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Review

Chlorogenic Acids and Caffeine from Coffee By-Products: A Review on Skincare Applications

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Abstract: Upcycling is a modern trend in the cosmetic sector, focusing on by-products reuse and waste reduction. Consumers are more aware of the origin of cosmetic products and their environmental impact, promoting the upcycling phenomenon. Converting these raw materials into products of higher quality or value contributes to the final product's sustainability. In fact, several agri-food by-products that are typically discarded have generated great interest, due to their value-added compounds with high functionality and/or bioactivity. Coffee is well known as a cosmetic ingredient, particularly due to the presence of phenolic compounds, such as chlorogenic acids, and caffeine. Caffeine is widely used in cosmetic formulations due to its photoprotector and anti-aging properties, as well as lipolytic action in cellulitis, and hair regrowth. Chlorogenic acids are powerful antioxidants and exhibit anti-aging and photoprotector abilities. Coffee by-products, such as coffee beans, possess these bioactive compounds and other chemical characteristics that can provide functional properties in cosmetic formulations. Coffee silverskin and spent coffee grounds are high-volume by-products of the coffee industry. Their use has been explored in different cosmetic formulations demonstrating safety, stability, acceptability as well as skin improvement, thus supporting their valorization as natural and sustainable new ingredients in skincare products.

Keywords: coffee silverskin; spent coffee grounds; extraction; bioactivities; cosmetic; upcycling

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1. Introduction

Coffee is one of the most widely consumed beverages in the world and its consumption is associated with various health benefits, such as reduction of type II diabetes risk, or protection against neurodegenerative diseases, which have been mostly attributed to two major groups of bioactives present, phenolic compounds and alkaloids [1,2]. These compounds also possess characteristics with dermacosmetic interest that have been explored over the years in regard to skin health and beauty, as well as hair care [3,4].

Considering that about 50% of the coffee fruit is discarded in its production, the coffee industry is responsible for generating large quantities of residues [5,6]. Their disposal constitutes a serious environmental hazard, especially due to their content of caffeine, tannins and polyphenols, which can present a phytotoxic effect when improperly discarded in the soil [5,7]. On the other hand, such bioactive compounds are a source of possible active ingredients for many industries, such as pharmaceutical or cosmetic ones [7]. Converting by-products into products of higher quality or value, an upcycling approach, represents the closing of the circle of a design aimed to increase the product overall sustainability, in a circular economy model [8].

Valorization is urgent, considering these by-products environmental impact and the socioeconomic advantages in its reuse, and should involve both industries and researchers to create strategies to promote their utilization. In that sense, this work aims to review the dermacosmetic potential of chlorogenic acids and caffeine, and summarize information related to coffee by-products application in cosmetic and hygiene products.

2. Methods

The bibliographic search was carried out using Science Direct, PubMed, Scopus, and Google Scholar databases using the keywords "coffee by-products", "coffee silverskin" or "spent coffee grounds" AND "cosmetic", "skin", "applications" or "extraction". Regarding bioactive compounds, "caffeine" or "chlorogenic acids" combined with "effects", "antioxidant", "anti-aging", "sunscreen", "antimicrobial" or "anti-inflammatory" was also searched. Search terms "sustainability", "upcycling" AND "cosmetic" or "by-products" were also explored. Relevance, citations and publishing year were factors involved in paper selection. Books related to cosmetic technology, active ingredients and skin physiology were also consulted.

3. Bioactive Compounds: Dermacosmetic Potential

Plants contain a variety of natural antioxidants produced as a response to environmental stressors, such as ultraviolet (UV) radiation or high temperatures, in order to preserve their physical and metabolic integrity [9]. Antioxidants protect skin against oxidative stress, so they are frequently added to anti-aging formulations, since oxidative stress plays a major role in the intrinsic, as well as the extrinsic, process of skin aging [9].

UV exposure is the main external factor in the aging process, promoting oxidizing effects through the generation of reactive oxygen species (ROS), thus photoprotector and anti-aging proprieties are tightly linked [9]. In addition, damage to the skin barrier from UV exposure creates an inflammatory response with the production of cytokines (e.g., IL-1α, IL-6, and TNF-α), proteolytic enzymes and oxidant species, therefore photoprotection is enhanced by anti-inflammatory properties [9]. ROS also play a fundamental role in the regulation of matrix metalloproteinases (MMPs), such as collagenase or elastase, which degrade fundamental extracellular matrix proteins, namely collagen and elastin, known to provide strength, flexibility, and firmness to the skin [9,10]. Another enzyme, hyaluronidase, has an increased expression with UV exposure and inflammatory processes, so the ability to inhibit this protein can also contribute to an anti-aging effect since hyaluronic acid is part of the natural moisturizer factor and vital to maintain skin's hydration and evenness [9].

Regarding intrinsic aging, collagen and elastin synthesis decreases with age, as does hyaluronic acid content; at the same time, expression of MMPs increases in fibroblasts and keratinocytes, leading to loss of skin elasticity and wrinkles [9].

