Recent Advances in the Development and Application of Green Extraction Techniques

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1. Introduction

Increased awareness towards environmental protection due to the recognized long-term effects of global industrialization and other anthropogenic actions, as well as imperatives posed to many industries to orient them towards sustainability and circular economy models, has imposed new trends and strategies in most technologies. In the exploitation of natural resources of both plant and animal origin, the extraction process is recognized as crucial, directly defining economic viability, sustainability, as well as compliance with strict requirements with respect to environmental impact and safety. More strict regulations with respect to environmental impact and raised awareness of the general population and consumers about the safety and origin of products established the necessity of adjusting existing technologies to new requirements. The implementation of green extraction processes, the replacement of conventional technologies, or translation to extraction processes involving cutting-edge technologies has become a challenge for industrial-scale processes. Modern extraction processes that are being developed not only provide safer and more environmentally friendly alternatives, but also successfully achieve improvements in efficiency and selectivity, providing reduced processing time and costs.

It can be said that trends in the development of new extraction techniques are oriented towards one of two important fields—analytical chemistry and technology/industry. In the sphere of analytical chemistry, coupling of the extraction, as a sample preparation step, with the analytical step, ensures improvement in reliability, accuracy, reproducibility, and overall measurement uncertainty by significantly reducing the time of analysis, particularly relevant in high sample throughput. Thus, the trends in the field of instrumental analysis consider miniaturization and the development of microextraction techniques, or so-called solvent-free extraction, for hyphenation with modern analytical instruments of high sensitivity and selectivity but low capacities, such as chromatographic systems (liquid or gas) or capillary electrophoresis. Membrane extraction, microextraction (dispersive liquid–liquid microextraction), or ‘solventless’ extraction (solid-phase microextraction) techniques are nowadays common in analytical practice, representing an integral part of commonly used analytical methods.

Industrial applications, however, must consider scalability from successfully developed lab-scale extraction to the industrial scale. As a major challenge, safety, sustainability, technical feasibility, and financial aspects must be considered [1].

Modern extraction techniques tend to increase extraction efficiency and selectivity, reduce processing time and costs, and assure the safety of the final extract by reducing solvent consumption and by replacing conventional solvents with greener and safer alternatives. Green extraction techniques thus imply the use of reduced quantities of conventional solvents, apply solvents with modified properties, or use the solvents relatively safe for the environment or of remarkably reduced toxicity and risks (GRAS—Generally Recognized as Safe). In addition to efficiently overcome the limiting steps of the extraction, such as...
strong bonds with the matrix, low solubility, low diffusivity, slow heating, poor contact with the matrix, etc., modern green extraction techniques prioritize significantly reducing the environmental burden, producing safer extracts richer in target chemicals.

Considering the above, the main goal of this Special Issue was to collect the latest research on the development and application of green extraction techniques.

2. Green Extraction Techniques

In this Special Issue, various green techniques were addressed encompassing subcritical water, microwave-assisted, enzyme-assisted, and ultrasound-assisted extraction and also addressing recent trends in extraction approaches, i.e., combined extraction techniques covering the current state-of-the-art in this field.

Mass transfer from a sample matrix to a solvent is an extremely complex process, accompanied by many limiting factors. The release of target compounds from a natural matrix depends on many factors, such as bond strength and the type of target compounds with matrix constituents, porosity of the matrix, i.e., the diffusivity of the target compounds, first through the pore filling matrix, and in later stages transfer into the extraction solvent. In the majority of extraction processes, convective mass transport is of utmost importance, since it reduces the thickness of the Prandtl diffusive layer at the matrix/solvent surface, reducing the necessary extraction time. The solubility of compounds in the selected solvent, but also viscosity, surface tension, and viscosity of the solvent, are highly dependent on the processing temperature and pressure.

