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Review

Valorization of SCG through Extraction of Phenolic Compounds and Synthesis of New Biosorbent

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Abstract: Coffee is considered to be one of the most renowned beverages and it is the second-most consumed product worldwide. Spent coffee grounds (SCGs) are the primary solid residue, which are generated during the coffee powder brewing in hot water or steam. The formation of huge amounts of these byproducts poses a severe threat to the environment, due to their organic nature and their high phenolic compounds concentration. Nevertheless, the latter are characterized as bioactive compounds with high antioxidant activity turning SCG into an economical raw matrix for the isolation of valuable components. Phenolic compounds that can be isolated from coffee byproducts can be potentially used as natural antioxidants in food, pharmaceutical, and cosmetics industries. Thus, the research community has focused its efforts on the optimization of phenolics extraction by the development of novel environmentally friendly techniques except for conventional maceration extraction using organic solvents. The objective of this review is to present an inclusive summary of the revalorization of SCGs and the potential uses of those solid residues through the recovery of phenolic compounds or the use of untreated or treated SCGs as biosorbents of valuable compounds from other food industry byproducts.

Keywords: biosorbent; food waste; polyphenols recovery; spent coffee grounds; waste management

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1. Introduction

Coffee is one of the most broadly consumed beverages, the second-most famous after water. Enjoying a cup of coffee is a daily routine and even a cultural habit in many countries since its consumption is linked with many significant moments of personal life. The increment in this beverage's popularity could be also associated with the health benefits it provides, based on recently published scientific findings [1]. According to the International Coffee Organization [2], the total consumption of coffee exceeded 9.9×10^6 Kg worldwide in 2021.

As lifecycle analysis "from farm to cup" reveals, increased coffee consumption results in accordingly high quantities of waste (spent coffee grounds, husks, defective coffee beans, etc.) that contribute to environmental threat [3]. The coffee peel, husks, and pulp, which comprise almost 45% of the cherry, are the principal byproducts of the coffee industry and could be a valuable raw material for several processes, such as caffeine and polyphenols extraction. Spent coffee ground (SCG) is the residue obtained during the brewing process. It is worth mentioning that 6 million tons of SCGs are generated per year and end up mostly in landfills [4]. This huge amount requires a waste management plan consistent with national legislation. The European Union promotes "waste hierarchy" and philosophy of waste management through definite directives [5,6]. The preferable waste management techniques in descending order of priority are as follows: (1) recycling, (2) reuse, (3) waste prevention, (4) disposal, and (5) recovery. For example, the company Nestle attempts to minimize this waste stream in Europe by using it as a source of renewable energy in more than 20 Nescafe factories [7].

In most of the coffee-producing industries, the byproduct is collected by specialized agencies that trade the byproducts for different purposes (bioenergy production, composting, mushroom growth). SCG contains large quantities of organic components, such as fatty acids, cellulose, hemicellulose, lignin, and other polysaccharides, that can be exploited as a source of value-added products. Thus, SCG has been investigated for biodiesel production [8], as a source of sugars [9], a precursor for activated carbon production [10], compost [11], and soil fertilizer in order to stimulate plant growth [12].

The increasing interest in SCG potential applications and valorization through several routes (biotechnological and/or physicochemical) is evident in the rising trend of publications (Figure 1), where, up until May of 2022, 1245 documents regarding SCG have been published.

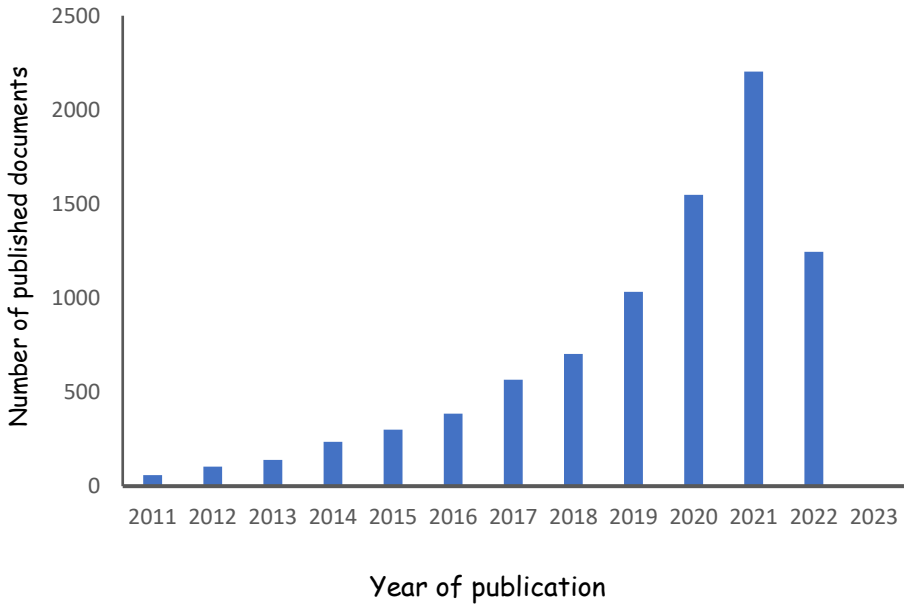

Figure 1. Scopus database results for published articles on SCG during the last decade (last accessed on 25 May 2022, query string entered: "spent coffee grounds").

SCG composition is abundant in phenolic chlorogenic acids and non-phenolic acids (caffeine and trigonelline) [13]. Phenolic compounds, although toxic to microorganisms, are valuable chemicals since they have a variety of activities, such as antimicrobial, antioxidant, anti-mutagenic, anti-allergenic, and anti-inflammatory, and are currently used in the fields of medicine, food technology, biology, and so on [14]. Up until now, various techniques have been reported for their extraction. From the water-based autohydrolysis [15] to ultrasound- and microwave-assisted solid–liquid extraction with alkyl alcohols [16,17], diverse maximum extraction rates have been obtained. The drawbacks of these methods are mainly concerned with safety issues (flammability, toxicity), increased cost, and, more importantly, environmental burdens [18]. Organic solvents are characterized by low boiling points and therefore their vapors are accumulated in the atmosphere during the extraction procedures. In addition, they are not biodegradable, and in the framework of sustainable development, their replacement with alternative environmentally benign components is crucial. The green chemistry has resulted in the introduction of innovative solvents, such as deep eutectic solvents (DES), which are characterized as "the organic reaction medium of the century" [19], and aqueous solutions of cyclodextrins [20].

In general, various approaches have been investigated as far as the recovery of polyphenols is concerned, and several techniques (extraction, adsorption, membrane and chromatographic separation) have been investigated independently or in combination [21]. However, researchers have pointed to adsorption, which is characterized as the most effective and low-cost method for the recovery of various compounds. The prohibitive cost

of most commonly used adsorbents and the need for their regeneration have resulted in the development of innovative, low-cost biosorbents with a high efficiency [22]. Although most of these sorbents comprise agricultural or food industry byproducts, they present many advantages. The most significant ones are their small cost, accessibility, and ease of regeneration [23]. The exploitation of SCGs for the removal of pollutants with adsorption has recently emerged.

The use of SCG as a biosorbent after the extraction of its phenolic content could be an integrated approach for the ultimate utilization of SCG, through the recovery of valuable byproducts and/or ingredients, while finally leading to full depollution. This approach moves beyond the state of the art, towards a holistic approach for SCG valorization. This review aims to provide a complete summary of all accomplished studies on the recovery of phenolic compounds from SCG and its use as a biosorbent. The prevailing methods for phenols recovery, the main parameters of the extraction and adsorption processes, and the achieved efficiencies are reviewed and discussed. The main objective is to access the status, recent developments, and future trends.

2. Spent Coffee Ground (SCG)

2.1. Production

Coffee is a beverage with a huge economical value and it is primarily cultivated in the equatorial regions. Coffea arabica (Arabica) and Coffea canephora var. robusta (Robusta) are considered to be the major varieties of the genus Coffea, which are typically cultivated for commercial manufacture. Specifically, the Arabica variety is the leader in the world production, as it accounts for about 75% of the global production and it is thought to be superior to Robusta due to its more gentle and flavorful taste [24], although Robusta is commonly used by the instant coffee industry for the manufacture of coffee brews [25].

During "fruit to cup" transformation, huge amounts of wastes, such as coffee silver skin, coffee pulp, coffee husk, and spent coffee grounds, are generated. The different types of coffee solid byproducts formed through the coffee processing are presented in Figure 2. During coffee beverage production, when roasted coffee powder contacts hot water or steam, components with characteristic flavors and other valuable constituents are released into the water, and solid waste with high moisture content, known as SCG, is generated [26]. According to Murthy and Naidu [27] and Mata et al. [28], around 650 kg of SCG is produced from 1 ton of coffee beans, while from 1 kg of soluble coffee approximately 2 kg of wet SCG is obtained.

SCG consists of different types of sugars, such as mannose, glucose, galactose, and arabinose, whereas it is primarily composed of neutral detergent fiber (45.2%) (hemicellulose, lignin, cellulose) and acid detergent fiber (29.8%) consisting of cellulose and lignin [29]. The physicochemical characteristics of SCG are presented in Table 1. According to Mussato et al. [9], SCG contains 46.8% mannose, 30.4% galactose, 19% glucose, and 3.8% arabinose. As far as lipids are concerned, SCG total lipids content is about 9.3–16.2%, 10–15%, and 14–15.4% for espresso coffee residues, filter, and industrial soluble coffee, respectively [7]. SCG fatty acid profile predominantly contains linoleic (44.2% of total lipids), palmitic (32.8% of total lipids), stearic (10.3% of total lipids), and oleic acid (7.1% of total lipids) [3,30]. The oil obtained from SCG is rich in omega-6 essential fatty acids with an ω-6/ω-3 ratio of 38.6–43.7 [31,32]. Moreover, two diterpenes, kahweol and cafestol, were isolated from SCG [31,32]. The concentration of diterpenes in coffee beans depends on the coffee species and the storage conditions as these compounds are sensitive to parameters such as heat, light, and acids.

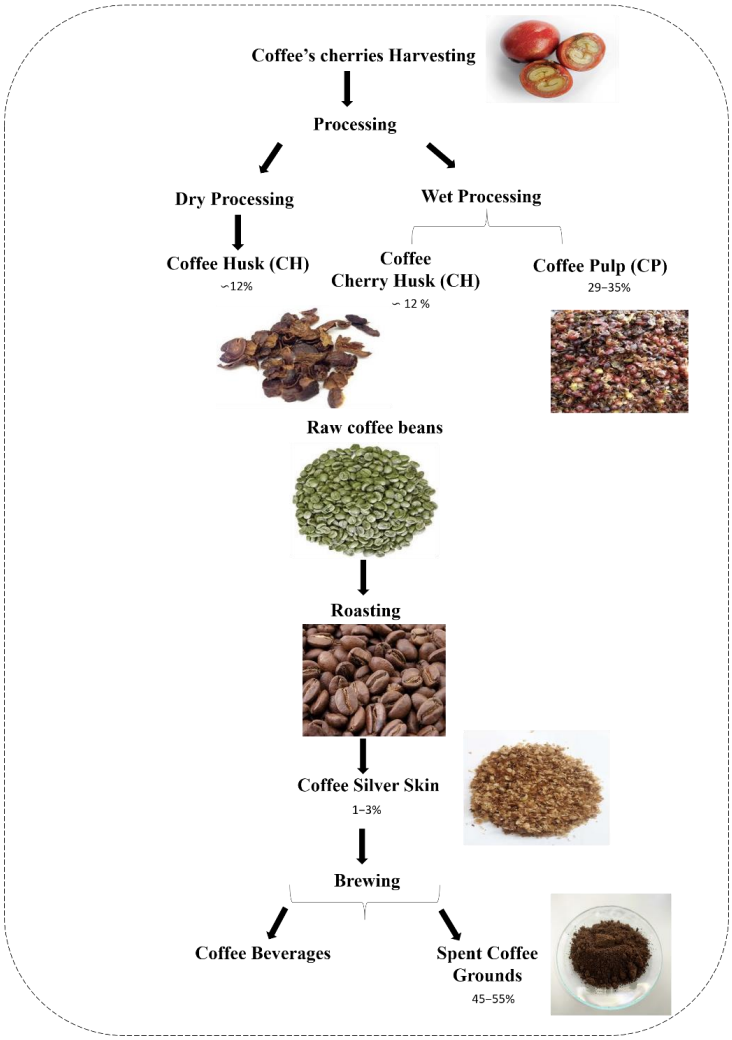

Figure 2. The main solid byproducts obtained from coffee processing.

