agronomy

Review

An Overview on Traditional vs. Green Technology of Extraction Methods for Producing High Quality Walnut Oil

Lubna Masoodi [1], Amir Gull [1], Farooq Ahmad Masoodi [1], Adil Gani [1], Jasia Nissar [1], Tehmeena Ahad [1], Gulzar Ahmad Nayik [2], Shaikh Ayaz Mukarram [3], Béla Kovács [3], József Prokisch [3], Hassan El-Ramady [3,4,*] and Svein Øivind Solberg [5,*]

1 Department of Food Technology, University of Kashmir, Hazratbal, Srinagar 190006, India
2 Department of Food Science & Technology, Government Degree College Shopian, Jammu and Kashmir 192303, India
3 Institute of Animal Science, Biotechnology and Nature Conservation, Faculty of Agricultural and Food Sciences and Environmental Management, University of Debrecen, 138 Böszörményi Street, 4032 Debrecen, Hungary
4 Soil and Water Department, Faculty of Agriculture, Kafrelsheikh University, Kafr El-Sheikh 33516, Egypt
5 Faculty of Applied Ecology, Agricultural Sciences and Biotechnology, Inland Norway University of Applied Sciences, 2322 Hamar, Norway
* Correspondence: hassan.elramady@agr.kfs.edu.eg (H.E.-R.); svein.solberg@inn.no (S.Ø.S.)

Abstract: Walnut oil is extremely nutrient dense. It has plenty of oil and is high in fatty acids, which have positive biological properties and have a favorable impact on blood lipids and lipoproteins. Walnut oil is low in saturated fatty acids and high in unsaturated fatty acids as well as being high in other vital nutrients. Walnut oil can be extracted using traditional as well as new and green technologies. It is low in saturated fatty acids and high in unsaturated fatty acids (monounsaturated and polyunsaturated fatty acids) as well as being high in other vital nutrients (e.g., selenium, phosphorus, and zinc). Walnut oil can be extracted using traditional as well as new and green technologies. The chosen extraction method has a significant impact on the lipids and other important components extracted. It is critical to select a suitable extraction process for the compounds of interest. In this study, different extraction methods are reviewed, demonstrating the significant benefits of new methods over previous approaches. New green technologies are ecologically benign and allow for shorter extraction times and yields that are comparable to those obtained using traditional methods. The new green technologies allow for higher-quality oils that are less vulnerable to oxidation processes than most of the old technologies.

Keywords: cold press; enzyme-assisted extraction; microwave-assisted extraction; supercritical fluid extraction; ultrasonic assisted extraction; walnut oil

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1. Introduction

The walnut (*Juglans* sp.) is an important temperate nut fruit in several countries, such as India. Since ancient times, walnut has been employed in human nutrition all across the world. Walnut kernels have a high protein and oil content, making them essential for human nutrition [1]. As a result, the walnut is considered a strategic species for human nutrition and is on the FAO priority plant list. Walnuts in India are found in different sizes and shapes. The Indian walnut is categorized into four categories viz., paper shelled, thin shelled, medium shelled and hard shelled [2]. The world production of walnuts exceeds almost 1,500,000 metric Mg (tons). China, the United States and Iran are the major producers, with about 25%, 20% and 11% of total global production, respectively [3]. In recent years, production in these countries has increased rapidly. India exported 1069.70 MT of walnuts to the world for the worth of INR 29.75 crores or USD 3.97 millions during the year 2021–2022 [4]; more than 90% of the country's walnut production comes from

Kashmir. The major importing countries of walnut from India are the United Arab Emirates, France, the U.K., Djibouti, Germany, and New Zealand. The major growing area in India are Jammu and Kashmir, Uttaranchal, Himachal Pradesh, and Arunachal Pradesh, with Jammu and Kashmir occupying the largest share in total area and production [4].

Traditionally, Kashmiri walnuts have enjoyed good demand in both domestic and international markets. Dried walnuts are preferred over fresh ones because of perishability. Walnuts can be added to breakfast cereals, baked goods, salads, pastas, and soups as a snack. The edible component of the walnut (kernel) is well known for its nutritional, health, and sensory qualities around the world. The nutritional and physiological benefits of walnuts have aided in their increasing popular demand. Walnuts are rich in many essential dietary fats as polyunsaturated fatty acids (PUFAs), such as omega-6 and omega-3. Due to the traditional idea of "shape compensation", walnuts have been consumed for thousands of years as the kind of nuts that are good for the brain [5]. This hypothesis has also been supported by research on walnut oil, which has anti-inflammatory qualities [6] and has been shown to improve memory in mice [7]. Due to walnut oil's excellent nutritional value as an edible oil, study on the oil has gained popularity in recent years. Walnut oil is used extensively in traditional medicine across the globe and is recommended as a beneficial food oil in the agro-industry. Nutrition research on walnut oil primarily focuses on the effect of walnut oil in digestive illnesses [6]. Since it has strong anti-aging effect in vivo [8] and can boost antioxidant capacity [9], walnut oil is a well-known functional food entrant for treating inflammatory bowel disease [10] and ulcerative colitis [11]. In situations of reducing ulcerative colitis and inflammatory bowel disease, the anti-inflammatory activity is more prominent. Moreover, antiaging and antioxidative potentials would be more advantageous for the health consequence of preventing memory decline. The method used in walnut oil's processing has a direct impact on its antioxidant capability [12]. As a result, the reports about the processing of walnut oil have garnered a lot of interest.

Market development efforts have intensified; as a result, walnuts are being used more in snacking, baking, and processed foods. The common methods of oil extraction may include the chemical (using a solvent) and mechanical extraction of oil from oilseeds [13]. The two categories of mechanical techniques are hot press and cold press. In the hot-press method, the influence of temperature on the breakdown of antioxidant components in the result is clearly obvious, despite the increased percentage of oil extraction [14]. The safest method for obtaining oil from oilseeds is cold pressing. In recent years, it has become widely used. The efficiency of mechanical methods may reach 80% for extracting oil, which is lower compared to that of chemical methods [15]. On the other hand, the chemical methods are often expensive and may have a risk of explosion and ignition, especially with using fire. During these processing operations to extract the edible portion (kernel), considerable quantities of broken kernels are produced. Despite their potential value, most of these broken kernels are underutilized. The use of broken kernels in the manufacturing of healthful food ingredients and high-value-added products can boost the walnut processing industry's profitability while also addressing environmental issues. So far, no work or study has been done to that extent in view of utilizing the walnut oil in bakeries and confectionery because of the lack of infrastructure, such as transport, oil extraction, power supply, roads, mandis, and packaging and processing facilities. Walnuts have attracted the attention of nutritionists and food scientists in recent years due to the high-value fatty acids found in their edible seed oil, such as omega-3 and omega-6 polyunsaturated fatty acids [16]. Walnut oil is created from the inedible flesh and kernel bits that are removed from the shell during the shelling process. The oils of diverse walnut species are fairly similar in terms of physico-chemical characteristics. They have a subtle, nutty odor and are pale yellow in color with a greenish tinge. Every year, a lot of broken walnut kernels are produced and somehow are not properly utilized.

