



# Removal and recovery of phenolic compounds from olive mill wastewater by cooling crystallization



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## HIGHLIGHTS

- Heat and mass balances in the cooling crystallization batch reactor.
- Depiction of the super-cooling and concentration distribution at various times.
- Determination of mass layer distance adjacent to the cooled surface.
- Comparative presentation of the % total recovery for the respective poly-phenol.

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## ABSTRACT

Phenolic compounds are among, the most complex and the most difficult to remove compounds from the by-products of olive mill wastewaters (OMW). Due to significant properties, including stability and anti-oxidative activity, the recovery of poly-phenols (PP) from OMW is of paramount importance. In the present work, trans-cinnamic acid and ferulic acid, model compounds for the PP present in OMW were removed by cooling crystallization from aqueous solutions. Cooling crystallization experiments were done in a batch reactor kept at constant temperature,  $T_{hot}$  (70 °C). Solutions of the two tested PP were prepared in the reactor and were allowed to equilibrate. Crystallization took place on the surface of a cylindrical ( $\varnothing$  25 mm,  $L$  = 120 mm) stainless steel (SS) metal tube immersed into the supercooled solution. The SS surface was cooled at a lower temperature,  $T_{cold}$ , with respect to the respective melting point, in the range between 0 and 25 °C. Preliminary experiments showed that the solubility of the tested PP solutions was 1 g L<sup>-1</sup> between 45 and 55 °C for trans-cinnamic acid and 3 g L<sup>-1</sup> at 50 and 60 °C for ferulic acid. These were the initial concentration values of the PP used in the cooling crystallization process in this study. For the calculation of the super-cooling with respect to each of the PP studied, the respective solubilities as a function of temperature were measured in the range 0–60 °C. The formation of PP crystal layers on the SS tube surface took place without any appreciable induction time. In the series of experiments done, the temperature and concentration profile in the batch reactor in the presence of the cooled SS surface were calculated on the basis of mass and heat transport equations for unstirred systems. The imposed super-cooling ( $\Delta T = T_{melt} - T_{cold}$ ) from the cold surface to the bulk solution, which is the driving force for the crystallization of the phenolic compounds on the SS surface, was thus estimated.

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## 1. Introduction

Olive mill wastewater (OMW) is classified as a hardly degradable waste because of the high organic load and the content of very high concentrations of phenolic compounds. The disposal of

untreated OMW into aquatic receptors has serious environmental consequences as it is responsible for water contamination, eutrophication, odour and aesthetic deterioration of the ecosystems [1,2]. It is imperative that all countries, engaged in the production of olive oil, follow the European community regulations [3] and develop financially viable treatment methods for OMW treatment. Despite the fact that to a large extent, OMW is disposed following a preliminary treatment (calcium oxide treatment [4]) there is increasing pressure for the efficient treatment of OMW. Higher

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## Nomenclature

$D_{AB}$	diffusion coefficient of the solution ( $\text{m}^2 \text{s}^{-1}$ )	$t$	Time (s)
$x_B$	association parameter of the solvent	$c$	concentration ( $\text{g L}^{-1}$ )
$M_W$	molecular weight of the solvent ( $\frac{\text{g}}{\text{g mol}}$ )	$c_{T_{\text{cold}}}^*$	solubility at temperature $T_{\text{cold}}$ ( $\text{g L}^{-1}$ )
$T$	absolute temperature (K)	$c_o$	initial concentration of the solution ( $\text{g L}^{-1}$ )
$T_{\text{cold}}$	temperature of the cooled surface (K)	$Q_l$	heat flux through the liquid ( $\frac{\text{W}}{\text{m}^2}$ )
$T_{\text{hot}}$	temperature of the hot wall (K)	$Q_{\text{cr}}$	heat flux through the crystal layer ( $\frac{\text{W}}{\text{m}^2}$ )
$T_{\text{int}}$	temperature of the interface (K)	$k$	thermal conductivity ( $\frac{\text{W}}{\text{m K}}$ )
$\bar{V}_A$	molecular volume of the solute ( $\frac{\text{cm}^3}{\text{g mol}}$ )	$k_{\text{cr}}$	thermal conductivity of the crystallized PP ( $\frac{\text{W}}{\text{m K}}$ )
$\mu$	viscosity of the solution (cP)	$n$	similarity ratio
$\alpha$	thermal diffusivity ( $\text{m}^2 \text{s}^{-1}$ )	$\rho$	density ( $\frac{\text{kg}}{\text{m}^3}$ )
$\delta_{\text{thermal}}$	distance of thermal boundary layer (m)	$C_p$	specific heat ( $\frac{\text{W}}{\text{kg K}}$ )
$\delta_{\text{mass}}$	distance from the cooled surface at which concentration difference is observed (m)	$R_1$	radius of the cooled cylinder (m)
$\delta_{\text{thick,cr}}$	thickness of crystal layer (m)	$h$	active length of the cooled cylinder (m)
$Le$	dimensionless Lewis number	$V$	volume of the crystallized material ( $\text{m}^3$ )
$x$	distance from the wall (m)		