Table 1. Chemical composition of spent coffee grounds.

Component	Content (% Wet Basis)	References
Moisture	1.18–74.72	[28,31,33]
Cellulose	12.40 ± 0.79	[34]
Hemicellulose	39.10 ± 1.94	[34]
Arabinose	3.60–6.00	[33,34]
Mannose	19.07–47.00	[33,34]
Galactose	16.43–30.00	[33,34]
Lignin	23.90 ± 1.70 Insoluble 17.59 ± 1.56 Soluble 6.31 ± 0.37	[34]
Fat	2.29–19.00	[28,33,34]
Ash	0.43–2.20	[31,33,34]
Protein	4.30–17.44	[9,31,33,34]
Total dietary fibers	36.87–60.46 Insoluble 50.78 ± 1.58 Soluble 9.68 ± 2.70	[31,34]

According to several studies, the protein content of SCG varies from 4.3 to 17.44% w/w, depending on the variety of coffee beans and the conditions used during instant coffee preparation [9,31,33,34]. This protein content is higher than that of coffee beans, possibly due to the non-extracted components during instant coffee preparation. In addition, the overestimation of SCG protein content may be attributed to various nitrogen-containing substances, such as caffeine, trigonelline, free amines, and amino acids, present in SCG [35]. As far as mineral composition is concerned, the roasted coffee beans have a total mineral concentration of about 4.6%, which is easily extracted by hot water, leading to a reduced content in soluble coffee solid wastes [30]. Potassium and magnesium comprise about 22 and 11%, respectively, of the SCG minerals [7].

2.2. Phenolic Compounds

Coffee beans and SCG are great sources of bioactive compounds, such as phenolic compounds, containing large amounts of chlorogenic acid and its derivatives (caffeoylquinic, p-coumaroylquinic, and feruloylquinic acid), as well as diesters of caffeic and ferulic acid with quinic acid [36], while the main phenolic compounds of coffee beans are presented in Figure 3. Traditionally, these compounds are characterized as chlorogenic acids and are considered to be powerful antioxidants associated with many health benefits [37–39]. Specifically, the aforementioned compounds are related to neurotrophic and neuroprotective properties [40–42] and these results initiated a boost in the manufacture of functional foods or supplements containing phenolic compounds from coffee industry waste.

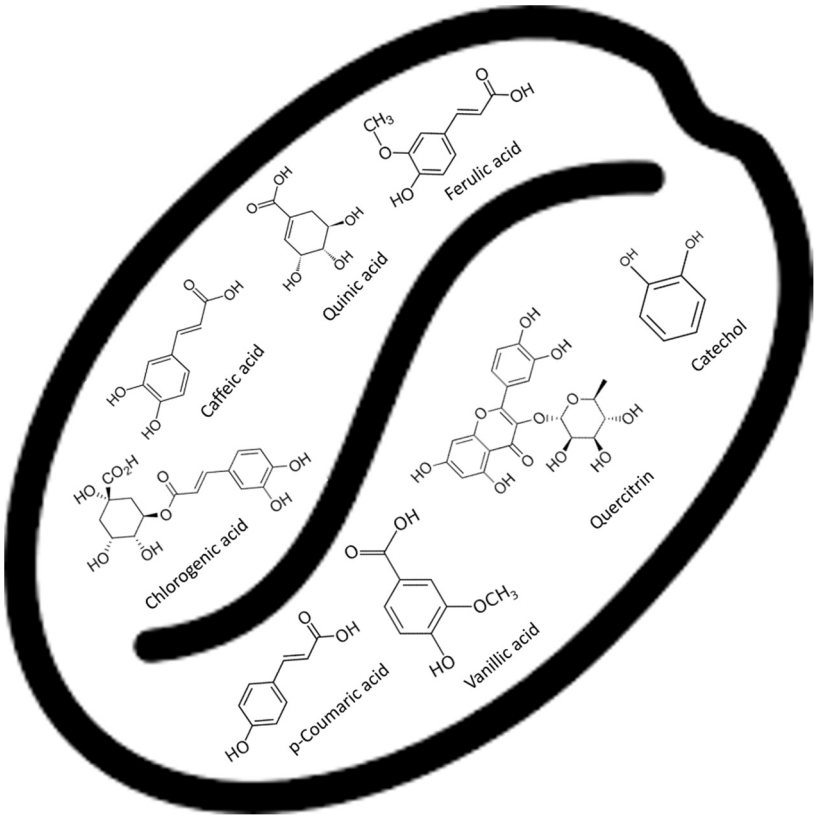

Figure 3. Main phenolic compounds of coffee beans.

Numerous studies on the phenolic content of SCG have been carried out and the main identified biophenols of SCG include vanillic acid, ferulic acid, sinapic acid, caffeic acid, p-coumaric acid, chlorogenic acid, quercitrin, catechol, quercitrin-3D-galactoside, and rutin [31,33]. Caffeoylquinic acids are the most plentiful phenolic compounds in SCG (Table 2). They are categorized as chlorogenic acids, which are water-soluble esters consisting of quinic acid and one or two molecules of caffeic acid, a trans-cinnamic acid. According

to Bravo et al. [43], as far as the composition of phenolic compounds is concerned, spent coffee grounds mainly consist of monocaffeoylquinic and dicaffeoylquinic acids. This composition is principally affected by the coffee species and the mechanism of coffee brews preparation (filter, espresso, and plunger). Ramalakshmi et al. [44] concluded that the major antioxidant in SCG is 5-caffeoylquinic acid (~6%), whereas Bravo et al. [43] found significant quantities of caffeoylquinic (6–13 mg/g) and dicaffeoylquinic (3–6 mg/g) acids, and Monente et al. [45] reported caffeic acid, p-coumaric acid, ferulic acid, 4-hydroxybenzoic acid, and sinapic acid.

Table 2. Caffeoylquinic acids and caffeine of spent coffee grounds (adapted from [43]).

Constituent	Content (mg/g)
Caffeoylquinic Acids	
3-*CQA	Arabica 1.10–1.64 Robusta 0.63–0.83
4-*CQA	Arabica 1.75–2.51 Robusta 0.97–1.16
5-*CQA	Arabica 2.48–3.59 Robusta 1.18–1.26
Total *CQAs	Arabica 5.33–7.74 Robusta 2.80–2.91
3,4-diCQA**	Arabica 2.34–2.53 Robusta 1.49–1.99
3,5-diCQA**	Arabica 1.09–1.26 Robusta 0.62–0.74
4,5-diCQA**	Arabica 1.46–2.07 Robusta 1.20–1.41
Total **diCQAs	Arabica 4.89–5.79 Robusta 3.31-4.10
Total *CQAs + **diCQAs	Arabica 11.05–13.24 Robusta 6.22–7.49
Caffeine	
Caffeine	Arabica 3.59–5.20 Robusta 5.73–8.09

***CQA**: monocaffeoylquinic acids, ****diCQA**: dicaffeoylquinic acids.

2.3. Management

SCG is a dark-colored solid waste with no commercial worth and is mainly discarded as solid waste in landfills or, to a small extent, is composted (Figure 4). During the disposal of SCG in landfills or during its burning, gases are emitted into the atmosphere. In general, SCG is considered to be a high pollutant and its toxicity is associated with the high organic content and the concentration of components such as caffeine, polyphenols, and tannins. Therefore, the proper management of SCG is crucial for environmental protection [46].

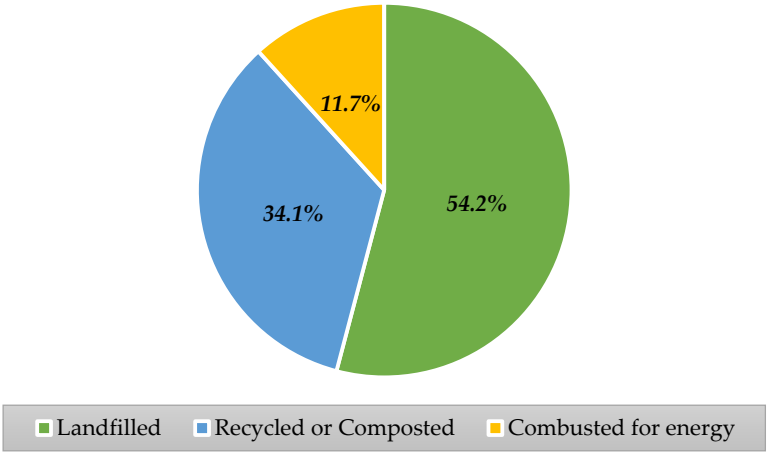

Figure 4. Management of coffee byproducts. Data from [47].

Nowadays, the rising awareness of waste management and environmental protection has stimulated the research for developing new techniques for the valorization of SCG. Currently, circular economy is an integral part of environmentally-friendly companies. In this regard, remarkable efforts for the utilization of a variety of food industry wastes are being made. As far as SCG is concerned, it can be potentially used as a source of fuels (bioethanol, biogas, biodiesel, bio-oil, hydrocarbon fuel, and fuel pellets) [48], biopolymers (polysaccharides, which can be used as dietary fibers) [49], biosorbents, polyurethane foams, carotenoids [3], and antioxidants, such as tannins [48,50,51], caffeine, and polyphenols [33] (Figure 5).

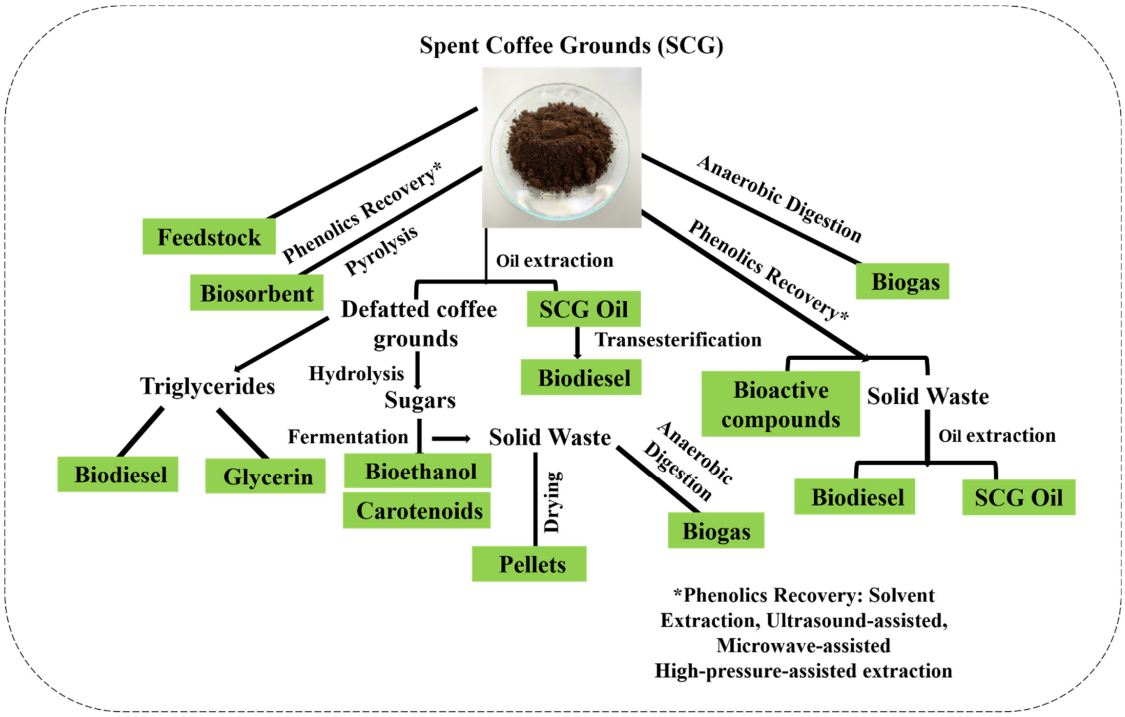

Figure 5. Valorization of spent coffee grounds.

