Ultrasound-Assisted Pretreatment and β-Cyclodextrin-aided Extraction

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Cyclodextrins (CDs) are a group of cyclic oligosaccharides consisting of subunits of α(1→4)-linked D-glucopyranose. Alpha-, β- and γ-CDs are the most common CDs, consisting of six, seven and eight glucose units, respectively, and they are obtained by enzymic starch degradation. Their shape has a truncated cone form, with hydroxyl functions directed towards the cavity's outer surface.

antioxidants β-cyclodextrin extraction polyphenols red grape pomace

1. Overview

Winemaking is a process that generates a large volume of solid waste biomass, which is currently under extensive investigation as a bioresource of precious polyphenolic compounds. These substances are retrieved from vinification side streams principally by deploying solid–liquid extraction methods. In this frame, the present investigation had as objective the development of an alternative, green extraction process for polyphenols, through integration of ultrasonication as a pretreatment stage, and subsequent extraction with aqueous β-cyclodextrin. Polyphenol recovery from red grape pomace (RGP) was shown to be significantly enhanced by ultrasonication pretreatment, and the use of β-cyclodextrin effectively boosted the aqueous extraction. Under optimized conditions, established by response surface methodology, the maximum yield in total polyphenols was 57.47 mg GAE g^{-1} dm, at 80 °C, requiring a barrier of 10.95 kJ mol^{-1}. The extract produced was significantly enriched in catechin and quercetin, compared to the aqueous extract, exhibiting also increased antiradical activity. These findings highlighted the value of the process developed for targeted recovery of certain polyphenols and the preparation of task-specific extracts.

2. Cyclodextrins

Globally, the agricultural activity related to food production has as a result the generation of wastes, which, according to FAO, in U.S.A. and in China only may exceed 47 million tons [1]. A large proportion of fruit, vegetable and cereal waste derives from industrial processing, and it is mainly composed of leaves, peels, roots, seeds and stems [2]. The improper handling and disposal of such materials, which are rich in organic load, may cause serious environmental pollution, and therefore their management and processing is of undisputed importance. On the other hand, the ongoing research on food waste valorization strategies integrated into a biorefinery concept has revealed the enormous potential of food side streams as bioresources of a vast variety of precious phytochemicals [3].

The wine industry has a crucial position in the agro-industrial sector, as grapes are one of the most important fruit crops worldwide [4]. The grape production was estimated around 77.8 metric tons in 2018 [5] and during vinification, approximately 25% of the grape mass results in grape marc. It has been estimated that the production of 6 L of wine is accompanied by approximately 1 kg of grape marc, which thus accounts for worldwide production of 10.5–13.1 million tons, on an annual basis. Grape marc consists principally of stems, skins, and seeds, which are the residues of grape crushing and juicing (pressing) steps. This bio-waste is particularly rich in multifunctional polyphenols, which belong to various classes, and they have been demonstrated to exhibit a range of biological activities [6].

The effective recovery of polyphenols from grape pomace has been a significant issue, and a wide diversity of methodologies have been developed for this purpose [7]. However, in compliance with the Green Chemistry principles, the objectives solicited by an eco-friendly extraction process should encompass the use of alternative non-toxic and reusable solvents, high extraction yields, production of a safe and high-quality extract/product, and minimum energy consumption [8]. It is of vital importance to choose a suitable solvent, as its physical-chemical properties will largely determine the extraction performance, as well as the means of appropriate downstream processing (e.g., evaporation, adsorption) [8].