In that sense, bioactive molecules that can slow down the rate of intrinsic skin aging processes, as well as diminish the impact of extrinsic factors, are of great interest in the development of anti-aging skincare products.

3.1. Chlorogenic Acids

Phenolic compounds are mainly found in green coffee beans as chlorogenic acids (CGAs), up to 12% in dry weight, and are the main antioxidants present [6,11]. The three major CGAs classes in coffee are caffeoylquinic acids (CQA), feruloylquinic acids (FQA) and dicaffeoylquinic acids (diCQA) [11]. Caffeoylquinic acids, are esters of caffeic acid and quinic acid, and present several isomeric forms, such as 5-caffeoylquinic acid, which is the most common in green coffee beans and often referred to as the chlorogenic acid [12]. CGAs are also the main group of phenolic compounds in post-roasting coffee by-products being reported at levels between 1–6%, a lower value than unroasted coffee beans, since they can be thermally degraded [6,11,13].

Chemical-based assays have shown that CGA can scavenge $ABTS^{\bullet+}$ and $DPPH^{\bullet}$ and hydroxyl radicals as well as superoxide anions and peroxylnitrite [14]. CGA also has been demonstrated to increase collagen synthesis in human dermal fibroblasts (HDFs) and upregulate the transcription of skin barrier genes in epidermal keratinocytes, such as the ones encoding for filaggrin, a protein which plays an important role in the skin's barrier function, without showing cytotoxicity [10].

Cho et al. [15] investigated CGA activity in mouse fibroblast cells under ultraviolet B (UVB) radiation. UV light has an adverse effect on dermal collagen not only by stimulating

MMP action, as mentioned before, but also through inhibition of collagen biosynthesis [15]. CGA inhibited intracellular ROS production and the expression of metalloproteinases MMP-1, 3, and 9, as well as the activity of enzyme xanthine oxidase, an enzyme associated with free radical generation [15]. On the other hand, in CGA-treated fibroblast cells, type-I procollagen (a collagen precursor) increased [15]. Due to conjugative bonds in their structures, phenolic compounds often exhibit UV absorption and photoprotective capacity which this study could also demonstrate [15]. Another study aimed to investigate the anti-aging ability of CGA on HDFs regarding ultraviolet A (UVA)-induced skin photoaging, since UVB mainly leads to the damage of the epidermal layer [16]. UVA rays penetrate more deeply into the human skin dermal tissue, hence UVA is the main contributor for skin photoaging [16]. This study demonstrated that CGA treatment increased the collagen biosynthesis and secretion in HDFs, especially in type 1 collagen, and decreased MMP-1 and MMP-3 expression [16]. In addition, CGA attenuated the decrease of fibronectin after UVA exposure, which may indicate its synthesis-promoting role in other extracellular matrix proteins [16]. Additionally, CGA reduced the accumulation of UVA-induced ROS, reduced DNA damage and promoted cell repair [16].

CGA treatment in human HaCaT cells reduced the amount of DNA breakage induced by UVB radiation as demonstrated by Cha et al. [17]. CGA scavenged DPPH$^{\bullet}$, superoxide anions and hydroxyl radicals generated by radiation, and was also capable of absorbing electromagnetic radiation in the UVB range, thus providing evidence of photoprotector ability [17].

CGAs also possess anti-inflammatory activity through inhibition of pro-inflammatory cytokines and reduced expression of COX-2 and iNOS [18]. A decrease in inflammatory molecules, IL-1β, IL6 and TNF-α, as well as COX-2 and nitric oxide, was observed in CGA-treated macrophage cells stimulated by LPS, without cytotoxicity [18].

Antibacterial activity was observed against *Klebsiella pneumoniae*, *Staphylococcus epidermidis*, and *Staphylococcus aureus*, with no cytotoxicity, at minimal inhibitory concentrations ranging from 31.3 to 250 µg/mL of coffee silverskin aqueous, hydroalcoholic and alcoholic extracts [19]. This antibacterial activity can be related to the presence of phenolic compounds, being CGA the most relevant, but also to other components, particularly melanoidins that have known antibacterial effect. [19].

3.2. Caffeine

Caffeine, a methylxanthine, is the main alkaloid present in coffee beans [20]. Its chemical structure is similar to cyclic adenosine monophosphate (cAMP) adenosine, thus most of its biological activity is mediated through an antagonist effect of the adenosine receptors leading to nervous system stimulation, cardiovascular and metabolic effects [2,21]. Potential protection against neurodegenerative diseases, such as Parkinson's disease, has also been studied [2].

Caffeine has become increasingly popular as an ingredient of cosmetic products due to its ability to penetrate the skin barrier and biological effects that improve skin and hair condition [21]. In fact, it is frequently used in different cosmetic formulations due to its antioxidant, UV-protective and lipolytic action [20]. Caffeine is also present in many fortifying and anti-hair loss products [21]. Hair follicles are sensitive to hormonal action, particularly dihydrotestosterone (DHT), which is produced when an enzyme, 5-α-reductase, converts testosterone to DHT, which shortens the anagen phase of the hair cycle [21]. Caffeine can stimulate hair growth in two ways: by improving microcirculation in the hair scalp, increasing nutrients delivery and oxygenation; and inhibiting 5-α-reductase [21].

