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Additional Information

# 1 Recovery of phenolic compounds from olive oil washing wastewater by 2 adsorption/desorption process

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10

## 11 Abstract

12 Agroindustry wastewater represents an opportunity to recover high added value antioxidants  
13 such as phenolic compounds. An adsorption/desorption process was investigated to recuperate  
14 these compounds using Purolite non-ionic resins (MN200, MN202, PAD900 and PAD950). The  
15 study was conducted on a model solution containing  $1.1 \text{ g}\cdot\text{L}^{-1}$  of tyrosol and  $0.2 \text{ g}\cdot\text{L}^{-1}$  of catechin,  
16 which are two of the main phenolic compounds found in olive mill wastewaters, and with the  
17 olive mill wastewater. The main objective was to determine the optimal concentration of resin  
18 and the best desorption solvent for the maximum recovery of phenolic compounds. For it, the  
19 process kinetics were determined, and the adsorption mechanisms were characterized by  
20 means of isotherm models. Results showed that the pseudo-second order kinetic model fitted  
21 to the experimental data, while the Langmuir isotherm correctly modelled the adsorption  
22 process for the MN resins, whereas the Freundlich isotherm was the model that best described  
23 the adsorption process with PAD resins. A resin concentration of  $40 \text{ g}\cdot\text{L}^{-1}$  and a 50% v/v ethanol-  
24 water solution were selected as the best options for recovering the phenolic compounds. The  
25 tests with olive oil washing wastewater showed that, for some of the resins, other compounds  
26 present, such as sugars, interfered with the adsorption of phenolic compounds, reducing the  
27 effectiveness of their recovery. Finally, the MN200 resin was selected as the best adsorbent. It  
28 achieved a recovery of 91% of the phenolic compounds present in the initial wastewater, being  
29 only 5% of the initial sugars present in the final stream.

30

31 **Keywords:** adsorption; desorption; non-ionic resins; olive oil washing wastewater; phenolic  
32 compounds recovery.

33

## 34           1. Introduction

35    In recent years, plant-based functional foods are receiving a great attention due to their natural  
36    availability and therapeutic potential, paying special attention to the phytochemicals present in  
37    edible plants. Among them, phenolic compounds are the most numerous and widely distributed  
38    group of bioactive molecules [1]. The high antioxidant capacity of natural phenolic compounds  
39    is beneficial for health, since they reduce free radicals through enzymatic regulation, being of  
40    great help against cardiovascular diseases, diabetes, osteoporosis and neurodegenerative  
41    conditions, among other diseases [2,3]. These antioxidant compounds are also found in agro-  
42    food wastes from different sectors, such as olive mill wastewaters (OMW) [4], table olive  
43    processing wastewaters [5] and effluents from pickle manufacturing, wine industry and citrus  
44    processing [6], among others.

45    Several studies have been focused on the investigation, design, development and optimization  
46    of processes to achieve the concentration and purification of the phenolic compounds from  
47    these wastewaters, such as electrocoagulation [7], liquid/liquid extraction [8], cooling  
48    crystallization [9], ultrasound treatment [10] and adsorption [11]. Among all the physical  
49    methods, adsorption is considered as the most economical, simple and effective one [12].

50    Adsorption is a separation process where one or more components are attracted to the surface  
51    of a solid adsorbent when they are in contact. The nature of the interaction depends on the  
52    properties of the compounds involved. This phenomenon is superficial, and it is produced by the  
53    action of forces on the surface of the adsorbent, which cause a net force normal to its surface.  
54    The adsorption process is composed of a series of interactions, including: mass transfer from the  
55    fluid phase to the external surface of the particle, pore diffusion in the solid phase, solute–solid  
56    interaction, hydrophobic and electrostatic attractions and hydrogen bonding [13]. The rate of  
57    the overall process can be controlled by one or several of these steps and it is dependent on the  
58    physico-chemical characteristics of the solute and adsorbent, particle size and affinities, and  
59    operating conditions. Equilibrium and kinetics information, as well as column operation  
60    parameters, are essential for practical operation [14].

61    Different materials have been tested as adsorbents for the selective adsorption of phenolic  
62    compounds, with activated carbon being the most used. However, the utilization of this material  
63    presents difficulties when the adsorbed compounds must be desorbed, being, the adsorption  
64    process very often irreversible [15]. Within synthetic adsorbents, resins are the most studied  
65    and used, due to their chemical stability, selectivity, adsorption capacity and low toxicity, which  
66    makes them very interesting for recovering compounds [14]. These resins have different

67 characteristics that distinguish them, such as polarity, material, particle size, specific surface  
68 area, and pore diameter. In general, they are relatively low cost, easy to pre-process and  
69 recover, and suitable for large-scale production [16].

70 The objective of this work was to evaluate the adsorption and desorption capacity of four non-  
71 ionic commercial resins (MN200, MN202, PAD900 and PAD950 distributed by Purolite) in order  
72 to find the best one to selectively recover the phenolic compounds present in olive mill  
73 wastewater. Firstly, the resins were tested with a model solution with a high concentration of  
74 phenolic compounds to find the best dose to recover the antioxidant compounds. Then, with  
75 the selected resin dose, the performance of the resins was validated with a real wastewater  
76 from olive oil production (olive oil washing wastewater, OOWW) to observe the impact of other  
77 substances on the behaviour of the resins. Until now, few studies have been carried out on the  
78 recovery of value-added compounds from real OOWW by means of non-ionic resins, considering  
79 both (adsorption and desorption). On the other hand, to date only one study has been found  
80 using a mixture of ethanol/water at 50% v/v without acidification as a solvent for the desorption  
81 of phenolic compounds [17]. However, the objective of that study was to investigate the binary  
82 interaction between phenol and tyrosol by comparing the behaviour of these with the resins  
83 separately, as with a binary solution. The study showed high desorption of tyrosol (94%) and  
84 phenol (85%), however it was not tested in real OMW. Another novelty of this work is the  
85 thorough characterization of the individual phenolic compounds adsorbed and desorbed by the  
86 resins.

## 87 **2. Material and Methods**

### 88 **2.1 Model Solutions**

89 The model solution was prepared with osmotized water and  $1.3 \text{ g}\cdot\text{L}^{-1}$  of phenolic compounds.  
90 This concentration was selected to simulate a real olive oil washing wastewater, being within  
91 the range characterized in other studies [18–20]. The model solution included  $1.1 \text{ g}\cdot\text{L}^{-1}$  of tyrosol  
92 (Maybridge, United Kingdom), representing the simple phenolic compounds of low molecular  
93 weight, and  $0.2 \text{ g}\cdot\text{L}^{-1}$  of catechin (Sigma Aldrich, Germany), which represents the class of  
94 flavonoids, with higher molecular weight. As the wastewaters from olive oil production have a  
95 pH value between 4.5 and 5.5 [21], hydrochloric acid (J.T. Baker, The Netherlands) was added in  
96 order to obtain a pH close to 5.

### 97 **2.2 Adsorption process**

98 The aim of adsorption tests was to evaluate the influence of resin dosage on the adsorption of  
99 phenolic compounds. To this purpose, two Macronet™ MN200 and MN202, and two Purosorb™

100 PAD900 and PAD950 resins, supplied all by Purolite, were evaluated at different concentrations  
 101 (10, 20, 30, 40, 50 and 60 g·L<sup>-1</sup>). The main physical properties of the resins are reported in Table  
 102 1. Before use, the resins were conditioned in a sodium hydroxide solution (2% w/v) for 60  
 103 minutes at 140 rpm. Then, they were washed twice with osmotized water for 5 min at the same  
 104 speed.

105 Table 1. Main physical properties of the employed resins (data from supplier).

Resin	Matrix	*Surface area (m <sup>2</sup> g <sup>-1</sup> )	*Pore diameter (Å)	*Pore volume (mL g <sup>-1</sup> )	Specific gravity	Particle size (mm)	Hydrophobicity
MN200	PS/DVB <sup>1</sup>	1100	700/15 <sup>#</sup>	0.4	1.04	0.5-0.7	Moderate
MN202	PS/DVB <sup>1</sup>	950	220/15 <sup>#</sup>	0.3	1.04	0.3-1.2	Moderate
PAD900	PDVB <sup>2</sup>	850	220	1.9	1.02	0.35-1.2	Moderate
PAD950	Polymethacrylic	450	120	0.6	1.1	0.35-1.2	Low

106 <sup>1</sup>PS/DVB: polystyrene crosslinked with divinylbenzene

107 <sup>2</sup>PDVB: Polydivinylbenzene

108 \*measured by nitrogen adsorption

109 # macropores/micropores

110

111 The different doses of resin studied, indicated above, were mixed with 200 mL of model solution  
 112 for 180 min at a constant stirring of 140 rpm at room temperature (21 ± 2°C). After adsorption,  
 113 the liquid phase, which contains the fraction of non-adsorbed phenolic compounds, was  
 114 separated from the solid matrix by filtration through a 0.2 µm membrane filter. Then, the  
 115 concentration of total phenolic compounds (TPhC) was measured with the Folin–Ciocalteu (FC)  
 116 method [22].- TPhC were expressed as tyrosol equivalents (Tyeq). All the adsorption  
 117 experiments were carried out in a Flocculator “FLOC-6 “ jar test apparatus, supplied by RAYPA.  
 118 The Adsorption efficacy (%Ads) related to total phenolic compounds was calculated as follows:

$$119 \quad \%Ads = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (1)$$

120 Being C<sub>0</sub> and C<sub>e</sub> the initial and equilibrium concentrations of the TPhC in the solution,  
 121 respectively. The adsorption capacity (q<sub>t</sub>) for every resin concentration (C<sub>r</sub>, g·L<sup>-1</sup>), at time t (min)  
 122 was also calculated according to Equation 2:

$$123 \quad q_t = \frac{C_0 - C_t}{C_r} \quad (2)$$

124 Where C<sub>t</sub> is the concentration of TPhC in the solution at a given time. The equilibrium adsorption  
 125 time was also calculated and the general models for adsorption kinetics were analysed (pseudo-

126 first order kinetic model and pseudo-second order kinetic model). Data were also plotted to find  
127 out whether they followed the behaviour of the Langmuir or Freundlich isotherms.

### 128 **2.3 Pseudo-first and Pseudo- second order kinetic models**

129 Kinetic parameters are useful for adsorption rate prediction, providing important information  
130 for designing and modelling the processes. For their determination, an assay was carried out  
131 following the same protocol described in the adsorption section (2.2). This time, 2 mL of each  
132 extract solution were withdrawn at time intervals of 1, 5, 10, 20, 30, 40, 60, 90, 120 and 180 min,  
133 to later determine their phenolic content. The tests were carried out for the different  
134 concentrations of resins considered. Then, two models were fitted to the experimental data to  
135 determine which best represents the process.

136 The Lagergren equation (Equation 3), better known as the pseudo first order kinetic equation  
137 [23], was the first model proposed to describe adsorption in a solid-liquid system, where the  
138 adsorption rate is based on the sorption capacity of the solids. The pseudo second order model  
139 [24] (Equation 4) indicates that the adsorption rate is proportional to the available sites on the  
140 sorbent surface. These two equations have been widely used to study adsorption from liquid  
141 solutions. The equations that describe these models are:

$$142 \quad \ln(q_e - q_t) = \ln q_e - k_1 \cdot t \quad (3)$$

$$143 \quad \frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \quad (4)$$

144 Where  $q_e$  ( $\text{mg} \cdot \text{g}^{-1}$ ) is the amount of solute adsorbed per gram of adsorbent at equilibrium;  $k_1$   
145 ( $\text{min}^{-1}$ ) is the pseudo first order rate constant and  $k_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) is the pseudo second order  
146 rate constant. For the determination of the constants, two graphics were plotted, one  
147 corresponded to  $\ln(q_e - q_t)$  versus time ( $t$ ) and the other to  $t/q_t$  versus time ( $t$ ). Then, performing  
148 a linear regression, it was possible to obtain  $q_e$  from each model as well as the model  
149 parameters.

