

# OPTIMIZATION AND MODELING OF TWO-PHASE OLIVE-OIL WASHING WASTEWATER INTEGRAL TREATMENT AND PHENOLIC COMPOUNDS RECOVERY BY NOVEL WEAK-BASE ION EXCHANGE RESINS

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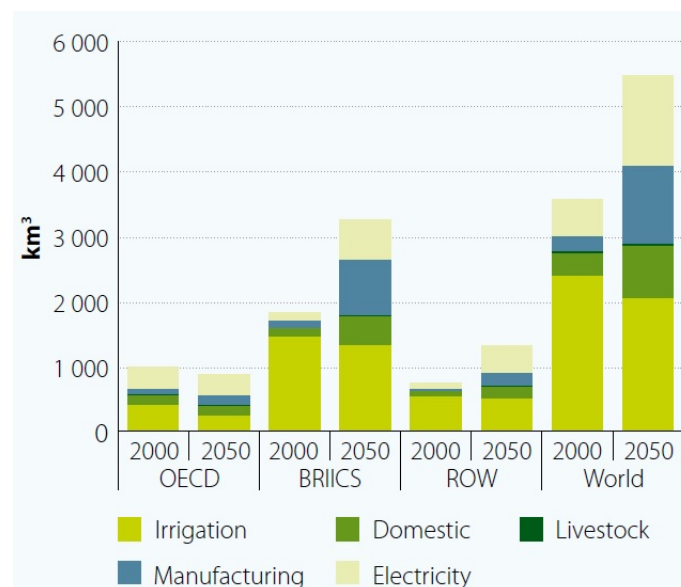
## Abstract

In light of the Circular Economy concept, recently emerged as a need for sustainable production, olive oil industry should be concerned to transform the whole process into environmentally friendly, which necessarily implies the treatment of the wastewater by-produced in olive mills. In this work, concentration and recovery of high-added value phenolic compounds from two-phase olive-oil washing wastewater (OOWW) and parallel effluent treatment by a ‘green process’ based on novel weak-base ion exchange (IE) resins was addressed. The key operating input factors of the resin process for the treatment and valorization of OOWW were studied, optimized and further modelled. A Box-Behnken design was implemented and the obtained data were analyzed by ANOVA and interpreted by RSM methodology. The process was ulteriorly modelled by a second-grade quadratic fitting equation comprising the significant operating variables. The optimization of the IE process performance (20.3 °C,  $pH_0$  6.7 and 114 g/L  $M_{resin}$ ) ensured up to 92.5 % recovery of total phenols concentration. Moreover, the purified stream presented good quality (56.6 – 83.7 mg L<sup>-1</sup> total phenols), following standard recommendations by the FAO. The obtained information would be of key importance for the scale-up of the proposed IE operation. Both the treatment and revalorization of OOWW would help implement a definite sustainable production process of olive-oil.

Keywords: Olive-oil washing wastewater, Ion exchange, Resins, Phenolic compounds, Wastewater reclamation, Sustainability.

## 1. Introduction

Water is a fundamental natural resource for all living beings, for every aspect of socio-economic development and the maintenance of healthy ecosystems. While there are sufficient freshwater resources worldwide nowadays to allow for continued agricultural and industrial development, the long-term unsustainable use of water resources is a growing concern for academics and governments. According to FAO, in the last century, the use of water increased almost twice the rate of population increase. Besides, most of that consumed water (70 %, approximately) is used for agricultural irrigation. If the forecasts are met, by 2050 the irrigated food production will increase by more than 50 % to meet the demand for food from a population that does not stop growing; therefore, the demand for water will also increase (see **Fig. 1**) [1,2]. To this fact, we must add the growing industrial growth that developing countries are experiencing, whose industries lack the technology and experience that provide years of research and development in other parts of the world. It is causing an unsustainable increase in water consumption for the process, cooling and cleaning necessities in the factories, to become seriously threatening. Moreover, in many cases direct discharge of the derived wastewaters in a wide range of regions is causing deterioration of the environmental quality. In this scenario, the reuse of regenerated wastewater in agriculture represents a potential solution that can generate a very positive environmental and economic benefit.



**Figure 1.** Global water demand in 2000 and 2050 [1].

Note: BRIICS (Brazil, Russia, India, Indonesia, China, South Africa);  
OECD (Organisation for Economic Co-operation and Development);  
ROW (rest of the world).

This graph only measures 'blue water' demand and does not consider rainfed agriculture.

The production of olive oil worldwide is around 3.3 million tons per year, of which about 95 % are produced in Mediterranean countries – mainly Spain, Italy, Greece, Tunisia, Turkey, Morocco, Portugal and Syria – where this industry is one of the main engines of the economy. In addition to these countries, although with much smaller productions, we should also mention Northern African nations such as Algeria, Egypt or Libya, European countries like Albania, Cyprus, France or Croatia, American countries such as Argentina, Chile or USA and states like Australia, China and the Middle East, where olive oil is a forceful emergent crop [3]. However, the excellent healthy properties of olive oil – increasingly known and recognized [4–9] – together with its versatility for incorporation into the diet, have led to a significant increase in its demand worldwide during the last decades and the consequent increase in effluents (olive mill wastewater, OMW) by-produced by these industries. The extraction process generates highly polluting effluents, which implies an important environmental problem both for its high polluting power and for the volumes by-produced. Spain, the main producer country worldwide, has not been oblivious to this increase that we mentioned, since in the last thirty years it has doubled its production to reach 1260 million tons per year, which is equivalent to 6300 million cubic meters of OMW per year (the capacity of 2 520 000 Olympic pools) [3,10]. OMW is a dark-colored liquid that contains high amounts of organic carbon, especially phenols, flavonoids and polyphenols, which are highly polluting. Its discharge into the environment causes a great environmental impact such as the coloration of natural waters, generation of bad odors, contamination in surface and underground waters, alterations in soil quality, threat to aquatic life and phytotoxicity. Industrial effluents from the olive oil industry, in addition to being very recalcitrant and organically contaminated, also have high saline toxicity [11,12].

European Environmental Regulations are increasingly stringent under ‘*Horizon 2020*’ (<http://ec.europa.eu/programmes/horizon2020/>) and the future ‘*Horizon Europe*’ ([https://ec.europa.eu/info/horizon-europe-next-research-and-innovation-framework-programme\\_en](https://ec.europa.eu/info/horizon-europe-next-research-and-innovation-framework-programme_en)), which is already being prepared. Industrial wastewater is being increasingly subjected to stricter environmental legislation, so its proper management is a key task [13,14]. There is a wide variety of processes described in the scientific literature for wastewater treatment. However, most of these conventional methods are expensive, in many cases complex, have important energy requirements and involve secondary pollution. The olive industry, consisting mainly of small oil mills scattered throughout

the national territory, is not willing to bear these high costs of wastewater purification to the detriment of its benefits. Therefore, it is necessary to develop new environmentally more sustainable manufacturing processes and wastewater treatment methods that are cheaper or that generate added value.

Today, there are two different technologies for the olive oil extraction process: two-phase continuous centrifugation system and three-phase continuous centrifugation. The main difference between both procedures is that in the first one the solid and the water are mixed in the same stream, while in the second the solid and the water appear separated in two different streams. On the other hand, the two-phase process consumes less water and energy, producing wastewater with a lower pollutant load; therefore, this technology is commonly called 'ecological' [10]. Thanks to these advantages, the two-phase process is the olive oil production procedure that is being imposed in the last decades in the main producing countries – Spain and others – where governments are encouraging public funds to replace the three-phase technology, which has environmentally less sustainable water needs.

However, in spite of everything, the problem related to the effluents generated is not yet solved. The solution most widely adopted so far by most oil mills has been the use of natural evaporation processes [15,16]. By building large artificial lagoons, oil mills can deposit their OMW waiting for solar energy and the favorable climatic conditions of these regions to evaporate it. Once most of the deposited water has evaporated, a concentrated residue containing the contaminating organic compounds will remain at the bottom of the ponds. Then, it will be collected and taken to a treatment plant for its final destruction. Nevertheless, although this has been the most used procedure during all these years, it presents important limitations:

- This method is subject to weather conditions so, depending on the geographical area of the oil mill, it can become quite slow and inefficient.
- The high seasonality of the olive industry – whose production is concentrated in a few months – together with the inefficiency of the method, leads in many cases to the lack of capacity of the artificial lagoons. Frequently, oil mills are forced to build new and larger ponds, with their corresponding associated economic costs.

