Optimization of preparation conditions of a novel low-cost natural bio-sorbent from olive pomace and column adsorption processes on the removal of phenolic compounds from olive oil mill wastewater

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Abstract
Olive oil mill wastewater (OMWW) poses an undeniable environmental problem due to its high organic loads and phenolic compound (PC) content. This study determined the optimal conditions for preparing a new bio-sorbent from olive pomace (OP) and the adsorptive treatment of OMWW by this bio-sorbent. The activation reaction was performed with hydrogen peroxide. The results of the combination effect optimization of the three preparation variables, the activation temperature (°C) $X_1$, the activation time (min) $X_2$, and the impregnation ratio $X_3$, are presented by the response surface methodology (RSM). The maximum adsorption capacity was obtained at an activation time of 240 min, a temperature of 80 °C, and a ratio equal to 6.2:1. The bio-sorbent was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffractometer (XRD). The adsorption process performance of this bio-sorbent was examined in batch (phenol solution) and fixed-bed columns (real effluent of OMWW). An adsorption capacity of 789.28 mg g$^{-1}$ and 643.92 mg g$^{-1}$ has been achieved for 4000 mg L$^{-1}$ concentration of PCs, respectively, for batch and fixed-bed column essays. The adsorption isotherm and kinetics were consistent with the Langmuir and pseudo-second-order models. Therefore, the Thomas model best fits the fixed-bed column experimental data. The bio-sorbent gave a high desorption percentage of PCs, which was above 60% using HCl (0.1M).

Keywords Bio-sorbent · Hydrogen peroxide · Olive oil mill wastewater · Olive pomace waste · Phenolic compounds · Regeneration

Introduction
The cultivation of the olive tree is part of the Mediterranean tradition. It is a symbol of civilization among the Mediterranean peoples and, at the same time, a favorite dish on their table. In addition to its main product, oil leaves two by-products: the olive pomace (OP) and the vegetation water, also called olive oil mill wastewater (OMWW). However, these effluents have a low economic value in Morocco (Lissaneddine et al., 2021a).

OMWW is viscous, acidic, and rich in organic matter (total sugars, nitrogenous substances, organic acids, PCs, fats) (Achak et al. 2009; Lissaneddine et al. 2021a). Olive oil extraction processes release huge amounts of OMWW into the environment in short time intervals (Annab et al. 2019). Therefore, the OMWW poses an undeniable environmental problem because of its high chemical oxygen demand (COD) content and the presence of PCs, since these PCs...
cause inhibition of seed germination and plant growth (Elayadi et al., 2020), and can consequently affect groundwater, surface water, and soil (Dhouib et al. 2006). However, these PCs have economic value if recovered, as they are characterized by a high antioxidant activity (Aissa et al. 2017). In addition, those PCs are considered additives for numerous consumable products (Cirimmina et al. 2017) and cosmetic uses (Galanakis et al. 2018). Therefore, PCs’ main appeal is that they offer an opportunity for high-added-value by-products that may reimburse the treatment expense of the OMWW and give a considerable edge for earnings.

Different techniques for PC removal from OMWW have been studied (adsorption, electro-adsorption, coagulation-flocculation, artificial wetlands, distillation, infiltration-percolation, and distillation) (Achak et al. 2009; Leone et al. 2017; Elayadi et al., 2020; Papaokonomou et al. 2019, Lissaneddine et al., 2022). But these processes show several limitations, such as being more expensive, generating large amounts of sludge, and incomplete removal of pollutants. However, researchers have focused on the adsorption technique, which is considered the cheapest, simple, and most effective method for removing and recovering different types of pollutants (Boumya et al. 2021; Lissaneddine et al. 2021a).

For large-scale applications, it is mandatory to carry out continuous flow treatment using a column model to evaluate the intended contact time in which the adsorbate attains equilibrium (Aziz et al. 2020; Lissaneddine et al., 2021b). Fixed-bed processes have advantages such as ease of operation, high efficiency, and lowest cost, and large wastewater flows can be treated by an adequate amount of porous material, and the possibility of regeneration (Aksu and Gönen 2004; Lakshmipathy and Sarada 2015; Aziz et al. 2020).

In similar recent works, they studied the activation of OP by CuO (Yuney et al. 2020), NaOH (Lissaneddine et al. 2021a), and KOH (Şirazi and Aslan 2021) to adsorb PCs from OMWW. However, those works performed a carbonization step at an elevated temperature during the adsorbent preparation. Moreover, their adsorbents were only tested under batch conditions on diluted OMWW (Yuney et al. 2020; Şirazi and Aslan 2021). These reasons make their adsorbent difficult to prepare and not scalable at the industrial level. Therefore, it is suggested in the present study to prepare a bio-sorbent in a simple activation step without carbonization. Furthermore, our work envisages removing PCs from the raw OMWW without dilution and at the natural pH of effluent without adjustment, which gives advantages for real application, since the problem of pH control in industrial wastewater treatment plants affects the treatment efficiency and increases the cost of the treatment (Alwan, 2008).

The objective of the present work was to prepare a bio-sorbent from OP and then employ it as a low-cost adsorbent for the recovery of PCs from OMWW, which represent a green circular economy approach. First, the MINITAB software was used to determine the optimal conditions for the preparation of the bio-sorbent. Then, batch adsorption experiments were performed under different operational conditions (contact time, initial solution pH, initial PC concentration, and temperature). Finally, a fixed-bed reactor was used to recover PCs and regenerate the bio-sorbent, targeting a large-scale application.

## Materials and methods

### Sample collection and physical-chemical characterization of OMWW

The OMWW samples were collected in the region of Marrakech-Safi of Morocco during the 2020/2021 olive oil extraction season.

Measurements of pH and electrical conductivity are performed by a probe Hanna HI 9829. According to the AFNOR standard (T 90-101), the chemical oxygen demand (COD) was estimated by oxidation with an excess of potassium dichromate in a hot and acidic environment. The Kjeldahl nitrogen, nitrite, nitrates, orthophosphate, total phosphorus, and sulfate are determined according to the standards AFNOR T90-110, AFNOR T90-013, RODIER 1984, AFNOR T90-022, AFNOR T90-023, and RODIER 7th EDITION, respectively. The concentration of PCs was determined by the Folin-Ciocalteau method (Singleton and Rossi, 1965) using caffeic acid as the standard.

### Preparation of bio-sorbent

In this study, we used an OP waste located in the Marrakech-Safi region, Morocco. After washing with distilled water, the OP was dried in an oven at 105 °C (SF7/S Stuart, UK) for 24 h. Hydrogen peroxide (H$_2$O$_2$) is a chemical agent used to produce a bio-sorbent with chemical activation. The dried OP samples were mixed without grinding with H$_2$O$_2$ solution (10%) at different temperatures (60, 70, and 80 °C), ratios (3.1:1, 4.6:1, and 6.2:1), and time (180, 240, and 300 min), under stirring (200 rpm). The resulting bio-sorbent was washed with distilled water and dried in an oven at 60 °C for 24 h.

