

## Electrosorption of phenolic compounds from olive mill wastewater: Mass transport consideration under a transient regime through an alginate-activated carbon fixed-bed electrode

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Amina Lissaneddine, Marie-Noëlle Pons, Faissal Aziz, Naaila Ouazzani, Laila Mandi, et al.. Electrosorption of phenolic compounds from olive mill wastewater: Mass transport consideration under a transient regime through an alginate-activated carbon fixed-bed electrode. Journal of Hazardous Materials, 2022, pp.128480. 10.1016/j.jhazmat.2022.128480. hal-03576656

## HAL Id: hal-03576656 https://hal.science/hal-03576656

Submitted on 16 Feb 2022

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1	Electrosorption of phenolic compounds from olive mill
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4	Amina Lissaneddine <sup>1,2,3</sup> , Marie-Noëlle Pons <sup>1</sup> , Faissal Aziz <sup>2,3</sup> , Naaila Ouazzani <sup>2,3</sup> , Laila
5	Mandi <sup>2,3</sup> , Emmanuel Mousset <sup>1,4</sup>
6	<sup>1</sup> Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France
7	<sup>2</sup> National Center for Research and Studies on Water and Energy (CNEREE), Cadi Ayyad
8	University, B. 511, 40000, Marrakech, Morocco
9	<sup>3</sup> Laboratory of Water, Biodiversity, and Climate Change, Faculty of Sciences Semlalia, Cadi
10	Ayyad University, B.P. 2390, 40000, Marrakech, Morocco
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12	ACCEPTED IN
13	JOURNAL OF HAZARDOUS MATERIALS
14	2022
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17	*Contact of the corresponding author: <u>emmanuel.mousset@cnrs.fr</u>

### 18 Abstract

Olive mill wastewater (OMWW) is an environmentally critical effluent, specifically due to its 19 high content of phenolic compounds (PCs), which are hazardous due to their antimicrobial 20 activities in water. However, their properties have good health effects at suitable doses. For 21 the first time, the electrosorption of PCs from actual OMWW has been proposed for their 22 possible recovery as value-added compounds, while decontaminating OMWW. A bio-sourced 23 alginate-activated carbon (AC) fixed-bed electrode was prepared based on the reuse of olive 24 pomace solid waste as powdered AC. At the optimal AC content (1% w/v), the internal ohmic 25 drop voltage was lower (2.26 V) and the mass transport coefficient was higher (9.7  $10^{-5}$  m s<sup>-1</sup>) 26 along with the diffusivity  $(7.3 \ 10^{-9} \ m^2 \ s^{-1})$ , which led to enhanced electrosorption rates. 27 Afterward, an optimal electrode potential was obtained (-1.1 V vs. Ag/AgCl), while higher 28 voltages led to faradaic reactions. Moreover, the adsorption capacity was lower (123 mg  $g^{-1}$ ) 29 than that of electrosorption (170 mg  $g^{-1}$ ) and was even higher (307 mg  $g^{-1}$ ) with actual 30 effluents. This was probably due to the influence of electromigration, which was confirmed 31 by new models that could predict the electrosorption kinetics well considering mass transport 32 and acid dissociation constants. 33

Keywords: Phenolic compounds; Activated carbon beads; Capacitive current; Fixed-bed
column reactor; Modeling

## 1. Introduction

The release of olive mill wastewater (OMWW) into the aquatic environment is a major issue 38 (Azzam and Hazaimeh, 2021; Esteves et al., 2021; Haddad et al., 2021; Lissaneddine et al., 39 40 2021a). These effluents are toxic; they have a high inorganic salt content (electrical conductivity ~ 5–23 mS cm<sup>-1</sup>) (Aharonov-Nadborny et al., 2016; Lissaneddine et al., 2021a) 41 and a high organic load, i.e., high chemical oxygen demand (COD) (~ 110 g-O<sub>2</sub> L<sup>-1</sup>) (Taylor 42 et al., 2015). They are especially saturated with aromatic molecules, particularly phenolic 43 compounds (PCs). They pose a serious environmental problem due to their phytotoxicity, 44 45 which inhibits the activity of plants and microorganisms (Elayadi et al., 2021, 2019). PCs also affect surface water and groundwater, threatening aquatic life and altering soil quality 46 (Elayadi et al., 2021). Moreover, hazardous OMWW is concentrated in a short period of time 47 48 each year since it is a seasonal activity. However, PCs also represent added-value molecules at reliable doses that can be recovered for subsequent valorization in the pharmaceutical, 49 cosmetic and food industries (Annab et al., 2019). Several physical, chemical, biological or 50 combined technologies have been proposed to remove PCs, including separation methods 51 (e.g., adsorption, membrane separation and ion exchange) and degradation techniques such as 52 53 advanced oxidation processes (e.g., electro-Fenton, heterogeneous photocatalysis)(Brillas and Garcia-Segura, 2020; Genethliou et al., 2020; He et al., 2020; Lissaneddine et al., 2021a; 54 55 Mousset, 2020; Mousset et al., 2021, 2018b, 2017, 2016a; Tundis et al., 2020; Ververi and 56 Goula, 2019; Yue et al., 2019a). Separation technologies offer the possibility to recover these added-value compounds under specific applied conditions instead of degrading them. 57 Electrosorption is gaining particular attention (Macías-garcía et al., 2019; Sahin et al., 2020) 58 59 due to its advantages of selectivity, desorption control and low energy requirements (Sahin et al., 2020; Yang et al., 2021). Electrode materials are of primary importance in such an 60 electrochemical system because they impact the electrosorption rates and yields. These 61

characteristics depend on the specific surface area, pore size distribution, electric 62 conductivity, surface function and wettability (Lissaneddine et al., 2021b; Sun et al., 2016; 63 Yue et al., 2019b). Three-dimensional (3D) particle electrodes provide a large electroactive 64 surface area and can be easily implemented in fixed-bed reactors to favor mass transfer 65 (Andrés García et al., 2018; Lissaneddine et al., 2021b; Macías-garcía et al., 2019; Yue et al., 66 2019b). Recently, 3D particle electrodes were shown to exhibit advantages in providing 67 additional active sites and enhanced mass transfer compared to two-dimensional (2D) 68 electrodes, which is conducive to improving the removal efficiency (Wang et al., 2021). 69 Various 3D and bio-sourced materials have been employed for adsorption technologies. For 70 71 instance, alginate offers advantages, as it acts as an embedding medium to assist in the preparation of easily separating and recycling adsorbents (Xu et al., 2021). It allows the 72 implementation of powdered materials that have a larger specific surface area than granular 73 74 adsorbents without the need for a postfiltration step to remove the fine adsorbent particles. Many researchers have employed beads with alginate coatings on several kinds of adsorbent 75 76 materials, such as activated carbon (AC) (Girijan et al., 2021), or functionalized them to be more efficient (Wadhawan et al., 2020). These composite beads have been tested to remove 77 organic pollutants in wastewater (Khan et al., 2021; Xu et al., 2021). In our recent article, bio-78 sourced beads based on a mixture of sodium alginate (SA) and powdered AC (SA-AC) made 79 from olive pomace waste were used for the elimination of PCs from OMWW by adsorption 80 (Lissaneddine et al., 2021a). However, pollutant transport within the beads is limited with 81 such technology. This phenomenon should be less limited when electrosorption is used, as 82 electromigration is favored, for example. To the best of the authors' knowledge, the 83 interesting properties of alginate composite beads have not previously been tested for 84 85 electrosorption.

