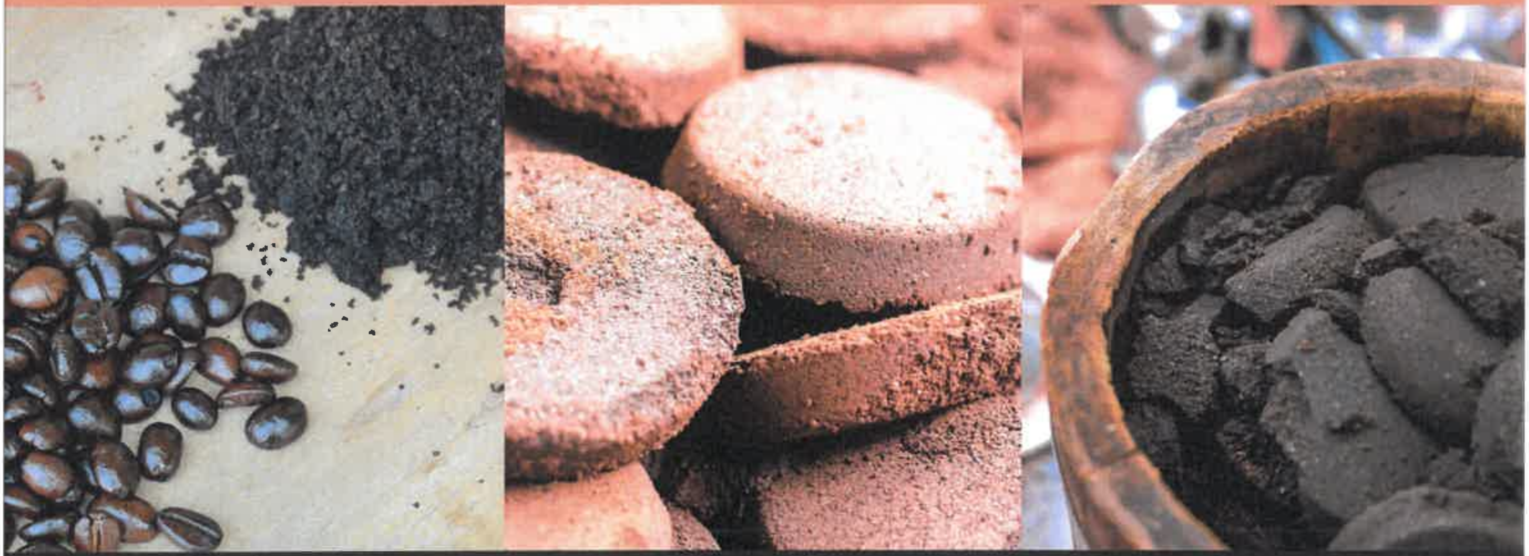
Handbook of Coffee Processing By-Products

Sustainable Applications



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525 B Street, Suite 1800, San Diego, CA 92101-4495, United States
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, United Kingdom

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Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-0-12-811290-8

For information on all Academic Press publications visit our website at
https://www.elsevier.com/books-and-journals

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Publisher: Nikki Levy
Acquisition Editor: Megan R. Ball
Editorial Project Manager: Jaclyn A. Truesdell
Production Project Manager: Lisa Jones
Designer: Greg Harris

Typeset by Thomson Digital

CHAPTER

State of the art in coffee processing by-products

1

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ABSTRACT

This chapter describes the steps involved in coffee processing from the field to the cup and the respective generation of by-products along the chain. The chemical composition of coffee husks, pulp, immature, and defective beans, coffee silverskin, and spent coffee grounds is detailed and methods for the sustainable management of these by-products are addressed, as well as legislative frameworks and policy recommendations. Although coffee by-products have a high potential of application in different fields, more integrated strategies with the involvement of coffee producers, industries, academic institutions, governmental and nongovernmental organizations are still needed to convert coffee by-products into really profitable substrates.

Keywords: coffee production; processing; waste; by-products; valorization; innovation; frameworks

1.1 INTRODUCTION

Coffee is one of the most popular beverages all over the world. Behind each hot and tasteful cup of coffee, which can be presented by so many different ways, a real journey is hidden. The genus *Coffea*, which belongs to the Rubiaceae family, embraces two of the more important plant species of the international coffee trade: *Coffea arabica* L. and *Coffea canephora* Pierre, widely known as Arabica and Robusta. *C. arabica* L., considering the different varieties and cultivated forms, originates about 65%–70% of the world coffee production. Its origin remounts to the mountains of Ethiopia (Yemen, AD 850) and it is an autogamic plant (self-fertile) (Alves et al., 2011; Ferrão, 2009). Its cultivation is carried out in regions of moderate temperature from tropical and subtropical areas. Some of the *C. arabica* varieties with higher commercial interest are the *typica* Cramer, the *bourbon* (B. Rodr.) Choussy, the *caturra* K.M.C., the *culumnaris* Ottotandr. ex Cramer, the *mokka* Hort. ex Cramer, and the *xanthocarpa* (Caminhoá) Froehner (Ferrão, 2009).

Handbook of Coffee Processing By-Products. http://dx.doi.org/10.1016/B978-0-12-811290-8.00001-3

Over the years, as the coffee market achieved great importance, an outstanding scientific and technical investment was performed. The preparation of new cultivars, ecologically well adapted, more productive, resistant to pests and diseases, giving origin to a commercial product of high quality, has been one of the fields in which success has been achieved. The selection and improvement of coffee have been fundamental tools in this process, which implied the use of hybridizations and crossings to assemble as many desirable characteristics as possible. Along this process, coffee plants that were not originally interesting due to the quality of the produced beverage were used to induce advantageous characteristics. Thus, besides the natural *C. arabica* varieties with their typical chromossomal and genetic composition, several others also have been emerging as a result of the genetic improvement (e.g., cultivar Catimor, cultivar Sarchimor) or, even, by natural and spontaneous crossing along the time (e.g., cultivar Mundo Novo, cultivar Bourbon-amarelo). Although not pure, their behavior in culture and their final product presents characteristics similar to those of natural Arabicas (Ferrão, 2009).

C. canephora Pierre, in turn, is indigenous from Equatorial African lowland forests from Guinea to Uganda and its cultivation was extended to Asia and South America. It is an allogamic species (self-sterile) that represents about 10%–25% of the worldwide coffee production. The organoleptic characteristics of these coffees are considered inferior to those of Arabica, but they contain higher levels of caffeine and total soluble solids. Besides, they present higher resistance to diseases, particularly to the coffee leaf rust (*Helimeia vastatrix*) and coffee berry disease (*Colletotrichum kahawae*). Also, their roasted seeds produce a "neutral" brew that easily accept the Arabica flavor, and because it is cheaper, *C. canephora* sp. have been assuming increased interest in international markets. Their applications are essentially to increase the body of the beverages (e.g., espresso coffee) and to produce instant coffee (Alves et al., 2011; Ferrão, 2009; Illy and Viani, 2005). We can cite as examples of varieties of this coffee species the *laurentii* De Wild, the *kouillensis* Pierre ex De Wild, the *ugandae* Cramer, and the *welwitschii* Chev (Ferrão, 2009). A summary of the main differences between Arabica and Robusta coffees is depicted in Table 1.1.

Besides the referenced main species—*C. arabica* L. and *C. canephora* Pierre—others can be listed, as *C. liberica* or *C. stenophyla*, but they present low economical importance compared to the first two, since from all the commercial coffees that

Table 1.1 Characteristics of Arabica and Robusta Coffees

Arabica Coffee	Robusta Coffee
• Superior cup quality • More appreciated organoleptic characteristics • Lower total soluble solids content • More vulnerable to pests and diseases	• Smaller bean size • Usually cheaper • Double caffeine content • Higher yield of extractable solids • More resistant to pests and diseases

currently circulate in the international market, about 98% correspond to Arabica and Robusta coffees (Ferrão, 2009).

