doi:10.1016/j.biortech.2016.09.001
5. Al-Dhabi NA, Ponmurugan K, Maran Jeganathan P (2017) Development and validation of ultrasound-assisted solid-liquid extraction of phenolic compounds from waste spent coffee grounds. Ultrason Sonochem 34:206–213. doi:10.1016/j.ultsonch.2016.05.005
6. Girotto F, Alibardi L, Cossu R (2015) Food waste generation and industrial uses: a review. Waste Manag 45:32–41. doi:10.1016/j.wasman.2015.06.008
7. Lopez-Barrera DM, Vazquez-Sanchez K, Loarca-Pina MG, Campos-Vega R (2016) Spent coffee grounds, an innovative source of colonic fermentable compounds, inhibit inflammatory mediators in vitro. Food Chem 212:282–290. doi:10.1016/j.foodchem.2016.05.175
8. Bravo J, Monente C, Juániz I, De Peña MP, Cid C (2013) Influence of extraction process on antioxidant capacity of spent coffee. Food Res Int 50(2):610–616. doi:10.1016/j.foodres.2011.04.026
9. Fki I, Allouche N, Sayadi S (2005) The use of polyphenolic extract, purified hydroxytyrosol and 3, 4-dihydroxyphenyl acetic acid from olive mill wastewater for the stabilization of refined oils: a potential alternative to synthetic antioxidants. Food Chem 93(2):197–204. doi:10.1016/j.foodchem.2004.09.014
10. Sampaio A, Dragone G, Vilanova M, Oliveira JM, Teixeira JA, Mussatto SI (2013) Production, chemical characterization, and sensory profile of a novel spirit elaborated from spent coffee ground. LWT Food Sci and Technol 54(2):557–563. doi:10.1016/j.lwt.2013.05.042
11. Machado C, Soccol CR, de Oliveira BH, Pandey A (2002) Gibberellic acid production by solid-state fermentation in coffee husk. Appl Biochem Biotech 102(1–6):179–191. doi:10.1385/ABAB:102-103:1-6:179
12. Franca AS, Oliveira LS, Ferreira ME (2009) Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds. Desalination 249(1):267–272. doi:10.1016/j.desal.2008.11.017
13. Nakamura T, Hirata M, Kawasaki N, Tanada S, Tamura T, Nakahori Y (2003) Decolorization of indigo carmine by charcoal from extracted residue of coffee beans. J Environ Sci Heal A 38(3):555–562. doi:10.1081/ESE-120016917
14. Hirata M, Kawasaki N, Nakamura T, Matsumoto K, Kabayama M, Tamura T, Tanada S (2002) Adsorption of dyes onto carbonaceous materials produced from coffee grounds by microwave treatment. J Colloid Interface Sci 254(1):17–22. doi:10.1006/jcis.2002.8570
15. Rufford TE, Hulicova-Jurcakova D, Zhu Z, Lu GQ (2008) Nanoporous carbon electrode from waste coffee beans for high performance supercapacitors. Electrochem Commun 10(10):1594–1597. doi:10.1016/j.elecom.2008.08.022
16. Jung KW, Choi BH, Hwang MJ, Jeong TU, Ahn KH (2016) Fabrication of granular activated carbons derived from spent coffee grounds by entrapment in calcium alginate beads for adsorption of acid orange 7 and methylene blue. Bioresour Technol 219:185–195. doi:10.1016/j.biortech.2016.07.098
17. Burton R, Fan X, Austic G (2010) Evaluation of two-step reaction and enzyme catalysis approaches for biodiesel production from spent coffee grounds. Int J Green Energy 7(5):530–536. doi:10.1080/15435075.2010.515444
18. Kondamudi N, Mohapatra SK, Misra M (2008) Spent coffee grounds as a versatile source of green energy. J Agric Food Chem 56(24):11757–11760. doi:10.1021/jf802487s
19. Couto RM, Fernandes J, da Silva MG, Simões PC (2009) Supercritical fluid extraction of lipids from spent coffee grounds. J Supercrit Fluids 51(2):159–166. doi:10.1016/j.supflu.2009.09.009
20. Bok JP, Choi HS, Choi YS, Park HC, Kim SJ (2012) Fast pyrolysis of coffee grounds: characteristics of product yields and biocrude oil quality. Energy 47(1):17–24. doi:10.1016/j.energy.2012.06.003

21. Li X, Strezov V, Kan T (2014) Energy recovery potential analysis of spent coffee grounds pyrolysis products. J Anal Appl Pyrolysis 110:79–87. doi:10.1016/j.jaap.2014.08.012
22. Yang L, Nazari L, Yuan Z, Corscadden K, Xu C, He Q (2016) Hydrothermal liquefaction of spent coffee grounds in water medium for bio-oil production. Biomass Bioenerg 86:191–198. doi:10.1016/j.biombioe.2016.02.005
23. Al-Hamamre Z, Foerster S, Hartmann F, Kröger M, Kaltschmitt M (2012) Oil extracted from spent coffee grounds as a renewable source for fatty acid methyl ester manufacturing. Fuel 96:70–76. doi:10.1016/j.fuel.2012.01.023
24. Cruz MV, Paiva A, Lisboa P, Freitas F, Alves VD, Simões P, Barreiros S, Reis MA (2014) Production of polyhydroxyalkanoates from spent coffee grounds oil obtained by supercritical fluid extraction technology. Bioresour Technol 157:360–363. doi:10.1016/j.biortech.2014.02.013