Therefore, the aim of the review is to evaluate many different processing techniques for oil extraction that could be employed so as to increase the walnut oil production and its utilization. This study also is an attempt at a major contribution to research on the extraction of walnut oil by demonstrating the benefits and drawbacks of different methods used in this extraction, with a focus on the operating principles of traditional and green extraction techniques.

2. Composition of Walnut Oil

Walnut oil is a high-quality oil that is frequently used in both food and medicine [17]. Naturally, the content of walnut oil in saturated fatty acids is low, but higher in polyunsaturated fatty acids, primarily linoleic and linolenic acids (Table 1). Oleic acid is the only monounsaturated fatty acid contained in walnut oil [18]. Walnut kernels typically contain 60% oil, which depends on the cultivar and may range from 52% to 70%. The principal component of walnut oil is triacylglycerols that account for 83–95% of the total oil fraction. These triacylglycerols are made up of tri-unsaturated and non-symmetrical di-unsaturated glycerides. The fatty acids in walnut oil are mostly unsaturated, with linoleic and oleic acids present in major quantities. Linoleic acid dominates the 2-position of the triacylglycerol. Figure 1 presents some photos of a walnut tree, fruits, and its nuts.

Table 1. The chemical composition of walnut oil (adapted from Dufoo-Hurtado et al. [19].

Property	Walnut
Specific Gravity (15 °C)	0.918
Refractive Index (25 °C)	1.45
Acid Value	0.7
Saponification Value	192
Iodine Value	152
Pollenske Value	0.2
Unsaponifiable Matter (g/100)	0.8
Solidification Value (°C)	−18.0

Figure 1. An overview of the walnut plant; the tree of walnut, and their green fruits in the three upper photos; in the middle some sections in the green walnut fruits, and the lower right photo represents the green and manure walnut fruits. Photos by Ayaz.

Walnut oil contains high amounts of PUFAs (e.g., linoleic and a-linoleic acids), monounsaturated, protein, dietary fiber, phytochemicals, and micronutrients. The human body cannot synthesize PUFAs, which are considered essential in the human physiology [20]. There is a need for knowing the chemical composition of the fatty acid in walnut oil, which may depend on the grown location. The fatty acid composition varies greatly: linoleic (49.7–72%), oleic (12.7–34%), and linolenic acid (9–25%), which are derived from stearic acids (1.4–2.5%) and the saturated palmitic (5.24–8.2%) [21]. Omega-3 PUFA may play a role in the prevention of coronary heart disease, arrhythmia illnesses, and thrombotic diseases, according to epidemiological and clinical studies [22]. Walnut oil also contains some components with pharmacological and cosmo-nutraceutical characteristics, such as phytosterols and tocopherols, in significant amounts, promoting its industrial application [23].

Pectic compounds make up roughly 2% of the anhydro-galacturonic acid in the edible section of walnuts. Pectic compounds, which are a type of dietary fiber, are primarily galacturonic acid polymers that can have a variety of physiological and nutritional effects, including hypo-cholesterolemic effects, enhanced fecal sterol excretion, and the ability to bind bile salts. The walnut kernels contain substantial amounts of phosphorus, magnesium, potassium and iron. Vitamins are abundant in walnut kernels. Walnut oil includes 30–300 IU of vitamin A per 100 g of kernel, 0.22–0.45 mg thiamin, 0.10–0.16 mg riboflavin, and 0.7–1.105 mg niacin. The unripe fruits as well as the leaves of walnuts are the best sources of vitamin C. Un-ripened walnuts are said to have a vitamin C content of 2400–3700 mg 100 g^{-1} and their antioxidant activity is 40–50 times more than that of citrus fruits. Walnut oil contains approximately 7.3–28.7 g-tocopherol, 1.0–8.2 g-tocopherol, 205–375.8 g-tocopherol, and 28.0–62.1 g-tocopherol g^{-1}. The amount of tocopherol in walnut oil varies between 100 and 436 mg kg^{-1}. According to Rabrenovic et al. [16], gamma-tocopherol dominates the tocopherol fraction and accounts for 88%. The existence of gamma-tocopherol in examined walnut oils is not established [24]. Astringency, coloring, enzyme inhibition, and antioxidant capabilities have all been linked to the presence of phenolic acids in food. Some phenolic acids, such as syringic, phenylacetic, vanillic, gallic acid, protocatechuic, caffeic, and ferulic acids, are detected in defatted kernels in very modest amounts, ranging from 0.02 to 0.20 μg-g^{-1} of kernels.

The total sterol content ranges from 12 to 20 mg-kg^{-1} of oil. Sterols are physiologically active compounds that make up the majority of unsaponifiable chemicals. According to Oliveira et al. [25], the sterol fraction in walnut oils contains campesterol (2%), 5-avenasterol (7%), and -sitosterol (>85%). Furthermore, cholesterol, stigmasterol, 7-stigmasterol, and 7-avenasterol have all been detected. A yellow–brown substance called juglone (5-hydroxy-1,4,-naphthoquinone) was revealed to be a compound connected to walnut resistance to fungus-caused scab. Juglone is abundant in the unripe hulls of the nuts and in all green and growing sections of the tree. Juglone levels in kernels, on the other hand, were either very low or non-existent [25].

Walnut oil's fatty acid makeup shows that it is prone to oxidation and rancidity [26]. Walnut oil is steady, influenced by antioxidants. In this connection, Savage et al. [27] demonstrated that walnut oil stored in the dark at ambient temperatures does not deteriorate and is moderately stable for more than four months. Walnut oil's strong natural antioxidant (vitamin E) concentration is expected to play a key role in its long-standing storage steadiness. It has a long shelf life and has an excellent sensory attribute as well as nutritional benefits.