Currently, more than 70 countries produce coffee. In 2015–16, the global coffee production was about 145 million of 60 kg bags, while the consumption rounded the 152.1 million. Brazil is the world's largest producer of coffee (~43 million 60 kg bags in 2015), followed by Vietnam (27.5 million 60 kg bags). Colombia and Indonesia are in third and fourth place, respectively (International Coffee Organization, 2016).

Along the several steps of coffee production (from the small producers to the big companies of coffee processing and roasting) a huge amount of residues is generated. For instance, in Brazil the production of coffee from 2008 to 2013 averaged 2.9 million tons, being generated about 1.4 million tons of wastes each year (Oliveira and Franca, 2015). Considering all the producing countries, coffee wastes and by-products constitute a source of severe contamination and a serious environmental problem. It is very important that coffee industries make an effort to valorize the by-products that result from coffee processing in order to increase the sustainability of the process. Simultaneously to an environmentally friendly approach, this can be seen as an opportunity to increase economical incomes and create new jobs. In fact, the different types of by-products are rich in valuable chemical compounds with potential applications in diverse biotechnological fields, such as pharmaceutical, food, or cosmetic ones.

The next subsections of this chapter detail the different steps of coffee beans processing (from the field to the fork) in order to show the variety of by-products generated in each phase and, subsequently, to highlight the suggested strategies to recover and use those by-products for innovative and useful applications.

1.2 COFFEE PROCESSING

1.2.1 THE POSTHARVESTING PROCESSING

The postharvesting processing aims to separate the seed from the remaining parts of the coffee fruit and guarantee a good preservation of the final product. Moreover, the technique has to be adequate in order to protect coffee from the acquisition of undesirable characteristics during all this process (Ferrão, 2009).

The coffee fruit has five layers of protective material that need to be removed in order to reveal the bean inside. From outside to inside, it is composed by:

1. the skin (epicarp or exocarp), a monocellular layer covered with a waxy substance; when ripe it can be red, yellow, or pink, according to the coffee variety;
2. the pulp (mesocarp), composed by a fleshy pulp and, in ripe fruits, a slimy pectinaceous layer of mucilage;
3. the parchment (endocarp), a thin polysaccharide covering;
4. the silverskin (or chaff), a thin tegument that directly coats the seed; and
5. two seeds with elliptical form (Farah and Santos, 2015; Instaurator, 2008).

The high quality of a commercial coffee can only be achieved when all (or almost all) the fruits are harvested in a perfect stage of maturation. However, this highly increases the costs of the process so, in a normal harvest, perfectly mature fruits (that should be the great majority) are usually mixed with some fruits that are excessively mature or, instead, immature (Ferrão, 2009). According to local conditions of the producer country, coffee processing can be performed by different methods (Alves et al., 2011). Each one has its own advantages and disadvantages; therefore it is not possible to select one as the best. It is possible to obtain commercial coffees of good quality using all the processes, if well conducted, and the technique selection depends a lot on the local possibilities (e.g., water availability) (Ferrão, 2009).

In the dry processing method, the cherries are dried and then mechanically dehusked. This process is used for most Brazilian, Ethiopian, and Haitian Arabica coffees, and for Robusta coffee in most parts of the world (Alves et al., 2011). In general, in this technique, excessively mature and immature beans are not usually separated from those perfectly mature and, thus, they will all compose the final batch. The fruits are harvested, and disposed in thin layers (5–10 cm) as quickly as possible. This, together with an adequate mixing along the process, should avoid pulp decomposition (due to its high content in water and sugars) that could originate the much-unappreciated "fermented beans" or "black beans." The drying process can be performed under the sun in yards (natural drying) or in mechanical dryers. The latest are recommended in regions where rain is frequent during the fruit-drying period or to finish the natural drying. During this process, the coffee beans detach from the parchment (endocarp) and after 3–4 weeks, depending on the drying conditions, the fruits are ready to be dehusked (moisture <12%). Nevertheless, if the dried fruits could rest (e.g., in silos) for some months before dehusking, the quality of the final product can be improved. During dehusking, the pericarp (skin, pulp, and parchment) is removed from the beans (Ferrão, 2009).

The wet method is a more sophisticated procedure compared to the previous one. It is based on depulp of the fruits, followed by fermentation. Although this process demands water in abundance and specific technical equipment, it generally allows the obtention of higher quality coffees with higher economical value. It is mainly used for Arabica coffees and coffees of higher quality (Alves et al., 2011; Ferrão, 2009). In order to be wet-processed, the fruits should be in a perfect state of maturation; therefore a careful selection of the cherries is needed, often with manual harvesting or with machinery that allows the separation of the mature beans. In this case, selection and washing tanks in which the coffee will be processed are unevenly disposed in a way that the materials can be separated by gravity. The well-mature beans present a slightly higher density than water and tend to deposit. The green and excessively mature fruits usually float. Therefore, it is possible to separate them and only the mature ones will proceed to the subsequent step: the depulping phase. This operation intends to remove the epicarp and the mesocarp of the fruit. At the end of depulping, the seed is still involved in the endocarp (Fig. 1.1). The gelatinous layer

