International Journal on Recent Advancement in Biotechnology & Nanotechnology
https://www.eurekajournals.com/biotech.html
ISSN: 2582-1571

Supercritical Fluid Extraction of Natural Dyes from botanical Waste-An Innovative Approach

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Abstract

Extraction is a vital prerequisite in most scientific studies involving the isolation and analysis of compounds from biological/environmental systems. Bioactive compounds are extracted from natural sources, and they have beneficial effects on human health. Fruits and vegetables are rich in carotenoids, phenolic compounds, and vitamin C, among others. Extraction processes for these compounds depend on several factors such as the technique that is used, the raw material, and the organic solvent. Conventional techniques generally require large amounts of organic solvents, high energy expenditure, and are time consuming, which has generated interest in new technologies that are referred to as clean or green technologies. The aim of present paper is to discuss the various advantages using green techniques- supercritical fluid extraction of bioactive compounds from fruit and vegetable wastes.Supercritical fluid extraction is the most effective and efficient way to extract valuable constituent botanicals. Supercritical Fluid Extraction (SFE) is the process of separating one component (the extractant) from another (the matrix) using supercritical fluids that is CO2 as the extracting solvent.

Keywords: Supercritical fluid extraction, Bioactive compounds, Natural dye.

Introduction

Fruits and vegetables have a crucial role in our diet and human life, and therefore, the demand for such important food commodities has increased very significantly. Processing industries are becoming a serious nutritional, economical, and environmental problem. The fruit and vegetable wastes are composed mainly of seed, skin, rind, and pomace, are good sources of potentially valuable bioactive compounds, such as carotenoids, polyphenols, dietary fibers, vitamins, enzymes, and oils. These phyto chemicals can be utilized in different industries, the food industry for the development of functional or enriched foods, the health industry for medicines and pharmaceuticals, and the textile industry for dying purposes.

So, fruits and vegetable waste are used in this study for extracting dyes from fruit waste is to avoid the environmental pollution.

Textile researchers and industrialists are subjected to challenges in discovering new development for the textile industry due to global concerns in environmental control. Current industries and social demands have raised awareness on the use of natural dyes as a source of textile coloration due to the hazardous implications from the processing and the usage of synthetic dyes [1]. Natural dyes are ecologically clean product, and this make them the best choice to replace synthetic dyes. The need for qualitative and non-perishable natural dyes is increasing [2,3].

The extraction of natural compounds depends on several factors, such as the extraction technique, raw materials, and the extraction solvent that are used. The techniques can be classified into conventional or non-conventional. Conventional techniques require the use of organic solvents, temperature, and agitation. Examples of this type of technique include Soxhlet, maceration, and hydro distillation. Modern techniques, or non-conventional techniques, are green or clean techniques due to reduced use of energy and the implementation of organic solvent, which are beneficial in relation to the environment [4] (Rodriguez Perez et al). In recent years, super critical fluid extraction has attracted attention as an environmentally friendly extraction method that does not use harmful organic solvents, in line with the concept of Green Chemistry. Supercritical fluid extraction (SFE) is a continuously evolving green technology for the separation of bioactive constituents from natural materials. The supercritical fluid is used extensively, especially in substance extraction. The extraction of many substances has reached the economic-scale industrial bulk production stage. However, the research on the wastewater-free dyeing technique replacing water as dissolvent is still at a development stage. This technique has reached the economic scale of mass production. Relevant studies on using supercritical carbon dioxide for extraction and purification have thus emerged since 1980s, including application to vegetable essential oil extraction [5,6], abstracting lecithin beneficial to human health, extracting β-carotene and lycopene from tomatoes or producing powder requiring strict particle size distribution and purity in pharmacy, extracting oligomer from polymer [7-10], and application to fluorine-containing polymer polymerization dispersion reaction and gas chromatography technique as dissolvent [11-13]. The application domains have extended continuously, so that the supercritical fluid technique has become an important part of chemical and chemical industry domains.

SC-CO_2 extraction is an alternative advanced green technology, which continuously increases its application field with beneficial factors including highly pure yield of extracts with no waste produced, shorter extraction time, automation, and lower solvent consumption [14-16]. In addition, the use of CO_2 as the extraction solvent provides nontoxic, non-polluting, high efficiency and operational flexibility with modest quality [17,18].