The use of SCG as a source of phenolic compounds and biosorbents is the subject of the present review. As far as the valorization of the other SCG components is concerned, various processes (pyrolysis, gasification) have been proposed to convert SCG into fuel, bio-oils, hydrogen-enriched fuel, liquid product mixture comparable to fossil fuel oil, and valuable biocide [7]. Bio-oils from SCG pyrolysis have high concentrations of various

carboxylic acids, which allow their further upgrade into biodiesel or other petrochemical products [52]. Potentially, 1.3 billion liters of biodiesel, based on approximately 8 million tons of worldwide produced coffee containing 10–15% lipids, could be included in the world fuel production from SCG [53]. Enzyme technology is usually used to hydrolyze SCG polysaccharides into precious food compounds, such as mannitol and higher mannosaccharide alcohols, or source raw material for bioethanol production [54]. The SCG cellulose and hemicellulose fractions can be used in sorbitol, formic acid, hydroxymethylfurfural, levulinic acid, arabitol, xylitol, mannitol, and, emulsificant production [9]. According to Sampaio et al. [55], alcohol production leads to a beverage with 40% ethanol alcohol, comparable to tequila and vodka, with a pleasant aroma and taste of coffee.

3. Extraction of Phenolic Compounds

SCG can be potentially used as a great source of valuable components with high antioxidant capacities, such as caffeic and chlorogenic acids, which can be utilized as natural antioxidants in food, cosmetics, and pharmaceuticals [56]. Various extraction techniques, including conventional maceration using organic solvents or novel methods such as ultrasound-assisted extraction, microwave-assisted extraction, and high-pressure extraction, are studied for the extraction of phenolic components.

3.1. Conventional Methods

Conventional extraction using organic solvents is the most widely used technique for the isolation of bioactive compounds. This method is based on the following stages: (1) penetration of organic solvent into the solid, (2) dissolution of bioactive compounds in the organic solvent and diffusion out of the matrix, and (3) recovery of bioactive compounds. A variety of parameters may increase the solubility, effectiveness, and recovery yield of extraction. Specifically, the type of solvent, particle size of the solid matrix, liquid (solvent)-to-solid ratio, extraction temperature, and duration of extraction are some of the factors that can affect the efficiency of extraction [57].

In the case of isolation of phenolic compounds from SCG, many studies have been carried out using conventional extraction with organic solvents (Table 3). Generally, choosing the appropriate solvent is considered to be crucial for solvent extraction, and this plays a principal role in the extraction efficiency. Especially, parameters such as polarity, cost, safety, selectivity, reactivity, stability, food grade, and potential reusability must be studied for the selection of a proper solvent [58]. Solvents with polarity near to the polarity of solute lead to better results. According to Table 3, mainly methanol and ethanol are used for the recovery of phenolic components from SCG. It can be observed that traditional extraction with organic solvents can lead to high yields ($\leq$90.35% using ethanol) [59].

Table 3. Recovery of phenolic compounds from SCG using conventional extraction method.

Operating Conditions	Solvent	Yield	Antioxidant Activity	References
T: 35 °C, L/S: 5 mL/g	Ethanol, 50% v/v	-	EC_{50}: 148.4 ± 30.4 (non-defatted) EC_{50}: 165.9 ± 6.8 mg/L (defatted)	[32]
T: 63.3 °C, t: 90 min, L/S: 30 mL/g	Ethanol, 45% v/v	90%	255.55 g SCG d.b./g DPPH	[60]
t: 90 min, L/S: 40 mL/g	Methanol, 60% v/v	89%	0.10 mM Fe(II)/g	[61]
T: 60 °C, t: 30 min, L/S: 50 mL/g	Ethanol, 60% v/v	-	EC_{50}: 1.47–3.67% v/v	[62]
T: 60 °C, t: 30 min, L/S: 50 mL/g	Water	-	EC_{50}: 2.33– 6.74% v/v	[62]
T: 80 °C, t: 30 min, L/S: 13.33 mL/g	Ethanol, 50% v/v	14.5 ± 0.3 mg GAE/g (dw)	-	[63]
T: 60 °C, t: 150 min, L/S: 50 mL/g	Ethanol, 30% v/v	87.3%	-	[46]
T: 60 °C, t: 90 min, L/S: 49 mL/g	Ethanol, 60% v/v	22.01 mg/g d.b.	-	[64]
T: 60 °C, t: 180 min, L/S: 50 mL/g	Ethanol, 30% v/v	90.35%	EC_{50}: 0.86% v/v	[59]

T: extraction temperature, t: extraction time, L/S: solvent to solid ratio; EC_{50}/IC_{50}: concentration of the sample necessary to decrease the initial DPPH concentration by 50%.

As far as the particle size of the solid matrix is concerned, typically, the finer the particle size is, the higher the efficiency. This phenomenon is based on the higher penetration of solvent when the particle size of the matrix is smaller, due to the increased specific surface area. In this case, an increase in solubility and recovery yield will be observed. Nevertheless, in the case of extremely fine components, excessive adsorption of solute on the solid matrix will be noticed. All studies regarding conventional extraction (Table 3) have stated that particle size is a factor of importance during phenolics extraction. The vast majority of them, however, studied SCG as it was collected from the coffee industry and did not employ any methods to alter the size of the waste particles in order to study its effect. Nonetheless, Ramón Gonçalves et al. [63] and Solomakou et al. [64] used SCG without grinding as pretreatment.

Traditionally, temperature significantly affects the solubility of the solute in a solution. However, even though an increase in temperature leads to higher extraction yields, excessively high temperatures have the opposite effect due to the decomposition of thermolabile components and evaporation of organic solvents. According to the literature, the extraction temperature for the removal of phenolic compounds from SCG ranges between 35 and 80 °C. The lowest temperature was employed by Acevedo et al. [32], whereas the majority of studies reported 60 °C as an optimum parameter of extraction. According to Solomakou et al. [64], who extracted phenolic components from SCG at 60 °C for 90 min with an L/S ratio of 49 mL/g using 60% (*v*/*v*) aqueous ethanol, this temperature appears to be the optimum extraction temperature (≤90% extraction yield) and was selected in order to prevent the degradation of sensitive bioactive compounds that can take place at higher temperatures. On the other hand, Ramón Gonçalves et al. [63] studied higher extraction temperatures, i.e., 80–120 °C, with the optimum being the lowest, although not achieving a higher recovery yield (14.5 mg GAE/g) in comparison with other studies.

The liquid-to-solid ratio plays a crucial role too. Specifically, higher liquid-to-solid ratios are associated with higher extraction yields. Nonetheless, extremely high ratios will lead to excessive volumes of solvent, which require more energy and time for concentration and solvent recovery. As presented in Table 3, the L/S ratios that have been used for the recovery of phenolic components from SCG range from 5 to 50 mL/g. The lowest ratio was used by Acevedo et al. [32], whereas the most frequently reported optimum ratio appeared to be 50 mL/g. According to Solomakou et al. [64], who investigated a wide range of L/S ratios (5–60 mL/g), the optimum value did not appear to be the highest of those studied, indicating that when increasing this parameter beyond a certain point, namely, a plateau, no further increase in yield can be observed.

3.2. Emerging Methods

The disadvantages of conventional maceration extraction led the scientists to focus their efforts on developing novel environmentally friendly extraction techniques for the extraction of valuable components from the food industry's byproducts, and specifically SCG. These novel methods are associated with minimization of energy consumption, shorter operation time, and higher phenolics recovery yield [56]. The primary methods studied for the recovery of phenolic components from the coffee industry's byproducts are presented in the following sections.

3.2.1. Ultrasound-Assisted Extraction (UAE)

UAE is considered to be a "green" extraction method, based on the application of sound waves in the frequency range of 20 kHz–100 MHz. Improved extraction yields achieved with UAE may be based on cavitational effects caused by the application of high-intensity ultrasounds. Large-amplitude waves move through a medium resulting in compression and shearing of solvent molecules and causing local changes in density and elastic modulus. As a result, the sinusoidal compression and shear waves will be distorted into shock waves at a limited distance from the ultrasonic transducer. The sudden decrease in pressure at the edge of the wave in the negative pressure cycle leads to the

formation of small bubbles that collapse in the positive pressure cycle and create turbulent flow conditions [65]. Furthermore, ultrasound causes swelling, hydration, and enlargement of the pores in the cell wall [66]. In addition, ultrasound collapse leads to a reduction in the particle size and increases the number of cells exposed to extraction by solvent and ultrasonic cavitation. An illustration of the UAE extraction method is represented in Figure 6.

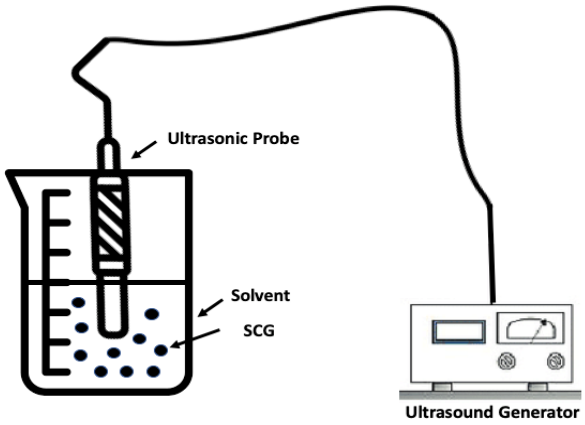

Figure 6. Setup of ultrasound-assisted extraction.

In general, UAE is considered a simple and cost-effective treatment that can be utilized on both small and large scales [67]. As a procedure, UAE is thought to be cost-effective due to the need for lower extraction duration, lower solvent volume, and lower temperatures involved (preservation of heat-sensitive components). Crucial parameters that must be taken into consideration are the type of solvent, the extraction time, the extraction temperature, the ultrasound power, and the liquid-to-solid ratio [68] (Figure 7).

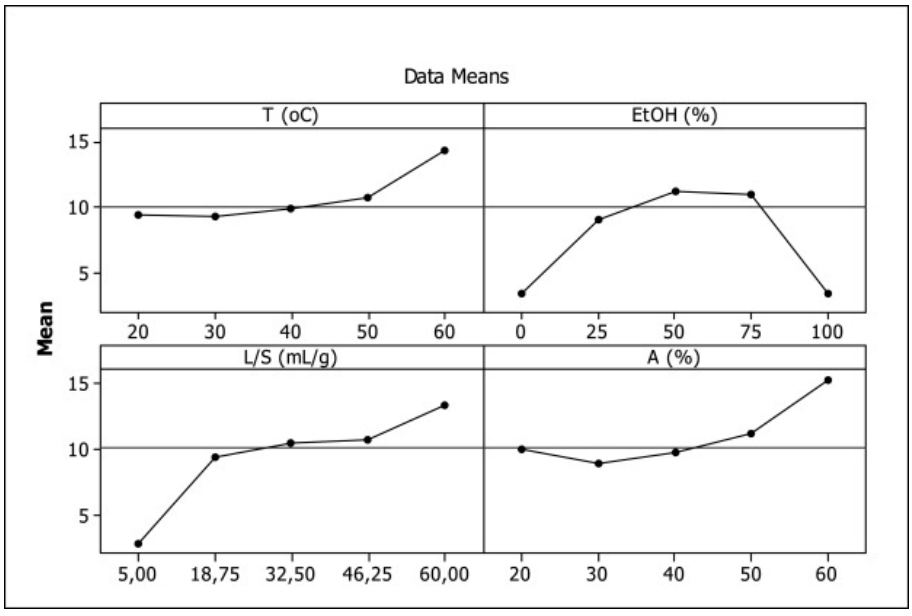

Figure 7. Main effects plot of temperature (T, °C), solvent concentration (EtOH, % *v*/*v*), liquid/solid ratio (L/S, mL/g), and amplitude level (A, %) on yield (Y, mg GAE/g dry SCG) during ultrasound-assisted extraction of phenolics from SCG (Reprinted from Sustainable Chemistry and Pharmacy Vol 25, Nikoletta Solomakou, Anastasia Loukri, Panagiota Tsafrakidou, Alexandra-Maria Michaelidou, Ioannis Mourtzinos, Athanasia M. Goula, Recovery of phenolic compounds from spent coffee grounds through optimized extraction processes, 100592, Copyright (2022), with permission from Elsevier [64]).

As far as the recovery of SCG phenols is concerned, only a few studies have been carried out using ultrasound-assisted extraction, achieving extraction efficiencies ranging from 9.51 to 941.04 mg GAE/g of SCG, under conditions which are mentioned in detail in Table 4.