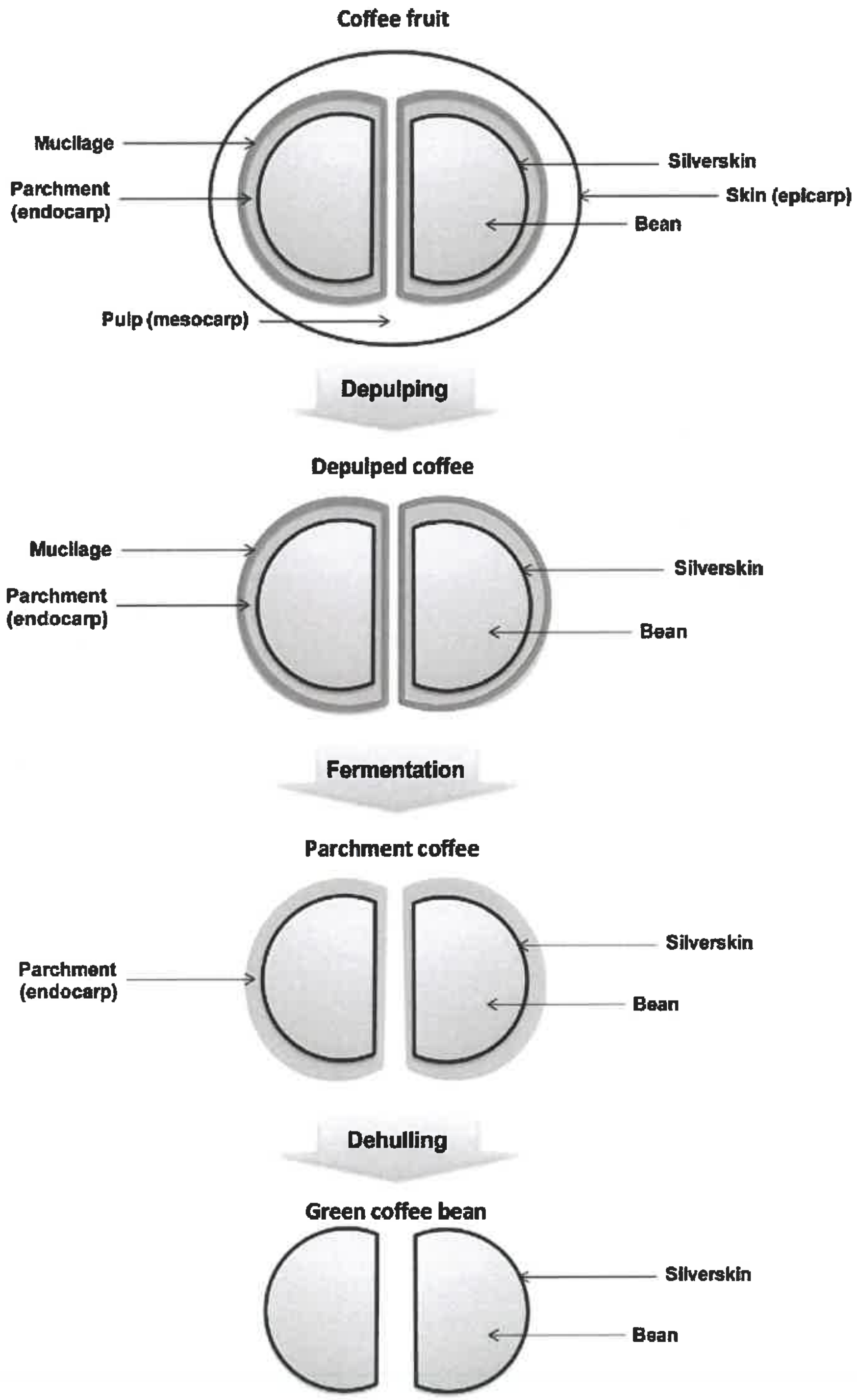


FIGURE 1.1 Coffee Processing Steps in the Wet Postharvesting Method

(mucilage) that coats the endocarp facilitates depulping by reducing the number of broken seeds and the strength to be applied. However, its tendency to retain water and slippery characteristics can impair the following phases. This mucilage, composed mainly by pectins, can be eliminated by fermentation, a process that involves a complex group of chemical and biological reactions. In this phase, the coffee stays in rest to allow the enzymatic and other processes to occur naturally, causing the degradation of mucilage. During this process, the temperature often increases, due to the alcoholic fermentation of the pulp sugar remaining, which is favorable to the enzymatic action of pectinases. The ideal time of fermentation is between 24 and 72 h. Otherwise, the color of the beans can be affected (fermented beans). Besides the natural action of pectinases, commercial enzymes or chemical agents can be also added to increase the efficiency of the process. However, it is still not a very common procedure (Ferrão, 2009).

In a third process, called "semidry" or "semiwashed," concepts of both dry and wet methods are combined. This method consists of washing and selecting the fruits in flotation tanks, followed by depulping, but excluding the fermentation step (Farah and Santos, 2015). Then, the depulped coffee, which contains the mucilage remains, can be directly dried. This process has been used in Central Africa and Brazil, producing the "natural depulped coffee". Both, wet- and semiwashed methods require an additional step for parchment removal, an inner membrane that stays adherent to the beans (Alves et al., 2011).

In addition, in the last years, the mucilage elimination by friction (mechanical action), instead of water, has been gaining supporters. Machines and equipments based on this principle have been appearing in the market, allowing the use of a method that simultaneously saves costs and water. In several regions where the dry-method was a tradition due to the water scarcity, these equipments were, indeed, very well accepted. These machines receive directly the fruits from the washing and calibration and, in sequence, remove the pulp, the mucilage, and wash the parchment coffee that is then ready to be dried and processed (Ferrão, 2009).

As previously referenced, along all of these types of processing, several by-products are generated. Just as an example, values described for washed Colombia coffee show that each 100 kg of mature fruits are constituted by 39 kg of pulp, 22 kg of mucilage, and 39 kg of parchment coffee (Ferrão, 2009). Therefore, considering the millions of bags produced in just 1 year, it can be highlighted that the amount of generated residues is extremely high. Fig. 1.2 summarizes the described postharvesting techniques and the main by-products generated in each one.

1.2.2 THE COFFEE ROAST

The roasting of raw beans is usually carried out in the consumer countries due to the friability and flavor characteristics of roasted beans, which would not resist the necessary movements of international circulation (Ferrão, 2009).

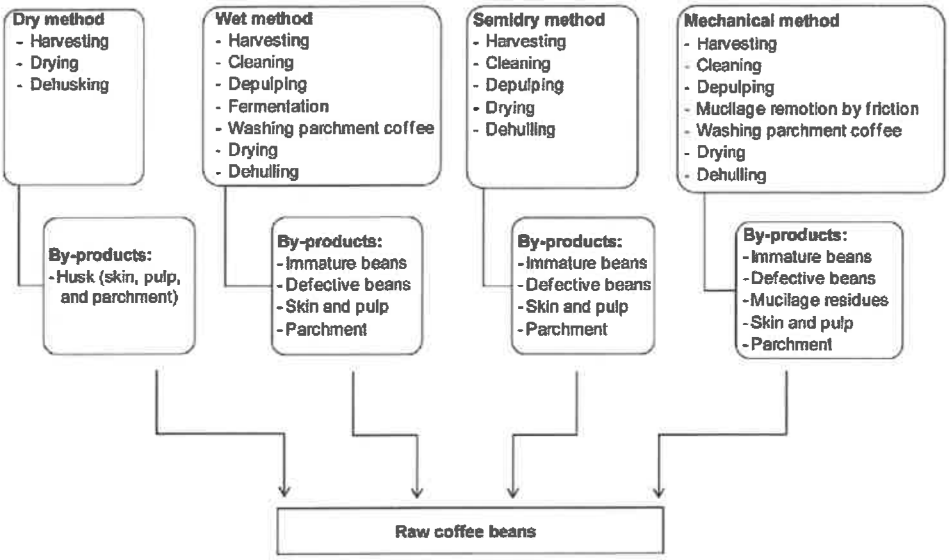


FIGURE 1.2 The Main Processes of Coffee Fruit Postharvesting Processing and the Respective Generated By-Products

After reception and confirmation of their quality, the beans are stored till roasting. When the bags are opened, coffee is usually subjected to a new cleaning step to remove any defective or immature beans, small stones, or metal pieces, for instance, by using a system of sieves and a metal detector, respectively.

Different types of roast can be employed, based on several points of view, namely mechanical, thermal, and operational. Summing up, the modern technologies present as basic principle the passage of a forced convective flow of hot gases through a moving bed of coffee beans. The beans movement can be created by rotation or by the flow of roasting gases (Illy and Viani, 2005).

The chemical composition of green beans is already very complex. During the roast, several physical and chemical reactions occur (with the formation and/or degradation of several chemical compounds), and consequently, the organoleptic characteristics of the beans are completely modified. At this stage, the silverskin (the thin tegument that coats the bean) is detached and can be separated from the final product by air flow, representing the main by-product of coffee roast industry (Fig. 1.3). Industrial data revealed that the roasting of about 4 tons of coffee produces about 30 kg of silverskin. Considering the millions of tons of coffee beans roasted annually all over the world, a huge amount of this by-product is produced. Since silverskin is not usually employed to prepare coffee beverages, it is discarded and often used as firelighters or dispatched to landfills (Costa et al., 2014). After roast, more cleaning steps can be performed. Then, the roasted beans can be directly packed or ground. In this last case, ground coffee can be sold as it is or used to prepare capsules or instant powder.

