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Review

Green Extraction of Phytochemicals from Fresh Vegetable Waste and Their Potential Application as Cosmeceuticals for Skin Health

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Abstract: The utilization of bioactive compounds from fresh produce waste, which is gaining attention in the agri-food and cosmetics industries, focuses on employing green extraction over conventional extraction methods. This emerging field addresses environmental concerns about food waste and the uses of bioactive phytochemicals for skin health. Modern green extraction methods aim to minimize the energy-intensive process and the use of harmful solvents. These techniques include ultrasound, microwave, and supercritical fluid extraction, pulsed electric field extraction, pressurized liquid extraction, and subcritical water extraction methods, which provide high efficacy in recovering bioactive phytochemicals from vegetable and root crops. The phytochemicals, such as carotenoids, polyphenols, glucosinolates, and betalains of fresh produce waste, exhibit various therapeutic properties for applications in skin health. These dietary antioxidants help to neutralize free radicals generated by UV radiation, thus preventing oxidative stress, DNA damage, and inflammation. The skin care formulations with these phytochemicals can serve as natural alternatives to synthetic antioxidants that may have toxic and carcinogenic effects. Therefore, this review aims to discuss different green extraction technologies, consumer-friendly solvents, and the beneficial skin health properties of selected phytochemicals. The review highlights recent research on major phytochemicals extracted from vegetables and root crops in relation to skin health.

Keywords: green processes; extraction techniques; bioactives; food waste; vegetables; phytochemicals; skin health

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1. Introduction

Skin is the largest organ in the human body and acts as an external defense system against environmental factors. The skin is the most susceptible organ to environmental carcinogenic factors such as pollutants, toxic compounds, and ultraviolet (UV) radiation, which can result in sunburn, DNA damage, and inflammation, leading to cancer [1]. Skin damage is mainly due to prolonged exposure to the sun, particularly UV radiation [2]. UV radiation is categorized into three different types, namely UVA (320–400 nm), UVB (280–320 nm), and UVC (200–280 nm) [3]. Among the types of UV radiation, the combination of UVA and UVB reaches the earth's surface, constituting 95% of UVA and 5% of UVB, which impacts skin health [3]. The intense effect of UV radiation is responsible for damaged skin due to the excessive generation of reactive oxygen species (ROS), which triggers oxidative damage [4,5]. This oxidative stress results in modifications in proteins and lipids, inflammatory responses, DNA damage, and the activation of signaling cascades impacting gene regulation, cell division, and apoptosis [5]. Antioxidants derived from plants can protect the skin against UV-induced oxidative stress and exert anti-inflammatory, anti-cancer, and anti-aging properties in the skin [1].

Secondary plant metabolites that are abundant in fruits and vegetables are known for their ability to promote skin health [6]. Generally, plant-based biologically active compounds (bioactive) isolated from food crops exert low toxicity and are cost-effective for developing cosmeceutical ingredients [7]. The demand for food is continuously growing due to the growing global population; conversely, significant amounts of food waste are being produced [8]. Fresh produce waste contains bioactives such as phenolic acids, carotenoids, glucosinolates, betalains, and flavonoids [9]. Food waste generated across the globe is about 40% of the whole food supply chain in the United States, followed by Central and East Asia and North Africa (32%), European countries (20%), and Latin America (6%), creating a significant impact on sustainability and climate change [10]. However, generating high-value products using innovative upcycling technologies not only reduces the impact of food waste on the environment but also contributes to the efficiencies in the agri-food industry through zero waste management [11].

Since fresh vegetable waste is highly perishable, a waste management strategy is required. This could include transportation, temporary low-temperature storage, removal of packaging and labels, sorting and cleaning, size reduction, dehydration, grinding, packaging, and long-term storage, among many other components that depend on the commodity. Once the fresh vegetable waste is upcycled and stabilized as above, extraction is the next step for the isolation and purification of bioactive phytochemicals from fresh vegetable waste [12] (Figure 1). In general, due to the high moisture content of fresh vegetables, the direct extraction of phytochemicals without dehydration is not practical. The recovery of phytochemicals is also influenced by the sample itself in terms of variety, geographical region, climate, stress, extraction parameters, etc. Therefore, standardization and quality control of the extracts to contain a consistent amount of targeted bioactive phytochemicals is required.

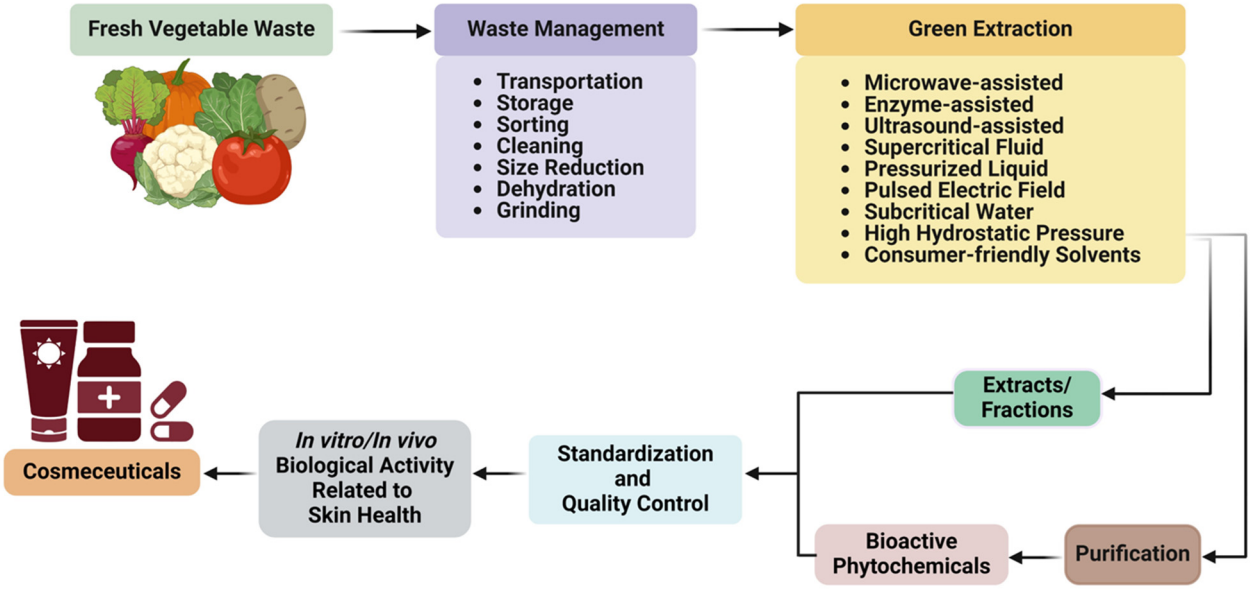

Figure 1. A schematic outline of the major processes involved in green extraction of phytochemicals from fresh vegetable waste.

In general, the phytochemical extraction methods are classified into conventional, such as Soxhlet extraction and maceration, and non-conventional advanced green extraction methods that can extract phytochemicals in a sustainable and consumer-friendly manner [13]. Conventionally used toxic solvents, such as methanol, cannot be used in extracting and isolating phytochemicals for cosmeceutical applications. Therefore, this review highlights consumer-friendly solvents and green extraction methods that have the potential to be used in cosmeceutical preparations. Extracted phytochemicals from fresh vegetable waste have been assessed for applications in skin health using in vivo and in vitro

experiments [8]. Bioactive phytochemicals obtained from vegetable and root crops, namely tomato, beetroot, kale, sweet potato, cauliflower, cucumber, and pumpkin, are reported to be effective in preventing several skin-related degenerative diseases. This review describes phytochemicals and green extraction methods, emphasizing the biological activity related to skin health and the applications to cosmeceutical development. The primary goal is to demonstrate how bioactive phytochemicals present in the mentioned vegetables and root crops have influenced skin health in relation to inflammation, skin aging, and cancer.

2. Methodology

The academic literature related to different green extraction methods for obtaining bioactive phytochemicals and their potential biological properties from vegetables and root crop waste, namely tomato, beetroot, kale, sweet potato, cauliflower, and pumpkin, for skin health applications, were reviewed. The literature search was conducted using scientific databases, including Scopus, NovaNet, ProQuest, PubMed, Springer Link, Science Direct, Web of Science, and Google Scholar from 2018 to 2024. Two hundred and five articles, including research papers and book chapters, were downloaded, of which 156 articles most relevant to the topic were selected for writing the review. The keywords used for the search are green extraction, consumer-friendly solvents, food waste, bioactive compounds, phytochemicals, carotenoids, vegetables, root crops, UV radiation, DNA damage, ROS, skin cancer, inflammation, oxidative stress, apoptosis, photoaging, and antioxidant properties.

3. Bioactive Compounds Abundant in Vegetables and Root Crops

Vegetables and root crops are significant parts of the human diet, containing rich sources of phytochemicals that play a crucial role in human health and well-being [14]. Major by-products from food processing, including peels, leaves, roots, bark, and midribs, are regarded as waste; however, they contain nutritional and functional values. Efforts are also being made to recover bioactive compounds present in the food wastes of vegetable and root crops. Extracted bioactive compounds can be used for supplemented foods, nutraceuticals, cosmetics, and pharmaceuticals. Vegetables, root, and tubers groups have a wide range of crops. However, only kale (*Brassica oleracea* var. *acephala*), cauliflower (*Brassica oleracea* var. *botrytis*), beetroot (*Beta vulgaris* subsp. *vulgaris*), sweet potato (*Ipomoea batatas*), tomato (*Lycopersicon esculentum*), and pumpkin (*Cucurbita* sp.) were selected in this review since they were identified as the top-most contributors to fresh produce waste in Canada. Also, these vegetables are abundant in known health-promoting bioactive compounds.