3. Traditional Extraction Technologies

The method used for extraction has a significant impact on the quantity and quality of lipids and other important components. It is critical to select a suitable extraction process for the compounds of interest. Scaling walnut oil into commercial production requires proper extraction technologies. Oil extraction is based on basic concepts, such as avoiding damaging the oil during the operation, extracting oil with the least number of impurities as feasible, reducing the amount of fat remaining in the cake, and extracting as much oil as possible from the raw material [28]. The concepts outlined apply to all extraction processes, despite the fact that their technologies differ.

3.1. Cold Press Extraction

Cold press extraction is a hydraulic extraction method that consumes less energy and is better for the environment than other oil extraction methods. It is a method widely used to extract oil from a wide range of matrices. For creating high-quality oils at low temperatures, the cold press process can be used. It does not utilize any solvents, and therefore it is safe for the environment. In other words, neither heat nor chemicals are used in cold-press extraction. Furthermore, customers are interested in these oils since they are natural and safe, as well as preventing diseases and promoting human health by containing a higher quantity of lipophilic phytochemicals, such as antioxidants. These oils are more nutrient dense than refined oils. They do have a number of benefits; however, one of the disadvantages of this technology is its low production. Another disadvantage of this method is that it is difficult to extract the same high-quality product each time. Cold-pressed oils, according to the Turkish Food Codex [29], are oils prepared only through mechanical means and that are appropriate for direct consumption without further heat treatment. To put it another way, cold-pressed oils are often ready to use directly. Zwarts et al. [26] investigated the fatty acid composition of walnut oil generated with a cold press. The overall oil content increased from 62.4 to 68.7% (by weight) compared to other methods. Many temperature-sensitive phenolic components are preserved, and no oxidation processes occur, as no heat is applied. Only washing with water, filtration, and centrifugation can be used to purify cold-pressed oils.

Expellers, expanders, and twin-cold systems are the three types of cold presses used. Twin-cold systems are now in operation in the laboratory and on a pilot scale, and optimization studies have gained traction. Soybean and cottonseed oil are also employed in the manufacturing of oil from raw materials that do not have a high oil content. Anderson's first press, dubbed Expellers, was introduced in 1902 and is still the most popular form of cold press. The heating system has become more versatile in response to the use of cold or hot presses. With the spinning cold, the oil extracted from the cake is withdrawn from the slit between the metal bars arranged at regular intervals [30]. Cold-press oil production processes are easy, environmentally friendly, and low cost, but the oil yield from raw materials is poor, and product quality is difficult to achieve [31]. Although many cold-extraction processes inhibit fatty acid breakdown in oils,, they have several demerits, such as the use of a hefty amount of solvents and lengthy processes that result in bigger sample losses, variability, and contamination.

The entire process of extracting walnut oil includes peeling green walnuts, cracking, pressing, filtering, and filling. A green walnut peeling machine must peel recently collected green walnuts. Green walnuts can be cleaned and dehulled simultaneously by a green walnut dehuller/peeling machine. It can dehull walnuts of different sizes. Beneath the hull, a hard shell covers the walnut. Therefore, a walnut-shelling machine is used to efficiently shell the nuts. There are two different kinds of walnut-shelling devices, one of which can preserve the kernel intact, and another that will not keep the walnut kernel whole, even though it can remove the shell. It is not necessary for the walnut kernel to be whole when pressing the oil. However, the kernels must be sufficiently dry in order to extract the oil. A hydraulic pressure in the machine's press chamber is used to compress walnuts kernels. To press walnut kernels, the equipment primarily uses cold, physical pressing. It is preferable to use dried walnut as a raw material (Figure 2). Even if the oil produced by a hydraulic oil press is sufficiently pure, filtering is often applied. Centrifugal oil filters are compatible with hydraulic oil presses. The machine primarily filters oil contaminants out using the centrifugal concept.

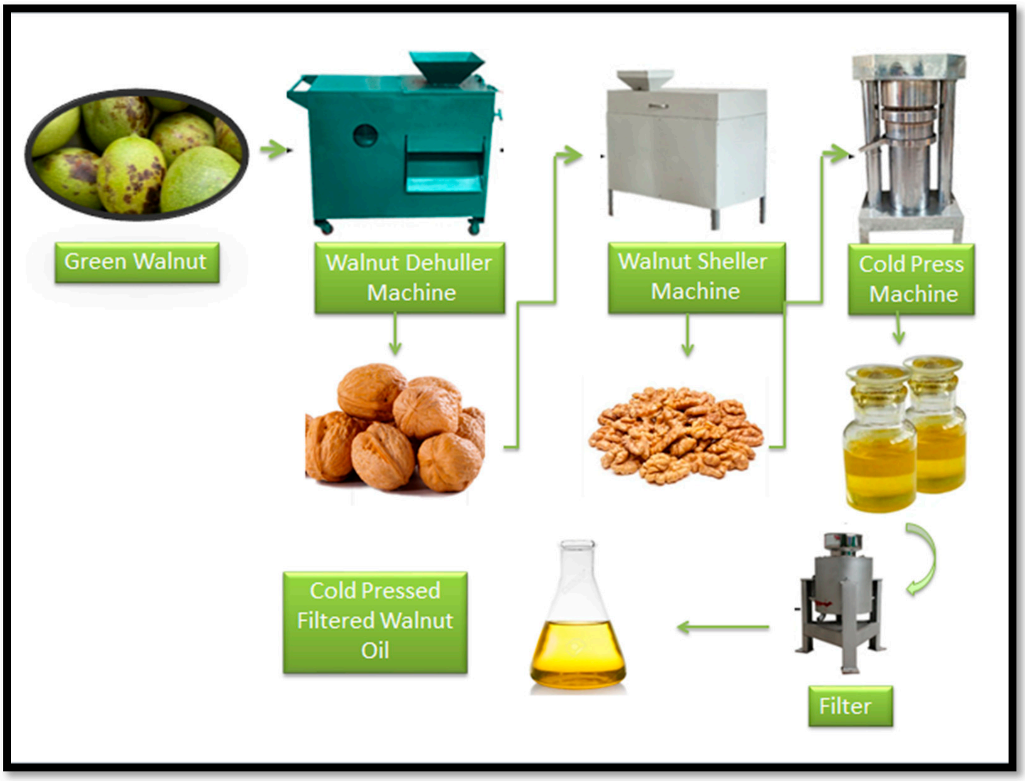

Figure 2. Graphical representation of cold oil extraction process.