### 150 **2.4 Freundlich and Langmuir Isotherms**

151 Adsorption isotherms describe the adsorption equilibrium of an adsorbate (phenolic compounds  
152 in this work) against a given dose of resin. The Langmuir model considers a monolayer  
153 adsorption with energetically identical sorption sites, where no interaction occurs between the  
154 adsorbed molecules. Equation 5 presents the linear form of the Langmuir isotherm.

$$155 \quad \frac{C_e}{q_e} = \frac{1}{k_L \cdot q_0} + \frac{1}{q_0} \cdot C_e \quad (5)$$

156 where  $q_0$  ( $\text{mg}\cdot\text{g}^{-1}$ ) is the maximum adsorption capacity and  $k_L$  is the Langmuir constant, which is  
157 obtained by the extrapolation of the analytical data.

158 On the other hand, the Freundlich model assumes a heterogeneous adsorption surface that is  
159 characterized by sorption sites at different energies. The linear form of the equation that  
160 represents the Freundlich isotherm corresponds to Equation (6).

$$161 \quad \log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

162 where  $K_f$  ( $(\text{mg}\cdot\text{g}^{-1}) (\text{mg}\cdot\text{L}^{-1})^{-1/n}$ ) and  $n$  are empirical coefficients.  $K_f$  is a measure of the adsorption  
163 capacity of the adsorbent and  $n$  is related to the adsorption intensity [25].

164 The isotherms were determined using the different resin concentrations tested. For this,  $\ln q_e$   
165 versus  $\ln C_e$  and  $C_e/q_e$  versus  $C_e$  were plotted. Then, adjusting to a linear regression, it was  
166 possible to obtain each coefficient.

## 167 **2.5 Desorption process**

168 For the best dosage selected from the adsorption experiments, the subsequent recovery of the  
169 adsorbed phenols was carried out by a desorption process. Several studies have concluded that  
170 ethanol is one of the best solvents for the desorption of phenolic compounds from olive mill  
171 wastewater adsorbed onto resins [26,27], however, this carries a high cost. A study performed  
172 by Frascari et al. [28] showed that 50% v/v mixture of deionized water and ethanol, acidified  
173 with HCl until reaching a concentration of  $2 \text{ mol}\cdot\text{L}^{-1}$  (pH -0.3), was the best option for the  
174 desorption of phenolic compounds from an ion exchange resin using OMW microfiltration  
175 permeate as feed. This acidification also entails an additional cost and could affect the  
176 equipment. No studies were found that used an ethanol/water mixture as a solvent without  
177 prior acidification to recover phenolic compounds and using non-ionic resins. In this way, the  
178 use of 50% v/v ethanol/water mixture without pH modification could lead to economical savings  
179 in comparison with the use of non-diluted ethanol.

180 After the adsorption tests, the resins were washed 3 times with osmotized water for 5 minutes  
181 at 150 rpm, then the resins were dried at  $50^\circ\text{C}$  for 3 hours. Then the two solvents, ethanol and  
182 a mixture of ethanol-water 50% v/v were tested in order to recover the highest amount of  
183 phenolic compounds. Absolute ethanol ( $\text{H}_3\text{CCH}_2\text{OH}$ ,  $\geq 99.5\%$ ) was purchased from VWR  
184 International. Resins were contacted with 100 mL of each solvent for 180 minutes at a constant  
185 rate of 140 rpm and room temperature ( $21 \pm 2^\circ\text{C}$ ). After desorption, the resins were washed  
186 again under the same protocol mentioned above and were reused for the next test.

187 Apart from FC method, for the individual determination of each phenolic compound, liquid  
188 chromatography coupled to mass spectrometry (LC-MS) was used. To that end, it was employed  
189 a 1260 Infinity II LC chromatograph coupled to a 6546 quadrupole-time-of-flight (qTOF) mass  
190 analyzer (Agilent Technologies, USA) with an electrospray interface (ESI). A Zorbax Extend C18  
191 column (4.6 x 100 mm, 1.8  $\mu\text{m}$ ) was used, operating at 40°C. The initial conditions for the mobile  
192 phases were set at the beginning of the analysis: 95% A and 5% B, where A was water and B was  
193 acetonitrile. Both mobile phases were acidified with a 0.5% of acetic acid. Afterwards, the  
194 following gradient was applied: 65% B at 12 min, 20% B at 14 min, 100% B at 18 min. That  
195 percentage was maintained during 3 minutes until 21 min of gradient program and then the  
196 initial conditions were reached in 3.5 minutes. A post-time for the re-equilibration of the column  
197 was set during 2.5 minutes. Injection volume was 10  $\mu\text{L}$  and the flow rate was fixed at 1 mL/min.  
198 The corresponding mass spectrometry conditions were described in Sánchez-Arévalo et al. (in  
199 press). Briefly, it was applied a capillary voltage of 3500V, nebulizer pressure of 30 psi and gas  
200 temperature of 200°C. In order to quantify the analytes, an external calibration was applied. To  
201 that end, standard solutions of tyrosol and catechin were prepared and diluted in ethanol/water  
202 50:50 (v,v) in the range of 0.2 – 50  $\text{g}\cdot\text{mL}^{-1}$ .

203 In addition, the concentration of total phenols in the liquid phase was measured to calculate the  
204 equilibrium desorption time. The desorption ratio (%Des), that is, desorption percentage of  
205 phenolic compounds from the total adsorbed, and adsorption-desorption recovery (%R) of  
206 phenolic compounds from the initial feed were calculated according to equation 7 and 8,  
207 respectively.

$$208 \quad \%Des = \frac{C_d \cdot V_d}{(C_o - C_e) \cdot V_o} \cdot 100 \quad (7)$$

$$209 \quad \%R = \frac{C_d \cdot V_d}{C_o \cdot V_o} \cdot 100 \quad (8)$$

210 where,  $C_d$  is the concentration of TPhC ( $\text{mg}\cdot\text{L}^{-1}$ ) in the desorption solution, and  $V_d$  and  $V_o$  are the  
211 volume of the desorption solution (solvent) and that of the initial feed (model solution) (mL),  
212 respectively.

## 213 **2.6 Test with olive oil washing wastewater**

214 Once the optimal dose of resin for the adsorption of phenolic compounds and the best solvent  
215 for their desorption were determined, the test was replicated with pre-treated olive oil washing  
216 wastewater (OOWW) (following the protocol reported in [20]). The samples were provided by  
217 an olive oil milling plant located in the Valencian Community (Spain) and were collected during



218 the 2020 olive oil production campaign. The OOWW corresponds to the residual water obtained  
219 at the exit of the vertical centrifuge after the olive oil washing step from a continuous two-phase  
220 olive mill. The same procedures indicated above were followed for the determination of  
221 adsorption and desorption efficiency. The determination of adsorption kinetics of the process  
222 was also carried out. Regarding the characterization of the supernatant after the adsorption  
223 process, in addition to the phenolic compounds, the sugar content and the chemical oxygen  
224 demand (COD) were also determined. For the determination of sugars concentration, the  
225 Sucrose/D-Glucose/D-Fructose colorimetric kit from r-biopharm (Germany) was employed,  
226 using glucose (Panreac, Spain) as a standard. For COD measurement, commercial kits supplied  
227 by Merck (Germany) were used. The phenolic compounds in the raw OOWW and from the  
228 desorption tests were determined with the LC-MS procedure described in the previous section.  
229 In this case, for the external calibration, standard solutions of citric acid, hydroxytyrosol, tyrosol,  
230 caffeic acid, *p*-coumaric acid, oleuropein, oleacein and dihydroxy-octadecanoic acid were  
231 prepared and diluted in ethanol/water 50:50 (v/v) in the range of 0.2 – 50 g·mL<sup>-1</sup>.

232 For the adsorption and desorption percentage of sugars and COD, equations 1 and 7 were used.  
233 In this case,  $C_0$  and  $C_e$  were the initial and equilibrium concentrations of sugars or COD in the  
234 feed solution, respectively;  $C_d$  was the concentration of sugars or COD in the desorption solution.  
235 All tests for both model solution and real wastewater were performed in triplicate.

### 236 **3. Results and discussion**

#### 237 **3.1 Tests with model solution**

##### 238 **3.1.1 Adsorption capacity**

239 Table 2 shows the adsorption of phenolic compounds for the different resins and dosages. The  
240 values correspond to the mean value together with the standard deviation. It can be seen that  
241 the highest adsorption percentage was achieved with the highest resin dosage (60g·L<sup>-1</sup>). As  
242 expected, this behaviour was observed for all the resins, which is mainly due to an increase in  
243 the number of available adsorption sites by increasing the surface area of the adsorbent [29].  
244 However, as the resin dose increases, the adsorption percentage showed less variation, with the  
245 PAD resin exhibiting practically similar adsorption percentage values at the three highest resin  
246 concentrations. Although the four resins achieved good adsorption percentages, the MN resins  
247 were able to retain the phenolic compounds almost completely, achieving percentages greater  
248 than 90% in some tests. The good performance of MN resins was also observed in studies  
249 performed by other authors. De Marco [30] showed that the MN202 resin was capable of  
250 retaining 99% of the phenolic compounds present in a vegetation water from the olive oil

251 extraction process. The MN200 resin was tested by Ferrer-Polonio [31] in order to separate  
 252 phenols from fermentation brines from table olive processing, achieving phenols removal  
 253 efficiencies higher than 90% with resin concentrations of 20 and 40 g·L<sup>-1</sup>.

254 Table 2. Adsorption of phenolic compounds for the different resins and dosages after 180  
 255 minutes treatment of the model solution.