Choosing the appropriate type of solvent plays an important role in UAE, due to its important impact on effectiveness. Specifically, a crucial characteristic of the solvent should be its low vapor pressure, increasing the collapsing of cavitation bubbles and therefore resulting in the augmentation of extraction yield. According to Syahir et al. [68], the most commonly used solvents in UAE are ethanol, n-hexane, and methanol. All studies conducted on the extraction of phenolics from SCG using ultrasound-assisted extraction employed the aforementioned solvents and, more specifically, aqueous solutions of ethanol and methanol. As far as ethanol is concerned, under optimum extraction conditions, ethanol was found to be at concentrations of 50–60% (v/v) and extraction of phenolics after 4.5 h at 28 °C was achieved up to 941.04 ± 37.25 mg GAE/g dry sample [69]. On the other hand, the use of aqueous methanol resulted in lower extraction efficiencies, leading up to 24.95 mg GAE/g. More specifically, according to Severini et al. [16], the maximum yield using methanol was achieved with an ultrasound pulse length of 4 min, a treatment time of 60 min, an L/S ratio of 50 mL/g, and a methanol/water ratio of 1.25.

Generally, increasing extraction time provokes an increase in extraction yield. However, at a certain point known as the "equilibrium state", further increase in extraction time does not affect yield. According to the literature, UAE time typically ranges around 30 min [70,71]. Similarly, in the case of extraction of phenolics from SCG using ultrasounds, it appears that the majority of researchers achieved satisfying extraction yields, ranging from 18.54 to 33.84 mg GAE/g SCG, under extractions for approximately 30 min (20–40 min). However, Ansori et al. [69] achieved the highest recorded extraction efficiencies, extending the extraction time up to 4.5 h.

Increasing extraction temperature leads to increased extraction yield, but this is highly dependent on the material under investigation. Higher temperatures result in increased solubility of the extracted compounds in the solvent and increased bubble collapsing speeds, thus increased solvent penetration into cell tissues. Generally, according to researchers, the optimum temperature for UAE ranges from 30 to 50 °C [71,72]. Indeed, the majority of studies on the extraction of phenolics from SCG utilizing UAE presented optimum temperatures that fall within this range, as very high temperatures may lead to degradation of phenolic compounds.

Extraction yield can also be influenced by ultrasonication power. More specifically, an increase in ultrasonic amplitude can increase yield, as more cavitation bubbles are formed that consequently collapse [68]. However, a certain plateau can be observed, beyond which an increase of ultrasonic power may lead to degradation and decomposition of bioactive compounds due to elevation of vapor pressure and temperature of the solvent [73].

Liquid-to-solid ratio greatly affects UAE, as it defines interactions between solvent and the matrix, until the point at which solvent is saturated. This effect of L/S is based on the driving force of the extraction, which is the concentration difference between the compounds in the matrix and the solvent. However, further increase of L/S beyond a certain point does not further increase extraction yield, additionally increasing operating costs and waste during the process of extraction [68]. In the case of phenolics extraction from coffee industry waste, conducted studies reported optimum conditions ranging from 9 mL/g, during which the minimum extraction yield was reported, up to 52 mL/g. During the latter, according to Solomakou et al. [64], the optimum L/S ratio was not the highest investigated (60 mL/g), leading to the conclusion that a plateau exists, a point beyond which increasing the L/S ratio does not induce a further increase of yield.

Table 4. Recovery of phenolic compounds from SCG using novel extraction methods.

Operating Conditions	Solvent	Yield	Antioxidant Activity	References
		Ultrasound-assisted extraction		
P: 244 W, T: 40 °C, t: 34 min, L/S: 17 mL/g	Ethanol	≤33.84 ± 0.59 mg GAE/g	-	[74]
T: 28 °C, t: 4.5 h	Ethanol, 60% *v*/*v*	941.04 ± 37.25 mg GAE/g dry sample	26.82 ± 2.92 mg Trolox Equivalents/g dry sample	[69]
After hydrothermal delignification of SCG, T: 40 °C, t: 40 min, L/S: 25 mL/g	Methanol, 100% *v*/*v*	20.3 mg GAE/g	-	[75]
P: 750 W, frequency: 20 kWh, T: 50 °C, t: 60 min, L/S: 20 mL/g,	Ethanol, 60% *v*/*v*	12.67 ± 0.31 mg GAE/g	EC_{50}: 10.94 ± 0.55 μg/mL	[76]
Amplitude: 60%, T: 25 °C, t: 15 min, L/S: 9 mL/g	Methanol, 80% *v*/*v*	≤9.51 ± 0.06 mg GAE/g	≤0.89 ± 0.04 mmol $FeSO_4$/100 g	[56]
Ultrasound pulse duration: 4 min, t: 60 min, L/S: 50 mL/g	Methanol/water, 1.25	19.29–24.95 mg GAE/g	134.90–174.73 μmol Trolox/g	[16]
Amplitude: 60%, T: 60 °C, t: 20 min, L/S: 52 mL/g	Ethanol, 50% *v*/*v*	18.54 mg GAE/g dry SCG	-	[64]
		Microwave-assisted extraction		
P: 966 W, t: 49 s, L/S: 20 mL/g	Methanol, 60% *v*/*v*	≤57.49 mg/g dry extract	1488 μmoles Trolox Equivalents/g	[77]
P: 80 W, t: 40 s, L/S: 9 mL/g	Ethanol, 20% *v*/*v*	≤398.95 mg GAE/g dry extract	DPPH: ≤90.69%, ≤3.02 mmol $FeSO_4$/L	[17]
P: 550 W, t: 180 s, L/S: 12 mL/g	Ethanol, 20% *v*/*v*	31.216 mg/g dry SCG	36.56–98.24% DPPH: 2.62–6.66 mmol Fe^{2+}/L	[78]
P: 600 W, t: 5 min, L/S: 60 mL/g	Ethanol, 68% *v*/*v*	31.79 ± 0.25 mg GAE/g dry SCG	-	[64]
		High-pressure-assisted extraction		
t: 60 min, L/S: 10 mL/g, T: 150 °C, P: 7 bar (0.7 MPa)	Ethanol, 50% *v*/*v*	43 ± 0.8 mg caffeic acid equivalents/g dried biomass	734 ± 11 μg trolox equivalents/g dried biomass	[79]
P: 300–500 MPa, T: 25 °C, t: 5–15 min, L/S: 9 mL/g	Methanol, 80% *v*/*v*	-	-	[56]

P: power, T: extraction temperature, t: extraction time, L/S: solvent-to-solid ratio.

3.2.2. Microwave-Assisted Extraction (MAE)

MAE is considered to be a potential alternative technology to the conventional solvent extraction for the isolation of polyphenol components from different matrices, and especially SCG [80]. Over the last few decades, solvent extraction is substituted with MAE for efficient and effective extraction of valuable constituents from a variety of food and agricultural residues [77]. Specifically, MAE is based on the use of microwave radiation in order to heat up a solute–solvent mixture. The heat treatment accelerates the diffusion of bioactive components out to the solvent, a fact that facilitates the recovery of value-added compounds. As a procedure, microwave-assisted extraction is not time-consuming (thus is less energy-consuming) and requires low solvent volumes [58]. According to conducted studies, MAE has been used for the extraction of several phytochemicals, such as polyphenols and specifically polyphenols of short-chain-like flavonoids and phenolic acids, with adequate recovery yields in short times and with low volumes of solvents [58]. An illustration of the MAE extraction method is represented in Figure 8.

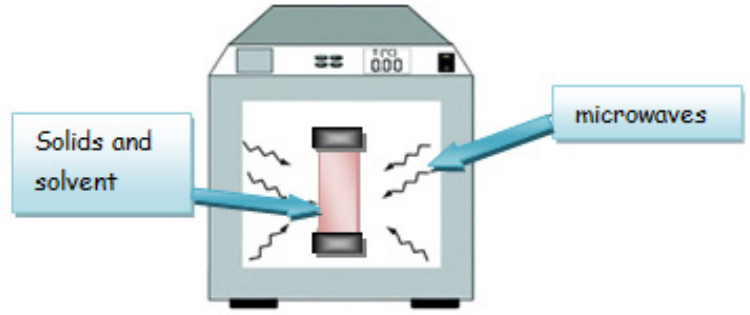

Figure 8. Setup of microwave-assisted extraction.

MAE, as an efficient extraction procedure, enables the simultaneous use of different variables, contrary to traditional methods. Moreover, surface overheating of the material is prevented, as there is no direct contact with a heating source [81]. Finally, as the use of chemicals can be avoided, MAE can be characterized as an ecofriendly method [82]. On the other hand, a possible drawback of MAE can be a phenomenon called "hot spot", during which a localized overheating can take place, caused by the uneven distribution of microwaves [83]. As can be seen in Table 4, recovery of phenolic compounds from SCG using MAE led to efficiencies ranging from 31.216 to 398.95 mg GAE/g dry SCG.

Crucial parameters that should be studied are the type of solvent, the microwave power, the frequency of microwaves, the process duration, the moisture content and the particle size of the solid matrix, the extraction temperature, the liquid-to-solid ratio, and the number of extraction cycles. The most critical factor that affects the whole procedure is the type of solvent, as it affects the solubility of the desirable compounds and the efficiency of the method. The solvent must be selected taking into account the capability for microwave radiation energy adsorption and its affinity to diffuse adequately. Solvents such as ethanol, methanol, and water are considered to be ideal for this technique [84]. On the contrary, solvents such as dichloromethane or hexane should be avoided owing to their inability to heat up under microwave conditions [85]. This fact can be confirmed by the current international literature, as researchers have solely used ethanol and methanol during MAE of phenolics from SCG.

As far as microwave power is concerned, generally, an increase in irradiation power can lead to a higher extraction efficiency [86]. Although during high microwave treatment an increase in temperature (superheating) can be observed, this phenomenon can be potentially harmful to sensitive compounds. Currently, studies on the recovery of phenolics from SCG utilizing microwaves have used microwave irradiation with power ranging from 80 to 966 W, with the highest yield being observed in the case of the lowest power. More specifically, Pavlović et al. [17] achieved a recovery yield of up to 398.95 mg GAE/g dry SCG using a power of 80 W with an extraction time of 40 s and an L/S ratio of 9 mL/g.

Furthermore, extraction time plays an important role. One of the advantages of MAE over the conventional extraction method is the very short extraction time. Typically, an increase in extraction time may positively affect the extraction yield, although, after a period distinctive to the matrix used, a longer extraction time does not significantly improve the efficiency [86]. Usually, extraction duration varies from a few minutes to half an hour depending on the matrix to avoid thermal degradation and oxidation [87]. The irradiation time is mainly dependent on the dielectric property of the solvent, while solvents such as ethanol, methanol, and water can rapidly heat, a phenomenon that can lead to a degradation of thermolabile compounds during extraction [88]. One of the purposes of MAE is the extraction of phenolic compounds in significantly shorter times, with the simultaneous optimum recovery of such compounds. Typically, extraction times vary from 40 s to a few minutes, as can be seen in Table 4 and Figure 9.

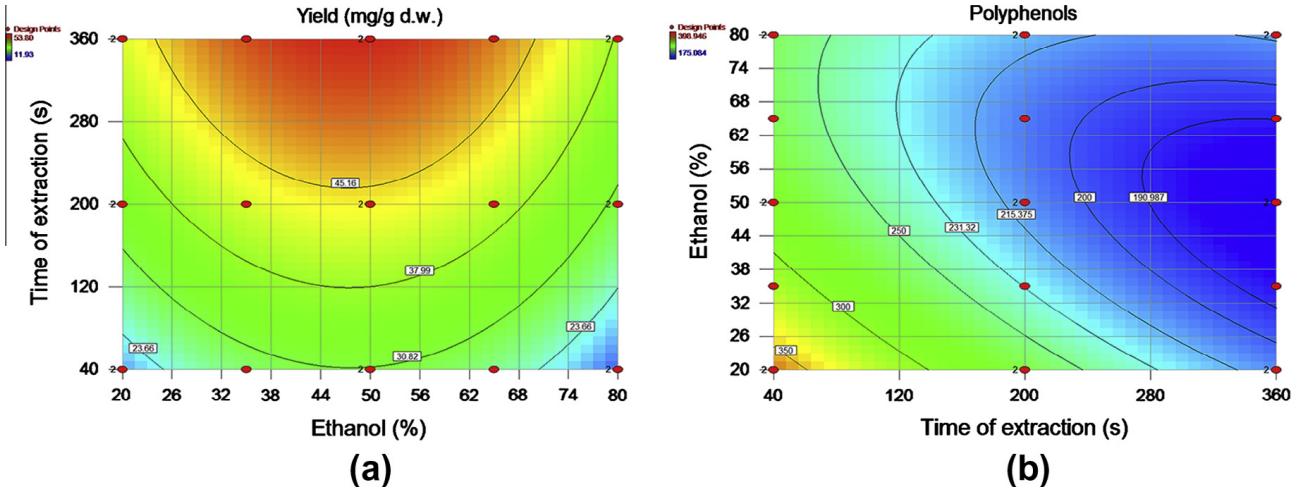

Figure 9. Contour plots for the effect of various factors on the extraction yield (**a**) and total polyphenol content (**b**) during microwave-assisted extraction of natural antioxidants from spent filter coffee (Reprinted from Separation and Purification Technology, Vol 118, Marija D. Pavlović, Aneta V. Buntić,Slavica S. Šiler-Marinković, Suzana I. Dimitrijević-Branković, Ethanol influenced fast microwave-assisted extraction for natural antioxidants obtaining from spent filter coffee, 503–510, Copyright (2013), with permission from Elsevier [17]).