To extract oil from oilseeds, there has been recently a renewed concern in employing mechanical-screw and continuous presses. In the case of new edible oils, although screw pressing will not totally replace solvent extraction in commodity oilseeds because it recovers a lower proportion of oil, it does provide a simple and dependable method of processing tiny amounts of seed [32]. The performance of a screw press is determined by the process used to prepare the raw material, which includes a variety of unit activities, such as cleaning, cooking, cracking, drying, or moistening to the desired moisture content. Although applying a heat treatment before or during pressing improves oil recovery, it can also have a negative impact on oil quality by raising oxidative indices. Another important process variable is the seed moisture content at the time of pressing. Moisture is known to increase the flexibility of seed materials and to aid press feeding by acting as a barrel lubricant. High moisture content, on the other hand, may result in poor oil recovery due to insufficient friction during pressing [33].

3.2. Solvent Extraction

Due to its quick evaporation and low energy cost, solvent extraction is commonly utilized in the industrial extraction of oils [34]. In 1855, carbon disulfide was utilized as a solvent in the first solvent extraction [35]. Hegzan is a frequently used solvent, despite the fact that a variety of other solvents have been employed in the past. A multicomponent solid, a solvent, is used in solvent extraction to dissolve the desired substance in the medium. This extraction process works by dissolving the oil in a solvent and then removing it from the environment. Solids have a slow diffusion rate, making it difficult to achieve equilibrium in this process [36]. It is the most ancient method of extraction, and the most used strategy as a benchmark for the process efficiency of other extraction methods, with the exception of a few niche applications, such as the extraction of thermo-sensitive compounds [37]. In general, this extraction process (solvent extraction) can remove roughly 99% of the oil contained in seeds, making it a preferred extraction method, while the solvent employed is recovered to about 60%. However, it requires long extraction durations, raises economic and environmental concerns, and cannot be agitated during the extraction; additionally, there is a risk of thermal breakdown of the target compounds due to high temperatures, no selective extraction is possible, and automation may be challenging [38]. The contact of oil with a solvent, the structure and the amount of solvent to dissolve the oil, the solution's ability to be easily removed from the environment, and temperature are all factors that affect solvent extraction. Oil is usually localized between cells; therefore, size reduction pre-treatment is required, so the surface area is increased, and the contact area is also increased. Additionally, the lower boiling point solutions are preferred [39]. Miraliakbari and Shahidi [40] reported that the Folch (chloroform/methanol, $v:v$ = 2:1) method applied for the extraction of walnut oil resulted in a greater oil yield. Crowe et al. [41] also evaluated the oxidized products of walnut oil extracted with hexane, methylene chloride, and Folch solution and discovered that the Folch method removed considerably more volatile chemicals. According to studies, the solvent extraction process yields 11.5% more oil in low- and medium-fat seeds than the cold-press method [42,43]. As a result, the extraction method has an impact on nutrient composition, flavor, and antioxidant properties. Furthermore, consumers are concerned about the other best options for the production of oil [44].

4. Green Extraction Technologies

Oil is extracted from seeds using traditional methods, such as expeller pressing, hydraulic pressing, and solvent extraction. Sometimes, the oil is simply mechanically pressed off the fruit and nut and utilized straight away without any further processing, as in case of the virgin olive oil. Due to its good solubilizing properties, ease of oil recovery and narrow boiling point (63–69 °C), hexane, as a petroleum ether, is frequently used for oil extraction. Unfortunately, such solvents have safety, environmental and health issues. Solvent alternatives are being sought by researchers who want to preserve oil quality and yield. Therefore, using green bio-based solvents as an alternative for oil extraction is a possibility. Furthermore, other emerging extraction methods have been developed using various green extraction technologies. Below, we provide an overview of the various technologies.

4.1. Bio-Based Solvents

Bio-based solvents have similar properties to those of standard solvents, which are derived from crop residues as renewable resources [45]. Fermentation or chemical transformation procedures can produce these solvents from four different cellulosic biomasses, including starch/sugar, protein, lignocellulosic, and oil based, as well as other food and forestry wastes [46]. Solvents can also be divided into groups based on their functional groups (ethers, esters, alcohols, and terpenes). The benefits of bio-based solvents are that they have high solvent strength, environmental safety, low cytotoxicity, and quasi and biodegradability, while their disadvantages include high boiling point, high viscosity, high cost, and off-flavor production [47]. Chaabani et al. [48] classified the lipid classes of Pistacia lentiscus oil generated by hexane and different bio-based solvents. These authors claimed that extracts made with 2-methyltetrahydrofuran, ethyl acetate, dimethyl carbonate, p-cymene, and hexane had greater triacylglycerols. Because alcohols have a high solvating activity for polar lipids, isopropanol and ethanol extracts are higher in phospholipids. The lipid class profile of ethyl lactate, limonene, and -pinene, on the other hand, is distinct, with considerable monoacylglycerol and diacylglycerol concentrations. The high boiling points of these solvents ranging from 154 to 155 °C may promote lipid breakdown and impair solvent efficiency. The most appropriate solvents may include 2-methyltetrahydrofuran and ethyl acetate, which can be used for hexane substitution after looking at the lipid content and global yield [48]. Only ethyl acetate and ethanol, out of all of the aforementioned bio-based solvents, are considered to be of food grade according to Directive 2009/32/CE of the European Parliament, which was issued on the 23rd of April.

4.2. Supercritical and Subcritical Fluid Extraction

Supercritical fluid extraction, a strong technology for separation processes, has sparked attention in the field of natural material extraction. Superior mass transfer capabilities and the capacity to alter solubility using system pressure, thermal efficiency, or a perpetuate are among the benefits of supercritical fluid. CO_2 is commonly used because of its near-room critical temperature, low cost and lack of residual issues [49]. It is also odorless, colorless, nontoxic, nonflammable, and noncorrosive. Supercritical and subcritical fluid extraction take advantage of the solvent characteristics to improve analyte extraction from samples. In contrast to the subcritical, the temperature and pressure employed for supercritical fluid extraction are higher than the critical point [50]. Oil extraction from natural sources is considered one of the most promising applications proposed for supercritical fluid extraction. In addition, it could be used to selectively extract certain end products with improved functional and/or nutritional properties for use in generating new designed foods to produce high extraction yields and quality [51]. Additionally, the fatty acid ranges for oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:3) were defined as 14.3 to 26.1% by weight, 49.3 to 62.3% by weight and 8.0 to 13.8% by weight, respectively. Oliveira et al. [25] investigated the compositions of free fatty acids, sterols, triglycerides, and tocopherols in walnut oil extracted by supercritical CO_2 extraction and Soxhlet extraction, finding that they were similar to those of oil obtained with n-hexane, and the oil extracted by supercritical CO_2 extraction was clearer than that extracted by n-hexane.