Dosage (g·L <sup>-1</sup> )	TPhC <sub>ads</sub>	Resin			
		MN200	MN202	PAD900	PAD950
10	% Ads	78.73 ± 1.43	59.88 ± 1.40	55.42 ± 0.42	51.66 ± 2.81
	mgTyeq·L <sup>-1</sup>	1001.35 ± 16.02	761.53 ± 15.26	704.89 ± 4.75	657.01 ± 31.29
20	% Ads	91.79 ± 0.94	70.28 ± 2.84	60.05 ± 0.54	59.23 ± 0.79
	mgTyeq·L <sup>-1</sup>	1167.34 ± 10.37	893.89 ± 29.12	763.71 ± 5.96	758.81 ± 7.93
30	% Ads	94.24 ± 0.48	80.08 ± 2.11	67.61 ± 1.03	59.83 ± 1.08
	mgTyeq·L <sup>-1</sup>	1198.54 ± 5.30	1018.52 ± 23.13	859.88 ± 11.45	760.91 ± 11.59
40	% Ads	95.68 ± 0.60	91.43 ± 1.06	74.23 ± 2.57	63.84 ± 1.43
	mgTyeq·L <sup>-1</sup>	1209.34 ± 7.57	1162.82 ± 13.43	944.08 ± 33.59	811.98 ± 9.09
50	% Ads	97.52 ± 0.09	91.81 ± 1.38	74.80 ± 0.46	63.57 ± 0.62
	mgTyeq·L <sup>-1</sup>	1240.33 ± 1.09	1167.60 ± 14.23	954.36 ± 3.08	812.27 ± 5.07
60	% Ads	98.28 ± 0.05	93.07 ± 1.50	74.18 ± 1.42	64.71 ± 0.64
	mgTyeq·L <sup>-1</sup>	1249.89 ± 0.54	1183.64 ± 15.07	953.05 ± 8.21	826.42 ± 6.06

256 TPhC<sub>ads</sub>= Total phenolic compounds adsorbed from the initial feed solution  
 257 %Ads= adsorption percentage of total phenolic compounds from the initial feed solution  
 258 mgTyeq·L<sup>-1</sup>= total phenolic compounds adsorbed in milligram tyrosol equivalents per liter of sample

259

260 The high adsorption percentage of the MN resins can be explained by their higher surface area  
 261 (1100 – 950 m<sup>2</sup>·g<sup>-1</sup>) compared to the PAD resins (850-450 m<sup>2</sup>·g<sup>-1</sup>). However, the MN202 and  
 262 PAD900 resins present similar surface area (950 and 850 m<sup>2</sup>·g<sup>-1</sup>, respectively), but the former  
 263 resin material could have a higher affinity with the analysed phenolic compounds, providing  
 264 greater adsorption ability. In particular, adsorption interaction mechanism depends on intrinsic  
 265 characteristics of the resin such as surface area, pore volume, pore size and functional groups  
 266 of the adsorbent surface [32]. Furthermore, the MN resins have two types of pores, micropores  
 267 (in the range of 10 to 30 Å), which are responsible for the adsorption of small molecules, and  
 268 macropores which act as "transport channels" that ensure the diffusion of small to large  
 269 molecules through the resin. This could allow better adsorption of tyrosol and catechin onto  
 270 MN202 resin than onto PAD900 resin.

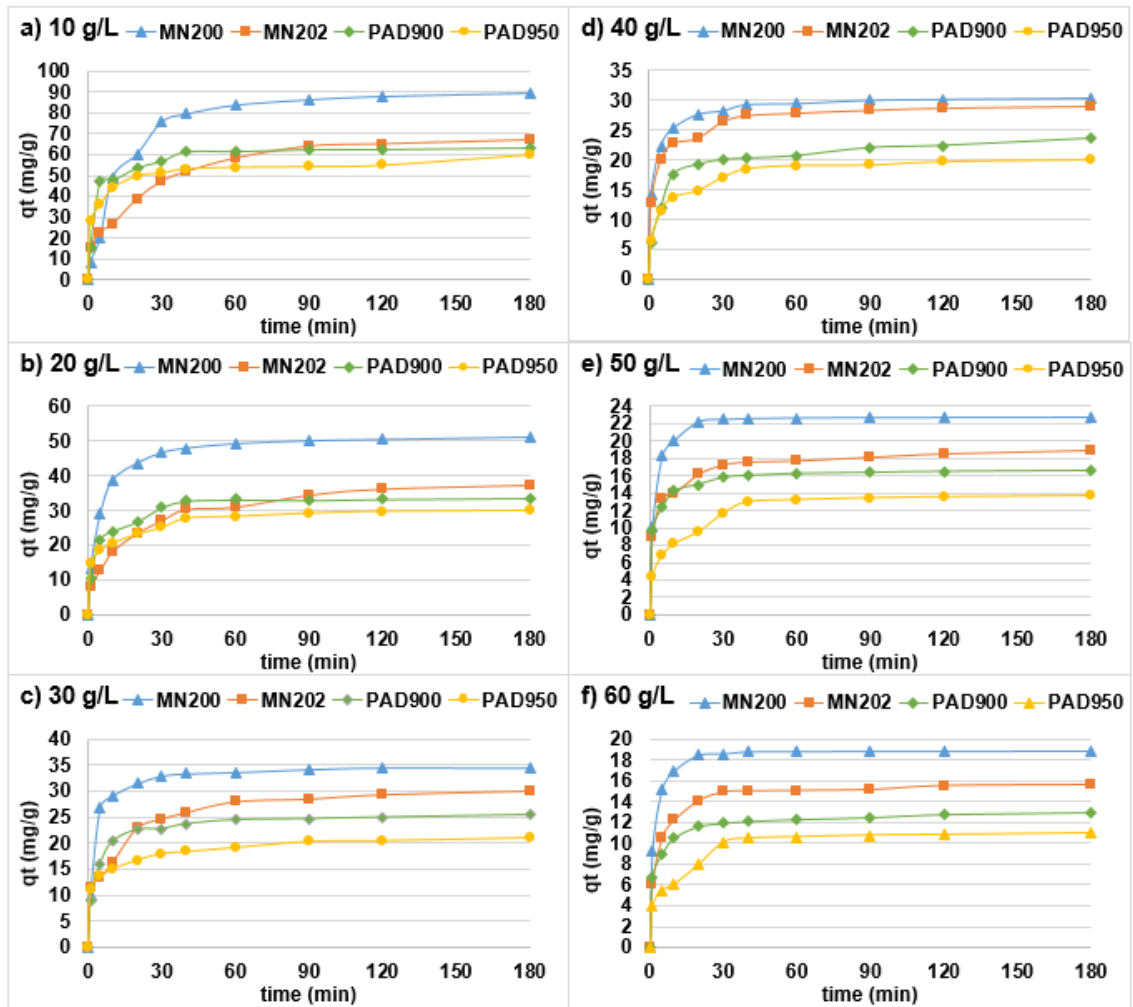
271 The low adsorption capacity of PAD950 resin may be due to its small pore diameter (120 Å).  
 272 Buran et al. [33] studied the separation of blueberry polyphenols and anthocyanins using

273 different cross-linked aromatic polymeric resins. These authors observed that the resin with the  
274 highest surface area had the lowest adsorption capacity, due to its very small pore envelope. It  
275 can be also explained considering the matrix, since this resin is the only one with an aliphatic  
276 matrix and with the lowest hydrophobicity. The MN and PAD900 resins are aromatic adsorbents  
277 with polystyrene- divinylbenzene (DVB) matrix, while the PAD950 resin is a polymethacrylic  
278 adsorbent. Valderrama et al. [34] reported that polystyrene-DVB adsorbents, including  
279 hypercrosslinked polystyrene, usually have a very hydrophobic surface, exhibiting a high affinity  
280 for solutes such as phenol or aniline with phenyl groups. In addition, the matrix of the PAD950  
281 resin presents greater affinity for aliphatic or semi aliphatic molecules than for aromatic ones.  
282 Different results were obtained by Silva et al. [35], who tested different resins for the adsorption  
283 of polyphenols from *Inga edulis* leaves. These authors found that the XAD-7 resin, made of an  
284 acrylic polymeric material (similar to the PAD950 used in this study), presented the best results  
285 in terms of adsorption capacity compared to the other resins based on styrene-divinylbenzene  
286 (similar to MN and PAD900 resins). It is important to note that these authors also pointed out  
287 that the use of the same resins for other phenolic extracts could lead to completely different  
288 results, concluding that the chemical nature of the adsorbent had more influence than its  
289 physical structure (surface area) on phenolic compounds adsorption.

### 290 **3.1.2 Kinetics of phenol adsorption**

291 Fig. 1 shows the amount of total phenolic compounds adsorbed per gram of resin during the  
292 adsorption process for all resins and concentrations tested. It can be seen that during the first  
293 minutes the adsorption was very fast, because all the active adsorption sites on the resin were  
294 available. Then, adsorption slowed down due to a decrease in the adsorption sites available,  
295 achieving finally the equilibrium.

296 As expected, initial adsorption was faster as resin concentration increased, reaching the  
297 equilibrium earlier. Furthermore, the adsorption kinetics showed that, in general terms, the  
298 amount TPhC absorbed did not significantly vary after 30 minutes. For the lowest resin  
299 concentration tested, the MN200 resin showed a higher amount of phenolic compounds  
300 adsorbed per gram of resin compared to the other resins. On the other hand, the PAD950 resin  
301 presented the lowest amount of phenolic compounds adsorbed in all the tests carried out,  
302 confirming the results of section 3.1.1. Regarding the contact time, the MN200 resin was the  
303 one that achieved the equilibrium in the shortest time, followed by the PAD900 resin.



304  
 305 Fig. 1. Variation of the amount of phenolic compounds adsorbed with time for all the resins,  
 306 using the model solution and different resin dosages: a) 10 gL<sup>-1</sup>, b) 20 gL<sup>-1</sup>, c) 30 gL<sup>-1</sup>, d) 40 gL<sup>-1</sup>,  
 307 e) 50 gL<sup>-1</sup> and f) 60 gL<sup>-1</sup> (results expressed in mg of tyrosol equivalents per gram of resin)

308 [Colour graph]

309

310 The analysis of the adsorption process based on kinetic models is presented in table 3. It can be  
 311 seen that the  $q_e$  values obtained by the pseudo-second order model are very close to the  
 312 experimental ones (Fig. 1), indicating a good approximation of the experimental adsorption data  
 313 to this model.

314 On the other hand, the pseudo-first order model yielded very low  $q_e$  values, being in some cases  
 315 incoherent and far from those obtained experimentally. As can be seen, the pseudo-second-  
 316 order model provided the best correlation for the phenols adsorption (obtaining an  $r^2$  close to  
 317 1). This infers that the adsorption rate depends on the adsorption capacity and not on adsorbate  
 318 concentration [36]. This behaviour was also observed by other authors [16,37], which supports  
 319 the affirmation that this kinetic model is characteristic of phenolic compounds.

320 Table 3. Kinetic parameters for the adsorption of phenolic compounds on the different resins  
 321 for the tests carried out with the model solution

Resin	dosage (g·L <sup>-1</sup> )	Pseudo-first-order			Pseudo-second-order		
		qe (mg·g <sup>-1</sup> )	k1(min <sup>-1</sup> )	r <sup>2</sup>	qe (mg·g <sup>-1</sup> )	k2(g·mg <sup>-1</sup> ·min <sup>-1</sup> )	r <sup>2</sup>
MN200	10	64.593	0.0385	0.9676	94.340	0.0012	0.9947
	20	29.973	0.0611	0.9741	51.813	0.0066	0.9997
	30	13.125	0.0513	0.8758	34.843	0.0172	0.9999
	40	13.197	0.0627	0.8805	30.675	0.0195	0.9999
	50	15.749	0.1823	0.9873	22.831	0.0573	0.9999
	60	10.710	0.1575	0.9459	18.939	0.0783	1
MN202	10	63.092	0.0432	0.9867	70.423	0.0014	0.9921
	20	27.268	0.0323	0.9669	38.610	0.0028	0.9943
	30	18.495	0.0392	0.9516	30.581	0.0060	0.9979
	40	12.929	0.0452	0.9122	29.326	0.0138	0.9996
	50	8.429	0.0577	0.9458	19.011	0.0202	0.9994
	60	5.384	0.0476	0.7800	15.748	0.0322	0.9997
PAD900	10	26.486	0.0469	0.9148	64.103	0.0062	0.9996
	20	18.666	0.0636	0.9240	34.130	0.0109	0.9994
	30	11.345	0.0504	0.9178	25.575	0.0157	0.9996
	40	11.127	0.0323	0.9101	23.641	0.0094	0.9978
	50	7.183	0.0774	0.9448	16.639	0.0437	0.9999
	60	4.897	0.0554	0.9280	12.987	0.0360	0.9996
PAD950	10	22.495	0.0539	0.9083	58.824	0.0047	0.9966
	20	16.188	0.0424	0.9528	30.488	0.0090	0.9988
	30	10.205	0.0375	0.9626	21.186	0.0129	0.9986
	40	10.944	0.0457	0.9119	20.325	0.0124	0.9988
	50	10.360	0.0624	0.9829	14.045	0.0158	0.9982
	60	8.685	0.0771	0.9666	11.211	0.0216	0.9982

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### 323 3.1.3 Adsorption isotherms

324 Table 4 summarizes the parameters and correlation coefficients when data were fitted to the  
 325 Freundlich and Langmuir isotherms. According to the r<sup>2</sup> values obtained, the Langmuir model  
 326 was the most appropriate for the MN resins, while the Freundlich model showed the best fit to  
 327 the data of the PAD resins. It is important to note that the Langmuir model did not provide  
 328 consistent values for PAD resins. The fact that the experimental data of the MN resins fit best  
 329 the Langmuir equation indicates a homogeneous nature of the adsorbent surface [38]. On the  
 330 contrary, the PAD resins presented a heterogeneous surface or surfaces with sites of varied  
 331 affinities, which is confirmed by the fitting to the Freundlich isotherm [37].