- Pollutant compounds that remain at the bottom of the ponds are concentrated and degraded over time, causing annoying bad odors and increasing their polluting power every year.
- Artificial lagoons must be properly protected and conditioned to prevent access by any animal and/or person that may fall into it and suffer an accident.
- Ponds cause a significant visual impact that remains even after the activity cessation.
- They are inevitably associated with the risk of leaks and overflows that can contaminate aquifers and surrounding land.
- Finally, artificial lagoons are an obstacle to the implementation of quality systems.

Accordingly, natural evaporation and artificial lagoons do not cease to be a provisional solution for the treatment of these agro-industrial effluents while exploring new feasible and reliable alternatives, more economical and environmentally sustainable.

According to recent research, OMW – this term includes two different wastewater streams that appear in the manufacturing process: wastewater that comes from the olive oil centrifugation, called olive-oil-washing wastewater (OOWW), and wastewater derived from the washing of the fruit (olives), called olives-washing wastewater (OWW) – could be an important source of natural antioxidants, due to its high content of phenolic compounds [17,13,14]. Only 2 % of the total phenolic content of the olives is transferred to the olive oil; the rest goes to OOWW (OWW does not normally contain phenolic compounds unless the olives have been collected quite ripe) [17,18]. This fact gives way to the possible obtaining of a product with high-added value, with applications in the food industry among other sectors. Hence, in recent years, the scientific community is focusing its efforts on the design, development and optimization of processes to concentrate and purify the phenolic compounds of OOWW. Besides, we must take into account that if the phenolic compounds remain in the wastewater, they will be oxidized and/or polymerized, conferring high phytotoxicity and recalcitrance to biological degradation [17,18]. Therefore, the achieved benefit is twofold: on the one hand, the toxicity of this wastewater is reduced, facilitating its subsequent treatment and purification and, on the other hand, an economic benefit is obtained that allows to alleviate the cost of purification.

In recent years, different methods have been investigated to remove phenolic compounds from polluted waters, including adsorption [19,20], chemical coagulation-flocculation

[21,22], extraction with solvents [23,24], ion exchange [25,26], membrane technology [27–29,13] and chemical oxidation and heterogeneous nano-catalysis [14,30–32]. Among them, we should highlight the recent use of membranes [33–35], adsorption [36,37] and ion exchange [38–41] for OOWW and three-phase OMW recuperation. Ion exchange (IE) technology is currently being extensively used for the elimination of inorganic and organic micropollutants from aqueous solutions [42–45]. There are many ion exchange resins in use. Among them, we highlight the polymeric resins that, thanks to their efficient removal of aromatic pollutants, are becoming a promising alternative to conventional ion exchangers [46–48]. Apart from its effectiveness, another of its strengths is related to its ease of regeneration by solvent washing, which allows the recovery of the target compounds easily and quickly. Besides, being a non-destructive regeneration, the resins can be reused [49,16].

In this scenario, the concentration and recovery of high-added value phenolic compounds from two-phase OOWW and the simultaneous treatment of the effluent by a novel IE resin were examined in this study. IE technology was chosen because it is an economical, simple and easily scalable technology; if it is properly optimized, it does not require high consumption of reagents and, in many cases, allows the recovery of the target compounds. In return, the regeneration of resins requires the use of chemical reagents (usually organic solvents) and, when they are depleted, they must be discarded. Therefore, to avoid secondary pollution, this recovery must be optimized [43,46,50,38,45].

To this end, a novel weak-base resin for the pursued objective was selected. The desired aim was the design and development of an ‘environmentally friendly process’ for the valorization and remediation of OOWW by-produced by the oil industry, environmentally respectful, effective and economically efficient for its possible subsequent transfer at industrial scale. This important industry is concerned with making the whole process environmentally sustainable, including the treatment of the wastewater generated in the oil mills. The effects of the main operating variables of the resin adsorption process, mainly the temperature, the effluent pH, the contact time and the resin dosage, were studied in a batch operation. Finally, water quality parameters for reusing the purified olive mill effluent for agricultural irrigation were checked in order to ensure the environmental impact is also reduced. To the authors’ knowledge, no previous research work on the recovery and reclamation of high-added value compounds from real two-phase OOWW through IE technology can be found in the scientific literature up to the present date.

## 2. Experimental

### 2.1. The effluent stream: olive-oil-washing wastewater

OOWW samples were collected in the middle of the production campaign, in January, from two oil mills in the Andalusian provinces of Granada ('Aceites La Purísima', Alhendín) and Jaén ('Cooperativa San Ildefonso', Pegalajar) (South of Spain). These oil mills operate with the modern two-phase olive oil extraction technology. The raw OOWW was taken directly from the vertical centrifuges in-situ and in real-time during the production process.

After collection, the raw OOWW was immediately used for the experiments, to use it as fresh as it is by-produced and thus avoid altering the natural characteristics of the effluent. Otherwise, samples of the raw effluent were kept refrigerated ( $-20\text{ }^{\circ}\text{C}$ ) to maintain them stable in case of further research experiments. The key physico-chemical characteristics of the raw OOWW are hereafter reported in the experimental results section.

### 2.2. Ion exchange resin characteristics

The physico-chemical properties of the selected resin are reported below in **Table 1**. The selected resin was a novel commercial weak-base anion exchange resin (Dowex 66<sup>®</sup>) purchased from Sigma Aldrich, presenting polyamide functional groups with hydroxyl ionic form on styrene-divinylbenzene macroporous matrix.

**Table 1.** Physico-chemical characteristics of the selected resin.

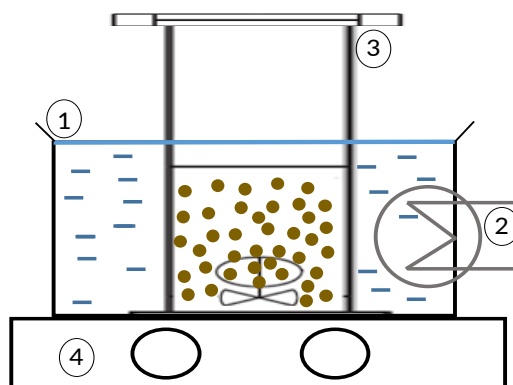
Resin's features	Value
Type of IE resin	Weak-base anionic
Resin model	Dowex 66 <sup>®</sup>
Matrix	Styrene-divinylbenzene (macroporous)
Functional group	Polyamide
Ionic form as shipped	OH <sup>-</sup>
Adsorption capacity (eq/L)	1.35
Moisture (%)	40–46
Density (g/L)	–
Operative pH range	0–7

### 2.3. IE experimental procedure

The OOWW resins-based treatment was studied by performing batch-mode experiments to obtain the key data of the IE process. A novel weak-base resin was chosen for the pursued objective. The goal was the design and development of a ‘green’ process for the valorization and remediation of the wastewater by-produced by the oil industry, economically efficient, effective and environmentally clean for its later scale-up at industrial scale. This aim is following the conception of this important industry, which is concerned with making the whole process environmentally sustainable, and this inevitably implies the treatment of the wastewater produced in the oil mills.

The experimental set-up used for the tests is shown in **Fig. 2**. 200 mL of OOWW samples were taken and placed into beakers (250 mL of maximum admissible volume). Then, the corresponding resin dosage (dry base) for the OOWW sample volume taken was calculated and introduced into the beaker, in which a magnetic stirrer was also introduced and, finally, the beakers were placed on stirring plaques (VELP® Scientifica, AGE series). The feed solution was continuously stirred (medium stirring speed) throughout the experiment. The resin was preconditioned in deionized water, in 50 mL magnetically-stirred beakers. The conditioned resin was subsequently filtered through a paper filter before placing them in the beakers.

The effects of the most important operational variables of the resin IE process, mainly the contact time ( $\tau$ ), the effluent pH ( $\text{pH}_0$ ), the temperature ( $T$ ) and the resin dosage ( $M_{\text{resin}}$ ), were studied in a batch operation. The contact time during the IE experiments was maintained up to 3 hours.



**Figure 2.** Experimental lab-scale set-up used for the IE experiments: 1) bath, 2) chiller system, 3) beaker, 4) stirring plaque



During the IE experiments, 100  $\mu\text{L}$  samples were periodically taken and poured into polypropylene flasks (every 15 min for the first operating hour, then every half an hour), to analyze them and dynamically evaluate the IE efficiency, specifically in terms of phenolic content. A final 20 mL sample of each experiment was taken to fully analyze the treated effluent at the end of  $\tau$ .

In order to determine the optimal  $M_{resin}$ , preliminary experiments were carried out to find the appropriate study range. The  $M_{resin}$  was varied from 3 g/L to 114 g/L. Otherwise, the impact of  $pH_0$  on the resin performance for the phenolic content recovery and reclamation of the OOWW stream was examined by varying the  $pH_0$  values in the range 2.5–8.5. For this purpose, the  $pH_0$  value was adjusted by adding 0.1 N NaOH or HCl solutions, depending on the desired value.

