Applications of Green Extraction of Phytochemicals from Fruit and Vegetables

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Abstract

Extraction is the widely used techniques in the process of phytochemicals, natural compounds (phenolic compounds, ascorbic acid, carotenoids, aroma compounds etc.) obtaining from plant material. Conventional solvent extraction methods are generally used for this purposes but, it has several disadvantages such as quite laborious, time-consuming, involve large amounts of solvents, target molecule degradation, the partial loss of volatiles and pose hazards to health and the environment. Some solvents (ethanol) require explosion proof facilities for production. Alternative extraction and separation techniques which are called "green extraction", provides environmentally sustainable extraction process for high value phytochemicals from plants for use in foods, pharmaceuticals, cosmetics and other products. Great improvements can be achieved with the use of green extraction techniques such as supercritical CO_2 extraction, ultrasound-assisted extraction (UAE), microwave-assisted extraction, pulse electric field (PEF), extraction with subcritical water and instant controlled pressure drop. The applications, principles, advantages and examples of green extraction has been summarised in this study.

Key words: Extraction, solvent, green extraction, phytochemicals, alternative methods

1. Introduction

Extraction is a way to separation of desirable, valuable components from mixture of liquid or solid medium [1]. There are various methods using in extraction of components such as maceration, solid-phase, steam or hydrodistillation, pressing, decoction, infusion, percolation, soxhlet extraction, supercritical CO_2, ultrasonic, microwave and Pulsed electrical field extraction.

Bioactive compounds and their precursors (antibiotics, chemopreventive agents, alkaloids, etc.) are extracted by the pharmaceutical industry, either with conventional methods, involving the use of chemical solvents or innovative procedure that uses supercritical carbon dioxide (SC-CO_2) extraction. Recent researches in extraction methods have extensively focused on minimizing the use of solvents [2,3].

Because of increasing energy prices and the controlling of CO_2 emissions, food industries are searched within new technologies, in order to reduce energy consumption, to obey legal regulations on emissions, product/process safety and control, and for cost reduction and increased quality as well as functionality [4].

Extraction of natural products has been largely used since the discovery of fire. There are many nations (Egyptians and Phoenicians, Jews and Arabs, Indians and Chinese, Greeks and Romans, and even Mayas and Aztecs) that possessed innovative extraction processes (maceration, alembic distillation, etc.) used even for perfume, medicine or food [2].

Fruit and vegetables include high amount of antioxidant compounds (ascorbic acid, α-tocopherol, carotenoids, phenolic compounds and flavonoids). They are used for production of various products except fresh consumption. In the apple juice production, Çam and Aaby

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[5] reported only 3-10 % percentage of phenolics extracted from apple, most of the phenolics remain in the pomace. New extraction methods can supply to extract more valuable compounds than conventional methods.

The plant tissue extracts are abundant soruce of valuable constituents for productions of nutraceutical or pharmaceutical. The trade for herbs for nutritional supplements (gren tea, melissa, blueberry) is around 6.7 billion € in Europe and 17.5 billion in the world. In this manner, the export and import values of medicinal plant raw material is 1 billion US$ in USA. The growth rate of this industrial area is about 6 to 8% [6].

It is necessary to establish technological innovations for environmental protection and the competitiveness of the globalized market. The twelve main principles of green chemistry are matched by the twelve basic principles of green extraction (engineering) that state the basis of sustainable processes [2]. The chemical substances especially used in the extraction is queried by the the directive REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals). The priority of REACH is to protect human health and the environment, beside the development and the competitiveness of EU chemicals industry. REACH regulate the control of chemicals, and also it is intended to have more information about the chemicals to share this information with the public [2,7].

The new extraction methods are environmentally pleasant and have low risks for the operators which are not exposed to chemical solvents side effects [7]. In this context, alternative methods instead of the solvent extractions, environmentally friendly, high efficiency extraction methods are summarized.

2. Green Extraction

The green extraction process is a method which is used to obtaine various plant extracts with minimum impact on the environment (lower energy and solvent consumption, etc.) [8]. “The green extract should be the result of a whole chain of values in both senses of the term, that is, economic an responsible, starting from the production and harvesting of the plant, the transformation process of extraction, and separation together with formulation marketing” [8].