332 Table 4. Isotherm parameters for total phenolic compounds adsorption for all the tests carried  
 333 out with the model solution

Resin	Langmuir				Freundlich		
	$k_L$ (L·mg <sup>-1</sup> )	$q_0$ (mg·g <sup>-1</sup> )	$R_L$	$r^2$	$k_f$ (mg·g <sup>-1</sup> )·(mg·L <sup>-1</sup> ) <sup>-1/n</sup>	1/n	$r^2$
MN200	0.0043	163.93	0.19	0.9955	1.41	0.75	0.9787
MN202	0.0015	136.99	0.38	0.9971	1.14	0.64	0.9411
PAD900	n.c.	n.c.	n.c.	n.c.	5746.23	2.03	0.9742
PAD950	n.c.	n.c.	n.c.	n.c.	792.27	3.31	0.9634

334 n.c. = not calculated (since the model did not fit properly the experimental data)  
 335

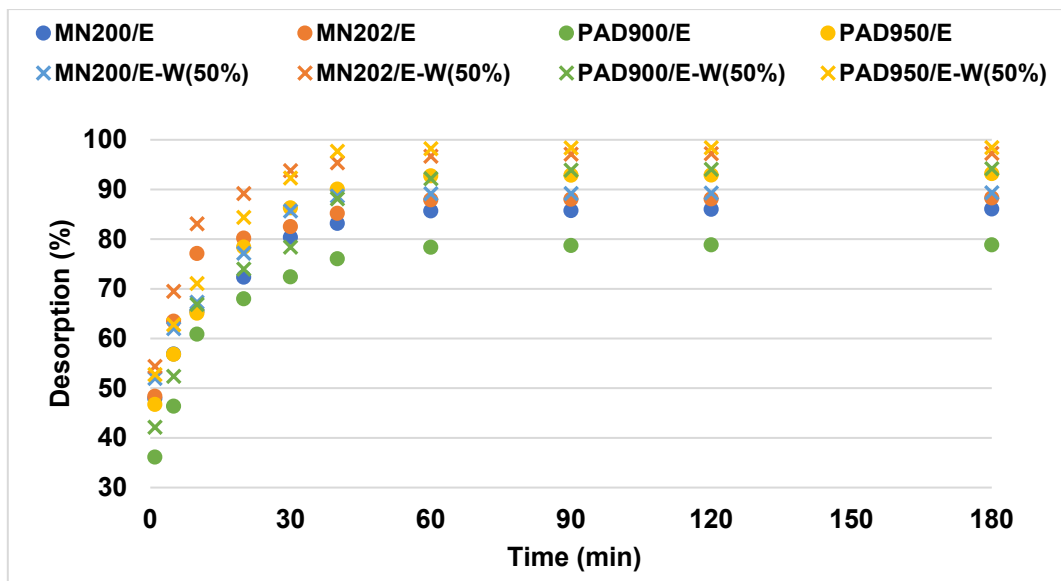
336 The dimensionless equilibrium parameter  $R_L$  was calculated for the MN resins. This parameter  
 337 is related to the  $K_L$  parameter (obtained with Langmuir model) through equation (7):

$$338 \quad R_L = \frac{1}{1 + K_L + C_0} \quad (7)$$

339 When  $R_L = 0$ , it is considered that the adsorption is irreversible, when  $0 < R_L < 1$  the adsorption  
 340 is favourable and when  $R_L > 1$  it is unfavourable. Both MN resins presented a value of  $R_L$  that  
 341 corresponds to favourable adsorption of phenolic compounds. MN200 resin had the lowest  $R_L$ ,  
 342 which means that it presents the best adsorption conditions. This agrees with the results of  
 343 adsorption percentages, where the MN200 resin showed the highest adsorption of total  
 344 phenolic compounds (Table 2). On the other hand, in the Freundlich model, the values of 1/n  
 345 are related to the adsorption intensity, being the adsorption favourable if they are lower than 1  
 346 [13]. Although the data of PAD resins fit the Freundlich model, the operating conditions tested  
 347 were not very appropriate for adsorption, as the 1/n values were greater than 1. On the other  
 348 hand, the MN resins presented 1/n values between 0.64 - 0.75, indicating a favourable  
 349 adsorption. The results also indicated that the PAD900 resin presented a significant higher  
 350 adsorption capacity than the PAD950 resin due to the higher  $k_f$  value, which is a parameter  
 351 related to the adsorption capacity [38].

### 352 3.2 Desorption

353 The adsorption tests showed that the adsorption of phenolic compounds did not present great  
 354 variation when the resin concentration increased from 40 to 60 g·L<sup>-1</sup>. Therefore, it was decided  
 355 to select the concentration of 40 g·L<sup>-1</sup> as the optimal one for the recovery of phenolic  
 356 compounds, taking into account that the cost of increasing the resin concentration from 40 to  
 357 60 g·L<sup>-1</sup> does not entail a measurable increase in the adsorption efficiency of these compounds.  
 358 For this reason, it was decided to analyse the desorption of phenolic compounds for the resin  
 359 dose of 40 g·L<sup>-1</sup>. Fig. 2 shows the desorption kinetics for two different eluents.



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Fig. 2. Desorption kinetics from previously saturated resins (dosage of  $40 \text{ g}\cdot\text{L}^{-1}$ ) using ethanol (/E) and a 50% v/v mixture of ethanol/water (/E-W(50%)) as eluents. (Results for the model solution).

[Colour graph]

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384 the recovery of phenolic compounds for all the tested resins. In addition, from an economic  
385 point of view, it is much more profitable (0.36 euros savings per test).

386 Within the non-ionic resins, the most often used for the recovery of phenolic compounds from  
387 OMW is Amberlite XAD16. Although good adsorption percentages of phenolic compounds with  
388 this resin have been published (greater than 80% in some cases), the percentage of desorption  
389 approached 50% [39]. Another study for the recovery of phenols from OMW, carried out by Ferri  
390 et al. [40], achieved adsorption/desorption percentages of 76% and 96%, respectively. In this  
391 case, the ENV+ was the best option for the entire process with acidified ethanol as eluent. A  
392 similar desorption percentage was observed by Caetano et al. [41] with the MN200 resin.  
393 Although, when they evaluated different resins (MN200, Dowex XZ and AuRIX 100) to remove  
394 phenols from an aqueous solution, the MN200 resin did not present the best adsorption  
395 percentages, it was the one that showed the highest recovery of phenolic compounds (90%)  
396 when using a methanol/water solution as a solvent.

397 Table 5 summarizes the results of the adsorption/desorption process when ethanol/water (50%  
398 v/v) solution was used as desorption solvent. Considering the entire process  
399 adsorption/desorption, the MN resins presented much higher adsorption percentages than the  
400 PAD resins, and globally showed the highest recovery of phenolic compounds from the model  
401 wastewater (which was 28 mgTyeq per gram of resin). It is important to emphasize that all the  
402 resins were used several times to determine the repeatability of the results. The resins did not  
403 lose their properties against the adsorption of phenolic compounds after three adsorption  
404 cycles.

405 Table 5. Summary table of adsorption/desorption process using a dosage of 40 gL<sup>-1</sup> of resin and  
406 ethanol/water 50% solution as desorption solvent for the model solution

Resin	% Ads.	% Des	% R	mgTyeq/g resin*
MN200	95.68 ± 0.60	92.74 ± 0.05	88.73 ± 0.04	28.21 ± 0.01
MN202	91.43 ± 1.06	96.99 ± 1.57	88.68 ± 1.43	28.19 ± 0.46
PAD900	74.23 ± 2.57	94.18 ± 4.27	69.90 ± 4.45	22.23 ± 1.42
PAD950	63.84 ± 1.43	98.37 ± 2.09	62.81 ± 1.96	19.97 ± 0.62

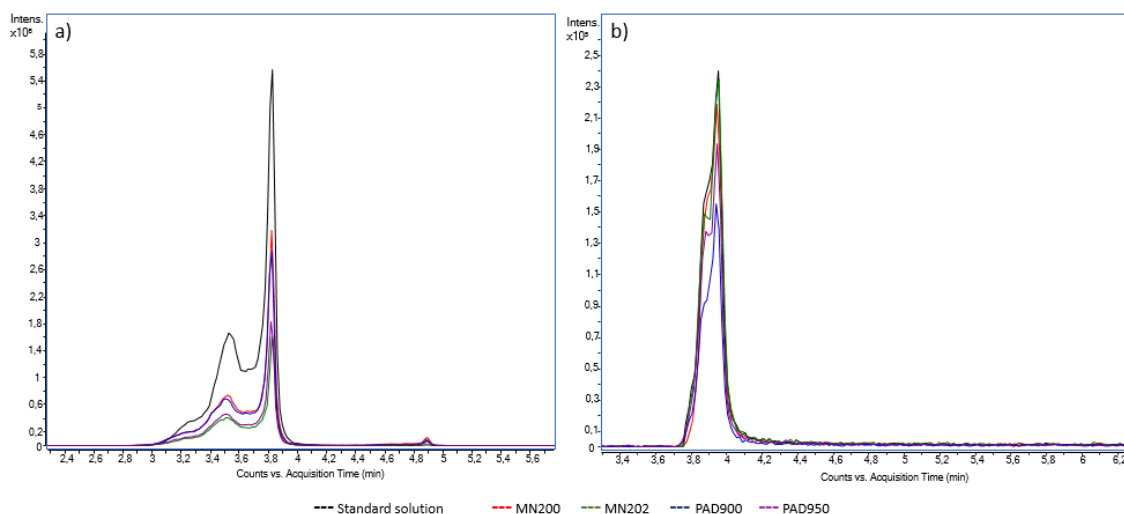
407 %Ads= adsorption percentage of phenolic compounds from the initial feed solution  
408 %Des= desorption percentage of phenolic compounds from the total phenolic compounds adsorbed  
409 %R=recovery percentage of phenolic compounds from the initial feed solution  
410 \*mgTyeq/g resin: recovered mg of total phenolic compounds in the final solution after desorption per grams of resin used

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412 To detect the specific concentration of catechin and tyrosol in the desorption solution, liquid  
413 chromatography coupled to mass spectrometry analyses were performed on the desorption  
414 samples obtained with the 50 % ethanol/water solution. This study was carried out with the



415 objective of analysing the affinity of the resins with the two different compounds present in the  
416 model solution.