### Characterization of bio-sorbent

The physicochemical characteristics of the bio-sorbent were studied using XRD. FTIR (ALPHA-P, Germany) was used to characterize the functional groups in the wavelength range of 400–4000 cm$^{-1}$. Examination of the grain morphology of the bio-sorbent was performed using SEM measurements (Fuveau, France), which were taken with a scanning...
microscope, the analysis of elements on the micro-scale and element distribution on the bio-sorbent by EDS analyzer (TEAM™ EDS). The pH_{PZC} (point of zero charge) determines the acidic or basic character of the bio-sorbent and knows its net surface charge according to the pH of the solution. Among the methods, allowing determining the pH of zero charges is the method of Lopez-Ramon et al. (1999). It introduces a fixed mass of bio-sorbent in 25 mL of a synthetic phenol solution (4 g/L) at different initial pH values. Then, the whole is agitated for 2 h at room temperature. The pH_{PZC} is the pH point where the pH_{final} versus pH_{initial} curve intercepts the pH_{final} = pH_{initial} line (Altenor et al. 2009). The BET method was used to calculate the specific surface area (S_{BET}) and the total volume (V_T) of bio-sorbent that had been previously outgassed and assessed by nitrogen adsorption at −196 °C (via a Micromeritics ASAP 2020 surface analyzer system). The average pore radius (r^-) was calculated from Eq. (1) (Lawal et al. 2020):

\[
r^- (nm) = \frac{2V_T}{S_{BET}} \times 10^3 \tag{1}
\]

### Experimental setup and procedure

#### Batch adsorption and isotherm studies

The bio-sorbent prepared was studied as an adsorbent for the adsorption of PCs from a phenol synthetic solution. The effect of contact time on the adsorption process of PCs was evaluated in the range of 0-240 min at optimum values of adsorbent dose 25 mg, initial concentration 4000 mg L^{-1}, pH 4.0, and temperature 25 °C with a stirring speed of 200 rpm (KS 3000i control, Germany). Concerning the study of the PC concentration effect on the adsorption capacity, a series of concentrations of a synthetic phenol solution was carried out 2000, 3000, and 4000 mg L^{-1}, for 240 min and at pH 4.0. This corresponds to the effect of pH; phenol solution was adjusted to values ranging from 2.0 to 12.0 by adding hydrochloric acid (HCl) or sodium hydroxide (NaOH) of equal concentrations to 1.0N. In order to study the effect of temperature, the adsorption process was performed at temperatures of 20, 40, and 60 °C in an adsorbent dose of 25 mg, in 25 mL of the phenol solution, at a concentration of 4000 mg L^{-1}, and pH 4.0.

The adsorption capacity was determined according to Eq. (7):

\[
q = \frac{C_0 - C_t}{W} \times V \tag{2}
\]

where \(C_t \text{ (mg L}^{-1})\) is the PC concentration after a certain time of contact with bio-sorbent, \(C_0 \text{ (mg L}^{-1})\) is the initial concentration of PCs, \(V\) is the volume of solution (L), and \(W\) is the amount of bio-sorbent (g).

#### Langmuir model

Langmuir model is based on several assumptions and adsorption is limited to monolayer adsorption. The energy of adsorption is assumed to be the same all over the surface; no interactions between adjacent molecules on the surface and molecules adsorb at fixed sites and do not migrate over the surface as given by Eq. (3). As a result, the Langmuir isotherm equation has the following by Okeola and Odebunmi (2010) and Aliakbarian et al. (2015):

\[
\frac{C_e}{q_e} = \frac{1}{K_L \times q_m} + \frac{C_e}{q_m} \tag{3}
\]

where \(q_e \text{ (mg g}^{-1})\) is the amount of PCs adsorbed at equilibrium; \(C_e \text{ (g L}^{-1})\) is the concentration of PCs at equilibrium; \(K_L \text{ (g L}^{-1})\) is the Langmuir constant related to the energy of adsorption (L g^{-1}); and \(q_m \text{ (mg g}^{-1})\) is the maximum adsorption capacity.

#### Freundlich model

The Freundlich isotherm mainly describes the adsorption equilibrium of sorption on a heterogeneous surface, given by Eq. (7). The Freundlich isotherm equation is expressed by Okeola and Odebunmi (2010) and Aliakbarian et al. (2015):

\[
\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \tag{4}
\]

where \(n\) is the adsorption intensity constant, and \(K_f\) is the Freundlich constant indicating adsorption capacity.

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**Fig. 1** Schematic diagram of the fixed-bed adsorption process
Column adsorption and isotherm studies

The column adsorption experiment was performed using a 30-cm high tube with a diameter of 0.5 cm. The column was surrounded by a polyester cylinder of 10-cm thickness to keep the constant temperature during experiments. The temperature was checked continuously by a thermometer fixed at the outlet of the column. Figure 1 shows the schematic of the experimental setup used for the PC adsorption study. First, 4.5 g of bio-sorbent was introduced into the column. Then, the real effluent of OMWW was introduced in upflow using a peristaltic pump (Antlia-3C Dutscher, France) at a constant flow rate of 0.5 mL min⁻¹. All experiments were performed at a temperature of 60 °C for 120 min. The treated OMWW at the exit of the column were collected at defined time intervals, and the PC concentrations were measured until the outlet concentration equals the input concentration.

Thomas model  The Thomas model (Thomas, 1944) is based on the assumption that the adsorption is of the Langmuir type; the adsorption kinetics obey reversible second-order kinetics. This model applies to a system with a constant flow rate and without axial dispersion. This model is given by Eq. (5) (Aksu and Gönen 2004):

\[
\frac{C}{C_0} = \frac{1}{1 + \exp \left( K_{TH} \times q_0 \times Q - K_{TH} \times C_0 \times t \right)}
\]

(5)

where \(K_{TH}\) (mL min⁻¹ mg⁻¹) is the Thomas rate constant; \(q_0\) (mg g⁻¹) is the adsorption capacity; \(m\) is the total amount of bio-sorbent sent to the column (g); and \(Q\) is the flow rate that circulates through the column (mL min⁻¹).

Yoon-Nelson model  The Yoon and Nelson model (Yoon and Nelson 1984) assumes that the decrease in adsorption probability for each adsorbate molecule is proportional to the solute adsorption probability and the adsorbate breakthrough probability (Gong et al. 2015). The Yoon-Nelson equation is written as follows:

\[
\frac{C}{C_0} = \frac{\exp \left( K_{YN} \times t - \tau \times K_{YN} \right)}{1 + \exp \left( K_{YN} \times t - \tau \times K_{YN} \right)}
\]

(6)

where \(K_{YN}\) is the Yoon-Nelson rate constant (min⁻¹) and \(\tau\) is the time required for 50 % adsorbate breakthrough (min).