Super Critical Fluid Extraction (SFE)

Supercritical fluid extraction is a green separation technology which has been developed in past two decades. Now a day this process is widely applied in extraction of natural products and bioactive compounds from different plants and food by products. Super critical fluids are increasingly replacing the organic solvents that are used in solvent extraction methods because of regulatory and environmental pressures on hydrocarbon and ozone- depleting emissions.

Supercritical fluid extraction (SFE) is an environment friendly extraction process that uses a supercritical fluid as an alternative to commonly be used organic solvent. SFE is a process based on the use of a solvent near their critical temperature and pressure to recover extracts from their solid matrices. This process is based on the fact that near the critical point of the solvent, its properties change rapidly with only slight variation of pressure/temperature.

Supercritical fluids may be any compound like water, carbon dioxide and ammonia that at the temperature and pressure above their critical point exhibit the properties of liquids and gases in an intriguing manner i.e., a state in which the fluid is compressible similar to gas along with density like a liquid. Thus, it is a state of unique properties that are different from those of either gases or liquids at standard conditions. Therefore a supercritical fluid has both the gaseous property of being able to penetrate anything and the liquid property of being able to dissolve materials into their components. The intrinsic low viscosity and high diffusivity of supercritical CO_2 has rendered supercritical fluid a faster extraction and efficient technique than traditional solvent.

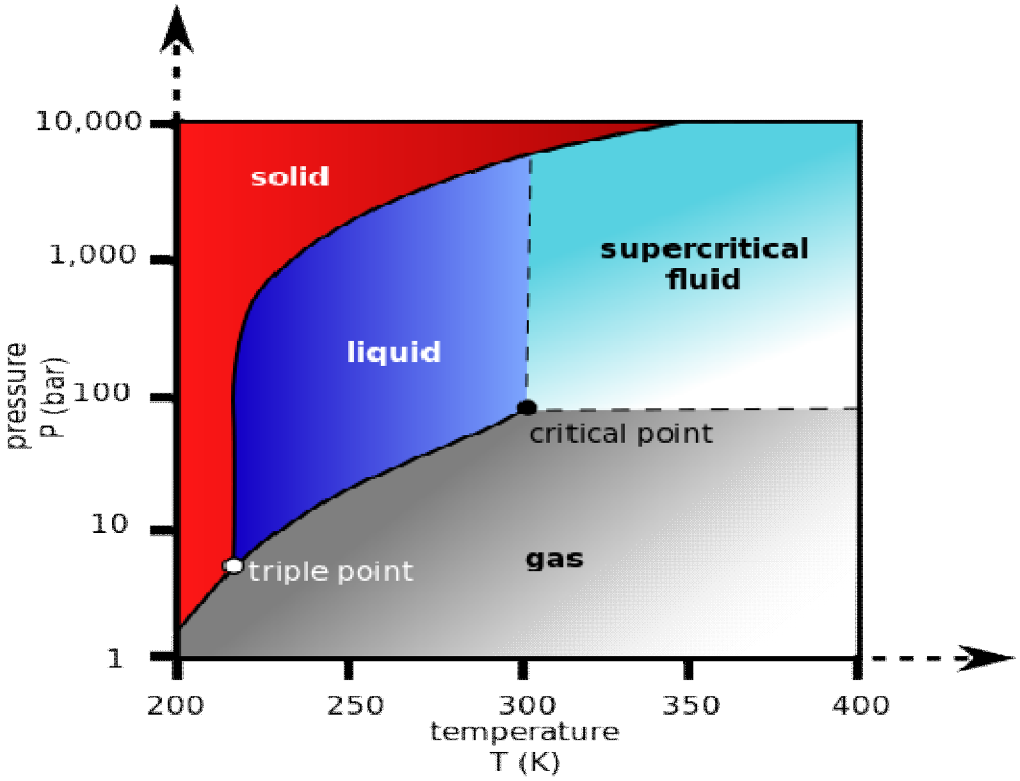

Figure 1.Phase Diagram for Carbon Dioxide in SFE

The figure shows the critical point above in temperature and pressure. At this point the substance does not exist in either the liquid or gas phase. For carbon dioxide the critical temperature is 31.1^{0}Cand pressure is 73.9MPa. Under those condition it is called “Super critical Fluid” and has properties between those of a liquid and a gas.