The abundant bioactive phytochemicals present in tomatoes are carotenoids, polyphenols, terpenes, and tocopherols. Major carotenoids such as lycopene, β-carotene, and lutein from tomato waste are used in the application of the cosmetic industry for preventing skin diseases [15]. The concentration of carotenoids in tomato skin was lycopene up to 4.9 μg/g of fresh weight (FW), and total phenolic content was around 2.8 mg gallic acid equivalence (GAE)/g FW [16]. Kale contains lutein, quercetin, sulforaphane, kaempferol, hydroxycinnamic acids, and other flavonoids [17,18]. In kale, lutein, violaxanthin, and neoxanthin are the most abundant carotenoids, and lutein content ranges from 5.1 to 38.2 mg/100 g FW [18]. Phytochemicals such as glucobrassicin, glucoibern, sinigrin, and gluconapin, along with kaempferol, ferulic acid, quercetin, and gallic acid are mostly present in cauliflower [19,20]. Beetroot contains bioactive phytochemicals, including carotenoids, gallic acid, betacyanin, betaxanthin, and betalains that are used for promoting health benefits like anti-carcinogenic and hepato-protective activities [21,22]. In beetroot, the leaves are discarded as waste and contain a significant amount of total phenolic content, betacyanins, and betaxanthins [23]. The bioactive compounds identified in sweet potatoes are β-carotene, phenolic acids (caffeic acid and chlorogenic acid), and flavonoids (quercetin, kaempferol, and apigenin) [24]. Pumpkins are grown commercially worldwide, and there are various species, such as *Cucurbita pepo*, *C. maxima*, *C. moschata*, *C. stilbo*, and *C. mixta*. Pumpkin is considered beneficial to human health because it contains carotenoids, phenolic compounds, provitamins, saponins, flavonoids, and phytosterols [25]. Bioactive compounds often exist in low concentrations

within plant tissues and are embedded in complex mixtures. Extraction is essential to separate these compounds to improve their bioavailability and to use them in food industry applications [26]. The recovery of the bioactive compounds of interest from vegetables and root crops involves conventional and green extraction methods.

4. Extraction Methods

4.1. Conventional Extraction Methods

Conventional method refers to the extraction of natural bioactive compounds using traditional techniques. These techniques involve using solvents such as methanol, ethanol, and water to extract bioactive compounds from the plant material. The material and solvents will be subjected to different treatments, such as distillation, filtration, and precipitation, to separate the phytochemicals or unwanted material from the solvents [27]. The most often used conventional extraction methods for extracting phytochemicals are Soxhlet extraction, maceration, and steam distillation. Most of these traditional methods require hazardous solvents that are harmful to the environment, have high energy consumption, involve the occurrence of thermal degradation, and are time-consuming and expensive [28]. To overcome these limitations, green extraction or non-conventional methods have been introduced, and they have been gaining attention due to their sustainable applications.

4.2. Advanced Green Extraction Methods

Green extraction technology, often known as non-conventional technology, has gained importance in recent years because of less time, solvent, and energy requirements and greater recovery of phytochemicals [29]. Non-conventional extraction techniques are guided by a set of principles, including innovation in the selection of renewable plant resources such as fruit and vegetable wastes, the use of alternative solvents, energy savings, coproduct use, obtaining a biodegradable and natural extract, and a reduction in the number of unit operations [30]. Petrochemical-based organic solvents are mostly volatile, flammable, and even toxic; therefore, alternative solvents are required to replace these solvents [31]. Microwave-assisted extraction (MAE), enzyme-assisted extraction (EAE), ultrasound-assisted extraction (UAE), supercritical fluid extraction (SFE), pressurized liquid extraction (PLE), pulsed electric field extraction (PEFE), subcritical water extraction (SWE), and high hydrostatic pressure extraction (HHPE) are some of the examples of emerging green extraction techniques.

4.2.1. Types of Green Extraction Methods

Microwave-Assisted Extraction (MAE)

The microwave-assisted extraction approach relies on the effect of oscillating non-ionizing electromagnetic field radiation with a frequency range of 300 MHz to 300 GHz [32]. Microwave heating has a direct impact on polar solvents, and it is based on two principles: ionic conduction and dipole rotation. An ionic conduction occurs when the electrophoretic transfer of ions generates an electrical field, and the displacement of polar molecules creates dipole rotation [33]. During the heating of the plant matrix, moisture present in the cell evaporates and generates pressure on the cell wall due to swelling. The pressure that builds up on the cell will rupture the cell and allow for easy penetration of the solvent to improve yield for extraction [34]. MAE is classified into two systems: open and closed systems. An open system consists of atmospheric conditions, the addition of solvent, and a higher sample throughout, whereas the closed system runs under high pressure, temperature, and faster extraction time [35]. The open system is commonly used to extract bioactive compounds, and closed systems are used to prevent the loss of volatile compounds. The factors influencing MAE are microwave power, extraction temperature, duration, and solvent amount [36]. Some of the advantages are cost-effective, less solvent usage, short extraction time, and less power. The major drawback is if solvents are non-polar, extraction efficiency might be poor (Table 1) [31,36,37].

Table 1. Summary of advantages and disadvantages of phytochemicals extraction methods.

Extraction Method	Advantages	Disadvantages
MAE	Quick, efficient, low-cost, room-temperature operation	Poor non-polar solvents, not for thermally labile compounds
EAE	High efficiency and selectivity, eco-friendly, low temperature	Expensive enzymes, time-consuming, pH and temperature sensitive
UAE	Easy to use, efficient, eco-friendly, versatile solvent selection	Multiple extractions needed, generate radicals, difficult to scale up
SFE	Non-toxic, cost-effective, rapid, recyclable supercritical fluid	High initial cost, limited for non-polar phytochemicals, parameter optimization needed
PEF	Shorter extraction time, high quality, non-thermal, increases cell permeability	High equipment maintenance cost, parameters are dependent on the texture and electric conductivity of raw material
PLE	Energy efficient, non-toxic solvents, simple equipment	High equipment cost, potential compound inactivation
SWE	Cost-effective, efficient, water as solvent	Higher temperatures may degrade sensitive compounds
HHP	Low time, high solubility, high yield	Possible structural changes in fragile materials

MAE, Microwave-assisted extraction; EAE, enzyme-assisted extraction; UAE, ultrasound-assisted extraction; SFE, supercritical fluid extraction; PEF, pulsed electric field extraction; PLE, Pressurized liquid extraction; SWE, subcritical water extraction; HHP, high hydrostatic pressure extraction.

Enzyme-Assisted Extraction (EAE)

Enzyme-assisted technology has been gaining attention during the last decade and is used to extract bioactive compounds such as polyphenols. The plant cell wall is composed of proteins and polysaccharides that act as a barrier during the extraction process. In EAE, protein coagulation and denaturation at high temperatures occur [38]. The principle is to disrupt the plant cell wall by the hydrolytic action of enzymes to release intracellular components under optimum conditions [39]. Enzymes such as pectinases, cellulases, and proteases are frequently used to disrupt the cell wall and membrane by enhancing the availability of polyphenols [36]. EAE helps to eliminate superfluous cellular wall components for improving system transparency and increases catalytic competence while preserving samples such as fruit peels with distinctive value to a larger extent [40]. The important parameters to consider for the EAE process are enzyme composition, concentration, particle size, hydrolysis duration, and enzyme-to-sample ratio. This technology has gained attention due to its long-term sustainability, environmentally friendly, and enhanced bioactive recovery [29]. The main drawbacks are time consumption, enzyme cost, and the great sensitivity of enzymes to pH and temperature (Table 1) [31,36]. Nevertheless, the cost can be decreased by incorporating an immobilization technique that reuses enzymes while maintaining their activity and specificity [29].

Ultrasound-Assisted Extraction (UAE)

Ultrasound-assisted extraction is one of the green extraction methods that can reduce extraction time, is easy to use, can be performed at room temperature, is economical, and has less thermal degradation of bioactive compounds [41]. The process encompasses a frequency of >20 kHz and has an energy intensity ranging from 10 to 1000 W/cm^2. The waves create alternative compression and rarefaction cycles in a liquid medium by exerting negative pressure in the medium to form cavities [42]. In UAE, cavitation bubbles are created in the liquid medium; energy is released, generating high pressure and temperature, enabling the process for extraction within a short period. Extraction using ultrasound involves diffusion, cell wall rupture, enhanced solvent penetration into the cell, and amplification of target compounds into the solvent (sponging effect) for better yield [43]. For effective extraction, particle size, frequency, temperature, pressure, time, solvent, and moisture are the major elements to be considered [30]. This method is mostly used for liquid–solid, liquid–liquid samples for processing. One of the major limitations is that at high temperatures and pressure, the probability of developing H and OH radicals

on the matrix from the decomposition of water vapor present in the bubbles is because of ultrasound (Table 1) [40]. The literature reported that low frequencies (20 to 40 kHz) extract higher yield, and lower temperature induces cavitation and minimizes viscous solvent [44].

Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction is a green technology that uses critical point temperature, pressure, and boiling point where solvents transform into supercritical state [45]. Supercritical fluid has pressure-dependent solvating power, and one such example is CO_2, which is regarded as safe (GRAS) because of its chemically inert, readily available, cheap, and non-flammable nature [46]. The properties of supercritical CO_2 exhibit liquid-like gas mass transfer, surface tension, solvent power, and gas-like low viscosity, which are considered for better extraction rates in a shorter time [47]. For the extraction of polar compounds, co-solvents such as ethanol can be used as supercritical CO_2, which has a low polarity index [48]. The essential idea of SFE is that it behaves as a single phase, preserving both gas and liquid properties at the same time with moderate pressure and temperature. For extraction of phytochemicals, CO_2 reaches a critical point at 31.1 °C and 7.38 MPa and returns to a gas state at room or mild temperatures to provide solvent-free at the end of the extraction step [49]. The added benefits of this technique are efficient, easy recovery for the solvent used and solvent consumption. However, SFE extraction is limited to non-polar compounds, and high pressure is required for processing (Table 1) [50].

Pulsed Electric Field Extraction (PEFE)

The pulse electric field technique is a non-thermal extraction method used to enhance the extraction by the disintegration of the cell membrane. In the PEFE process, short-duration pulses (microseconds to milliseconds) with high-voltage intensity can pass through the phytochemical samples within the two electrodes [51]. The principle is based on the external electrical force, applied to the pores inside the membrane, which increases the cell permeability; this is referred to as electroporation or electro-permeabilization [52]. Electroporation is influenced by field strength, energy, pulse shapes, and the number of pulses applied. It also depends on reversible and irreversible membrane permeabilization out of its irreversible process, which is effective for extraction [53]. In general, the low time (milliseconds) and the specific energy of 1–10 kJ/kg enhance the recovery of bioactive compounds without raising the temperature or damaging the structure of the plant matrix [54]. The advantages include low energy, low processing cost, higher yield efficiency, environmentally friendly (no petrochemical solvents), and quick process (Table 1). Despite having many benefits, sample dependence on electrical conductivity and texture, supply of high-power equipment, and especially safety for workers [54].

Pressurized Liquid Extraction (PLE)

Pressurized liquid extraction, also known as accelerated solvent extraction (ASE), is another innovative technology that uses less solvent and has fast extraction of compounds. In this method, high pressure is used to maintain solvents in a liquid state at high temperatures above the solvent boiling point. The process enhances the mass transfer and solubility, thus allowing the cells to permeabilize by speeding up the extraction [52]. This method avoids the use of organic solvent, which is similar to Soxhlet extraction, except that the pressure should be below the boiling point, preventing thermolabile compounds [44]. The factors essential for the functioning of PLE are solvent polarity and toxicity, number of extraction cycles, temperature, pressure, time, and particle size [55]. For the extraction, the temperature ranges from room temperature to 200 °C and pressure between 35 and 200 bar [52]. PLE is particularly effective for selective extraction since the polarity of the solvent changes with temperature. The rule of thumb for selecting solvents ('like dissolves like') was followed, indicating the use of polar solvents and non-polar solvents [30,36]. The benefits of PLE are the recovery of polyphenols at various temperatures, energy-

saving, non-toxic, and protection of sensitive compounds. The disadvantage of PLE is the destruction of extracted bioactive compounds (Table 1) [44].

Subcritical Water Extraction (SWE)

Subcritical water is a process in which water is heated to a temperature below its boiling point of 100 °C and its critical temperature of 374 °C with sufficient pressure to maintain the liquid state [56]. Water is used as a solvent in extraction due to its properties. The hydrogen bond in the water breaks down at higher pressure and temperature, decreasing surface tension, dielectric constant, and viscosity, thereby increasing the diffusivity to penetrate the plant matrix [57]. This process is known as subcritical water extraction or pressurized hot water extraction, which can be used to extract essential oils, bioactive compounds, and other valuable materials from plant materials. Water is a polar solvent that has a dielectric constant of approximately 80 at room temperature, and the value decreases when there is a temperature rise, which is similar to ethanol by showing a less polar solvent nature [58]. The major advantages of this extraction are the low cost and non-toxic nature of the solvent. The system operates at low temperatures so that there is less energy consumption. The main disadvantage is that temperature and pressure need to be controlled based on the compounds to be extracted, and the initial cost of the system is high (Table 1) [59].

High Hydrostatic Pressure Extraction (HHPE)

High hydrostatic pressure (HHP) is a non-thermal extraction method that uses pressure ranging from 200 to 600 MPa based on mass transport phenomena [60]. According to mass transfer theory, pressure is increased in a short period, disrupting plant tissue and cell walls and enhancing the mass transfer of solvents into the extracted material [61]. Based on phase behavior theory, applied pressure increases the permeability of the cell, leading to cell component diffusivity and greater solubility of the compound [62]. Under this pressure, the rate of dissolution is large, and penetration of the solvent is faster in a short period [61]. In comparison to conventional extraction, HHP has several advantages, namely uniform pressure distribution, low temperature (room temperature), less solvent consumption, high diffusion rate, higher purity, and yield of extracts [63]. The extraction can be performed at room temperature, which prevents thermal degradation of thermosensitive components. Nonetheless, the major obstacle faced by HHP applications is the cost of the equipment (Table 1) [60].

4.3. Types of Consumer-Friendly Solvents

Bioactive phytochemicals are extracted traditionally using aqueous-organic solvents such as acetone, hexane, methanol, petroleum ether, and chloroform, which are harmful to the environment and particularly in topical applications [64]. Green or consumer-friendly solvents are the substitution for petroleum-based solvents used in conventional extraction methods to minimize the environmental impact and address the use of less polluting alternative solvents [65]. The green alternative solvents should be easily available and have low toxicity, the ability to recycle, and high efficiency for the extraction used [66]. The most well-known green solvents are supercritical fluids, bio-based solvents, ionic liquids, oil-based, and deep eutectic solvents.

4.3.1. Food-Grade Ethanol

In most cases, food-grade ethanol is produced through wet milling, a process that separates starches and sugars from corn components. The impurities result in significantly lower concentrations than those found in dry-milled corn fermentation, which produces cyclic and heterocyclic compounds [67]. Unlike most other solvents, food-grade ethanol is 100% pure and free from additives, making it a safe and non-hazardous solvent. Ethanol is used for the extraction of bioactive compounds since it is a grade, low-cost, and environmentally friendly solvent. Food-grade ethanol was used to extract bioactive phytochemicals

using the shaking method in tomatoes. The tomato peel extract was recovered for the production of low-cost biosorbent, and the results showed high polyphenols and flavonoid content compared to lycopene [68].

4.3.2. Ionic Liquids

Ionic liquids are a type of liquid salt composed of inorganic anions and unsymmetrical organic cations below their low melting point. The nitrogen-based cations such as imidazolium, pyridinium, phosphonium, pyrrolidinium, and cholinium combined with halide anions (Cl^-, Br^-, F^-), acetate, nitrate (NO^{3-}), and hydrogen sulfate ($HSO_4{}^-$) [69]. The use of ionic liquids as a solvent for extracting phytochemicals is that they can effectively dissolve lipophilic (fat-soluble) and hydrophilic (water-soluble) compounds [70]. Ionic liquids are more effective compared to traditional solvents as they are used at low temperatures and preserve the stability of heat-sensitive compounds. Ionic liquid properties consist of high ionic conductivity, non-flammability, and high thermal and chemical stability [71]. Among the ionic liquids available, the most studied is 1-alkyl-3-methylimidazolium combined with Cl^-, Br^- counterions [72]. Ionic compounds facilitate the release of bioactive compounds by modifying cell walls and tissues. Ionic liquids are limited due to their high costs and potential toxicity [69].

4.3.3. Deep Eutectic Solvents

Deep eutectic solvents (DES) are eutectic mixtures, which are mixtures of two or more substances that are liquid at room temperature and have a lower melting point than any of the individual components [73]. In the mixture, the melting point is lower for the individual component due to the formation of new hydrogen bonds between the molecules [74]. The hydrogen bonds acceptor and donor lower the energy required to separate the molecules, leading to a low melting point [73]. DES are the new generation of ionic liquids and used as solvents for the extraction of bioactive compounds [75]. The mixtures used are often inexpensive, readily available, and cost-effective compared to organic solvents. DES were developed to overcome the limitation of ionic liquids [76]. The common DES are choline chloride mixed with amine, alcohol, sugar, and acid, which serve as hydrogen bond donors. The two influential factors are polarity and viscosity when optimizing the extraction of phytochemicals with DES [74]. Recent research has shown that effective extraction of tomato by-product is performed by DL-menthol as a hydrogen-bond acceptor (HBA) and lactic acid as a hydrogen-bond donor (HBD), using DES as extraction solvents. UAE was performed at a temperature of 70 °C, 8:1 mol HBA/mol HBD, for 10 min. The optimal yield indicated for the extraction of lycopene is 1447 mg/g FW from tomato by-products [77].