Moreover, the operating temperature was varied from 15 to 35  $^{\circ}\text{C}$ . This choice was motivated by the need not to exceed the temperature point at which phenolic compounds begin to degrade, and thus avoiding any loss; for that, a maximum temperature of 35  $^{\circ}\text{C}$  was chosen. On the other hand, a minimum temperature of 15  $^{\circ}\text{C}$  was adopted, since it is in the range of the conditions experienced during the olive-oil production campaign, and operating at a temperature point below this one would not be economically efficient. The operating temperature was maintained during the experiments ( $T_{\text{set point}} \pm 0.1$   $^{\circ}\text{C}$ ) by immersing the beakers in a controlled-temperature water bath, connected to a chiller (7306 model, PolyScience<sup>®</sup>).

The extent of the IE equilibrium data of the total phenolic concentration was determined by calculating their uptake from the liquid phase. The OOWW sample was contacted with the resin until equilibrium was achieved. The flask containing the effluent solution was continuously stirred throughout the course of the experiments. The removal efficiency (%) was determined by measuring the residual amount of the target species in the liquid phase, then calculating the sorption percentage with the following equation:

$$\% \text{ sorption} = \frac{c_0 - c_e}{c_0} \cdot 100 \quad (1)$$

where  $c_0$  and  $c_e$  are the initial and equilibrium concentration (mg/L), respectively.

#### 2.4. IE process optimization and modeling

In order to optimize the IE purification process of the OOWW feedstream, a Box-Behnken design (BBD) was implemented. This BBD consisted of a total number of 15 experiments, comprising the triplication of the central point. The obtained results were thereafter expressed in the shape of response surface methodology (RSM) [38]. RSM is a collection of mathematical and statistical methods based on the adjustment of an experimental data set to a second-order polynomial model equation, in order to describe the behavior of a data series and thus being able to make statistical predictions [51]. The approach is useful for designing, developing, optimizing operational conditions of the system to achieve target values of the response and improving processes where the response is affected by several variables, determining the range that meets them. This multivariate statistic method is the most popular and used, particularly in optimization processes, since it is capable to obtain the relevant amount of information from very few experimental points and, from them, to predict the behavior of the system.

In 1960, Box and Behnken [52] developed a family of efficient designs for multi-level factors that allow the adjustment with quadratic models. It is a creative design based on the construction of incomplete balanced blocks. The Box-Behnken design has a number of relevant features, which provide a sufficient number of profiles to test the goodness of the fit [52].

For the determination of total phenolic compounds IE efficiency of the weak-base resin under evaluation, three levels were established for each of the process variables examined. This meant adopting a central point level (0) and two extreme levels (minimum and maximum,  $-1$  and  $+1$  respectively) for each operating variable: effluent pH ( $pH_0$ ), temperature ( $T$ ) and resin dosage ( $M_{resin}$ ) (see **Table 2**). The optimization of the model was carried out with *Statgraphics Centurion XV*. Otherwise, the contact time ( $\tau$ ) was followed up to 3 hours.

The experimental conditions of the system were randomly established by combining among the maximum, medium and minimum point values of each studied variable, considering some technical considerations of olive oil production framework. This design is rotatable, which implies that the accuracy in the calculation of the response is uniform throughout the experimental region. Moreover, the central point, meaning the point at the ‘central’ conditions for the studied variables, that is, the medium value for the  $pH_0$ ,  $T$  and  $M_{resin}$  studied, was triplicated to provide the reproducibility of the model.

**Table 2.** Ranges and coded values of the examined IE resin variables.

Factor/Level	pH <sub>0</sub>	Temperature, °C	M <sub>resin</sub> , g/L
- 1	2.5	15	6
0	5.5	25	60
+ 1	8.5	35	114

When using the RSM method, the process response is given by an empirical equation comprised of the corresponding coefficients deducted from the fitting of the experimental data of the examined system.

The surface represented by this polynomial equation, named ‘response surface’, adopts the following form for a three-variable system:

$$y \tag{2}$$

where  $y$  is the response function and  $x_1$ ,  $x_2$  and  $x_3$  are the factors under study.

The use of second-order polynomial equations with cross terms allows the representation of the concavities or convexities of the surface. By solving this equations system, the optimum for the  $x_1$ ,  $x_2$  and  $x_3$  variables can be calculated by differentiating Eq. (3), as follows:

$$\frac{\delta y}{\delta x_1} = b_1 + 2b_{11}x_1 + b_{12}x_2 + b_{13}x_3 = 0 \tag{3}$$

$$\frac{\delta y}{\delta x_2} = b_2 + 2b_{22}x_2 + b_{12}x_1 + b_{23}x_3 = 0 \tag{4}$$

$$\frac{\delta y}{\delta x_3} = b_3 + 2b_{33}x_3 + b_{13}x_1 + b_{23}x_2 = 0 \tag{5}$$

The statistical multifactorial analysis was additionally implemented with *Statgraphics Centurion XV* software, for the determination and quantification of the potential complex relative impacts of the input parameters considered in the studied IE purification process.

### 2.5. Analytical methods

Both the OOWW feedstream as well as the liquid phase during the dynamic operation of the resins adsorption process were characterized by measuring their main physico-chemical parameters: pH, electrical conductivity (EC), chemical oxygen demand (COD),

total suspended solids (TSS) and total phenolic compounds (TPhs). All measurements were made at least in triplicate.

EC and pH measurements were evaluated with a Crison conductivity-meter and pH-meter (GLP 21 and GLP 31 models) respectively, provided with autocorrection of temperature (25 °C). Every day, the equipment was calibrated using buffer standard solutions also supplied by Crison (4.01, 7.00 and 9.21 for the pH-meter; 1413  $\mu\text{S}/\text{cm}$  and 12.88  $\text{mS}/\text{cm}$  for the conductivity-meter).

COD and TSS were analyzed following standard methods [53]. A Helios Gamma UV-Visible spectrophotometer (Thermo Fisher Scientific, UK) at 620 nm was used to analyze the COD, whereas MFV6047 glass microfiber filters (FILTER-LAB®) were employed to quantify the TSS.

TPhs concentration, expressed in mg/L of Gallic Acid Equivalent (GAE), was measured following the Folin-Ciocalteu method [53]. Folin-Ciocalteu's reagent consists of a mixture of phosphomolybdate and phosphotungstate that, at basic pH, become reduced to oxides of an intense blue color which were measured by spectrophotometry at 765 nm in the Helios Gamma UV-Visible spectrophotometer (Thermo Fisher Scientific, UK).

The reagents used for the analytical methods were sulfuric acid (96 %, PanReac), sodium hydroxide (98 %, PanReac), citric acid monohydrate (99.5 %, PanReac), gallic acid monohydrate (99 %, PanReac AppliChem), sodium carbonate (1 N, PanReac AppliChem), potassium dichromate (99.5 %, PanReac), Folin-Ciocalteu's reagent (2 M, PanReac AppliChem), mercury(II) sulfate (99 %, PanReac) and silver sulfate (99 %, PanReac). All the reagents used were of analytical grade without any purification or modification of their properties.

## *2.6. Regeneration and reuse of the chosen resin*

After each batch IE experiment with the OOWW feedstream, the selected resin was regenerated according to the following procedure: first of all, the resin was separated from the liquid phase by filtration through a paper filter, after which the used resin was regenerated with NaOH solution (2 % w/v) and, finally, the resin was washed with double distilled water (20 min) to remove excess base. This procedure was performed immediately after each IE experiment (IE/regeneration cycle).

### 3. Results and discussion

#### 3.1. Effluent characteristics and IE experimental performance

Beforehand, characterization following standard methods of the raw effluent stream taken in-situ from the vertical centrifuges (OOWW) was carried out. The main physico-chemical parameters of the OOWW stream measured in this work – pH, EC, COD and TPhs – are summarized in **Table 3**. It can be highlighted a low pH (acidic) and high COD, and particularly a considerable concentration of phenolic compounds of up to 775.9 mg/L.

**Table 3.** Main physico-chemical characteristics of raw OOWW.

Parameter	Value
pH	5.1 – 5.5
EC (mS/cm)	1.9 – 2.2
COD (mg/L)	13393.0 – 16060.0
TSS (mg/L)	3400.0 – 3460.0
Total phenolic compounds (mg/L)	748.7 – 775.9

Phenolic compounds are naturally present in vegetation decay, but also in domestic wastewaters and in a wide range of industrial effluents, including those from plastics, leather, oil refineries, olive mills, paint, pharmaceutical and steel industries, among others. On one hand, they are regarded as refractory, persistent and phytotoxic compounds even if present in low concentrations. Because they can accumulate in the environment, their removal from wastewaters before discharge into land or water bodies is necessary. Nevertheless, on the other hand these species generally have valuable radical scavenging, antioxidant, antimicrobial and anticarcinogenic properties and thus are very much in demand among pharmaceutical, cosmetic, biotechnological and food industries. Phenolic compounds enhance protection from oxidative stress in biomolecules such as lipids, proteins and DNA, as they help eliminate free radicals in cells [54]. As a result of their properties, but also owed to the fact that currently these compounds are chemically synthesized to satisfy the high demand of those sectors, they present a high market price.