Moreover, different studies have already demonstrated the performance of 3D electrodes for 86 the electrosorption of organic compounds (e.g., acid red 88, orange II, methylene blue and 87 metribuzin) from wastewater (Lissaneddine et al., 2021b). Matrix effects have rarely been 88 considered, while a supporting electrolyte has always been added in electrosorption 89 experiments (Lissaneddine et al., 2021b). However, matrix effects are known to interfere with 90 the electrochemical process efficiency, and the addition of salts constitutes a supplementary 91 source of pollution (Lissaneddine et al., 2021b; Mousset, 2020; Mousset et al., 2020, 2019, 92 2018a). Moreover, the few existing models of organic electrosorption do not include the 93 physico-chemical properties of the compounds or mass transport phenomena, although they 94 are of primary importance in the process efficiency (Lissaneddine et al., 2021b). 95

It is within this context that a detailed investigation has been carried out for the first time to 96 understand and predict the electrosorption of PCs from simulated and actual OMWW. The 97 prepared SA-AC beads were newly implemented as a 3D electrode for electrosorption 98 experiments. The effect of the main parameters, i.e., the electrode preparation (crosslinking 99 100 agent and AC content) and experimental conditions (applied electrode potential), on the electrosorption kinetics and capacity are stated in detail. In addition, novel theoretical models 101 are proposed to predict the evolution of the electrosorption of organic compounds in 102 103 simulated and real effluents, considering the mass transport and difference in acid dissociation constants (pKa) of the PCs. 104

105

#### 106 **2. Experimental**

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## 2.1. Effluent preparation and characterization

108 Two kinds of effluents were studied: one was a simulated OMWW that was used to optimize 109 the operating parameters, and the second was an actual OMWW. The latter was employed to 110 study the matrix effect by comparison with the simulated effluent.

Simulated OMWW was prepared using potassium chloride (KCl) (6 g L<sup>-1</sup>) and phenol (4 g L<sup>-1</sup>) and adjusted to pH 4 using hydrochloric acid (HCl) (Sigma Aldrich, Saint-Quentin-Fallavier, France) to be representative of the average characteristics of actual OMWW (Lissaneddine et al., 2021a). The phenol content was determined by UV–visible spectrophotometry (Shimadzu UV-2600 spectrophotometer) at the maximum absorption wavelength of 269 nm (Adebayo and Areo, 2021).

Real OMWW was collected from modern oil mills located in the region of Marrakech in 117 Morocco during the olive oil extraction season from December to March in the 2020/2021 118 119 campaign when the main products were PCs (Lissaneddine et al., 2021a). The main characteristics were pH = 4.8,  $[Cl^{-}] = 8.5 \text{ g } L^{-1}$ , conductivity = 16 mS cm<sup>-1</sup>, and total PCs = 120 10.6 mg  $L^{-1}$ ; details of the characteristics are described elsewhere (Lissaneddine et al., 2021a). 121 The total PC content was measured by the Folin-Ciocalteu method using meta-phosphoric 122 acid, petroleum ether, ethyl acetate and methanol as reagents (Sigma Aldrich, Saint-Quentin-123 Fallavier, France) (Singleton, V. L., & Rossi, 1965). All commercially available reagents 124 were used without further purification, while ultrapure water (18.2 M $\Omega$  cm) (PureLab ELGA 125 Classic, Veolia Water, Antony, France) was used in all experiments and analyses. 126

127

128

## 2.2. Preparation and characterization of the 3D porous electrode

The porous material (SA-AC beads) was prepared based on activated carbon of olive pomace
according to a previous paper (Lissaneddine et al., 2021a). First, a mixture of a hydrogel of

sodium alginate (BioChemica) (1%) was fabricated at 60 °C. Second, AC powder was added 131 to the alginate hydrogel with constant stirring for 24 h to obtain a homogeneous dispersion. 132 Next, the dispersed solution was poured dropwise into a crosslinking solution for bead 133 solidification. The presence of a crosslinking agent leads to competition between the gelling 134 reaction and polyelectrolyte complex, which also results in the formation of a more porous gel 135 (Mi et al., 2002). Two crosslinking agents (iron(III) (Fe) and calcium(II) (Ca)) were used in 136 bead preparation, both at 100% weight per volume (% w/v). The proportions in % w/v of AC 137 (0%, 0.5%, 0.75%, 1%, 2%, and 3%) were varied in the SA-AC bead preparation process. The 138 surface area (Brunauer-Emmett-Teller (BET) analysis), surface morphology (scanning 139 electron microscopy (SEM)), elemental composition (energy-dispersive X-ray spectroscopy 140 (EDS)) and surface function (Fourier transform infrared spectroscopy (FTIR)) of the initial 141 beads have been described previously (Lissaneddine et al., 2021a). 142

The electrochemical properties of the prepared SA-AC beads electrode were evaluated using a 143 potentiostat (AMETEK, Massy, France) in a three-electrode system whose design is described 144 in Section 2.3. The SA-AC beads, a graphite rod and a Ag/AgCl electrode were employed as 145 the working electrode, counter electrode and reference electrode, respectively. The 146 electroactive surface of the porous material was determined by cyclic voltammetry (CV) with 147 -0.2 to 0.8 V vs. Ag/AgCl as the voltage range and 0.01 V s<sup>-1</sup> as the scan rate. The 148 electroactive surface area (A in  $cm^2$ ) was calculated according to the Randles-Sevcik equation 149 (Eq. 1) from the peak currents determined with the polarization curve (Mousset et al., 2016b). 150

151 
$$I_P = 2.69 \times 10^5 \times AD^{1/2} n^{3/2} \gamma^{1/2} C$$
 (1)

where  $I_p$  is the peak current (in A), *n* is the number of electrons participating in the redox reaction (*n*=1), *D* is the diffusion coefficient of  $[Fe(CN)_6]^{3-}$  (7.60×10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup>), *C* is the concentration of  $[Fe(CN)_6]^{3-}$  (1×10<sup>-5</sup> mol cm<sup>-3</sup>) and  $\gamma$  is the scan rate.