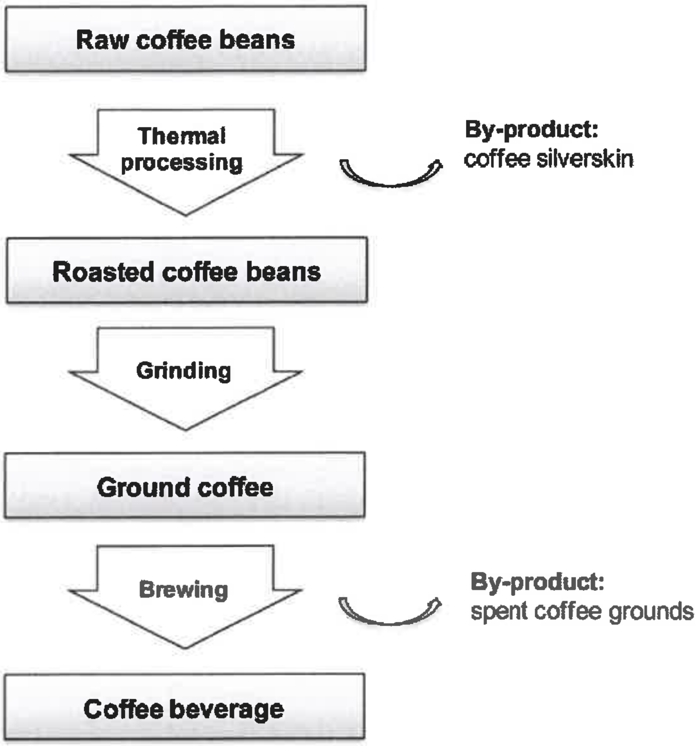


FIGURE 1.3 Raw Coffee Beans Processing and Generated By-Products

1.2.3 THE COFFEE BEVERAGE

The coffee beverage can be prepared by many different ways, namely by decoction (e.g., boiled coffee, Turkish coffee, percolator coffee), infusion (e.g., filtered and napoletana coffees), and pressure (e.g., press-pot, mocha, and espresso coffees) (Petracco, 2001). The composition of the final beverage will depend not only on the brew method (e.g., coffee grinding degree, powder/water ratio, water temperature, time of extraction) but also on the coffee species used to prepare the commercial blend. Moreover, different studies have been showing differences in the extractability of compounds according to coffee roast conditions (Alves et al., 2007; Alves et al., 2010a,b). By this way, the composition of the residue that remains after coffee beverage preparation will vary, too. However, a main conclusion can be achieved: the chemical compounds of coffee are not all extracted along brewing and the residue is still rich in different chemicals with important bioactivities.

In the same perspective, and considering the industrial preparation of instant/soluble coffee, several methods can be employed for its preparation, which in general are based on the production of a dried soluble portion of coffee aqueous extracts by percolation, concentration, and dehydration (e.g., evaporation, freeze-drying, spray-drying) (Alves et al., 2011). In this case, coffees with a higher roast degree (preferably Robusta) are usually employed in order to increase the yield of extraction. Besides, the spent coffee from the instant coffee industries is more exhaustively extracted, compared to the "richer", but more disperse spent coffee resulting from beverage preparation at coffee shops, restaurants, and homes. Soluble coffees are consumed all over the world, representing more than 70% of coffee consumed in Great Britain, Ireland, and Australia, >50% in Japan, >40% in USA and Canada, ~20% in Spain, and ~5% in Portugal. In this last case, it represents a consumption of more than 100 ton of imported soluble coffee per year (Ferrão, 2009). This type of coffee is appreciated essentially for its easiness of preparation for consumption.

Depending on the conditions of coffee extraction different weight percentages of spent coffee can be achieved. This worthless residue is normally simply discarded into dustbins, and finally, sent to landfills (Low et al., 2015).

1.3 COFFEE BY-PRODUCTS COMPOSITION AND POTENTIAL APPLICATIONS

Coffee processing by-products include those derived from postharvesting processing, coffee roasting, and coffee consumption, namely, immature/defective beans, husks, skin and pulp, parchment, silverskin, and spent coffee. Along the years, an increase in these wastes has been observed, directly related to the rise of coffee consumption in the world. Being these by-products a great source of bioactive compounds, their valorization and use can be of interest for different industries and fields, such as food, pharmaceutical, or cosmetic ones. Although all of the coffee by-products could be used for new purposes, a lot still needs to be done by both industries and researchers to achieve a real economic feasibility. The dispersion of the residues, the high perishability of the majority, together with the high cost for their separation, collection, and transportation to industrial facilities where they could be treated and transformed, makes this process a real challenge.

1.3.1 COFFEE HUSKS/PULP

Coffee husks are the main solid residues obtained during coffee dry processing. They are composed of the dried skin, the pulp, the mucilage, and the parchment, all together in a single fraction (Esquivel and Jiménez, 2012). On a dry-weight basis, husks represent about 12% of the cherry, and for each ton of harvested coffee fruit, about 0.18 tons of coffee husks are produced (Murthy and Naidu, 2012).

In contrast, the wet-processing method allows the recovery of the skin and pulp in one fraction, which is generally called coffee pulp (40%–50% of the fresh weight of coffee berries) (Dias et al., 2015; Esquivel and Jiménez, 2012; Hernandez et al., 2009). Coffee pulp is produced in large amounts: generally, about 1 ton is obtained from every 2 tons of produced coffee (Murthy and Naidu, 2012; Roussos et al., 1995). In 2008, only in Mexico, the coffee pulp production was estimated in 707 million dry tons (Torres-Mancera et al., 2013).

Several studies have been carried out to assess the chemical composition of coffee husks and coffee pulp. Franca and Oliveira (2009) compiled data from different authors, describing that husks are composed (in dry weight) by protein (8%–11%), lipids (0.5%–3%), minerals (3%–7%), carbohydrates (58%–85%), reducing sugars (14%), caffeine (~1%), and tannins (~5%). According to Bekalo and Reinhardt (2009), coffee husks contain 24.5% of cellulose, 29.7% of hemicelluloses, 23.7% of lignin, and 6.2% of ash. Coffee husks are also known for their high content in secondary metabolites, such as caffeine and polyphenols (Esquivel and Jiménez, 2012; Murthy and Naidu, 2012; Pandey et al., 2000). Mullen et al. (2013) described 5-O-caffeoylquinic acid as the major phenolic present in Arabica and Robusta coffee husks from Mexico and India (0.2–1.9 mg/g). Other compounds were also identified although in minor amounts (in the μg/g range), namely quercetin-3-O-rutinoside, quercetin-3-O-glucoside, quercetin-3-O-galactoside, (+)-catechin, and (−)-epicatechin, and procyanidin dimers, trimers, and tetramers. In general, the phenolic profile of the husks varied widely according to the geographical origin and species. For example, total procyanidin contents varied from 1.3 μg/g (Chinese Robusta husks) and 534 μg/g (Indian Robusta husks) and total flavonols ranged from 5 μg/g (Indian Robusta husks) to 261 μg/g (Mexican Arabica husks) (Mullen et al., 2013).

When compared to husks (1.2%), coffee pulp presented a higher total phenolic content (1.5%) (Murthy et al., 2012). Ramirez-Coronel et al. (2004) being identified four major classes of phenolic compounds in Arabica coffee pulp, namely flavan-3-ols, hydroxycinnamic acids, flavonols, and anthocyanidins. Also, in fresh coffee pulp, Ramirez-Martinez (1988) reported the presence of 5-caffeoylquinic acid (identified as the major phenolic), epicatechin, 3,4-dicaffeoylquinic acid, 3,5-dicaffeoylquinic acid, 4,5-dicaffeoylquinic acid, catechin, rutin, protocatechuic acid, and ferulic acid. Other phenolics have been found by other authors, such as 5-feruloylquinic acid (Clifford and Ramirez-Martinez, 1991), cyanidin-3-rutinoside, and cyanidin-3-glucoside (Esquivel et al., 2010). The soluble and bound hydroxycinnamates in Arabica coffee pulp from seven cultivars were evaluated by Rodríguez-Durán et al. (2014), considering three ripening stages. Chlorogenic acid was the main phenolic acid (94%−98%) in the soluble fraction, whereas caffeic acid was the most abundant hydroxycinnamate found in the bound fraction (72%−88%). Ferulic and *p*-coumaric acids were detected, too, although in small amounts. Considering the ripening stage, the maximum content of total hydroxycinnamates in pulp was at the semiripe stage. However, its concentration decreased at the ripe stage in six of the seven studied cultivars. In addition, coffee pulp is very rich in fiber (~61%) and has a high content of protein and sugars (~12% and 14%, respectively), minerals (especially potassium), tannins, and caffeine (Murthy et al., 2012). It is also described that yellow coffee varieties have higher proanthocyanidin content than the red ones (De Colmenares et al., 1994). This group of compounds largely contributes to organoleptic features, such as bitterness and astringency (Ramirez-Coronel et al., 2004).

