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Review Article

Subcritical water extraction for phytochemicals from vegetables and vegetable waste: A review of recent advances

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Abstract
Subcritical Water Extraction (SWE) has emerged as an innovative and sustainable technique for extracting valuable phytochemicals from vegetables. Under subcritical water conditions, by which operating water at elevated temperatures and pressures below its critical point, SWE enhances its ability to dissolve a broad spectrum of bioactive compounds, including polar substances like glucosinolates and phenolic acids, as well as nonpolar compounds such as flavonoids and carotenoids. Compared to conventional solvent-based methods, this green extraction approach has the benefit of higher efficiency in extraction and reduced environmental impact, along with lower capital costs. SWE has been successfully applied to recover important phytochemicals, such as sulforaphane from broccoli and quercetin from kale. Extraction yields and phytochemical stability are influenced by factors including types of plant, temperature, pressure, solid-to-solvent ratio, extraction time, and pH conditions. The valourisation of vegetable waste materials like carrot peels, cauliflower stems make SWE align towards circular economy principles. Despite scaling up challenges, as generally seen in equipment design and energy consumption, SWE has a huge potential for broad industrial use in areas of food, nutraceutical, pharmaceutical and cosmetic. This review focuses on recent advances, the synergistic effects, environmental and economic merits of the SWE technology and is followed by its prospects in this field.

Keywords: Subcritical Water Extraction, Phytochemicals, Vegetables, Green Extraction

Introduction

Vegetables are a vital source of essential nutrients, including vitamins, dietary fibre, proteins, and minerals necessary for human growth and development [1]. Beyond these nutrients, vegetables are rich in phytochemicals, as seen in bioactive, non-nutrient plant compounds generated through secondary metabolism that offer powerful antioxidant effects and contribute to health promotion and disease prevention [2-6]. Compounds such as polyphenols, flavonoids, and glucosinolates have demonstrated potential in delaying chronic diseases like diabetes, cancer, and cardiovascular disorders [7, 8, 9].

The increasing prevalence of lifestyle-related chronic conditions worldwide has escalated the demand for phytochemicals in food products, nutraceuticals, and pharmaceuticals [9]. Traditional extraction methods, including Soxhlet extraction and maceration, rely heavily on organic solvents, which are often toxic, non-renewable, and environmentally harmful [10]. Moreover, these methods can be inefficient, selective, and sometimes degrade sensitive phytochemicals due to prolonged exposure to heat [11].

Green extraction technologies have emerged to respond to these limitations, aiming to reduce environmental impact while improving extraction efficiency and product safety. Among them, Subcritical Water Extraction (SWE) has gained significant attention as a sustainable alternative. SWE utilises water at elevated temperatures (120–374°C) and pressures (typically 5–25 MPa) to alter its physicochemical properties, enabling it to dissolve both polar and moderately nonpolar compounds effectively. This process eliminates the need for organic solvents, achieving higher extraction yields with a lower environmental footprint [10].

This process is solvent-free, and environmentally benign. Moreover, it offers distinct advantages over traditional and other advanced extraction methods. Unlike conventional solvent extraction, SWE eliminates the use of hazardous organic solvents, reducing environmental impact and improving product safety [10]. Compared to supercritical CO_2 extraction, which primarily targets nonpolar compounds, the adjustable polarity of SWE enables efficient recovery of a broader array of bioactives without co-solvents [12]. The technique also benefits from higher extraction efficiency, shorter processing times, and lower capital and operational costs relative to many green extraction alternatives [13].

The application of SWE for phytochemical recovery from vegetables has demonstrated notable success [14] . For instance, a study reported that the extraction using SWE yielded approximately 200 mg of phenolic compounds from onion skin under controlled heating and pressurisation conditions [15]. SWE has also proven effective in extracting bioactive compounds from various vegetable sources [16]. Consequently, SWE represents a novel and sustainable approach for extracting phytochemicals not only from fresh vegetables, but also from vegetable waste streams [17]. This environmentally friendly and efficient technique offers significant advantages over conventional extraction methods. Moreover, SWE supports circular economy principles by valourising vegetable by-products into phytochemical-rich extracts, advancing sustainable practices in the food and pharmaceutical industries [18].

Despite these advantages, challenges remain in scaling up SWE technology for industrial applications, particularly in equipment design, optimising energy consumption, and refining the process conditions to preserve the integrity of thermosensitive compounds. Addressing these challenges is critical to fully realise SWE's industrial potential.

Accordingly, this review provides a comprehensive and critical review of recent advances of SWE as a viable and effective technique for the phytochemical recovery from vegetables and associated food by-products. The paper explains the principles of SWE, its main concepts, among the changes in water properties under subcritical conditions, translated to the basis of the unusual solvent possibilities of SWE. Also, it compares the SWE with conventional and green extractions by outlining its advantages, disadvantages and industrial relevance. This review combines with the recent research findings and investigates not only the environmental and economic value of SWE but also its relation to the principles of the circular economy, as well as the problem of scale-up and deals with the issue of compound instability. Ultimately, the article identifies knowledge gaps and future directions required to streamline SWE technology and enhance its wider application in the food, nutraceutical, pharmaceutical, and related industries.

Principle of subcritical water extraction

Subcritical Water Extraction (SWE) is an advanced green extraction technology that utilises water as a solvent at elevated temperature (typically 100°C to 374°C) and pressure below its critical point (5 to 25 MPa) to maintain it in a liquid state [12,19]. Under these subcritical conditions, water undergoes significant changes in its physical and chemical properties, transforming it from a highly polar solvent at ambient conditions into a medium capable of dissolving a wide spectrum of bioactive compounds, both polar and moderately nonpolar [17, 20, 21]. These conditions emulate the role of organic solvents like methanol and ethanol with no associated environmental risk.