Besides antioxidant and anti-inflammatory properties, epidemiological studies have also suggested that caffeine consumption reduces the incidence of non-melanoma skin cancer [21,22]. Caffeine can also be incorporated in skincare products such as a sunscreen adjuvant acting in synergy as a photoprotector and a photo stabilizer [23]. Sunscreens with 2.5% content in caffeine were prepared by Rosado et al. [23] and their efficacy was assessed in vitro and in vivo. Both assays showed higher sun protection factor (SPF) values for the

caffeine formulated sunscreen combined with chemical and physical filters, compared to the caffeine-free sunscreen, reporting an increase of, approximately, 25% in the in vivo anti-UVB protection [23]. It has been suggested that topical caffeine can prevent UVB-induced carcinogenesis by its sunscreen function, but also by enhancing apoptosis in DNA damaged cells [24,25].

The potential of caffeine as a therapeutic agent against photoaging was explored by Eun Lee et al. [22] considering a possible inhibitory effect of MMPs (collagenase and elastase) and tyrosinase activity. The bioassays were performed with different caffeine concentrations between 10 and 1000 μg/mL. This work revealed that caffeine strongly inhibited collagenase followed by elastase, in a concentration-dependent manner, and had a week inhibition activity towards tyrosinase (only the highest caffeine concentration tested, 1000 μg/mL, had statistically different results for this enzyme) [22].

Tables 1 and 2 summarize some of the most important biological activities demonstrated by CGA and caffeine, respectively, with dermacosmetic impact.

Table 1. Chlorogenic acids skin-related benefits documented in scientific literature.

Chlorogenic Acids Dermacosmetic Activities	
Antioxidant and anti-aging	Ability to scavenge free radicals [14] Xanthine oxidase inhibition [15] Down-regulation of MMP-1, MMP-3, and MMP-9 [15,16] Up-regulation of procollagen synthesis [15,16]
Photoprotective and anti-cancer	UV-B absorption [15,17] Protection against UV-induced DNA damage [16,17]
Anti-inflammatory	Downregulation of pro-inflammatory molecules [18] iNOS and COX-2 inhibition [18]
Antibacterial	Growth inhibition of *Klebsiella pneumoniae*, *S. epidermidis*, and *S. aureus* [19]

Table 2. Caffeine skin-related benefits documented in scientific literature.

Caffeine Dermacosmetic Activities	
Thermogenic and anti-cellulite	Lipolytic action through inhibition of phosphodiesterase activity in adipocytes [21]
Antioxidant and anti-aging	Inhibition of lipid peroxidation induced by ROS [7] Collagenase and elastase inhibition [22]
Photoprotective	SPF enhancer [23] Inhibit the development of UVB-induced skin cancer [25] Induce apoptosis in UV-damaged keratinocytes [25]
Hair growth stimulant	Increase blood circulation and inhibition of 5 α-reductase [21]

4. Coffee By-Products: Chemical Composition, Extraction Methods and Safety

Coffee by-products derive from the different stages of coffee production, from post-harvest processing to roasting and coffee consumption [5]. These by-products include defective coffee beans, husks/pulp, parchment, silverskin and spent coffee grounds [5]. Although most processing steps occur in producing countries with tropical and subtropical locations, such as Brazil or Colombia, the roasting industry is present worldwide [5].

Figure 1 shows the coffee processing scheme and by-products originated.