4.3.4. Natural Deep Eutectic Solvents

The replacement of synthetic compounds in DES led to a new class, namely natural deep eutectic solvents (NaDES), consisting of a eutectic mixture of at least two components, an HBA and an HBD, that have a significantly lower melting point when combined than each component at a proper molar ratio [78]. They are typically composed of natural organic compounds such as amino acids, sugar, chloride, and hydroxide. The NaDES are non-toxic, biodegradable, environmentally friendly, and have lower costs compared to synthetic solvents [79]. The properties of NaDES are low volatility, low cost, non-flammability, and biocompatibility, and they can be directly applicable to food, pharmaceuticals, and cosmeceuticals [80]. A common example of NaDES is a mixture of choline chloride and glycerol, which is less expensive and non-toxic compared to traditional solvents used in the extraction of bioactive compounds from plants [81]. The extraction of β-carotene from pumpkin using natural deep eutectic solvents was studied [82]. An improvement in the final yield of β-carotene and recovered 90% of carotenoids was observed due to the high stability of NaDES. The different types of NaDES were compared in the study, and NaDES caprylic acid and capric acid composed of C8:C10 (3:1) fatty acids were selected. The UAE

was performed using C8:C10 (3:1) NaDES solvent at 50 °C in 10 min with a fixed frequency at 57 kHz.

4.3.5. Edible Oil-Based Extractions

Edible oils are used as alternative solvents for extraction and purification of bioactive phytochemicals and are compatible with cosmeceuticals. Different types of edible oils are produced from fruits or seeds by cold-press extraction and other methods, namely olive, canola, sunflower, flaxseed, rapeseed, and avocado. Vegetable oils are non-volatile, safe, cheaper, and easy to regenerate for the extraction of bioactive compounds. Most vegetable oils are used as solvents or co-solvents that are enriched phytochemicals to combine with innovative green extraction methods for better-quality extracts [83]. The recovery of carotenoids uses oil as a solvent to enhance the stability, and there is no degradation of the compound. Flaxseed oil contains omega-3 fatty acids, and it is used in the extraction of carotenoids from carrots with microwave-assisted extraction. The recovery of carotenoids was observed at 78% and it increased the phenolic content due to the properties of flaxseed oil [84]. A similar extraction solvent (flaxseed oil) is used for the recovery of β-carotene, that is, 78 mg/g of dry weight (DW) using a high shear disperser technique with 750 W power, 45% duty cycle, and 12 min [85]. Apart from the above mentioned, canola oil is used as the solvent by maceration extraction method using 1 g of pumpkin pulp waste in 10 mL of oil at 60 °C for 22 min in dark conditions, resulting in 62% DW of total carotenoid content [86].

5. Recovery of Phytochemicals from Vegetables and Root Crops Using Green Extraction Methods and Its Role in Skin Photoprotection

The skin of the human body serves as a crucial protective barrier and interfaces with the environment, playing a significant role in maintaining homeostasis. However, skin is susceptible to various physical and chemical agents that can disrupt its structure and function. Many of these environmental toxins and their metabolites have oxidizing capabilities, which either directly or indirectly cause the production of ROS. ROS are short-lived molecules generated during normal aerobic metabolism and are implicated in the activation of proliferative and cell survival signaling pathways, as well as the alteration of apoptotic pathways involved in skin disorders. To counteract the deleterious effects of toxicants, the skin possesses a range of antioxidant defense mechanisms.

Kale, cauliflower, beetroot, tomato, sweet potato, and pumpkin are abundant in carotenoids, betalains, polyphenols, and glucosinolates, which have antioxidant protection against oxidative damage caused by ROS and toxic agents. These protective compounds also serve as cell protectors within the human body. Globally, fresh produce waste is a significant underutilized biomass, which contains bioactive phytochemicals. Bioactive-rich waste is utilized by extracting the components using green extraction techniques to provide high-quality value-added ingredients, which have increasing demand. The selection of appropriate extraction technologies is necessary to effectively recover bioactive phytochemicals. The extraction of bioactive phytochemicals is accomplished by various green extraction techniques to reduce the environmental impact due to toxic solvents, enhance yield, and reduce the extraction time. The main objective of this review is to address the concerns related to health with an emphasis on skin health, environment, and economy for the United Nation's sustainable development goals. This paper also provides an overview of the role of oxidative stress in skin toxicity, the skin's antioxidant defense mechanisms, and the challenges associated with translating antioxidant research into cosmeceutical product development.

5.1. Kale (Brassica oleracea L. var. acephala)

Among the Brassicaceae family, kale is one of the well-known and traditionally used vegetables in Mediterranean countries [87]. Kale contains a high concentration of carotenoids, glucosinolates, and phenolic acids. Additionally, it also has a greater an-

tioxidant capacity than many other vegetables [88]. Kale is known as a superfood for its remarkable risk-reduction functions against type 2 diabetes, bacterial infections, certain cancers, rheumatic disorders, anemia, obesity, and bone weakness [89,90].

5.1.1. Green Extraction Methods Are Reviewed for the Identification of Phytochemicals in Kale

The most used green extraction method reported in the literature for kale is UAE. In kale, phenolic acids and flavonoids were extracted using the UAE method. The prominent results were shown with 80% aqueous ethanol compared to other solvents such as methanol [91]. The optimum conditions are 60 °C and 1 h of extraction time. In addition, the UAE method was used with 80% methanol for 15 min at 10 °C to extract phenolic compounds [92]. On the other hand, supercritical fluid extraction is used to extract carotenoids, such as lutein, with extraction conditions including CO_2 with 5% methanol as an organic modifier at 39 °C for 30 min (Table 2) [93]. These techniques are advantageous for reduced time and lower temperatures for extracting heat-sensitive phenolics. The reported extractions showed that UAE is an environmentally friendly, green, and cost-effective method for the extraction of phytochemicals from kale (Table 2). However, methanol should not be used as a cosolvent when the products are targeted for cosmeceuticals.

Table 2. Green phytochemical extraction methods reported for vegetables and root crops.

Extraction Method	Optimized Extraction Conditions	Recovered Phytochemicals	Yield	References
Kale (*Brassica oleracea* L. var. *acephala*)				
UAE	80% aqueous Ethanol, 60 °C, 20 kHz, 1 h	Benzoic acid (0.49 µg/g DW), Vanillic acid (1.46 µg/g DW), Trans-ferulic acid (3.38 µg/g DW), Trans coumaric acid (2.49 µg/g DW)		[91]
UAE	15 mL methanol, 10 °C, 15 min	Kaempferol (58 ± 4 mg/100 g FW), Quercetin (44 ± 4 mg/100 g FW), Total Flavonoids (646 ± 12 mg/100 g FW)		[92]
SFE	CO_2 with 5% methanol, 35 °C, 30 min	Lutein (0.69 ± 0.03 mg/g DW)		[93]
Cauliflower (*Brassica oleracea* var. *botrytis*)				
EAE	Pre-treatment: 85% phosphoric acid, 50 °C, pre-treatment: 16 h, extraction: 5 h	Isothiocyanates (0.49 mg/g FW)		[94]
UAE	2 M NaOH, 60 °C, 30 min	Non-extractable phenolics (Blade: 6109 µg GAE/g DW; Petiole: 940 µg GAE/g DW)		[95]
UAE	70% aqueous ethanol, 70 °C, 30 min	Glucosinolates (3.22 µmol/g FW)		[19]
Beets (*Beta vulgaris* subsp. *vulgaris*)				
MAE	Sample/solvent (1:20), 50 °C, 5 min	Betacyanins (3.08 mg/g) DW, Betaxanthins (1.74 mg/g DW)		[96]
UAE	Sample/solvent (1:20), 80 °C, 30 min	Betacyanins (3.87 mg betanin/g DW) DW, Betaxanthins (8.61 mg betaxanthin/g DW)		
SWE	Sample/solvent (1:20), 150 °C, 5 min	Betacyanins (0.03 mg/g DW, Betaxanthins (0.19 mg/g DW)		
UAE	30% ethanol, 30 °C, 30 min, 44 kHz	Betalains (6.86 mg/g DW)		[97]
UAE	1:20 solid–liquid ratio, 30 °C, 16 min	Betaxanthin, Betacyanin (949 µg/g DW, 562 µg/g DW)		[98]
SFE	20 mL ethanol as co-solvent, 35 °C, 400 bars	Phenolic content (2.80 mg/g DW)		[99]
PLE	Ethanol, 40 °C, pressure—10 MPa, flowrate—3 mL/min	Phenolic content (252 mg GAE/g DW)		[100]