Desorption

Desorption gives the bio-sorbent a chance for reuse. The desorption tests were done in the same way as the adsorption experiments. First, the bio-sorbent was saturated with PCs and then washed with distilled water in the first series. Next, desorption of the bio-sorbent was done with 0.1M HCl solution at 60 °C. Then, the bio-sorbent is reused for further PC adsorption tests. Finally, the desorbed amount of PCs was calculated by Eq. (7).

\[
\text{Desorbed} = \frac{q_r}{q_0} \times 100\%
\]

(7)

where \(q_r\) and \(q_0\) (mg g⁻¹) are the adsorption capacities of the PCs after and before regeneration, respectively.

Statistical analysis

The effect of process parameters on the optimal bio-sorbent preparation conditions and adsorption capacity was analyzed using the MINITAB statistical software.

The MINITAB software is a statistical technique used to identify significant parameters to determine the optimal bio-sorbent preparation conditions. The three parameters chosen for the experiment were the activation temperature \(X_1\), activation time \(X_2\), and rate \(X_3\). Each parameter has three different levels (coded as −1, 0, and +1): activation temperature (60, 70, and 80 °C), activation time (180, 240, and 300 min), and rate (3.1:1, 4.6:1, and 6.2:1) (Table 1). The three parameters studied yielded twelve experimental designs.

Modeling of the optimal bio-sorbent preparation conditions was based on the second-order polynomial equation (Eq. (8)):

\[
Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ij} X_i^2 + \sum_{i=1}^{k} b_{ij} X_i
\]

(8)

where \(b_0\) is the constant, \(b_i\) is the linear effect of input factor \(x_i\), \(b_{ij}\) is the linear interaction effect between input factors \(x_i\) and \(x_j\), \(b_{ij}\) is the quadratic effect of input factor \(x_i\), and \(n\) is the number of factors.

In addition, the statistical software MINITAB was used to study the effect of operating conditions on the adsorption capacity. Finally, an analysis of variance was performed to determine the significance of the interactions and effects between the operating conditions.

| Process variables | Units | Symbols | Levels |
|-------------------|-------|---------|--------|
| Activation time   | min   | \(X_1\) | −1 0 1 |
| Activation temperature | °C   | \(X_2\) | 60 70 80 |
| Ratio             |       | \(X_3\) | 3.1:1 4.6:1 6.2:1 |

Table 1  Actual and coded values of independent variables used for Minitab
Results and discussion

Physicochemical properties of the OMWW

The physicochemical analysis of the studied OMWW (Table 2) shows these effluents have an acidic pH (4.81), indicating that OMWW is an acidic effluent. The same pH value was observed by Bouknana et al. (2014), Lee et al. (2019), Dehmani et al. (2020), and Lissaneddine et al. (2021a). Table 2 shows a lower electrical conductivity (12 mS cm⁻¹) than that found by Lissaneddine et al. (2021a), Elayadi et al. (2021), and El Ghadraoui et al. (2021). The chemical oxygen demand (80 g O₂ L⁻¹) is high and is also characterized by a predominance of toxic substances and the presence of PCs (Vuppala and Shaik, 2021). OMWW is also characterized by inorganic loadings such as potassium (4.8 g L⁻¹) and sodium (0.3 g L⁻¹).

Characterization of the bio-sorbert

Figure 2 shows the FTIR spectrum of OP (a) and bio-sorbent before (b) and after (c) adsorption of the PCs. FTIR spectra were obtained in the wavelength range of 480-4000 cm⁻¹. The FTIR spectrum of OP waste (Fig. 1a), the peak at 3416 cm⁻¹, can be attributed to the -OH stretching vibration. The peak at 2928 cm⁻¹ is due to C-H stretching vibrations in aliphatic CH, CH₂, and CH₃. The peaks at 1461 and 1743 cm⁻¹ were attributed to the symmetrical stretching vibrations of CH₂ and C=O groups, respectively (Wang et al. 2019). The FTIR spectrum of bio-sorbent (Fig. 2b) at 3416 cm⁻¹ corresponds to the -OH of hydroxyl functional groups. The peak at 1743 cm⁻¹ is probably related to the stretching vibration of carboxyl groups or C=O of lipids (Oladipo et al. 2019; Toumi et al. 2018b). The band at 1380 cm⁻¹ is attributed to the symmetrical stretching vibration CH₂ (Allwar, 2020). The peak at 1033 cm⁻¹ can be attributed to the bending vibration of the -OH group (Nasrullah et al. 2018). The FTIR spectrum of bio-sorbent (Fig. 2c) after adsorption shows that some peaks are shifted to different wavenumbers or disappear after the adsorption of the PCs, indicating that the functional groups present on the adsorbent are involved in the adsorption of phenol (Oliveira et al. 2016). Notably, the carboxyl group shifted to 1745 cm⁻¹, suggesting the involvement of the carboxyl group during the adsorption process (Blazquez et al. 2010; Oladipo et al. 2019). Furthermore, the peak of the -OH stretching vibration is shifted to 3425 cm⁻¹, and this shift confirms that the -OH group was responsible for the adsorption of phenol onto the bio-sorbent (Yuney et al. 2020). Finally, a new peak is observed at 1225 cm⁻¹, which is probably related to the vibration of the C-O group of polyphenols such as hydroxytyrosol, and tyrosol (Oliveira et al. 2016), and the R-CO-OR, the stretch of the phenolic hydroxyl (Yuney et al. 2020).

Biosorption can be explained by the interaction between the functional groups present on the bio-sorbent and the PCs, considering two types of chemical and physical interactions. Foremost, biosorption involves different mechanisms such as coordination, complexation, microprecipitation, or electrostatic attraction (Veglio and Beolchini, 1997). Therefore, identifying these processes and the characterization of the active sites of the bio-sorbent are essential steps for optimizing the operating conditions in the development of the adsorption capacity of PCs.

SEM analysis allows visualization of the bio-sorbent pores. This analysis was performed to determine the elements present on the surface of the samples by EDX. The
results obtained from olive pomace before and after chemical activation at the same magnifications are presented in Fig. 3.

Figure 3a shows that the surface of the olive pomace does not contain pores or voids. However, after activation (Fig. 3b), relatively more homogeneous pores with constant diameters appeared on the external surface of the bio-sorbent, improving the porosity consequently, a high number of pores on the surface of the bio-sorbent.

The EDX analysis of the OP before and after activation allowed the elemental analysis of the elements present on the external surface. The analysis shows that both materials are composed mainly of carbon atoms and contain oxygen (Table 3). After activation (Table 3), Mg and Cu appear on the surface.