417

418 Fig. 3. Chromatogram of the desorption solution when 50% v/v ethanol/water mixture was  
419 used as eluent for the most efficient adsorption conditions (40 g/L of resin using the model  
420 solution). a) catechin b) tyrosol  
421 [Colour graph]

422

423 Fig. 3 shows the chromatograms of the samples from the desorption process with ethanol/  
424 water mixtures for the two phenolic compounds. In both cases, the black line represents the  
425 standard solution. As expected, all the resins showed desorption of both compounds. Catechin  
426 desorption sequence was MN200>PAD900>PAD950>MN202, while for tyrosol the sequence  
427 was MN202>MN200>PAD950>PAD900 (from the highest concentration in the sample to the  
428 lowest one). The concentration sequence observed for tyrosol followed the trend shown in table  
429 5, where the MN resins provided a higher concentration of desorbed phenolic compounds  
430 compared to PAD resins. This result was expected since the model solution had a higher  
431 concentration of tyrosol than catechin. Regarding the desorption of catechin, the MN200 resin  
432 showed the largest desorption percentage (99.4% tyrosol and 96.6% catechin). However,  
433 greater concentration of this compound was observed in the samples from PAD900 resins in  
434 comparison with those from the MN202 resin. After desorption from the MN202 resin, 30% of  
435 the catechin present in the initial model solution (59.72 ppm) was recovered, while in the case  
436 of the PAD900 resin the amount present in the desorption solution corresponded to 88 % of the  
437 catechin in the initial model solution (175.06 ppm). The PAD950 resin presented a similar  
438 behaviour to the MN202, desorbing only 35.5% of catechin from the initial total in the model  
439 solution. Therefore, these resins could have a higher affinity for catechin (flavonoids, large

440 compounds) compared to tyrosol (simple phenol, smaller compounds), adsorbing it but not  
441 allowing desorption.

### 442 3.3 Tests with OOWW

#### 443 3.3.1 Adsorption process

444 Once it has been shown that the resins were capable of adsorbing phenolic compounds and  
445 desorbing them almost entirely, it was studied whether the presence of other compounds could  
446 affect the performance of these adsorption resins. It has been reported that the adsorption  
447 yields of phenolic compounds can be affected by competitive adsorption and, at the same time,  
448 by the interaction among them [42].

449 Table 6. Characterization of pre-treated olive oil washing wastewater (OOWW)

Parameter	Pre-treated OOWW
pH	5.18 ± 0.05
Conductivity (mS·cm <sup>-1</sup> )	4.36 ± 0.03
COD <sup>a</sup> (mgO <sub>2</sub> ·L <sup>-1</sup> )	27208.5 ± 341.2
TPhC <sup>b</sup> (mg tyrosol eq.·L <sup>-1</sup> )	1440.01 ± 11.81
Sugars (mg glucose ·L <sup>-1</sup> )	1491.20 ± 21.12
%Sug <sub>Glu</sub> <sup>c</sup>	59.64
%Sug <sub>Fruc</sub> <sup>d</sup>	22.31
%Sug <sub>Suc</sub> <sup>e</sup>	18.04

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<sup>a</sup> COD: chemical oxygen demand

<sup>b</sup> TPhC: Total phenolic compounds

<sup>c</sup> %SugGlu: percentage of glucose with respect to total sugars

<sup>d</sup> %SugFruc: percentage of fructose with respect to total sugars

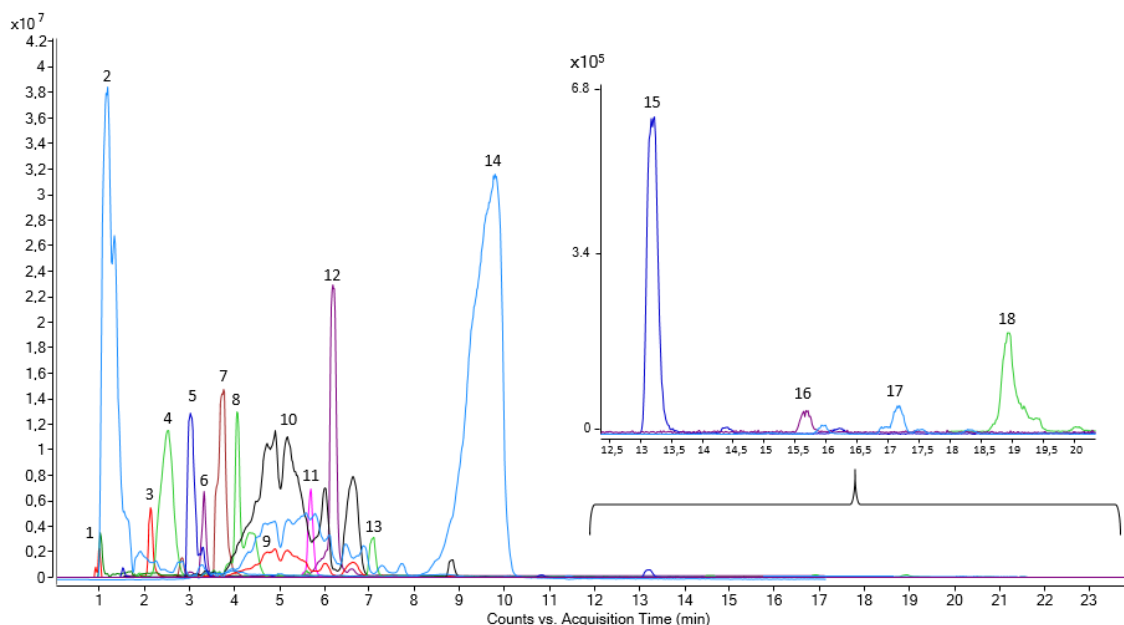
<sup>e</sup> %SugSuc: percentage of sucrose with respect to total sugars

455

456 Before starting the adsorption tests, pre-treated OOWW was characterized. It can be observed  
457 in table 6 that, apart from a high concentration of phenolic compounds, OOWW had a high  
458 organic load and a significant presence of sugars. These characteristics, together with an acidic  
459 profile, are typical of the wastewaters coming from the oil mills [20]. With regards to sugars,  
460 glucose and fructose are the ones at the highest concentrations. This was expected since these  
461 monosaccharides are the main sugars in most fruits [43]. Another fact to take into account is  
462 that the concentration of phenolic compounds is similar to that of the model solution used in  
463 the adsorption/desorption study.

464 In addition, the identification of the specific phenolic compounds present in the sample was  
465 carried out. More than twenty-five phenolic compounds were found, of which 13 could be  
466 identified. Fig. 4 shows 18 identified compounds, including organic acids, simple phenols,  
467 phenolic acids, secoiriodoids, flavonoids and fatty acids derivatives. The aldehydic form of  
468 decarboxymethyl elenolic acid, dihydroxy-hexadecanoic acid and dehydroxy-octadecatrienoic

469 acid were also found, although they are not visible in the chromatogram due to the scale. Table  
 470 7 contains the concentrations of all identified compounds.



471  
 472 Fig 4. Chromatogram of detected compounds in OOWW by LC-ESI-qTOF-MS. The number  
 473 correspond to the compound presented in table 7.

474 [Colour graph]

475 Table7. Concentration of the detected compounds in OOWW by LC-ESI-qTOF-MS

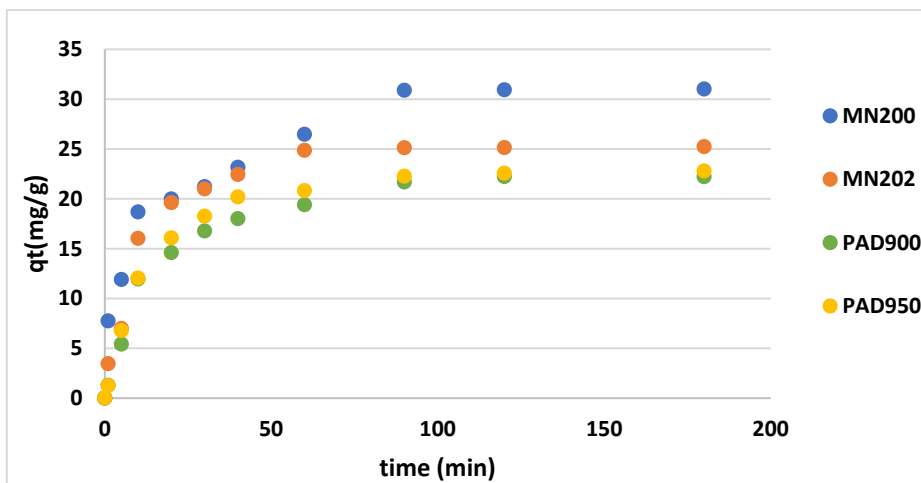
	<b>Detected Compound</b>	<b>Rt (min)</b>	<b>ppm</b>	<b>SD</b>
1	Malic acid	1.02	7.96	0.015
2	Citric acid	1.19	353.47	0.491
3	Quinic acid	1.01	149.25	0.153
4,8	hydroxy-decarboxymethyl elenolic acid (isomer 1+2)	3.95	40.44	0.007
5	hydroxytyrosol glucoside	3.02	1.70	0.004
6	hydroxytyrosol	3.30	1.15	0.000
7	acyclodihydroelenolic acid hexoside	3.95	86.84	0.010
9	tyrosol	5.90	529.62	0.927
10	hydroxy-elenolic acid	5.91	18.64	0.050
11	galocatechin	5.70	2.52	0.001
12	decarboxymethyl elenolic acid	6.21	174.56	0.159
13	p-coumaric acid	7.08	0.91	0.000
14	elenolic acid	9.79	17.52	0.310
15	luteolin	13.23	0.07	0.017
16	apigenin	15.70	0.30	0.075
17	trihydroxy-octadecadienoic acid	17.20	1.05	0.001
18	trihydroxy-octadecenoic acid	18.82	0.49	0.071
19	Aldehydic form of decarboxymethyl elenolic acid	7.10	1.35	0.005
20	dihydroxy-hexadecanoic acid	19.83	0.25	0.000
21	dehydroxy-octadecatrienoic acid	22.95	0.15	0.001

476

477 It can be seen that the measured phenolic compounds encompass different classes of  
 478 compounds, being secoiridoids the most abundant family. However, simple phenols were the  
 479 compounds at the highest concentrations (61%), being tyrosol and hydroxytyrosol among them.  
 480 These compounds have been recognized as antioxidant, anti-inflammatory and antimicrobial,  
 481 with promising applications in cosmetics, food and medical areas [44,45].

482 Fig. 5 shows the adsorption of phenolic compounds from OOWW by the selected resins. It can  
 483 be seen that, as for the model solution, during the first minutes the adsorption is faster. After  
 484 ten minutes of testing, a high adsorption is already observed. Then, the increase becomes less  
 485 abrupt. However, comparing with the model solution, it takes more time to reach an  
 486 equilibrium, i.e. after 90 minutes. Regarding the behaviour of the resins, a similar but more  
 487 pronounced trend was observed. Clearly, the results were better for the MN200 resin in  
 488 comparison with those yielded by the other resins, while the PAD900 had the worst  
 489 performance. Regarding the mass of phenolic compounds adsorbed by the resin, MN202 and  
 490 PAD900 resins decreased their yield compared to that obtained with the model solution.  
 491 Therefore, it can be inferred that, for these resins, there were compounds in the wastewater  
 492 that interfered with the adsorption of phenolic compounds. This was expected since the  
 493 presence of various adsorbates in solution can generate competition for active site effects,  
 494 which lead to a worse adsorption of the target compounds [46].