3. The Main Principles of Green Extraction

Green extraction can be defined as the invention, design and application of chemical products and processes to decrease or to eliminate the use and generation of dangerous chemicals. The other definition type is expressed as follows: “Green Extraction is based on the discovery and design of extraction processes (supercritical fluid extraction, ultrasound extraction, subcritical water extraction, controlled pressure drop process, pulsed electric field, and microwave extraction) which will reduce energy consumption, allows use of alternative solvents and renewable natural products, and ensure a safe and high quality extract/product” [2].

There are three major solutions to identify to design and demonstrate green extraction for optimal consumption of raw materials, solvents and energy: (1) improvement and optimisation of current processes; (2) using special equipment; and (3) innovation of processes and procedures but at the same time in determination of alternative solvents [2]. There are comparable advantage and disadvantage of extraction methods between conventional and new techniques. This differences are given in Figure 1.

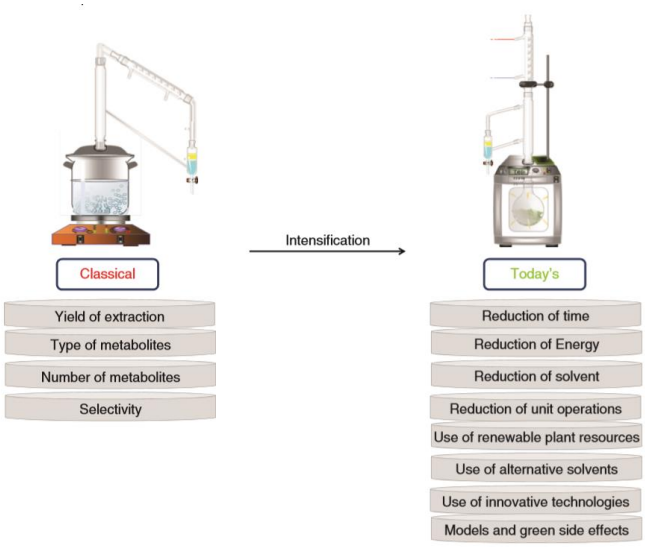

Figure 1. Comparision of extraction methods: conventional and new technologies [8].

Green extraction is a way to protect both environment and human health and provide more ecologic, economic and innovative methods, for that reason this method is the new concept of the 21 th century [8].

4. The Major Six Principles of Green Extraction

4.1. Principle 1: Selection of New Varieties and the Usage of Renewable Plant Raw Materials

Because of the increasing demand of natural products and extracts, the over-exploitation of natural plant resources occurs. History reports several examples of plant extinction cause of overutilization; therefore the protection of biodiversity is mandatory in the respect of future generations. All renewable resources must be favoured either with intensive cultivation or in vitro growth of plant cells or organisms in green extraction. A quarter of existing medicines are extracted from plants, the best known example is the anti-cancer paclitaxel (Taxol®) extracted from the bark of the western yew (Taxus brevifolia). During the 1970s no less than 30 tonnes of bark were collected for clinical trials: only 1 g of taxol is produced for 10 kg of dry bark after extraction and purification. Therefore a large number of research projects have been aimed at finding alternatives to felling trees of this threatened species. Since 1980, Semisynthesis prepare paclitaxel and docetaxel (Taxotere®) from the natural precursor, 10-deacetylbaccatine III, extracted from needles and branches (renewable resource) of different yew tree species [2].

4.2. Principle 2: Use of Available Solvents and Water or Other Agro Based Solvents

Current regulations on the petrochemical solvents and Volatile Organic Compounds (VOCs) have a direct effect in reducing the consumption of this chemicals. The manufacturer have to demonstrate the risk of using organic solvents during the extraction and give an information about safety of ingredients as regards to solvent traces. Most organic solvents are flammable depending on their volatility. Many solvents are toxic and causing environmental pollution. Manufacturer are leading to environmentally friendly products, taking into account

environmental and economic characteristics. The agro or bio-solvents which are green solvents preferred instead of petrochemical solvents. Wood, starch, vegetable oils or fruits etc. are renewable resource produced from biomasses. This bio-solvents with high solvent power are non-toxic, non-flammable and biodegradable. Because of high viscosity, high boiling point and off-flavors, they have some limitations and drawbacks. [2]. Alternative solvents for green extraction is given in the Table 1.