Tafel slopes were obtained from linear sweep voltammetry (LSV) with -2 to 2 V vs. Ag/AgCl 155 as the voltage range and 0.01 V  $s^{-1}$  as the scan rate and were used to calculate the exchange 156 current density  $(I_0)$  of the 3D porous electrode (Adnan et al., 2021b; Fang et al., 2017; 157 Mousset et al., 2016b). Electrochemical impedance spectroscopy (EIS) using the frequency 158 range from 50,000 to 0.1 Hz and an amplitude of 10 mV was performed to characterize the 159 working electrode/electrolyte interface using the equivalent electrical circuit (EEC) method 160 (Mousset et al., 2016b). The EIS data were fitted using ZSimpWin data analysis software 161 (AMETEK, Massy, France). 162

163

164

## **2.3.** Electrochemical setup and procedure

165 The electrosorption performance achieved with the SA-AC beads working electrode was tested on a fixed-bed column reactor (2.6 cm internal diameter) (Fig. 1) using a graphite rod 166 (210 mm length, 12 mm diameter) (Final Advanced Material, Didenheim, France) as a current 167 collector to connect SA-AC beads (35 g) with the potentiostat in monopolar mode. The 168 average particle size of the SA-AC beads was 2 mm, and the height of the bed electrode was 9 169 cm. The counter electrode was a graphite rod (100 length, 8 mm diameter) (Final Advanced 170 Material, Didenheim, France) and was considered the anode. A nonconductive 171 polytetrafluoroethylene (PTFE) mesh (with a pore diameter of 1 mm) was placed between the 172 cathode and the anode to avoid contact in between without interfering with the electrosorption 173 mechanism. In all experiments, 100 mL of effluent was introduced with ascending flow using 174 a peristaltic pump (Fisher Scientific, Illkirch-Graffenstaden, France) at a constant flow rate of 175 10 mL min<sup>-1</sup>. The cathode potential was varied from -0.8 to -1.3 V vs. Ag/AgCl, and the open 176 circuit (OC) was tested for the blank experiment in the absence of an applied voltage. The 177 electrosorption capacity (q in mg  $g^{-1}$ ) was calculated according to Eq. 2 (Li et al., 2016): 178

179 
$$q = \frac{(C_0 - C_e) V}{m}$$
 (2)

180 where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of the pollutant, respectively 181 (mg L<sup>-1</sup>), *V* is the volume of the circulated solution (L), and *m* is the adsorbent mass of the 182 SA-AC electrode (g).

The mass transfer coefficients ( $k_m$ ) within the column were determined by LSV using the limiting-current technique with solutions containing 0.05 M K<sub>3</sub>Fe(CN)<sub>6</sub>, 0.10 M K<sub>4</sub>Fe(CN)<sub>6</sub> and 0.50 M Na<sub>2</sub>CO<sub>3</sub> (Sigma Aldrich, Saint-Quentin-Fallavier, France) (Adnan et al., 2021b; Cañizares et al., 2006; Selman and Tobias, 1978). The internal ohmic resistances were determined according to Eq. 3 (Adnan et al., 2022; Miller et al., 2019):

$$\sum RI = E_{cell} - |E_c| - |E_A| \tag{3}$$

189 where  $\sum RI$  is the ohmic drop,  $E_{cell}$  is the cell voltage, and  $|E_A|$  and  $|E_C|$  are the absolute 190 values of the anode and cathode potentials, respectively.

191 The electroactivity of phenol (4 g  $L^{-1}$ ) was assessed by LSV performed from -2 to 2 V vs. 192 Ag/AgCl at 0.01 V s<sup>-1</sup> scan rate using KCl (6 g  $L^{-1}$ ) as the supporting electrolyte. This was 193 performed to determine whether the direct electroreduction and/or electrooxidation of phenol 194 could occur.



with the simulated effluent since the phenol molecule (pKa = 9.95) is uncharged at the applied pH of 4. Although the setup is under forced convection within the column, the low flow rate would imply that the diffusion of phenol toward the 3D porous material does not occur in the stationary regime. Supposing that the beads are all spherical and have the same diameter (~ 3.5 mm), the phenol rate toward the 3D porous material ( $r_c$ ) can obey Fick's law under the transient regime according to Eq. 4 (Miomandre et al., 2005):

208 
$$r_c = -\frac{1}{s} \frac{dC}{dt} = \frac{1}{V} (C_t - C_t^{el}) \sqrt{\frac{D}{\pi t}}$$
 (4)

where *D* is the diffusion coefficient of phenol, *S* is the specific surface area of the beads, *t* is time, and  $C_t$  and  $C_t^{el}$  are the concentrations of phenol in the solution and at the electrode surface at time *t*, respectively.

212  $C_t^{el}$  can be expressed as a function of  $C_0$ , as follows:

213 
$$C_t^{el} = C_0 - C_{t-1}$$
 (5)

where  $C_{t-1}$  and  $C_0$  are the concentrations of phenol at time t-1 and t = 0 (in min), respectively, in the discrete model.

216 Then, 
$$C_t - C_t^{el}$$
 can be expressed according to Eq. 6:

217 
$$C_t - C^{el} = C_t + C_{t-1} - C_0$$
 (6)

After incorporating Eq. 5 into Eq. 4 and integrating Eq. 4 from  $C_t = C_0$  to  $C_t$ , Eq. 7 can be obtained:

220 
$$\ln(C_t + C_{t-1} - C_0) = \frac{2S\sqrt{D}}{\pi V} t^{\frac{1}{2}} + \ln(C_0)$$
 (7)

When dealing with real effluents (OMWW), a mixture of PCs with different pKa values (3.0–
4.0 to 10.0–11.0) should be considered (Lissaneddine et al., 2021a). Therefore, the influence
of the electromigration of ionic PCs must be added to Eq. 4:

224 
$$r_c = -\frac{1}{s} \frac{dC}{dt} = \frac{1}{V} (C_t - C_t^{el}) \sqrt{\frac{D}{\pi t}} + j_k$$
 (8)

225 with

226 
$$j_k = \frac{F}{RT} Z_k D_k C_k E = \frac{F}{RT} Z_k D_k C_k \rho_s j_{app}$$
(9)

where  $j_k$ ,  $D_k$ ,  $Z_k$  and  $C_k$  are the flux, diffusion coefficient, valence and concentration of the charged PCs (*k*), respectively; *R* is the gas constant; *T* is the absolute temperature; *F* is the Faraday constant; *E* is the electric field;  $\rho_s$  is the solution resistivity; and  $j_{app}$  is the applied current density.

After integrating Eq. 8 from 
$$C_t = C_0$$
 to  $C_t$ , Eq. 10 can be obtained:

232 
$$t^{\frac{1}{2}} = \frac{X + \sqrt{X^2 - 4YZ}}{2Y}$$
 (10)

233 with

$$234 X = \frac{2S\sqrt{D}}{\pi V} (11)$$

$$235 \quad Y = \frac{FZ_k D_k \rho_s j_{app}}{RT} \tag{12}$$

236 
$$Z = ln\left(\frac{C_t + C_{t-1} - C_0}{C_0(C_t - C_0)}\right)$$
(13)

The fittings of the models with experimental results were evaluated with the root mean squareerror (RMSE) as written in Eq. 14 (Adnan et al., 2021a):

239 
$$RMSE = \sqrt{\frac{\sum_{i=1}^{K} (y_i - y'_i)^2}{K}}$$
 (14)

240 where  $y'_i$  is the experimental value,  $y_i$  is the model value and *K* is the number of iterated 241 values.