Şirazi and Aslan (2021) observed similar texture characteristics using OP activated by KOH. This shows that the OP’s SEM surface before activation has a porosity less than that of the adsorbent after activation, which is similar to the present study results.

The XRD patterns for pure and activated OP are shown in Fig. 4. The XRD patterns of OP before and after activation are very similar, suggesting that no alteration of the OP structure occurred during the preparation of the bio-sorbent. This is normal because we only did a chemical activation without carbonization. The two diffractograms showed

Table 3 EDX spectra of OP before and after chemical activation

| Element | OP Atomic % | Bio-sorbent Atomic % |
|---------|-------------|----------------------|
| C       | 74.13       | 70.50                |
| O       | 24.46       | 29.10                |
| Si      | 0.26        | 0                    |
| P       | 0.26        | 0                    |
| S       | 0.17        | 0                    |
| K       | 0.54        | 0                    |
| Ca      | 0.18        | 0                    |
| Cu      | 0           | 0.22                 |
| Mg      | 0           | 0.18                 |
| Totals  | 100         | 100                  |

Fig. 5 pH_{ZPC} of bio-sorbent
peaks located at $2\theta = 22.31^\circ$ (Trache et al. 2014), 39.16°, 45.43°, 61.58°, 77.65°, and 84.47°, which is attributed to the native cellulose. While the other constituents of OP are mainly amorphous, this is explained by the appearance of the spectrum of Schneider and Brebner (1985) and Zhang et al. (2015).

The pH at which the zero surface charge is called the point of zero charges (pzc). The surface’s electrokinetic properties are defined by pH$_{PZC}$ (Yagub et al. 2014). The plot $pK_f = f(pH)$ is shown in Fig. 5. Results show that pH$_{PZC}$ of the bio-sorbent was around 8.64.

The surface of the bio-sorbent is characterized by a pH$_{PZC}$ of 8.64, suggesting a basic character (Yuney et al. 2020). When the solution pH is higher than the phenol pKa ~9.9, a negligible amount of neutral phenol molecules exist in the solution, while phenolate anions ($C_6H_5O^-$) are the dominant attracted species to the positively charged adsorbent surface. On the contrary, at pH lower than phenol pKa ~9.9, phenol molecules exist in neutral forms that favor $\pi-\pi$ stacking, hyperdophobic, and/or scattering interactions between $p$-electrons in the carbon chain of the adsorbing and aromatic phenolic ring (Ververi and Goula 2019; Yuney et al. 2020). This is consistent with the result obtained by Şirazi and Aslan (2021) since the KOH-activated OP, pH$_{PZC}$ for adsorbent, was 8.0.

The textural characteristics of the bio-sorbent are presented in Table 4. The adsorbent’s specific surface area ($S_{BET}$) was 905 m$^2$ g$^{-1}$, and the total pore volume ($V_T$) value was 0.822 cm$^3$ g$^{-1}$. These results show the effect of the activating agent on OP, thus maintaining higher adsorption capacities.

### Process optimization

#### Optimization of preparation conditions for bio-sorbent

The preparation variables are presented in a design matrix; their ranges and responses (adsorption capacity (mg g$^{-1}$)) are displayed in Table 5. The statistical software MINITAB is applied to compare and correlate the independent variables in Table 5. It was applied to develop polynomial regression equations representing all quadratic expressions suggested by MINITAB. The equation expression was selected according to the sequential sum of the square model, which is based on the highest order of the polynomial where the model was not aliased and the extra terms were significant (Sahu et al. 2010; Garba and Rahim, 2015; Salman 2014). There was a clear correlation between the experimental and predicted data, as indicated by the model $R^2$ value of 0.9745 for adsorption capacity. The final empirical model equation for the $Y_q$ response of the adsorption capacity is given by Eq. (9):

$$Y_q = 686 - 3.72X_1 - 13.9X_2 + 85X_3 + 0.00583X_1^2 + 0.190X_2^2 + 58.3X_3^2 + 0.0292X_1X_2 - 2.98X_2X_3$$

Table 6 presents the variance (ANOVA) results of the full factional design using the statistical software MINITAB. The model $F$-value was recorded at 21.20, enlightening that the model was significant. On the other hand, high values

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**Table 4** Textural characteristics of bio-sorbent

| Parameters     | $S_{BET}$ (m$^2$ g$^{-1}$) | Total pore volume (cm$^3$ g$^{-1}$) | $r_r$ (nm) |
|----------------|-----------------------------|-----------------------------------|------------|
| Value          | 905                         | 0.822                             | 1.816      |

**Table 5** Minitab experimental design

| Run | Level | Variables | Responses $q$ (mg g$^{-1}$) |
|-----|-------|-----------|-----------------------------|
|     |       | $X_1$ | $X_2$ | $X_3$ |                |
| 1   | −1    | 240   | 60   | 3.1:1 | 273.21          |
| 2   | +1    | 180   | 60   | 4.6:1 | 123.21          |
| 3   | −1    | 240   | 60   | 6.2:1 | 326.78          |
| 4   | +1    | 180   | 80   | 4.6:1 | 416.35          |
| 5   | −1    | 180   | 70   | 3.1:1 | 340.71          |
| 6   | +1    | 240   | 80   | 6.2:1 | 737.49          |
| 7   | −1    | 180   | 70   | 6.2:1 | 305.35          |
| 8   | +1    | 300   | 60   | 4.6:1 | 292.85          |
| 9   | −1.682| 240   | 80   | 3.1:1 | 551.78          |
| 10  | +1.682| 300   | 70   | 6.2:1 | 510.71          |
| 11  | 0     | 240   | 70   | 4.6:1 | 332.14          |
| 12  | 0     | 240   | 70   | 4.6:1 | 332.14          |
| 13  | 0     | 300   | 70   | 3.1:1 | 489.00          |
| 14  | 0     | 240   | 70   | 4.6:1 | 332.14          |
| 15  | 0     | 300   | 80   | 4.6:1 | 656.00          |
of $R^2$ (0.9745) and Adj-$R^2$ (0.9285) were estimated, indicating that the selected model can describe 92.85% of the total variation in adsorption capacity data. The parameters having a p-value probability value of less than 0.05 are significant. In this case, $A$, $B$, and $C^2$ are the significant model terms.

Values superior to 0.1 are considered non-significant terms.