The water phase diagram (**Figure 1**) shows the distinct physical states of water, solid (ice), liquid, and gas (vapour) based on pressure and temperature, highlighting the subcritical and supercritical regions while addressing SWE. This diagram also illustrates the critical thermodynamic points where a phase change occurs, as the triple point (approximately 0.01°C and 0.006 MPa) and critical point (374°C and 22 MPa) to delineate the transitions between phases [22]. The subcritical region, indicated between the boiling point and critical point at high pressure (yellow-shaded zone), represents conditions where water remains in its liquid phase despite high temperatures, because the pressure was increased above atmospheric pressure [23]. The subcritical liquid phase is vital in SWE, as water, at this state, undergoes considerable physicochemical transformations. Here, its physicochemical character changes drastically and thus, water behaves as a tuneable solvent that can well dissolve both polar and strongly nonpolar phytochemicals. By maintaining water at temperatures typically between 100°C and

374°C and pressures sufficient to prevent vaporisation, the extraction process harnesses these altered solvent properties to improve mass transfer and solubility of target compounds [24]. On the other hand, beyond the critical point, water attains the supercritical state, possessing properties distinct from either liquid or gaseous phases, as SWE primarily exploits the liquid subcritical state to achieve green and efficient extraction. This phase diagram gives fundamental knowledge on the conditions under which SWE will be a handy and eco-friendly method of phytochemical extraction of vegetables [13].

Figure 2 presents a schematic diagram of a typical SWE installation, operating under controlled elevated temperature and pressure, ensuring liquid water remains in a subcritical state throughout the extraction. In this process, the vegetable matrix is loaded into a stainless-steel extraction reactor vessel (8). It is heated by an element (3) where immersed in an inner salt bath (2), ensuring uniform heat transfer. The isolation chamber (1) thermally insulates the system and maintains pressure conditions. The internal temperature is constantly controlled via the operation panel (7) through a temperature sensor (4). The mixer (5) stirs under the power of the stirring motor (6), which assures homogenous mixing that promotes solvent contact and mass transfer of the plant materials. This configuration is an exemplary setup that SWE employ elevated temperature and pressure to manipulate the solvent capabilities of water that minimises polarity, viscosity and surface tension, enabling the extraction of a wide phytochemical range with enhanced extraction efficiency [25].

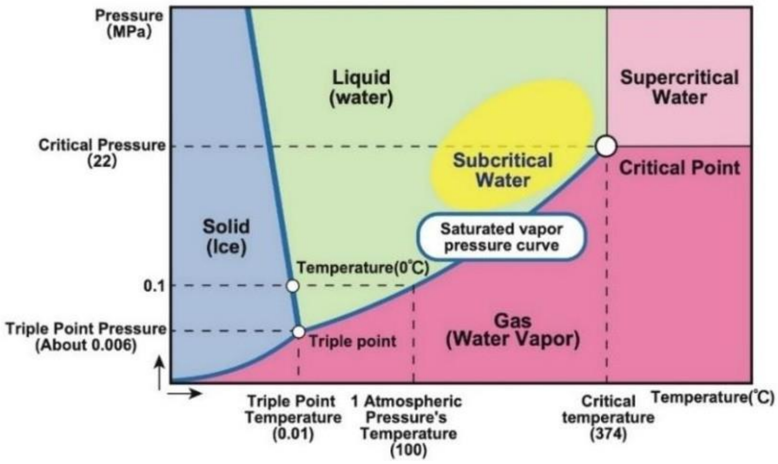

Figure 1. Water Phase Diagram
(source: https://www.jandwtrading.co.jp/)

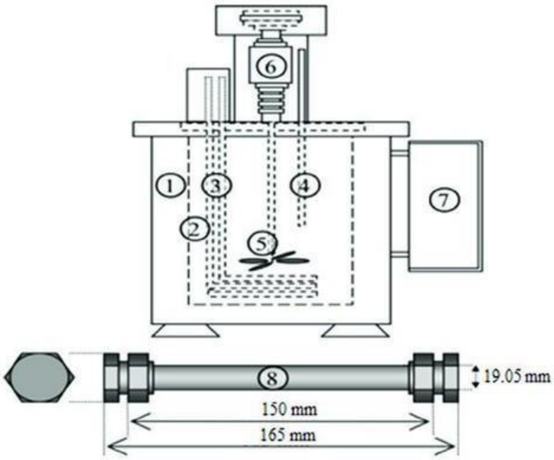

Figure 2. Schematic Diagram of The Subcritical Water Extraction Setup. (1) isolation chamber providing thermal and pressure insulation; (2) inner salt bath ensuring even heating; (3) heater (4000 W) supplying heat; (4) temperature sensor; (5) mixer for homogenisation; (6) stirring motor; (7) operation panel for controlling process parameters; (8) stainless steel reactor. (Source: Copyright © 2018 [25])

Changes in water properties (dielectric constant, viscosity, diffusivity)
A key factor empowering this enhanced extraction ability is the change in water's dielectric constant with temperature and pressure. The dielectric constant measures the polarity of the solvent. At room temperature, water's dielectric constant is approximately 80, becoming highly polar and effective at dissolving polar compounds [22]. However, as the temperature increases, and reaching subcritical temperatures, the dielectric constant drops sharply to approximately 27 at 250°C, approaching values comparable to organic solvents like methanol (~33) or ethanol (~24) at ambient temperatures [26]. This polarity reduction means water can dissolve less polar, and even nonpolar compounds such as carotenoids, flavonoids, and other hydrophobic phytochemicals thereby enhancing the extraction efficiency of diverse bioactive compounds [27].

Similarly, the viscosity and surface tension of water reduce substantially in the subcritical region, aiding rapid mass transfer since the solvent can infiltrate more actively into solid plant matrices to improve diffusion rates [27]. All these physicochemical alterations contribute to efficient extraction and fractionation of phytochemicals from complex vegetable tissues compared to conventional aqueous extraction [28].