Table 2. *Cont.*

Extraction Method	Optimized Extraction Conditions	Recovered Phytochemicals	Yield	References
Sweet potato (*Ipomoea batatas*)				
UAE	58% ethanol, 80 °C, 40 min, 178 W	Polyphenols (3.87 mg/g FW)		[101]
UME	72% ethanol, 57 °C, 76 s	Flavonoids (91.6 ± 3.37% *w*/*w* DW)		[24]
UAE	83% polyethylene glycol, 64 °C, 80 min	Phenolic compounds (83.7 CE/100 g DW)		[102]
Tomato (*Lycopersicon esculentum*)				
SFE	5% ethanol, 55 °C, 120 min	β-carotene, Lycopene 53.9 mg/g DW		[103]
SFE	CO_2 solvent, 60 °C, 0.79 bar, 80 min	Lycopene (0.86 mg/ 100 g DW), Oleoresin (1.5 mg/100 g DW)		[104]
SFE	15.5% ethanol, 59 °C, 30 min, 350 bar	β-carotene (99 ± 2.8%,), lutein (98.5 ± 2.2%,), lycopene (36.2 ± 6.2%)		[50]
PEF	Acetone, solid–liquid ratio 1:40 g/mL, 50 °C, 480 min	Carotenoids (84.0 ± 8.3 mg/100 g FW)		[105]
UAE	NaDES DL-methanol and lactic acid—8:1 mol BBA /mol HBD, 70 °C, 10 min	Lycopene (1446 µg/g DW)		[77]
Pumpkin (*Cucurbita* sp.)				
MAE	5 g in 50 mL corn oil (1:10), 45 °C, 30 min	Carotenoids (Pulp: 31.1 µg/g DW, Peel: 34.9 µg/g DW), phenolic compounds (Pulp: 527 mg GAE/g DW, Peel: 554.5 mg GAE/g DW)		[106]
UAE	5 g in 50 mL corn oil (1:10), 22–25 °C, 30 min	Carotenoids (Pulp: 32.7 µg/g DW, Peel: 38.1 µg/g DW), phenolic compounds (Pulp: 555 mg GAE/g DW, Peel: 588 mg GAE/g DW)		
MAE	6 g in 60% ethanol, 2.45 GHz, 100 °C, 20 min	Phenolic compounds (35.0 mg/g DW)		[107]
UAE	60% ethanol, 40 °C, 20 min	Phenolic compounds (34.2 mg/g DW)		
SFE	CO_2 fluid, ethanol: water (80:20), 70 °C, 3 h	Carotenoids (11.5 mg/100 g DW), phenolic compounds (353 mg GAE/100 g DW)		[108]
SWE	Water, 120 °C, 3 h at 5 MPa	Carotenoids (15.2 mg/100 g DW), phenolic compounds (213 mg GAE/100 g DW)		
SFE	CO_2 with ethanol, 47.7 °C, 60 min	β-carotene (20.5 mg/100 g DW), α-tocopherol (9.5 mg/100 g DW)		[109]
UAE	NaDES caprylic acid: capric acid of C_8:C_{10} (3:1), 50 °C, 52.5 w/cm^3 power, 10 min	β-carotene (151.4 µg/mL DW)		[82]

MAE, Microwave-assisted extraction; EAE, enzyme-assisted extraction; UAE, ultrasound-assisted extraction; UME, ultrasonic–microwave synergistic extraction; SFE, supercritical fluid extraction; PEF, pulsed electric field extraction; PLE, Pressurized liquid extraction; SWE, subcritical water extraction; DW, dry weight; FW, fresh weight. CE, catechin equivalents; GAE, gallic acid equivalents; *v*/*v*, volume/volume; NaOH, sodium hydroxide; CO_2, Carbon dioxide; BBA/HBD, hydrogen bond acceptor/hydrogen bond donor; NaDES, natural deep eutectic solvents; kHz, kilohertz; W, watt.

5.1.2. Antioxidant Properties of Kale as Bioactive in Skin Health

Moreover, recent studies have highlighted the potential health benefits of certain phytochemicals found in kale, including flavonoids such as kaempferol, quercetin, fisetin, and luteolin, as well as carotenoids and isothiocyanates such as lutein and glucoraphanin, respectively. The phytochemicals are known for their anticancer properties. For example, flavonoids have demonstrated properties that modify ROS, disrupt protein function impede cell cycle progression, induce apoptosis and autophagy, and prevent the growth of malignant cells. Among these, kaempferol has been identified as the most effective in reducing proinflammatory cytokines such as interleukin (IL)-6 and tumor necrosis factor-alpha (TNF-α), protecting against UVB-induced photoaging of human splenic fibroblasts (HSF) and human keratinocytes (HaCaT) cells [110]. Similarly, bioactives such as quercetin, luteolin, and lutein have exhibited protection against skin aging, carcinogenesis,

and inflammation by inhibiting the expression of matrix metalloproteinase-1 (MMP-1), cyclooxygenase-2 (COX-2), prostaglandin E2 (PGE2) synthesis, and skin erythema while also preventing collagen degradation [111–113]. Additionally, another flavonoid found in kale is fisetin, which exhibits promising results against UV-induced skin damage by reducing the appearance of fine lines and wrinkles, and inhibiting the activity of various enzymes such as MMP-1, MMP-2, COX-2, and epidermal hyperplasia, while also enhancing collagen production within the deeper layers of the skin and increasing expression levels of nuclear factor erythroid 2-related factor-2 (Nrf2) [114]. The regular consumption of spray-dried kale and the glucoraphanin-enriched kale extract by mice prone to skin aging experienced significant enhancements in epidermal and dermal thickness for 43 weeks. The positive effect was significant in the glucoraphanin-enriched kale group compared to those consuming spray-dried kale [115]. Interestingly, the blue fenugreek kale extract showed promising results in reducing ultraviolet A (UVA) and H_2O_2-induced protein carbonylation in human dermal fibroblasts (HDFs) by enhancing skin moisture content and hydration levels without significant alterations in wrinkle severity, skin sagging, elasticity, or inflammatory markers. These findings underscore the potential of kale-derived bioactive compounds to mitigate oxidative stress and inflammation, showing promising results in addressing concerns of skin health and aging (Table 3).

Table 3. Various dietary phytochemicals of vegetables and root crops with anti-inflammatory and anti-photoaging properties.

Phytochemicals	Experimental Model	Marker Measured	References
Kale (*Brassica oleracea* L. var. *acephala*)			
Kaempferol	UV radiation on HDFs and HaCaT cells	↑Radical scavenging, ↓IL-6 and TNF-α, ↑Cytokines inhibitory potency	[110]
Quercetin	UVA-induced skin aging in skin cells and human skin tissue	↓PKCδ and JAK2 Kinase, ↓MMP-1, ↓COX-2, ↓collagen degradation, ↓AP-1, ↓NF-κB, ↓ERK/JNK/Akt/STAT3	[111]
Fisetin	UVB-induced photodamage in hairless mice	↓MMP-1/2, ↓COX-2, ↓IL-6, ↓NF-κB, ↑Nrf2	[114]
Luteolin	UVB-induced DNA damage in HaCaT cells	↓cyclobutane pyrimidine dimers, ↓COX-2, ↓prostaglandin E2 production	[112]
Lutein	UVB-induced acute inflammation in hairless mice	↓acute inflammatory responses, ↓epidermal hyperproliferation	[113]
Cauliflower (*Brassica oleracea* var. *botrytis*)			
Luteolin	UVB-induced skin barrier damage in SD rats and HDFs	↑Collagen expression, ↓SIRT3, ↓ROS, ↓MAPK, ↓MMPs	[116]
Caffeic acid	UVB-induced skin carcinogenesis in HDFs and Swiss albino mice skin	↓CPD formation, ↓DNA damage, ↓ROS, ↑PTEN, ↓PI3K and AKT Kinase	[117]
Sulforaphane	UVB-induced skin aging in HaCaT cells	↓AP-1, ↑Nrf2, No significant protection with post-UVB supplementation	[118]
	UVR-mediated skin damage in SKH-1 hairless mice	↑Nrf2, ↓NF-kB signaling, ↓MIF	[119]
Glucoraphanin	UVB-induced skin carcinogenesis in SKH-1 hairless mice	↓AP-1, ↑Nrf2, ↓TPA-induced ornithine decarboxylase, ↓tumor incidence	[120]
Beets (*Beta vulgaris* subsp. *vulgaris*)			
Caffeic acid	UVB-induced photo carcinogenesis in mouse skin	↓Lipid peroxidation, ↓iNOS/VEGF/TGF-β, ↓tumor multiplicity, ↑PPARγ, ↓COX-2, ↓ NF-κB	[117]
Betanin	DMBA–UV-B-induced skin carcinogenesis in female hairless mice	↓Skin tumors, ↓skin papillomas, ↑tumor latency	[121]
Rutin	UVB-induced skin damage in mice	↓ROS; ↓MMP-1; ↑Collagen I/III; ↓ COX-2; ↓iNOS	[122]