Subcritical fluid extraction is a relatively recent technology for extracting less-polar chemicals using only water in a short 30 min extraction time (Figure 3). At a temperature between 100 and 374 °C, subcritical water is kept in a liquid condition under high pressure [52]. During the extraction, high temperatures reduce the viscosity and density of the solvent, allowing it to penetrate deeper into the sample matrix [53]. Moreover, there is an improvement in diffusivity between gas and liquids with the increase in temperature [54]. Pereira et al. [55] reported that subcritical extractions are considered clean methods due to the solvent being able to be recovered and re-used in the process in a closed loop.

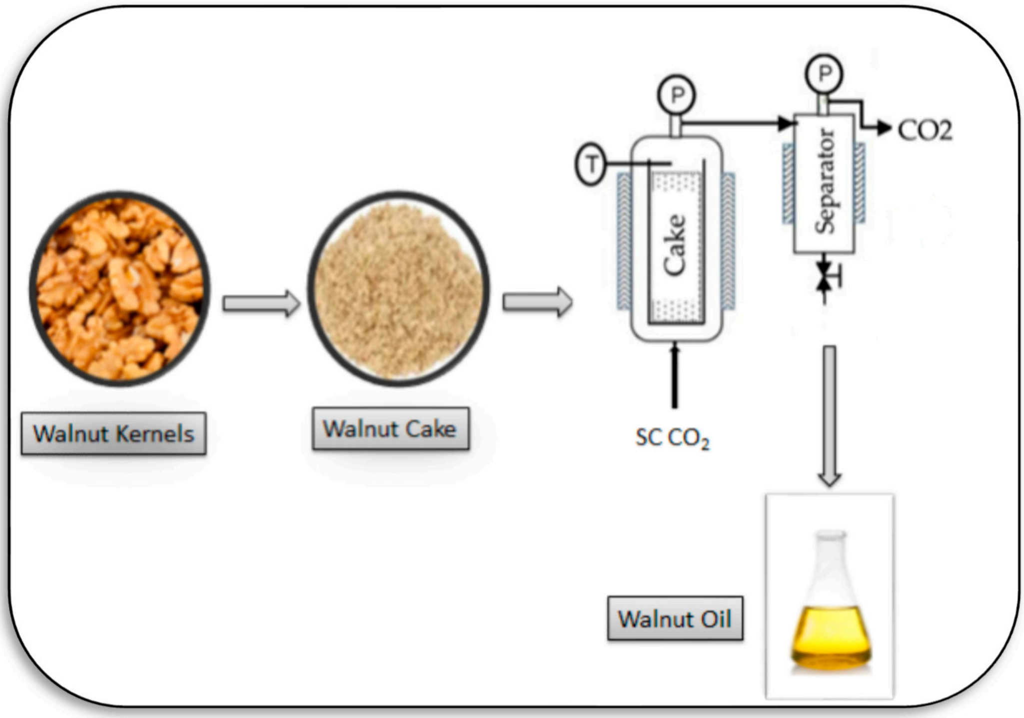

Figure 3. Supercritical fluid extraction method.

Because they are colorless and affordable, propane and N-butane are the most often employed subcritical fluids in oil extraction [52,56]. They also have strong lipophilic compound dissolving power and can be employed at lower critical temperatures and pressures, resulting in a high-quality product with minimal damage [57]. Subcritical fluid extraction has a number of advantages over traditional extraction methods, including a shorter extraction time, a smaller solvent volume, increased efficiency and safety, better oil quality preservation due to the lower extraction temperature, and cheaper utility and total investment costs [58]. Moreover, the reduced subsequent refining procedure is related to the little remaining solvent in the oil [56]. Zanqui et al. [59] used subcritical n-propane to extract Brazil nut oil. With 6 MPa, 60 °C, and 60 min, the highest extraction yield of 63.1% was obtained utilizing Brazil nut particles with a granulometry of 1.40 mm. The yield of this extraction was 8.4% lower than that of solvent extraction. The subcritical fluid extraction, on the other hand, was 15.5 times faster than the usual approach. However, both techniques had identical fatty acid compositions, indicating that subcritical fluid extraction retains the purity of fatty acids. In contrast to the oils recovered by subcritical fluid extraction, the oils extracted by solvent extraction showed the presence of oxidized triacylglycerols, which can cause health concerns when consumed. Furthermore, when compared to conventional extraction, the amounts of tocopherols, squalene, and phytosterols in oils extracted using subcritical fluid extraction were higher (24, 238, and 87%, respectively). This could be due to the photosensitive chemicals' degradation or the lower affinity of the solvent utilized in solvent extraction. In the Xinjiang region, Qi et al. [58] looked at how subcritical fluid extraction affected the oil quality of three different native almond cultivars (SC-ZP, SC-9 and SC-TX). SC-ZP had the largest fat, protein, and total amino acids content, as well as the highest extraction yield (41.5%); however, it was only 6.1% higher than cold-press extraction. Both approaches provided fatty acid compositions that were not significantly different. The values for iodine, peroxide, and saponification obtained with the subcritical fluid extraction were lower than those obtained with the cold press, indicating that the oil extracted with subcritical fluid extraction had better antioxidant activity. As a result, subcritical fluid extraction might be useful for producing high-quality almond oils.