The Pareto chart

The presentation of the relative importance of the main effects and their interaction was achieved using the Pareto chart, as shown in Fig. 6. The individual factors and the likely combinations obtained are represented as bars. To show whether the effects studied differ significantly from zero, the $t$-test was used (Abdel-ghani et al. 2016). For a 97.45% confidence level and nine degrees of freedom, the $t$-test value was found to be equal to 2.57. The values on the horizontal axes are the $t$-test values for each effect and their interaction (Carmona et al. 2005; Rathinam et al. 2011; Saadat and Karimi-Jashni 2011). Variables $A$, $B$, and $C^2$ have an absolute value greater than 2.57, which places them on the right side of the vertical line and makes them significant, while all other factors have an absolute value below the reference line, making them insignificant. By analyzing the Pareto chart, it can be seen that $B$, $A$, and $C^2$ have the greatest influence on the adsorption of PCs in the bio-sorbent. On the other hand, the effect of ratio ($C$) made the smallest contribution to the adsorption of PCs into bio-sorbent because it is far from the reference line of the Pareto chart.

Contour plots and response surface

The 3D contour plots and response surface show the interactive effects of several parameters on the response. The contour plots and response surface were acquired by the Minitab software to indicate the adsorption efficiency of PCs considering independent factors such as activation time, activation temperature, and ratio shown in Fig. 7. The effect of activation time, ratio, and activation temperature was investigated using response surface methodology (RSM) by the Minitab software. From Table 6, the $F$-value of the model is 21.20, and the p-value is 0.002. The model terms were considered significant when the p-value was less than 0.05. The contour plot (Fig. 7a) for the interaction between activation time and ratio shows that at a time of 240 min and a ratio of 6.2:1 (3), the interaction was declared significant. The interaction between activation temperature and ratio (Fig. 7b) shows that at a ratio of 3.2:1(1) and a temperature of 80°C, the adsorption of PCs is significant. The interaction between activation temperature and activation time (Fig. 7c) indicates at a time of 240 min and a temperature of 80°C, the biosorption is significant.

The optimal conditions for bio-sorbent preparation using response optimization were obtained at ratio = 6.2:1 (3), activation time = 300 min, and activation temperature = 80°C. Anisi et al. (2021) determined that the optimal conditions for the preparation of zeolitic imidazolate framework-8 were found as follows: ligand/salt molar ratio of 10.4, solvent/salt ratio of 702.7, and temperature of 52.9°C, which resulted in an uptake of 1120 mg g$^{-1}$ olive oil from an aqueous solution.

Adsorption efficiency

Batch adsorption

Effect of initial concentration The driving force is very important by the initial concentration of PCs to overcome all the mass transfer limitations between the two phases, liquid and solid (Liu et al. 2019).

The plot of adsorption capacity versus time at different concentrations is presented in Fig. 8. The maximum adsorption capacity is 789.28 mg g$^{-1}$, at the initial phenol concentration of 4000 mg L$^{-1}$ and 210 min. This increase in adsorption capacity with increasing concentration was
Fig. 7 The representative contour plots and 3D-response surface of effect for the interaction between the activation time (min) and ratio (a), activation temperature (°C) and ratio (b) and the activation time (min) and activation temperature (°C) (c) on capacity adsorption (mg g⁻¹)
attributed to the fact that this concentration was the driving force in order to overcome the resistance in the mass transfer of PCs between the liquid phase (phenol solution) and the solid phase (bio-sorbent surface), resulting in the increase of their transfer rate into the adsorbent (Lissaneddine et al. 2021a). Comparing the results with different studies, the adsorption of PCs on activated carbon by Achak et al. (2009) reported a decrease in adsorption efficiency with an increase in the initial concentration. This phenomenon was attributed to activated carbon adsorbing more phenolic compounds at low initial concentrations than higher initial concentrations. On the other hand, in the study of Lissaneddine et al. (2021a) on the use of SA-AC beads for the adsorption of PCs, an increase in adsorption capacity was observed with the increase in initial concentration. Again, this is due to the increasing amount of PCs in the solution, which causes a rise in the mass transfer driving force (Liu et al. 2019).

**Adsorption isotherm** When the adsorption process reached equilibrium, the adsorption isotherms were analyzed to describe the distribution of PCs between the solid and liquid phases (Liu et al. 2019). Several models have been proposed to describe this relationship during the adsorption of PCs, the main ones being the isothermal models of Langmuir and Freundlich. However, some assumptions are applicable according to the Langmuir theory. First of all, all sites are energetically equivalent, i.e., the energy of the adsorption sites is considered equal. At the same time, they can contain at most one adsorbate molecule, forming a monolayer on the adsorbent surface. In addition, the surface of the adsorbent is assumed to be homogeneous, with the identification of the active sites. Moreover, there is no interaction between the adsorbed molecules (Swenson and Stadie 2019).

On the contrary, Freundlich’s theory considers the heterogeneous adsorption surface, while several layers of adsorbate molecules can be formed. Furthermore, this theory considers that interactions between adsorbed molecules occur (Dada et al. 2012; Osagie and Owabor 2015). Figure 9 shows the adsorption isotherm of PCs with the bio-sorbent. The adsorption capacity of PCs increased with the increase of PC concentration until it reached 830 mg g⁻¹ on an initial concentration of 6000 mg L⁻¹. The driving force of mass transfer is the increase of the PC concentration in the solution (Li et al. 2019).

From the linear regression data (Table 7) in Fig. 10 (a and b), it is clear that the model with a correlation coefficient ($R^2 = 0.9898$) indicates that the active adsorption sites of PCs on the bio-sorbent are energetically homogeneous. Significant monolayer coverage of PCs on the outer surface of the bio-sorbent is formed without any interaction between the PCs (Mojoudi et al. 2019). Therefore, the Langmuir model represents the best model for the adsorption of PCs onto the bio-sorbent with a maximum adsorption capacity of 1125 mg g⁻¹. Several recent studies on removing phenolic compounds through olive pomace have been exhibited. However,
the majority of the work shows a low adsorption capacity, namely Aliakbarian et al. (2015) (156.2 mg g\(^{-1}\)), Aly et al. (2018) (16.5 mg g\(^{-1}\)), Yangui and Abderrabba (2018) (246.4 mg g\(^{-1}\)), Lissaneddine et al. (2021a) (114 mg g\(^{-1}\)), and Vavouraki et al. (2021) (178 mg g\(^{-1}\)). Yet, our study, using an eco-friendly activation of the biomaterial, shows a very high value of adsorption capacity that reached 789.28 mg g\(^{-1}\), which is close to the theoretical one (1125 mg g\(^{-1}\)) calculated from the Langmuir model.

**Effect of contact time**  The effect of contact time allowed the essential parameters during adsorption. Adsorption time can vary depending on the nature of the adsorbent and adsorbate, while it is affected by different parameters, such as concentration of PCs in the solution, temperature, and pH of the phenol solution. In all cases, the equilibrium is reached at a given time; this is the state in which the increase of the contact time does not significantly increase PC adsorption efficiency. The equilibrium time varies with the studied adsorbents, such as SA-AC beads (120 min) (Lissaneddine et al. 2021a), pomegranate seed (20 min) (Papaoikonomou et al. 2019), the raw clay (10 min) (Chaari et al. 2020), MgCl\(_2\)-impregnated activated carbons (60 min) (Hamadneh et al. 2020), and hydroxyapatite-sodium alginate composite (Benaddi et al. 2021).

