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# Microfiltration for the recovery of polyphenols from winery effluents

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ABSTRACT

Winery effluents are attractive sources for the recovery of antioxidant compounds, particularly polyphenols. In this study, the aqueous extraction associated with microfiltration for the recovery of polyphenols present in the effluent (wine lees) from the second racking of red winemaking was investigated. To decrease the charge of the suspended solids and then use the effluent as feed for the microfiltration, dilutions combined with vacuum filtration were tested. In total recirculation mode, two flat-sheet microfiltration membranes (V0.2 and MFP5 membranes) were studied, while in concentration mode a hollow fiber membrane (PAM-Membranas Seletivas) was used. Higher dilution factors of the effluent resulted in higher permeate fluxes, and the membrane with a larger pore size showed higher propensity to fouling. At the optimal conditions, a solution diluted 10 v/v followed by microfiltration led to the achievement of a limpid permeate, rich in polyphenols. This represents a recovery rate of 21% of the total content of polyphenols.



## 1. Introduction

Polyphenols are secondary metabolites typically found in plants. They are characterized by having one or more phenolic groups in their structure [1], and can be classified into different groups, namely phenolic acids, flavonoids, stilbenes and lignans [2].

These phenolic compounds have high antioxidant properties, acting as free-radical scavengers, electron or hydrogen donors and strong metal chelators, evidencing their potential human health benefits [3]. Furthermore, according to Ky et al. [4], they can prevent the oxidation of nucleic acids, proteins and lipids, which may initiate degenerative diseases such as cancer, heart disease, dermal disorders and aging.

Based on these properties, phenolic compounds have become of interest for food, pharmaceutical and cosmetic industries, especially those polyphenols from natural sources. Nowadays, consumers are changing their consumption habits, which means the market is demanding naturally processed, additive-free and safe products, rather than synthetic ones [5].

In fact, agro-industrial by-products are cheap, abundant and sustainable resources, rich in antioxidants, specifically polyphenols [6]. In this regard, in the last few years, several studies have been carried out aiming to establish conditions for polyphenols recovery from a myriad of agro-industrial wastes, such as olive mill wastewaters [7–9], pomegranate wine lees [10], wood extracts [11] and sour cherry pomace [12], among others. The vast amount of literature in winemaking by-products is particularly concerned with grape pomace [13–16]. In contrast, there are few studies on the recovery of polyphenols from effluents or wine lees [17,18].

According to European Council Regulation (EC) 1493/1999 on the common organisation of the wine market, wine lees are defined as the residue accumulating in vessels containing wine after fermentation, during storage or after authorised treatment as well as the residue obtained from filtering or centrifuging it [19].

In wineries, effluents from first and second rackings are also generated in large amounts and, consequently, they are an environmental problem that requires appropriate treatment. On the other hand, effluents from the second racking can also be a valuable source for the recovery of polyphenols, since they are mainly composed of microorganisms, tartaric acid, inorganic matter and phenolic compounds [20].

The aforementioned researches, regarding to polyphenols recovery, are mainly focused on organic solvent extraction, employing methanol, ethanol, ethyl acetate, etc. However, solvents are not always "food friendly" and do raise consumer concerns regarding their safe utilization within the food chain [21]. For this purpose, efficient and environmentally friendly processes should

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**Nomenclature**

| | |
|---|---|
| DF | dilution factor |
| GAE | gallic acid equivalent |
| Jp | permeate flux |
| Lp | hydraulic permeability |
| MF | microfiltration |
| MSP | membrane separation processes |
| NF | nanofiltration |
| PI | polyimide |
| PVDF | polyvinylidene fluoride |
| PWP | pure water permeation flux |
| SRR | solute recovery rates |
| TOC | total organic carbon |
| TMP | transmembrane pressure |
| TS | total solids |
| TSS | total suspended solids |
| UF | ultrafiltration |
| VCF | volumetric concentration factor |
| v/v | volume/volume |

be developed for the recovery, concentration and purification of the polyphenols present in agro-industrial wastes.

On this subject, membrane separation processes (MSP) become an alternative for this matter, as they have inherent characteristics such as low energy requirement, no additives, mild operating conditions, separation efficiency and easy scaling up. In fact, microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) have already been widely used in the recovery, concentration and fractionation of value-added products from agro-industrial wastes [17,22–28]. Nevertheless, the use of MSP for the recovery of value-added products from wine lees is still a matter of research. Previous studies have shown that around 2% of polyphenols were recovered from wine lees generated during second racking, coupling sedimentation process to UF [17]. Subsequently, by means of UF/NF, polyphenols and polysaccharides were fractionated [22]. However, MF has not been sufficiently studied for this purpose, especially for the recovery of the polyphenols present in wine lees from the second racking.

