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Review

Supercritical fluid extraction of vegetable matrices: Applications, trends and future perspectives of a convincing green technology

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ABSTRACT

Along more than a decade, R&D on supercritical fluid extraction (SFE) of vegetable matrices has been increasingly reported in the literature. Aiming at portraying the current state of this field and its evolution in terms of raw materials, products, modes of operation, optimization, modeling techniques, and closeness to industrial application, a large compilation of almost 600 essays from 2000 to 2013 has been deeply analyzed in order to unveil those indicators and their trends. Furthermore, strengths and weaknesses are identified, and some remarks that may drive upcoming research are provided.

Globally, more than 300 species are reported in the literature, with prevalence of the extraction of seeds (28% of works) and leaves (17%). The main families of extracted compounds, cosolvents and operating conditions adopted are critically examined, being possible to conclude that researchers investigate many times working regions far from the optimum due to practical limitations or absence of experimental optimization. Current phenomenological, statistical and semi-empirical approaches are reviewed, along with scale-up studies, and economic analysis. In the whole, the most comprehensive picture over SFE of vegetable matrices is provided in this review, highlighting pertinent aspects and opportunities that may further consolidate the convincing route of this technology for the next years.

Contents

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1. Introduction

In the last 13 years (2000–2013), the extracts of more than 300 plant species have been studied using supercritical fluid extraction (SFE) technology. It is worth noting the major share of SFE research covers vegetable biomass [1,2]. While many extracts and pure components of these species are already in use for human nutrition and health purposes, others represent potentially new applications involving plants whose knowledge, in most of the cases, has been empirically established or still lacks scientific coverage.

The remarkable interest of scientific community on this technology has been driven by the great versatility of carbon dioxide, the most used solvent in supercritical state, whose properties can be tuned in order to provide extracts with desirable compositions (selectivity enhancements), while at the same time it ensures an innocuous separation process both to human health and to the environment. Other solvents (e.g. ethane, propane) have also been object of research but their use is not as widespread as carbon dioxide, and for this reason the emphasis of this review is on supercritical carbon dioxide (SC-CO_2).

Among the vast group of species that have been studied under the scope of SFE, some have appeared in great number in literature since 2000. It is the case of grape (*Vitis vinifera* L.) [3–25] tomato (*Solanum lycopersicum* L.) [26–35], thyme (*Thymus vulgaris* L.) [36–44], eucalypt (*Eucalyptus* spp.) [45–53], coffee (*Coffea* spp.) [54–62], sunflower (*Heliantus annuus* L.) [63–69], flax (*Linum usitatissimum*) [70–75], rosemary (*Rosmarinus officinalis* L.) [76–83], red pepper (*Capsicum anuum* L.) [84–90], and rice (*Oryza* variety) [91–97].

In what concerns food related species, the great expansion of nutraceuticals market in recent years, as an emerging sector comprising the use of dietary substances for prevention of diseases [98], has been attracting the attention of researchers and food industry. In this context, SFE is advantageously positioned as a sustainable and safe extraction option for the preparation of plant extracts for supplements and nutrient enriched products in which, as Perrut anticipated in 2000 [99], the *natural* character of the preparation mode has a high marketing value. Besides those requisites, when SFE is applied to eatable raw materials as a pretreatment for removal of compounds (e.g. cleaning of rice), other advantages are also observed, such as the enhancement of product shelf life and, eventually, the shortening of the cooking time [1]. In addition, research on this field has also explored the valorization of residues from main stream processes [100,101].

As a result, a substantial number of dairy plant products has been object of SFE technology, such as, among others, apricot (*Prunus armeniaca* L.) [102–106], carrot (*Daucus carota* L.) [107–110], cashew (*Anacardium occidentale* L.) [111–114], cocoa (*Theobroma cacao*) [115–117], garlic (*Allium sativum* L.) [118–121], ginger (*Zingiber officinale*) [122–126], ginseng (*Panax* spp.) [127–130], laurel (*Laurus nobilis* L.) [131–135], orange (*Citrus sinensis* L.) [136–140], oregano (*Origanum* spp.) [141–145], pumpkin (*Cucurbita* spp.) [146–150], soybean [151–156], turmeric (*Curcuma longa* L.) [157–161], and wheat germ (*Triticum* spp.) [162–167].

