Purpose: Phenols are compounds with high antioxidant activity and positive impact on human health and their isolation and purification, from agricultural by-products, is of interest for the production of cosmetics, nutritional and pharmaceutical supplements.

Method: In the present study, a preliminary design of a treatment plant is presented, based on experiments carried out with three materials rich in phenolic compounds. The proposed process for the separation the phenols implements physicochemical methods such as solvent extraction, filtration through membranes, adsorption/desorption on resins and vacuum evaporation. The materials tested were olive mill wastewater (OMW), grape marc and olive leaves.

Results: The final products of the proposed process were rich in phenolic compounds, with the OMW final concentrate containing 378 g/L phenols in gallic acid equivalents, 84.8 g/L being hydroxytyrosol. The final concentrate of olive leaf extract contained 98 g/L phenols in gallic acid equivalents, and the final concentrate of grape marc phenols 190 g/L in gallic acid equivalents, containing 4.7 g/L catechin.

Conclusions: The combination of solvent extraction, membrane filtration, resin adsorption/desorption and vacuum evaporation proved to be effective for the separation and purification of phenols contained in agro-industrial by-products, with the final concentrates that occurred containing high amounts of high-added value phenolic compounds. As a result, the design of a new process was possible, for the separation and purification of phenols contained in agro-industrial by-products.

Keywords: Phenols, membrane filtration, resin adsorption, olive mill wastewater, grape marc, olive leaves
1. Introduction

Phenols are important compounds, abundant in nature known for their antioxidant activity. They are present in most plants in great variety and may differ not only from plant to plant but also with the season, maturity and region. In the recent years, the naturally occurring phenolic compounds have received increased interest, because of the benefits they offer to human health [1, 2]; as a result, their isolation for the production of high-added value products is of great interest. In the present study, a separation process is illustrated, for the purification of phenols contained in agro-industrial by-products. The results of the separation, isolation and purification of the phenolic content of three plant materials or by-products, rich in phenolic compounds were used for the designing of a complete treatment process. The used materials were olive mill wastewater (OMW), grape marc and olive leaves and the suggested process includes solid-liquid extraction, membrane filtration and resin adsorption/desorption.

1.1 Olive mill wastewater (OMW)

OMW is a by-product of the three-phase extraction systems during the production of olive oil. The phenolic compounds contained in the waste originate from olive fruits and vary depending on the tree variety, region of cultivation and degree of maturation, etc. [3]. Because of their partition coefficient, most phenolic compounds of olive fruits end up in the wastewater produced and not in olive oil. Oleuropein is the most common phenolic compound of unripe olive fruits, but during maturity, it is hydrolyzed to several simpler phenolic compounds like hydroxytyrosol and Tyrosol [3].

1.2 Olive leaves

Olive leaves is a by-product of olive fruit harvesting and initial stages of olive oil extraction, during their separation from olive fruits. Olive leaf extracts have been proven to be rich in phenolic compounds, with the most prominent one being oleuropein, which, unlike in the olive fruit, it is not hydrolyzed to simpler phenols [4]. Oleuropein can be either bound to a sugar molecule (Oleuropein glycoside) or be present in its free form (Oleuropein aglycon). Other important olive leaf phenols are luteolin, verbascoside, rutin and caffeic acid, in much lower concentrations [5]. According to Silva et al. [6], around 1200-1700 mg of phenols are contained in 100 g of fresh olive leaves, although this concentration varies with region, harvesting period and olive tree variety.
1.3 Grape marc

Grapes used for winemaking are rich in phenolic compounds, with most of their phenolic content being concentrated in their skin and seeds [7]. Grape marc occurs after the extraction of the juice for winemaking and mainly consists of the phenol-rich parts of the grape, making it an excellent material for phenol extraction. Both red and white grapes have a significant phenolic content, but red grapes have much higher levels of phenols. The most important phenolic compounds found in grapes are catechin, epicatechin, trans-resveratrol and quercetin [7, 8].

1.4 Solid-liquid extraction

Solid-liquid extraction is the separation of target compounds from a solid matrix through the use of the appropriate solvent. Usually, the solid residue is the by-product, although in some cases the removal of undesirable compounds is the target of the process. An example of solid-liquid extraction is the use of hexane for the extraction of vegetable oils from oilseeds. This type of processes is widespread in the food industry.