The physical characteristics of the plant matrix and its moisture content may affect the extraction efficiency. Finer particles increase the contact surface, providing the area for higher penetration of irradiation, thus increasing the extraction yield [89]. However, an excessively fine plant matrix may lead to technical difficulties during filtration or centrifugation [90]. Generally, the suggested particle size ranges from 2 to 100 mm [87]. As far as sample moisture content is concerned, it has been reported that high moisture content may be beneficial, as moisture acts as a solvent that evaporates during MAE and causes the disruption of the cell wall by pressure.

Moreover, the liquid-to-solid ratio also plays a principal role in the process efficiency. Generally, in conventional solvent extraction, the higher the solvent volume, the higher the recovery yield. In the case of microwave extraction, two different aspects are reported [84]. Possibly, in some cases, a higher solid-to-liquid ratio leads to lower recovery yields due to the fact that the same amount of microwave energy corresponds to a larger amount of solids, while the contact surface area decreases, thus decreasing the extraction of compounds [91,92]. Liquid-to-solid ratios reported in the literature for the MAE of SCG phenolics vary between 9 and 60 mL/g, with the highest extraction efficiency being reported by Pavlović et al. [17], reaching up to 398.95 mg GAE/g dry SCG.

3.2.3. High-Pressure-Assisted Extraction (HPE)

High-pressure-assisted extraction is considered to be an emerging method that is based on the application of high pressures (100–900 MPa) to a food matrix [93]. During this procedure, pressure leads the air in plant tissues to leak, interrupting the cell membrane, a fact that facilitates the contact between solvent and extracted phenolic compounds [94,95]. High pressures keep solvents below their boiling point (liquid state), leading to higher solubility of solutes and higher penetration of solvent in the matrix [57]. Compared to conventional extraction, high-pressure-assisted extraction is a novel rapid method that requires smaller volume of solvents [96]. Table 4 presents studies on the extraction of phenolic components from SCG with high-pressure-assisted extraction.

The most critical parameters influencing the recovery yield are pressure, solvent type, liquid-to-solid ratio, time, and temperature. As far as solvent type is concerned, the solvent should be selectively soluble with polarity close to that of the target compounds [97]. Ethanol (20–100%) is considered to be the most common solvent in high-pressure extraction

of compounds, such as phenolic compounds, flavonoids, anthocyanins, etc., from plant materials [97–99]. As far as the extraction of SCG phenolics using HPE techniques, although the literature is rather scarce, da Silva et al. [79] used 50% (v/v) ethanol, achieving a yield of 43 mg caffeic acid equivalents/g dry SCG, with the main effects on total polyphenol yield and antiradical power being presented in Figure 10, whereas another study conducted by Okur et al. [56] utilized 80% (v/v) methanol.

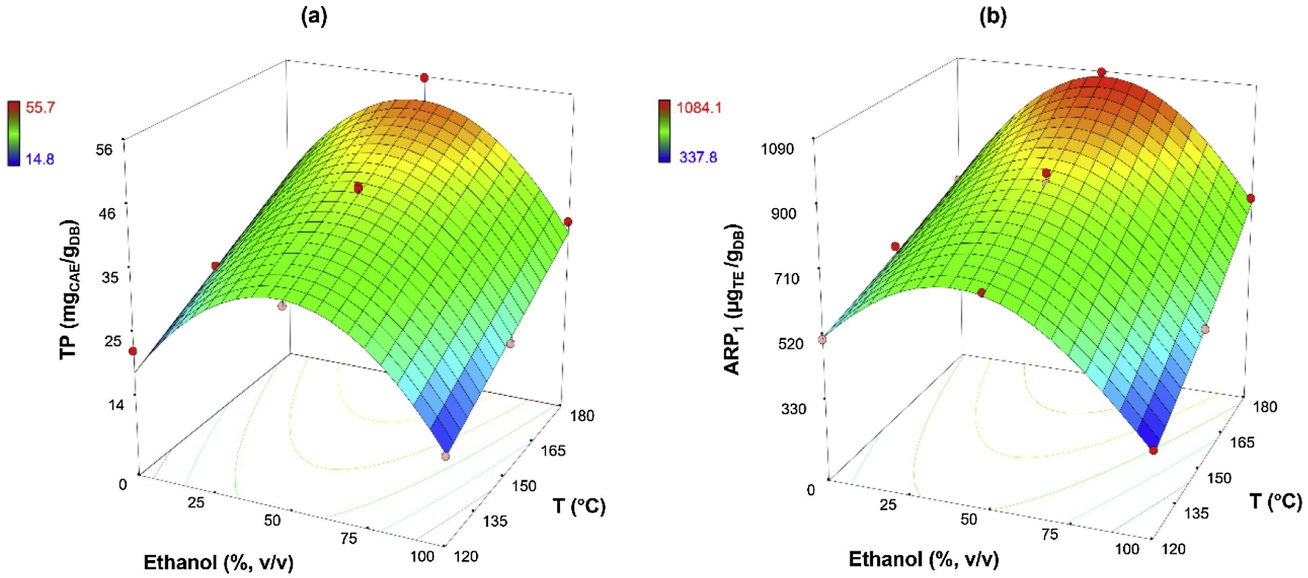

Figure 10. Response surfaces plots for the effect of various factors on total polyphenol yield (TP) (**a**) and antiradical power (ARP_1) (**b**) for high-pressure-assisted extraction of phenolics from SCG (pressures ranging from 2 to 20 bars) (Reprinted from Chemical Engineering Research and Design, Vol 177, Milena Fernandes da Silva, Margherita Pettinato, Alessandro Alberto Casazza, Maria Inês Sucupira Maciel, Patrizia Perego, Design and evaluation of non-conventional extraction for bioactive compounds recovery from spent coffee (*Coffea arabica* L.) grounds, 418–430, Copyright (2022), with permission from Elsevier [79]).

Pressure during HPE can generally be increased up to 600 MPa [100], whereas higher pressure assists the extraction of desired compounds and lowers the required extraction time. This phenomenon is based on the fact that increased pressure can lead to increased solvent strength and solubility of compounds and decreased dielectric constant of water [97]. Regarding studies specifically on the use of HPE on coffee industry wastes, operation pressures ranged from 0.7 to 500 MPa.

Generally, the raw material to solvent ratio affects the efficiency of extraction in HPE. As the ratio increases, the extraction yields show an increasing trend; however, an increase above a certain point, namely, a plateau, does not lead to a further increase in efficiency [97]. Similar L/S ratios have been employed in the few studies performed on HPE of SCG phenolics, i.e., 9 and 10 mL/g, while the investigation of this effect on the total yield should be considered a topic of interest.

Higher temperatures during HPE can increase efficiency, as diffusion of the solvent into the material is favored. Meanwhile, the desorption of solutes from the raw material is also increased [100]. Temperatures during this type of extraction can typically range between 20 and 60 °C [101]. Another effect of higher temperatures is the decrease of viscosity and surface tension of liquid solvents [97].

The efficiency of HPE is highly dependent on the extraction time. Longer times assist in the complete contact of solvent and matrix, thus increasing yield. In addition, this prolonged contact can cause the inflation of the matrix, increasing the amount of solvent that can penetrate the raw material [102]. As can be seen in Table 4, this parameter has been investigated in the field of SCG phenolics recovery in the ranges of 5 to 60 min.

4. Use as Biosorbents

Lately, limitations of commercially available adsorbents have led the research community to the development of novel adsorption materials (biosorbents) from industrial and agricultural byproducts. These biosorbents are low-cost, abundant, and effective, whereas their revalorization is beneficial as these solid wastes can be reused and not be disposed of in landfills, posing a severe threat to the environment.

Only a few studies have been carried out using coffee industry byproducts as biosorbents, and these are presented in the following sections. The first report on the revalorization of coffee wastes for the removal of pollutants from wastewaters was published in 2003. Matos et al. [103] investigated several biosorbents, including coffee bean skins, for the elimination of zinc and copper ions in swine breeding wastewater. Recently, treated or untreated spent coffee grounds have become one of the most investigated coffee byproducts for the removal of toxic components [33].

The exploitation of spent coffee grounds wastes for the removal of pollutants has recently emerged, as is shown in Table 5, whereas a common setup of this process is presented in Figure 11. Regarding the use of SCG for the removal of pollutants from wastewaters, Franca et al. [104] studied the recovery of dye (methylene blue) from aqueous solutions, pretreating SCG with drying at 105 °C for 5 h and achieving yields up to 98%. Meanwhile, Hirata et al. [105], using microwave-treated SCG, investigated the adsorption of the same dye and also gentian violet. Similarly to Franca et al. [104], Solomakou et al. [106] also used coffee industry waste after pretreatment at 105 °C until a final moisture content of 4%, for the removal of phenolics from another food industry waste, namely, olive mill wastewater, and pure gallic acid aqueous solutions. The literature on the use of SCG for the removal of phenolics compounds is rather limited, while yields achieved (45.44 and 70.69%, respectively) are considered to be satisfactory, given the fact that SCG was not chemically or thermally activated. Indeed, it has been proven that adsorption capacity can be considerably boosted after thermal or chemical pretreatment. Generally, pretreatments increase the number of available adsorption sites and improve adsorption-related physicochemical properties, such as porosity and surface area [107].

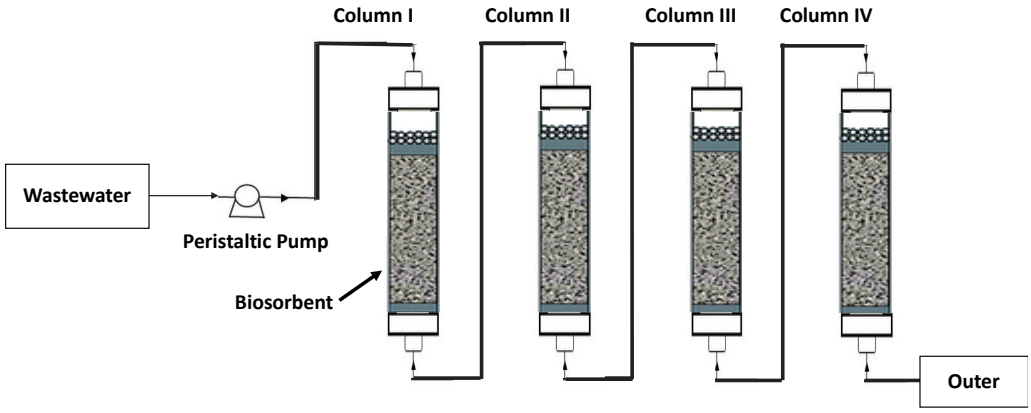

Figure 11. Fixed-bed columns setup for continuous adsorption on SCG.

With the ultimate purpose of increasing yield, several studies have employed the use of pretreated SCG for the removal of different types of dyes. More specifically, Namane et al. [108] used chemically activated SCG with $ZnCl_2$ and H_3PO_4 for the removal of phenols and dyes from aqueous streams, Ramón Gonçalves et al. [63] studied KOH-treated SCG for the adsorption of methylene blue, and Safarik et al. [109] used magnetically modified SCG for the treatment of water-soluble dyes and xenobiotics, presenting yields that reached up to 73.4 mg of dye/g of SCG.

Finally, many researchers focus their studies on the development of innovative techniques using SCG for the removal of heavy metal ions and depollution of contaminated waters [110–113], achieving remarkable adsorption capacities up to 97%.

Table 5. Use of SCG as biosorbent.