4.3. Ultrasonic-Assisted Extraction

Ultrasonic-assisted extraction is also simple and is relatively low priced when compared to other new unconventional extraction techniques; it has a high efficiency that stems from machine-driven effects; it allows for improved solvent penetration; it is not reliant on the solvent used; it employs a lower solvent/solid sample ratio; and it is not dependent on the solvent used (Figure 4). It also cuts down on extraction times and temperatures, reducing the amount of thermolabile chemicals lost. Ultrasound waves have frequencies between 10 Hz and 20 kHz, which are greater than audible [60]. This extraction method uses the energy of ultrasonic waves to cause compression and expansion cycles [61]. A series of microbubbles form, grow, and collapse inside the liquid phase during the transmission of this mechanical vibration, which is known as acoustic cavitation [62]. When the ultrasonic energy is insufficient to keep the bubble in the vapor phase, the bubble implodes [60]. A horn transducer and an ultrasonic water bath are used in an ultrasonic probe system. The fact that the transducers are not in direct contact with the sample is the major advantage of the technique [63]. Wong et al. [64] investigated the influence of ultrasonic-assisted extraction and ethanol on hazelnut oil extraction and it was found that ultrasonic-assisted extraction obtained the greatest oil production of 79.8% at 380 °C for 90 min, which was 51.2% higher than other treatments. Furthermore, the walnut oil prepared with ultrasonic-assisted extraction had a lower quantity of free fatty acids, which, when present in large concentrations, cause an undesirable taste and odor. In terms of oil oxidation, the ultrasonic-assisted extraction resulted in a drop in iodine value, most likely due to a reduction in the number of unsaturation sites. Due to the generation of free radicals and volatile chemicals, the peroxide value increased as the ultrasonic extraction temperature increased, reducing the extracted oil's oxidation stability.

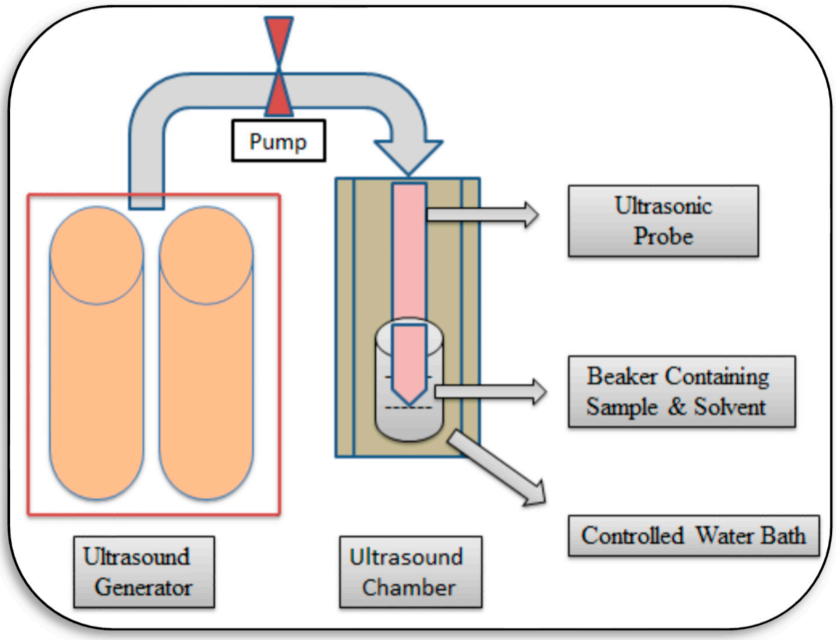

Figure 4. Ultrasonic assisted extraction.

4.4. Microwave Assisted Extraction

It is a non-ionizing electromagnetic radiation with a frequency (300 MHz to 300 GHz) that is used to directly alter the components of the sample [65]. The mechanics of ionic conduction and dipole rotation convert electromagnetic energy to heat [66]. The principle of microwave assisted extraction is that high pressure on cell walls and organelles causes physical changes in the matrix, which lead to solvent diffusion across the sample matrix, and thus a solute is released from the sample matrix into the solvent, enhancing extraction efficiency. There are two types of microwave-assisted extraction instruments in terms of target compound extraction conditions: open vessel and closed vessel. In an open vessel, the chemicals are extracted at barometric pressure, and the solvent is refluxed, while in a closed system, controlled temperature and high pressure are employed. The solvent can be heated above its critical boiling point [37]. The effects of microwave power (250–450 W), liquid-to-solid ratio (4–8 mL g^{-1}), duration (40–60 min), and temperature (65–85 °C) on tiger nut oil extraction were investigated by Hu et al. [67]. The results showed that microwave-assisted extraction with a mixture of petroleum ether and acetone yielded a 24.1% oil extraction yield, which was 24.5% less effective than solvent extraction. Microwave irradiation can also increase the breaking of the structure and lessen the interaction of bioactive chemicals in tiger nuts, resulting in a rapid release of bioactive substances into the oil. This could explain why oil extracted by microwave-assisted extraction versus solvent extraction has more beneficial components (tocopherol, total phenolic, phytosterols, and phospholipids). As a result, the oil obtained through microwave-assisted extraction is of higher quality and more resistant to oxidation (Figure 5).

4.5. Enzyme-Assisted Extraction

Enzymes are biodegradable, non-hazardous, and have the ability to catalyze reactions with a high selectivity [68]. In mild conditions, several enzymes can dissolve or disintegrate the cell wall and membranes in aqueous solutions. Enzyme-assisted extraction is considered a promising technology that employs particular enzymes to aid in the extraction of compounds via the hydrolysis of polysaccharide and cell wall cracking, because some molecules are scarcely accessible to a solvent under typical extraction conditions [69]. Enzyme-assisted extraction offers benefits, such as economical operating costs and rapid extraction [70]. Moreover, the chemical makeup, cell wall structure, and placement of the oil droplet within the seed must all be taken into consideration when choosing an enzyme [71]. In addition, the oil-to-water ratio should be taken into account during oil extraction optimization trials in addition to more general factors, such as pH, temperature, particle size, and enzyme concentration. Enzymes require moisture to function, and low moisture levels in oilseeds cause the production of thick suspension, which inhibits enzyme activity. Furthermore, the enzymatic reactions are carried out under mild circumstances, which is beneficial to the extraction of thermolabile chemicals and saves a lot of energy [72]. Nonetheless, emulsification of the extracted oil is unavoidable, and this comes at a hefty expense. Gonzalez-Gomez et al. [73] investigated the best settings for enzyme-assisted extraction to produce superior walnut oil and also reported the optimal conditions for walnut oil extraction (pH 4.0, temperature 41.5 °C, and 86 min), with a yield of 75.4%. The enzyme-assisted extraction extracted walnut oil had a five-fold higher antioxidant potential than the solvent extraction extracted oil, indicating improved oil stability, which could be due to the increased total tocopherol content achieved with the new alternative technology. Moreover, fatty acids (MUFA and PUFAs) were better conserved under enzyme-assisted extraction conditions because polyunsaturated fatty acids were degraded during extraction with organic solvents. As a result, the oil extracted from walnut kernels utilizing enzyme-assisted extraction was more oxidatively stable and of higher quality than oil produced using the traditional approach. Commonly used enzymes for enzyme-assisted aqueous extraction from some walnut kernels include Alcalase, As1398, protizyme, papain chymotrypsin, nutrias, protamex and trypsin [74]. Typically, protein surrounds oil droplets since it is a key component of the cell wall. Proteins and pectin made up the majority of the cell walls in walnut kernels, rapeseed oil and soybean. Thus, increasing oil output was achieved by degrading these components utilizing combinations of protease, cellulase, pectinase, and other enzymes [71]. Despite having a number of benefits, the usage of enzyme-assisted extraction is still constrained by the lengthy processing time and challenging drying procedure following enzymatic treatment. The need for a large quantity of enzyme (often >1% of the weight of the oilseed ingested) contributes to its expensive price. Moreover, the development of such procedures has been constrained by the lack of commercially available enzymes. A further issue with enzyme-assisted extraction is that it is highly challenging to prevent the oil from becoming emulsified, necessitating a post-extraction de-emulsification phase in order to recover and improve the oil output [75]. The aqueous enzymatic emulsion de-emulsification approach was utilized by Tabtabaei et al. [76] to destabilize the oil in water emulsions so that free oil could be recovered before being used industrially. A comparison between different extraction technologies of walnut oil, including the advantages and disadvantages, is tabulated in Table 2.