Once the OOWW stream was characterized, IE experiments with the chosen weak-base anion exchange resin were conducted in order to simultaneously treat the OOWW effluent and recover the phenolic fraction. The impacts of the main operating factors, that is, the

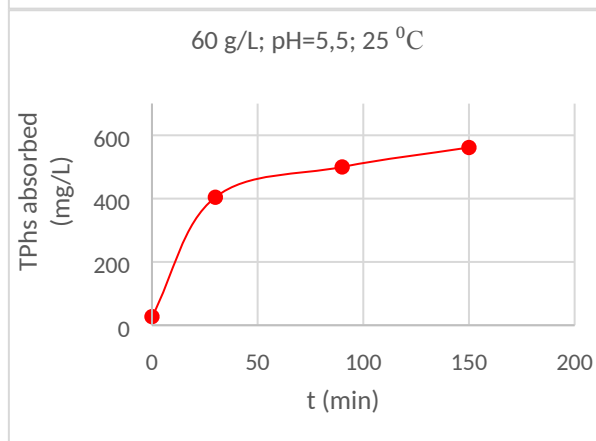
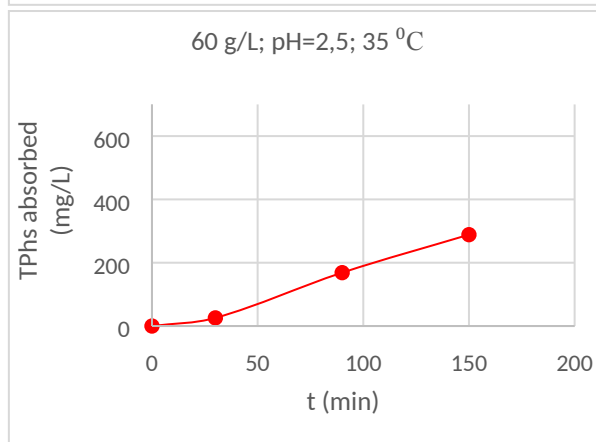
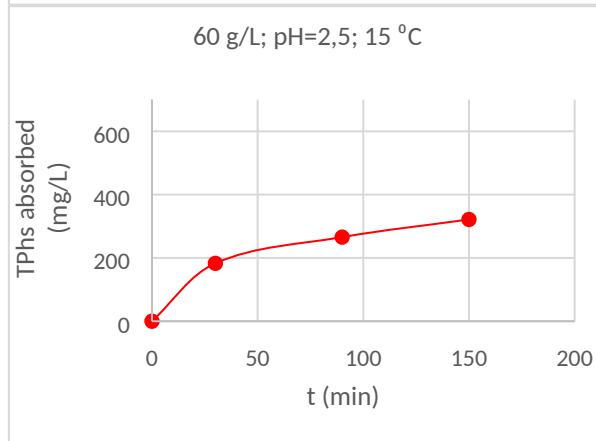
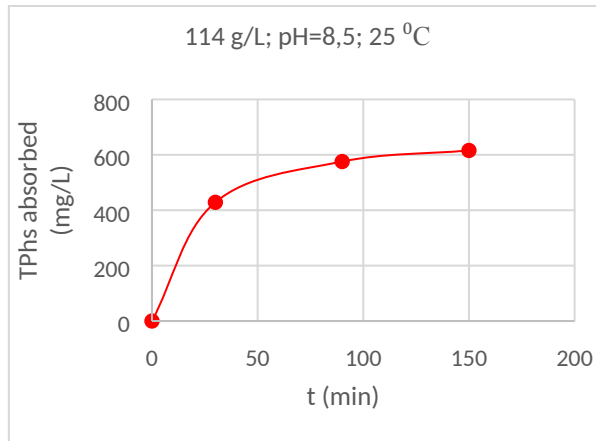
resin dosage ( $M_{\text{resin}}$ ), contact time ( $\tau$ ), effluent pH ( $\text{pH}_0$ ) and temperature ( $T$ ), were examined in batch experiments. The key operating variables of the IE process performance were studied, optimized and further modelled.

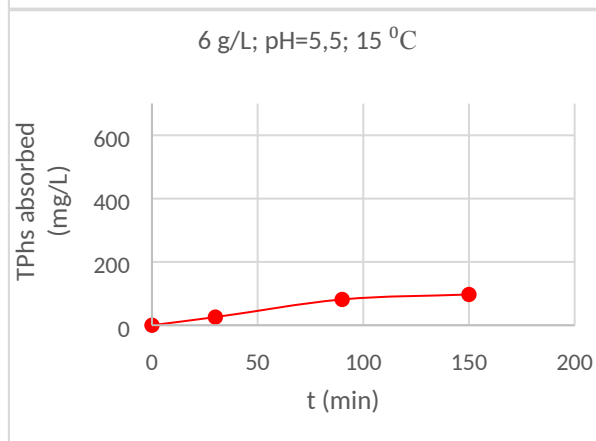
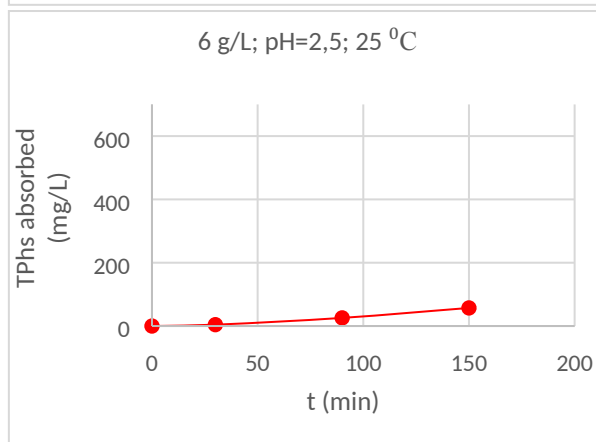
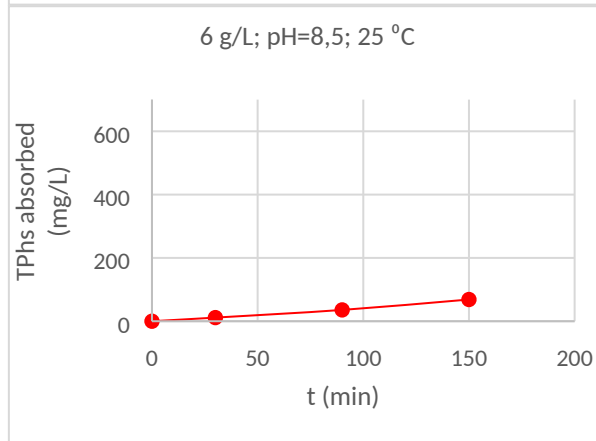
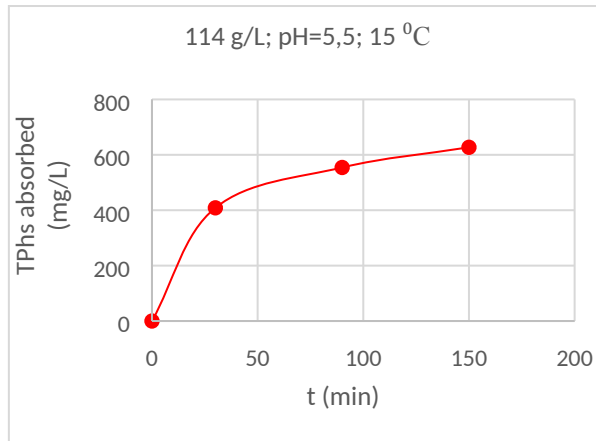
For this purpose, samples were periodically withdrawn to evaluate the dynamic behaviour of the IE process – concretely in terms of phenolic concentration uptake efficacy – under the different conditions set-up during the duration of IE experiments, which were carried out up to a total contact time ( $\tau$ ) of 3 hours. During the course of the IE experiments, the OOWW solution was continuously stirred at medium-low speed in order to permit an effective contact between the solid resin matrix and the compounds in the effluent, as well as to avoid the destruction and pulverization of the resins particles (this issue was observed in preliminary tests, due to the low mechanical resistance of the polymeric particles). Results of randomized OOWW weak-base anion IE resin purification experiments are summarized in **Table 4**. The dynamic IE performance data obtained are as well graphically shown in **Fig. 3**.