Pretreatment	Conditions	Adsorbed Compound	Yield	References
Drying at 105 °C for 5 h	stirring 100 rpm, pH 3–11, r: 5–30 g/L, C_0: 50–500 mg/L, T: 25 °C, t: 15 min–12 h	Methylene blue from aqueous solution	47–98%	[104]
-	pH 2–10, r: 25 g/L, C_0: 0–200 mM, T: 25 °C, t: 2 h	Cadmium	≤91.04%	[110]
Grinding, sieving, washing, and drying at 110 °C for 3 h	stirring 300 rpm, r: 10 g/L, C_0: 10 mg/L, T: 25 °C, t: 3 h	Lead ions from aqueous solutions	≤97%	[111]
Drying until decrease of moisture content by 50%, carbonization at 800, 1000, and 1200 °C	r: 3.33 g/L, C_0: 100 mg/L, T: 25 °C, t: 10 days	Indigo carmine	100%	[114]
Drying to constant weight, chemical activation with $ZnCl_2$ and H_3PO_4	r: 10 g/L, C_0: 0.5 g/L, T: 30 °C, t: 5 days	Phenols and dyes from aqueous steams	-	[108]
Treatment with hot water, drying at 100 °C for 24 h, soaking in 1 M KOH for 24 h, drying at 105 °C for 12 h, carbonization at 500 °C	pH 7-9, C_0: 20–40 ppm, T: 25 °C, t: 2–4 h	Aniline yellow dye	≤88.72%	[115]
Treatment with potassium hydroxide, carbonization at 850 °C	stirring 350 rpm, C_0: 10 mg/L	Methylene blue	-	[63]
Magnetic modification	r: 3 g/L, t: 3 h	Water-soluble dyes and xenobiotics	73.4 mg of dye/g dried adsorbent	[109]
Removal of phenolics, drying at 100 °C	t: 20 min, T: 30 °C, pH: 8, C_0: 162.5 mg/L, S/L: 0.02 g/mL (OMW) t: 20 min, T: 40 °C, pH: 6, C_0: 50 mg/L, S/L: 0.03 g/mL (gallic acid)	OMW phenolics, pure gallic acid aqueous solutions	45.44% (OMW) 70.69% (gallic acid)	[106]
-	r: 0.1 and 1 g/L, C_0: 100 mg/L, T: 24 °C, t: 24 h	Lead ions from drinking water	≤95%	[112]
Air drying for 6 h	r: 10 g/L, t: 12 h	Cu, Zn, Cd, and Pb cations from aqueous solutions	≤94.9%	[113]

r: Adsorbent dosage, C_0: initial concentration of the adsorbed compound, T: adsorption temperature, t: adsorption time.

5. Future Challenges

The extraction of phenolic compounds from SCG allows the sustainable production of bioactive compounds and should be the way forward. However, the food industry is slow at embracing the valorization approach for valuable compounds wastes. The degradation and/or consistency of SCG wastes as raw materials for the production of other food ingredients can be a major concern or issue. The stability of SCG and of its phenolic extracts has to be considered, since there is limited research in this field. Published works have mainly been focused on a single theme: extraction efficiency. Future investigations should pay more attention not only to the thorough collection of SCG but also to the purification and stability of its products.

In addition, most of the studies on the valorization of SCG are restricted to the laboratory scale and only very few studies have been commercialized to scaling-up processes so far. This demands multidisciplinary approaches to transform the studies related to SCG valorization from the laboratory scale to the industrial scale. Valorization of SCG could be developed by establishing links between academia and industry, estimating how the type and quantity of byproducts can be inserted, for example, in the agricultural sector, treating these byproducts adequately in addition to a possible undertaking to give added value to byproducts by taking advantage of their nutritional characteristics. Future research is needed to strengthen the available knowledge in this area, including characterization of bioactive compounds, and practical applications in the food and pharmaceutical industries.

Although coffee waste has been successfully exploited in the food and pharmaceutical industries, other areas, such as renewable energies, remain poorly explored. SCG has a relatively high caloric value and, thus, it could be exploited through combustion as fuel. It

remains necessary to increase the production yield of bioethanol, which is severely affected by the presence of phenolic compounds.

6. Conclusions

The coffee industry is one of the most profitable in the world, as it is not only limited to the preparation of beverages and food. Wastes derived from coffee processing owing to their composition have a high potential for use as a source of phenolic compounds, lipids, and carbohydrates for the production of many value-added products. Many studies have been carried out to extract phenolic compounds from SCG. Solid–liquid extraction is the conventional method. However, nonconventional extraction techniques remain a developing field. In addition, the production of adsorbent materials for decontamination processes has been extensively studied in recent years. SCGs and their carbonaceous materials show a high removal capacity for heavy metals synthetic dyes, drugs, and pesticides.

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Nomenclature

Symbol	Description
A	Amplitude level
ARP1	Antiradical power
C_0	Initial concentration of the adsorbed compound
CH	Coffee cherry husk
CP	Coffee pulp
CQA	Monocaffeoylquinic acids
diCQA	Dicaffeoylquinic acids.
DES	Deep eutectic solvents
DPPH	α, α-diphenyl-β-picrylhydrazyl (free radical scavenging method)
EC_{50}/IC_{50}	Concentration of the sample necessary to decrease the initial DPPH concentration by 50%
EtOH	Aqueous ethanol
GAE	Gallic acid equivalent
HPE	High-pressure-assisted extraction
L/S	Solvent to solid ratio
MAE	Microwave-assisted extraction
r	Adsorbent dosage
SCG(s)	Spent coffee ground(s)
T	Temperature
t	Time
P	Microwave power
UAE	Ultrasound-assisted extraction

References

1. Kourmentza, C.; Economou, C.N.; Tsafrakidou, P.; Kornaros, M. Spent coffee grounds make much more than waste: Exploring recent advances and future exploitation strategies for the valorization of an emerging food waste stream. *J. Clean. Prod.* **2018**, *172*, 980–992. [CrossRef]
2. International Coffee Organization. Available online: http://www.ico.org (accessed on 23 May 2022).
3. Karmee, S.K. A spent coffee grounds based biorefinery for the production of biofuels, biopolymers, antioxidants and biocomposites. *Waste Manag.* **2018**, *72*, 240–254. [CrossRef]

4. Getachew, A.T.; Chun, B.S. Influence of pretreatment and modifiers on subcritical water liquefaction of spent coffee grounds: A green waste valorization approach. *J. Clean. Prod.* **2017**, *142*, 3719–3727. [CrossRef]
5. European Union Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives. *Off. J. Eur. Union* **2008**, *51*, 3–30.
6. European Union Council Directive 1999/31/EC on the landfill of waste. *Off. J. L* **1999**, *182*, 1–19.
7. Campos-Vega, R.; Loarca-Piña, G.; Vergara-Castañeda, H.A.; Oomah, B.D. Spent coffee grounds: A review on current research and future prospects. *Trends Food Sci. Technol.* **2015**, *45*, 24–36. [CrossRef]
8. Caetano, N.S.; Silva, V.F.M.; Melo, A.C.; Mata, T.M. Potential of spent coffee grounds for biodiesel production and other applications. *Chem. Eng. Trans.* **2013**, *35*, 1063–1068.
9. Mussatto, S.I.; Carneiro, L.M.; Silva, J.P.A.; Roberto, I.C.; Teixeira, J.A. A study on chemical constituents and sugars extraction from spent coffee grounds. *Carbohydr. Polym.* **2011**, *83*, 368–374. [CrossRef]
10. Kante, K.; Nieto-Delgado, C.; Rangel-Mendez, J.R.; Bandosz, T.J. Spent coffee-based activated carbon: Specific surface features and their importance for H2S separation process. *J. Hazard. Mater.* **2012**, *201*, 141–147. [CrossRef] [PubMed]
11. Gomes, T.; Pereira, J.A.; Ramalhosa, E.; Casal, S.; Baptista, P. Effect of Fresh and Composted Spent Coffee Grounds on Lettuce Growth, Photosynthetic Pigments and Mineral Composition. In Proceedings of the VII Congreso Ibérico de Agroingeniería y Ciencias Horticolas, SECH e SEAgIng, Madrid, Spain, 26–29 August 2014; pp. 1–5.
12. Ribeiro, J.P.; Vicente, E.D.; Gomes, A.P.; Nunes, M.I.; Alves, C.; Tarelho, L.A.C. Effect of industrial and domestic ash from biomass combustion, and spent coffee grounds, on soil fertility and plant growth: Experiments at field conditions. *Environ. Sci. Pollut. Res.* **2017**, *24*, 15270–15277. [CrossRef] [PubMed]
13. Abrahão, F.R.; Rocha, L.C.R.; Santos, T.A.; do Carmo, E.L.; Pereira, L.A.S.; Borges, S.V.; Pereira, R.G.F.A.; Botrel, D.A. Microencapsulation of bioactive compounds from espresso spent coffee by spray drying. *LWT* **2019**, *103*, 116–124. [CrossRef]
14. Kovalcik, A.; Obruca, S.; Marova, I. Valorization of Spent Coffee Grounds: A review. *Food Bioprod. Process.* **2018**, *110*, 104–119. [CrossRef]
15. Ballesteros, L.F.; Ramirez, M.J.; Orrego, C.E.; Teixeira, J.A.; Mussatto, S.I. Optimization of autohydrolysis conditions to extract antioxidant phenolic compounds from spent coffee grounds. *J. Food Eng.* **2017**, *199*, 1–8. [CrossRef]
16. Severini, C.; Derossi, A.; Fiore, A.G. Ultrasound-assisted extraction to improve the recovery of phenols and antioxidants from spent espresso coffee ground: A study by response surface methodology and desirability approach. *Eur. Food Res. Technol.* **2017**, *243*, 835–847. [CrossRef]
17. Pavlović, M.D.; Buntić, A.V.; Šiler-Marinković, S.S.; Dimitrijević-Branković, S.I. Ethanol influenced fast microwave-assisted extraction for natural antioxidants obtaining from spent filter coffee. *Sep. Purif. Technol.* **2013**, *118*, 503–510. [CrossRef]
18. Ruesgas-Ramón, M.; Figueroa-espinoza, M.C.; Durand, E. Application of Deep Eutectic Solvents (DES) for Phenolic Compounds Extraction: Overview, Challenges, and Opportunities. *J. Agric. Food Chem.* **2017**, *65*, 3591–3601. [CrossRef] [PubMed]
19. Alonso, C.; Pérez, R.; Bazaga, P.; Medrano, M.; Herrera, C.M. MSAP markers and global cytosine methylation in plants: A literature survey and comparative analysis for a wild-growing species. *Mol. Ecol. Resour.* **2016**, *16*, 80–90. [CrossRef]
20. Diamanti, A.C.; Igoumenidis, P.E.; Mourtzinos, I.; Yannakopoulou, K.; Karathanos, V.T. Green extraction of polyphenols from whole pomegranate fruit using cyclodextrins. *Food Chem.* **2017**, *214*, 61–66. [CrossRef]
21. Goula, A.M.; Gerasopoulos, D. Integrated olive mill waste (OMW) processing toward complete by-product recovery of functional components. In *Olives and Olive Oil as Functional Foods: Bioactivity, Chemistry and Processing*; Wiley: New York, NY, USA, 2017; pp. 177–204.
22. Ververi, M.; Goula, A.M. Pomegranate peel and orange juice by-product as new biosorbents of phenolic compounds from olive mill wastewaters. *Chem. Eng. Process. Intensif.* **2019**, *138*, 86–96. [CrossRef]
23. Nasuha, N.; Hameed, B.H. Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea. *Chem. Eng. J.* **2011**, *166*, 783–786. [CrossRef]
24. Bertrand, B.; Guyot, B.; Anthony, F.; Lashermes, P. Impact of the Coffea canephora gene introgression on beverage quality of C. arabica. *Theor. Appl. Genet.* **2003**, *107*, 387–394. [CrossRef] [PubMed]
25. Clarke, R.J.; Vitzthum, O.G. *Coffee: Recent Developments*; Blackwell Science Ltd.: Hoboken, NJ, USA, 2001.
26. Zuorro, A.; Lavecchia, R. Spent coffee grounds as a valuable source of phenolic compounds and bioenergy. *J. Clean. Prod.* **2012**, *34*, 49–56. [CrossRef]
27. Murthy, P.S.; Madhava Naidu, M. Sustainable management of coffee industry by-products and value addition—A review. *Resour. Conserv. Recycl.* **2012**, *66*, 45–58. [CrossRef]
28. Mata, T.M.; Martins, A.A.; Caetano, N.S. Bio-refinery approach for spent coffee grounds valorization. *Bioresour. Technol.* **2018**, *247*, 1077–1084. [CrossRef] [PubMed]
29. Vardon, D.R.; Moser, B.R.; Zheng, W.; Witkin, K.; Evangelista, R.L.; Strathmann, T.J.; Rajagopalan, K.; Sharma, B.K. Complete utilization of spent coffee grounds to produce biodiesel, bio-oil, and biochar. *ACS Sustain. Chem. Eng.* **2013**, *1*, 1286–1294. [CrossRef]
30. Cruz, R.; Cardoso, M.M.; Fernandes, L.; Oliveira, M.; Mendes, E.; Baptista, P.; Morais, S.; Casal, S. Espresso Coffee Residues: A Valuable Source of Unextracted Compounds. *J. Agric. Food Chem.* **2012**, *60*, 7777–7784. [CrossRef]
31. Acevedo, F.; Rubilar, M.; Scheuermann, E.; Cancino, B.; Uquiche, E.; Garcés, M.; Inostroza, K.; Shene, C. Spent coffee grounds as a renewable source of bioactive compounds. *J. Biobased Mater. Bioenergy* **2013**, *7*, 420–428. [CrossRef]