495



496  
 497 Fig. 5. Mass (mg) of total phenolic compounds from olive oil washing wastewater absorbed per  
 498 gram of resin over time for all resins tested at a dose of 40 g/L  
 499 [Colour graph]

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501

502 The use of OOWW produced a delay in the adsorption process, multiplying by three the  
 503 equilibrium time compared to that measured with the model solution, where equilibrium was  
 504 reached after half an hour of contact time.

505 Another aspect to highlight is that the pH of the OOWW was not modified for the tests. This is a  
 506 factor to be taken into account since the pH has an important effect on the adsorption of  
 507 phenolic compounds [47]. Frascari et al. [28] compared five resins (four neutral and one ion  
 508 exchange resin, three of them with the same matrix (microporous styrene-divinylbenzene) as  
 509 the resins used in this work), for the recovery of phenolic compounds from OMW. For the  
 510 neutral resins, they reported a decrease in the absorbed percentage when pH increased, so they  
 511 decided to work at the natural pH of the OMW (pH=4.2). Caetano et al. [41] also tested different  
 512 resins for the recovery of phenolic compounds from aqueous solution. They reported that, in  
 513 the case of the non-functionalized resin, under acidic conditions (pH = 3), greater adsorption  
 514 capacities were measured than under alkaline conditions (pH = 11). This indicates a preference  
 515 for the molecular form of phenol over phenolate, which involves an increase in electrostatic  
 516 repulsion. Therefore, it should be emphasized that the analysed resins presented a good  
 517 performance of adsorption of phenolic compounds without varying the feed pH.

518 Table 8. Kinetic parameters of adsorption of phenolic compounds from olive oil washing  
 519 wastewater

Resin	dosage (g·L <sup>-1</sup> )	q <sub>e</sub> (exp.) (mg·g <sup>-1</sup> )	Pseudo-first-order			Pseudo-second-order		
			q <sub>e</sub> (mg·g <sup>-1</sup> )	k <sub>1</sub> ·10 <sup>-2</sup> (min <sup>-1</sup> )	r <sup>2</sup>	q <sub>e</sub> (mg·g <sup>-1</sup> )	k <sub>2</sub> ·10 <sup>-3</sup> (g·mg <sup>-1</sup> min <sup>-1</sup> )	r <sup>2</sup>
MN200	40	30.946	34.726	5.70	0.831	30.362	3.595	0.9918
MN202	40	25.163	15.331	7.95	0.926	26.316	6.055	0.9966
PAD900	40	22.035	19.939	4.17	0.968	23.866	3.600	0.9932
PAD950	40	22.540	20.206	4.65	0.981	23.213	4.234	0.9944

520

521 Regarding the adsorption kinetics of phenolic compounds, it can be seen in Table 8 that again,  
 522 the pseudo-first order model did not provide consistent data on the solute adsorbed per gram  
 523 of sorbent at equilibrium, with values below those experimentally obtained. As in the model  
 524 solution, the pseudo second order model was the one that most accurately fitted to the  
 525 experimental data of adsorption of phenolic compounds. Pseudo-second order kinetics indicates  
 526 that the process is dominated by adsorption on active sites, so it is the best fitting model when  
 527 the adsorbent has many active sites [48]. Previously, it was commented that the amount of  
 528 adsorbed phenolic compounds for some of the resins was smaller than in the case of the model  
 529 solution. It can also be observed that the experimental q<sub>e</sub> value was approximately 12% lower

530 for the MN202 resin and 6% lower for the PAD900 resin than the values experimentally obtained  
 531 with simulated water (28.74mg·g<sup>-1</sup> vs 25.16 mg·g<sup>-1</sup> and 22.68 vs 22.03 mg·g<sup>-1</sup>, respectively). This  
 532 shows the existence of other compounds that occupy adsorption sites on the resins, thus  
 533 reducing the separation efficiency of phenolic compounds. The MN200 resin, however, did not  
 534 present significant variation (+2%) in the experimental q<sub>e</sub> compared to that obtained with the  
 535 simulated wastewater; the PAD950 resin showed an improvement in the performance, with a  
 536 q<sub>e</sub> 10% higher than that obtained with the simulated solution. This may be due to the  
 537 compounds present in each sample. The MS only presents one type of flavonoid and simple  
 538 phenol, while the OOWW presents a variety of phenolic compounds, which can have more  
 539 affinity with the PAD950 resin. Studies reported by Casas et al. [37] indicate that the PAD950  
 540 resin present high adsorption capacity for phlorotannins, a type of tannin present in seaweed  
 541 *Sargassum muticum*. It has been reported the presence of tannins in OOWW [49], therefore that  
 542 could explain the higher PAD950 adsorption.

543 In order to find out whether sugars and COD (which includes the rest of organic compounds in  
 544 OOWW in addition to sugars and TPhC) interfered the phenolic compounds adsorption, the  
 545 theoretical COD of the adsorbed phenols (COD<sub>PhC.ads</sub>) and sugars (COD<sub>Sug.ads</sub>) was calculated. This  
 546 parameter was calculated following the correlation proposed by [31]. As total phenols are  
 547 expressed in mgTYL<sup>-1</sup> and 1 mol of tyrosol requires 9.5 mol of O<sub>2</sub> for its oxidation, 2.2mg O<sub>2</sub> per  
 548 mg of tyrosol are needed. In the case of glucose, 1 mole of glucose needs 6 mol of O<sub>2</sub> for its  
 549 oxidation, i.e. 1.1mg O<sub>2</sub> per mg of glucose. Thus, the equations used for the calculation were the  
 550 following:

$$551 \quad COD_{PhC.ads} = (C_{0,PhC} - C_{e,PhC}) \cdot 2.2 = C_{PhC.ads} \cdot 2.2 \quad (8)$$

$$552 \quad COD_{Sug.ads} = (C_{0,Sug} - C_{e,Sug}) \cdot 1.1 = C_{Sug.ads} \cdot 1.1 \quad (9)$$

553 Being C<sub>0,PhC</sub> and C<sub>0,Sug</sub> the initial concentration of total phenols and sugars, respectively, and C<sub>e,PhC</sub>  
 554 and C<sub>e,Sug</sub> the concentration of total phenols and sugars, respectively, in the liquid phase when  
 555 adsorption equilibrium was achieved. Finally, C<sub>PhC.ads</sub> and C<sub>Sug.ads</sub> are the concentrations of total  
 556 phenols and sugars adsorbed on the resins expressed in (mgTyeqL<sup>-1</sup>) and (mg glucose ·L<sup>-1</sup>),  
 557 respectively. These results can be expressed in percentages (Eq. 10 and 11):

$$558 \quad COD_{PhC.ads}(\%) = \frac{COD_{PhC.ads}}{COD_{ads}} \cdot 100 \quad (10)$$

$$559 \quad COD_{Sug.ads}(\%) = \frac{COD_{Sug.ads}}{COD_{ads}} \cdot 100 \quad (11)$$

560 Being  $COD_{ads}$  the difference between initial COD in the samples ( $COD_0$ ) and COD in the liquid  
561 phase when the adsorption equilibrium was reached ( $COD_e$ ). The results of the adsorption of  
562 phenolic compounds, sugars and COD are presented in Table 9. The theoretical percentage of  
563 COD that corresponded to the total phenolic compounds and sugars adsorbed is also shown in  
564 the table. The results followed the same trend that was observed with the model solution. The  
565 MN200 resin presented the largest adsorption of phenolic compounds, while the PAD950  
566 showed the smallest one. The low TPhC adsorption of PAD950 resin is again attributed to its  
567 small pore size. According to the literature, the smallest the diameter of the pores of the resin,  
568 the lowest the diffusion of the adsorbate molecules from the aqueous phase to the pores of the  
569 adsorbent [50]. Interestingly, this resin was the only one that did not exhibit a decrease in the  
570 adsorption of phenolic compounds in comparison with the model solution. The MN202 resin  
571 was the one that presented the greatest decrease in TPhC adsorption (19% lower). However,  
572 this resin showed a high adsorption of phenolic compounds, again being the MN resins the ones  
573 that exhibited the best performances. This is directly related to the material of the resins.  
574 Studies carried out by Kammerer et al. [51] observed that resins with a polystyrene-based matrix  
575 (the same matrix as MN resins) exerted a significantly greater polyphenol binding than  
576 polyacrylamide-based resins as a result of stronger hydrophobic interactions and hydrogen  
577 bonding due to their higher hydrophobicity. In that study, the authors also reported the impact  
578 of saccharides and amino acids on apple polyphenols adsorption on resins. They concluded that  
579 the presence of glucose, fructose and sucrose could affect the adsorption of some phenolic  
580 compounds on both neutral and ion exchange resins. They observed that the adsorption of  
581 catechin in a non-ionic resin was less effective when glucose and sucrose were present. On the  
582 contrary, the adsorption of caffeic acid was better in the presence of all the sugars together or  
583 separately. They attributed it to the possibility of a multilayer adsorption on the resin surface,  
584 which might be enhanced in the presence of sugars through hydrogen bridges. Carbohydrates  
585 might enhance the formation of several layers of some compounds that do not normally interact  
586 directly with the resin; significantly improving the recovery rates. This might also explain the  
587 slightly higher adsorption (+5%) exhibited by the PAD950 resin compared to the model solution.

588 To know how selective the resins are for these compounds and how many other organic  
589 substances they can remove, the adsorbed COD corresponding to phenolic compounds and  
590 sugars was determined. The MN200 resin showed the highest percentage of adsorbed COD  
591 linked to phenolic compounds (52.4%). This means that this resin is more selective than the  
592 others towards phenolic compounds, since more than 50% of the adsorbed COD corresponds to  
593 these antioxidant compounds. This resins also yielded the lowest COD removal related to sugar

594 adsorption (12.86%). The MN202 and PAD950 resins also presented a low percentage of COD  
 595 removal corresponding to adsorbed sugars. This implies a small competition between phenolic  
 596 compounds and sugars on the adsorption sites of these resins. On the other hand, MN202 also  
 597 had a removal of COD linked to phenolic compounds similar to that of PAD950 resin (between  
 598 32-39%).