242 The lower the RMSE value is, the more suitable the model.

243 **3. Results and discussion** 

244

## 3.1. Electrochemical characterization of the 3D porous electrodes

The electrochemical properties of the initial SA-AC beads electrodes were determined to evaluate their electrochemical performance as an active electrode material. The electroactive surface area ( $I_0$ ), charge transfer resistance ( $R_{CT}$ ) and electrical double-layer capacitance ( $C_{DL}$ ) values were not impacted by the content of AC in the beads. Therefore, only their average values were reported.

The electroactive surface area of porous electrodes determines the number of polarized active 250 sites, which in turn determines the rate and yield of electrosorption. In addition, the 251 252 electroactive surface area is a key parameter for the electrosorption efficiency (Zhu and Zhao, 2019). CV showed that the beads possessed a large electroactive surface area of  $23 \times 10^3 \pm 5.5$ 253  $\times 10^3$  cm<sup>2</sup> (Fig. 2a). Comparatively, previous studies estimated surfaces with areas of 0.14 cm<sup>2</sup> 254 with an oxidized activated carbon electrode (Derylo-Marczewska et al., 2019), 0.93 cm<sup>2</sup> with 255 an AC nanotube-supported palladium electrode (Wang et al., 2010) and 531 cm<sup>2</sup> with an 256 activated carbon fiber electrode (Ergan and Gengec, 2020). The value obtained with SA-AC 257 emphasized that the encapsulation of AC in the beads allowed a large electroactive surface 258 area to be maintained compared to porous electrodes proposed in the literature. This is of 259 260 prime interest to achieve high electrosorption capacity. This is in agreement with the adsorption ability of SA-AC beads determined in a previous study, in which the BET specific 261 surface area of SA-AC beads was 523  $m^2 g^{-1}$  and the porous nature of the adsorbent was 262 shown (total pore volume of 0.308 cm<sup>3</sup> g<sup>-1</sup>), as confirmed by FTIR, SEM and EDS 263

(Lissaneddine et al., 2021a).  $I_0$  was determined to evaluate the catalytic performance of the 264 265 electrode and electron transfer across the electrode (Sharma et al., 2013; Situmorang et al., 2020). The  $I_0$  calculated from the Tafel slopes was 3.24 mA (Fig. 2b). This value was high 266 compared to the values of electrodes based on other materials described in the literature, such 267 as activated carbon derived from rice husk (0.06 to 0.17 mA) (Jiao et al., 2020) and 268 ammonium bicarbonate and activated carbon (0.084 to 1.5 mA) (Li et al., 2014). Knowing 269 270 that a higher  $I_0$  leads to a quicker response to a change in potential (Sharma et al., 2013; Sun and Chen, 2016), better electrode performance is expected. 271

272 To further characterize the porous electrode/electrolyte interface, EIS data were obtained after validation of impedance spectra with the linear Kramers-Kronig transform (KKT) technique 273 (Fasmin and Srinivasan, 2015) (Fig. 2c). The chi-squared residues ( $\chi^2$ ) calculated by using 274 275 the KKT technique to fit the experimental spectra and the Randle-type EEC model for fitting along with KKT were determined to be  $1.5 \ 10^{-5}$  and  $9.3 \ 10^{-7}$ , respectively. Among all the EEC 276 models tested, the best agreement with EIS spectra was obtained with the Randle-type circuit 277 model shown in Fig. 3. This model further demonstrated that exchanges with the electrolyte 278 occur directly within the SA-AC beads, not at the bead and current collector surfaces. This 279 can also explain why the parameters related to the electrode/electrolyte interface 280 (electroactive surface area,  $I_0$ ,  $R_{CT}$  and  $C_{DL}$ ) were relatively constant, regardless of the AC 281 load within the beads. The associated  $R_{\rm CT}$  and  $C_{\rm DL}$  values of the EEC model were 1.7± 0.7  $\Omega$ 282 and 0.15  $\pm$  0.084 µF cm<sup>-2</sup>, respectively.  $R_{\rm CT}$  was low compared with  $R_{\rm CT}$  values of other 283 reported porous electrodes, such as almond shell-based activated nanoporous carbon (5.8  $\Omega$ ) 284 (Jain and Tripathi, 2014), activated carbon (4.2  $\Omega$ ) (Tian et al., 2020) and Cu<sub>2</sub>O-doped 285 activated carbon (9.39  $\Omega$ ) (Zhang et al., 2015). This trend of  $R_{CT}$  compared with other porous 286 materials corroborated the higher  $I_0$  value in the present case. This would therefore promote 287 electrosorption on the SA-AC beads electrodes. In addition, a higher  $C_{DL}$  value was found 288

compared to that of activated carbon (0.0058  $\mu$ F cm<sup>-2</sup>) (Tian et al., 2020), which should increase the electric double layer and, therefore, the electrosorption efficiency (Lissaneddine et al., 2021b). This is discussed in the next subsection.



Fig. 2. Electrochemical properties of the prepared SA-AC beads electrode using CV (a), LSV
(b) and EIS (c).



Fig. 3. Scheme of the EEC model integrated into the 3D porous electrodes.

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299

## 298**3.2.** Electrosorption efficiency

## **3.2.1.** Effect of the iron and calcium contents in the beads

To optimize the stability of the bio-sourced adsorbent during electrosorption, iron or calcium was added to the beads during preparation (Fig. 4). The results show that the electrosorption capacities were similar, on the order of  $204 \pm 3 \text{ mg g}^{-1}$  and  $197 \pm 10 \text{ mg g}^{-1}$  after 240 min for Fe and Ca, respectively.

To select the optimal element, the electrical conductivities of the two porous electrodes (Fe 304 305 and Ca) were compared by EIS measurements. Fig. 4b illustrates the Nyquist representations. The  $R_{\rm CT}$  values were ranked as follows: Fe (1.7  $\Omega$ ) < Ca (2.6  $\Omega$ ). The  $R_{\rm CT}$  value of Fe is 1.5-306 fold less than that of Ca, highlighting a slight increase in electrode conductivity achieved with 307 Fe. This trend was assumed to be due to differences in electron hopping, polarons and ionic 308 radii. The transition energy between  $Fe^{2+}$  and  $Fe^{3+}$  is 0.2 eV (Iqbal and Farooq, 2007), which 309 indicates pronounced electron hopping and, hence, a rapid increase in conductivity with iron. 310 Similar results have been observed in a previous study involving doping magnesium 311

aluminate with divalent and trivalent metal ions. The magnesium aluminate doped by  $\text{Fe}^{3+}$ had lower resistivity, i.e., higher conductivity, than that doped with Ca<sup>2+</sup> (Iqbal and Farooq, 2007). This is because the ionic radius of Ca<sup>2+</sup> (0.99 Å) is larger than that of Fe<sup>3+</sup> (0.64 Å) and the small polaron and electron hopping achieved with iron (Iqbal and Farooq, 2007).