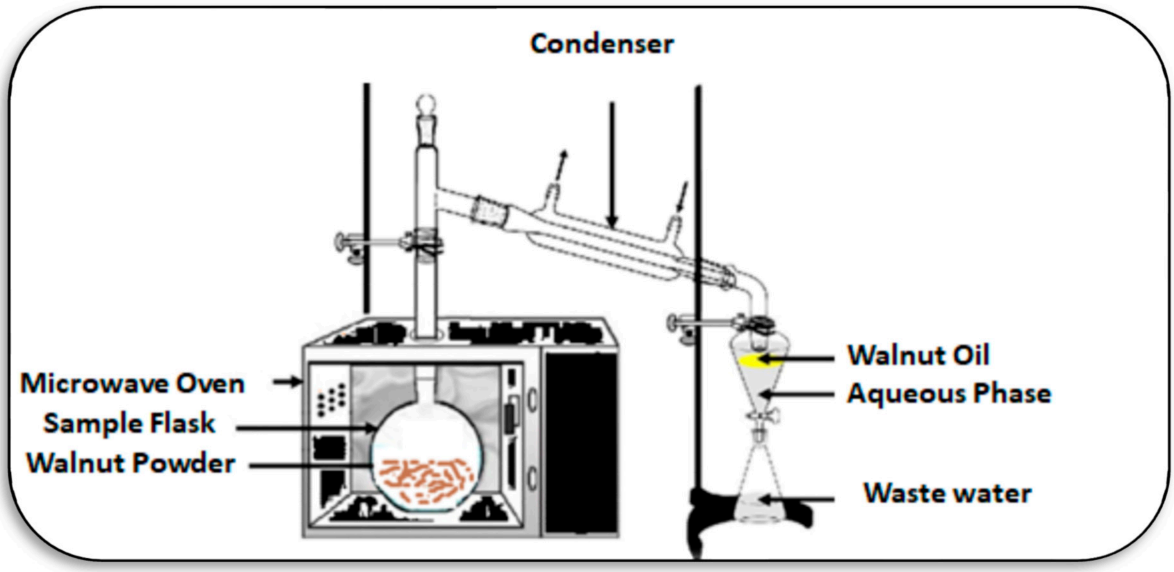

Figure 5. Microwave assisted walnut oil extraction.

5. Applications of Walnut Oil

Walnut oil has recently attracted the attention of consumers and food scientists due to its high nutritional value, sensory attributes, and nutraceutical potential, and it is quickly becoming a popular food product in a number of developed and developing countries. Walnut oil (an expensive cooking oil) is used in a variety of food preparations, including cold meals, because it is a dietary supply of important fatty acids (Huffman et al., 2011) [77]. Walnut oil is edible, pale in color, has a delicate flavor and has a nutty flavor. Walnut oil is often used to make salad dressings since the oil emulsifies sauces. It is not used for cooking or the heat treatment of products because of the presence of unsaturated fatty acids (70%) that induce oxidation and a disagreeable taste as well as aroma. Walnut oil is an essential component of the nutraceutical sector as an alternative health care treatment due to its high unsaturated fatty acid content, particularly linoleic acid, oleic acid, and linolenic acid [78]. According to epidemiological studies, walnut oil not only decreases blood cholesterol, but it may also be utilized as a nutrition and health care oil (Zhao et al., 2010) [79]. In this regard, more information about the green extraction technologies in agriculture can be found in the works of Ferreira et al. [80], and Desai et al. [81].

Table 2. Overview of different extraction technologies of walnut oil with advantages and disadvantages. References are provided for the various statements.

Extraction Technology	Advantages	Disadvantages	Refs.
Cold-Press Extraction	Hydraulic extraction method Consumes less energy Eco-friendly High quality oils at low temperatures	Low Production Hard to extract uniform quality of oil	[31,82]
Solvent extraction	Inexpensive method, but very simple Temperature during the extraction system could be maintained	Requires excessive extraction times Uses large amounts of extractants (solvent) No need for agitation to accelerate extraction process Compound sensitive to heat may be thermally decomposed	[82,83]
Supercritical and Subcritical fluid extraction	Solvent (CO_2) is inexpensive For all methods, solvent recycling could be achieved Pure extraction yield could be obtained	Desired compounds may loss with improper solvent selection Highly expensive because it requires specialized equipment	[75,84]
Ultrasonic-Assisted Extraction	High efficiency for large-scale commercial applications High oil yield, high extract quality, and reduced solvent consumption Easy to handle with reduced working time	This method depends totally on ultrasound unit Oil extraction is weak Existence of a dispersed phase may contribute to an ultrasound wave attenuation	[63,64]
Microwave-Assisted Extraction	For both laboratory and industrial scales is applicable High returns on capital investment are expected Less time consuming than conventional methods	Very poor efficiency for solvents or non-polar target compounds or for extremely viscous solvents For heat sensitive compounds is not appropriate Difficult to operate and expensive equipment	[37,67]
Enzyme-Assisted Extraction	Higher extraction yield Higher quality of extract Oxidation stability Eco-friendly	High cost Non-availability of enzymes on a commercial scale	[71,73,74]