The disposal of coffee husks/pulp represents an environmental burden, especially due to their chemical composition, namely their content in caffeine and tannins (Giannetti et al., 2011; Salmones et al., 2005). For instance, tannins are considered antinutritional factors and are the reason why the amount of coffee pulp in animal feed should be limited to 10% (Pandey et al., 2000).

Nevertheless, other approaches have been suggested to use coffee husks/pulp namely as fertilizers, for composting or vermicomposting, as biosorbents, for bioethanol production or caffeine extraction (Bonilla-Hermosa et al., 2014; Gurram et al., 2016; Hughes et al., 2014; Murthy et al., 2012; Mussatto et al. 2011a; Pandey et al., 2000; Shemekite et al., 2014; Tello et al., 2011). Their content in tannins and fermentable sugars makes them ideal substrates for bioprocesses, too. Considering that gallic acid can be produced by microbial hydrolysis of tannic acid by tannase, secreted by microorganisms, coffee pulp was suggested as a potential raw material to produce gallic acid by microbial transformation (Bhoite et al., 2013).

The extraction and recovery of bioactive compounds, as phenolic acids and related compounds, is one of the most promising applications to valorize these by-products (Murthy and Naidu, 2012). The production of value-added products, such as enzymes, organic acids, flavor and aroma compounds has also been studied (Pandey et al., 2000; Rodríguez-Durán et al., 2014).

Besides, strategies that detoxify coffee husks and pulp from their phytotoxic compounds and antinutritional factors, or at least that degrade them to a plausibly safe level, led to different possibilities of use, namely as biofertilizer, feed, or even as a substrate for the production of edible mushrooms.

For instance, Brand et al. (2000) tested biological detoxification of coffee husk by filamentous fungi (Rhizopus, *Phanerochaete*, and *Aspergillus* spp.) using a solid-state fermentation system in which coffee husk was used as the sole source of carbon and nitrogen source. *R. arrizus* LPB-79 showed great results on the degradation of caffeine and tannins (87% and 65%, respectively), which were obtained in 6 days (pH = 6.0; moisture: 60%). With *P. chrysosporium* BK, maximum degradation rates of 70.8% and 45% for caffeine and tannins, respectively, were obtained in 14 days (pH = 5.5; moisture: 65%). An *Aspergillus* strain, isolated from the coffee husk, showed the best biomass formation on coffee husk extract-agar medium. Optimization assays were carried out using a factorial design and surface response experiments with *Aspergillus* sp. The best detoxification rates achieved were 92% for caffeine and 65% for tannins. These results showed good prospects of using these fungal strains, in particular *Aspergillus* sp., for the detoxification of coffee husk.

1.3.2 IMMATURE AND DEFECTIVE COFFEE BEANS

The presence of defective and immature beans results from problems during harvesting and preprocessing operations (Franca and Oliveira, 2008). According to Ramalakshmi et al. (2007), the defective coffee beans represent about 15%–20%

of coffee production on a weight basis. The most important defects are black, sour, or brown, immature, bored or insect-damaged, and broken beans. The immature beans, which result from immature fruits, normally contribute to beverage astringency. Both black and sour defects are associated with bean fermentation and decrease significantly the quality of the beverage. Immature-black beans usually fall on the ground while immature, remaining in contact with the soil where they suffer fermentation (Franca et al., 2005; Mazzafera, 1999). In the case of green coffee, it is possible to differentiate defective and nondefective (healthy) beans by color, size, acidity levels, sucrose levels, and the presence of histamine. However, in the case of roasted coffee, only an evaluation of the volatile profile will effectively provide the means for differentiation. The macro differences could be observed based on the volume of immature coffee beans, which is lower. Likewise, defective beans attain a lighter roasting degree than nondefective ones under the same roasting conditions (Franca and Oliveira, 2008; Vasconcelos et al., 2007). Mazzafera (1999) described that nondefective beans are heavier and present higher moisture contents compared to immature and black beans. Protein and oil levels are higher in nondefective beans, but free amino acids (especially asparagine) and soluble phenol contents are higher in defective beans. The amount of 5-caffeoylquinic acid was approximately 35% higher in immature coffees, which is in accordance with data published by Farah et al. (2005) that also reported significantly higher levels of all chlorogenic acids in immature beans.

The total mineral content of defective coffee beans is higher (~6% dry basis) comparing to nondefective ones (~5% dry basis). Potassium is the predominant mineral, followed by calcium and magnesium (Oliveira et al., 2006; Vasconcelos et al., 2007). Lower sugar and sucrose contents were observed in immature beans comparatively to healthy ones, showing that the amount of sugar is primarily associated with the developmental stage of the fruit (Mazzafera, 1999; Vasconcelos et al., 2007). In addition, higher caffeine levels have been associated to the presence of defective or low quality coffees (Franca et al., 2005; Mazzafera, 1999). Trigonelline, together with caffeine, receives considerable attention in coffee chemistry research, because this alkaloid is responsible for aroma compounds production. During roasting, trigonelline is partially degraded to produce two important compounds—pyridines and nicotinic acid (vitamin B3). According to Franca et al. (2005), trigonelline levels were about 1% in nondefective, immature and sour coffee beans, but lower values (~0.8%) were found for black-immature beans. In addition, significantly lower levels of 5-caffeoylquinic acid were detected.

Regarding lipids, the fatty acid composition of oils from defective beans was not significantly different from healthy mature coffee beans (Oliveira et al., 2006). Oliveira et al. (2006) reported that linoleic and palmitic acids are the predominant fatty acids, with averages of 44% and 34%, respectively, while miristic and palmitoleic acids are present in trace amounts.

According to literature, in Brazil, the defective beans are separated from the nondefective ones prior to commercialization in the international market and dumped in the Brazilian internal market, thus depreciating the quality of the roasted coffee consumed in that country (Franca et al., 2005). The extraction of the oil (Oliveira et al., 2006) or their bioactive compounds, such as chlorogenic acid or caffeine, for potential applications in the food and pharmaceutical sectors, can be considered an alternative use for those low-grade coffee beans.

1.3.3 SILVERSKIN

Coffee silverskin is a thin layer that is directly in contact with the coffee bean. Strongly adherent, it is only detached during roasting, because it does not expand like the bean during the thermal processing. It is the main by-product of coffee-roasting industries, which have to collect it mandatorily. Coffee silverskin is currently used as direct fuel (such as firelighters), for composting and soil fertilization (Costa et al., 2014; Mussatto et al., 2011a). Compared to the other coffee by-products, it is a relatively stable product due to the lower moisture content (~7%) (Borrelli et al., 2004) acquired during the roast, and it could be easily gathered for further processing. However, the produced amount is lower compared to other coffee by-products, since silverskin represents a minor fraction of coffee production. Even so, based on data kindly provided by an industrial coffee roaster, which revealed that for 120 tons of roasted coffee about 1 ton of silverskin is produced, and considering the millions of coffee bags produced around the world every year (see Section 1.1), this by-product presents a huge potential for being used and valorized.