This can further explain why in this study, beads prepared with Fe displayed slightly higher electrosorption capacities. Since the increase in material conductivity has previously been demonstrated to increase the electrosorption efficiency (Lissaneddine et al., 2021b), the selected optimal element of crosslinking agent used for beads preparation was Fe.



Fig. 4. Effect of the presence of iron or calcium in beads preparation on the electrosorption efficiency of phenol (a) and on the electrode conductivity estimated from the Nyquist plot (b). The operating conditions were as follows: anode: graphite rod; cathode: graphite rod and 35 g SA-1% w/v AC beads; cathode potential: -1.2 V vs. Ag/AgCl; electrolyte: 6 g L<sup>-1</sup> KCl and 4 g L<sup>-1</sup> phenol; flow rate: 10 mL min<sup>-1</sup>; and m/V = 0.35 g mL<sup>-1</sup>.

- 327
- 328

## **3.2.2.** Influence of AC percentage

The influence of AC percentage, i.e., the adsorbent dose, on phenol electrosorption kinetics in simulated OMWW is illustrated in Fig. 5a. First, the electrosorption capacity increased

rapidly over time as the active sites became accessible. With increasing time, the active sites 331 tended to be saturated so that the electrosorption capacity slowly increased until adsorption 332 equilibrium was finally reached. Second, the electrosorption capacity increased for all 333 percentages of AC tested with increasing time. In addition, there was an increase in 334 electrosorption capacity with increasing percentages of AC up to 1% w/v (183 mg g<sup>-1</sup>). This 335 336 trend was in agreement with the literature, in which the phenol adsorption capacity increased 337 with increasing powdered AC content in alginate gels (Jodra and Mijangos, 2003). Moreover, a further increase in the percentage of AC (3% w/v) led to a decline in the electrosorption 338 capacity of phenol to  $178 \text{ mg g}^{-1}$ . 339

Interestingly, the trend of  $k_m$  evolution with AC percentages (Fig. 5b) was similar to the 340 behavior of phenol electrosorption (Fig. 5a). The  $k_{\rm m}$  values increased from 8.9 10<sup>-5</sup> m s<sup>-1</sup> for 341 0% w/v AC to 9.7  $10^{-5}$  m s<sup>-1</sup> for 1% w/v AC and decreased to 8.1  $10^{-5}$  m s<sup>-1</sup> for 3% w/v AC. 342 This further confirmed that electrosorption occurred mainly within the beads, as suggested by 343 the EEC model (Section 3.1), not at the graphite rod and bead interfaces. Moreover, this 344 suggests that the electrosorption capacity strongly depended on the diffusivity of the phenol 345 346 within the beads. It has been previously shown that when AC particles are trapped in SA gels, the PCs diffuse into the micropores of the SA gels and are adsorbed by the AC enveloped in 347 the SA matrix (Chung et al., 2003). The increase in the amount of AC could then increase the 348 diffusivity and, therefore, the mass transport. At an AC content that is too high (3% w/v), AC 349 may agglomerate, which could lead to a reduction in the elasticity of the hydrogel network 350 351 and the formation of a denser network (Thakur, 2018; Tiwari et al., 2012). In a previous adsorption work, AC agglomerated in the beads, which led to an increase in the diffusional 352 path length and a decrease in the adsorption capacity (Araga et al., 2017; Iqbal et al., 2016). In 353 354 addition, the mass transfer coefficient has been shown to decrease with increasing adsorbent particle size (Krishna, M. S., Raju, G. J., & Rao, 1966). These statements agree with the 355

decreased electrosorption capacity of phenol at 3% w/v AC. To better visualize the mechanism of electrosorption with an increase in AC content within the beads, a scheme is proposed in Fig. 6. This drawing highlights the constant external diffusion layer regardless of AC content, while the internal diffusion within the beads is affected. Mass transport is then influenced along with the electrosorption efficiency.

Furthermore, increasing the percentage of AC possibly decreased the internal ohmic 361 resistance of the SA-AC bead electrode from 2.9 V (0% w/v AC) to 2.2 V (1% w/v AC) (Fig. 362 5c), which subsequently resulted in a higher electrosorption capacity. A further increase in 363 AC content (3% w/v AC) led to an increase in  $\sum RI$  to 2.7 V. The reasons for this latter trend 364 could be explained as follows. The mass transport coefficient decreased for 3% w/v AC (Fig. 365 5b), and according to the results of Fang et al. (2005, 2006), the delayed transport of the ions 366 367 into electrode (modified activated carbon aerogel) pores resulted in an increase in the internal ohmic resistance (Fang et al., 2005; Fang and Binder, 2006). Consequently, the AC 368 percentage influenced ion transport and the internal ohmic resistance. Bian et al. (2016) 369 370 demonstrated that the electrosorption performance significantly improved with a decrease in the electrode's internal ohmic resistance (14 to 3.6  $\Omega$ ) for inorganic compounds on a 371 membrane capacitive deionization reactor (Bian et al., 2016). This was further evidenced in 372 this study for organic compound electrosorption on a fixed-bed column reactor with beads 373 electrode. To conclude,  $\sum RI$  seemed to be correlated with mass transport as well as the AC 374 content in the beads and the related electrosorption efficiency. 375

Based on these results, the optimum percentage of AC was taken as 1% w/v for the nextelectrosorption experiments.



Fig. 5. Effect of AC percentage (% w/v) on the evolution of the electrosorption capacity of phenol (a), mass transport (b) and internal ohmic resistance (c). The operating conditions were as follows: anode: graphite rod; cathode: graphite rod and 35 g SA (100% Fe)-AC beads; cathode potential: -1.2 V vs Ag/AgCl; electrolyte: 6 g L<sup>-1</sup> KCl and 4 g L<sup>-1</sup> phenol; flow rate: 10 mL min<sup>-1</sup>; and m/V = 0.35 g mL<sup>-1</sup>.



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**Fig. 6.** Mechanism of phenol electrosorption in SA-AC beads with increasing AC content.