Figure 11 shows the sorption equilibrium obtained after about 150 min, and then remains stable with an adsorption capacity value of 789.28 mg g\(^{-1}\). Adsorption can be considered a two-step process, a rapid initial adsorption step, attributed to many sites on the bio-sorbent for PC adsorption. This rapid step leads to a rapid increase in the amount of PCs accumulated on the bio-sorbent surface. Existing residual sites are then difficult to occupy by PCs, as repulsive forces develop between the PCs on the solid surface of the bio-sorbent and the bulk phase (Lissaneddine et al. 2021a). In addition, PCs are small molecules and can diffuse into the internal pores (Papaoikonomou et al. 2019), thus reducing the driving force for mass transfer (Din et al. 2009). Obviously, during the slow step, the molecules encounter greater resistance to entering the adsorption sites (Lissaneddine et al. 2021a; Achak et al. 2009).

**Adsorption kinetic**  The adsorption kinetic study provides important information to predict the adsorption process. In this work, two linear kinetic models studied the adsorption of PCs from the phenol solution by the bio-sorbent.
as a function of time, including pseudo-first-order and pseudo-second-order.

From Fig. 12, both models show clear linearity of the equation with a correlation value of $R^2 = 0.9656$ for pseudo-first-order kinetics and a correlation of $R^2 = 0.9929$ for pseudo-second-order kinetics. Therefore, according to Table 8, the model with the experimentally calculated maximum equilibrium sorption capacity value approximately equal to that determined theoretically is the pseudo-first-order. Therefore, the adsorption kinetics of PCs on the biosorbent is of pseudo-second-order type. Furthermore, this model assumes that the sorption of PCs is mainly controlled by chemisorption, which includes valence changes through electron exchange or partitioning between the biosorbent and PCs. Therefore, external adsorption occurs more often than micropore adsorption (Abdelhay et al., 2018; Tao et al. 2019).

In a batch test, the biosorbent removed 789.28 mg g\(^{-1}\) of PCs. Compared to olive pomace treated with H\(_3\)PO\(_4\)+2MHNO\(_3\) (28.57 mg g\(^{-1}\)) (Soudani et al. 2013), HCl + ZnCl\(_2\) (78.74 mg g\(^{-1}\)) (Temdrara et al. 2015), and H\(_3\)PO\(_4\) (110.30 mg g\(^{-1}\)) (Soudani et al. 2017), the biosorbent of this study showed better removal efficiency of PCs.

The adsorption capacity as a function of time at different pH values is shown in Fig. 13. A significant effect of pH on the adsorption of PCs was observed. It can be explained by the $\pi-\pi$ electron donor-acceptor interactions between the aromatic ring of the PCs (electron acceptor) and the free oxygen of the surface basic sites (electron donor) (Moreno-Castilla 2004; Dabrowski et al. 2005; Hamdaoui and Naffrechoux 2007). The adsorption capacity of PCs on the biosorbent increases from 380 to 803 mg g\(^{-1}\) for pH values between 2 and 4, and the maximum adsorption of PCs is reached at pH equal to 4.0. If the pH value exceeded 4.0, there is a decrease

![Fig. 12 Adsorption kinetics: pseudo-first-order (a) and pseudo-second-order (b) kinetics models of PCs derived from OMWW effluent on bio-sorbent](image)

![Fig. 13 Effect pH (at 25 °C; volume = 25 mL; bio-sorbent = 25 mg and PC concentration = 4000 mg L\(^{-1}\))](image)

### Table 8 Values of characteristic constants for two models of adsorption kinetic

|                      | Pseudo-first-order | Pseudo-second-order |
|----------------------|--------------------|---------------------|
|                      | $q_{exp}$ (mg g\(^{-1}\)) | $q_{theo}$ (mg g\(^{-1}\)) | $K_{lag}$ (min\(^{-1}\)) | $R^2$ | $q_{exp}$ (mg g\(^{-1}\)) | $q_{theo}$ (mg g\(^{-1}\)) | $K_b$ (mg g\(^{-1}\) min\(^{-1}\)) | $R^2$ |
|                      | 789.28             | 1096                | 0.0318                | 0.9656 | 789.28             | 806                | 0.0022                | 0.9929 |

**Effect pH** pH is a more important parameter in the adsorption process. The pH affects the sorption mechanisms onto the bio-sorbent surface and the nature of physicochemical interactions between the bio-sorbent adsorption sites and the PCs (Achak et al. 2009). In addition, pH can also affect the surface charge of the adsorbent (Aksu and Gönen 2004).
in the adsorption capacity of PCs. This decrease can be attributed to the phenol ionization to phenolate ions since the absorption of this later is prevented by hydroxyl ions presented on the adsorbent (Halhouli et al., 1995). The adsorption capacity is higher at acidic pH than at basic pH. The pH of the OMWW is acidic, which is advantageous in this study, so pH adjustment would not be necessary during effluent treatment. Therefore, OMWW can be used directly without pH adjustment in large-scale treatment systems, which minimizes costs during treatment. A study by Alwan (2008) showed that pH adjustment in industrial wastewater treatment plants influences the treatment efficiency, which leads to an increase in wastewater treatment cost.

**Effect of temperature**  Temperature is one of the most important parameters during the sorption process (Masomi et al. 2015). Figure 14 shows the plot of adsorption capacity versus time at different temperatures. The maximum adsorption capacity is found to be 857 mg g⁻¹ at a temperature of 60 °C. The increase in adsorption capacity with increasing temperature can be attributed to the increase in temperature promoting the polymerization phenomenon between the PCs, increasing adsorption efficiency. Furthermore, this increase in adsorption capacity can be associated with an increase in adsorbent swelling, allowing more active sites of the bio-sorbent to become available to the adsorbate (Ververi and Goula 2019). However, the temperature is a parameter that depends on other characteristics of the adsorbent and the solution (Moreno-Castilla 2004). Masomi et al. (2015) studied the adsorption of PCs on activated carbon and found better removal of PCs at a temperature of 20 °C. This result can be attributed to the exothermic nature of the adsorption process.