Solvents can be used for the removal of phenols from a solid matrix, and their transfer to a solution [9-13], with the most common ones being water, methanol, ethanol, ethyl acetate and other organic solvents, pure or in mixtures. Important parameters of the extraction are the physical characteristics of the solid, the solvent used, temperature and agitation. In the present work, safe for food solvents such as mixtures of water and ethanol were used in different percentages.

1.5 Membrane filtration

Membrane filtration is a relatively new separation technique that has many applications in chemical process industries. This technology is mature enough to compete with other well-established separation techniques. After phenols have been transferred to a solution, membrane filtration can be used for their separation according to their molecular weight. The most important membrane applications are Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO). Membrane filtration is a separation method with relatively low energy consumption (compared to techniques where phase change takes place) and facilitates the preservation of phenols as it takes place at low temperatures. Membrane filtration has already been tested for the separation of phenolic compounds from agro-industrial by-products [14-19].
1.6 Resin adsorption

Adsorption resins have been used for the adsorption of polar compounds like phenols [20-26]. Their application enabled further separation of the target compounds through their difference in polarity from less polar compounds, like carbohydrates. After the removal of carbohydrates, phenols can be further concentrated through vacuum evaporation, leading to highly enriched phenolic extracts with high added-value.

2. Materials and methods

The preliminary design of the treatment plant is based on experimental results published by the authors in previous works [19, 27-29], where more information about the materials used and the analytical techniques implemented can be found. Some brief information will be presented herein.

2.1 Feed Materials

OMW used was obtained from a 3-phase olive mill during January of 2013 in the region of Patras, Greece. The membrane filtration experiments were carried out immediately after sample collection. The RO concentrate, rich in simple phenols, as well as all intermediate samples during membrane processing, were kept at -20°C.

The grape marc used was produced from Merlot grapes of the 2013 harvesting season, from the region of Achaia, Greece, after the extraction of their juice. The olive leaves used originated from “Koroneiki” olive tree variety and were collected in December 2014, from the region of Ilia, Greece. Solid samples were refrigerated at -20 °C until used for the preservation of their phenolic content. Prior to every experiment, the solid samples were defrosted and ground.

2.2 Analytical Techniques

Phenols (Ph) were measured with the Folin-Ciocalteu method [30], using gallic acid as standard with spectrophotometric method at 760 nm, and carbohydrates (Ch) were measured with L-tryptophan reagent and glucose as standard at 525 nm [31].

The HPLC–diode array detection (DAD) model, Agilent 1200 series system was used for the determination of free low-molecular-weight phenolic compounds contained in OMW. The analytical column used was Luna C18(2) 100 Å (250 x 4.6 mm, i.d., 5 µm particle size) with security guard
cartridge C18 (4 x 3 mm) by Phenomenex. The separation of OMW phenols was achieved by gradient elution according to [32]. Standards of phenolic compounds of p-coumaric acid, gallic acid, tyrosol and cinnamic acid as well as caffeic acid, vanillic acid, oleuropein, and hydroxytyrosol were purchased from Merck and Sigma-Aldrich, respectively. The only phenolic compounds detected in appreciable amounts in the samples, as identified by comparison of their retention time and spectra with those obtained from the corresponding standards, were gallic acid, hydroxytyrosol and tyrosol.

The HPLC WATERS 2695 system, coupled with a WATERS 2996 Photo Diode Array Detector, was used for the determination of the free low-molecular-weight phenolic compounds contained in grape marc. The analytical column used was Prodigy C18, 100 Å (250 x 4.6 mm, 5 μm particle size), coupled with a 0.5 μm inline filter (KrudKatcher Ultra), both supplied by Phenomenex. The separation was achieved by gradient elution according to [33] with some modifications. Standards of phenolic compounds of (+)-catechin, (-)-epicatechin, trans-resveratrol, quercetin and rutin were purchased from Sigma-Aldrich. The only phenolic compounds detected in appreciable amounts in the samples, as identified by comparison of their retention time and spectra with those obtained from the corresponding standards, were (+)-catechin, (-)-epicatechin and rutin, while the presence of quercetin, although identified, was below 1 ppm.

2.3 Separation processes
The membrane used to obtain the results presented herein were a tubular UF membrane (Ceramic Zirconia, 0.24 m², 100 nm pore size), a spiral wound NF membrane (polymeric, 2.4 m², molecular weight cut-off: 470 Da, determined experimentally in the lab through filtration of PEG solutions with different MW) and a spiral wound RO membrane (polymeric, 2.5 m², 99% rejection of NaCl) supplied by HAR SpA, Milan, Italy. Cross-flow filtration was carried out in all the membrane filtration steps.