Some green extraction techniques, such as subcritical water extraction, modify the properties of conventional solvents by applying high pressures and temperatures. In these techniques high pressures and temperatures improve not only the penetration of the solvent into the pores of a solid matrix, but they also modify the overall physico-chemical properties of the solvents, such as polarity, surface tension, viscosity, and density. Thus, in these conditions, solvents act as completely distinct solvents, according to their mobility, polarity, solvating properties, and diffusivity. Taking advantages of the green properties of water, several studies explored it as an extraction solvent [2–4]. Švarc-Gajić et al. [2] proposed a new strategy to valorize oilseed cake biowastes by subcritical water extraction. These authors [1], for the first time, comprehensively characterized the extraction of relevant compounds from pumpkin, flax, and hemp seed cakes when exposed to different gaseous environments and homogenous catalysis. The presented data unequivocally demonstrated the chemical and nutritional value of the aqueous oilseed cake extracts and the high interest of their incorporation in the food, pharmaceutical, and cosmetic sectors. In addition, in the context of the valorization of natural resources, Rodríguez-Seoane et al. [3] applied subcritical water for the recovery of bioactive compounds from *Paulownia elongata x fortune* (bark, leaves, and petioles) with the final aim of using the extracts for the development of enriched biopolymer-based hydrogels. The results indicated that the extraction temperature had a crucial influence on the color, rheological, and textural properties of the hydrogels, which displayed high potential applicability in food and other related industries [3]. Moreover, the adequacy of the extraction technique for valorization of underexplored natural resources in a green and sustainable approach was proven. Gianni et al. [4] also successfully used water as a solvent for extraction of tannins from *Pinus sylvestris*, but in this case in a conventional solid–liquid extraction.

Some of the modern extraction techniques, such as microwave-assisted extraction aim to overcome slow heat transfer by direct absorption of the microwave energy, avoiding slow convection and conduction. Not all solvents are efficiently heated in a microwave field, since heating is closely related to the dielectric properties that must be adjusted for this extraction approach, either by using a solvent mixture, where one solvent is serving as an indirect heating medium, or by assuring that the matrix itself has adequate dielectric properties for efficient heating in the microwave field. Al Rubaiy et al. [5] selected ethyl acetate as optimal solvent for the microwave-assisted extraction of antioxidants from koji rice fermented with *Aspergillus flavus*. The obtained extracts exhibited promising
characteristics, namely, 2 h of stability at neutral pH and high temperatures (ca. 185 °C), suggesting new strategies to produce microbial antioxidants. Pontillo et al. [6] also tested microwave-assisted extraction and compared it with conventional solid-liquid extraction for the recovery of antioxidant compounds from *Rosmarinus officinalis* L. leaves. Additionally, this research team optimized an enzyme-assisted extraction step to be used as pretreatment. In enzyme-assisted extraction, the sample matrix is treated with different enzymes, mostly pectinases or proteases, to break the bonds of the target compounds with the matrix, which is often a limiting factor to efficient recovery. Pretreatment with enzymes improves recovery of the target compounds, reducing solvent consumption and saving time. Thus, a greener strategy was developed to obtain high added-value extracts from rosemary leaves [6].

Ak et al. [7] also performed a comparative assessment of traditional and non-traditional techniques for the extraction of bioactive compounds from *Calendula officinalis* L. (marigold), which included the greener approach of ultrasound-assisted extraction. In this technique, the choice of solvents is unlimited, since the solvent serves as a medium through which the ultrasounds are propagated, causing cavitation, followed by fast adiabatic compression that releases an enormous amount of energy in the form of heat. The liberated energy generates free radicals that can cause the degradation of the extracted compounds. The solvents in this extraction technique are chosen according to the solubility of the target chemical class. The technique also offers the possibility of using solvent mixtures, where one solvent serves as a medium that is miscible with the pore-filling medium, or a sample matrix, to assure good indirect solvation by the second solvent, which has high selectivity towards target compounds. These authors [7] clearly showed the marked effect of the extraction technique on the obtained phytochemical profile, which also varies with the used plant part (roots, leaves, or flowers). Ultrasonication was also used as a pretreatment step in the study of Grigorakis et al. [8], which is a relevant example of the combination of this method with novel citrate-based deep eutectic solvents. Deep eutectic solvents are a new generation of solvents intended to replace toxic organic solvents and to overcome the major drawbacks of their use, such as their low biodegradability and high toxicity. These have properties similar to ionic liquids and are prepared by mixing two compounds acting as hydrogen bond donors and hydrogen bond receptors. The melting point of a selected chemical pair must be significantly lower in comparison to the sample. The attained data showed the superior extraction efficiency of the optimum (lactic acid and sodium citrate dibasic) deep eutectic solvent coupled with ultrasonication for *Salvia fruticosa* polyphenols when compared with previously reported extraction schemes [8].