The fluid used in SFE is carbon dioxide (CO_2) which is the most common and reliable supercritical fluid solvent that has been extensively studied for its potential applications in various fields [19]. Supercritical carbon dioxide is a fluid state of carbon dioxide where it is held at or above its critical temperature and critical pressure. Carbon dioxide usually behaves as a gas in air at standard temperature and pressure (STP) or as a solid called dry ice when frozen. If the temperature and pressure are both increased from STP to be at or above the critical point for carbon dioxide, it can adopt properties midway between a gas and a liquid i.e. super critical state. In this state CO_2 has both gas like and liquid like qualities, and it is this dual characteristic of supercritical fluid that provides the ideal condition for extracting compounds with a high degree of recovery in a short period of time. The CO_2 act as the best solvent due to its low critical temperature 31.1^{0}C and low critical pressure,7.39 MPa which are relatively easier to attain, wide availability, environmentally friendliness, nontoxic, inexpensive, non-flammable, and non-polluting supercritical fluid solvent for the extraction of natural products [20].

Because CO_2 is nonpolar, a polar organic co-solvent or (modifier) can be added to the supercritical fluid for processing polar compounds. By controlling the level of pressure

Changes in properties for a SCF are as follows: (i) Liquid like density (ii) Reduction in surface tension (iii) low viscosity (iv) Gas like CO2

Why CO2 is a supercritical fluid (SCF)?

These properties of CO2 make it qualified to be an SCF. (i) Low critical pressure (74 atm) and low critical temperature (32^0 C) (ii) Relatively non-toxic (iii) Non-flammable (iv) Available as high purity (v) Low cost (vi) Easily removable from extract (vii) It has polarity like liquid pentane at supercritical conditions and thus, best suited for liophilic compounds.

Table 1.List of compounds with their critical temperature and pressure to be used as supercritical fluids

S. No	Compound	Critical temperature (°C)	Critical pressure (bar)
1	Carbon dioxide	31.3	72.9
2	Ammonia	132.4	112.5
3	Water	374.15	218.3
4	Nitrous oxide	36.5	71.7
5	Xenon	16.6	57.6
6	Krypton	-63.8	54.3
7	Methane	-82.1	45.8
8	Ethane	32.28	48.1
9	Ethylene	9.21	49.7
10	Propane	96.67	41.9
11	Pentane	196.6	33.3
12	Methanol	240.5	78.9

Schematic Diagram of Supercritical fluid extraction-SCFE apparatus

Supercritical fluid extraction-SCFE is the process of separating one component from another using supercritical fluids as the extracting solvent.

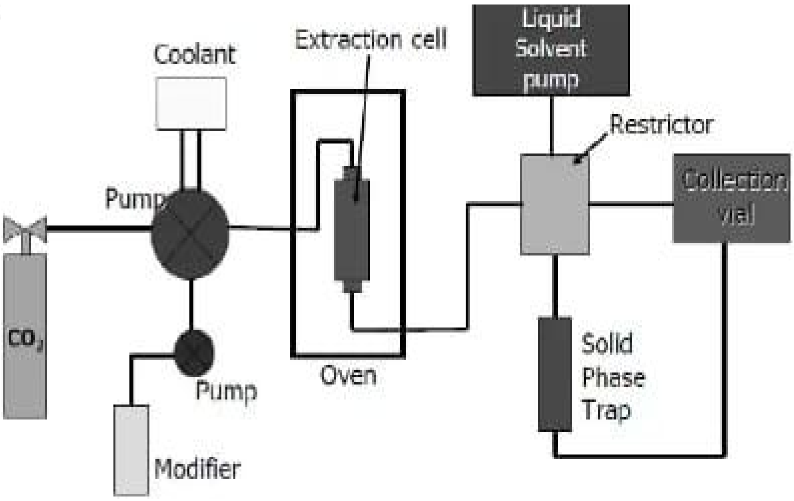

Figure 2.

