# Modeling and optimization of two-phase olive-oil washing wastewater phenolic compounds recovery and treatment by novel weak-base ion exchange resins

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**Abstract**

In the present work, the concentration and recovery of high-added value phenolic compounds from two-phase olive mill wastewater (OMW) and the simultaneous effluent treatment by a 'green process' based on resins adsorption/ion exchange was studied. Olive oil is produced by a technological procedure based on physical operations, without use of chemicals. This industry is concerned to make the whole process environmentally friendly, which includes the treatment of the wastewater produced in the mills. The proposed weak-based IE process was statistically optimized and modelled. Results showed the resin performance was optimal at the raw effluent pH and ambient temperature conditions, which means no acidification or basification, nor cooling or heating would be needed. This would imply important savings for the scale-up of the process in real mills. The examined resin ensured minimum 72.4% phenols adsorption after 2 h contact time. The effluent could be partially discharged on suitable terrains or disposed to biological treatments, avoiding phytotoxicity or inhibition due to the phenolic content. The obtention of this concentrated pool of added-value antioxidant compounds for food, cosmetics, pharmaceutical and biotechnological industrial sectors could help counter-balance the economic feasibility of the reclamation process.

**Keywords:** Olive mill wastewater, Ion exchange, Resins, Phenols, Wastewater reclamation, Sustainability.

## 1. Introduction

More than 3 million tons of olive oil are produced annually worldwide, being Mediterranean countries, mainly Spain, Italy, Greece and Portugal, the major producers, but also the Northern African countries and other European nations, as well as the USA, the middle East, Australia and China, where olive oil is a pushful emergent crop. However, the significant boom in the demand of olive oil worldwide in the last decades has in parallel led to an equivalent increase of the effluents (olive mill wastewater, OMW) by-produced.

Different methods have been proposed to eliminate phenolic compounds from OMW, including chemical oxidation, chemical coagulation, extraction with solvents, membrane technology and adsorption (Paraskeva and Diamadopoulos, 2006; Ochando-Pulido et al., 2017). Among them, we should remark the use of membranes and adsorption for three-phase OMW and OMW reclamation (Ochando-Pulido et al., 2017).

In this scenario, polymeric adsorbents have become a promising choice for the efficient removal of aromatic pollutants. They present several advantages, especially those about regeneration, which can be accomplished by simple, nondestructive means, such as solvent washing, thus providing the potential for target compounds recovery.

To this end, a weak-base resin was examined and optimized with the objective to design a 'green' process for valorization (thorugh added-value phenols recovery) and remediation of OMW for its feasible ulterior transfer at industrial level.

## 2. Experimental

### *2.1. IE resin and experimental set-up*

The physico-chemical characteristics of the selected resin are fully reported elsewhere (Ochando-Pulido et al., 2018). The adsorbent was a novel commercial weak-base anion exchange resin (Dowex 66®, Sigma), with polyamide functional groups and hydroxyl ionic form on styrene-divinylbenzene macroporous matrix.

### *2.2. Effluent*

Raw OMW was collected during winter campaign from olive mills operating with two-phase centrifugation technology (OMW2) in region of Andalucia (Table 1).

### *2.3. Physico-chemical analyses*

Analyses of chemical oxygen demand (COD), suspended solids (TSS), phenolic compounds, iron, electrical conductivity (EC) and pH were performed following standard methods (Greenberg et al., 2005). Folin-Cicolteau method was used to measure the phenolic content in the samples. A Helios Gamma UV-visible spectrophotometer (Thermo Fisher) was used for COD, total phenols and total iron analyses.

*2.4. Optimization and modeling*

Statistical impact of the main operating variables - pH ($pH_0$), temperature (T) and resin dosage ($M_{resin}$), as well as contact time (τ) - on the resin performance in terms of phenols adsorption was carried out throughout statistical software Statgraphics Centurion XV, used for the design of experiments and process optimization.

## 3. Results and Discussion

First, the physicochemical characterization of the effluent is reported in **Table 1**, in which it can be seen a significant concentration of phenolic compounds, up to 775.9 mg/L.

**Table 1.** OMW2 physicochemical characterization.

| Parameter | Raw |
|---|---|
| pH | 5.0 - 5.2 |
| EC, mS $cm^{-1}$ | 1.8 - 2.1 |
| COD, g $L^{-1}$ | 13393.0 - 13964.5 |
| Total phenols, mg $L^{-1}$ | 749.3 - 775.9 |

The impacts of the main operating variables on the weak-base anionic resin towards TPhs adsorption efficiency (TPhs absorbed, mg) is reported in **Fig. 2**. Upon increasing the $M_{resin}$ above 60 g/L, a very high and fast TPhs adsorption efficiency was yielded. Otherwise, an increase of the operating T led to a decrease of the TPhs uptake efficiency for the examined resin. The resin was highly efficient at ambient T conditions. Increasing the operating T above ambient conditions (T > 25 °C) led to a decrease of the global uptake efficiency towards TPhs. This is quite relevant, given that the effluent could be driven from the exit of the vertical centrifuges at the outlet T directly to the resins process, without the need nor to heat nor cool the stream, giving a sensible economical boost to the IE process, since the operating T is a key variable from a technical-economical point of view. On another hand, TPhs uptake efficiency increased upon incrementing the $pH_0$ from acidic conditions ($pH_0$ = 2.5) to values of 5.5 (raw effluent $pH_0$), but decreased if the $pH_0$ was further increased up to 8.5.

The effects statistically examined of each input factor on the resins TPhs adsorption efficiency is reported in **Fig. 2**. The optimised parameters showed that the resin performance was optimal at the raw effluent pH and ambient temperature conditions, which means no acidification or basification, nor cooling or heating would be needed. This would imply important savings for the scale-up of the process in real mills from a cost-efficiency point of view.

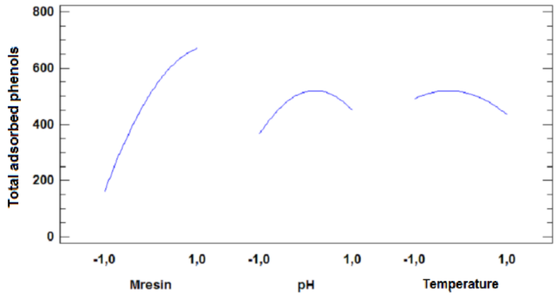


**Fig. 1**. Impacts of the main operating variables on the weak-base anionic resin TPhs adsorption efficiency.

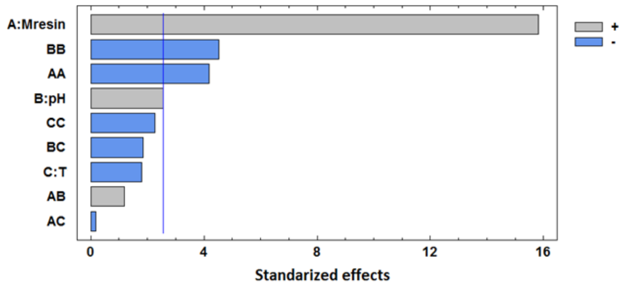


**Fig. 2.** Standarized Pareto chart for IE process.

## 4. Conclusions

OMW could be partially discharged on suitable terrains or directed to biological treatments, avoiding phytotoxicity due to the phenolic content. The obtention of this concentrated pool of added-value antioxidant compounds for food, cosmetics, pharmaceutical and biotechnological industrial sectors could help counter-balance the feasibility of the reclamation process.

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