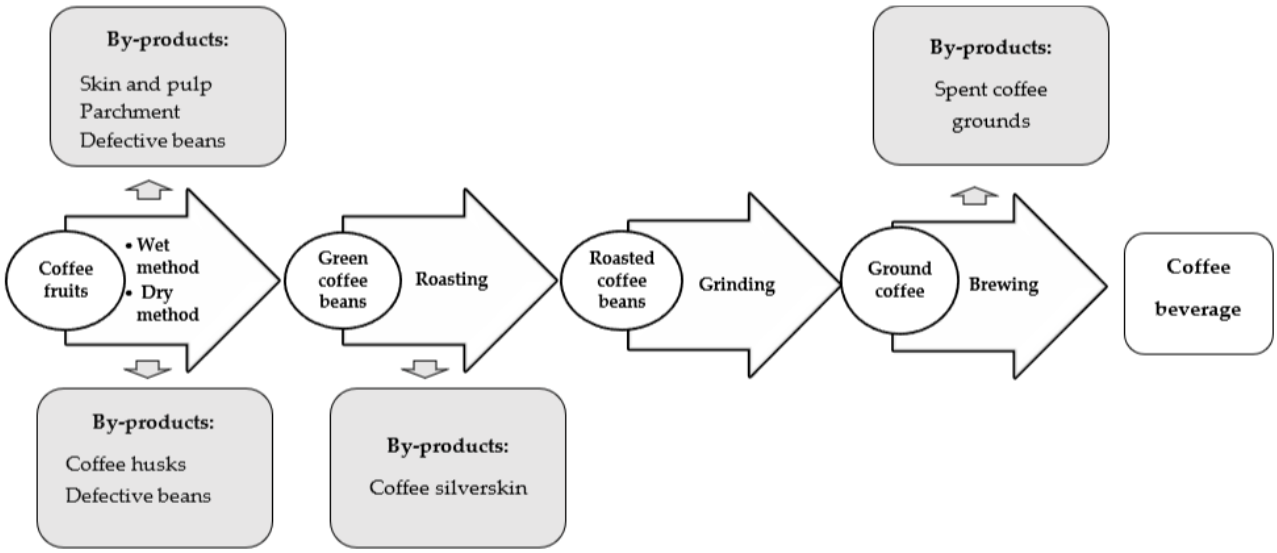

Figure 1. Coffee by-products from the coffee fruit to the coffee beverage. Adapted from [5].

4.1. Coffee Silverskin

Coffee silverskin (CS) is a thin layer covering the green coffee seeds, which detaches during the thermal processing of the beans, being the only by-product from the roasting stage [5,7]. Nowadays, it is mostly used as fertilizer or combustible, so its valorization is crucial [7]. Along with CS, spent coffee grounds (SCG), a by-product obtained after the coffee beverage preparation, are the most studied by-products, and thus the focus in this review [26].

CS has a high content of dietary fiber (56–62%) and is also very rich in protein (16–19%), and minerals, particularly potassium, magnesium, and calcium [13,26,27]. This by-product also presents low water percentage, which contributes to its stability, and low-fat content (2–4%), mainly saturated fatty acids [5,7,11,13]. CS has shown in several studies antioxidant activity and this ability is partially associated with its phenolic content, mainly chlorogenic acids and its derivatives [7]. In addition, tocopherols (α, β, γ, and δ) and tocotrienols (β, γ, and δ) were found in CS, α-tocopherol being the major one [7]. Other compounds may contribute to an antioxidant synergistic effect such as caffeine, and Maillard reaction products, such as melanoidins, which are produced during roasting [13]. CGAs are thermolabile, thus the intensity of roasting conditions can cause a reduction in the total amount [6].

CS content in CGAs will depend not only on roasting conditions, but also geographical origins and coffee species [11,14]. Contrary to CGA, caffeine content after roasting is not markedly reduced [2,28]. In CS, the concentration ranges from 0.44 to 1.25 g/100 g, depending on the coffee species [7].

4.2. Spent Coffee Grounds

After roasting, coffee beans are ground, and the beverage is prepared from the treatment of the coffee powder with hot water or steam, producing the last coffee by-product, spent coffee grounds (SCG), one of the major ones in the coffee industry [11,26,29].

SCG are solid residues with high moisture but, similarly to CS, they also present high amounts of dietary fiber [30]. Cellulose is more abundant in CS, while hemicellulose is more abundant in SCG according to Ballesteros et al. [30]. SGCs are also rich in proteins (14–17%) and minerals such as potassium and magnesium [26,30,31].

Fat content has been reported at about 2% by Ballesteros et al. [30] but other studies have reported up to 30% [31,32]. This variability can be due to the different preparation methods employed to prepare the beverage. SCG oil has been studied for cosmetic applications due to its unsaponifiable fraction and richness in unsaturated fatty acids such as linoleic acid, a natural occurring substance in the skin lipid matrix, essential to maintain

skin barrier integrity and hydration [29,33]. The unsaponifiable fraction includes diterpenes, kahweol and cafestol, which are also known for their beneficial effects on skin such as UVB photoprotection, anticarcinogenic, anti-inflammatory, and antioxidant activities [32].

Ballesteros et al. [30] demonstrated that SCG and CS have similar antioxidant potential (20.04 and 21.35 µmol TE/g dry material, respectively) when analyzed by the DPPH• scavenging assay, but SCG showed a higher antioxidant potential in the FRAP assay compared to CS. As for CS, most of SCG antioxidant potential is related to the presence of phenolic compounds, particularly CGA, such as 5-cafeolyquinic acid [5]. Maillard reaction products, such as melanoidins, are also present in considerable amounts [5,26]. Although the caffeine content in SCG is lower than that in coffee beans, various caffeine concentrations (0.007 to 0.5%) have been reported, depending on the extraction process and SCG source [31].

Most SCGs are currently being incinerated or discarded in landfills [26]. Alternative applications have been investigated, not only in skincare products, but also as food ingredients, biofuel, adsorbents, bioplastics or as materials for the construction industry [26].

Besides its richness in bioactive compounds and antioxidant activity, CS and SCG extracts have also been described as having interesting functional properties related to its fiber content, including emulsifying activity and emulsion stability, which can benefit cosmetic formulations [30].

It is worth noting that, due to their natural origin, by-products composition may vary, depending on the plant species *(Coffea arabica* or *Coffea canephora*, also known as arabica and robusta coffees, respectively), geographical origin, cultivation conditions, harvesting processing method, and type of roasting [6].