Supercritical fluid extraction-SCFE is a two-step process, which uses a dense gas as solvent usually carbon dioxide above its critical temperature (31°C) and critical pressure (74 bar) for extraction. The natural product is powdered and charged into the extractor. Carbon dioxide is fed to the extractor through a high-pressure pump (100-350 bar). The extract charged carbon dioxide is sent to a separator (60-120 bar) via a pressure reduction valve. At reduced temperature and pressure conditions, the extract precipitates out in the separator. The extract-free carbon dioxide stream is introduced several times for effective extraction of all the dye material from the natural product

Steps involved in Supercritical fluid Extraction

Introduction of feed into extractor (Solid Feed) or extractor in modified column either Co-currently or counter-currently

↓

Formation of mobile phase: mixing of solutes with supercritical fluid

↓

Exposure of mobile phase to pressures (50-500atm) and temperatures ambient to (30^0C) near or above the critical point for enhancing the mobile phase solvating power.

↓

Isolation of dissolved solute by precipitation

The unique feature of supercritical fluid extraction using CO_2 is that the density of the supercritical fluid could be easily tuned by modifying the temperature and pressure applied to give the solvent for class-selective extraction (21,22). However, CO_2 is nonpolar in nature as it does not possess a permanent dipole moment and hence, its ability to dissolve and extract polar compounds is limited. The selectivity of CO_2 towards polar compounds could be amplified by the addition of polar solvents such as alcohol or water. (23,24)SCFE is superior over the traditional solvent extraction of natural dyes because it uses a clean, safe, inexpressible, nonflammable, nontoxic, and nonpolluting solvent-carbon dioxide (CO_2). . The intrinsic low viscosity and high diffusivity of super critical CO_2 has rendered supercritical fluid a faster extraction and efficient technique than traditional solvent. SCFE is a superior technique over traditional solvent extraction for natural dyes.

Table 2.Comparison of conventional organic solvent and supercritical carbon dioxide extraction and pretreatment methods

Organic solvent	**Disadvantages**
Soxhlet extraction and purification	Uses harmful organic solvents
Solvent extraction & purification	Process is complicated and time-consuming Long pre-processing time Higher sample concentration required Trace residual solvent
Supercritical carbon dioxide	**Advantages**
Carbon dioxide	Uses safe carbon dioxide
Carbon dioxide & ethanol, etc.	Simple process that can be automated Fast pre-processing and extraction Selective extraction possible Online SFE-SFC Prevention of sample oxidation, operation at low temperature

When compared to Soxhlet extractions, supercritical fluid extractions have proven to be capable of providing extractions up to 25 times faster with equivalent recovery while using up to 30 times less solvent.

Advantages of Super Critical Fluid Technology

1. Selectivity-CO_2 polarity varies greatly depending upon the pressure it is exposed to. This makes CO_2 a tunable solvent which allows the user to find the precise conditions for extraction of the compounds of interest while leaving unwanted compounds behind.
2. No residual solvents-given the gaseous state of CO_2 at atmospheric conditions, the resulting extract does not require the long rotavapor time needed to dry solvent extracted analytes.
3. Faster-given the high diffusivity and low viscosity of CO_2 in its supercritical state the extractions typically take a fraction of the time compared to solvent extractions.
4. Higher Yield-due to increased temperature and pressure, supercritical CO_2 can penetrate many matrices that solvents cannot thereby allowing for greater surface area contact which in turn increases yield.
5. Low Operating Cost-Cost Per Extraction is significantly lower as the cost of CO_2 is much lower than the equivalent amount of solvent.
6. Environmentally Friendly

Conclusion

SC-CO2 Extraction technology is emerging as high valued, green and efficient extraction technology finding wider application as food ingredient industry is catching up with its materials engineering and pharmaceutical counterparts and expanding beyond extraction. SC-CO2 offers solutions for problems such as product purity, process efficiency, health, and environmental impact.

SCF-based technologies offer important advantages over organic solvent technology, such as ecological friendliness and ease of product fractionation. The main advantages of using SCF for isolation of natural products include solvent free products, no coproducts, and low temperatures in the separation processes for their beneficial health effects.

Recent demand has tended towards implementation of extraction and formulation processes that enable the transition to ‘green’ technologies, without further use of environmentally and health hazardou organic solvents.

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