Nevertheless, SWE has limitations. Although some more hydrophobic compounds can be solvated better, the uncompensated polarity of subcritical water is still substantially greater than that of pure organic solvents. This dynamic makes full recovery of highly nonpolar substances uncertain. Additionally, high temperatures applied during SWE may lead to thermal degradation or transformation of heat-sensitive phytochemicals, and decrease the extract quality and yield [29].

Recent advancements have focused on using modifiers and optimising extraction parameters to overcome these shortcomings. For example, to improve the solubility of hydrophobic compounds, small amounts of co-solvent may be added, such as ethanol or organic acids, to reduce the thermal degradation, by enabling milder extraction conditions [30]. Similarly, manipulating the pH of the SWE extraction medium can be an alternative to preserve its bioactivity [31]. For SWE, in mild acidic conditions (pH 4 to 6) in SWE, phytochemicals' stability and solubility can be enhanced. Thus, adjusting pH adjustment by adding weak acids or buffers before SWE extraction can extend the variety of compounds.

In addition, integrating SWE with other novel technologies like ultrasound or microwave-assisted technology has been utilised with success to increase the extraction yield at lower temperatures and shorter timeframes, reducing thermal risks. Continuous-flow SWE systems have also been developed to grant more control over the extraction parameters and enhance scalability for industrial purposes [32].

In a nutshell, the positive alterations in the dielectric constant, viscosity, and diffusivity of water at the subcritical conditions are the basis of the SWE efficacy. However, it is essential to recognise and deal with the limitations of the method, particularly in the case of nonpolar, heat-sensitive compounds, by controlling pH, the use of co-solvents and hybrid technologies in maximising the yield of extraction and enriching the profile of bioactive compounds.

General process flow of SWE
The process of SWE is a straightforward process to allow efficient extraction of bioactive compounds from plant materials. The preparation of the vegetable matrix begins with the preparation of raw materials, usually cutting or grinding, and drying. Since solvent access to the surface is increased, more contact is built. After sample preparation, the plant material is inserted into a high-pressure extraction vessel, which is built to withstand extreme temperatures and pressures used for SWE in the order of 5–25 MPa and 100°C to 374°C.

After the material is loaded into the extraction vessel, the system is heated and pressurised to subcritical conditions and maintains its liquid form. In this phase, the hot temperature softens plant cell walls, making the phytochemicals targeted for solubilisation accessible to the solvent. This process is notably faster and more efficient than conventional extraction methods during this stage [33].

The water and the dissolved compounds in solution are separated from the remaining residual solid. The liquid extract is subjected to concentration and purification processes, and the concentrated and purified extract is used. The resulting product is an aqueous extract for various applications in food and beverages, pharmaceuticals, and cosmetics containing phytochemicals that are known for promoting health [34]. **Figure 3** shows the general process flow of SWE.

Key parameters affecting SWE efficiency
The efficiency of SWE is greatly influenced by temperature, pressure, extraction time, and solid-to-solvent ratio. Temperature has a dual role in altering the physicochemical properties of water and facilitating the desorption and diffusion of phytochemicals from plant cells. Excessive temperatures can degrade heat-sensitive compounds, and thus, the optimisation process must be carried out

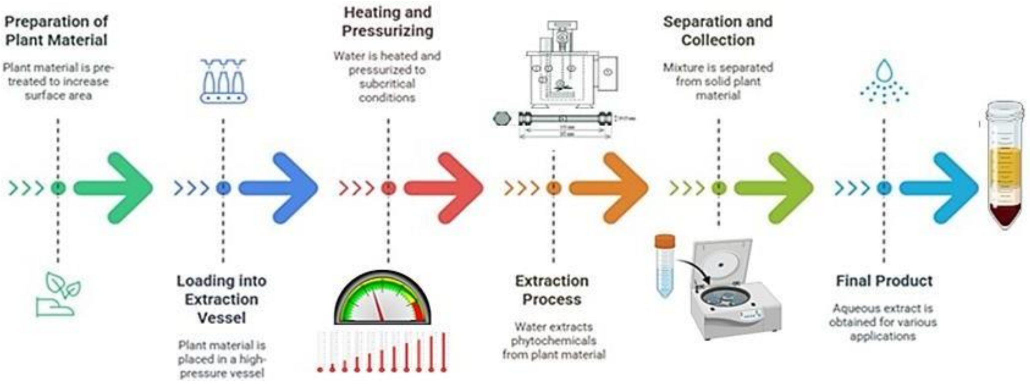

Figure 3. General Process Flow of Subcritical Water Extraction (SWE)

carefully [18]. Pressure is adjusted to keep the water in the liquid phase and has an insignificant effect on solubility, although it may influence system safety and equipment design [18].

Extraction time is another critical parameter, as long extraction times can yield more extract but pose a risk of compound degradation and energy inefficiency [35]. At a solid-to-solvent ratio, concentration gradients and mass transfer driving force will differ. The optimised ratio yields optimal recovery, while unneeded solvent consumption is reduced [36]. Furthermore, the scalability and performance of industrial setups of SWE systems (such as batch or continuous flow systems) also depend on their design. **Table 1** summarises the key parameters that affected SWE.

Temperature

Temperature is one of the most critical parameters in SWE, as it significantly influences the physicochemical characteristics of water, such as viscosity, surface tension, and dielectric constant [37]. Generally, as temperature increases, the dielectric constant of water decreases, enhancing its ability to solvate both polar and nonpolar compounds more effectively [38]. Previous studies have reported phytochemical extraction from various vegetables at temperatures ranging from 120 to 250 °C [12, 36]. However, certain valuable compounds are thermally unstable at elevated temperatures, possibly leading to reduced yields and diminished bioactivity due to thermal degradation [39]. Therefore, it is essential to optimise the extraction temperature for each phytochemical to maximise yield and preserve bioactivity. Many studies have demonstrated that temperatures between 120 and 250 °C to be the effective temperature to extract a wide range of phytochemicals, including phenolic compounds, flavonoids, and carotenoids from different vegetables. Nonetheless, high temperatures may adversely affect sensitive compounds, emphasising the need for careful temperature optimisation during SWE.