The resins used were supplied by Sigma-Aldrich. Amberlite XAD4 (matrix: styrene-divinylbenzene, 20-60 mesh) was used for the OMW experiments and XAD16N (matrix: styrene-divinylbenzene, 20-60 mesh) for the grape marc extract and olive leaf extract experiments. Both resins have been reported to yield good adsorption results for phenols [24, 25, 34], and had only small differences in their adsorption capacities in the experiments carried out for the selection of the most appropriate resin per material treated.
3. Results and discussion

The processes presented herein are based on the results published in previous works of the authors [19, 27-29] which will be briefly discussed. The results from the treatment of OMW were used as a basis for the design presented herein [19, 27], but the same processes can be used for the treatment of solid by-products, rich in phenolic compounds, such as grape marc and olive leaves, with an extra step of particle size reduction and by using the feeding tank for the extraction of the phenolic compounds from the solid matrix of the by-product. The process has been tested by the authors for both grape marc phenols [28] and olive leaf phenols [29].

3.1 Proposed separation process

The main conclusions from the previously published work of the authors were that through the synergy of different physicochemical separation techniques, the phenolic content of both liquid and solid by-products can be concentrated to very small volumes. In the case of solid by-products, the first step is the solvent extraction of the phenolic compounds. Water-ethanol mixtures proved capable of this extraction. In the case of grape marc, a mixture of 50% v/v ethanol was the optimum solvent, while in the case of olive leaves pure water yielded the best results. In the case of grape marc, the ethanolic content of the extract had to be reduced prior to membrane filtration. This was achieved through vacuum evaporation (the same equipment is used later-on in the process) and the addition of water. 80 L of grape marc extract occurred from 20 kg of grape marc and 75 L of olive leaf extract occurred from 20 kg of olive leaves.

After the phenolic content was transferred to a liquid phase, the next step of the proposed process was the separation according to molecular weight. This can be achieved with the inline filtration through membranes with decreasing molecular weight cut-off. The membranes used for this kind of separation were UF, NF and RO. The volume balances of the membrane filtration can be observed in Fig. 1. RO was only used in the case of OMW, as the phenolic content of the other materials was distributed at higher molecular weights, and the NF filtrate (NFt) did not contain sufficient amounts of phenols to facilitate an extra filtration step. As it can be observed in Fig. 3, all the suspended solids were removed in the UF step, while the final filtrate of the process appeared free of any colored compound.
Figure 1: Volume balances of membrane processes developed for the fractionation of the phenolic content of (a) OMW, (b) grape marc extract and (c) olive leaf extract.

During the separation according to their molecular weight, low-molecular-weight phenolic compounds were concentrated in the NF/RO concentrate (NF$_c$/RO$_c$). Carbohydrates followed a similar trend in their distribution in the membrane process fractions, with lower molecular weight carbohydrates being concentrated alongside lower-molecular-weight phenolic compounds (Table 1).

Table 1: Distribution of carbohydrates (Ch) and phenols (Ph) during the proposed membrane filtration process.

<table>
<thead>
<tr>
<th>Sample</th>
<th>OMW</th>
<th>Grape marc extract</th>
<th>Olive leaf extract</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ch (mg/L)</td>
<td>Ph (mg/L)</td>
<td>Ch (mg/L)</td>
</tr>
<tr>
<td>Initial</td>
<td>13340</td>
<td>2650</td>
<td>2204</td>
</tr>
<tr>
<td>UF$_c$</td>
<td>19370</td>
<td>6590</td>
<td>6122</td>
</tr>
<tr>
<td>UF$_f$</td>
<td>10930</td>
<td>2170</td>
<td>1106</td>
</tr>
<tr>
<td>NF$_c$</td>
<td>11970</td>
<td>2640</td>
<td>1882</td>
</tr>
<tr>
<td>NF$_f$</td>
<td>5090</td>
<td>860</td>
<td>443</td>
</tr>
<tr>
<td>RO$_c$</td>
<td>14060</td>
<td>2090</td>
<td>-</td>
</tr>
<tr>
<td>RO$_f$</td>
<td>210</td>
<td>40</td>
<td>-</td>
</tr>
</tbody>
</table>
For two out of three materials tested, NF contained lower concentrations of phenolic compounds. This can be attributed to the different phenolic compounds in each material. After HPLC analysis of the NF of the materials the apparent rejection of the membrane regarding low-molecular-weight phenols was calculated and is presented in Fig. 2, in comparison with polyethylene glycols (PEGs) of different molecular weights. The membrane used appeared to reject phenols at a higher percentage compared to PEGs of similar molecular weight. This can be explained by the different shape of the molecules, as phenols are expected to have more bulk because of the benzene ring they contain, while PEGs are mostly linear molecules. The most prominent phenolic compounds of OMW are tyrosol and hydroxytyrosol that are not rejected at high percentages by the NF membrane used. On the other hand, grape marc extract contains mostly catechin, epicatechin and their polymers, and olive leaf extract contains mostly oleuropein which has a molecular weight of 378 Da, that are rejected by the membrane by more than 70%. As a result, only in the case of OMW a third step of membrane filtration (RO) was justified. The NF of OMW was rich in higher-molecular-weight phenols that can still be exploited with the proposed method, but the RO was used, as it contained the more valuable, lower-molecular-weight phenolic compounds.