**Thermodynamic studies**  The thermodynamic parameters (ΔG°, ΔH°, and ΔS°) were calculated by using the following equations (Eq. (10) and Eq. (11)):

\[
\Delta G^o = \Delta H^o - T \times \Delta S^o
\]

\[
\ln K_c = -\frac{\Delta H^o}{R \times T} + \frac{\Delta S^o}{R}
\]

Plotting ln(K_c) as a function of 1/T (Fig. 15) allows the calculated ΔH°, ΔG°, and ΔS°. The thermodynamic parameters for the adsorption of PCs onto the bio-sorbent are given in Table 9. The value of ΔG° for all three temperatures was obtained negative, confirming the spontaneous and feasible adsorption of PCs on the bio-sorbent. In addition, the ΔG° values for physisorption are less than −20 kJ mol⁻¹, and chemisorption is greater than −80 kJ mol⁻¹ (Turco et al. 2019). In this work, ΔG° was −4229.38, −4355.49, −4732.51, and −5036.33 J mol⁻¹, which indicated the adsorption of PCs with the bio-sorbent is chemisorption. In addition, ΔH° and ΔS° are other critical thermodynamic parameters that provide information about the adsorption process of PCs. In this study, the positive value of ΔH° was 30.82 kJ mol⁻¹, which demonstrates the endothermic nature of the adsorption process.
of the adsorption process of PCs with the bio-sorbent. As for $\Delta S^0$, a positive value was obtained $\Delta S^0 = 49.26 \, \text{J mol}^{-1} \, \text{K}^{-1}$, so the increased randomness can explain it at the liquid/solid interface during the adsorption process (Sun et al., 2019). These outcomes are identical to those of Lissaneddine et al. (2021a), who have found that $\Delta S^0 = 74 \, \text{J K}^{-1} \, \text{mol}^{-1}$ and $\Delta H^0 = 29 \, \text{kJ mol}^{-1}$.

### Fixed-bed column

A continuous fixed-bed column adsorption process using a bio-sorbent as a sorbent was considered an alternative method to separate PCs from OMWW. Figure 16 shows the breakthrough curves for the adsorption of PCs on biosorbent in a fixed-bed column adsorption system at 60 °C.

In Fig. 16, $C_0$ is the initial concentration of PCs entering the column, and $C_t$ is the concentration of PCs leaving the column every 15 min. All PCs were adsorbed in the first 40 min, resulting in a low concentration of PCs in OMWW output. During the adsorption process, the concentration of PCs in the treated effluent gradually increases. The bio-sorbent sites are saturated, and the adsorption zone progresses vertically in the column (Kundu and Gupta 2005). In our work, the $q_e$ value reached 643.92 mg g$^{-1}$ for $C_i = 4251 \, \text{mg L}^{-1}$ and $Q = 0.5 \, \text{mL min}^{-1}$, while the removal rate was 74% (Table 10).

Using Yoon-Nelson and Thomas’s empirical models, the mathematical analysis of PC adsorption study data on fixed-bed columns was carried out. The model proposed by Yoon-Nelson considers the adsorption probability of each molecule to be directly proportional to the breakthrough probability of the adsorbate on the adsorbent and the adsorption probability of the adsorbate (Ajmani et al. 2020). The Thomas model is a theoretical model commonly applied in analyzing column adsorption data. It is based on the assumptions of the Langmuir isotherm model and the second-order kinetic model of the batch adsorption process (Ajmani et al. 2020). The Yoon-Nelson and Thomas model parameters for the PC adsorption on the bio-sorbent in a fixed-bed column are presented in Table 11.

![Fig. 16 Predicted and experimental predicted breakthrough curves for PC adsorption by the bio-sorbent (PC concentration = 4251 mg L$^{-1}$; pH = 4.0; and contact time = 120 min)](image)

**Table 10** Parameters of breakthrough curves of the packed bed column for PC adsorption onto the bio-sorbent

| $C_i$ (mg L$^{-1}$) | $Q$ (mL min$^{-1}$) | $V_e$ (mL) | $m_{total}$ (mg) | $R$ (%) | $q_e$ (mg g$^{-1}$) |
|--------------------|-------------------|------------|-----------------|--------|------------------|
| 4251               | 0.5               | 60         | 4500            | 74     | 643.92           |

**Table 11** Parameters of Thomas and Yoon-Nelson model for the adsorption of PCs into bio-sorbent in a fixed-bed column

| Model   | Parameters | Value         |
|---------|------------|---------------|
| Thomas  | $K_T$ (mL mg$^{-1}$ min$^{-1}$) | 0.00144       |
|         | $q_0$ cal (mg g$^{-1}$) | 547.78       |
|         | $R^2$      | 0.94571       |
|         | MAE        | 0.0104        |
|         | RMSE       | 0.10          |
| Yoon-Nelson | $K_{YN}$ (min$^{-1}$) | 0.3411       |
|         | $t_{cal}$ (min) | 57            |
|         | $R^2$      | 0.9571        |
|         | MAE        | 0.0125        |
|         | RMSE       | 0.12          |

![Fig. 17 Adsorption-desorption cycles for OMWW (PC concentration 4000 mg L$^{-1}$, 120 min)](image)
From Table 11, the Yoon-Nelson model correlates $R^2 = 0.9572$, demonstrating that the Yoon-Nelson model was approachable and could describe the adsorption of PCs in continuous mode on the bio-sorbent. Table 11 shows that the mean absolute error (MAE) values were 0.0125 and 0.0104 for the Yoon-Nelson and Thomas model, respectively. In contrast, the two models’ root means square error (RMSE) values were calculated as 0.12 and 0.10, respectively. The RMSE and MAE values of the Thomas model were lower than those of the Yoon-Nelson model. The Thomas model fits the experimental data; the results followed Langmuir kinetics (Chue 2010).

Desorption

The desorption study aims to elucidate the adsorption process, the recovery of PCs, and the adsorbents’ reuse. In the first adsorption cycle, the bio-sorbent was saturated with PCs with a removal rate of 74%. Then, the bio-sorbent was washed with distilled water and treated with 0.1M HCl solution for 120 min at room temperature for phenol recovery, which reached 64% of the total adsorbed amount (Fig. 17). After that, the adsorption/desorption process was duplicated several times, and the efficiency of the bio-sorbent in removing/desorbing PCs was analyzed. During the second reuse cycle, the adsorption rate decreases from 74 to 37% and from 64 to 32% for the desorption rate. This shows that the bio-sorbent is a good sorbent with excellent reusability and stability. Several studies on the desorption of PCs for adsorbent regeneration have been performed. According to Lissaneddine et al. (2021a), who used sodium alginate-activated carbon beads, the percentage of desorption of PCs was 58.5%. Yuney et al. (2020) used CuO-coated OP, reaching 77% of the PC concentration desorbed.

To sum up, the study’s main achievement was using the olive industry’s solid waste as the bio-sorbent for treating the same industry wastewater, targeting a green circular economy. Furthermore, the valorization of vegetable waste, the olive pomace, for the preparation of natural bio-sorbents shows better efficiency in removing phenolic compounds from OMWW ($q_m = 789 \text{ mg g}^{-1}$). Moreover, the production was done in a simple step of chemical activation by hydrogen peroxide, which is cheaper and not toxic since this activating agent contains the same water molecule (H2O2). The application of resource-saving technologies, such as adsorption using locally available materials and resource recovery to obtain value-added by-products (e.g., phenolic compounds), will be cost-effective on an industrial scale (Aziz et al. 2020).