Organic solvents used in the extraction prosesses have disadvantages; flammable, volatile, and often toxic. They are also responsible for environmental pollution and the greenhouse effect [2].

Table 1. Alternative Solvents for Green Extraction [2].

Solvent	Extraction Technique (Application)	Solvent Power			Health & Safety	Cost	Environmental Impact
		Polar	Weakly Polar	Non-Polar			
Solvent-free	Microwave Hydrodiffusion and Gravity (antioxidants, essential oils)	+++	+		+++	+	+++
	Pulse Electric Field (antioxidants, pigments)	+++	+		+++	+	+++
Water	Steam distillation (essential oils)	++	+		+	++	+
	Microwave-assisted distillation (essential oils)	+++	+++	+	+	+	++
	Extraction by sub-critical water (Aromas)	+	++		+	+	+
CO_2	Supercritical fluid extraction (decaffeination of tea and coffee)	−	+	+++	+	+	+
Ionic liquids	Ammonium salts (Artemisinin)	−	+	+++	−	−	++
Agrosolvents	Ethanol (pigments and antioxidants)	+	+	−	−	++	+
	Glycerol (polyphenols)	+	+	−	−	+	+
	Terpenes such as *d*-limonene (fats and oils)	−	−	++	−	+	+
Petrochemical solvents	*n*-Hexane (fats and oils)	−	+	+++	−−−	++	−−−

Safety, environmental and economical aspects are forcing industry to turn to greener solvents [2]. Ideal solvent properties are given in Figure 2.

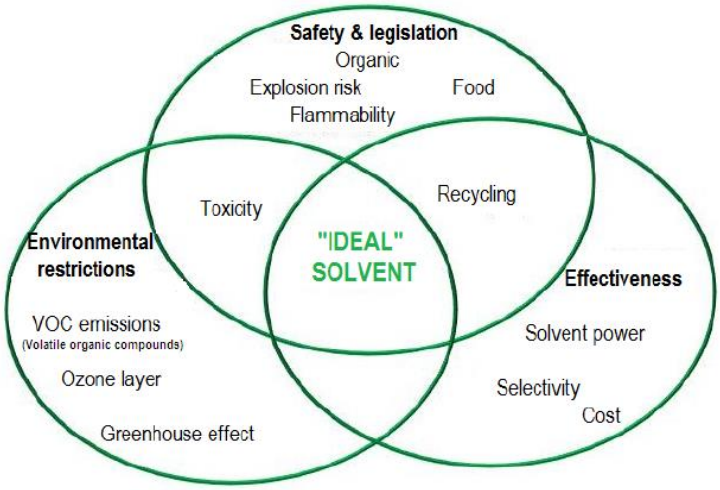

Figure 2. Ideal solvent properties using in extraction [8].

Among green solvents, the agro- or bio-solvents have an important position in the replacement of petrochemical solvents [2].

4.3. Principle 3: Redution of Energy Consuming and Using New Technologies

The industry of natural products is a very competitive field for manufacturers. For that reason, they are using optimized processes in order to survive. The R&D, industrial, and cost control departments are always searching more effective and cost-efficient ways to extract botanicals. Almost all of the industry members are aware that reducing of the carbon footprint of their processes are needed. So, the green extraction principles of reduction of energy consuming and reduction of unit operation steps and ensuring safety and process control are available for industries. These new extraction technologies at production size (pressurized liquid extraction, microwave-assisted extraction, etc.) will definitely benefit those industries in the quest for more efficient extraction process on a long-term basis [8].

Microwave is a non-contact heat source and at the same time it can provide a more effective and selective heating. Distillation can be completed in minutes instead of hours with help of microwave. In this method, plant compounds are extracted in a microwave reactor with or without using organic solvents or water under different process conditions depending on the experimental procedure. The first Microwave-Assisted Extraction (MAE) of essential oils (EOs) was put forward as compressed air microwave distillation (CAMD) [9]. The other short time extraction process is Turbo distillation method. It is developed to reduction of energy and consumption of water during boiling and cooling in hydrodistillation. The turbo extraction lets a notable agitation and mixing with a shearing and destructive effect on plant materials. So, distillation time is shortened by a factor of 2 or 3. In addition, it is an alternative technique for extraction of EOs from spices or woods which are comparatively difficult to distill [10].