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## 3.2.3. Effect of the cathode potential

The electrode potential is the driving force of the electrosorption efficiency. Preliminary experiments were performed by applying an anode potential and using the beads as the working electrode. However, the beads could not support the high voltage involved under oxidation conditions, meaning that they were not stable (data not shown). Subsequent experiments were therefore performed by applying a cathode potential. The influence of varying the cathode potential from -0.8 to -1.3 V vs. Ag/AgCl on the phenol electrosorption efficiency compared to the OC condition is shown in Fig. 7. The electrosorption capacity

increased with decreasing applied potential from -0.8 to -1.2 V vs. Ag/AgCl, reaching a 396 maximum electrosorption capacity of 170 mg g<sup>-1</sup> at equilibrium (Fig. 7a). It has been 397 previously demonstrated that the potential can impact the electrosorption capacity of 398 uncharged molecules (Gileadi, 1966), which was the case for phenol (pKa = 9.95) considering 399 a solution pH of 4. However, the electrosorption capacity decreased to 73 mg g<sup>-1</sup> when the 400 applied potential equaled -1.3 V vs. Ag/AgCl. At this range of cathode potentials, water 401 (H<sub>2</sub>O) reduction starts to occur according to Eq. (15), in which hydrogen gas (H<sub>2</sub>) is produced 402 403 on the surface of the 3D electrode (Ziati and Hazourli, 2019).

$$404 \quad 2H_2O + 2e^- \to H_2 + 2OH^- \tag{15}$$

This H<sub>2</sub> electrogeneration reaction limits the availability of the active sites on the cathode 405 surface (Adnan et al., 2021a; Hazourli et al., 1996). The involvement of this faradaic reaction 406 therefore strongly reduced the electrosorption capacity to 73 mg  $g^{-1}$ , which was even lower 407 than that under OC conditions (123 mg  $g^{-1}$ ). In this latter case, the absence of electric current 408 409 emphasized the gain (38%) obtained with electrosorption at optimal voltage compared with 410 the adsorption mechanism alone. To further assess whether electrooxidation or electroreduction of phenol can occur, an LSV curve was plotted in the presence of phenol and 411 KCl (Fig. 7b). Neither reduction nor oxidation peaks could be observed between -2 and 2 V 412 vs. Ag/AgCl. This means that no electron transfer occurred between phenol and the 413 electrodes. Thus, it was assumed that only capacitive phenomena were involved (i.e., 414 electrosorption including adsorption). Uncharged molecules such as phenol at pH 4 can 415 electrosorb because electrode polarization induces the replacement of solvent molecules with 416 the organic compound at the interface (Gileadi, 1966). This enhances electrosorption (Gileadi, 417 1966). 418

The energy requirement is an important economic parameter to consider in electrosorption process optimization. Considering the electrosorption efficiency as a function of specific charge values (Fig. 7c), decreasing the applied potential increased the specific charge. The maximum electrosorption capacity (approximately 170 mg  $g^{-1}$ ) was only reached after 0.28 Ah L<sup>-1</sup> at -1.1 V vs. Ag/AgCl, compared to 2 Ah L<sup>-1</sup> at -1.2 V vs. Ag/AgCl. This means that the energy requirement would be 7 times lower at -1.1 V vs Ag/AgCl.

Thus, the applied cathode potential was -1.1 V vs. Ag/AgCl for the next electrosorptionexperiment with real OMWW.

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Fig. 7. Effect of cathode potential (V vs. Ag/AgCl) on phenol electrosorption considering the
contact time (a), LSV with SA-AC beads as the working electrode (b), and effect of cathode
potential on specific charge (c). Operating conditions: anode: graphite rod; cathode: graphite
rod and 35 g SA (100% Fe)-1% w/v AC beads; electrolyte: 6 g L<sup>-1</sup> KCl and 4 g L<sup>-1</sup> phenol;

flow rate: 10 mL min<sup>-1</sup>; and m/V = 0.35 g mL<sup>-1</sup>.

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## 3.2.4. Multicomponent effect with actual effluent

Electrosorption experiments with real OMWW were carried out under optimal conditions: 1% 437 w/v AC, 100% w/v Fe and -1.1 V vs. Ag/AgCl cathode potential (Fig. 8). The results showed 438 that the maximum electrosorption capacity of PCs was higher (307 mg g<sup>-1</sup>) than that with 439 phenol solutions (164 mg  $g^{-1}$ ) in simulated OMWW. This difference could be explained by 440 the presence of multiple PCs with different physico-chemical properties, such as diverse pKa 441 values. The main PCs identified in actual OMWW have been listed in a previous paper 442 (Lissaneddine et al., 2021a), and their pKa values ranged from 3.0-4.0 to 10.0-11.0. Since the 443 444 pH of the solution was between 4 and 5, the compounds, whose pKa values are equal to or below this pH value, predominantly exist in their acidic form. In contrast, the PCs, whose pKa 445 is higher than the solution pH, primarily exist in their basic form. In addition, it is usually 446 447 assumed that the acidic forms of the PCs remain uncharged because the hydroxyl (OH/O<sup>-</sup>) and carboxyl (COOH/COO) groups are protonated. In contrast, their basic forms are ionized since 448 these groups are deprotonated (Baransi et al., 2012; Liu et al., 2020). The charged PCs were 449 therefore subjected to electromigration in addition to diffusion near the electrode. Although 450 the SA-AC beads surfaces was negatively charged (cathode), electrostatic repulsion between 451 the negatively charged PCs and the negatively charged SA-AC beads surfaces could still 452 promote contact with the beads (Parida and Pradhan, 2010). The electrostatic repulsion could 453 454 also be explained by the molecular complexation of PCs in OMWW. The polarizability of

PCs depends on the combination of dispersion interactions and hydrophobic effects, which is 455 the main driving force for the molecular complexation of PCs in OMWW (Bouknana et al., 456 2019). In addition, since the hydraulic flow of the negative fixed-bed electrode is less than 457 that of the positive counter electrode, electromigration can also favor the contact of PCs 458 within the fixed-bed electrode before reaching the anode. Therefore, the electrosorption rates 459 and yields were maximized. The influence of electromigration was previously observed with 460 other organic compounds (e.g., acid red 88, orange II, and methylene blue) in simulated 461 effluents (Lissaneddine et al., 2021b; Sun et al., 2016; Yue et al., 2019b). The present results 462 newly demonstrated the influence of electromigration with a multicomponent system 463 containing organics in an actual effluent. 464

Based on this trend, the SA-AC beads electrode can be used to separate not only phenol but also other PCs (47%) from actual OMWW by electrosorption for subsequent valorization in future research studies.



469 Fig. 8. Effect of contact time on the electrosorption of PCs from real OMWW under optimal
470 operating conditions. Operating conditions: anode: graphite rod; cathode: graphite rod and 35

471 g SA (100% Fe)-1% w/v AC beads; cathode potential: -1.1 V vs. Ag/AgCl; flow rate: 10 mL

 $min^{-1}$ ; and *m*/*V* ratio = 0.35 g mL<sup>-1</sup>.

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# 473 473 474 **3.3.** Theoretical evolution of organic compound electrosorption in simulated and actual effluents

The models developed in Section 2.4 were used to predict the electrosorption evolution of phenol in simulated OMWW as a function of AC content (Fig. 9a) and PCs in real OMWW (Fig. 9b). All the RMSE values were lower than  $2.95 \times 10^{-2}$ , which confirmed the good agreement of the model with the experimental data. Thus, diffusion in simulated effluent and diffusion along with electromigration in real effluent are the main phenomena involved in the kinetics of organic compound electrosorption.