Conclusion

In this paper, we are interested in testing the effectiveness of a new low-cost bio-sorbent in removing PCs from OMWW in a continuous flow. The optimum condition of preparation of the bio-sorbent was determined using the statistical software MINITAB. The structure of bio-sorbent was characterized by FTIR and Brunauer, Emmett, and Teller $S_{BET}$. The adsorption of PCs depended on the contact time, initial concentration, pH solution, and temperature. The Langmuir isotherm best represented the equilibrium adsorption data, and the adsorption capacity was found to be $789.28 \text{ mg g}^{-1}$. The adsorption kinetics was described well by the pseudo-second-order model. The positive $\Delta H^o$ value demonstrated that the adsorption was endothermic, and the negative $\Delta G^o$ indicated the spontaneous adsorption reaction. Thomas is the best model that was better at predicting PC column adsorption. For the process reusability in two cycles, the desorption yield decreased from 74 to 37%; however, the desorption yield decreased from 64 to 32%. Therefore, bio-sorbent can be stated among the effective alternatives for PC sorption since it provides ready separation and easy recycling from low-cost solutions.

Data Availability The datasets and materials used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Author contribution Imane HAYDARI (data curation) (writing—original draft) (interpretation). Amina LISSANEDDINE (optimization) (review and editing). Khalid AZIZ (modelization) (review and editing). Naaila OUAZZANI (review and editing). Laila MANDI (review and editing). Ayoub El GHADRAOUI (participating in data curation). Faïsal AZIZ (supervision) (review and editing).

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Declarations

Ethics approval and consent to participate We all declare that the manuscript reporting studies do not involve any human participants, human data, or human tissue, so it is not applicable.

Consent for publication Our manuscript does not contain data from any individual person, so it is “not applicable.”

Competing interests The authors declare no competing interests.

References

Abdel-Ghani NT, El-Chaghaby GA, Elgammal MH, Rawash ESA (2016) Optimizing the preparation conditions of activated carbons from olive cake using KOH activation. Xinxing Tan Cailiao/
New Carbon Materials. https://doi.org/10.1016/S1872-5805(16)60027-6
Abdelhay A, al Bsoul A, Al-Othman A, Al-Anazeh NM, Jun’mh I, Al-Taani AA (2018) Kinetic and thermodynamic study of phosphate removal by water from adsorption onto (Arundo donax) reeds. Adsorp Sci Technol. https://doi.org/10.1177/0263617416684347
Achak M, Hafidi A, Ouazzani N, Sayadi S, Mandi L (2009) Low cost biosorbtor “banana peel” for the removal of phenolic compounds from olive mill wastewater: kinetic and equilibrium studies. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2008.11.036
Aissa I, Kharrat N, Aloui F, Sassi A, Sellami M, Bouaziz M, Gargouri Y (2017) Equilibrium biosorption of lead(II) from aqueous solutions by solid waste from olive oil production. Chem. Eng. J. https://doi.org/10.1016/j.cej.2010.03.085
Boukana D, Hammouti B, Salghi R, Jodeh S, Zarrouk A (2014) Physicochemical characterization of olive oil mill wastewaters in the eastern region of Morocco. J Mater Environ Sci. 10.22159/jmesc.2018v5i15.28840
Boumna W, Taoufik N, Achak M, Barksa N (2021) Chemically modified carbon-based electrodes for the determination of paracetamol in drugs and biological samples. J Pharm Anal. https://doi.org/10.1016/j.jpharma.2020.11.003
Cañizares P, Carmona M, Baraza O, Delgado A, Rodrigo MA (2006) Adsorption equilibrium of phenol onto chemically modified activated carbon F400. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2005.09.037
Carmona MER, da Silva MAP, Ferreira Leite SG (2005) Biosorption of chromium using factorial experimental design. Process Biochem. https://doi.org/10.1016/j.procbio.2004.02.024
Chahri I, Touil A, Medhioub M (2020) Adsorption-desorption of phenolic compounds from olive mills wastewater using Tunisian natural clay. Chinese J Chem Eng. https://doi.org/10.1016/j.cjche.2020.12.020
Chue KH (2010) Fixed bed sorption: setting the record straight on the Bohart-Adams and Thomas models. J Hazard Mater. https://doi.org/10.1016/j.jhazmat.2010.01.019
Cirimmina R, Meneguzzo F, Delisi R, Pagliaro M (2017) Olive biophenols as new antioxidant additives in food and beverage. Chemistry Select. https://doi.org/10.1002/slct.201601900
Dabrowski A, Podkościelny P, Hubicki Z, Barczak M (2005) Adsorption of phenolic compounds by activated carbon - a critical review. Chemosphere 58:1049–1070. https://doi.org/10.1016/j.chemosphere.2004.09.067
Dada A, Olalekan A, Olatunya A, Dada O (2012) Langmuir, Frumkin, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk. IOSR J Appl Chem. https://doi.org/10.9790/5736-0313845
Dehmani Y, Ed-dra A, Zennouhi O, Bouymajane A, Rhazi F, Nassiri L, Abouarmandasse S (2020) Heliyon chemical characterization and adsorption of oil mill wastewater on Moroccan clay in order to be used in the agricultural field. Heliyon. https://doi.org/10.1016/j.heliyon.2020.e03164
Dermeche S, Nadour M, Larrroche C, Mouli-Mati F, Michaud P (2013) Olive mill wastes: biochemical characterizations and valorization strategies. In Process Biochemistry. https://doi.org/10.1016/j.procbio.2013.07.010
Dhoub A, Aloui F, Hamad N, Sayadi S (2006) Pilot-plant treatment of olive mill wastewaters by Phanerochaete chrysosporium coupled to anaerobic digestion and ultratillation. https://doi.org/10.1016/j.procbio.2005.06.008
Din A T M, Hameed B H, Ahmad A L (2009) Batch adsorption of phenol onto physicochemical-activated carbon shell. doi. https://doi.org/10.1016/j.jhazmat.2008.05.009
El Ghadraoui A, Ouazzani N, Saf C, Ahmali A, Hejiaj A, Aziz F, Del Bubba M, Mandi L (2021) Behaviour of physicochemical and microbiological characteristics of vertical flow constructed wetland substrate after treating a mixture of urban and olive mill wastewaters. Environ Sci Pollut Res. https://doi.org/10.1007/s11356-021-14874-7
Elayadi F, Achak M, Benich N, Belaqziz M, El Adlouni C (2020) Factorial design for optimizing and modeling the removal of organic pollutants from olive mill wastewater using a novel low-cost
