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Research article

Isolation of organic compounds with high added values from agro-industrial solid wastes

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A B S T R A C T

Phenols are organic compounds with high antioxidant activity. Occurring mainly in plants, where they act as pigments or even as part of defense mechanisms against insects and herbivores. Given the positive impact on on human health, their isolation and purification from agricultural products is of particular interest for the production of nutritional, pharmaceutical and cosmetics supplements. In our study different materials rich in phenolic compounds were used, in order to separate the phenolic content and maximum condensation using physicochemical methods such as solvent extraction, filtration through membranes, adsorption/desorption on resins and vacuum distillation. The materials tested were solid wastes from winery, cocoa residuals, olive leaves, etc. The first step for the treatment was the extraction of phenolic content using water-ethanol solutions which was initially optimized. Then, sequential membrane filtration of the extracts by Ultrafiltration membranes, Nanofiltration and Reverse Osmosis was performed to separate the contained compounds, based on their molecular weight. To remove non-polar compounds, with similar molecular weights with phenols, methods of adsorption/desorption on specific resins were developed, in order final ethanolic solutions rich in phenolic compounds to be obtained. Finally, the ethanol was removed by vacuum evaporation at low temperatures. The purification of olive leaf phenols is illustrated in details in the present work. The final obtained concentrate, was a rich phenolic concentrate and contained 98 g/L phenols in gallic acid equivalents. This technique, after modification, can be applied to a variety of phenol-rich byproducts, allowing the operation of phenol separation plant adjustable to local agricultural activities.

1. Introduction

Olive tree and vineyard cultivations have a long history in the Mediterranean countries, and even today consist an important cultural, economic and environmental aspect of the area. Together with the precious products (extra virgin olive oil and wine) large amounts of agricultural byproducts are co-produced every year, causing significant environmental problems. The problem from the uncontrolled disposal of byproducts to the environment can be reduced by the exploitation and purification of their phenolic content.

Phenolic compounds are important phytochemicals, abundant in nature. They are present in most plants in great variety, and may differ not only from plant to plant, but also with season, maturity and region. Their role may be to act as pigments, or even a defense mechanism for plants (Morales-González, 2013). Phenols are characterized as antioxidants, with beneficial health effects for humans (Yu et al., 2009); as a result their isolation for the production of high-added value products is of great interest. In our studies, different plant materials or byproducts, rich in phenolic compounds were examined for the purification of their phenolic content, through solid-liquid extraction, membrane filtration and resin adsorption/desorption. In the present work, the study was focused on the extraction of oleuropein from olive leaves which has been named as an excellent phenolic compound with antimicrobial and antioxidant activities (Pereira et al., 2007; Japón-Luján et al., 2006; Tsakona et al., 2012; Silva et al., 2006). Generally, phenols were identified for their antioxidant, antimicrobial, anti-inflammatory, anti-HIV, antiviral, antitumor, hypotensive, hypoglycemic, antiallergenic, cardio-protective, anti-thrombotic, vasodilatatory and hepatoprotective activity (Morales-González, 2013;

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Yu et al., 2009; Pereira et al., 2007; Japón-Luján et al., 2006; Tsakona et al., 2012; Silva et al., 2006).

Solid-liquid extraction can be utilized for the treatment of solid byproducts, rich in phenols, in order to move the targeted compounds from the solid matrix to a solution. Phenolic compound extraction from a solid matrix is commonly achieved through solvent extraction with different techniques (Spigno and De Faveri, 2007; Yilmaz and Toledo, 2006; Makris et al., 2007; Spigno et al., 2007; Wang et al., 2008; Proestos and Komaitis, 2008; Bouaziz and Sayadi, 2005; Markin et al., 2003; Soto et al., 2011). This extraction can be further enhanced with the use of ultrasounds or microwaves, increasing its efficiency (Wang et al., 2008; Proestos and Komaitis, 2008). The most common solvents used are water, methanol, ethanol, ethyl acetate and other organic solvents, pure or in mixtures of water-ethanol (Pereira et al., 2007; Japón-Luján et al., 2006), or water–methanol (Silva et al., 2006; Bouaziz and Sayadi, 2005) or just pure water (Pereira et al., 2007; Markin et al., 2003). Water-ethanol mixtures are preferred in the food industry, as they do not affect the human health. Important parameters of the extraction are the composition of the solvent, temperature, solid/solvent ratio and duration, use of microwaves or ultrasound (Pereira et al., 2007; Wang et al., 2008). Another extraction technique involves supercritical fluids, like supercritical CO_2.