Table 3. *Cont.*

Phytochemicals	Experimental Model	Marker Measured	References
Sweet potato (*Ipomoea batatas*)			
Myricetin	UVB-induced wrinkle formation in SKH-1 hairless mice	↓MMP-9, ↓Raf kinase, ↓MEK/ERK	[123]
Cyanidin-3-O-glucoside,	UVB-induced cell damage in human HaCaT cells	↑Bcl-2, ↓p53, ↓ROS, ↓Caspase-3	[124]
β-carotene	UVA-induced photoaging in HaCaT cells	↓MMP-1, ↓MMP-3, ↓MMP-10	[125]
Caffeoylquinic acid (CQA)	UVB-induced damage in human HaCaT cells	↓ROS, ↓Nrf2, ↓TNF-α, ↓COX-2, ↓IL-6, ↓IL-1β	[126]
Tomato (*Lycopersicon esculentum*)			
Quercetin	UVB-induced oxidative damage in JB6 P+ mouse epidermal C141 cells	↓ROS, ↑Catalase, ↑GSH/GSSG, ↓DNA Damage/Apoptosis, ↓NF-κB	[127]
β-carotene	36 healthy adults	Diminished erythema intensity 24 h post-irradiation	[128]
Lycopene	65 healthy volunteers	↓HO1, ↓ICAM1, ↓MMP1	[129]
Delphinidin	UVB-mediated oxidative stress in Human HaCaT Keratinocytes and mouse skin	↓Apoptosis/DNA damage, ↓Nuclear Antigen, ↑Lipid peroxidation, ↑Caspases/Bax/Bid/Bak, ↓Bcl-2/Bcl-xL	[130]
Fisetin	UV-induced photodamage in human skin fibroblasts	↓ERK/JNK/p38 phosphorylation, ↓IκB, p65 (NF-κB subunit), ↓ROS/PGE2/NO	[131]
Pumpkin (*Cucurbita* sp.)			
Syringic acid, Ferulic acid,	UVA-induced photoaging in HFF-1 cells	↓ROS, ↑GSH, ↑GPx, ↑SOD, ↑CAT, ↓MDA, ↓Keap1 protein,	[132]
Caffeic acid	UVB radiation effects in human HaCaT keratinocytes	↓COX-2, ↓MMP-1, ↓PGE2, ↓MAPK, ↓EGFR	[133]
Extracts			
Blue fenugreek kale extract	UVA and H_2O_2 induced protein carbonylation (PA) in HDFs, followed by a randomized, double-blind, placebo-controlled clinical trial on 59 volunteers for 56 days.	↓PA, ↓TEWL, ↑skin moisture content level, ↑skin hydration. No significant difference was observed in wrinkle severity, skin sagging, elasticity, and inflammatory markers.	[134]
Glucoraphanin-enriched kale (GEK) extract	GEK diet on skin aging in senescence-accelerated mouse prone 1 (SAMP1) mouse.	↑Nrf2, ↑HO-1, ↑collagen production, ↑thickness of the epidermis	[115]
Beetroot extract	UVB-induced sunburn in epidermal cells in rats	↓TNF-α, ↓sunburn, ↓IL-6	[135]
Purple-fleshed sweet potato anthocyanin extract (PSP-AE)	UVB-induced photoaging in BALB/c- mouse skin	↓TNF-α, ↓IL-6, ↓Kinase, ↓MMP-1, ↓NF-κB	[136]
Pumpkin seed extract	Pumpkin seed extract Doxorubicin-induced normal NIH-3T3 fibroblasts	Dose-dependent reduction in cell senescence percentages	[137]

↑, increase; ↓, decrease; Akt, protein kinase B; Bcl-2, B-cell lymphoma 2; Bax, Bcl-2 Associated X-protein; COX, cyclooxygenase; CPD, cyclobutane pyrimidine dimers; ERK, extracellular signal-regulated kinases; GSH/GSSG, glutathione (reduced/oxidized form); HaCaT, human keratinocytes; HO1, heme oxygenase1; IL-6, interleukin-6; iNOS, inducible nitric oxide synthase; IL-1β, interleukin 1β; ICAM1, intercellular adhesion molecule 1; IκB, inhibitor of kappa B; JNK, c-jun N-terminal kinases; JAK2, Janus kinase 2; MAPK, mitogen-activated protein kinases; MMP, matrix metalloproteinases; MIF, macrophage migration inhibitory factor; MEK, mitogen-activated protein kinase kinase; NF-κB, nuclear factor kappa-light-chain-enhancer of activated B cells; Nrf2, nuclear factor erythroid 2–related factor 2; NO, nitric oxide; PKCδ, protein kinase C delta; PTEN, phosphatase and tensin homolog; PI3K, phosphoinositide 3-kinases; PPARγ, peroxisome proliferator-activated receptor gamma; p53, tumor protein p53; PGE2, prostaglandin E2; ROS, reactive oxygen species; STAT3, signal transducer and activator of transcription 3; SIRT3, Sirtuin 3; TEWL, trans epidermal water loss; TNF-α, tumor necrosis factor-alpha; TPA, 12-O-tetradecanoylphorbol-13-acetate; TGF-β, transforming growth factor beta; VEGF, vascular endothelial growth factor.

5.2. Cauliflower (Brassica oleracea var. botrytis)

Cauliflower belongs to the Brassicaceae family and produces a variety of secondary metabolites, which have been shown to have beneficial effects on human health [138]. Cauliflower is recognized as a rich source of glucosinolates and polyphenols that exhibit antioxidant, anticarcinogenic, and cardio-protective properties in humans [139]. Cruciferous vegetables contribute to a significant amount of food waste generated each year [19]. The issue has been resolved by recent research focusing on the use of enzymes to extract phytochemicals from cauliflower.

5.2.1. Different Green Extraction Methods for Phytochemical Recovery from Cauliflower

The EAE of phytochemicals from cauliflower was performed using cellulases and xylanases from Bacillus subtilis strain wild type (WT) and its derivate OS58 as enzymatic pre-treatment before cyclic pressurized extraction [94]. The formidable Gram-positive soil bacterial Bacillus subtilis-derived OS58 demonstrated better sustainable extraction efficiency in the pre-treatment process. The extraction of glucosinolates (sinigrin and glucoiberin) from cauliflower was optimized by an ultrasound-assisted technique using 70% aqueous methanol solvent at 70 °C for 30 min (Table 2) [19]. The analysis of non-extractable phenolics (NEP) in cauliflower was performed by combining UAE and alkaline hydrolysis methods. The results showed higher extraction efficiency for the NEP in cauliflower using 2 M sodium hydroxide (NaOH) at 60 °C for 30 min [95].

5.2.2. Plant Bioactive Compounds from the Cauliflower as Powerful Antioxidant in Skin Health

The concentration of glucosinolates in cauliflower and their enzymatic degradation into bioactive chemicals, such as sulforaphane, form a critical part of its health-promoting potential (Table 3) [118,140–143]. A comprehensive study exploring the chemoprotective effects of sulforaphane in hairless mice exposed to UV light revealed the protection mechanisms that were Nrf2-independent and inhibition of NF-κB signaling [119]. It has been reported that HaCaT cells were protected from UVB exposure by sulforaphane in high concentrations (10 μM and above) and post-exposure exhibited cytotoxic effects [118]. Glucoraphanin is one of the glucosinolates; it showed protective properties against UV-induced skin carcinogenesis through Nrf2 upregulation and AP-1 modulation while upregulating Nrf2 [120]. Sulforaphane-containing broccoli sprout extracts are considered a promising approach to reducing the development of skin tumors post-UV radiation. Furthermore, the polyphenols found in cauliflower, particularly caffeic acid, inhibited UVB-induced DNA damage and apoptotic cell death in HDFs [117]. In addition, luteolin significantly reduced oxidative stress, MMP activation, and collagen expression, protecting skin cells from UVB radiation-induced photoaging through the SIRT3/ROS/Mitogen-Activated Protein Kinase (MAPK) axis [116]. These findings highlight the protective effects of these phytochemicals and their potential applications in skin health.

5.3. Beets (Beta vulgaris subsp. vulgaris)

Beetroot contains bioactives such as betalains, carotenoids, phenolic acids, and flavonoids. These phytochemicals account for natural anti-inflammatory, anti-hypertensive, antibacterial, and antianemia properties that are expressed by distinct parts of the plant [144].

5.3.1. Green Extraction Methods for Extracting Valuable Compounds from Beetroot

Various extraction methods have been used to extract these phytochemicals from different parts of the beetroot (Table 2). UAE was performed for the recovery of betalains from dried beetroot waste with a yield of 6.9 mg/g DW. The optimum conditions for extracting betalains were 30% ethanol as solvent, 30 °C for 30 min, and 44 kHz sonication power [97]. A similar study was conducted using beetroot leaves for the recovery of polyphenols, betaxanthins, and betacyanins. In this study, the response surface methodology (RSM) was used for the optimization of sonication parameters, and the results showed that extraction was

efficient using a solvent of 1:20 solid–liquid ratio at 30 °C for 16 min compared to traditional methods [98]. The extraction of polyphenols from beetroot leaves using CO_2 as a supercritical fluid, ethanol as a co-solvent, 35 °C, 400 bar, with 0.17 mL/min flow rate obtained total phenolic content (TPC) of 3.4 mg GAE/g DW [99]. An overview of the PLE technique was used to extract phenolic compounds present in beetroot waste. To determine the extraction, the optimum conditions were a temperature of 40 °C, a pressure of 10 MPa, and a flow rate of 3 mL/min were used, and extracts assessed TPC of 252 mg GAE/g DW [100]. A comparative study of UAE, MAE, and SWE methods to obtain betacyanins and betaxanthins from beetroot was interpreted [96]. The extraction parameters of sonication, microwave, and subwater are temperature and time given as 80 °C for 30 min, 50 °C for 5 min, and 150 °C for 5 min were used respectively with constant ratio of sample and solvent (1:20). The highest yield 3.9 mg/g DW and 8.6 mg/g DW of betacyanins and betaxanthins were obtained using sonication method (Table 2). This demonstrates the effectiveness of the sonication method in the recovery of bioactive compounds from beets.