Table 1. Parameters in SWE and their impact on extraction efficiency

Parameter	Effect on Extraction	Typical Range
Temperature	Higher temperature increases the solubility of bioactive compounds	100°C to 374°C
Pressure	Higher pressure maintains water in a subcritical state, increasing extraction efficiency	Up to 25 MPa
Extraction Time	Longer extraction times improve yield but may affect compound stability	10 minutes to 2 hours
Solid-to-Solvent Ratio	Affects extraction efficiency and phytochemical yield	1:10 to 1:20 (w/v)
pH	Affects the solubility of compounds, especially in vegetables with varying pH	4 to 7 (neutral to slightly acidic)
Types of Plant Material	Influences the extraction efficiency due to the matrix structure and compound distribution	Leaves, stems, roots, peels, seeds, etc.

Pressure

Although temperature is the dominant parameter of SWE, pressure is also critical to keep the water in liquid form. Extraction pressure of SWE can range from 5 to 25 MPa, depending on the desired temperature [40]. Maintaining pressure is necessary to prevent water from vaporising at higher temperatures, which confirms the need to conserve the solvent properties of water [38]. Most compounds are not affected by pressure, but this factor affects the total safety and the energy consumption of the system, as well as how the extractor apparatus is designed [32]. In this way, optimising the pressure with temperature directly connects to system efficiency and safety.

Time

Extraction duration is another critical factor influencing SWE efficiency. Higher yield and mass transfer of bioactive compounds are obtained by prolonged extraction time, since deeper penetration of water into the plant matrix is possible during longer extraction duration [41]. It was found that heat-sensitive components, such as antioxidants, degrade under prolonged exposure to high temperature, which results in a decrease in the nutritional value and function of the extracts [32]. Therefore, it is necessary to identify the optimal extraction times for each vegetable and the phytochemical to obtain as much extraction as possible without compromising the structure of the component.

Solid-to-Solvent Ratio (SSR)

SWE relies on specific settings, such as the solid-to-solvent ratio. This setting affects how well the extraction works and how much plant chemicals are produced based on this ratio. SSR refers to the amount of plant material relative to the volume of water used in the extraction process [42]. Using more solvent compared to the solid plant material usually helps move target compounds into the solvent better by creating a stronger difference in concentration, which encourages diffusion. The relationship is not strictly linear and can become nonlinear; the more solvent used, the more dilution effects will reduce the yield. A study bt Mikucka et al. (2022) on distillery stillage showed that the maximum TPC and TFC were obtained in a ratio of 1:15 (w/v). Increasing the ratio to 1:15 gave a substantial extraction improvement, and beyond 1:30 or 1:50, little or less increase in extraction was obtained because equilibrium had been reached, and dilution effects occurred [43]. Therefore, the solid-to-solvent ratio became an important factor for getting more of the compounds while also making the extraction process more efficient, cost-effective, and environmentally friendly [44, 45].

pH

pH of the extraction medium is essential for the level of solubility and stability of bioactive compounds during SWE [15]. Water on the other side of the saturation line is more reactive. Even small changes in pH can produce big differences in the degree to which compounds are ionised and, therefore, the degree to which they are soluble [46]. Some phenolic acids and flavonoids will be more soluble in slightly acidic conditions, and very high or low pH conditions may lead to hydrolysis or degradation [47]. Polyphenols are stabilised in a more acidic environment, while Polyphenols in an alkaline solution will always degrade, dimerise and oxidise [48]. For instance, malvain 3-O-glucoside exhibits different colours under different pH conditions [49]. Heating significantly reduces the content of total anthocyanins when the pH is between neutral and alkaline [50]. The varied pH characteristics of vegetables (which commonly have naturally varying pH throughout the vegetable, depending on the type of tissue, either leaves or stems dictate the extraction. Around the pH range of about 4–7, it optimises the extraction while minimising unwanted side reactions [47]. SWE is intentionally controlled at its pH extremes to maximise yield without degradation of heat- and pH-sensitive phytochemicals.

Type of plant material

The type and composition of plant material significantly influence the SWE efficiency. Variations in cell structure, moisture content, and phytochemical concentrations among different vegetables affect the solubility and extraction efficiency of individual compounds [38]. For example, glucosinolates in broccoli and kale are present at relatively low concentrations in plant tissues and thus, optimised SW parameters is required to achieve higher extraction yields [51]. Furthermore, all vegetable matrices contain phenolic compounds, carotenoids and flavonoids, which require different extraction conditions to maximise the yield and bioactivity [12].

Key phytochemicals extracted from vegetables using SWE

SWE is employed in various industries to extract phytochemicals from vegetables. This method utilises specific temperature and pressure conditions under which water performs an extraction process that is both sustainable and preserves the integrity of sensitive compounds [12]. Phytochemicals such as phenolic acids, flavonoids, glucosinolates, carotenoids, and sulforaphane are compounds that carry various health benefits[52, 53].

Colouring, flavouring and aroma of vegetables contribute significantly to human health as they contain abundant antioxidant, anti-inflammatory and anticancer properties [54, 55]. It has become a popular method to produce high yields of these compounds from various vegetables for use in the food and pharmaceutical industries. Also, flavonoids and carotenoids have been shown to protect cells from oxidative stress [56], and lauded compounds such as glucosinolates and sulforaphane have been proven extensively to combat cancer [57]. Hence, the compounds found in berries possess attributes that reduce the risk of contracting chronic diseases, including cardiovascular and neurodegenerative disorders [58, 59]. **Table 2** shows the key phytochemicals obtained from vegetables and the extraction conditions.