Membrane filtration can then separate phenolic compounds according to their molecular weight. The most important, size exclusion, membrane applications are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The advantages of membrane application include: low energy consumption compared to other separation methods that involve phase change, high selectivity and low temperatures (crucial when handling thermally unstable compounds like phenols). Membrane filtration was already tested and found useful for the isolation and purification of phenols from olive mill wastewaters (Zagklis et al., 2015; Cassano et al., 2013; Ochando-Pulido et al., 2013), and other agricultural byproducts such as grape marc pomace (Zagklis et al., 2015) or other fruit byproducts (bergamot juice, kiwifruit juice, citrus and carrot juices) (Conidi et al., 2011; Cassano et al., 2003, 2008). Membrane filtration of this type of extracts (olive leaves) is not well documented in literature, but in the UF step, removal of suspended solids is expected, while in the NF step the phenolic content of the extract should be retained, as oleuropein has higher molecular weight (541 g/mol) than the MWCO of the membrane used (470 g/mol).

Further treatment of the phenol enriched concentrate can be carried out through resin adsorption/desorption of polar compounds like phenols. In the experiments presented by Li et al. (2011), the adsorption/desorption of olive leaf extracts on synthetic macroporous resins, resulted in 13-fold increase of the total flavonoids concentration while, according to the results of Bayçın, Altıok, Ülkü and Bayraktar (Bayçın et al., 2007), silk fibroin was successfully used as adsorbent for the separation of oleuropein. As shown in our previous work (Zagklis et al., 2015; Zagklis and Paraskeva, 2015), the use of resins can separate the polar phenols from the non polar carbohydrates of the plant material. Carbohydrates are present in most plant extracts, hindering the concentration of phenolic compounds. As they have similar molecular weights to phenols, they cannot be separated with membrane filtration, but this is possible with the use of adsorption resins. Finally, after the removal of carbohydrates, the purified phenolic compounds can be further concentrated through vacuum evaporation for increased concentrations of phenolic compounds.

In the present work a detailed experimental investigation was performed for the extraction, isolation and purification of phenols in olive leaves using a combination of solid-liquid extraction, membrane filtration and resin adsorption/desorption, for the production of phenolic concentrates. The final products of the proposed process contain a large percentage of the byproducts' phenolic content, in a small fraction of the initial volume.

The novelty of the process that was developed lies in the different stages of phenol separation, first according to their molecular weight in the stage of membrane filtration where lower-molecular-weight phenolic compounds with high-added value are separated from polyphenols. Then the low-molecular-weight phenolic compounds are further purified according to their polarity through an adsorption/desorption process on selective resins consisting of three stages: adsorption, carbohydrates desorption with water and finally phenols desorption with ethanol.

2. Materials and methods

2.1. Olive leaves

The olive leaves used in this study originated from "Koroneiki" olive tree variety, and were collected in December 2014, from the region of Ilia, Greece. The sample was refrigerated at −25 °C until used, for the preservation of its phenolic content. Prior to every experiment, the samples were defrosted and ground.

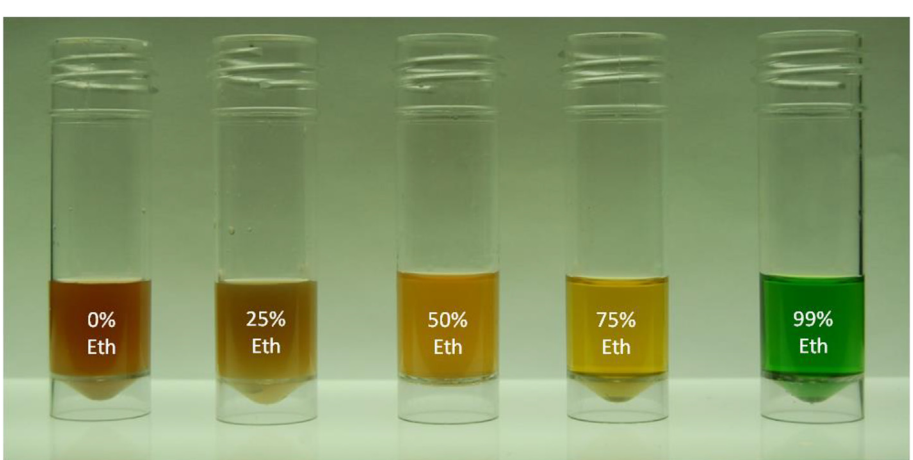

Fig. 1. Olive leaf extracts, with different hydro-ethanolic mixtures.

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