Figure 2: Comparison of NF membrane apparent rejection of polyethylene glycols and olive mill wastewater and grape marc phenols, according to their molecular weight. T: tyrosol, H: hydroxytyrosol, G: gallic acid, C: catechin, and R: rutin.
The similar distribution of phenols and carbohydrates posed a serious problem for the further concentration of phenolic compounds. Vacuum evaporation of the membrane fraction of interest was attempted, but after the removal of a small amount of water the sample became very viscous and could not be further concentrated because of the presence of high amounts of carbohydrates.

Figure 3: Samples obtained during the membrane filtration of (a) OMW, (b) grape marc extract and (c) olive leaf extract.
For the separation of low-molecular-weight phenols from low-molecular-weight carbohydrates, resin adsorption/desorption was used. After batch adsorption experiments, using the fraction concentrated in NF (olive leaves, grape marc) or RO (OMW), containing the low molecular weight phenols, XAD4 and XAD16N were proven to successfully adsorb phenolic compounds. A three-step resin process was then developed. The first step was the adsorption of phenols, the second step was the desorption of adsorbed carbohydrates with the use of water as eluent and the final step was the desorption of phenols with the use of ethanol as eluent. As a result, most of the carbohydrates were removed, while the majority of phenolic compounds were retrieved in an ethanolic solution.

The removal of carbohydrates and the retrieval of phenols in ethanol facilitated the concentration of phenols through vacuum evaporation and the recovery of ethanol for further use in the process. The final concentrates (Fig. 4) were rich in phenolic compounds with concentration ranging from 100 to 380 g/L in gallic acid equivalents (Table 2). 1 ton of OMW treated with the proposed process would lead to the production of approximately 0.5 L of final concentrate, 1 ton of grape marc would lead to the production of approximately 1.5 L of final concentrate and 1 ton of olive leaves would lead to the production of approximately 3 L of final concentrate.

![Figure 4: Final concentrates that occurred through the proposed process, from (a) OMW, (b) grape marc and (c) olive leaves.](image)

**Table 2:** Results from the gradual concentration of phenols after the proposed membrane filtration process.

<table>
<thead>
<tr>
<th>Sample</th>
<th>OMW</th>
<th>Grape marc</th>
<th>Olive leaves</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume/mL</td>
<td>Ph g/L</td>
<td>Ch g/L</td>
</tr>
<tr>
<td>Membrane fraction</td>
<td>2000</td>
<td>2.64</td>
<td>12.34</td>
</tr>
<tr>
<td>Desorbed</td>
<td>1500</td>
<td>3.36</td>
<td>3.84</td>
</tr>
<tr>
<td>Final concentrate</td>
<td>9</td>
<td>377.5</td>
<td>293.92</td>
</tr>
</tbody>
</table>
Here, it must be noted that in the case of olive leaf extract, the separation of phenols from carbohydrates was achieved at a lower extend compared to OMW and grape marc extract. This may have been caused by the presence of oleuropein-glycoside, which is expected to be a prominent phenolic compound contained in olive leaf extract. Oleuropein-glycoside contains a glucose molecule, and as a result it contributes to the concentration of both phenols and carbohydrates. Microorganisms or enzymes (β-glycosidase, esterase) can be used to convert oleuropein-glycoside to oleuropein-aglycon, and even produce hydroxytyrosol [35-37], enabling better separation and the production of higher value final concentrate.