Ongoing research suggests that SWE not only focuses on isolating phytochemicals but also facilitates the development of functional foods with numerous therapeutic potentials. SWE is widely employed across various industries to extract phytochemicals from vegetables, utilising specific temperature and pressure conditions that enable a sustainable extraction process while preserving the integrity of sensitive compounds. Important phytochemicals such as phenolic acids, flavonoids, glucosinolates, carotenoids, and sulforaphane exhibit diverse health benefits [52, 53]. These compounds contribute to the colour, flavour, and aroma of vegetables, and play a significant role in promoting human health due to their abundant antioxidant, anti-inflammatory, and anticancer properties [54, 55].

SWE has become a popular technique for producing high yields of these bioactive compounds from various vegetables for applications in the food and pharmaceutical industries. Flavonoids and carotenoids, for instance, have demonstrated protective effects against oxidative stress [56], in cells, while glucosinolates and sulforaphane are extensively recognised for their anticancer activities [57]. Furthermore, phytochemicals found in berries possess attributes that help reduce the risk of chronic diseases, including cardiovascular and neurodegenerative disorders [58, 59].

Phenolic compounds

The most extracted phytochemicals are phenolic compounds, such as flavonoids, phenolic acids, and tannins, which are well known for their antioxidant and anti-inflammatory properties. SWE has proven to be an effective method for extracting phenolic compounds from several vegetables and even vegetable byproducts. For example, SWE has been applied to extract total phenolic content from onion skins, achieving significantly higher yields compared to the conventional method [7]. Moreover, phenolic compounds extracted by SWE exhibit significantly greater antioxidant activity than those obtained through traditional methods, making SWE a promising technique to maximise the health benefits of phenolic compounds derived from vegetables [72].

Flavonoids

Flavonoids, a subclass of phenolic compounds, have been extensively studied for their antioxidant, anticancer, and anti-inflammatory properties. [15]. Kale, spinach, and broccoli are abundant in flavonoids, and these compounds can be easily extracted using SWE. The extraction of flavonoids is greatly enhanced at higher temperatures to allow the breaking down of plant cell walls to release these compounds into the solvent [38].

Glucosinolates

The sulphur-containing compounds present in cruciferous vegetables such as broccoli, kale and cauliflower are getting more attention due to their potential anticancer properties, primarily attributed to glucosinolates. SWE has been proven to be effective at extracting glucosinolates from broccoli, as high yields of glucosinolates are produced in a shorter period than conventional methods [73]. Extraction efficiency is strongly influenced by temperature and pressure higher temperatures enhance the solubility of glucosinolates in subcritical water [12]. Additionally, high pressure and combined thermal processing can retard degradation of glucosinolates, a common issue encountered during prolonged high-temperature or harsh solvent extractions [74]. Thus, SWE is an excellent method to extract glucosinolates from fresh and residual vegetable materials, contributing to the sustainable use of vegetable waste [38].

Carotenoids

The vegetable pigments β-carotene, lutein and zeaxanthin belong to the carotenoid group, which functions as fat-soluble substances found in carrots, spinach and sweet potatoes. Human health relies on these compounds to enhance vision and strengthen the immune system, and as sources of antioxidant protection [75]. SWE exhibits superior capabilities in extracting carotenoids from various vegetables, as compared to traditional methods that usually require organic solvents [76]. SWE provides an environmentally friendly solution to carotenoid recovery by replacing dangerous solvents, thereby reducing the overall pollution impact. The extraction of carotenoids requires temperature control and pressure adjustments because higher temperatures help carotenoids dissolve into liquids [10]. Studies indicate SWE functions as a method to obtain carotenoids from carrot and pumpkin residues, thus promoting sustainable management of vegetable waste materials [12].

Table 2. Phytochemicals extracted from vegetables and vegetable by-products

Vegetable	Extracted Phytochemicals with concentration	Extraction Conditions	Reference
Broccoli (*Brassica oleracea*)	Sulforaphane (42.3 µg/g DW) Glucosinolates (8.6 – 12.4 mg/g DW) Glucoraphanin (3.2 – 4.8 mg/g DW)	100-160°C, 10-30 min	[17, 60]
Onion Skin Waste (*Allium cepa*)	Quercetin (15.4 ± 0.4 mg/g DW) Quercetin-4'-glucoside (8.4 ± 0.1 mg/g DW) Kaempferol(3.2 – 5.7 mg/g DW) Total flavonoids (42.6 – 67.8 mg QE/g DW)	105-180°C, 5-30 min Optimal extraction at 145°C for 15 min;	[61, 62, 63]
Cauliflower leaves	Kaempferol derivatives(18.9 mg/g) Isothiocyanates(7.2 mg/g)	135°C with 10 min residence time demonstrated 2.4× higher bioactivity	[64, 65]
Kale stems	Flavonoids (26.8 mg/g) Glucosinolates (15.4 mg/g) Carotenoids (392 µg /g DW)	Continuous flow extraction at 140°C selectively recovered intact bioactive compounds	[14]
Tomato (*Solanum lycopersicum*)	Lycopene (5.2 – 8.7 mg/100 g DW) β-carotene (2.4 – 3.9 mg/100 g DW) Total phenolics (28.6 – 42.3 mg GAE/g DW)	150°C, 10 MPa, 20 min	[66]
Spinach	Lutein (65.3 mg/100 g) Total flavonoids (246.5 mg/100 g) Apigenin (170 mg/kg) Quercetin (50 mg/kg) Kaempferol (30 mg/kg) Capsanthin (12.4 – 18.7 mg/100 g DW)	Rapid extraction at 125°C preserved thermolabile compounds	[67, 68, 69]
Bell Pepper (*Capsicum annuum*)	β-carotene (4.6 – 8.2 mg/100 g DW) Total carotenoids (28.4 – 42.6 mg/100g DW) Total phenolics (18.4 – 26.3 mg GAE/g DW) β-carotene, (28.6 mg/100g)	145°C, 7 MPa, 20 min	[70]
Carrot leaves	Total phenolic content (42.83 ± 1.85 mg GAE/g DW)	110–230 °C), time (0–114 min)	[71]

Sulforaphane

Research on sulforaphane, a secondary metabolite in broccoli, continues due to its widespread popularity [77]. Studies have shown that vegetables in the Brassicaceae family, including broccoli, contain the isothiocyanate compound called sulforaphane [78]. In food science, sulforaphane is recognised as a naturally occurring compound with potent anticancer and health-promoting properties [74]. Sulforaphane appears in vegetables as the glucoraphanin glycoside compound alongside its isothiocyanate chemical structure [79, 80]. Broccoli contains sulforaphane/glucoraphanin as its main functional compound, with concentrations ranging from 44 to 171 mg per 100 g dry weight (DW) in broccoli and up to 1153 mg per 100 g DW in broccoli sprouts [81].