The good fitting with real effluent data further supported the estimated average valence of ionic PCs, which was 3.8. This value was obtained by weighting the valence of each PC charged in solution at a pH of 4.8 based on the ratio of their basic form to their average concentration in real effluent. The main ionic PCs identified in actual OMWW were gallic acid (valence of 5), ferulic acid (valence of 5), caffeic acid (valence of 4), cinnamic acid (valence of 2), and coumaric acid (valence of 3) according to a previous study (Lissaneddine et al., 2021a).

488 Furthermore, based on the slope values  $(\frac{2S\sqrt{D}}{\pi V})$  of  $\ln(C_t + C_{t-1} - C_0) = f(t^{1/2})$  (Eq. 7), the 489 diffusivity constant for phenol could be estimated as a function of AC content  $(D_{X\%})$  as 490 follows (Eq. 16):

491 
$$D_{X\%} = \frac{\pi V^2}{4S^2}$$
 (16)

492 The evolution of  $D_{X\%}$  as a function of AC content is plotted in Fig. 9c. The trend followed 493 that of the electrosorption capacity of phenol at different AC percentages (Fig. 5a), i.e., optimal diffusion (7.3  $10^{-9}$  m<sup>2</sup> s<sup>-1</sup>) at 1% w/v AC. This was also consistent with the  $k_m$  value evolution (Fig. 5b). This further corroborated the fact that the electrosorption capacity strongly depended on the diffusivities of the PCs within the beads.



Fig. 9. Experimental (symbol) versus theoretical correlations (continuous line) as a function of  $t^{1/2}$  in simulated OMWW as a function of AC content (a) and PCs in real OMWW and (b) effect of the percentage of AC on the diffusion coefficient (c).

## 501 Conclusions

This study proposed a novel approach to remove PCs from simulated and actual OMWW by implementing electrosorption onto SA-AC beads as porous bio-sourced electrodes. The impacts of key parameters (crosslinking agent (iron and calcium), AC content and cathode potential) on the removal efficiency of PCs were explored. The main new insights are listed as follows:

- The higher conductivity obtained with the Fe crosslinking agent led to a slightly
   higher electrosorption efficiency than that obtained with Ca.
- The AC content within the beads impacted the mass transfer and diffusion coefficients
   as well as the internal ohmic resistance. An optimal AC amount was observed (1%
   w/v) because an excessively high concentration implied agglomeration.
- A cathode potential of -1.1 V vs. Ag/AgCl was found to be optimal considering the electrosorption capacity and energy requirements. Too high voltage leads to faradaic reactions that hamper the electrosorption mechanism. Electrosorption was better than adsorption efficiency, while uncharged phenol electrosorption could still occur.

The electrosorption efficiency was higher with real wastewater than with simulated
 effluent. This could be due to the presence of multiple organic components that have
 different pKa values.

New discrete models were proposed to understand and predict the electrosorption
efficiency. The kinetics were mainly limited by diffusion in the transient regime in the

synthetic effluent, while the electromigration of ionic PCs also impactedelectrosorption with real OMWW.

• The results of the EEC model along with the kinetic models confirmed that electrosorption mainly occurred within the beads, not at the 3D electrode/electrolyte interface, unlike what is often assessed.

The good electrosorption efficiency obtained for PCs removal from OMWW is promising for 526 PCs recovery for subsequent valorization. The reusability of porous electrodes is also an 527 important indicator when evaluating the electrosorption performance of materials. Since the 528 529 organic compounds were trapped in the beads, electrosorption may be more irreversible and, therefore, desorption may be less easy. This is the subject of incoming research that will 530 provide a more detailed evaluation of the particle cathode stability and reusability. A further 531 532 possibility is to combine electrosorption for recovery with a degradation process for the 533 elimination of unwanted compounds, which is also the subject of ongoing research.

534

## 535 Acknowledgments

This work was funded by the PHC TOUBKAL 2019 Project (French-Morocco bilateral program, grant number 41525VG). The authors would like to thank the National Center for Studies and Research on Water and Energy (Cadi Ayyad University\_Morocco) and Laboratoire Réactions et Génie des Procédés (LRGP), CNRS/Université de Lorraine (France), and the European regional development fund program (CPER SusChemProc) for their technical and scientific support of this work.

#### 543 **References**

- Adebayo, M.A., Areo, F.I., 2021. Removal of phenol and 4-nitrophenol from wastewater
  using a composite prepared from clay and Cocos nucifera shell: Kinetic, equilibrium and
  thermodynamic studies. Resour. Environ. Sustain. 3, 100020.
  https://doi.org/10.1016/j.resenv.2021.100020
- Adnan, F.H., Mousset, E., Pontvianne, S., Pons, M., 2021a. Mineral cathodic electroprecipitation and its kinetic modelling in thin-film microfluidic reactor during advanced
  electro-oxidation process. Electrochim. Acta 387, 138487.
  https://doi.org/10.1016/j.electacta.2021.138487
- Adnan, F.H., Pons, M.-N., Mousset, E., 2021b. Mass transport evolution in microfluidic thin
  film electrochemical reactors: New correlations from millimetric to submillimetric
  interelectrode distances. Electrochem. commun. 130, 107097.
  https://doi.org/10.1016/j.elecom.2021.107097
- Adnan, F.H., Pontvianne, S., Pons, M.N., Mousset, E., 2022. Unprecedented roles of
  submillimetric interelectrode distances and electrogenerated gas bubbles on mineral
  cathodic electro-precipitation: Modeling and interface studies. Chem. Eng. J. 431.
  https://doi.org/10.1016/j.cej.2021.133413
- Aharonov-Nadborny, R., Raviv, M., Graber, E.R., 2016. Soil spreading of liquid olive mill
  processing wastes impacts leaching of adsorbed terbuthylazine. Chemosphere 156, 220–
  227. https://doi.org/10.1016/j.chemosphere.2016.04.104
- Andrés García, E., Agulló-Barceló, M., Bond, P., Keller, J., Gernjak, W., Radjenovic, J.,
  2018. Hybrid electrochemical-granular activated carbon system for the treatment of
  greywater. Chem. Eng. J. 352, 405–411. https://doi.org/10.1016/j.cej.2018.07.042