Following a major trend of western pharmaceutical industry of integrating oriental folk medicine species that have been used for centuries in natural formulations for a myriad of health problems, extracts of a significant number of species used in those contexts have been prepared using SFE. Although many species are still to be recognized for their health/nutrition benefits by health authorities such as World Health Organization, others have seen their bioactivity confirmed, such as on the cases of *Acorus calamus* [168], *Andrographis paniculata* [169], *Azadirachta indica* [170–173], *Curcuma longa* [157–161], *Cyperus rotundus* [174], *Ocimum gratissimum* [175,178,179], *Panax ginseng* [127,129], *Taxus baccata* L. [180]. Its application has been directed by the interest to isolate and quantify phytopharmaceuticals existing in those extracts so that further pharmacological studies can then be carried out in order to confirm the respective bioactivities. An elucidating perspective on this research path was recently published for the case of triterpenoid compounds, either with respect to their extraction with SC-CO_2 [181], either in terms of the corresponding bioactivity studies that support their therapeutic potential [182].

This review intends to document and systematize the progresses of supercritical CO_2 extraction research upon natural extracts, with emphasis on raw materials, products, modes of operation, optimization, modeling techniques, and closeness to industrial application. A large compilation of almost 600 essays from 2000 to 2013 has been deeply analyzed in order to unveil indicators and trends. It is expected that this compilation and discussion provide hints and suggestions to researchers with respect to the different aspects that contribute to the final viability of SFE technologies and, thus, to its widespread implementation at commercial level.

The review is structured in the following way: Section 2 is devoted to the presentation of biomass matrices and naturally occurring molecules, followed, in Section 3, by the focuses of SFE research. In Section 4, aspects related to the operation of SFE units, the impact and optimization of process variables are covered. Modeling is introduced in Section 5, and discussed in terms of empirical, simplified, comprehensive and statistical approaches. The next two sections highlight the scale-up (Section 6) and economic analysis (Section 7). Final remarks conclude the review in Section 8.

2. Biomass matrices and naturally occurring molecules

When overviewing the field of vegetable matrices extracts for a period larger than a decade, a vast group of species arises as issue of SFE research, hence revealing the strong interest and attention that supercritical fluids have conquered. A wide-ranging compilation of works in this field is presented in Table 1, sorted by the scientific names of plant species substrates. Information regarding the vegetable species, target molecules and operating conditions (pressure, temperature, solvent flow rate, and cosolvent content) are provided for each SFE publication, as well as the respective analytical techniques employed and complementary features about each work.

Considering the representative number of works covered in this review, it is possible to depict some structural tendencies regarding the directions research has followed in this field, such as the characteristics of the biomass matrices that have been most studied. Accordingly, Fig. 1 presents a statistical distribution of the vegetables matrices types mostly found on SFE publications. It becomes clear that supercritical fluids have been mainly applied to the extraction of seeds and leaves. Together, they represent 45% of the plant fractions of all the works considered, being seeds the biggest fraction (28%), and leaves (17%). They are followed by fruits (10%), roots (7%), flowers (5%), rhizomes (3%) and bark (2%). On the other hand, parts such as stems, branches, and woods seem not to justify individual studies of SFE, being instead included only in cases where matrices comprise mixtures of components, such as aerial parts, which account for 9% of the researched matrices. In addition, processed vegetables like pomace or husks represent 5% of the 544 SFE publications considered.

In view of the vast diversity of molecules found in natural matrices, vegetables are typically matter of research for more than one application. Depending on the species and plant component studied, SFE processes can be devoted to many naturally occurring compounds. Furthermore, SFE extracts obtained from vegetable matrices are typically mixtures of the following family