Comparison of SWE with conventional methods (soxhlet, ultrasonic, solvent)

The effectiveness of SWE in extracting bioactive compounds from vegetables is compared to Soxhlet extraction, ultrasonic-assisted extraction and solvent extraction in shown in **Table 3**.

Table 3 presents a comprehensive comparison between SWE and the three common extraction methods, Soxhlet, ultrasonic extraction and conventional solvent extraction. Referring to the comparison of SWE with these conventional extraction methods, it is clear that SWE possesses numerous benefits. SWE enables new rates of extraction, comparable to conventional extraction-based rates. Though commonly used, Soxhlet extraction is a time-consuming process that consumes heavy amounts of organic solvents compared to continuous solvent extraction, which is faster and does away with hazardous solvents [82]. Also, ultrasonic-assisted extraction is faster than conventional methods as sound waves are used to break the plant cell walls. However, ultrasonic-assisted extraction cannot match the SWE efficiency of extracting plant matrix compounds. Ethanol-based solvent extraction enables the recovery of diverse compounds. However, it is solvent-intensive and time-consuming, potentially compromising the stability of heat-sensitive phytochemicals SWE uses only water as a solvent under milder conditions, which better maintains bioactive compounds [76]. SWE, therefore, represents an improvement over other small-scale extraction techniques due to its efficiency and versatility."

Solvent usage

SWE emerges as the only extraction method that operates without solvents and utilises subcritical water as its primary processing medium. Thus, the environment can benefit significantly from SWE as it replaces harmful organic solvents with water in its subcritical state [76]. Soxhlet, ultrasonic, and solvent extraction all rely on organic solvents, that causes environmental damage and complicates waste disposal. Herrero et al. mention that SWE method is more environmentally friendly than other natural product extraction methods since numerous toxic organic solvents are eliminated using SWE [83].

Processing conditions

The operating conditions of SWE differ from those of conventional methods due to its distinct processing parameters. For example, SWE requires temperatures spanning from 100°C to 374°C, exceeding those used by conventional techniques that work with temperatures between ambient and boiling points. The expanded temperature range controls water polarity, thus permitting the extraction of compounds across the polar and non-polar spectra [84]. As for pressure, SWE sets itself apart from other extraction methods because a high pressure of up to 3000 psi is needed, alongside elevated temperatures [85]. SWE's pressure requirements create technical challenges. However, these same conditions also enable distinctive extraction capabilities.

Table 3. Comparison of SWE and conventional extraction methods

	Extraction Method			
Parameters	**SWE**	**Soxhlet Extraction**	**Ultrasonic Extraction**	**Solvent Extraction**
Solvent Used	Water (solvent-free)	Organic solvents	Organic solvents or water	Organic solvents
Extraction Time	Short to moderate (minutes to hours)	Long (hours)	Short (minutes)	Short to moderate (minutes to hours)
Temperature	100°C to 374°C (subcritical)	Ambient to boiling	Ambient to boiling	Ambient to boiling
Pressure	High pressure (up to 3000 psi)	Atmospheric pressure	Atmospheric pressure	Atmospheric pressure
Extraction Efficiency	High, selective for both polar and non-polar compounds	Moderate to high	Moderate	Moderate to high
Environmental Impact	Green, solvent-free, low waste	High (solvents used)	Moderate (solvents often used)	High (solvents used)
Cost	Moderate (due to energy usage)	High (due to solvent use and time)	Moderate (energy and solvent use)	Moderate to high (solvent and processing costs)
Health and Safety	Safe (no toxic solvents)	Risky (due to solvents)	Safe (depending on solvent)	Risky (due to solvents)

Efficiency and selectivity

SWE shows excellent extraction capacity and allows selection of both polar and non-polar compounds through changes in temperature, along with pressure control. While the extraction capability of Soxhlet and conventional Solvent Extraction remains moderate to high, SWE surpasses them by enabling the extraction of various compounds from one source [85]. Meanwhile, the extraction performance of ultrasonic extraction is moderate, and the system requires less processing duration. Chemat et. al explained that SWE enables extraction yields with equal or superior results while using less time than typical methods used for extraction [38].

Economic and safety considerations

SWE demonstrates average energy cost requirements for maintaining high pressure and temperature. However, its advantage lies in providing lasting economic benefits through eliminating solvent purchases and waste disposal expenses generally seen in traditional techniques [86]. The safety aspect of SWE adopts minimal toxic impairments since solvent-based extraction systems require hard-to-handle chemical substances. Zhang et al. explained that replacing organic solvents with water at subcritical conditions creates safer work environments with lower environmental exposure risks during extraction [87].

Processing time

Compared with Soxhlet extraction, SWE requires a significantly shorter processing time.Ultrasonic extraction offers competitive processing speed for certain applications. However, SWE achieves superior efficiency when processing materials over time frames ranging from minutes to hours [88]. Rodríguez-Meizoso et al. reported that SWE shortens extraction periods by 75% relative to traditional solvent extraction processes without generating inferior yield results [89].