4.3. Bioactives Extraction

In order to incorporate bioactive plant metabolites into cosmetic formulations, they must be effectively extracted from dried or fresh material, preferably using green extraction techniques and solvents [34]. Some conventional extraction methods usually use large quantities of organic solvents, such as methanol, which are not appropriate for direct dermal use [34]. In that sense, several studies have proposed different methods for phenolic and caffeine extraction in coffee by-products including conventional (solid–liquid extraction) and non-conventional methods (ultrasound, microwave, supercritical fluid, subcritical water or pulsed electric field assisted extraction), using dermatologically safe solvents, such as water and ethanol, in different ratios [35].

The richness in bioactive compounds depends significantly on the extraction method [35]. Changes in extraction parameters, such as solvent type and ratio or temperature, gives rise to qualitative and quantitative differences in active substances [36]. Cost effectiveness and ecological impact should also be considered when choosing an extractive method [37].

Table 3 reviews the methods described in the literature for phenolic compounds and caffeine extraction of CS and SCG.

Table 3. Different extraction methods applied to coffee silverskin and spent coffee grounds.

By-Product	Method	Optimal Experimental Conditions	Reference
Coffee silverskin	Solid–liquid extraction	Ethanol:water (50:50) 40 °C for 60 min Constant stirring at 600 rpm	[36]
Coffee silverskin	Subcritical water extraction	1 g/50 mL water 1.0–5.3 Mpa 180–270 °C for 17–42 min	[38]
Coffee silverskin	Pulsed electric field extraction	12 kV and 100 A Ethanol:water (62.67:37.33) Number of pulses: 1000 PEF strength: 1.37 kV/cm 75 min	[39]

Table 3. *Cont.*

By-Product	Method	Optimal Experimental Conditions	Reference
Coffee silverskin	Ultrasound-assisted extraction	10 g/50 mL solvent Ethanol:water (70:30) 40 kHz for 120 min at 20 °C	[40]
Spent coffee grounds	Solid–liquid extraction	0.3 g/25 mL solvent Ethanol:water (25:75) Constant stirring for 15 min at 60 °C	[41]
Spent coffee grounds	Ultrasound-assisted extraction	7 g/210 mL ethanol 55 kHz for 2 h at room temperature	[42]
Spent coffee grounds	Ultrasound-assisted extraction	10 g/50 mL solvent Ethanol:water (70:30) 40 kHz for 120 min at 20 °C	[43]
Spent coffee grounds	Supercritical fluid extraction	CO_2 100 bar 323.15 K	[42]
Spent coffee grounds	Microwave-assisted extraction	Sample: solvent ratio of 1:6 Ethanol:water (20:80) 40 s at 240 W	[44]
Spent coffee grounds	Microwave-assisted extraction	2 g/20 mL Ethanol:water (54:46) 500 W 10 min at 423 K	[45]
Spent coffee grounds	Subcritical water extraction	6 g 240 °C 40 bar	[46]
Spent coffee grounds	Subcritical water extraction	14.1 g/L extract 5.0 MPa 37.9–55.0 min at 160–180 °C	[47]

4.4. Safety

Regarding coffee by-products safety, one concern can be the presence of mycotoxins, such as ochratoxin A (OTA), produced by *Aspergillus ochraceus* and *Penicillium verrucosum*, classified as a possible human carcinogen (group 2B) by the International Agency for Research on Cancer [13,26]. In fact, some studies described silverskin extracts safe in this context, but others, such as Toschi et al. [20] quantified OTA levels higher than those fixed by the European Commission for roasted and soluble coffee since there is no specific OTA regulation limit for CS [13,20]. To minimize the presence of this mycotoxin good practices of coffee harvesting, storage, and transport should be adopted [13].

Another compound that can be present in CS is 5-hydroxymethylfurfural (HMF) [48]. HMF is formed during coffee roasting, and is cytotoxic, irritating to the eyes, skin and mucous membranes at high concentrations, thus when using CS extracts, this component should be quantified in order to guarantee the safety of the cosmetic product [48].

When choosing new ingredients for cosmetic formulations, data on cyto- and genotoxicity, skin irritation, photosensitization, dermal absorption or allergenicity are extremely important [49]. Toxicity assays should be performed in order to avoid the presence of irritant constituents and cytotoxicity of these compounds can be evaluated using MTT and LDH assays as well as in vitro models to test skin or eye irritation [50]. In vivo assays, such as the occlusive patch test, should also be performed, to evaluate acute irritant reactions in human volunteers, offering a more reality adjusted safety profile [48].

Research shows CS and SGC are safe for topical use, with no evidence of cytotoxicity or skin irritation [33,48,51–53].

5. Coffee By-Products in Cosmetic Formulations

5.1. Vehicle and Emollient

Considering the high content of unsaturated fatty acids in SCGs, research has been carried out to evaluate this raw material as an alternative to vegetable oils used in cosmetic products. Deficiency of ceramides, cholesterol, essential fatty acids, and triglycerides can result in an increase in transepidermal water loss (TEWL) and skin dryness [29]. Substances with emollient action are often used to improve skin hydration and maintain skin barrier proprieties while providing softness to the skin [54].