5.3.2. Natural Bioactive Compounds from Beets and Their Function in Skin Health

Beetroots are rich in betalains, which are organic pigments (chromoalkaloids) that exhibit antioxidant properties and are synthesized into betacyanins (red-purple) and betaxanthins (yellow-orange) from tyrosine [145,146]. Betalains possess anti-inflammatory and anti-cancer activities, scavenging free radicals [147]. In the context of skin health, betalains counteract UVB-induced oxidative damage, evidenced through in vitro, in vivo, and human intervention studies. Betanin, a component of beetroot extracts, inhibits skin carcinogenesis in HOS:HR-1 strain mice, resulting in a delay in tumor development induced by diethyl nitrosamine (DEN) in both short-term and long-term treatments using the extract [121]. This study confirms that betanin increases tumor latency by effectively inhibiting skin tumors and papillomas. Furthermore, recent research has demonstrated the efficacy of beetroot extract in mitigating UVB-induced sunburn by reducing levels of TNF-α and IL-6 in rat epidermal cells. The beetroot-rich extract possesses other phytochemicals, such as betacyanin, rutin, and caffeic acid, that exhibit promising potential in skin health. Administration of caffeic acid, both topically and intraperitoneally before UVB exposure, resulted in the downregulation of COX-2, NF-κB, and transforming growth factor-beta (TGF-β) while also upregulating tumor protein p53, resulting in reduced tumor multiplications in Swiss albino mice skin [117]. Moreover, a study on the preventive impact of rutin in mice revealed significant downregulation of MMP-1 and MMP-3, COX-2, and upregulation of Collagen I and III, highlighting the potential of betalains in promoting skin health [122]. These summarized findings suggest that beetroot bioactives have the potential to be an effective chemo-preventive agent against skin cancer (Table 3) [148,149].

5.4. Sweet Potato (Ipomoea batatas)

Sweet potato is an important staple food cultivated in Asia but has not been explored for its nutraceutical and cosmeceutical potential [24]. Sweet potato contains abundant anthocyanins, flavonoids, and phenolic acids, with health benefits against cancer, cardiovascular, and neurodegenerative diseases.

5.4.1. Sweet Potato Extraction Methods for Their Bioactive Phytochemicals

The extraction of flavonoids from sweet potato leaves was performed by using RSM coupled with MAE. The optimum extraction conditions were 72% ethanol, 57 °C, and 76 s with a solid–liquid ratio of 1:40 g/mL for two consecutive extractions to achieve higher extraction efficiency of flavonoids [24]. UAE was employed to extract polyphenols and anthocyanin from purple sweet potato at 58% ethanol, 80 °C, and 40 min with pH 2.5. The UAE method was compared to conventional methods, resulting in a higher content of anthocyanin in purple sweet potato [101]. Anthocyanins were extracted from purple sweet potatoes using UAE with polyethylene glycol PEG. The best extraction efficiency resulted from 83% PEG, 64 °C, 80 min, and solid–liquid ratio of 1:42 g/mL [102]. These

studies demonstrate the efficacy of novel extraction techniques in maximizing the yield of bioactive compounds from sweet potatoes (Table 2).

5.4.2. Phytochemical Components of Sweet Potato and Its Antioxidant Properties in Skin Health

Sweet potatoes are abundant in cyanidin, myricetin, and caffeoylquinic acid, demonstrating their potent capacity to scavenge superoxide radicals (Table 3). The purple-fleshed sweet potato anthocyanin extract (PSP-AE) has significant anti-photoaging properties in the UVB-induced BALB/c-nu mice skin model, effectively suppressing oxidative stress and skin inflammation via a range of mechanisms [136]. PSP-AE significantly reduces pro-inflammatory cytokines (TNF-α and IL-6) and lipid peroxidation and ameliorates skin damage by enhancing antioxidant enzyme (superoxide dismutase, catalase, and glutathione peroxidase) activities, suppressing NF-κB activation, and inhibiting MAPK protein phosphorylation. It is noted that one of the key components of PSP-AE, cyanidin, exhibits similar protective properties, as shown by its ability to inhibit ROS, caspase-3, Bcl-2, and p53 in HaCaT cells, hence reducing cell damage [124]. These results show the strong anti-inflammatory and antioxidant properties of cyanidin and demonstrate how effective they are as natural anti-photoaging agents for maintaining skin health. Furthermore, myricetin has been investigated for its anti-aging properties in UV-exposed SKH-1 mice, where it protects keratinocytes from UVB-induced damage, inhibits wrinkle formation, and prevents skin carcinogenesis [123]. In addition to flavonoids, sweet potatoes also contain β-carotene, a carotenoid with potent antioxidant properties that inhibits apoptosis and downregulates significant MMPs linked to photoaging [125]. Moreover, caffeoylquinic acid has shown protective effects on HaCaT cells, including scavenging of ROS, reduction in pro-inflammatory cytokines (IL-6, IL-1β), and stimulation of antioxidant enzymes through the activation of the Nrf2 pathway [126]. These findings illustrate the diverse and beneficial effects of sweet potato phytochemicals on skin health and the aging process.

5.5. Tomato (Lycopersicon esculentum)

Tomato is one of the most extensively consumed vegetables in the world. It contains a variety of bioactive phytochemicals, particularly carotenoids, which help in the prevention of cancer and cardiovascular diseases and protect against macular degeneration and delayed aging [105].

5.5.1. Different Green Extraction Techniques of Tomato Extracts

The extraction of carotenoids such as β-carotene, lutein, and lycopene from the flesh and peels of tomatoes has been successfully achieved through the SFE method using 15.5% ethanol as the solvent at 59 °C and 30 min. Among the extracted carotenoids, lycopene recorded the highest concentration [50]. A similar extraction method study was observed for β-carotene and lycopene from the by-products of tomato using 5% ethanol at 55 °C for 2 h [103]. In tomatoes, the goal was to improve the extraction of carotenoids from skins, particularly lycopene and β-carotene, by using carbon dioxide as an extraction fluid of SFE [104]. The temperature, extraction duration, and pressure were at 60 °C, 80 min, and 550 bar, respectively. The effects of pre-treatment using PEF were investigated for extraction temperature on the recovery of carotenoids from tomato peels [105]. The PEF pre-treatments at 5 kV/cm field strengths and 5 kJ/kg total specific energy input resulted in greater total carotenoid content. To determine the best PEF processing by pre-treating tomato peels before acetone extraction at various temperatures between 20 and 50 °C. Increasing the extraction temperature did not result in a higher recovery yield of total carotenoids in the extracts, regardless of whether a PEF pre-treatment was used. Furthermore, high-performance liquid chromatography (HPLC) analysis demonstrated that the major carotenoid recovered was lycopene, with no degradation [105].

5.5.2. Bioactive Compounds and Biological Activities of Tomato Extracts in Skin Health

Carotenoids demonstrate a wide range of bioactive properties, including antioxidative, antibacterial, anti-aging, anti-inflammatory, antidiabetic, anticancer, cardio-protective, neuro-protective, and hepato-protective effects, among others [150–153]. Among these bioactives, β-carotene is known as a protectant against sun light-induced skin damage [128]. Interestingly, a study with 36 healthy participants found that daily supplementation of β-carotene or a carotenoid mixture (β-carotene, lutein, and lycopene) increased skin total carotenoid levels and decreased UV-induced erythema. Lycopene is identified as the most potential singlet oxygen quencher among carotenoids [154]. Moreover, lycopene and lutein-rich tomato complex significantly prevented oxidative stress induced by UVA/B radiation by upregulating the expression of heme-oxygenase, intercellular adhesion molecule, and MMP-1 providing further evidence of its protective properties [129]. Delphinidin, an anthocyanin found in tomatoes, has been extensively studied for its impact on apoptosis and cell cycle inhibition, demonstrating potential in safeguarding against UVB–induced damage [155]. Pre-treatment of HaCaT cells with delphinidin for 24 h and topically applied on SKH-1 hairless mice skin resulted in significant reductions in UVB-induced apoptosis, oxidative stress, and DNA damage, particularly in reducing cyclobutane pyrimidine dimers (CPD). Fisetin, another phytochemical found in tomatoes, possesses potential antitumor, antioxidative, and anti-inflammatory properties [131]. Fisetin effectively inhibited the expression of COX-2, MMP-1, MMP-3, and MMP-9 induced by UVB irradiation in human skin fibroblasts. Fisetin showed inhibitory effects on ROS, PGE2, and nitric oxide (NO) generation. In summary, the findings from various studies show the significant capacity of tomato phytochemicals to alleviate DNA damage, suppress apoptosis, regulate nuclear antigen expression, and counteract ROS. Consequently, these bioactives hold immense potential as therapeutic agents for the treatment of oxidative damage-related conditions, including photoaging and skin cancer (Table 3).

5.6. Pumpkin (Cucurbita sp.)

Pumpkins are cultivated worldwide for decorative, commercial, and agricultural uses. The pumpkin peel, pulp, and seed are rich in phytochemicals such as carotenoids, phytosterols, phenolic compounds, and flavonoids [156]. The functional components reported in pumpkins exert health benefits such as antioxidative, anti-inflammatory, anti-cancer, anti-bacterial, and anti-diabetic properties in humans [25].