4.4. Principle 4: Production of Co-Products with Reductionof Waste

After extraction processes, there are revealed some materials such as waste, by-product and co-product. Generally, waste is any material that an industrial producer wants to get rid of or

eliminate (waste disposal centre, incineration, landfill, etc.). "A by-product is a residual product that appears during the manufacture or distribution of a finished product". It is unintentional, unpredictable and accidental. It can be used an ingredient in production process or used directly. Orange is one of the major crops in the processing industry in 2012 due to a total production of 68 million tons. 95% of orange is used to production of orange juice. 3 kg of oranges are necessary for production of 1 l of orange juice. For that reason, there is a high potential for valorization of the by-products. Moreover, the whole orange tree can be used for nutritional, pharmacological, or cosmetic purposes as well as by-products [8].

A co-product is a material that created during a single production process and at the same time as the main product. The main final product and the co-product always have to meet specifications for their properties. However, each can be used directly for a specific application. Otherwise, co-products have economic value and a specific market for it, a pricing, etc. Oil cakes (rape, sunflower, flax), spent cereal grain (wheat, barley), beet pulp, potato fibre and proteins, are some examples of food industry co-products [11].

4.5. Principle 5: Reducing Unit Operation Steps and Safety Controlled Processes

It is necessary to decrease the number of stages in the process to a reducing in costs and energy consumption. A single-stage process could ideal. In the green extraction, supercritical extraction has an advantages; using a clean solvent and obtaining extract at the minimum number of operation stage. Natural products obtaining by solvent extraction could be complete more than single unit operation. In the extraction of β-carotene from carrots, there is a several steps: (1) dry the raw material (carrot) (apolar solvent, n-hexane extract the β-carotene); (2) to increase surface area dry carrot sample grind or shred; (3) extraction of β-carotene with n-hexane; (4) liquid and pomace separate from each other; (5) n-hexane and β-carotene seperate according to boiling point differences and recycle the n-hexane. And then, molecular distillation or vacuum drying achieve to remove residual traces [2]. Ultrasound application is an advantages extraction techniques. It reduces process time, increases yield and improves quality and flavor of extract. Low enegry consumption is an another advantages of ultrasound in extraction process. Cavitation bubbles which are generated from ultrasound generator caused to icrease to micro-jets to destroy essential oils glands so as to make possible the mass transfer rate and the release of plant EOs'. This cavitation effect is depend on the operating conditions (e.g. ultrasonic frequency, intensity, temperature, treatment time, etc.). Beside the yield improvement, Ultrasound-Assisted Extraction (UAE) indicated less thermal degradation, high quality and a good flavor of extract [12].

Because of the usage of non-toxic, non-explosive, environmental friendly, cost effective, time saving and selectivity-adjustable solvent in supercritical carbon dioxide fluid extraction, it is advantageously, too [13]. PEF assisted extraction reduces extraction time as the pulsed electric fields (PEF) provide cell membrane permeabilization. Cell membrane is exposed to a sufficiently intense electric field of short time (milliseconds to microseconds),during PEF treatment. For that reason PEF enhances extraction of compounds such as lipids and carotenoids [14].

4.6. Principle 6: Production of Biodegradable Extract with "Green" Values

After drying and purification of product, the purified extract is analyzed to ensures that it satisfy the acceptance criteria. The harmony of specifications is matched with the aim process yield (mass yield, active yield). Naturex has been developing to test method for rosmarinic

and carnosic acids. This methods are used worlwide to identified as market standarts. The rate of carnosol and carnosic acid gives to ensure that carnosic acid has not been degraded in carnosol throughout the process [8].

Conclusions

Green extraction is a useful process and it is also positive effect to environment and operators. And it is provide to decrease harmful side effects of conventional extraction solvents which are used in food contact processes. There is necessary to need to design new studies and rapid integration with industrial applications for a good future.

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