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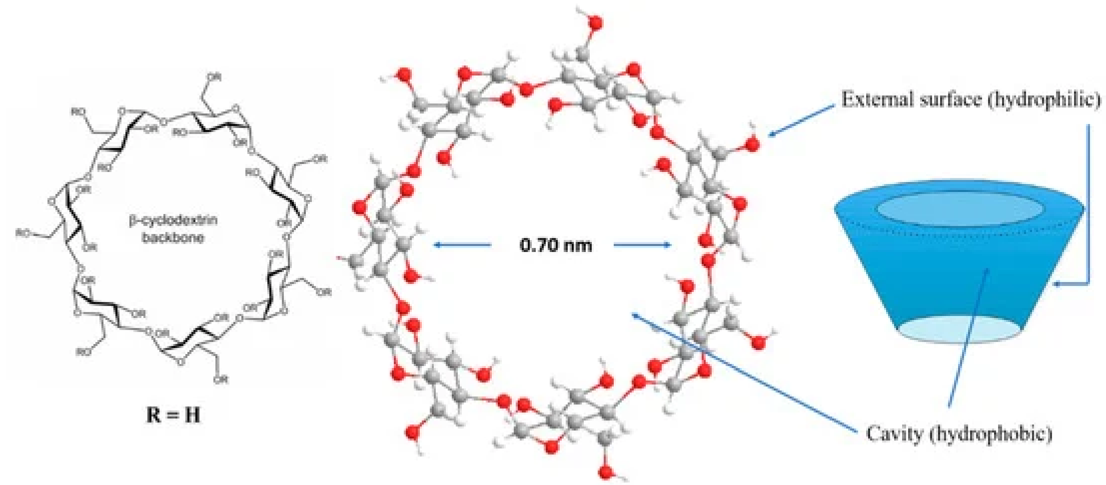

Figure 1. Structure of β-cyclodextrin.

This three-dimensional structure of the CD molecules is characterized by an external hydrophilic surface and an internal hydrophobic cavity, providing both water solubility and the ability to encapsulate appropriately sized hydrophobic molecules inside the cavity, producing inclusion complexes [9]. The use of CDs for the extraction of polyphenolic compounds is a state-of-the-art trend, offering unparalleled "green extraction" possibilities. This is because, while common organic solvents used for the recovery of polyphenols (e.g., ethanol, ethyl acetate, etc.)

show excellent potential for the dissolution and extraction of polyphenols, their use is of significant environmental concern [7]. Aqueous systems containing CDs may be regarded as green extraction media, with a potential of replacing organic solvents in such processes.

The use of various cyclodextrins has been stressed as a way towards fostering aqueous polyphenols extraction and achieving increased yields. This has been demonstrated for various polyphenol classes of red grape pomace (RGP) [10], polyphenols of vine shoots [11], catechin and epicatechin of RGP [12], flavone glycosides and rosmarinic acid from *Salvia fruticosa* [13], polyphenols of potato peels [14], and flavanone glycosides from orange peels [15].

3.

The use of various types of cyclodextrins as green enhancers of aqueous polyphenol extraction has been gaining a high appreciation. The investigation presented herein is proposing for the first time a green high-performance process of red grape pomace polyphenol recovery, using ultrasonication pretreatment and β-cyclodextrin-aided extraction. The most important findings may be summarized as follows:

- Optimization through response surface methodology demonstrated that incorporation of β-cyclodextrin in an aqueous medium at a level of 1.5% and ultrasonication pretreatment for 30 min may significantly increase the extraction yield in total polyphenols.
- The maximum yield, after carrying out a temperature assay, was 57.47 mg GAE g^{-1} dm, at 80 °C. Taking into consideration the bibliographic data from previous studies, but also the relatively low activation energy determined, the process developed is effective, green, with low energy demands.
- The extracts obtained were characterized by high (506.54 μg g^{-1} dm) and quercetin (151.17 μg g^{-1} dm) content and relatively high antiradical activity. This outcome may be important for the production of extracts fortified in selected polyphenolic phytochemicals and enable task-specific extractions.

Since β-cyclodextrin is an approved food additive, it could be part of the final product formulation. Thus, polyphenol-enriched extracts could be directly used in foods/pharmaceuticals/cosmetics, the appropriate composition and concentration provided. Such an option would be particularly appealing, since current trends suggest ingredient production based on functionality rather than purity. Therefore, the extracts produced with the methodology proposed could be for specific applications rather than for general use.

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