**Table 4.** Results of randomized OOWW weak-base anion IE resin purification experiments.

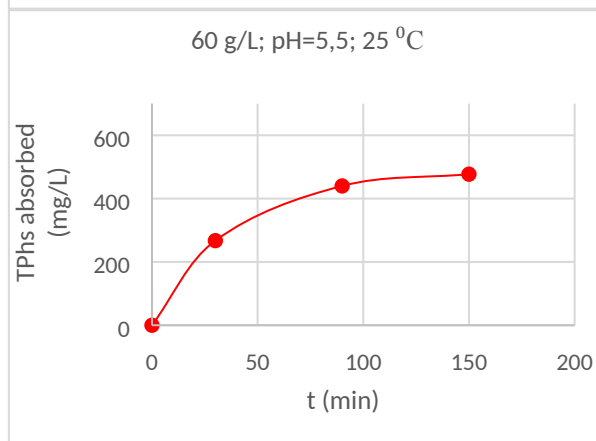
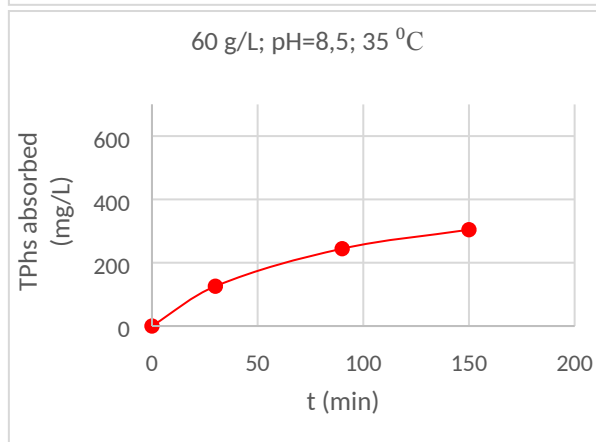
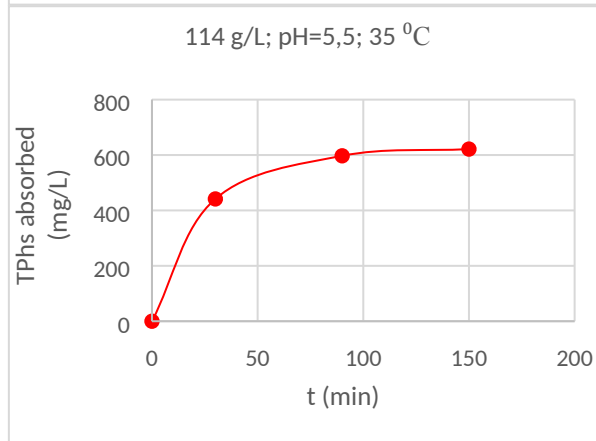
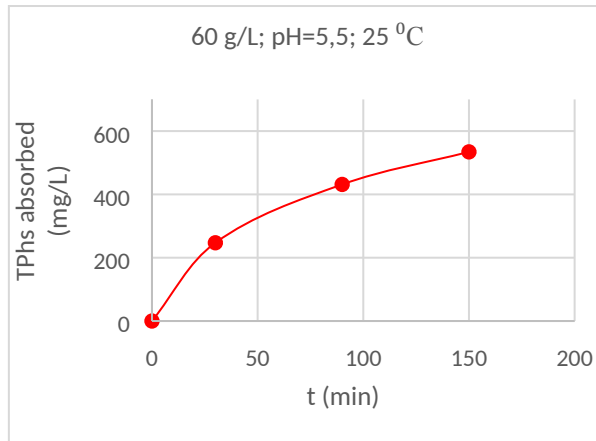
Experiment	$M_{\text{resin}}$	$\text{pH}_0$	$T$	TPhs ads., mg/L	%TPhs ads., %
1	1	1	0	615.72	<b>79.36</b>
2	0	-1	-1	321.43	41.43
3	0	-1	1	288.57	37.19
4	0	0	0	534.28	71.36
5	1	0	-1	627.15	<b>80.83</b>
6	-1	1	0	68.57	8.84
7	-1	-1	0	57.15	7.37
8	-1	0	-1	97.15	12.52
9	0	0	0	534.29	68.86
10	1	0	1	621.43	<b>80.10</b>
11	0	0	0	477.15	61.50
12	-1	0	1	107.15	13.81
13	0	1	1	304.29	39.22
14	0	0	0	536.5	69.15
15	0	1	-1	505.72	65.18

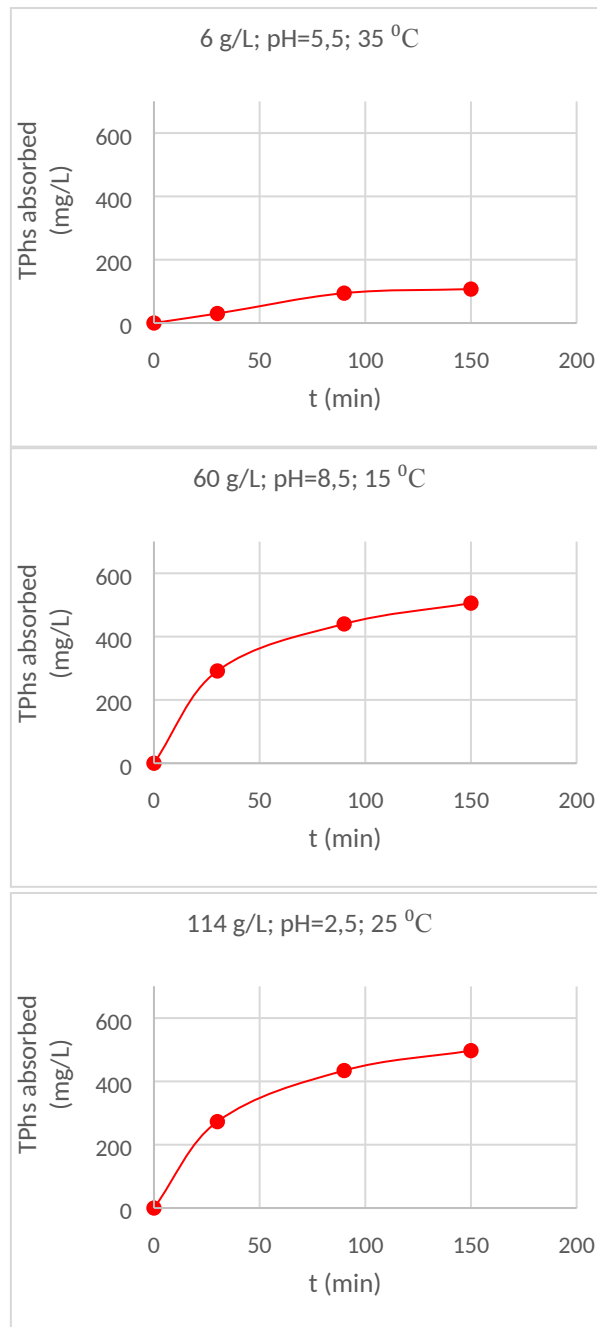
T: temperature;  $M_{\text{resin}}$ : resin dosage;  $\text{pH}_0$ : effluent pH; TPhs<sub>ads</sub>: total phenolics concentration adsorption.











**Figure 3.** Dynamic adsorption efficiency patterns of TPBs of the weak-base IE resin.

Regarding the determination of the optimal resin dosage, preliminary tests were carried out beforehand so as to define the adequate  $M_{resin}$  range [16]. In those tests, different resin dosages (3 g/L and 6 g/L) were examined, whilst the rest of operating variables were kept at the central point, that is, unadjusted pH (raw OOWW  $pH_0$ ) and ambient temperature (25 °C). As a result of the use of these low  $M_{resin}$  dosages (3 and 6 g/L) it was observed that very low uptake efficiencies towards the target species, unfeasible for industrial process scale-up, could be achieved. With a resin dosage of 3 g/L, the %TPBs

efficiency was found to be 12.6 %, value that grew up to just 16.9% for 6 g/L. Therefore, it was decided to further increment the  $M_{resin}$  to the values in **Table 4**, that is, 60 and 114 g/L. By doing this, a central point (60 g/L) equally spaced ( $\pm 54$  g/L) from the maximum and minimum extremes (6 and 114 g/L) were defined for the ulterior optimization and modelling of the IE process.