Ribeiro et al. [29] applied the lipid fraction of SCG in the development of cosmetic formulations. Their physicochemical characterization, stability, biological effects, and sensory acceptability were evaluated and compared with formulations containing green coffee oil and without coffee oil. The epidermal capacitance, TEWL and skin surface lipids were evaluated with a Corneometer CM 820®, a Tewameter TM 210® and a Sebumeter SM 810® (Courage & Khazaka, Koln, Germany), respectively. The physical characterization of the spent coffee oil cream revealed lower particle size values when compared to the other formulations, suggesting a better stability. Spent coffee oil cream was non-irritating to the skin, lowered TEWL and increased sebum levels. However, odor was poorly evaluated by volunteers, meaning this aspect should be improved when using these raw materials.

Another study by Sousa et al. [33] compared different vegetable oils in cosmetic formulations including SCG oil. The effects of the formulations were assessed by volunteers by measuring the epidermis water content and the TEWL two hours after application, and 20 days after daily application using a Corneometer CM 825® and a Tewameter TM 300® (Courage & Khazaka, Koln, Germany) respectively. The irritation evaluation and sensory analysis were also effectuated. Physicochemical characterization of the creams—namely pH, droplet size and viscosity—revealed an acceptable pH and pseudoplastic behavior for cutaneous application, as well as well-formed droplets with small size variation, which predicts greater stability of the emulsified system. Results also demonstrated a non-irritant effect, significant hydration increase and TEWL reduction with no significant difference between the hydration profiles of the SCG cream when compared with the reference cream. In addition, the formulated creams' sensorial qualities were found acceptable by volunteers.

5.2. Antioxidant and Anti-Aging

Rodrigues et al. [55] evaluated the hyaluronidase inhibitory effect of CS in vivo. Previously, it was found by Furusawa et al. [56] that CS had a significant reducing effect against hyaluronidase, attributed, in this study, to the presence of acidic polysaccharides composed of uronic acid. The analysis by Rodrigues et al. [55] was performed on 20 volunteers incorporating a silverskin extract in a base cream. After a period of use, the skin hydration and firmness of volunteers were evaluated by comparing the cream containing silverskin with an equal base formulation with a supplementation of 1.5% hyaluronic acid (HyaCare® Filler CL, Evonik Industries AG, Essen, Germany) as a control. Methodology included visual evaluation, biometric analysis, and sensorial evaluation. Skin elasticity and firmness was compared for both creams using Cutometer®(Courage & Khazaka, Koln, Germany) and visual images from Visioface® (Courage & Khazaka, Koln, Germany) and PRIMOS® (Canfield, Fairfield, New Jersey, USA), allowing a more detailed skin surface evaluation, noticeably, wrinkle depth and roughness. The CS-based cream provided similar results to hyaluronic acid regarding skin hydration and firmness, as well as volunteer acceptance.

Rodrigues and colleagues [51] also studied a hand cream formulation containing 2.5% of CS extract that demonstrated to be safe for topical use by in vitro analysis using reconstituted human epidermis (RHE) models (EpiSkin™ and SkinEthic™, SkinEthics Laboratories, Lyon, France). In another study, a body formulation containing CS and another food by-product obtained from *Medicago sativa* (also containing a high percentage of antioxidants) was evaluated by both in vitro and in vivo safety tests as well as physical and chemical proprieties considering rheological behavior, color, antioxidant content and microbiological analysis, during 180 days at different temperatures [57]. The results showed

that the formulation retained antioxidant activity and stability during storage and provided evidence for in vitro and in vivo topical safety.

Ribeiro et al. [53] also combined SCG extracts in carboxymethylcellulose hydrogels for topical application. SCG extracts properties, such as the antioxidant capacity, as well as elastase and tyrosinase inhibitory activity were assessed, showing promising results for anti-aging and skin lightening formulations. In vitro cytotoxicity as well as release and permeation assays through synthetic membrane and human skin of bioactive substances from the hydrogels were performed. Results showed that extracts incorporation lowered apparent viscosity, when compared with a control gel without extracts addition, resulting in a less resistant structure to breakdown. Formulations allowed delivery and permeation of bioactive substances without toxicity.

Another research project aimed to develop an exfoliating body cream using SCG, with the purpose of obtaining a cosmetic product with both exfoliating and antioxidant properties [58]. Exfoliating products seek to mechanically remove dead cells and impurities present in the skin, through the solid abrasive particles that compose them, decreasing the thickness of the stratum corneum and enhancing the penetration of active compounds from later cosmetic application [58]. In this study 4, 6, and 8% of SCG formulations were developed and the exfoliating capacity was measured, using a Mexameter MX 16® (Courage & Khazaka, Koln, Germany) and skin pH [58]. Rheological profile, antioxidant capacity and sensory analysis were also explored. With respect to the analysis of the exfoliating capacity, the three formulations showed similar behavior. The 6% SCG cream showed a high content of antioxidants and polyphenols combined with good texture parameters, such as, adhesiveness and cohesiveness. After exposure to the exfoliating cream, the skin presented an increase in wettability and softness as expected with this form of skincare product.