Environmental and economic advances of SWE

Subcritical water extraction (SWE) or pressurised hot water extraction has gained substantial recognition for using hot water under pressure, providing environmental advantages and cost-effectiveness against conventional extraction methods. The advantages of this method support natural product industries while aligning with the sustainability objectives of green chemistry. This section reviews the environmental and economic advantages by consulting peer-reviewed studies to show its potential as a green extraction method for different applications.

Environmental advance 1: Solvent-free, green extraction

SWE stands out as the most environmentally advantageous extraction technique, as it eliminates the need of organic solvents. The extraction process through conventional methods requires hexane, methanol, acetone and petroleum ether solvents, leading to environmental pollution and health hazards and toxicity [76]. Rodríguez-Meizoso et al. established that organic solvents contribute notably to volatile organic compounds (VOCS) emissions, generating air pollution; therefore, they pollute water systems in improper disposal scenarios [89].

The extraction method of SWE depends solely on water, eliminating all environmental dangers that result from organic solvents. Plaza et al. explained that water offers several advantages as a green solvent, including its non-toxicity, non-flammability, availability, and environmental compatibility [76]. Final extracts from SWE methods do not contain dangerous solvent residues, which both improve product safety and avoid extra steps to eliminate solvent remnants [28]. Chemat et al. revealed SWE can replace traditional solvent extraction to decrease environmental indicators by as much as 90% in specific applications, highlighting its major environmental advantages [38].

Environmental advance 2: Reduced carbon footprint

SWE implements methods which decrease the emission of carbon dioxide during operation. Rodríguez-Meizoso et al. found that SWE is more energy-efficient than conventional methods across all stages, including production, extraction, and waste management [89]. SWE reduces total energy requirements because it eliminates costly and power-hungry recovery and recycling procedures that conventional extraction requires [76]. The extraction lifecycle of SWE processes achieves a lower carbon footprint as it eliminates the requirements for manufacturing solvents and their transportation, along with waste disposal [87]. When SWE systems are calibrated, they extract products quickly, leading to a decrease in energy consumption per manufactured unit. The optimised implementation of SWE extraction resulted in time savings between 30% and 75% relative to standard solvent extraction processes with equivalent or improved yields of crucial compounds [90].

Environmental advance 3: Waste reduction and minimisation

The implementation of SWE enables manufacturers to decrease waste output within extraction systems. Conventional extraction practices produce large waste effluents through solvent consumption because spent solvents need specialised processing before they can be discarded [91]. As organic solvents are removed, SWE reduces the number of hazardous wastes and reduces disposal expenses. The water waste produced by SWE systems consists of water-soluble plant materials, which are efficiently processed through standard wastewater treatment procedures [84]. This feature makes basic waste management processes became possible, leading to diminished environmental impact compared to organic solvent waste streams. In the SWE systems, operators have the option to recycle water, which improves their waste minimisation capabilities. Ong et al. demonstrated that proper water treatment enables recycling of SWE process water, reducing both water consumption and sewage output during extraction [86].

Economic advantage 1: Long-term cost effectiveness

The upfront spending on SWE equipment remains higher than standard extraction tools, but numerous economic factors make it cost-effective throughout its operational period. Firstly, ongoing operational savings will be substantial after the elimination of the cost of organic solvent. Mustafa et al. reported that solvent costs comprise 30-60% of total operational expenses in conventional extraction methods, depending on solvent type and recovery efficiency [85]. Plaza et al. revealed that SWE operations generate considerable economic advantages through eliminating solvent costs related to the purchase period, storage needs and disposal requirements, particularly among large extraction facilities [76]. Next, cost-effective facility design and operational needs can benefit from the reduced requirement for typical safety measures, which are normally required to handle flammable and toxic solvents (specialised storage, ventilation systems, explosion-proof equipment) [28]. The superior extraction capability of SWE plays an essential role in delivering economic benefits to operations. Mustafa et al. demonstrated that SWE can reach extraction yields equivalent to or surpassing bioactive compound yields while shortening process durations, which improves manufacturing throughput and decreases operational costs per product unit [85].

Economic advantage 2: Reduced post-processing requirements

Conventional solvent extraction requires long procedures for removing solvent residues from extracts, using energy-consuming methods like evaporation and distillation, and vacuum drying [38]. The extra processing operations both raise manufacturing expenses and weaken heat-vulnerable bioactive elements. Through SWE, most post-processing steps become unnecessary, or greatly minimised. Teo et al. stated that simple cooling or filtration will remove water from SWE extracts without degrading thermolabile compounds and reduce the extraction process expenses [84]. Quality control procedures become simpler, and less analytical testing will be needed because solvent residues are absent from the product [92]. The energy costs needed to dry extracts will decrease because the extraction method provides enhanced efficiency by eliminating the steps involved in solvent recovery. The energy efficiency of SWE extraction persists as favourable when including energy requirements for water removal in comparison to conventional methods, according to [87].

Economic advantage 3: Versatility and process integration

SWE demonstrates economic advantages through its ability to integrate processes and create diverse product lines. Ko et al. conducted an experimental study and showed that adjusting temperature and pressure settings enables SWE to extract different bioactive compound categories one at a time from raw materials, thus achieving maximum feedstock value and generating multiple product lines [61]. The selective extraction feature enables processors to start their operations by extracting valuable compounds under gentle conditions before proceeding to extract secondary compounds through stronger methods [91]. This sequential extraction procedures lead to increased product value production from raw materials, resulting in a reduction in expenditure. SWE systems provide opportunities to combine with green processing technologies, including ultrasound and microwave assistance to improve both extraction efficiency and economic performance [76]. Combining SWE extracts with continuous processing protocols leads to advancement in economic results, as it combines both process intensification with reduced manpower needs [93].