Thereafter, high %TPhs uptake efficiency was attained within certain conditions set for the IE experiments (runs 1, 5 and 10), which could enhance the feasibility of the process scale-up. The maximum TPhs uptake by the weak-base resin from the effluent occurred around 2.5 h contact time, point at which approximately the resin became saturated. As it can be seen in **Table 4**, a maximum total phenols adsorption of 625.15 mg/L was yielded by the chosen resin, corresponding to %TPhs uptake efficiency as high as 80.83 %, by loading  $M_{resin}$  equal to 114 mg/L, setting the operating temperature at 15 °C and upon the raw pH of the effluent ( $pH_0 = 5.5$ ). The pH increment in the outlet stream proportional to the phenols uptake efficiency for each assay pointed for IE as the dominant process responsible of TPhs uptake by the resin, being phenolic compounds replaced by the resin's hydroxyl ions [40,48]. Otherwise, a contact time of 90 minutes (experiment 10) was observed to be sufficient to achieve an asymptote in %TPhs uptake efficiency.

The efficiencies here found are also beyond those observed in previous studies by the authors with Amberlyst A26 strong-base and Amberlite IRA-67 weak-base anion exchange resins, in which adsorption efficiencies towards phenol in aqueous solutions (initial TPhs concentration investigated equal to 200 mg/L) up to 74.2% were reported for the former (Amberlyst A26) whereas lower uptake efficiency was attained (22.1 %) with the latter (Amberlite IRA-67) [40,48].

### *3.2. Statistical IE performance analysis and modelling*

One approach to meet the investors' need to trust a certain technology is to guarantee that the process will be properly optimized. In this context, prediction and modelling of the system response is key for the success in the design and operation control. However, prediction and modelling of IE processes is often difficult and complex. With this goal, a Box-Behnken design (BBD) comprising a whole number of 15 experiments as a function of  $T$ ,  $pH_0$  and  $M_{resin}$  was implemented in the present work. The obtained data were then analyzed by ANOVA and interpreted by RSM methodology for the optimization of the IE process.

The impact of each of the studied operating variables on the IE process yield, focusing on %TPhs uptake efficiency, was evaluated. A statistical multifactorial analysis was used as a tool to quantitatively determine each of the potential conjugated effects of the input variables on the IE process. The objective was to estimate the relative significance of the main operating variables as well as their squared effects on the response of the system (%TPhs uptake). The lower the p-value, the more significant the effect of a singular factor on the response expected. ANOVA results for %TPhs uptake are given in **Table 5**.

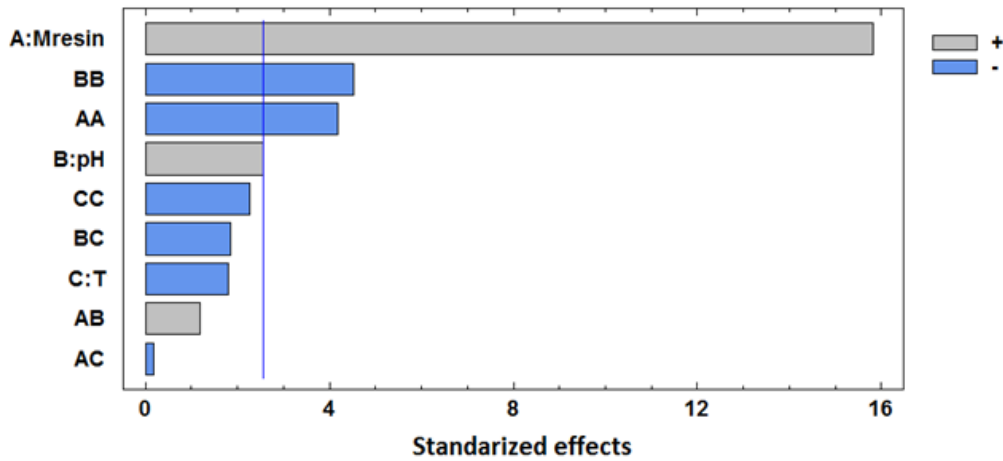
**Table 5.** Analysis of variance (ANOVA) of Box-Behnken design (BBD) for %TPhs uptake.

Source	Sum of square (SS)	Degree of freedom (DF)	Mean square (MS)	F-ratio	p-value
A: $M_{resin}$	51583.8	1	51583.8	250.13	<b>0.0000</b>
B: $pH_0$	13612.5	1	13612.5	6.60	0.0501
C: T	6613.08	1	6613.08	3.21	0.1333
AA	35960.2	1	35960.2	17.44	<b>0.0087</b>
AB	2870.28	1	2870.28	1.39	0.2912
AC	61.7796	1	61.7796	0.03	0.8694
BB	42198.2	1	42198.2	20.46	<b>0.0063</b>
BC	7103.96	1	7103.96	3.44	0.1226
CC	10502.2	1	10502.2	5.09	0.0737
Pure error	10311.6	5	2062.31		
Total error	63458.3	14			

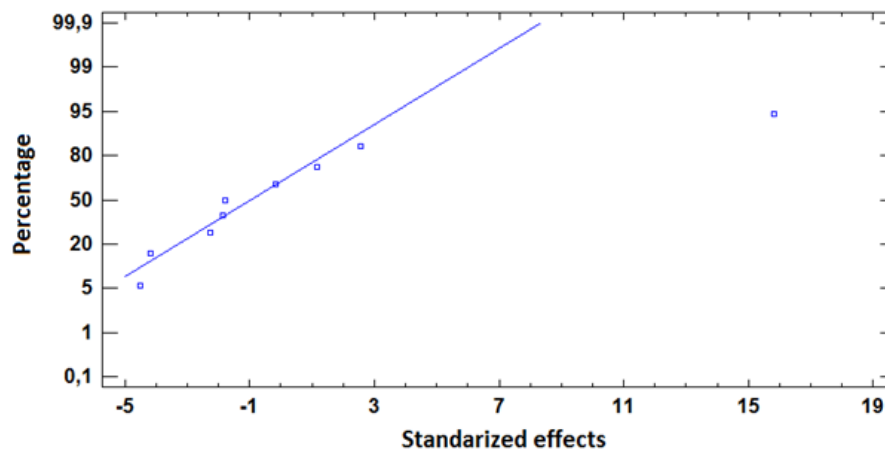
The variability of %TPhs IE uptake was divided in pieces for each of the examined effects separately, such that each factor's statistical significance was analyzed by comparing its mean square with the experimental error estimated. As a result of the p-values resulting for each of the examined operating parameter, it was possible to confirm that  $pH_0$  and  $M_{resin}$  influence more notably on %TPhs uptake performance of the weak-base resin (p-value < 0.05, almost negligible) than  $T$  (see **Table 5**).

This is graphically depicted for ease of comprehension in the Pareto Chart in **Fig. 4**, and confirmed by the normal probability graphic for %TPhs IE uptake (**Fig. 5**). As it can be observed in **Table 4** and **Fig. 4**, both  $pH_0$  and  $M_{resin}$  exhibit quantitatively more impact on %TPhs uptake than  $T$ , based on the p-values for these variables and their squared effects

withdrawn from the ANOVA (p-values < 0.05), concretely  $pH_0^2$ ,  $M_{resin}^2$  and  $M_{resin}$  (see **Table 5** and **Fig. 4**). It could be highlighted a statistically significant correlation among  $pH_0^2$ ,  $M_{resin}$  and  $M_{resin}^2$  at 95 % confidence level. On the contrary,  $B$ ,  $C$ ,  $AB$ ,  $AC$ ,  $BC$  and  $CC$  terms resulted not to have significant impact on %*TPhs* uptake.



**Figure 4.** Standardized Pareto chart for OOWW IE purification process.



**Figure 5.** Normal probability graph of the OOWW IE purification process.

Subsequently, by correlating the theoretical %*TPhs* uptake values with the operating input factors by means of multiple non-linear regression, a second-grade quadratic model equation was inferred, in which the factors found to have no significant effect on the system response (%*TPhs* uptake) were discarded:

$$\%TPhs \text{ uptake} = 515.24 + 253.929 \cdot M_{resin} - 98.6875 \cdot M_{resin}^2 - 106.905 \cdot pH_0^2$$

A p-value equal to 0.002 was obtained for the model following ANOVA analysis. This value well under 0.05 pin-points for a significant correlation between %*TPhs* uptake

and  $pH_0^2$ ,  $M_{resin}$  and  $M_{resin}^2$  according to the model equation at 95.0% confidence level. The statistic  $R^2$  confirmed that the model could explain 98.37% of the variability of %TPhs uptake. Moreover, it should be highlighted that the adjusted  $R^2$ , adequate in order to compare models consisting in a different number of independent variables, was quite satisfactory (95.45%) (**Table 6**). This supports the goodness of the proposed model as a function of  $pH_0^2$ ,  $M_{resin}$  and  $M_{resin}^2$ .