5.3. Photoprotector

As mentioned before, the constituents of coffee's lipid fraction have valuable properties for formulating products with photoprotector ability, such as antioxidants and UVB protection.

Wagemaker et al. [59] characterized the lipid fraction and determined the SPF of 10 different species of coffee. All presented high content of oil and wax, a rich composition of unsaturated fatty acids and unsaponifiable matter. *Coffea arabica* exhibited the highest SPF when compared with the other species.

A synergistic effect in SPF value (up to 20% increase) when green coffee oil was associated with a chemical filter was observed by Chiari et al. [60]. Since many chemical sunscreen agents induce photoirritation and photosensitization, reducing their concentration by adding an SPF booster can be advantageous [60]. Another advantage in this study is the use of oil from green beans that are not used for coffee production because of lower quality, such as defective or immature beans, increasing product sustainability [60].

With that in mind, Marto et al. [52] studied SCG oil and green coffee oil (GCO) from defective coffee beans in sunscreen formulations. The GCO was extracted using mechanical pressing, whereas the lipid fraction of SCG was extracted with supercritical CO_2. As previously stated, polyphenols are excellent candidates in sunscreens considering their ability to defend against UV damage by their antioxidant, anti-inflammatory and radiation absorbing capacity. In this work, two water-in-oil emulsions (W/O) stabilized by physical sunscreens (titanium dioxide and zinc oxide), that differed on the oil phase composition, were developed: one containing 35% of the lipid fraction of SCG, and the other incorporating 35% GCO. The emulsion was a surfactant-free system, which can reduce the risk of skin irritability associated with these ingredients, being stabilized by the solid particles titanium dioxide and zinc oxide [52]. A Texture Analyzer was used to examine both formulations for hardness, elasticity, compressibility, adhesiveness, and cohesiveness of the emulsion, and rheology studies were performed. Mechanical proprieties in both formulations only differed in adhesiveness since the presence of SCG oil caused an increase in this parameter. Since this was a W/O emulsion it was able to promote moisture retention

and water resistance. In fact, the results showed in vitro and in vivo water resistance, with the SCG oil sunscreen being the most effective. Both emulsions showed high values of SPF with a suitable UVA/UVB ratio, but GCO formulation presented an SPF value of 82.3 ± 10.350 while SCG oil formulation presented 51.9 ± 5.550, which is possibly related to the fact that the coffee roasting process diminishes the content of polyphenolic compounds [52]. In conclusion, SCG oil was presented as an alternative in cosmetic use since no irritative or allergic reactions on the occlusive patch test occurred, and the formulation had broad SPF protection and good rheological and mechanical behavior [52].

5.4. Anti-Cellulite

Cellulite is a complex problem involving the microcirculatory and lymphatic system, the extracellular matrix, and the presence of excess subcutaneous fat in the adipose tissue [21]. Caffeine exert a lipolytic activity by inhibiting phosphodiesterase in adipocytes, an enzyme that is responsible for the degradation of cAMP [21]. The consequent increase in cAMP promotes lipase activity, which hydrolyses triglycerides [21]. Additionally, caffeine can improve the microcirculation of blood vessels, which can improve the appearance of cellulite [21].

A formulation was developed for cellulite treatment using caffeine extracted from CS and incorporated in nanostructured lipid carriers (NLCs) [61]. The incorporation of CS did not influence the nanoparticle size, and the formulation showed good chemical stability for up to 180 days at different temperatures and relative humidity [61]. In vivo permeation of caffeine in CS extracts evaluation, through pig ear skin, showed an improved penetration of nanoparticles [61]. It should be noted that due to caffeine's hydrophilic nature only about 30% of caffeine from the extracted CS was able to be incorporated in these lipid nanoparticles [61].

Table 4 reviews the applications of coffee by-products found in the literature.

Table 4. Cosmetic application of coffee by-products.

By-Product	Formulation	Accomplishments	Limitations	Reference
CS extract	Hand cream	No cytotoxicity No skin and ocular irritancy	NR	[51]
CS extract	Anti-aging cream	Improvement of skin hydration and firmness Similar results to control Organoleptic acceptance	NR	[55]
CS extract	Body cream containing two food by-products	Antioxidant and physical stability No toxicity Skin hydration improved Consumer acceptance	NR	[57]
CS extract	Anti-cellulite NLC formulation with caffeine	Good stability in 180 days Improved caffeine skin permeation vs. CS extract alone	Skin model limitations Only 30% of extracted caffeine could be incorporated	[61]
SCG oil	W/O creams with 10% SCG oil	Decrease in TWEL Increase in skin moisture Non-irritant Sensory acceptability, similar to control	NR	[33]
SCG oil	O/W cream	Cosmetic acceptance Decrease in TWEL Increase in hydration and sebum levels	Unpleasant odor	[29]

Table 4. *Cont.*

By-Product	Formulation	Accomplishments	Limitations	Reference
SCG oil	W/O sunscreens with physical filters	Skin compatibility Water resistance in vitro and in vivo Surfactant-free	NR	[52]
SCG extracts	Hydrogel	Elastase and tyrosinase inhibition No cytotoxicity Formulation allowed release and permeation of bioactive substances	Extracts addition altered rheological behavior	[53]
SGC (dried)	Exfoliating body cream with 4, 6 and 8% SCG	Good texture qualities Exfoliating capacity Emulsion stability 6% of SCG cream showed the best performance	NR	[58]

NR, None reported.