32. Acevedo, F.; Rubilar, M.; Scheuermann, E.; Cancino, B.; Uquiche, E.; Garcés, M.; Inostroza, K.; Shene, C. Bioactive Compounds of Spent Coffee Grounds, a Coffee Industrial Residue. In Proceedings of the III Symposium on Advanced Magnetic Materials and Applications, Taiwan, China, 21–25 July 2013; Volume 212.
33. Cerino-Córdova, F.J.; Dávila-Guzmán, N.E.; León, A.M.G.; Salazar-Rabago, J.J.; Soto-Regalado, E. Revalorization of coffee waste. In *Coffee-Production and Research*; IntechOpen: London, UK, 2020; p. 133. ISBN 183880885X.
34. Ballesteros, L.F.; Teixeira, J.A.; Mussatto, S.I. Chemical, functional, and structural properties of spent coffee grounds and coffee silverskin. *Food Bioprocess Technol.* **2014**, *7*, 3493–3503. [CrossRef]
35. Delgado, P.A.; Vignoli, J.A.; Siika-aho, M.; Franco, T.T. Sediments in coffee extracts: Composition and control by enzymatic hydrolysis. *Food Chem.* **2008**, *110*, 168–176. [CrossRef]
36. Farah, A.; Donangelo, C.M. Phenolic compounds in coffee. *Braz. J. Plant Physiol.* **2006**, *18*, 23–36. [CrossRef]
37. Yen, W.-J.; Wang, B.-S.; Chang, L.-W.; Duh, P.-D. Antioxidant properties of roasted coffee residues. *J. Agric. Food Chem.* **2005**, *53*, 2658–2663. [CrossRef] [PubMed]
38. Rawel, H.M.; Kulling, S.E. Nutritional contribution of coffee, cacao and tea phenolics to human health. *J. Verbrauch. Leb.* **2007**, *2*, 399–406. [CrossRef]
39. Brezová, V.; Šlebodová, A.; Staško, A. Coffee as a source of antioxidants: An EPR study. *Food Chem.* **2009**, *114*, 859–868. [CrossRef]
40. Sul, D.; Kim, H.-S.; Lee, D.; Joo, S.S.; Hwang, K.W.; Park, S.-Y. Protective effect of caffeic acid against beta-amyloid-induced neurotoxicity by the inhibition of calcium influx and tau phosphorylation. *Life Sci.* **2009**, *84*, 257–262. [CrossRef] [PubMed]
41. Jeong, C.-H.; Jeong, H.R.; Choi, G.N.; Kim, D.-O.; Lee, U.K.; Heo, H.J. Neuroprotective and anti-oxidant effects of caffeic acid isolated from Erigeron annuus leaf. *Chin. Med.* **2011**, *6*, 25. [CrossRef]
42. Kim, S.Y. Neuroprotective and Neurotrophic Agents. In *Research Focus on Natural Products and the Body's Immune and Inflammatory Systems*; Suk, K., Ed.; Nova Science Publishers: New York, NY, USA, 2007; pp. 23–39.
43. Bravo, J.; Juaniz, I.; Monente, C.; Caemmerer, B.; Kroh, L.W.; De Peña, M.P.; Cid, C. Evaluation of spent coffee obtained from the most common coffeemakers as a source of hydrophilic bioactive compounds. *J. Agric. Food Chem.* **2012**, *60*, 12565–12573. [CrossRef]
44. Ramalakshmi, K.; Rao, L.J.M.; Takano-Ishikawa, Y.; Goto, M. Bioactivities of low-grade green coffee and spent coffee in different in vitro model systems. *Food Chem.* **2009**, *115*, 79–85. [CrossRef]
45. Monente, C.; Bravo, J.; Vitas, A.I.; Arbillaga, L.; De Peña, M.P.; Cid, C. Coffee and spent coffee extracts protect against cell mutagens and inhibit growth of food-borne pathogen microorganisms. *J. Funct. Foods* **2015**, *12*, 365–374. [CrossRef]
46. Seo, H.S.; Park, B.H. Phenolic compound extraction from spent coffee grounds for antioxidant recovery. *Korean J. Chem. Eng.* **2019**, *36*, 186–190. [CrossRef]
47. U.S. Environmental Protection Agency (EPA). Recycling Basics. 2017. Available online: https://www.epa.gov/recycle/recycling-basics (accessed on 5 August 2017).
48. Rajesh Banu, J.; Kavitha, S.; Yukesh Kannah, R.; Dinesh Kumar, M.; Preethi; Atabani, A.E.; Kumar, G. Biorefinery of spent coffee grounds waste: Viable pathway towards circular bioeconomy. *Bioresour. Technol.* **2020**, *302*, 122821. [CrossRef]
49. Simões, J.; Nunes, F.M.; Domingues, M.R.; Coimbra, M.A. Extractability and structure of spent coffee ground polysaccharides by roasting pre-treatments. *Carbohydr. Polym.* **2013**, *97*, 81–89. [CrossRef] [PubMed]
50. Low, J.H.; Rahman, W.A.W.A.; Jamaluddin, J. Structural elucidation of tannins of spent coffee grounds by CP-MAS 13C NMR and MALDI-TOF MS. *Ind. Crops Prod.* **2015**, *69*, 456–461. [CrossRef]
51. Choi, B.; Koh, E. Spent coffee as a rich source of antioxidative compounds. *Food Sci. Biotechnol.* **2017**, *26*, 921–927. [CrossRef] [PubMed]
52. Kan, T.; Strezov, V.; Evans, T. Catalytic pyrolysis of coffee grounds using NiCu-impregnated catalysts. *Energy Fuels* **2014**, *28*, 228–235. [CrossRef]
53. Jenkins, R.W.; Stageman, N.E.; Fortune, C.M.; Chuck, C.J. Effect of the type of bean, processing, and geographical location on the biodiesel produced from waste coffee grounds. *Energy Fuels* **2014**, *28*, 1166–1174. [CrossRef]
54. Jooste, T.; García-Aparicio, M.P.; Brienzo, M.; Van Zyl, W.H.; Görgens, J.F. Enzymatic hydrolysis of spent coffee ground. *Appl. Biochem. Biotechnol.* **2013**, *169*, 2248–2262. [CrossRef]
55. Sampaio, A.; Dragone, G.; Vilanova, M.; Oliveira, J.M.; Teixeira, J.A.; Mussatto, S.I. Production, chemical characterization, and sensory profile of a novel spirit elaborated from spent coffee ground. *LWT-Food Sci. Technol.* **2013**, *54*, 557–563. [CrossRef]
56. Okur, I.; Soyler, B.; Sezer, P.; Oztop, M.H.; Alpas, H. Improving the Recovery of Phenolic Compounds from Spent Coffee Grounds (SCG) by Environmentally Friendly Extraction Techniques. *Molecules* **2021**, *26*, 613. [CrossRef]
57. Zhang, Q.-W.; Lin, L.-G.; Ye, W.-C. Techniques for extraction and isolation of natural products: A comprehensive review. *Chin. Med.* **2018**, *13*, 20. [CrossRef] [PubMed]
58. Alara, O.R.; Abdurahman, N.H.; Ukaegbu, C.I. Extraction of phenolic compounds: A review. *Curr. Res. Food Sci.* **2021**, *4*, 200–214. [CrossRef]
59. Zuorro, A.; Lavecchia, R. Influence of extraction conditions on the recovery of phenolic antioxidants from Spent Coffee Grounds. *Am. J. Appl. Sci.* **2013**, *10*, 478–486. [CrossRef]
60. da Silva Araújo, C.; Vimercati, W.C.; Macedo, L.L.; Pimenta, C.J. Effect of solvent, method, time and temperature of extraction on the recovery of phenolic compounds and antioxidants from spent coffee grounds. *Int. J. Food Eng.* **2022**, *18*, 325–336. [CrossRef]