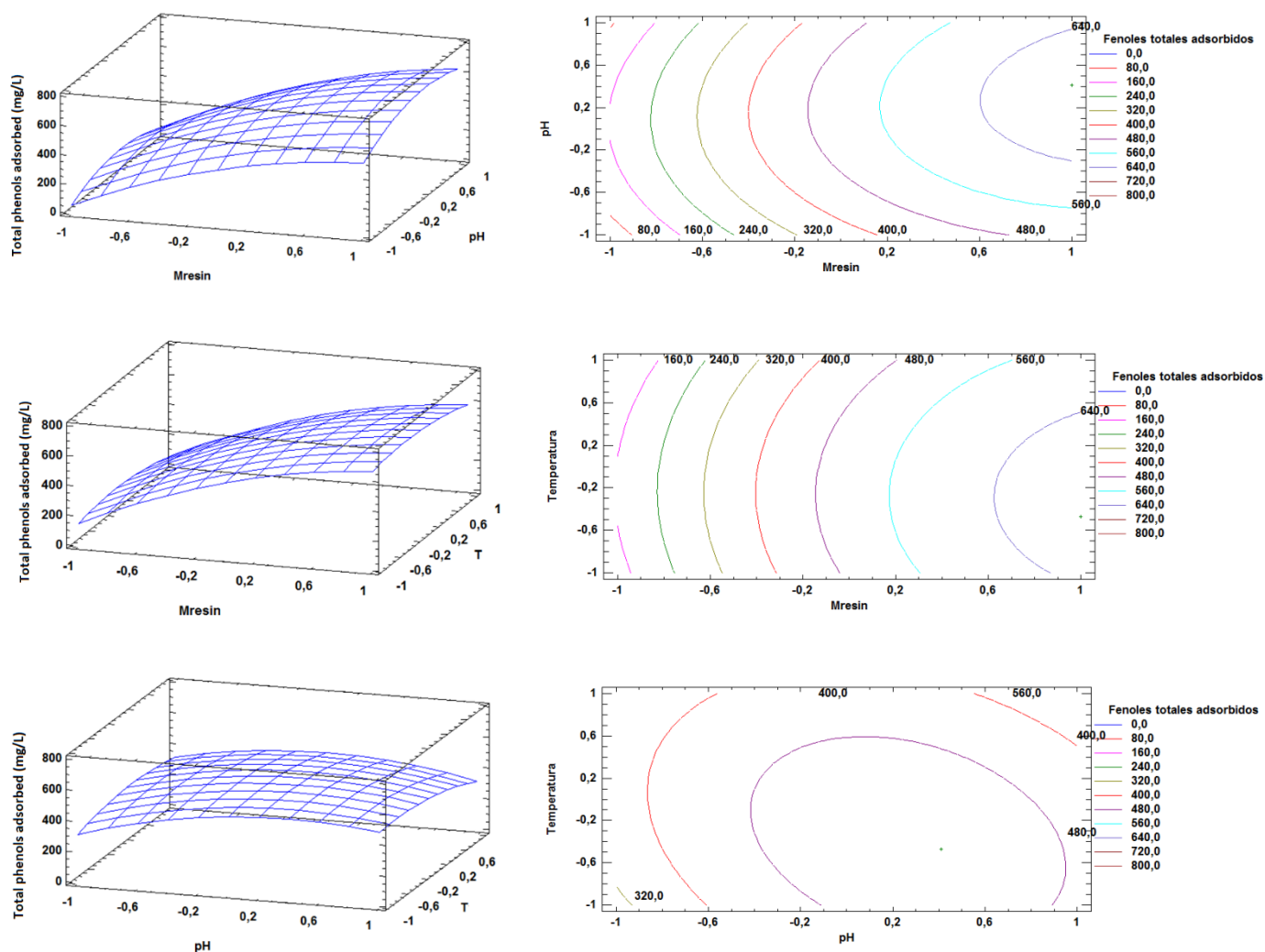
The error estimation showed a value for the residues standard deviation equal to 45.4127 and a mean absolute error (MAE) of 23.3173. Durbin-Watson statistic equal to 3.2147 (p-value = 0.9974), close to 2, confirms that the residuals vary randomly, whereas the p-value below ensures no sign of serial autocorrelation among the residues at 95.0% confidence level. In addition, there was no significant structure unexplained by the model given that the Lag 1 residual autocorrelation (−0.6197) tended to zero (see **Table 6**).

**Table 6.** Summary of goodness of Box-Behnken design ANOVA for %TPhs uptake.

Statistic parameter	Value
$R^2$ (%)	98.375
$R^2_{adjusted}$ (%)	95.4502
Estimated standard error	45.4127
Mean standard error (MAE)	23.3173
Durbin-Watson statistic	3.2147 (p = 0.9974)
Lag 1 autocorrelation residual	−0.6197

### 3.3. Response surfaces, contour plots and process optimization

The IE resin process was ulteriorly optimized using *Statgraphics Centurion XV.I* software. Each of the main process variables – contact time ( $\tau$ ), effluent pH ( $pH_0$ ), temperature ( $T$ ) and resin dosage ( $M_{resin}$ ) – was optimized in order to maximize %TPhs adsorption efficiency of the weak-base anionic resin. A central point (0) and two equally-distanced extreme levels (minimum and maximum, −1 and +1 respectively) were established for each operating variable. The resulting response surfaces and contour plots for the proposed OOWW IE purification process are shown in **Fig. 6** (comprising  $M_{resin}$  vs. feedstream  $pH_0$ ; (ii)  $M_{resin}$  vs. system  $T$ ; (iii)  $pH_0$  vs. system  $T$ ).



**Figure 6.** Estimated response surfaces and contour plots for the proposed OOWW IE purification process: (i)  $M_{resin}$  vs. feedstream  $pH_0$ ; (ii)  $M_{resin}$  vs. system  $T$ ; (iii)  $pH_0$  vs. system  $T$ .

As it can be observed, %TPhs uptake was enhanced much considerably upon augmenting the **resin dosage** up to 60 g/L. This resulted in an increased number of active sites available for IE, and in faster approach to equilibrium (see **Fig. 6**). By loading a quantity of  $M_{resin}$  beyond 60 g/L, very high and fast %TPhs adsorption was provided by this resin. The Dowex 66<sup>®</sup> weak-base resin yielded IE efficiencies towards the target phenolic species of 43.5 % after 15 min, 58.9 % after 1 h, and finally 72.4% after the total contact time (3h), which might be significant for the process feasibility at real industrial scale. Otherwise, slightly higher efficiency (77.9%) was attained by incrementing the  $M_{resin}$  up 114 g/L, being the uptake efficiency of TPhs incremented up to 77.9 %. However, this means that the uptake capacity expressed in  $mg\ TPhs_{adsorbed}/g_{resin}$  were equal to 93.57 mg/g at 60 g/L  $M_{resin}$  vs. lower (53.0 mg/g) upon an increment of the  $M_{resin}$  to 114 g/L. It was observed that the increase of  $M_{resin}$  loaded enhanced the %TPhs adsorption efficiency until

an asymptote approached around  $\sim 110$  g/L, beyond which no significant improvement of IE process efficiency was noted. These uptake efficiencies at raw OOWW  $pH_0$  are higher than those achieved by Caetano et al. on phenols adsorption on AuRix 100 weak base anion exchange resin (46.2 mg/g at pH = 3 and 75.8 mg/g at pH = 11)[46]. Also, Galanakis et al. achieved uptake lower efficiencies, equal to 43.5 mg/g (pH = 3) and 76.8 mg/g (pH = 11) for Dowex XZ strong anion exchange resin [23].

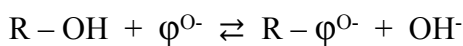
In that regard, as shown in **Fig. 6** the **feedstream  $pH_0$**  was noted to affect very significantly ( $pH_0^2$ ) the system response ( $\%TPhs$ ). A minimum for  $\%TPhs$  uptake (40.5 %) was attained upon the lowest  $pH_0$  of the effluent ( $pH_0 = 2.5$ ), which increased considerably (72.4 %) with an increment of the  $pH_0$  up to the central point, corresponding to the raw effluent (unmodified)  $pH_0$ . Thereafter, the uptake efficiency towards TPhs again decreased upon further incrementing the  $pH_0$  of OOWW up to alkaline conditions (47.1 % at  $pH_0 = 8.5$ ). Therefore, as per the pattern of the  $\%TPhs$  as a function of OOWW  $pH_0$ , the raw effluent  $pH_0$  could be chosen as a feasible value. It is also worth pointing not only the high but also fast TPhs adsorption efficiency provided by the weak-base Dowex 66<sup>®</sup> resin upon the raw effluent pH conditions.