Silverskin is rich in protein (19%) and dietary fiber (62%), especially the soluble one (86% of total dietary fiber) (Borrelli et al., 2004). It contains 18% of cellulose and 13% of hemicellulose, being this last composed by xylose (4.7%), arabinose (2.0%), galactose (3.8%), and mannose (2.6%) (Carneiro et al., 2009). Napolitano et al. (2007) reported fat contents varying from 1.6% to 3.3% and caffeine levels ranging from 0.8% to 1.4%. Both were dependent on the geographical origin of the samples. In terms of fat composition, the detected profile varied according to the method used for lipids extraction (Toschi et al., 2014). With a classic Soxhlet extraction with *n*-hexane, triacylglycerols were found to be the major components of lipids (48%), followed by free fatty acids (21%), esterified sterols (15%), free sterols (13%), and diacylglycerols (4%). In what concerns to the fatty acids profile, C18:2*n*-6 and C16:0 were the major ones (29% and 28%, respectively), followed by C22:0 and C20:0 (11% each) (Toschi et al., 2014).

According to Ballesteros et al. (2014), silverskin is also an interesting source of minerals (5% of ash), containing mainly potassium (21,100 mg/kg of dry silverskin), calcium (9,400 mg/kg), magnesium (3,100 mg/kg), sulfur (2,800 mg/kg), phosphorous (1,200 mg/kg), and iron (843 mg/kg), among others. Nevertheless, the authors also reported the presence of aluminum (470 mg/kg). Borrelli et al. (2004) found that ochratoxin A levels were below to 4 μg/kg, the maximum level suggested by the Istituto Superiore Sanità, Italy. However, Toschi et al. (2014) found 5- to 9-fold higher levels: from 17.8 to 36.1 μg/kg, which should be more explored due to safety issues.

Silverskin antioxidant activity, due to melanoidins (formed through Maillard reactions during roasting) and phenolic compounds, has also been shown in different studies (Ballesteros et al. 2014; Borrelli et al., 2004; Costa et al., 2014), highlighting the potential of this by-product as an alternative functional ingredient for the food industry. In fact, the amount of water-soluble melanoidins of this by-product is about 4.5%, comparable to that observed in coffee brews (Borrelli et al., 2004). In what concerns total phenolics content, Costa et al. (2014) described 302.5 ± 7.1 mg of gallic acid equivalents (GAE) per liter of extract, which was prepared using 1 g of silverskin in 50 ml of ethanol:water (1:1). The authors also found tannins (0.43 ± 0.06 mg tannic acid equivalents/L) and flavonoids (83.0 ± 1.4 mg epicatechin equivalents/L). In another study, Toschi et al. (2014) reported 0.39–0.73 g gallic acid equivalents per 100 g of silverskin. Using HPLC, Narita and Inouye (2012) were able to detect 1.1 mg of 5-caffeoylquinic acid per gram of silverskin.

It was found that, in association with its antioxidant activity, silverskin aqueous extracts have in vitro antiglycative properties, protecting against the formation of advanced glycation end-products and trapping of carbonyl reactive species, such as methylglyoxal (Mesías et al., 2014). Moreover, silverskin showed to be efficient as prebiotic, namely for bifidobacteria. Instead, *Lactobacillus* spp. and coliforms showed a limited aptitude to use silverskin for their growth, while *Bacteroides* spp. and clostridia growth was inhibited (Borrelli et al., 2004).

Based on its promising health benefits, Martinez-Saez et al. (2014) used coffee silverskin to prepare a novel antioxidant beverage for body weight control and Mussatto et al. (2011a) suggested that the incorporation of silverskin in flakes, breads, biscuits, and snacks can be an interesting approach. Moreover, Pourfarzad et al. (2013) used coffee silverskin after subjected to a treatment with alkaline hydrogen peroxide to give higher quality, shelf life, sensory, and image properties to Barbari flat bread, simultaneously reducing the caloric density and increasing dietary fiber content of the product.

In another perspective, Mussatto et al. (2011a) suggested that the chemical composition of silverskin opens up possibilities for innovative applications. For instance, cellulose and hemicelluloses can be converted to polysaccharides, oligosaccharides, and monosaccharides using acid treatments or enzymes. Subsequently, those sugars can be used to produce added-value compounds (e.g., glucose into ethanol or butanol, manose into mannitol) (Mussatto et al., 2011a).

Finally, silverskin has also been a focus of study for the cosmetic field. Rodrigues et al. (2015) demonstrated with in vitro and in vivo assays that silverskin extracts are not irritants and can be regarded as safe for topical application. In another study, Rodrigues et al. (2016) reported for the first time the successful use of silverskin as a cosmetic active ingredient with similar results to hyaluronic acid in the improvement of skin hydration and firmness.

1.3.4 SPENT COFFEE GROUNDS

Spent coffee grounds are the main by-product of the coffee brewing process and are obtained by both domestic brew preparation (at coffee shops, restaurants, homes) or during the industrial preparation of instant coffee. They consist of a dark brown solid residue with high moisture, being those from the first origin richer in chemical compounds compared to spent coffee from instant coffee industries. This is understandable since for soluble coffee production, extraction is maximized in order to obtain the highest yields.

Ballesteros et al. (2014) analyzed the nutritional composition of spent coffee grounds derived from mixtures of Arabica and Robusta coffee varieties, provided by a coffee roaster industry, highlighting the richness of this by-product in polysaccharides, lignin, and protein. The ash content is a minority, representing 1.3% w/w, and being composed by a variety of elements, including potassium, calcium, magnesium, sulfur, phosphorus, iron, manganese, boron, copper, and others. Potassium is the most predominant element. These minerals are micronutrients that could have different body functions, such as hormonal and enzymatic activities, electrolyte balance, and normal growth.

The fat content of fresh spent coffee grounds is about 2% w/w (Ballesteros et al., 2014; Jiménez-Zamora et al., 2015). In turn, different authors reported that dried spent coffee contains between 13% and 18% of oil (Al-Hamamre et al., 2012; Kulkarni and Dalai, 2006; Petrik et al., 2014). According to Couto et al. (2009), palmitic (C16:0) and linoleic (C18:2) acids are the major fatty acids and comprise about 35% each of the total fatty acid content of the extracted oil. Coffee oil is also rich in vitamin E, namely α- and β-tocopherols (no other vitamers are present), and according to Alves et al. (2010b) only a small percentage (approximately 1%) of the total tocopherol amount in the coffee cake is extracted during the preparation of classic espresso coffee. Although the use of servings or capsules may increase 5-fold the amount of vitamin E extracted into the brew, 95% of the original tocopherols still remains in the coffee cake. This makes spent coffee grounds a very rich source of this liposoluble antioxidant vitamin. This goes in accordance to Gross et al. (1997) that stated that lipids and several hydrophobic compounds are mainly retained in the spent coffee.

Regarding protein, the reported contents in spent coffee grounds range between 14% and 17.5% w/w (Ballesteros et al., 2014; Mussatto et al., 2011b; Ravindranath et al., 1972). The suitability of the proteins in spent coffee grounds is considered poor due to its thermal history and contents of phenolics and melanoidins (Monente et al., 2015). According to Lago et al. (2001), glutamic acid and leucine are the predominant amino acids, but in lower amounts than in coffee beans.

The content of total dietary fiber is about 62% w/w, being the insoluble portion predominant: 5 times higher than the soluble fraction (Ballesteros et al., 2014; Jiménez-Zamora et al., 2015). Hemicellulose (constituted by mannose, galactose, and arabinose) and cellulose are the most representative polysaccharides (Ballesteros et al., 2014; Mussatto et al., 2011b). In terms of sugars, the spent coffee is composed by ~37% mannose, ~32% galactose, ~24% glucose, and ~7% arabinose. Xylose is not present (Ballesteros et al., 2014). Lignin, a macromolecule composed by a great variety of functional groups, is also present in significant amounts (~24% w/w) (Ballesteros et al., 2014; Stewart, 2008).