6. Walnut Crop Residues and Their Valorization

The agricultural sector is very rich in wastes and/or restudies, which can be used in several industries. So, turning wastes into useful by-products can be considered a "true treasure" [85]. Walnut crops are really a treasure under different levels of its production and consumption (Figure 6). It is reported that approximately 40–60% of the weight of the walnut fruit are waste by-products that generate during walnut production [86]. These large amounts are beneficial wastes due to their easy availability, high hardness and sturdiness, low cost, least moisture content, and biodegradability [87]. These wastes also have several applications in the pharmacology and chemical industries, the general marketing of nuts, the food and beverage industry, the metal industry, the industry of cosmetics, perfume, oil extraction, and the bio-sorbent of hazardous materials, as well as in the field of energy [86,88–91]. The industry of oil extraction of walnuts itself is considered an important source for producing wastes from walnuts depending on the used pretreatment and processing technologies [92]. More potential of solid wastes from the walnut industry were confirmed, such as bioactive compounds and bioherbicides [93], solar energy-driven water evaporation [85], converting into value-added carbon nanomaterials [94], and producing biochar for removing pollutants from water/wastewater [95] or polluted soils [96].

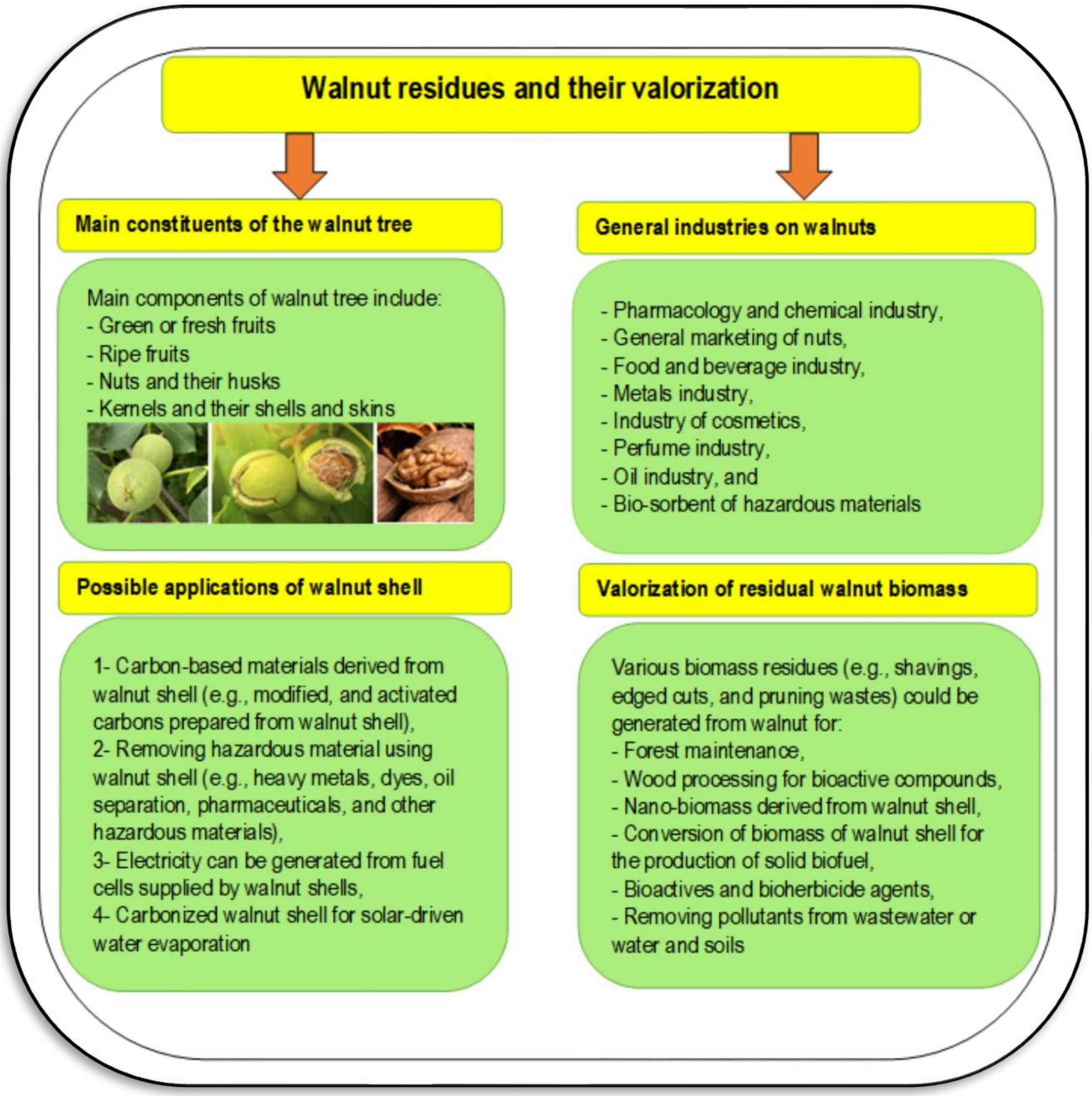

Figure 6. Walnut crops are one of the most important plants, which several industries can establish based on the walnut wastes, including pharmacology, food industry, cosmetics, metals, and perfume industry. Sources: [86,89,90].

7. Conclusions

In this review, essential information regarding oil extraction was provided, and the benefits, drawbacks, and operating principles of traditional and green extraction techniques were assessed. Due to the wide range and lengthy history of extraction as a separation technique, it is only used for working oil extraction, particularly when using a cold press, cold squeezing, or cold pressing. The cold press is preferred because of its many application areas, ease of use, lack of labor, low cost, environmental friendliness, absence of harmful organic solvents, and capacity for high-quality production. However, new extraction technologies offer an effective alternative for recovering oils from nuts. Supercritical fluid extraction, subcritical fluid extraction, ultrasonic-assisted extraction, microwave-assisted extraction, and enzyme-assisted extraction mitigate some of the limitations of traditional extraction processes by using less time and energy, using fewer organic solvents, and producing an oil with good antioxidant activity, resulting in less extraction of photosensitive bioactive components. Several studies have already reported encouraging results from the use of such new techniques to recover oils from nuts (walnuts). Several studies discovered different oil yields for different nut classes, different circumstances, and different extraction techniques, demonstrating that no single methodology or set of variables can be applied globally. Nonetheless, the evolving technologies described in this study appear to increase oil quality when compared to older processes.

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