3.2 Preliminary plant design

The phenol separation method presented in this study can be applied to a variety of plant materials or by-products. Although a complete techno-economic analysis of the whole process has not been carried out, initial analysis of the process, not including the resin part, was promising [7]. In this study, a preliminary design for a phenols extraction plant is presented, along with the expected distribution of phenols during the process. Results obtained from the OMW treatment experiments were used as a basis for the process design, but the same plant can be used for solid by-products, by adding an initial particle size reduction step and converting the initial waste storage tank to an extraction tank. The feed of the plant was chosen to be 1.1 m³/h of extract or wastewater, but this purely theoretical and can be rescaled. For simplicity reasons, all the steps of the process are considered to be carried out in batch mode with one-hour duration (apart from the resin process), after which, the treated sample passes to the next treatment step.

The main factors that will determine the sustainability of the plant will firstly be the market demand and price of the final product, and secondly the management of the large volumes of occurring secondary products.

In the pretreatment of the liquid sample (after the extraction if the initial material is solid), a flotator, decanter, vertical separator and filter bags are used in line (Fig. 5). This pretreatment is essential for the protection of the membrane process that follows, through the removal of the solids present in the sample. During pretreatment, other modifications of the initial samples can be carried out as well, for example, enzymatic treatment of olive leave extracts for enhanced oleuropein concentration, or better phenols-carbohydrates separation.
Figure 5: Proposed pretreatment for the samples treated in the phenol extraction plant.

The final effluent of the pretreatment process will then be fed to the membrane process, where separation through size exclusion of the compounds takes place (Fig. 6). This step may include UF, NF and RO steps, depending upon the intended separation. More than one NF steps with different MWCO can also be used in line, depending upon the molecular weights of the target compounds and their intended fractionation.

If the characteristics of the occurring final filtrate are appropriate, it may be implemented in the membrane cleaning process. After the membrane separation step, the concentrate enriched in phenolic compounds will be led to the resin adsorption/desorption process.
Figure 6: Membrane separation step of the proposed phenol extraction plant.

The resin adsorption/desorption process is presented in Fig. 7. It consists of an adsorption step, a carbohydrate desorption step with water as eluent and a phenol desorption step with ethanol as eluent. The selection of the appropriate resin is crucial and depends upon the treated material. Moreover, the resin lifespan should be examined, as it is an expensive material that can impact the economic feasibility of the process.

The final product of the resin process will be a phenol enriched ethanolic solution. Finally, vacuum evaporation will further concentrate the phenols contained in the ethanolic solution and enable solvent recovery (Fig. 8).
Figure 7: Resin adsorption/desorption step of the proposed phenol extraction plant.

Figure 8: Vacuum evaporation step of the proposed phenol extraction plant.
The initial design of the phenols purification plant is for 12 h of operation per day, with three resin adsorption/desorption cycles. With the capacity presented herein and 12 h operation, the plant would be able to treat 13.2 m$^3$/d of OMW, or about 3 ton/d of solid by-products, such as grape marc and olive leaves.

The water and ethanol requirements of the plant are presented in Table 3. The high washing water requirements can be partly covered by the final permeate of the membrane process, and the ethanol requirements through solvent recycling, although eventually enrichment of the ethanol solution will be needed.

**Table 3:** Water and ethanol requirements of the extraction plant.

<table>
<thead>
<tr>
<th></th>
<th>m$^3$/d</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washing Water</td>
<td>20</td>
<td>The pH needs to be neutralized before discharge</td>
</tr>
<tr>
<td>Desorption Water</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td>Desorption Ethanol</td>
<td>1.16</td>
<td>A portion can be recovered in the concentration of the final product</td>
</tr>
</tbody>
</table>

An important factor for the sustainability of the plant will be the management of the occurring secondary products (Table 4). The large quantities of the products that are expected are not easily manageable; as a result, their final treatment or use should be decided and organized, prior to the plant operation. Some possible uses are proposed in Table 4, but further investigation is needed for their suitability.

**Table 4:** Occurring secondary products and possible uses.

<table>
<thead>
<tr>
<th>By-product</th>
<th>Description</th>
<th>m$^3$/d</th>
<th>Possible use</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Large solids</td>
<td>1.2</td>
<td>Animal feed or composting</td>
</tr>
<tr>
<td>2</td>
<td>UF concentrate</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>NF concentrate, high concentration of polyphenols</td>
<td>2.04</td>
<td>Food additive, natural antioxidant</td>
</tr>
<tr>
<td>4</td>
<td>RO filtrate</td>
<td>6.6</td>
<td>Discharged or used for membrane cleaning</td>
</tr>
<tr>
<td>5</td>
<td>Resin effluent 1, high concentration of sugars and low concentration of phenolics</td>
<td>2.34</td>
<td>Food Additive</td>
</tr>
<tr>
<td>6</td>
<td>Resin effluent 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Distillate, mainly ethanol</td>
<td>1.16</td>
<td>Recycled in the resin process after further enrichment in ethanol</td>
</tr>
</tbody>
</table>