Besides, in addition to its interesting nutritional profile, spent coffee also contains a wide range of components formed through the Maillard reactions during the roast, such as melanoidins (Borrelli et al., 2004). In fact, based on its chemical composition, authors have been suggesting the potential interest of spent coffee for different industries, such as cosmetic, nutraceutical, or even pharmaceutical (Esquivel and Jiménez, 2012; Mussatto et al., 2011a).

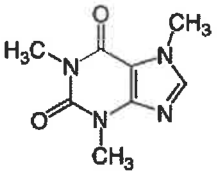
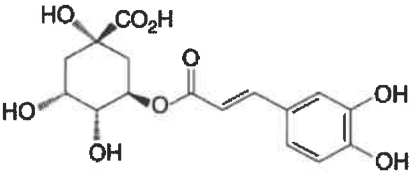
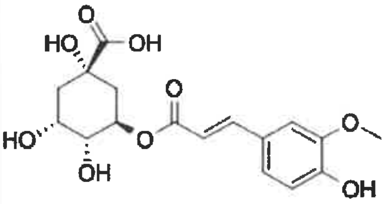
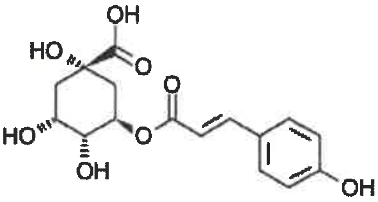
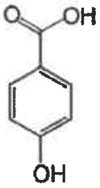
Several studies determined the bioactivity of spent coffee ground extracts, using different solvents and methods (Bravo et al., 2012; Panusa et al., 2013; Ramalakshmi et al., 2009). Ramalakshmi et al. (2009) compared the DPPH scavenging activity and the oxygen radical absorbance capacity (ORAC) of methanolic extracts of spent coffee grounds and low-grade green coffee beans. No significant differences in radical-scavenging activity between samples were observed, with results ranging between 82% and 92%, respectively, for coffee beans and spent coffee. Bravo et al. (2012) reported that the antioxidant capacities of the aqueous spent coffee extracts depends on the coffee brew preparation, ranging between 46.0% and 102.3% for filter, 59.2% and 85.6% for espresso, and almost 42% for plunger, in comparison to their respective coffee brews.

Most of this antioxidant activity seems to be due to the phenolic compounds present in this by-product. Panusa et al. (2013) extracted and analyzed spent coffee grounds in order to evaluate the recovery of relevant natural antioxidants. The results showed total phenolics ranging between 17 and 35 mg of GAE/g dry sample. Other studies reported slightly lower values: 16–19 mg GAE/g (Mussatto et al., 2011c; Zuorro and Lavecchia, 2012). Chlorogenic and caffeic acids are the most relevant phenolic components in this by-product (Maydata, 2002). Such compounds can play an important role in health due to their antioxidant properties. Nevertheless, their contents are mainly dependent on coffee species and beans maturity. Among phenolics, the main compounds are caffeoylquinic acids, feruloylquinic acids, *p*-coumaroylquinic acids and mixed diesters of caffeic and ferulic acids with quinic acid (Esquivel and Jiménez, 2012; Farah and Donangelo, 2006). According to Ramalakshmi et al. (2009) the major antioxidant compound present in spent coffee is chlorogenic acid (5-caffeoylquinic acid): almost 6%. Bravo et al. (2012) also demonstrated that spent coffee had relevant amounts of total caffeoylquinic acids (6.22–13.24 mg/g), mainly dicaffeoylquinic acids (3.31–5.79 mg/g), which were 4- to 7-fold higher than in their respective coffee brews. Panusa et al. (2013) reported that the total content of chlorogenic acid and derivatives varied between 1.65 and 6.09 mg 5-caffeoylquinic acid equivalents/gram dry basis. More recently, Monente et al. (2015) assessed the total phenolic compounds in spent coffee ground extracts and reported that free and bound caffeoylquinic, dicaffeoylquinic, caffeic, ferulic, *p*-coumaric, sinapic, and 4-hydroxybenzoic acids were detected. According to the same study, phenolic compounds with one or more caffeic acid molecules were approximately 54% linked to macromolecules, such as melanoidins.

Besides chlorogenic acid and its derivatives, methylxanthines are present in spent coffee and caffeine is the major one recovered, representing 1%–2% of dry matter (Esquivel and Jiménez, 2012). According to Bravo et al. (2012), the caffeine content ranged from 3.59 to 8.09 mg/g of spent coffee, depending on the preparation of coffee brews with the most common coffeemakers (filter, espresso, plunger, and mocha). In another study, different levels of caffeine were detected in extracts of spent coffee from capsules and coffee bars, varying between 0.96 and 0.97 mg/g and 5.99 and 11.50 mg/g, respectively (Panusa et al., 2013).

Table 1.2 summarizes some of the bioactive compounds most commonly found in spent coffee grounds. These chemical components are not all completely

Table 1.2 Chemical Structures of Some of the Most Commonly Found Compounds in Spent Coffee Grounds

Name	Chemical Structure	References
Caffeine		Bravo et al. (2012); Panusa et al. (2013); Ramalakshmi et al. (2009)
Caffeoylquinic acids		Bravo et al. (2012); Panusa et al. (2013); Monente et al. (2015)
Feruloylquinic acids		Bravo et al. (2012); Monente et al. (2015); Panusa et al. (2013)
p-Coumaroylquinic acids		Panusa et al. (2013)
4-Hydroxybenzoic acids		Monente et al. (2015)

extracted during beverage preparation, and a considerable amount of different chemical compounds are speculated to remain in the spent coffee grounds, which are most often thrown away as a waste. To date, some potential applications have been proposed to use spent coffee, for example, for the production of fuel for industrial boilers (Silva et al., 1998), as animal feed (Givens and Barber, 1986), as substrate for fungus growth (Machado et al., 2012), as raw material to produce fuel ethanol (Machado et al., 2012; Rocha et al., 2014), as adsorbent for the removal of heavy metals (Yeung et al., 2014), or for preparation of a distilled beverage with coffee aroma (Sampaio et al., 2013). In spite of these possible applications, spent coffee grounds are still underutilized as a valuable material for industrial processes. Nevertheless, several studies describing its bioactivity, sugars, and even amino acids contents have also been performed aiming to find alternatives for the use of this residue (Ballesteros et al., 2014; Bravo et al., 2012; Campos-Vega et al., 2015; Lago et al., 2001; Monente et al., 2015; Mussatto, 2015; Mussatto et al., 2011a,b,c).

1.4 LEGISLATIVE FRAMEWORKS AND POLICY RECOMMENDATIONS

Sustainability is a dynamic process in which long-term environmental, social, and economical requirements should be fulfilled by an integrated way without compromising the capacity of future generations to meet their own needs (World Commission on Environment and Development, 1987).

As mentioned before, the wastes produced along the coffee chain in both producing and importer countries are undoubtedly a source of contamination and a serious environmental problem. For that reason, several efforts have been made to investigate and develop processes for their valorization and use. Nevertheless, integrated strategies are still necessary always having in mind the sustainability of the coffee chain.