6. Further Applications

6.1. Acne

Four main factors are known to influence the development of acne, namely sebaceous gland hyperplasia with excess sebum production (seborrhea), follicular epidermal hyperproliferation, colonization by *Propionibacterium acnes* and subsequent inflammation with release of inflammatory mediators and immune response [54]. Since CGA has demonstrated anti-inflammatory and antimicrobial activities, a work by Luo et al. [62] tried to assess the effects of CGA on the underlying mechanisms of acne. Ears of ICR mice, induced by living *P. acnes*, were used as a model for skin inflammation. It was found that CGA treatment diminished the induced ear swelling, redness and erythema and significantly downregulated the expression of inflammatory cytokines. Further analysis also suggested that CGA significantly decreased lipogenesis since the contents of triglycerides, cholesterol and free fatty acids were significantly reduced after CGA treatment. Both findings can suggest that CGA could be a potential anti-acne agent by targeting sebum production and inflammation.

6.2. Wound Healing

Topical CGA beneficial effect in wound healing was evaluated in carbopol hydrogels with 10% extract from green and roasted press cake (a coffee residue after oil extraction) in mouse model [63]. Both significantly reduced the wound area size on the inflammatory phase, but green coffee showed the best result on the wound reduction, being similar to the positive control, corroborating the fact that this extract showed the highest concentration of phenolic compounds [63].

6.3. Nutraceuticals

Besides topical use, coffee by-products can use can also be explored in nutraceuticals. A study in human volunteers with xerotic skin, by Fukagwa et al. [64], provided results that the ingestion of coffee phenolic extracts improved skin barrier function as well as microcirculation and hydration. These results could be extrapolated to coffee by -products that contain similar phenolic compounds and endorse its study in nutraceuticals for dermatological conditions associated with dryness and epithelial disfunction.

7. Commercially Available Products

Some companies have already started to adopt the upcycling concept in the cosmetic sector by developing ingredients based in coffee by-products.

Kaffe Bueno, a Copenhagen-based company, recycles SCG by fractioning these residues into different compounds to be incorporated in skincare products, food or nutraceuticals [65].

Koffee' Up™ (Givaudan Active Beauty, Vernier, Switzerland) is a sustainable oil derived from upcycled *C. Arabica* SCG, with antioxidant and anti-aging claims [66].

SLVR' Coffee™ (Mibelle Biochemistry, Buchs, Switzerland) is the first upcycled ingredient that is based on coffee silverskin. Efficacy studies have shown that this ingredient improves skin resistance by increasing the functionality of the skin barrier, decrease the TWEL and increase skin hydration [67].

8. Conclusions

Numerous works demonstrate coffee by-products' rich composition, biological properties and toxicological safety. Dermacosmetic potential is mainly due to the phenolic compounds and caffeine present. Considering the anti-aging growing market and the cosmetic industry awareness in sustainability practices, there is an opportunity in reusing these by-products. Coffee silverskin and spent coffee grounds are distributed around the world and their ecotoxicological burden urges the need for valorization. Their incorporation in cosmetic formulations has been successful and recently, some companies have developed cosmetic ingredients based on these by-products with antioxidant and anti-aging claims, a step forward in coffee production sustainability.

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Abbreviations

CS	Coffee silverskin
SCG	Spent coffee grounds
UVROS	UltravioletReactive oxygen species
MMPs	Matrix metalloproteinases
CGA	Chlorogenic acids
CQA	Caffeoylquinic acids
FQA	Feruloylquinic acids
diCQA	Dicaffeoylquinic acids
$ABTS^{\bullet+}$	2,2′-azino-bis 3-ethylbenzothiazoline-6-sulfonic acid
$DPPH^{\bullet}$	2,2-diphenyl-1-picrylhydrazyl
HDFsUVBUVA	Human dermal fibroblastsUltraviolet B Ultraviolet A
COX-2	Cyclooxygenase-2
iNOS	Inducible nitric oxide synthase
LPS	Lipopolysaccharide
cAMP	Cyclic adenosine monophosphate

DHT	Dihydrotestosterone
FRAP	Ferric reducing antioxidant power
SPF	Sun protection factor
OTA	Ochratoxin A
HMF	5-hydroxymethyl furfural
MTT	3-4,5-dimethylthiazol-2,5-diphenyltetrazolium bromide
LDH	Lactacte dehydrogenase
TEWL	Transepidermal water loss
RHE	Reconstituted human epidermis
GCO	Green coffee oil
W/O	Water-in-oil
NLC	Nanostructured lipid carriers
O/W	Oil-in-water

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