25. Pan W, Perrotta JA, Stipanovic AJ, Nomura CT, Nakas JP (2012) Production of polyhydroxyalkanoates by Burkholderia cepacia ATCC 17759 using a detoxified sugar maple hemicellulosic hydrolysate. J Ind Microbiol Biotechnol 39(3):459–469. doi:10.1007/s10295-011-1040-6
26. Lane A (1983) Anaerobic digestion of spent coffee grounds. Biomass 3(4):247–268
27. Leifa F, Pandey A, Soccol CR (2001) Production of Flammulina velutipes on coffee husk and coffee spent-ground. Brazilian Archives of Biology and Technology 44(2):205–212. doi:10.1590/S1516-89132001000200015
28. Pushpa SM, Manonmani H (2008) Bioconversion of coffee industry wastes with white rot fungus Pleurotus florida. Res J of Environ Sci 2(2):145–150. doi:10.3923/rjes.2008.145.150
29. Cruz GM (1983) Resíduos de cultura e indústria. Informe Agropecuário 9:32–37
30. Mussatto SI, Carneiro LM, Silva JP, Roberto IC, Teixeira JA (2011) A study on chemical constituents and sugars extraction from spent coffee grounds. Carbohydr Polym 83(2):368–374. doi:10.1016/j.carbpol.2010.07.063
31. Claude B (1979) Étude bibliographique: utilisation dês sous-produits du café. Café Cacao Thé Paris 23(2):146–152
32. Givens D, Barber W (1986) In vivo evaluation of spent coffee grounds as a ruminant feed. Agric Wastes 18(1):69–72
33. Ramalakshmi K, Rao LJM, Takano-Ishikawa Y, Goto M (2009) Bioactivities of low-grade green coffee and spent coffee in different in vitro model systems. Food Chem 115(1):79–85. doi:10.1016/j.foodchem.2008.11.063
34. Passos CP, Coimbra MA (2013) Microwave superheated water extraction of polysaccharides from spent coffee grounds. Carbohydr Polym 94(1):626–633. doi:10.1016/j.carbpol.2013.01.088
35. Passos CP, Moreira AS, Domingues MRM, Evtuguin DV, Coimbra MA (2014) Sequential microwave superheated water extraction of mannans from spent coffee grounds. Carbohydr Polym 103:333–338. doi:10.1016/j.carbpol.2013.12.053
36. Simões J, Maricato É, Nunes FM, Domingues MR, Coimbra MA (2014) Thermal stability of spent coffee ground polysaccharides: galactomannans and arabinogalactans. Carbohydr Polym 101:256–264. doi:10.1016/j.carbpol.2013.09.042
37. Namane A, Mekarzia A, Benrachedi K, Belhaneche-Bensemra N, Hellal A (2005) Determination of the adsorption capacity of activated carbon made from coffee grounds by chemical activation with ZnCl 2 and H 3 PO 4. J Hazard Mater 119(1):189–194. doi:10.1016/j.jhazmat.2004.12.006
38. Silva M, Nebra S, Silva MM, Sanchez C (1998) The use of biomass residues in the Brazilian soluble coffee industry. Biomass Bioenerg 14(5):457–467. doi:10.1016/S0961-9534(97)10034-4
39. Sprules RK (1999) Coffee-based solid fuel composition. In: Google Patents, (1999)
40. Limousy L, Jeguirim M, Dutournié P, Kraiem N, Lajili M, Said R (2013) Gaseous products and particulate matter emissions of biomass residential boiler fired with spent coffee grounds pellets. Fuel 107:323–329. doi:10.1016/j.fuel.2012.10.019
41. Choi IS, Wi SG, Kim S-B, Bae H-J (2012) Conversion of coffee residue waste into bioethanol with using popping pretreatment. Bioresour Technol 125:132–137. doi:10.1016/j.biortech.2012.08.080
42. de Melo MM, Barbosa HM, Passos CP, Silva CM (2014) Supercritical fluid extraction of spent coffee grounds: measurement of extraction curves, oil characterization and economic analysis. J Supercrit Fluids 86:150–159. doi:10.1016/j.supflu.2013.12.016
43. Abdullah M, Koc AB (2013) Oil removal from waste coffee grounds using two-phase solvent extraction enhanced with ultrasonication. Renew Energy 50:965–970. doi:10.1016/j.renene.2012.08.073
44. Romeiro G, Salgado E, Silva R, Figueiredo M-K, Pinto P, Damasceno R (2012) A study of pyrolysis oil from soluble coffee ground using low temperature conversion (LTC) process. J Anal Appl Pyrolysis 93:47–51. doi:10.1016/j.jaap.2011.09.006
45. Neves L, Ribeiro R, Oliveira R, Alves MM (2006) Enhancement of methane production from barley waste. Biomass Bioenerg 30(6):599–603. doi:10.1016/j.biombioe.2005.12.003
46. AOCS (1997) Official method of analysis and recommended practices, 5th edn, Ba 6-84, Cd 8-53 and Ce 2-66. American Oil Chemists Society, Champaign
47. APHA, AWWA, WPCF (1999) Standard methods for the examination of water and wastewater, 20th ed. American Public Health Association, American Water Works Association, Water Environment Federation, Washington DC
48. Van Ginkel SW, Oh S-E, Logan BE (2005) Biohydrogen gas production from food processing and domestic wastewaters. Int J Hydrogen Energ 30(15):1535–1542. doi:10.1016/j.ijhydene.2004.09.017
49. Kong F, Engler C, Soltes E (1992) Effects of cell-wall acetate, xylan backbone and lignin on enzymatic hydrolysis of aspen wood. Appl Biochem and Biotechnol 34–35:23–35. doi:10.1007/BF02920531