599

600 Table 9. Removal percentages for each resin after reaching the equilibrium and study of  
 601 adsorption of COD for all the resins tested when the olive oil washing wastewater was treated

Removal percentage (%)	MN200	MN202	PAD900	PAD950
<sup>a</sup> TPhC <sub>ads</sub>	91.89 ± 0.97	74.31 ± 0.18	69.99 ± 0.92	66.95 ± 0.79
<sup>b</sup> Sug <sub>ads</sub>	23.60 ± 0.28	29.47 ± 0.60	54.38 ± 0.84	41.71 ± 1.73
<sup>c</sup> COD <sub>total.ads</sub>	19.11 ± 0.06	20.89 ± 0.25	25.96 ± 1.20	22.99 ± 0.86
<sup>d</sup> COD <sub>PhC.ads</sub>	52.37 ± 0.62	39.01 ± 0.40	27.37 ± 1.06	31.95 ± 0.85
<sup>e</sup> COD <sub>Sug.ads</sub>	12.86 ± 0.13	15.72 ± 0.19	35.32 ± 0.75	19.28 ± 0.43

602 <sup>a</sup>TPhC<sub>ads</sub>: Percentage of total phenolic compounds adsorbed from the initial feed solution

603 <sup>b</sup>Sug<sub>ads</sub>: Percentage of sugars adsorbed from the initial feed solution

604 <sup>c</sup>COD<sub>Total.ads</sub>: Percentage of total COD adsorbed from the initial feed solution

605 <sup>d</sup>COD<sub>PhC.ads</sub>: COD percentage corresponding to the adsorbed phenolic compounds

606 <sup>e</sup>COD<sub>Sug.ads</sub>: COD percentage corresponding to the adsorbed sugars

607

608 With respect to the PAD900 resin, it showed a greater adsorption of COD linked to sugars than  
 609 to phenolic compounds (1.3 times higher). Therefore, in this case, the sugars competed for the  
 610 resin sites, thus interfering with the adsorption of the phenolic compounds. The adsorbed COD  
 611 represented by sugars together with that represented by phenolic compounds gives percentage  
 612 values between 51-65%. Frascari et al. [52] reported that in addition to carbohydrates, the  
 613 presence of proteins was detected in non-phenolic COD desorbed after an adsorption process  
 614 performed in a continuous flow column for OMW valorisation. This implies that the resins  
 615 adsorbed organic compounds other than sugars and phenols. With these results, it can be  
 616 inferred that the phenolic compounds adsorbed by the MN200 resin contained fewer impurities  
 617 than those adsorbed by the other resins. In this way, it can be commented that, although the  
 618 resins are specific for phenolic compounds, they also adsorb other compounds, which interferes  
 619 with the performance of the resins for the adsorption of phenolic compounds. However, all the  
 620 resins presented adsorption percentages of phenolic compounds higher than 66%, with the  
 621 MN200 resin presenting values higher than 91%. Chaari et al. [53] achieved adsorption  
 622 percentages of phenolic compounds from OMW between 77.61% and 84.21% using calcined  
 623 clay as adsorbent at acidic pH. In this work, by means of the MN resins, greater percentages can

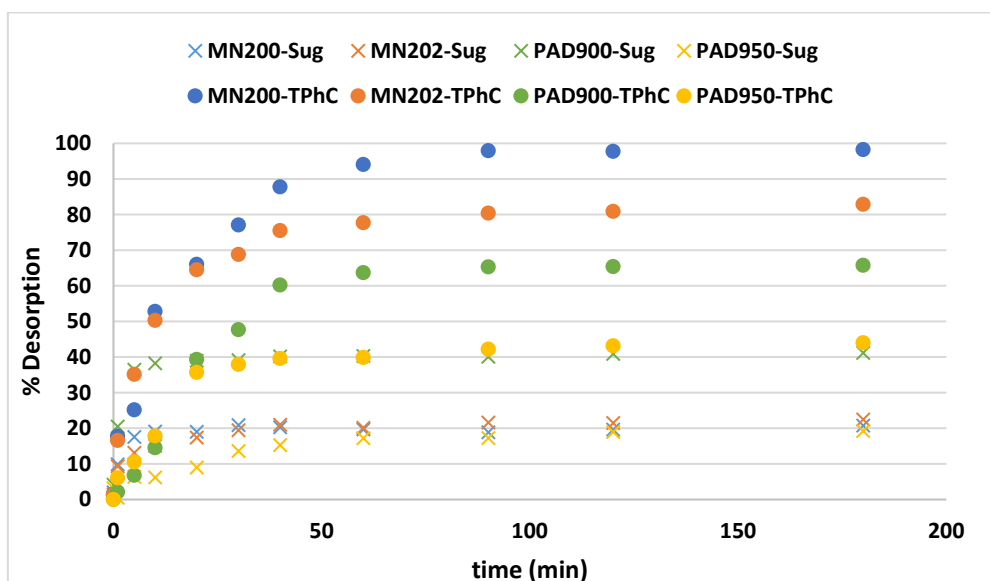


624 be achieved without acidifying the medium and with easily recoverable adsorbents. Ochando-  
 625 Pulido et al. [54] tested different resins for the recovery of phenolic compounds from OOWW.  
 626 They achieved the highest rejection percentage with an ionic resin (95.3%). However, with the  
 627 non-ionic resins tested only 70.5% adsorption of phenolic compounds was reached with a resin  
 628 dose of 60 g·L<sup>-1</sup>. In this case, the MN resins presented better performance, while the PAD resins  
 629 presented similar adsorption to the one reported by those authors. Moreover, in our work a  
 630 lower resin concentration was used. This demonstrates the high affinity of these resins against  
 631 phenolic compounds. The studies carried out by Zagklis et al. [55], using an reverse osmosis  
 632 OMW concentrate as feed, showed similar percentages of adsorption of sugars and phenolic  
 633 compounds using non-ionic resins (XAD4, XAD7 and XAD16). The best result was obtained with  
 634 the XAD4 resin, with 35.8% and 93.1% adsorption of sugars and phenolic compounds,  
 635 respectively. Although the MN200 resin has a slightly lower adsorption of phenolic compounds  
 636 (-1.21%), it has 12.2% less adsorption of sugars.

### 637 3.3.2 Desorption process

638 As in the desorption tests with the model solution a 50% v/v ethanol/water solution was the  
 639 one that reached the highest percentages of desorption, this eluent was the one selected for  
 640 the tests with OOWW. Desorption percentages of phenolic compounds and sugars are shown in  
 641 fig.6. It is important to highlight that the percentage of desorption is calculated based on the  
 642 amount adsorbed by each resin, not on the total amount in the initial sample. The results  
 643 obtained for phenolic compounds were completely different from those observed for the model  
 644 solution.

645



646

647 Fig 6. Desorption of Phenolic compounds (TPhC) and sugars (Sug.) using a 50% v/v  
648 ethanol/water mixture as solvent for 40 g/L resin dose when the olive oil washing wastewater  
649 was treated.  
650 [Colour graph]

651

652 The obtained sequence (from the highest to the lowest desorption percentage) was  
653 MN200>MN202>PAD900>PAD950, while the sequence with the model solution was  
654 PAD950>MN202>PAD900>MN200. The MN200 resin improved the desorption percentage,  
655 exceeding 98% (92% with model solution). However, the rest of the resins presented lower  
656 desorption percentages than those obtained with the simulated solution. The lowest percentage  
657 was observed for the PAD950 resin (45%), desorbing less than half of the adsorbed phenolic  
658 compounds. In this case, it is possible that the affinity between the resin and the adsorbed  
659 compounds is so strong that their desorption is not enhanced. This was also commented in the  
660 section 3.2 for the model solution. This was also observed by Buran et al. [33] in their  
661 adsorption/desorption studies of blueberry phenolic compounds. They attributed it to the great  
662 affinity of the resinous material towards phenolic compounds (mainly anthocyanins and  
663 flavonols). The resin was made of a polar phenol formaldehyde polymer (dipole moment = 1.80),  
664 while the other adsorbents were made of styrene-divinylbenzene co-polymer (dipole moment  
665 = 0.30). In our case, the PAD950 resin is made of an acrylic material, which has a similar dipole  
666 moment to phenolic compounds [35]. Thus, it could explain that a significant amount of phenolic  
667 compounds were irreversibly adsorbed.

668 Regarding the percentages of desorbed sugars, it can be clearly seen that they are significantly  
669 lower than the desorption percentages of phenolic compounds. PAD900 resin offered the  
670 highest and PAD950 resin the lowest sugar desorption ratio. Although in the previous section  
671 high COD linked to adsorbed sugars was obtained for the PAD900 resin, these were not  
672 completely desorbed. These are valuable results for the objective of recovering phenolic  
673 compounds, since, regardless of whether the resins can adsorb sugars, they were not completely  
674 desorbed, so a concentrated stream of relatively pure phenolic compounds can be obtained.  
675 Nevertheless, sugars adsorption can affect the durability of the resin, since extra cleaning would  
676 be needed to remove the not desorbed sugars (and other compounds), affecting its useful life.

677 Table 10 shows a summary of the adsorption/desorption process for the recovery of phenolic  
678 compounds from OOWW. It can be seen that the MN resins presented the best results in terms  
679 of recovery of phenolic compounds from the initial sample (table 6), obtaining a recovery of 90%  
680 with the MN200 resin. On the other hand, the solution obtained after the desorption step

681 showed a 18 times lower concentration of sugars (73ppm) compared to the concentration of  
 682 phenolic compounds (1310.97ppm). That means that the obtained extract contained only 5% of  
 683 the initial sugar content of the OOWW. This implies a great purity of the phenolic compounds.  
 684 Similar results were obtained with the MN202 resin, where the concentration of sugars in the  
 685 final solution was 11 times lower than that of the phenolic compounds present. The purity of  
 686 the final stream followed the following sequence MN200>MN202>PAD950>PAD900.

687 Table 10. Summary of adsorption/desorption of phenolic compounds and sugars from OOWW,  
 688 using a resin dosage of 40 gL<sup>-1</sup> and a 50% v/v ethanol/water mixture as eluent

	Resins			
	MN200	MN202	PAD900	PAD950
<sup>a</sup> TPhC. <sub>ads</sub> (%)	91.89 ± 0.97	74.31 ± 0.18	69.99 ± 0.92	66.95 ± 0.79
<sup>b</sup> TPhC. <sub>des</sub> (%)	99.07 ± 0.25	69.22 ± 1.32	50.94 ± 0.25	44.52 ± 0.88
<sup>b</sup> TPhC. <sub>des</sub> (ppm)	1310.97 ± 1.22	915.92 ± 5.32	674.12 ± 0.88	589.12 ± 3.22
<sup>c</sup> Sug. <sub>ads</sub> (%)	23.60 ± 0.28	29.47 ± 0.60	54.38 ± 0.84	41.71 ± 1.73
<sup>d</sup> Sug. <sub>des</sub> (%)	20.04 ± 0.94	22.48 ± 0.54	41.18 ± 0.56	19.23 ± 1.06
<sup>d</sup> Sug. <sub>des</sub> (ppm)	73.00 ± 6.28	98.80 ± 4.82	255.80 ± 6.06	119.60 ± 13.09
<sup>e</sup> TPhC. <sub>rec</sub> (%R)	90.90 ± 0.56	76.11 ± 1.14	60.01 ± 1.37	40.91 ± 0.37

689 <sup>a</sup>TPhC.<sub>ads</sub>= total phenolic compounds adsorbed from the initial feed solution

690 <sup>b</sup>TPhC.<sub>des</sub>= total phenolic compounds desorbed from the total adsorbed

691 <sup>c</sup>Sug.<sub>ads</sub> =total of sugars adsorbed from the initial feed solution

692 <sup>d</sup>Sug.<sub>des</sub> =total of sugars desorbed from the total adsorbed

693 <sup>e</sup>TPhC.<sub>rec</sub>= total phenolic compounds recovery from the initial feed solution

694

695 The study carried out by Ochando-Pulido et al. [56] achieved a slightly higher recovery of  
 696 phenolic compounds (92.5%) from OOWW. However, they used an ion exchange resin, and they  
 697 worked under certain operational conditions (effluent at 20.3 °C, pH 6.7 and resin dose of 114  
 698 g·L<sup>-1</sup>) that implied changes in the system. In our case, we worked without modifying the pH of  
 699 the effluent and the resin dose was much smaller (40 g·L<sup>-1</sup>). All this makes the recovery process  
 700 of phenolic compounds proposed in this work more profitable from an economic point of view.