Supporting the circular economy model valorisation of agricultural and food waste

SWE is promoting the circular economy through the recognition of agricultural and food processing by-products. These materials are commonly used as waste in traditional methods, producing disposal costs and the loss of valuable resources. SWE is a green technology that acquires valuable compounds from waste materials [88]. Rodríguez-Meizoso et al. showed that SWE extracts bioactive molecules, including antioxidants and phenolic compounds, from different food processing by-products, which include fruit pomace and vegetable peels and seed residues and spent coffee grounds [89]. The compounds obtained from the waste extraction processes can become components for pharmaceutical products, including cosmetics and functional foods and food supplements, leading to value chain development from discarded residues. Ko et al. demonstrated that extracts obtained by SWE from citrus peels contained more flavonoids while showing enhanced antioxidant properties than conventional solvent removal processes, thus proving SWE's effectiveness for waste conversion [61]. The marketable products that SWE creates from waste streams enable the circular economy principle of closed material loops in production cycles. **Figure 4** illustrates the advantages and disadvantages of SWE.

Resource efficiency and sustainability

SWE implements multiple means to achieve resource efficiency. Firstly, removing organic solvents from chemical processing techniques helps protect the depletion of existing petrochemical materials throughout their production period. SWE extraction procedures use water that can be treated as it supports water preservation activities [86]. SWE extraction support resource conservation because it improves the efficiency of bioresource utilisation. Khajenoori et al demonstrated that SWE achieves superior efficiency in essential oil extraction from aromatic plants compared to hydro distillation using reduced starting material requirements [94]. SWE showcases flexible processing by processing dried biomass or fresh or wet biomass simultaneously, thus lowering feedstock preparation and especially drying energy costs [85]. The production efficiency improves across the whole manufacturing process thanks to the integration of processing flexibility.

Industrial applications and case studies food and nutraceutical industries

As an extraction method, SWE enhances the development of products in the food and nutraceutical sectors. Plaza et al reported that the outcomes of polyphenols and antioxidants, alongside additional bioactive compounds from various food substances, achieved higher quality through SWE extraction compared to traditional approaches [76]. Ko et al. demonstrated that SWE effectively extracted polyphenolic compounds from grape pomace, producing higher yields of 30% using no solvent residue [18]. Researchers applied beverage products with pure high-quality extracts while showing the industrial feasibility of SWE methods. The industrial SWE processing system developed by Mustafa et al, successfully extracted rosemary antioxidants with better environmental performance and lower extraction costs than usual methods [85].

Pharmaceutical and cosmetic applications

In pharmaceutical applications, SWE offers advantages beyond environmental benefits and cost savings. SWE extracts achieve particular importance in pharmaceutical ingredients as all organic solvent residues are eliminated while regulatory limits still apply [38]. One pharmaceutical manufacturer reported switching to SWE to replace conventional plant extraction method [94]. Through this modification, the business achieved significant savings of 40% in processing expenses, together with superior extract quality and absolute elimination of residue contaminants. Processing costs is also decreased by 40%, together with better extract purity and no trace residues of solvents. Mustafa et al. proved that SWE successfully obtained natural preservatives and active ingredients from plant samples for cosmetic use [85]. The production of water-based extracts from SWE generated product solutions simpler than solvent-based extracts, which lowered manufacturing expenses.

Challenges and future directions

SWE requires specialised equipment equipped with safety features due to its high-pressure operating conditions, which leads to higher initial capital costs than conventional extraction [28]. Also, the high operating temperatures may restrict the use of thermolabile compounds due to their sensitivity to heat. Research should focus on creating integrated SWE platforms by integrating them with ultrasound or microwave energy technologies for raising extraction yield rates at lower operational temperatures [95]. The implementation of continuous-flow SWE systems as part of process intensification approaches demonstrates potential benefits for economic success and industrial adoption [96]. However, the elevated temperatures may not be suitable for highly thermolabile compounds, potentially limiting applications for certain heat-sensitive materials.

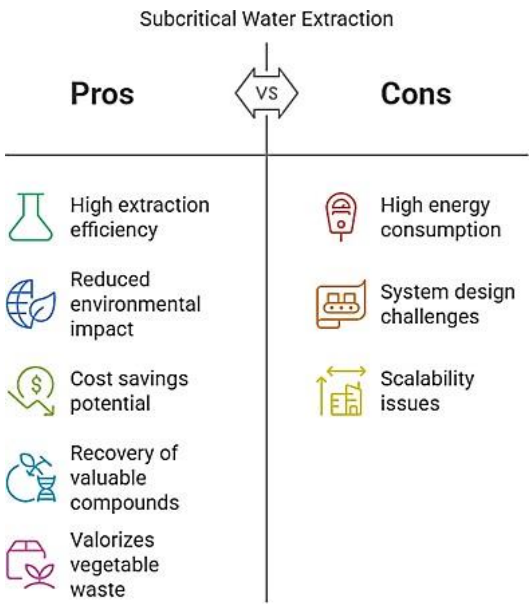

Figure 4: The Advantages and Disadvantages of Subcritical Water Extraction (SWE)

Future direction of SWE should create hybrid systems by integrating SWE with alternative sustainable technologies, including ultrasound and microwave techniques, to optimise extraction efficiency, while maintaining operating temperatures below ambient [95] . The implementation of continuous-flow SWE systems as process intensification methods demonstrates the potential economic viability enhancement and industrial-scale modes of operation. The extent of compound extraction through temperature-pressure profile development will enable SWE to increase its application range in diverse fields. The ability to manipulate extraction settings for choosing compound types stands as a major potential advancement of SWE technology [87].

Conclusion

The principle behind SWE is using water heated under pressure as an extraction medium. It is a promising green technology. Water acts as a good solvent for both polar and nonpolar compounds at elevated temperatures, allowing for the efficient extraction of phytochemicals without the intervention of organic solvents. The method is shown to surpass conventional techniques dramatically in terms of reduced environmental impact and carbon emissions, as well as minimised post-processing requirements and thus, contribute to economic benefits. However, despite these merits, equipment engineering and industrial-scale implementation of such designs remain challenging, signalling a need for further research and technological developments in this field.

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