In this paper, MF was applied to the treatment of the effluent from the second racking, with or without using previous water dilution of the effluent. The process was applied in order to recover polyphenols on the permeate. Polyphenols are preferably soluble in organic solvents and have low solubility in water. At the same time, polysaccharides are highly soluble in water and the interactions among these groups of molecules enhance the solubility of the polyphenols in aqueous solutions [29].

In the light of these considerations, this paper proposes the optimization of a sequence of aqueous extraction and microfiltration for the recovery of polyphenols from the wine lees generated during the second racking of Merlot grape winemaking.

## 2. Materials and methods

### 2.1. Wine lees

Wine lees from the second racking, obtained of the red wine production using Merlot grapes, were collected in a winery located in the Vale dos Vinhedos Region in Brazil, stored at −20 °C and defrosted to room temperature before use.

A schematic diagram of the experiments is shown in Fig. 1, where before or after dilutions, the effluent was subject to filtration and/or microfiltration.

### 2.2. Vacuum filtration

Aliquots of 100 mL of the effluent were filtered through filter paper under vacuum, using a Buchner funnel coupled to a water aspirator, with a flow rate of 0.57 mL $cm^{-2}$. Different solutions, one without dilution and three prepared after 3, 5 and 10 v/v dilutions in deionized water ($A_1$, $A_2$, $A_3$ and $A_4$) were investigated in order to determine the best conditions for the recovery of polyphenols in the filtered solution ($A_{1F}$, $A_{2F}$, $A_{3F}$ and $A_{4F}$), respectively. These experiments were carried out in triplicate. For subsequent MF experiments, under a flow rate of 2.8 mL $cm^{-2}$, aliquots of 500 mL were filtered until a total volume of 5 L was achieved.

### 2.3. Membranes characterization

Permeation experiments were carried out with three commercial membranes: a V0.2 membrane, a PVDF flat-sheet membrane with 0.2 μm pore size supplied by Synder Filtration, USA; a MFP5 membrane, a fluoro polymer flat-sheet membrane with 0.5 μm pore size supplied by Alfa Laval, Denmark; and a polyimide (PI) hollow fiber membrane with 0.4 μm pore size supplied by PAM-Membranas Seletivas, Brazil.

Membranes were first compacted through the circulation of deionized water (with a conductivity of less than 2 μS $cm^{-1}$) that was pressurized at 1 bar for 3 h. This compaction avoids the influence of pressure effects on the membranes' structure in subsequent experiments. They were characterized in terms of their hydraulic permeability (Lp), as described elsewhere [30], at transmembrane pressures (TMP) of 0.3, 0.5, 0.7 and 1 bar.

### 2.4. Microfiltration permeation experiments

Permeation experiments were performed in laboratory flat-cell units with a membrane surface area of $14.6 \times 10^{-4}$ $m^2$, using the V0.2 and MFP5 membranes. A schematic illustration is presented in Fig. 2. Experiments were conducted in total recirculation mode, where the permeate and the retentate streams were recirculated to the feed tank to study the variation in the permeate fluxes and the solute rejection coefficients.

These permeation runs were performed at a feed flow rate of 150 L $h^{-1}$ and with four values of TMP, 0.3, 0.5, 0.7 and 1 bar. Four variations of the effluent from the second racking as feed solutions were used (Fig. 1): without any pretreatment (solution B), filtered with filter paper under vacuum without any dilution (solution $C_{VF}$), diluted 10 v/v in deionized water (solution $D_{DIL}$) and diluted 10 v/v in deionized water and filtered with filter paper under vacuum (solution $E_{DIL\text{-}VF}$). The stabilization time for each experimental run was 15 min. Between each run, membranes were washed until the Lp reached at least 90% of the initial value. Samples were taken at the beginning and at the end of each experimental run and the average concentration of these two samples was considered the feed concentration. The feed temperature was kept at 25 ± 1 °C in all experiments by using a heat exchanger coupled to an ultrathermostatic bath.

After the optimization of the MF operating parameters, a separate run was conducted in concentration mode to determine the variation of the permeate flux and the solute recovery rates as a function of the volumetric concentration factor (VCF).