3. Future Trends and Challenges

In the last decades, the principles of green chemistry have been clearly encouraged and implemented to support an imperative of World Sustainable Development. Considering an environmental protection perspective, green chemistry practitioners have been involved in the development of a plethora of promising extraction techniques. Some of these techniques have become relatively mature (principally on the laboratory scale) being successfully applied to various fields, such as the environment, food industry, pharmacology, among other strategic sectors, while others (for example, based on specifically designed green solvents, such as deep eutectic solvent), are still emerging.

New extraction techniques that have a perspective in industrial applications combine conventional approaches with modern technologies, overcoming major bottlenecks of the processes, targeting major driving forces of the particular process, and adjusting to specific matrices. Microwaves can, thus, be combined with classical Soxhlet or Clevenger distillation to shorten processing time. In the improvement of the extraction processes, the logical next step is to combine two or more modern extraction techniques, creating hybrid extraction techniques intended for continuous technological processes and scaling-up, resulting improved efficiency and selectivity towards target compounds, as well as reduced processing time, which is a very important parameter for industrial processing. Thus, in many food technologies, it is not uncommon to assist filtration with ultrasound.
propagation, since ultrasonic waves trigger the agglomeration of fine particles. To reduce energy consumption and thermal degradation of the target molecular class, either microwaves or ultrasound can be combined with enzyme-assisted extraction. Simultaneous irradiation of the matrix with ultrasound and microwaves is one of the most promising hybrid extraction techniques that can significantly shorten the extraction step, which is, in most cases, the time-limiting step of the overall technological process. Being developed at the lab scale, the process proved to be easily scalable to industrial processes dealing with different matrices. Similarly, the improvement in the extraction efficiency can be achieved by combining pulsed electrical field and microwave heating, producing another modern hybrid extraction technique. In this way, by combining different phenomena, i.e., fast disruption of cellular walls by a pulsed electric field, and fast heating by direct conversion of microwave energy into heat, the process simultaneously overcomes the major limiting step of the extraction process.

Another combined extraction technique, benefiting from fast microwave heating of the sample/solvent mixture, is a technique coupled with Instantaneous Controlled Pressure Drop (DIC—Déntente Instantanée Contrôlée). The DIC process targets the sample matrix’s limitations by increasing its porosity, and thus the diffusivity of the solvent, by thermomechanical processes involving the consecutive exposure of the sample to a vacuum and steam. The process starts by establishing a vacuum condition, followed by rapid exposure to steam for a few seconds, and returning again to the vacuum state (~5 kPa) [9]. The sudden change in pressure causes auto-evaporation of the water inside the sample cells, leading to increases in cell porosity and permeability. This combination of electromagnetic (microwave heating) and mechanical (DIC) processes, in addition to being very efficient in the extraction of different matrices, can also conveniently be used for microwave-assisted drying.

Hyphenation of ultrasound and supercritical fluid extraction, i.e., inserting an ultrasound probe into the extraction vessel, is an example of another modern coupled extraction technique. This combined technique exploits the cavitation phenomenon of the ultrasound propagation, provoking cell wall disruption, with good solvating properties and selectivity of supercritical carbon dioxide, which is most frequently used. By this combined approach, strong matrix effects, i.e., the strong dependence of the yield on matrix, which are the most limiting factors in supercritical fluid extraction, are minimized.

4. Conclusions

In conclusion, the trend that is clearly recognized in the development of green extraction processes is the combination of different mechanisms to improve yields and reduce time, costs, and, most importantly, solvent consumption, thus overcoming the limitations of single techniques and reaching synergistic results. In addition to improvements in efficiency and selectivity, conventional solvents are being replaced with safer and greener alternatives. Improvement in extraction, orienting towards greener strategies, is a crucial technological step and one of the most important prerequisites for sustainable technological development and environmental protection.

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