efficiency in treating OMW is related with the possibility to extract high added value products, such as poly-phenols (PP) [5–9]. The treatment methods currently employed are either physicochemical, biological or combination methods. Physicochemical methods include coagulation–flocculation [10], membrane filtration [11,12] and oxidation [13]. Biological treatment of OMW may be either aerobic or anaerobic digestion [14] and composting [15]. Despite the need for efficient treatment of OMW, it seems that the cost involved in the different methods applied so far, is a prohibitive factor for their wider application, especially taking into account the fact that the olive mills are rather small seasonal and family units. An additional disadvantage, contributing to the high operational cost is the lack of selectivity of recovery of the various OMW components, among which high added value products (e.g. PP) are included, that may be used as pharmaceutical products [16].

An interesting alternative treatment method for OMW is cooling crystallization that may be applied directly to the fluid. During this process it is possible to separate the various components according to their freezing points (FP). Considering the solvent as “impurity” it is obvious that the FP of the various components of interest depends on their concentration and the presence of other compounds as well. Cooling crystallization has, so far, been successfully applied industrially for the purification of a number of compounds including phenol [17]. Chianese and Santilli calculated the solid layer growth of pure  $\epsilon$ -caprolactam, mixtures of  $\epsilon$ -caprolactam and water and pure naphthalene by applying the integral formulation approach [18]. Choi and Kim separated successfully acetic acid and water by single-stage melt crystallization, finding out the corresponding effective distribution coefficients for various crystal growth rates [19]. Ulrich and Özoğuz used a binary mixture of dodecanole with 3.3 mass% of decanole to improve the process of melt crystallization. They pointed out the way to control the process by controlling the growth rate of the crystal coat. By introducing the procedure of sweating, effective purification was achieved [20]. Hengstermann et al. examined both the effect of supercooling and water content on the crystal morphology of acrylic acid. It came out that by increasing the supercooling and water content, needlelike crystals were formed and the occurring cavities had larger length [21]. Jones and Mullin predicted the crystal size distribution of seeded potassium sulphate solutions both numerically and experimentally and reported the beneficial effect of controlled cooling on the improvement of the product crystal size distribution and on the reduction of the quantity of the formed

nuclei [22]. Kim and Ulrich calculated both theoretically and experimentally the impurity distribution in static layers crystallizations for the binary eutectic mixture of caprolactam and water. The theoretical impurity distributions proved to verify the corresponding experimental data [23]. Huang et al. by examining aqueous solutions of potassium nitrate found out that nucleation capacity decreases and growth capacity increases with increasing seed load [24]. Parisi and Chianese worked on the crystallization of benzylidimethylketale from the binary eutectic system with benzyl. They developed a model for solid layer growth by taking into account the crystal surface undercooling and the impurity segregation in the solid–melt boundary layer [25].

OMW may be considered as a “melt” from which compounds like the PP can be selectively removed by cooling crystallization. In the present work, two representatives among the family of PP contained in the OMW, namely trans-cinnamic acid (TCA) and ferulic acid (FA) were selected for the investigation of the possibility of their selective removal by cooling crystallization from their aqueous solutions. The layer crystallization on a cooled surface was selected from solutions in which the freezing point for the selected poly-phenols was in the range 45–55 °C for 1 g L<sup>-1</sup> of TCA and 50–60 °C for 3 g L<sup>-1</sup> of FA. More specifically, the present work includes the calculation of the PP concentration distribution based on the heat and mass balance in the reactor which was designed so that a variable temperature gradient could be applied. Depending on the temperature of the cooled surface, the temperature gradient could be controlled. From the temperature and concentration profiles the super-saturation distribution in the reactor, the PP layer distance and the crystal layer thickness, formed on the cooled surface as a function of time, were calculated theoretically and experimentally measured for TCA and FA solutions.

## 2. Materials and methods

### 2.1. Chemical reagents – Analysis

The test PP compounds, TCA and FA were obtained in crystalline form (Sigma Aldrich). Stock solutions of the PP were prepared using deionized, triply distilled water. The total mass of the crystals deposited on stainless steel (SS) surface of a cylinder ( $\emptyset$  25 mm,  $L$  = 120 mm), immersed in the supercooled solution, was measured from the total phenol concentration measured in the FA

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