5.6.1. Bioactives of Pumpkin Extracts Using Different Extraction Methods

The recovery of bioactive compounds in pumpkin seeds was reported using different extraction methods [107]. The phenolic compounds were extracted at 40 °C for 20 min and compared with the use of different solvents such as 60% ethanol and ternary mixture (30:49:21 *v*:*v*:*v* of hexane, ethanol, and water). The findings for MAE indicated that the optimum conditions were a concentration of 60% ethanol, 100 °C, and 20 min at 2.45 GHz. The UAE results from the above-mentioned optimum conditions concluded that the use of a ternary mixture has a better recovery of phenolics in pumpkin seeds compared to MAE [107]. The carotenoids were extracted from pumpkin peel and pulp using corn oil as a green solvent with UAE and MAE. The best conditions for UAE were 22–25 °C and 30 min, whereas the MAE experiment setup was 45 °C for 30 min. In the comparison of both green extraction techniques for total carotenoid and phenolic content, UAE recorded the highest yield for the pumpkin variety (*Cucurbita maxima* var. *Gold nugget*) [106]. An overview of SWE and SFE to extract carotenoids and phenolic compounds using green solvents was provided [108]. For SWE, the maximum yield of phytochemicals mentioned was obtained using water as a solvent at 120 °C for 3 h with 5 MPa. On the other hand, SFE optimal parameters were at 70 °C for 3 h by pumping carbon dioxide fluid followed by ethanol: water (80:20) as solvent. The total amount of carotenoids was the highest using SWE, and the total phenolics content was maximum using SFE in the above-mentioned comparative study of pumpkin peel extract. The extraction of β-carotene and α–tocopherol

from pumpkin was evaluated using the SFE method with optimal extraction conditions at 47.5 °C for 60 min and ethanol as co-solvent. The maximum yield obtained from pumpkin was β-carotene [109].

5.6.2. Potential Phytochemicals in Pumpkin to Fight against Skin Health

The therapeutic potential of syringic acid present in pumpkin was investigated against UVB-induced skin damage and demonstrates significant inhibitory effects on key biomarkers, including prostaglandin E2, MMP-1, and COX-2 [133]. These results highlight its function in focusing on molecular pathways linked to UVB-induced cellular damage, suggesting syringic acid as a potential treatment for UVB-induced skin damage. Furthermore, a phenolic acid mixture (PAM) was found with syringic acid that provided protection against UVA-induced damage by reducing cell cycle arrest, oxidative damage, ROS accumulation, Keap1 protein, and malondialdehyde (MDA) [132]. The PAM increases the activity of intracellular antioxidant markers (GSH, GPx, SOD, and CAT), impairs cell cycle regulatory proteins (p53, p21, and p16), and increases collagen secretion and cell survival. Pumpkin seed has the potential to act as an anti-aging agent due to its intrinsic antioxidant properties, which include the presence of tocopherol. Given this, the author discovered that pumpkin seed extract reduced senescence in doxorubicin-induced normal fibroblast NIH-3T3 cells without causing cytotoxicity [137]. Tocopherol's ability to prevent aging-related cell damage was highlighted by molecular docking, which suggested the molecule's significance in anti-aging through its interaction with cytochrome CYP3A4. These results highlight the anti-aging properties of pumpkin seed extract and recommend additional investigation into how well it might protect against aging-related cellular damage.

6. Conclusions and Future Directions

In conclusion, recovery of bioactive phytochemicals from fresh vegetable waste involves complex mechanisms coupled with various emerging technologies (Figure 2). The trend toward green extraction techniques has been progressing in the food, nutraceutical, and cosmeceutical industries to overcome the drawbacks of conventional methods. These methods improve yield, reduce processing time, eliminate the use of toxic solvents, and result in better overall quality and safe natural extracts. The most investigated methods for extracting phytochemicals are ultrasound- and microwave-assisted extractions. The implementation of green alternative solvents provides insight into the use of the resulting products in cosmeceuticals. This review summarizes green extraction methods and the potential to apply phytochemicals extracted from vegetables and root crops against UV-induced skin damage and photoaging. In addition, phytochemicals show promising results in reducing ROS production, preventing apoptosis, inhibiting MMPs, modulating inflammatory pathways, and promoting collagen synthesis.

Over the last few decades, food waste has become a significant and growing global issue. Thus, there is a potential to recover bioactive phytochemicals from food waste, especially from fresh vegetable and root crop waste. Green extraction technologies can be used to isolate phytochemicals from fresh produce waste for applications in skin health. Future research should be focused on developing environmentally friendly, scalable, and economical extraction processes, as well as entire food waste management strategies, to optimize the yield of bioactive phytochemicals. The various extraction methods with consistent quality are required for formulating standardized skin care products. Moreover, proper pre-clinical and human clinical studies should be performed to assess the mechanism of action, safety, and the efficacious doses of these phytochemicals before using them as cosmeceuticals in skin care products. However, establishing and promoting a comprehensive framework with industries, academia, and policymakers can ensure economic viability and contribute toward sustainable developmental goals.

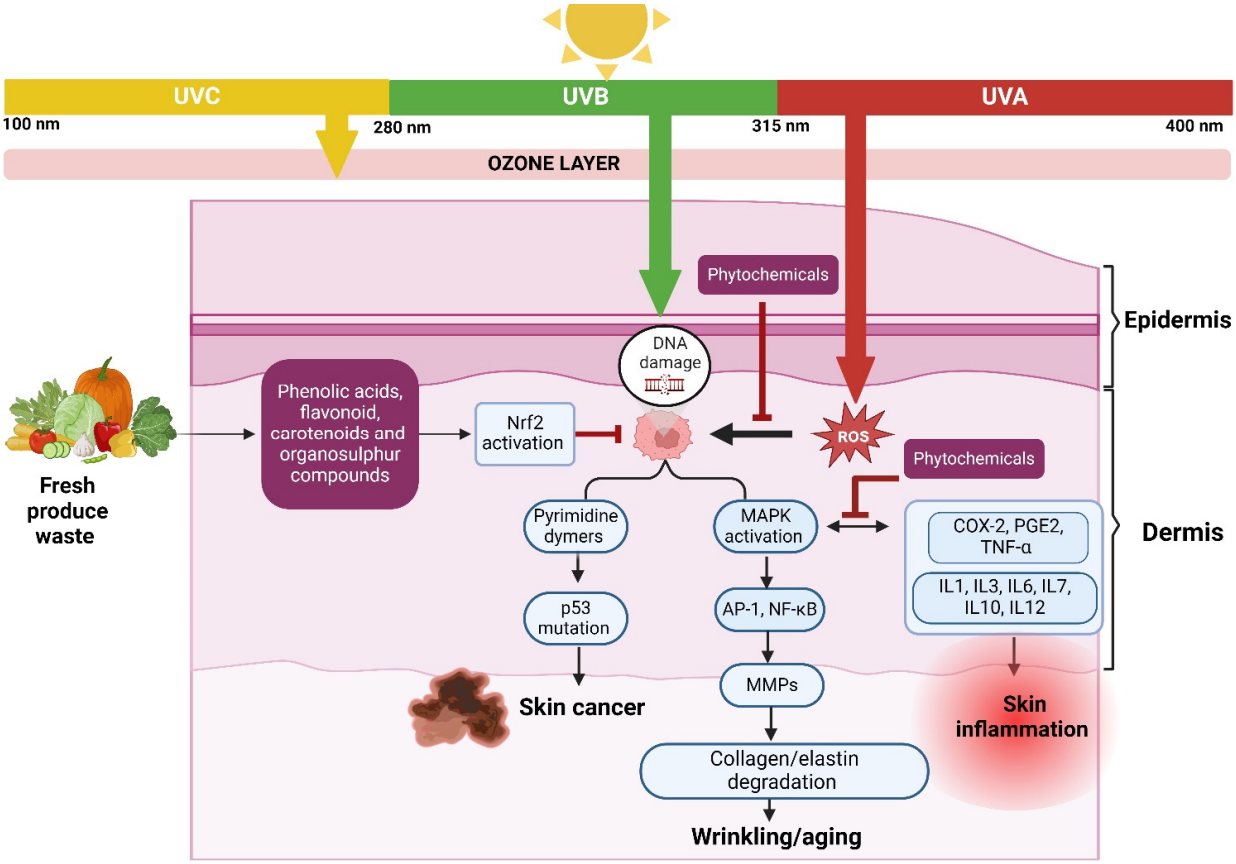

Figure 2. Photoprotective potential of phytochemicals against ultraviolet radiation (UVR) induced skin cancer, skin inflammation, and skin aging. Abbreviations Nrf2: Nuclear factor erythroid 2-related factor 2; p53, Tumor protein p53; MAPK, Mitogen-activated protein kinase; AP1, Activator protein 1; NF-κB, nuclear factor kappa-light-chain-enhancer of activated B cells; MMPs, Matrix metalloproteinases; COX-2, Cyclooxygenase-2; PGE2, Prostaglandin E2; TNF-α, Tumor necrosis factor-alpha; IL, Interleukin.

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