These patterns could be explained by the fact that phenolic compounds are present in molecular form at acidic pH conditions, and therefore the uptake takes place by adsorption mechanism on the free polymeric surface:



where  $S^*$  and  $S\varphi^{OH}$  represent the active and occupied adsorption sites of the resin.

Whereas phenolates ( $\varphi^{O^-}$ ) start to form as the solution pH increases to more alkaline conditions, and the removal of phenolic compounds thereby begins to take place predominantly by ion exchange of phenolate ions with  $OH^-$  co-ions of the resin.



These two mechanisms occur during phenolic species uptake into the resin solid phase [25]. IE mechanism is supported by the pH increment registered in the treated effluent stream proportional to the removal efficiency, whilst both IE and adsorption occurred at the raw effluent pH conditions, at which phenol dissociation is minor. If the medium is further basified, the  $\%TPhs$  decrease observed could be explained by competitiveness of hydroxyl species in solution of the basifying medium, as well as to an excessive



hydroxylation of the active sites of the weak-base resin hindering the linkage of phenolate ions to the active sites. These results are in line with those obtained by Bertin and Carmona et al. on Amberlite IRA-420 strong-base anion exchange resin [55,56]. Moreover, in previous research by the authors of this work studying removal of molecular phenol from aqueous solutions, analogous behaviour was observed: if the effluent was first driven through the cationic resin, this caused the drop of the solution pH to very acidic by proton exchange, which resulted in utterly low phenol removal efficiencies, but if the feedstream was made to pass first through the anionic resin, hydroxyl anions release led to an increase of the pH conditions, enhancing phenol removal.

On another hand, the resin performance was also observed to be affected by the system operating **temperature (Fig. 6)**. For this variable, a maximum value of 35 °C was set justified by the need to avoid overcoming the  $T$  point at which phenolic species begin to be degraded, with the goal to minimize any loss of the target compounds, and a minimum of 15 °C, similar to the conditions in the mills during the olive-oil production campaign in autumn-winter; operating at a temperature below this (stream cooling) would not be justified from an economic point of view. From the data withdrawn, it can be noted that higher and faster IE efficiency took place when the operating temperature was nearby ambient conditions (22 – 25 °C). A higher operating temperature ( $T > 25$  °C) resulted in a decrease of TPhs uptake for the weak-base Dowex 66<sup>®</sup> resin, as it can be noted in **Fig. 5**. At the end of  $\tau$  (3 h), a corresponding value of TPhs adsorption efficiency of 72.4 % was achieved at an operating temperature of 25 °C (~ambient  $T$ ), 43.5 % of which was yielded in the initial moments (15 min) and 58.9 % after 1 h. An increase of the operating  $T$  otherwise led to a reduction of the uptake towards TPhs (e.g. 28.2 % TPhs uptake decrease if the  $T$  was set at 35 °C). Finally, a contact between 60 – 90 minutes was observed to be sufficient to achieve an asymptote in %TPhs uptake efficiency.

These results are supported by former studies by the authors on molecular phenol removal from aqueous solutions on Amberlite IRA-67s polymeric resin, [57,58], in which it was found that phenol uptake was certainly influenced by the system temperature. In that case, it was possible to achieve 60 % phenol removal upon the minimum operating temperature tested (298 K), whilst a  $T$  increment up to 318 K led to 20 % less effective phenol removal (%TPhs = 40 %). In the same line, Roostaei and Tezel reported the decrease of phenols uptake capacity with an increase of the system  $T$  on a series of adsorbents comprising activated carbon, activated alumina and silica gel, among others [59]. Also, Zhu et al. [60]

pointed molecular phenol adsorption on MCl (N-butylimidazolium strong-base anion exchange resin functionalized with Cl<sup>-</sup>) in an acidic medium to be exothermic whereas endothermic when anion exchange of phenolate predominates. Analogous patterns were noted at acidic pH in other research works on IRA96C, NDA103 and Purolite A-510 resins [61,62]. These observations contrast with the conclusions by Ku et al. [63], who did not find a significant impact of  $T$  on phenol adsorption onto Purolite A-510 resin.

Finally, IE process optimization was carried out. Results are summarized in **Table 7**. The optimised parameters of the studied IE process for %TPhs uptake maximization were estimated to be 20.3 °C,  $pH_0$  equal to 6.7 and 114 g/L  $M_{resin}$ , which permitted ensure %TPhs uptake up to 92.5 %. The determination beforehand of the most adequate and feasible operating conditions is key to optimize the IE process and thus enhance its stable performance. Summing up, the optimization of the present IE process considering  $T$ ,  $pH_0$  and  $M_{resin}$  pin-pointed for an operating  $T$  in the range from 20 – 25,  $pH_0$  between 5.5 – 6.7 and 110 – 114 g/L  $M_{resin}$ , which ensured %TPhs uptake up to 89.2 – 92.5 %. In conclusion, the chosen Dowex 66<sup>®</sup> resin was capable to ensure high %TPhs uptake efficiencies at ambient temperature conditions, without implying heating nor cooling of the effluent stream. Thus, OOWW could be straightly driven to the IE resin column from the outlet of the vertical centrifuges, enhancing the process intensification scale-up in the mills and boosting the valorization and treatment process in terms of specific energy consumption. Moreover, as per the pattern of the %TPhs as a function of the OOWW  $pH_0$ , the effluent could be directly driven at its raw  $pH_0$  into the resins revalorization and treatment process, which would also imply the needless to modify OOWW pH to achieve high process performance, having important implications for the cost-efficiency of the process. Since the physico-chemical composition of the effluent, olive oil washing wastewater, may be quantitatively different depending of the different regions but qualitatively similar, the results of the optimization and modelling of this work could be extrapolable.

**Table 7.** Optimised parameters values for the IE purification process of OOWW stream.

Factor	T, °C	$M_{resin}$ , g/L	pH	Predicted adsorbed TPhs, mg/L	Predicted adsorbed TPhs, %	R <sup>2</sup>
Optimal value	20.3	114	6.7	716.9	92.4	98.81
Optimal range	20 – 25	110 – 114	5.5 – 6.7	692.1 – 716.9	89.2 – 92.4	98.81

The outlet purified stream upon the optimized operating conditions presented good quality, that is, total phenols load lowered to 56.6 – 83.7 mg L<sup>-1</sup>. The standards recommended by the Food and Agricultural Association (FAO) for reusing regenerated water for irrigation (for instance in the proper olive fields) could be fulfilled, as well as the water quality standards established by the Guadalquivir Hydrographical Confederation (Spain) for discharge in public waterways. The applied regeneration protocol achieved up to 99.5 % restore of the resin capacity for at least 5 cycles. To conclude, the obtention of this concentrated pool of added-value antioxidant compounds could help counter-balance the economic feasibility of OOWW reclamation. Both the treatment and revalorization of OOWW would help implement the concept of circular economy to the whole olive-oil production process.

#### 4. Conclusions

The key operating input factors of IE process with novel Dowex 66<sup>®</sup> weak-base resin for the treatment and valorization of OOWW throughout phenolic compounds (*TPhs*) recovery were studied, optimized and further modelled. A Box-Behnken design as a function of  $T$ ,  $pH_0$  and  $M_{resin}$  was implemented and the obtained data were analyzed by ANOVA and interpreted by RSM methodology.

The optimization of the IE process performance for %*TPhs* uptake maximization (20.3 °C,  $pH_0$  6.7 and 114 g/L  $M_{resin}$ ) ensured up to 92.5 % recovery. Moreover, the process was ulteriorly modelled accurately by a second-grade quadratic fitting equation based on the significant operating variables found.

The determination beforehand of the most feasible operating conditions is key to optimize the IE process and thus enhance its stable performance. The obtained information would be rather important for the scale-up of the proposed IE operation from a cost-efficiency point of view, since this weak-base resin was capable to work highly efficiently at ambient temperature conditions, key from the technical-economical side, and no acidification or basification of the effluent was found to be necessary to improve significantly the optimal process performance. The OOWW stream could thus be directly driven from the exit of the vertical centrifuges at its outlet temperature straightly to the IE resin column, permitting the economic feasibility of the process intensification.

The purified stream upon process optimization presented good quality (total phenols load lowered to 56.6–83.7 mg L<sup>-1</sup>). The standards recommended by the Food and Agricultural Association (FAO) for reusing regenerated water for irrigation, for example in olive fields, could be fulfilled, as well as the water quality standards established by the Guadalquivir Hydrographical Confederation (Spain) for discharge in public waterways. Both the treatment and revalorization of OOWW would help implement the concept of circular economy to the whole olive-oil production process.

## 5. Acknowledgements

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