International Coffee Organization (2005) spread a copy of a document about the potential uses of coffee wastes and by-products that was prepared by a team working on the reformulation of a project entitled "Use of coffee by-products and alternative uses for low-grade coffee" submitted by Costa Rica and approved by the Council in 2003. The development of a full-scale project was coordinated with the International Center for Science and High Technology, United Nations Industrial Development Organization (ICS-UNIDO). In that document, Rathinavelu and Graziosi summarize several of the different possibilities of coffee wastes/by-products applications, namely in the production of feed, beverages, vinegar, biogas, caffeine, pectin, pectic enzymes, protein, and compost. This could be seen as a way to inspirit ICO members and community to give attention to such practices, in addition to publicize the relevant work that was being developed.

Currently, in the European Union, Directive 2008/98/EC on Waste (Waste Framework Directive) is the core legislative act that regulates waste management, strengthening the actions that must be taken in order to prevent wastes and introducing an approach that takes into account the whole life-cycle of products. One of the aims of this directive was to repeal and replace Directive 2006/12/EC, because key concepts, such as the definitions of waste, recovery, and disposal needed to be clarified and measures for waste prevention had to be strengthened. Moreover, the introduction of an approach that takes into account the whole life-cycle of products and not only the waste phase was a very relevant issue. One of the main focuses of Directive 2008/98/EC is, therefore, the reduction of the environmental impacts of waste generation and waste management by increasing the waste economic value: the recovery of wastes is encouraged in order to conserve natural resources. Thus, the main aim of waste policies should be to minimize the negative effects of the generation and management of waste on both human health and environment. Waste policies should also aim to reduce the use of resources and incentive the application of the waste hierarchy. This concept lays down a priority order of what represents the best environmental option in waste legislation and policies, except when technical feasibility, economic viability or environmental protection are not possible to be achieved. In general, the following priority order in waste prevention and management should be applied:

1. prevention;
2. preparing for reuse;
3. recycling;
4. other recovery (e.g., energy recovery); and
5. disposal.

In this context, Member States shall take measures to encourage the options that deliver the best overall environmental outcome, which may require specific waste streams departing from the hierarchy whenever justified. One of the main aims of this Directive is, indeed, to help the European Union to be closer to a "recycling society" (European Union, 2008).

The polluter-pays principle is a guiding principle at European and international levels, according to which the waste producers and the waste holders should manage the wastes in order to guarantee the protection of the environment and human health. The introduction of extended producer responsibility in Directive 2008/98/EC is the basis to support the design and production of goods taking into account the efficient use of resources during their whole life-cycle, including their repair, reuse, disassembly and recycling without compromising the free circulation of goods on the internal market.

Still, according to this Directive, a substance that results from a production process not primarily aimed to produce that item can be considered a by-product and not a waste, only if this is consistent with the protection of the environment and human health, and under environmental licenses or general environmental rules. Therefore, the following conditions have to be met:

1. further use of the substance is certain;
2. the substance can be used directly without any further processing other than normal industrial practice;
3. the substance is produced as an integral part of a production process; and
4. further use is lawful.

Considering this, Member States shall take the necessary measures to guarantee that waste management is performed without endangering human health or environment (especially water, air, soil, plants, or animals), without causing a nuisance (through noise or odors), and without adversely affect the countryside or places of special interest.

The European Coffee Federation (ECF) was founded in 1981 to represent the interests of both the coffee trade and roasting industry. Their members have been working together and in partnership with stakeholders in the coffee chain to guarantee that coffee products are manufactured in a responsible way. ECF is a founding partner in the Sustainable Coffee Program that brings together coffee industries, trade, and export partners, governmental and nongovernmental organizations, among others, aiming to bring sustainable coffee production to scale to meet increasing requirements, to improve farmer livelihoods, and sustain natural resources. In 2014, a consortium of leading coffee companies and stakeholders was selected to run a pilot for the European Commission's Product Environmental Footprint (PEF) project. Among other objectives, the coffee PEF pilot aimed to engage with European Union policy developments, to help developing future ones, and to create methodologies to evaluate and improve the environmental performance of coffee based beverages (European Coffee Federation, 2014).

The general concept of the circular economy, which is based on the maintenance of natural resources in the economy as long as possible, while simultaneously their economic value and technical properties are preserved, is highly applicable to the coffee chain. Among other things, a chain of value should involve cross-sector collaborations that create business opportunities for developing innovative products or processes that emerge from the use of resources that were previously considered wastes (Talmon-Gross et al., 2016). Indeed, circular economy is inspired in industrial ecology that regards the flow of material and energy through industrial systems in a way similar to the natural ecosystem: in nature, nothing is wasted and nutrients are recycled in a closed loop. In accordance, circular economy proponents aim to make use of all wastes as input for further value creation (Pike, 2016).

The transition to a circular economy is a great challenge, but the opportunities that rise from all coffee by-products produced along the chain can represent a clear picture of this model. As described along this chapter, such products are rich in nutrients and several bioactive compounds, being added-value substrates. It is thus essential to develop strategies to collect those by-products and create new opportunities of business that can offer a more efficient and profitable use of the different resources in the circular economy. This will certainly have crucial implications not only in small businesses, but also in the global economy. Moreover, consumers are increasingly concerned about the social and environmental impacts of the products they consume, including coffee, being often motivated to also become part of the solution (Pike, 2016; Talmon-Gross et al., 2016). Recently, some initiatives and companies have been created based on the use of coffee by-products to create new products. An example is the firm bio-bean (http://www.bio-bean.com/), from London, that collect spent coffee grounds from coffee shops and convert them into biofuels (e.g., barbecue coals and biomass pellets), being the first company in the world to industrialize this process. The possibility of selling the pellets back to coffee shops to be used, for instance, on coffee roast, can create a true circular economy: the waste becomes the input power for the production activities that created it. Besides, coffee shops give this firm free-of-charge material (in both directions) instead of paying disposal fees to send spent coffee grounds to landfills (Pike, 2016).

Although successful attempts, such as the case of bio-bean, have been created, to date, a lot still needs to be performed to recover all the potential that all coffee by-products present. Governmental organizations can play here a crucial role in promoting changes in the economic behavior, encouraging the adoption of circular economic practices, and promoting public policies for waste reduction (Pike, 2016). However, an interconnected system composed by producers, distributors, and also consumers, together with governments and organizations, entrepreneurs, and researchers is mandatory in order to achieve a true circular economy.

1.5 CONCLUSIONS

In general, coffee by-products represent a relevant environmental burden due to their production in high amounts and their richness in phytotoxic and/or antinutrient compounds (e.g., caffeine, tannins, and polyphenols) that can limit their use directly for soil and feed applications. However, they can be a good source to extract such compounds, which in turn, can be used for food, cosmetic, or pharmaceutical fields. Furthermore, coffee by-products are very rich in polysaccharides and contain high protein and mineral contents, what makes them a product with high biotechnological value (Mussatto et al., 2011a). Several studies have been performed by industries and academic institutions in order to valorize and use the different coffee by-products produced along the coffee chain (in both producer and consumer countries) in distinct perspectives. Nevertheless, the great majority is still dispatched for landfields or used for energy production. Although National and European legislation has been created for waste management in general, specific recommendations and policies about coffee waste/by-products are still lacking in both producing and consumer countries. Integrated strategies in which industry, academic institutions, governmental and nongovernmental organizations are involved together are crucial to transform coffee by-products in really profitable substrates.

ACKNOWLEDGMENTS

Francisca Rodrigues and M. Antónia Nunes are thankful for the research grant from project UID/QUI/500006/2013.

The authors thank the financial support to the project Operação NORTE-01-0145-FEDER-000011—Qualidade e Segurança Alimentar uma abordagem (nano)tecnológica. This work was also supported by the project UID/QUI/50006/2013—POCI/01/0145/FED-

ER/007265 with financial support from FCT/MEC through national funds and cofinanced by FEDER. Francisca Rodrigues and M. Antónia Nunes is thankful for the research grants from project UID/QUI/50006/2013.

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