An important issue that could affect the operation of the plant is the seasonality of the by-products treated. The by-products examined in this study cover the months from September to March, but for the continuous operation of the plant, more by-products should be examined. Some examples and proposals for such materials are presented in Table 5. As phenolic compounds are abundant in nature,
several different plant materials can be chosen for treatment, allowing the plant feed to be adjusted to the by-products that occur near its location.

Table 6: Possible plant materials for extraction of high added value compounds.

<table>
<thead>
<tr>
<th>Source</th>
<th>Main product</th>
<th>Harvesting period</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tomato by-products</td>
<td>Quercetin, Hydroxycinnamic acid and lycopene</td>
<td>May-August</td>
<td>[38, 39]</td>
</tr>
<tr>
<td>Coffee by-products</td>
<td>Hydroxycinnamic acids</td>
<td>All year</td>
<td>[39, 40]</td>
</tr>
<tr>
<td>Citrus by-products</td>
<td>Hesperidin</td>
<td>November-March</td>
<td>[39, 41]</td>
</tr>
<tr>
<td>Apple, pear by-products</td>
<td>Hydroxycinnamic acids</td>
<td>September-January</td>
<td>[39, 42]</td>
</tr>
<tr>
<td>Strawberry by-products</td>
<td>Anthocyanins</td>
<td>May-July</td>
<td>[39, 43]</td>
</tr>
<tr>
<td>Mediterranean aromatic plants (dyclamus, marjoram, vitex, teucrium, rosemary)</td>
<td>Phenolic acids</td>
<td>June-August</td>
<td>[44]</td>
</tr>
</tbody>
</table>

4. Conclusions

In the results presented herein, solid-liquid extraction, membrane filtration and resin adsorption/desorption were combined for the purification of phenols contained in OMW, grape marc and olive leaves.

It must be noted that for the solid materials examined, correct extraction was crucial for maximizing the phenolic concentration. Moreover, pretreatment of the samples can greatly affect the results, as for example reduction of olive leaf particle size may increase the amount of phenols extracted, with lower extraction duration.

During membrane filtration, the extracted compounds were fractionated according to their molecular weight. The presence of organic solvents like ethanol can affect the rejection of polymeric membranes and change their molecular weight cut-off, and it should be removed prior to filtration. In the UF step, the solids contained in the samples were removed. The complex and higher-molecular-weight compounds were concentrated in the NF step, while low-molecular-weight at the RO step.

Because of their similar molecular weight distribution, phenols and carbohydrates could not be separated by size exclusion during the membrane filtration step, but this was achieved through adsorption/desorption on resins. After the selective adsorption of the phenolic compounds of the membrane concentrate of interest, water was used to desorb the adsorbed carbohydrates and ethanol for the desorption of phenols. This type of separation can be limited by the presence of complex compounds, like phenol-glycosides. This can possibly be tackled with the enzymatic treatment of the concentrate, prior to adsorption.
During the resin process, the solvent of the phenolic compounds was changed from water to ethanol, facilitating their further concentration through evaporation. The final product of the proposed process contained a large amount of the phenols contained in the initial plant material, in a very small fraction of the initial volume.

Apart from the plant materials examined in this study, the proposed process can be employed for the treatment of any material rich in phenolic compounds. The application of the proposed process to a number of seasonal agricultural by-products would enable the establishment and continuous operation of a phenol extraction plant, adaptable to regional agricultural activities. Some materials that could be investigated are by-products from coffee extraction, from the cultivation of tomatoes, citruses, apples, pears, strawberries and Mediterranean aromatic plants like dyclamus, marjoram, vitex, teucrium, rosemary and the waste occurring from the two-phase extraction of olive oil.

Another important parameter of the process that should be examined is the stabilization of the phenolic compounds contained in the final product. Several techniques, like freeze drying and encapsulation, may be examined for their effect on the stability of the separated phenols, and the use of chromatographic separation could be tested for the production of purified single phenols.

A detailed techno-economic analysis will be carried out for the validation of the economic feasibility of the process, which will heavily depend on the demand and pricing of the final products of the process.

5. Acknowledgements

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