61. Mussatto, S.I.; Ballesteros, L.F.; Martins, S.; Teixeira, J.A. Extraction of antioxidant phenolic compounds from spent coffee grounds. *Sep. Purif. Technol.* **2011**, *83*, 173–179. [CrossRef]
62. Panusa, A.; Zuorro, A.; Lavecchia, R.; Marrosu, G.; Petrucci, R. Recovery of Natural Antioxidants from Spent Coffee Grounds. *J. Agric. Food Chem.* **2013**, *61*, 4162–4168. [CrossRef] [PubMed]
63. Ramón-Gonçalves, M.; Alcaraz, L.; Pérez-Ferreras, S.; León-González, M.E.; Rosales-Conrado, N.; López, F.A. Extraction of polyphenols and synthesis of new activated carbon from spent coffee grounds. *Sci. Rep.* **2019**, *9*, 17706. [CrossRef] [PubMed]
64. Solomakou, N.; Loukri, A.; Tsafrakidou, P.; Michaelidou, A.-M.; Mourtzinos, I.; Goula, A.M. Recovery of phenolic compounds from spent coffee grounds through optimized extraction processes. *Sustain. Chem. Pharm.* **2022**, *25*, 100592. [CrossRef]
65. Li, H.; Pordesimo, L.; Weiss, J. High intensity ultrasound-assisted extraction of oil from soybeans. *Food Res. Int.* **2004**, *37*, 731–738. [CrossRef]
66. Vinatoru, M. An overview of the ultrasonically assisted extraction of bioactive principles from herbs. *Ultrason. Sonochem.* **2001**, *8*, 303–313. [CrossRef]
67. Shirzad, H.; Niknam, V.; Taheri, M.; Ebrahimzadeh, H. Ultrasound-assisted extraction process of phenolic antioxidants from Olive leaves: A nutraceutical study using RSM and LC–ESI–DAD–MS. *J. Food Sci. Technol.* **2017**, *54*, 2361–2371. [CrossRef]
68. Syahir, A.; Sulaiman, S.; Mel, M.; Othman, M.; Sulaiman, S.Z. An Overview: Analysis of Ultrasonic-Assisted Extraction's Parameters and Its Process. In *Proceedings of the IOP Conference Series: Materials Science and Engineering*; IOP Publishing: Bristol, UK, 2020; Volume 778, p. 12165.
69. Ansori, N.U.R.I.; Zainol, M.K.; Zin, Z.M. Antioxidant Activities of Different Varieties of Spent Coffee Ground (SCG) Extracted Using Ultrasonic-Ethanol Assisted Extraction Method. *Univ. Malays. Teren. J. Undergrad. Res.* **2021**, *3*, 33–42. [CrossRef]
70. Teng, H.; Chen, L.; Huang, Q.; Wang, J.; Lin, Q.; Liu, M.; Lee, W.Y.; Song, H. Ultrasonic-assisted extraction of raspberry seed oil and evaluation of its physicochemical properties, fatty acid compositions and antioxidant activities. *PLoS ONE* **2016**, *11*, e0153457. [CrossRef] [PubMed]
71. Yang, L.; Yin, P.; Fan, H.; Xue, Q.; Li, K.; Li, X.; Sun, L.; Liu, Y. Response surface methodology optimization of ultrasonic-assisted extraction of Acer truncatum leaves for maximal phenolic yield and antioxidant activity. *Molecules* **2017**, *22*, 232. [CrossRef] [PubMed]
72. Buddin, M.; Rithuan, M.Z.A.; Surni, M.S.A.; Jamal, N.H.M.; Faiznur, M.F. Ultrasonic assisted extraction (UAE) of Moringa oleifera Seed Oil: Kinetic study. *ASM Sci. J.* **2018**, *11*, 158–166.
73. Zhou, Y.; Zheng, J.; Gan, R.-Y.; Zhou, T.; Xu, D.-P.; Li, H.-B. Optimization of ultrasound-assisted extraction of antioxidants from the mung bean coat. *Molecules* **2017**, *22*, 638. [CrossRef] [PubMed]
74. Al-Dhabi, N.A.; Ponmurugan, K.; Maran Jeganathan, P. Development and validation of ultrasound-assisted solid-liquid extraction of phenolic compounds from waste spent coffee grounds. *Ultrason. Sonochem.* **2017**, *34*, 206–213. [CrossRef]
75. Arauzo, P.J.; Lucian, M.; Du, L.; Olszewski, M.P.; Fiori, L.; Kruse, A. Improving the recovery of phenolic compounds from spent coffee grounds by using hydrothermal delignification coupled with ultrasound assisted extraction. *Biomass Bioenergy* **2020**, *139*, 105616. [CrossRef]
76. Caballero-Galván, A.S.; Restrepo-Serna, D.L.; Ortiz-Sánchez, M.; Cardona-Alzate, C.A. Analysis of extraction kinetics of bioactive compounds from spent coffee grounds (Coffea arábica). *Waste Biomass Valorization* **2018**, *9*, 2381–2389. [CrossRef]
77. Budaraju, S.V.R.N.; Mallikarjunan, K.P.; Petit, R. Comparison and Optimization of Solvent Extraction and Microwave Assisted Extraction of Phenolic Compounds from Spent Coffee Grounds. In Proceedings of the 2017 ASABE Annual International Meeting, Washington, DC, USA, 16–19 July 2017; American Society of Agricultural and Biological Engineers: St. Joseph, MI, USA, 2017; p. 1.
78. Ranic, M.; Nikolic, M.; Pavlovic, M.; Buntic, A.; Siler-Marinkovic, S.; Dimitrijevic-Brankovic, S. Optimization of microwave-assisted extraction of natural antioxidants from spent espresso coffee grounds by response surface methodology. *J. Clean. Prod.* **2014**, *80*, 69–79. [CrossRef]
79. da Silva, M.F.; Pettinato, M.; Casazza, A.A.; Maciel, M.I.S.; Perego, P. Design and evaluation of non-conventional extraction for bioactive compounds recovery from spent coffee (*Coffea arabica* L.) grounds. *Chem. Eng. Res. Des.* **2022**, *177*, 418–430. [CrossRef]
80. Upadhyay, R.; Ramalakshmi, K.; Rao, L.J.M. Microwave-assisted extraction of chlorogenic acids from green coffee beans. *Food Chem.* **2012**, *130*, 184–188. [CrossRef]
81. Xie, Z.; Yang, J.; Huang, X.; Huang, Y. Microwave processing and properties of ceramics with different dielectric loss. *J. Eur. Ceram. Soc.* **1999**, *19*, 381–387. [CrossRef]
82. Karunanithy, C.; Muthukumarappan, K.; Gibbons, W.R. Sequential extrusion-microwave pretreatment of switchgrass and big bluestem. *Bioresour. Technol.* **2014**, *153*, 393–398. [CrossRef] [PubMed]
83. Sun, J.; Wang, W.; Yue, Q.; Ma, C.; Zhang, J.; Zhao, X.; Song, Z. Review on microwave–metal discharges and their applications in energy and industrial processes. *Appl. Energy* **2016**, *175*, 141–157. [CrossRef]
84. Zhang, H.-F.; Yang, X.-H.; Wang, Y. Microwave assisted extraction of secondary metabolites from plants: Current status and future directions. *Trends Food Sci. Technol.* **2011**, *22*, 672–688. [CrossRef]
85. Dudley, G.B.; Richert, R.; Stiegman, A.E. On the existence of and mechanism for microwave-specific reaction rate enhancement. *Chem. Sci.* **2015**, *6*, 2144–2152. [CrossRef]
86. Kaufmann, B.; Christen, P.; Veuthey, J. Parameters affecting microwave-assisted extraction of withanolides. *Phytochem. Anal. An Int. J. Plant Chem. Biochem. Tech.* **2001**, *12*, 327–331. [CrossRef] [PubMed]

87. Nour, A.H.; Oluwaseun, A.R.; Nour, A.H.; Omer, M.S.; Ahmad, N. Microwave-assisted extraction of bioactive compounds. In *Theory and Practice*; Springer: Berlin/Heidelberg, Germany, 2021; pp. 1–31.
88. Shams, K.A.; Abdel-Azim, N.S.; Saleh, I.A.; Hegazy, M.F.; El-Missiry, M.M.; Hammouda, F.M.; Bohouth, E.; Tahrir, E. Green technology: Economically and environmentally innovative methods for extraction of medicinal & aromatic plants (MAP) in Egypt. *J. Chem. Pharm. Res* **2015**, *7*, 1050–1074.
89. Huie, C.W. A review of modern sample-preparation techniques for the extraction and analysis of medicinal plants. *Anal. Bioanal. Chem.* **2002**, *373*, 23–30. [CrossRef]
90. Mandal, V.; Mohan, Y.; Hemalatha, S. Microwave assisted extraction—An innovative and promising extraction tool for medicinal plant research. *Pharmacogn. Rev.* **2007**, *1*, 7–18.
91. Gao, M.; Huang, W.; RoyChowdhury, M.; Liu, C. Microwave-assisted extraction of scutellarin from Erigeron breviscapus Hand-Mazz and its determination by high-performance liquid chromatography. *Anal. Chim. Acta* **2007**, *591*, 161–166. [CrossRef]
92. Ballard, T.S.; Mallikarjunan, P.; Zhou, K.; O'Keefe, S. Microwave-assisted extraction of phenolic antioxidant compounds from peanut skins. *Food Chem.* **2010**, *120*, 1185–1192. [CrossRef]
93. Yaldagard, M.; Mortazavi, S.A.; Tabatabaie, F. The principles of ultra high pressure technology and its application in food processing/preservation: A review of microbiological and quality aspects. *African J. Biotechnol.* **2008**, *7*, 2739–2767.
94. Sadus, R.J. *High Pressure Phase Behaviour of Multicomponent Fluid Mixtures*; Elsevier: Amsterdam, The Netherlands, 2012; ISBN 0444596666.
95. Teles, A.S.C.; Chávez, D.W.H.; Coelho, M.A.Z.; Rosenthal, A.; Gottschalk, L.M.F.; Tonon, R.V. Combination of enzyme-assisted extraction and high hydrostatic pressure for phenolic compounds recovery from grape pomace. *J. Food Eng.* **2021**, *288*, 110128. [CrossRef]
96. Nieto, A.; Borrull, F.; Pocurull, E.; Marcé, R.M. Pressurized liquid extraction: A useful technique to extract pharmaceuticals and personal-care products from sewage sludge. *TrAC Trends Anal. Chem.* **2010**, *29*, 752–764. [CrossRef]
97. Khan, S.A.; Aslam, R.; Makroo, H.A. High pressure extraction and its application in the extraction of bio-active compounds: A review. *J. Food Process Eng.* **2019**, *42*, e12896. [CrossRef]
98. Spigno, G.; Tramelli, L.; De Faveri, D.M. Effects of extraction time, temperature and solvent on concentration and antioxidant activity of grape marc phenolics. *J. Food Eng.* **2007**, *81*, 200–208. [CrossRef]
99. Xi, J. Effect of high pressure processing on the extraction of lycopene in tomato paste waste. *Chem. Eng. Technol. Ind. Chem. Equip. -Process Eng.* **2006**, *29*, 736–739. [CrossRef]
100. Prasad, K.N.; Yang, B.; Zhao, M.; Wei, X.; Jiang, Y.; Chen, F. High pressure extraction of corilagin from longan (Dimocarpus longan Lour.) fruit pericarp. *Sep. Purif. Technol.* **2009**, *70*, 41–45. [CrossRef]
101. Shin, J.-S.; Ahn, S.-C.; Choi, S.-W.; Lee, D.-U.; Kim, B.-Y.; Baik, M.-Y. Ultra high pressure extraction (UHPE) of ginsenosides from Korean Panax ginseng powder. *Food Sci. Biotechnol.* **2010**, *19*, 743–748. [CrossRef]
102. Chen, R.; Meng, F.; Zhang, S.; Liu, Z. Effects of ultrahigh pressure extraction conditions on yields and antioxidant activity of ginsenoside from ginseng. *Sep. Purif. Technol.* **2009**, *66*, 340–346. [CrossRef]
103. De Matos, A.T.; Brandao, V.S.; Neves, J.C.L.; Martinez, M.A. Removal of Cu and Zn from swine raising wastewater using organic filters. *Environ. Technol.* **2003**, *24*, 171–178. [CrossRef]
104. Franca, A.S.; Oliveira, L.S.; Ferreira, M.E. Kinetics and equilibrium studies of methylene blue adsorption by spent coffee grounds. *Desalination* **2009**, *249*, 267–272. [CrossRef]
105. Hirata, M.; Kawasaki, N.; Nakamura, T.; Matsumoto, K.; Kabayama, M.; Tamura, T.; Tanada, S. Adsorption of dyes onto carbonaceous materials produced from coffee grounds by microwave treatment. *J. Colloid Interface Sci.* **2002**, *254*, 17–22. [CrossRef] [PubMed]
106. Solomakou, N.; Tsafrakidou, P.; Goula, A.M. Holistic Exploitation of Spent Coffee Ground: Use as Biosorbent for Olive Mill Wastewaters After Extraction of Its Phenolic Compounds. *Water Air Soil Pollut.* **2022**, *233*, 173. [CrossRef]
107. Papaoikonomou, L.; Labanaris, K.; Kaderides, K.; Goula, A.M. Adsorption–desorption of phenolic compounds from olive mill wastewater using a novel low-cost biosorbent. *Environ. Sci. Pollut. Res.* **2021**, *28*, 24230–24244. [CrossRef] [PubMed]
108. Namane, A.; Mekarzia, A.; Benrachedi, K.; Belhaneche-Bensemra, N.; Hellal, A. Determination of the adsorption capacity of activated carbon made from coffee grounds by chemical activation with ZnCl2 and H3PO4. *J. Hazard. Mater.* **2005**, *119*, 189–194. [CrossRef]
109. Safarik, I.; Horska, K.; Svobodova, B.; Safarikova, M. Magnetically modified spent coffee grounds for dyes removal. *Eur. Food Res. Technol.* **2012**, *234*, 345–350. [CrossRef]
110. Kim, M.-S.; Kim, J.-G. Adsorption characteristics of spent coffee grounds as an alternative adsorbent for cadmium in solution. *Environments* **2020**, *7*, 24. [CrossRef]
111. Lavecchia, R.; Medici, F.; Patterer, S.; Zuorro, A. Lead removal from water by adsorption on spent coffee grounds. *Chem. Eng. Trans.* **2016**, *47*, 295–300.
112. Tokimoto, T.; Kawasaki, N.; Nakamura, T.; Akutagawa, J.; Tanada, S. Removal of lead ions in drinking water by coffee grounds as vegetable biomass. *J. Colloid Interface Sci.* **2005**, *281*, 56–61. [CrossRef]
113. Utomo, H.D.; Hunter, K.A. Adsorption of divalent copper, zinc, cadmium and lead ions from aqueous solution by waste tea and coffee adsorbents. *Environ. Technol.* **2006**, *27*, 25–32. [CrossRef] [PubMed]

114. Nakamura, T.; Hirata, M.; Kawasaki, N.; Tanada, S.; Tamura, T.; Nakahori, Y. Decolorization of indigo carmine by charcoal from extracted residue of coffee beans. *J. Environ. Sci. Health Part A* **2003**, *38*, 555–562. [CrossRef] [PubMed]
115. Pagalan, E., Jr.; Sebron, M.; Gomez, S.; Salva, S.J.; Ampusta, R.; Macarayo, A.J.; Joyno, C.; Ido, A.; Arazo, R. Activated carbon from spent coffee grounds as an adsorbent for treatment of water contaminated by aniline yellow dye. *Ind. Crops Prod.* **2020**, *145*, 111953. [CrossRef]