701 One of the latest studies on the valorisation of phenolic compounds from solid oil mill residues  
 702 by means of adsorption/desorption [57] showed recovery percentages of total phenols between  
 703 74.6% - 70.31%, using contents of resin of 100 and 50 g·L<sup>-1</sup>, respectively. In addition, these  
 704 authors worked under acid conditions. In our case, we could obtain higher recovery percentages  
 705 without acidifying the feed solution. It is important to note that this study was conducted using  
 706 the solid residue from olive oil production, which was submitted to an extraction process with  
 707 hydroalcoholic solutions. The feed solution for the adsorption process was the dealcoholized  
 708 extract acidified to pH 2.8.

709 Table 11 shows the final concentration of individual phenols, organic acids, fatty acid derivatives  
710 and sugars in the eluent of each resin. The final recovery of phenolic compounds and sugars  
711 through the adsorption/desorption process is also presented. It is important to highlight that  
712 sugar concentrations were not obtained by LC-MS, but by colorimetric kits as explained in  
713 section 2.6. A difference in the total concentration of phenolic compounds is observed when the  
714 desorption results obtained with FC and LC-MS are compared. This may be due to different  
715 reasons, such as interference with other compounds or that there are phenolic compounds not  
716 detected with LC-MS methodology, but quantified with FC. Some studies have concluded that  
717 fructose and sucrose could react with the FC reagent and be measured as phenolic compounds,  
718 affecting the final total phenolic compounds values [58]. Nevertheless, the FC method is the  
719 prevailing method for the determination of the total concentration of these compounds in food  
720 samples and, according to Olmo-García et al. [59], it can be considered a valid and reliable  
721 method when global concentration is pursued. These authors mentioned that, although all the  
722 published options for the quantification of phenolic compounds are valid, the main limitation is  
723 the disparity of criteria regarding the expression of the results on the quantification of phenolic  
724 compounds. Thus, the results are not comparable. From table 11 the chemical classes that are  
725 predominant in the final solution of each resin can be inferred. In addition, recovery percentages  
726 of the main individual phenolic compounds and sugars are shown.

727 In can be seen from table 11, that the highest concentration of phenolic compounds was found  
728 in the final elution solution obtained with the MN200 resin, being 3.6 times greater than that  
729 from the PAD950 resin. In general, all the resins presented a high concentration of tyrosol in the  
730 final stream. The MN200 resin was able to recover all the phenolic compounds present in the  
731 initial OOWW sample. This resin was the one that, considering all the simple phenols together,  
732 achieved the highest recovery. However, this resin did not present the highest recovery of  
733 hydroxytyrosol, having a similar performance to the PAD900 resin (recovery of 42-43%). The  
734 highest recovery of hydroxytyrosol was achieved with the MN202 resin and was 87%. On the  
735 other hand, this compound was not found in the desorption solution obtained with the PAD950  
736 resin. Therefore, it can be concluded that the recovery of small phenolic compounds, such as  
737 simple phenols, by the MN resins is possible.

738 Regarding the phenolic acid, the MN202 resin presented by far the largest recovery, with the  
739 MN200 resin only recovering a 12%, while in the eluent from the PAD resins this compound was  
740 not detected. Once again, the MN202 resin was the one that presented the greatest recovery of  
741 secoiriodoids (90%), followed by the MN200 resin with 68.72%. The same trend was observed  
742 with the flavonoids, obtaining largest recovery percentages with the MN resins. Similar results

743 were presented by Yangui et al. [60] when studying the recovering phenolic compounds from  
744 OMW with MN202 and FPX66 resin, at a resin concentration close to that presented in this study  
745 ( $50 \text{ gL}^{-1}$ ). Obtaining the greatest phenolic acid (100% p-coumaric acid and caffeic acid) and  
746 flavonoids (91.3% catechin) recovery with the MN202 resin.

747 Depending on which compounds are to be recovered, one MN resin is more suitable than the  
748 another. To recover simple phenolic compounds, the MN200 resin is more suitable, while  
749 MN202 would be the one selected to recover phenolic acids, secoiriodoids and flavonoids.

750 Taking into account the concentration of total phenolic compounds, as with the FC method  
751 (table 10), the MN200 resin was the one that presented the best performance, obtaining a total  
752 recovery of 89.75%.

753 Regarding sugars, the solution obtained with the PAD900 resin was the one that presented the  
754 greatest concentration of sugars, being almost similar to the concentration of total phenolic  
755 compounds (equivalent to almost 40% of the concentration of total phenolic compounds in the  
756 extract). In general, glucose showed the highest concentration in the samples in comparison  
757 with the rest of the sugars. The MN resins were the ones that obtained desorption solutions  
758 with the lowest concentration of sugars, thus being the purest ones.

759 Table 11. Specific concentration of phenolic compounds, organic acids, fatty acids and sugars in the eluent for each resin and recovery percentage of the  
 760 phenolic compounds and sugars.

Chemical class	Detected Compound	Resins							
		MN200		MN202		PAD900		PAD950	
		<sup>a</sup> ppm	<sup>b</sup> %Recovery	<sup>a</sup> ppm	<sup>b</sup> %Recovery	<sup>a</sup> ppm	<sup>b</sup> %Recovery	<sup>a</sup> ppm	<sup>b</sup> %Recovery
Simple phenols	Hydroxytyrosol	0.49 ± 0.01	42.61	1.00 ± 0.05	86.96	0.48 ± 0.07	41.74	0.00 ± 0.00	0.00
	Tyrosol	548.17 ± 18.55	100.00	166.76 ± 0.09	31.49	213.92 ± 14.55	40.39	156.34 ± 6.25	29.52
	Hydroxytyrosol glucoside	1.58 ± 0.08	92.94	1.08 ± 0.01	63.53	1.07 ± 0.06	62.94	0.73 ± 0.11	42.94
Phenolic acid	p-coumaric acid	0.11 ± 0.00	12.09	0.99 ± 0.13	100.00	0.00 ± 0.00	0.00	0.00 ± 0.00	0.00
Secoiriodoids	Hydroxy decarboxymethyl elenolic acid 1+2	8.81 ± 0.14	21.79	38.50 ± 0.37	95.20	1.94 ± 15.18	4.80	1.00 ± 0.14	2.47
	Elenolic acid glucoside	0.71 ± 0.04	34.66	1.73 ± 0.02	84.46	0.00 ± 0.03	0.00	0.00 ± 0.00	0.00
	Hydroxy elenolic acid	18.06 ± 1.00	96.89	5.55 ± 0.56	29.77	8.49 ± 0.43	45.55	4.03 ± 0.24	21.62
	Decarboxymethyl elenolic acid	104.85 ± 3.19	60.07	170.67 ± 0.14	97.77	49.83 ± 6.53	28.55	22.72 ± 0.90	13.02
	Acyclodihydroelenolic acid hexoside	83.80 ± 0.20	96.50	83.97 ± 0.01	96.70	39.59 ± 0.11	45.59	31.04 ± 0.33	35.74
Flavonoids	Elenolic acid	17.46 ± 0.62	99.66	5.08 ± 0.24	29.00	7.44 ± 0.70	42.47	2.73 ± 0.19	15.58
	Apigenin	0.26 ± 0.00	86.67	0.10 ± 0.01	33.33	0.11 ± 0.01	36.67	0.05 ± 0.00	16.67
	Luteolin	0.04 ± 0.00	57.14	0.06 ± 0.00	85.71	0.00 ± 0.00	0.00	0.00 ± 0.00	0.00
Organic acids	Gallocatechin	2.19 ± 0.02	86.90	2.54 ± 0.05	100.00	1.73 ± 0.11	68.65	1.62 ± 0.14	64.29
	Quinic acid	143.92 ± 3.06	96.42	118.45 ± 0.05	79.36	98.91 ± 0.13	66.27	105.93 ± 14.59	70.97
	Malic acid	8.54 ± 0.30	100.00	4.34 ± 0.00	54.48	5.36 ± 0.13	67.37	6.10 ± 0.91	76.57
	Citric acid	368.28 ± 9.82	100.00	256.82 ± 0.03	72.66	230.67 ± 0.22	65.26	249.74 ± 24.28	70.65
Fatty acids derivatives	Trihydroxy-octadecadienoic acid	0.37 ± 0.03	34.87	0.93 ± 0.01	88.10	0.19 ± 0.02	17.72	0.05 ± 0.00	4.29
	Dihydroxy-hexadecanoic acid	0.11 ± 0.02	42.14	0.34 ± 0.05	100.00	0.02 ± 0.00	9.23	0.05 ± 0.00	18.01
	Trihydroxy-octadecenoic acid	0.00 ± 0.00	0.00	0.00 ± 0.00	0.00	0.00 ± 0.00	0.00	0.49 ± 0.02	99.47
	Dehydroxy-octadecatrienoic acid	0.14 ± 0.01	95.68	0.11 ± 0.01	73.09	0.11 ± 0.01	74.33	0.13 ± 0.01	89.86
Sugars	Glucose	64.00 ± 3.00	7.20	72.00 ± 4.50	8.10	115.20 ± 12.00	12.95	87.50 ± 6.00	9.84
	Fructose	6.00 ± 0.10	1.80	20.80 ± 1.00	6.25	86.60 ± 6.40	26.03	25.50 ± 1.20	7.67
	Sucrose	3.00 ± 0.00	1.12	6.00 ± 0.00	2.23	54.00 ± 7.00	20.08	6.60 ± 0.00	2.45

761 <sup>a</sup>ppm= from in the desorption eluent

762 <sup>b</sup>%Recovery= from the initial concentration in the OOWW sample

763 **4. Conclusions**

764 The adsorption/desorption capacity of four resins was studied in order to find the best resin  
765 dose and eluent to recover phenolic compounds, firstly from a simulated solution that contained  
766 catechin and tyrosol and, secondly, from olive oil washing wastewater.

767 All the resins tested with the model solution showed high adsorption towards phenolic  
768 compounds. The adsorption capacity of the resins increased with increasing their dose in  
769 solution. The greatest increase in adsorption efficiency occurred when the dose was augmented  
770 from 10 to 40 gL<sup>-1</sup>; then the change from 40 to 60 gL<sup>-1</sup> did not generate a significant variation in  
771 adsorption.

772 With the model solution, the MN resins achieved adsorption percentages greater than 90%,  
773 being the MN200 the resin that presented the highest total phenolic compounds adsorption  
774 ( $97.41 \pm 0.07$  %, for a resin dosage of 60 g·L<sup>-1</sup>). The pseudo-second order kinetic model provided  
775 the best fitting of the experimental data for all the resins. For the MN resins, the adsorption  
776 process was properly described by the Langmuir isotherm model, while the adsorption onto the  
777 PAD resins was better fitted by the Freundlich isotherm model.

778 From the tests performed with the model solution, a 50%v/v ethanol/water mixture was  
779 observed to be the best eluent to recover the phenolic compounds, being the MN202 the resin  
780 that yielded the highest desorption efficiency of phenolic compounds.

781 The adsorption-desorption of phenolic compounds from olive oil washing wastewater yielded a  
782 similar behaviour as that observed with the model solution, with the MN resins presenting the  
783 best performance. The adsorption of phenolic compounds onto PAD resins was worse than onto  
784 MN resins due to interferences with sugars that competed for the active sites of the resins.

785 The resins tested showed good affinity for the phenolic compounds, presenting high  
786 percentages of adsorption/desorption. In this way, an extract rich in phenolic compounds of  
787 high purity could be obtained. The MN200 resin showed the best performance, being almost  
788 90% of the initial phenolic compounds recovered, with low presence of sugars (about 5%).

789 In summary, this work has shown that it is possible to revalue mill waste using  
790 adsorption/desorption technology, since bioactive compounds with promising health benefits  
791 can be recovered with high purity.

792

793

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