566	Annab, H., Fiol, N., Villaescusa, I., Essamri, A., 2019. Journal of Environmental Chemical
567	Engineering A proposal for the sustainable treatment and valorisation of olive mill
568	wastes. J. Environ. Chem. Eng. 7, 102803. https://doi.org/10.1016/j.jece.2018.11.047
569	Araga, R., Soni, S., Sharma, C.S., 2017. Fluoride adsorption from aqueous solution using
570	activated carbon obtained from KOH-treated jamun (Syzygium cumini) seed. J. Environ.
571	Chem. Eng. 5, 5608–5616. https://doi.org/10.1016/j.jece.2017.10.023
572	Azzam, M.O.J., Hazaimeh, S.A., 2021. Olive mill wastewater treatment and valorization by
573	extraction/concentration of hydroxytyrosol and other natural phenols. Process Saf.
574	Environ. Prot. 148, 495–523. https://doi.org/10.1016/j.psep.2020.10.030
575	Baransi, K., Dubowski, Y., Sabbah, I., 2012. Synergetic effect between photocatalytic
576	degradation and adsorption processes on the removal of phenolic compounds from olive
577	mill wastewater. Water Res. 46, 789–798. https://doi.org/10.1016/j.watres.2011.11.049
578	Bian, Y., Liang, P., Yang, X., Jiang, Y., Zhang, C., Huang, X., 2016. Using activated carbon
579	fiber separators to enhance the desalination rate of membrane capacitive deionization.
580	Desalination 381, 95–99. https://doi.org/10.1016/j.desal.2015.11.016
581	Bouknana, D., Jodeh, S., Sbaa, M., Hammouti, B., 2019. A phytotoxic impact of phenolic
582	compounds in olive oil mill wastewater on fenugreek "Trigonella foenum-graecum."
583	Environ. Monit. Assess.
584	Brillas, E., Garcia-Segura, S., 2020. Benchmarking recent advances and innovative
585	technology approaches of Fenton, photo-Fenton, electro-Fenton, and related processes: A
586	review on the relevance of phenol as model molecule. Sep. Purif. Technol. 237, 116337.
587	https://doi.org/10.1016/j.seppur.2019.116337

588 Cañizares, P., Marcos, I.F. De, Rodrigo, M.A., Lobato, J., 2006. Measurement of mass-

- transfer coefficients by an electrochemical technique. J. Chem. Educ. 83, 1204–1207.
  https://doi.org/10.1021/ed083p1204
- Chung, T., Tseng, H., Juang, R., 2003. Mass transfer effect and intermediate detection for
  phenol degradation in immobilized Pseudomonas putida systems 38, 1497–1507.
  https://doi.org/10.1016/S0032-9592(03)00038-4
- Deryło-Marczewska, A., Skrzypczyńska, K., Kuśmierek, K., Świątkowski, A., ZienkiewiczStrzałka, M., 2019. The adsorptive properties of oxidized activated carbons and their
  applications as carbon paste electrode modifiers. Adsorption 25, 357–366.
  https://doi.org/10.1007/s10450-019-00016-6
- Elayadi, F., Adlouni, C. El, Achak, M., Herradi, E. El, Krati, M. El, Tahiri, S., 2019. Effects
  of raw and treated olive mill wastewater (OMW) by coagulation- flocculation, on the
  germination and the growth of three plant species ( wheat , white beans , lettuce ).
  Moroccan J. Chem. 1, 111–122.
- Elayadi, F., Boumya, W., Achak, M., Chhiti, Y., 2021. Experimental and modeling studies of
  the removal of phenolic compounds from olive mill wastewater by adsorption on
  sugarcane bagasse. Environ. Challenges 4, 100184.
  https://doi.org/10.1016/j.envc.2021.100184
- Ergan, B.T., Gengec, E., 2020. Dye degradation and kinetics of online Electro-Fenton system
  with thermally activated carbon fiber cathodes. J. Environ. Chem. Eng. 8, 104217.
  https://doi.org/10.1016/j.jece.2020.104217
- Esteves, B.M., Morales-Torres, S., Maldonado-Hódar, F.J., Madeira, L.M., 2021. Integration 609 610 of olive stones in the production of Fe/AC-catalysts for the CWPO treatment of synthetic and real olive mill wastewater. Chem. Eng. J. 411. 611 https://doi.org/10.1016/j.cej.2021.128451 612

- Fang, B., Binder, L., 2006. A modified activated carbon aerogel for high-energy storage in
  electric double layer capacitors. J. Power Sources 163, 616–622.
  https://doi.org/10.1016/j.jpowsour.2006.09.014
- Fang, B., Wei, Y.Z., Maruyama, K., Kumagai, M., 2005. High capacity supercapacitors based
  on modified activated carbon aerogel. J. Appl. Electrochem. 35, 229–233.
  https://doi.org/10.1007/s10800-004-3462-6
- Fang, Z., Cao, X., Li, Xuexiao, Wang, H., Li, Xianning, 2017. Bioresource Technology
  Electrode and azo dye decolorization performance in microbial-fuel-cell- coupled
  constructed wetlands with different electrode size during long- term wastewater
  treatment. Bioresour. Technol. 238, 450–460.
  https://doi.org/10.1016/j.biortech.2017.04.075
- Fasmin, F., Srinivasan, R., 2015. Detection of nonlinearities in electrochemical impedance
  spectra by Kramers–Kronig Transforms. J. Solid State Electrochem. 19, 1833–1847.
  https://doi.org/10.1007/s10008-015-2824-9
- Genethliou, C., Kornaros, M., Dailianis, S., 2020. Biodegradation of olive mill wastewater
  phenolic compounds in a thermophilic anaerobic upflow packed bed reactor and
  assessment of their toxicity in digester effluents. J. Environ. Manage. 255, 109882.
  https://doi.org/10.1016/j.jenvman.2019.109882
- Gileadi, E., 1966. Electrosorption of uncharged molecules on solid electrodes. J. Electroanal.
  Chem. 11, 137–151. https://doi.org/10.1016/0022-0728(66)80073-6
- Girijan, S., Kumar, M., Gomber, S., 2021. Starch and powdered activated carbon amended
  alginate-biomass beads for metronidazole and bulk organic matter removal: Synthesis,
  optimization, reaction kinetics and reusability. J. Environ. Chem. Eng. 9, 106102.
- 636 https://doi.org/10.1016/j.jece.2021.106102

- Haddad, K., Jeguirim, M., Jellali, S., Thevenin, N., Ruidavets, L., Limousy, L., 2021. Biochar
  production from Cypress sawdust and olive mill wastewater: Agronomic approach. Sci.
  Total Environ. 752, 141713. https://doi.org/10.1016/j.scitotenv.2020.141713
- Hazourli, S., Bonnecaze, G., Astruc, M., 1996. Adsorption et electrosorption de composes
  organiques sur charbon actif en grains partie I Influence du potentiel imposé et du
  nombre de cycles adsorption and electrosorption of organic compounds on granular
  activated carbon part I- Influence of applied. Environ. Technol. 17, 1275–1283.
  https://doi.org/10.1080/09593330.1996.9618457
- He, F., Hemmatifar, A., Bazant, M.Z., Hatton, T.A., 2020. Selective adsorption of organic
  anions in a flow cell with asymmetric redox active electrodes 1–26.
- Iqbal, M., Iqbal, N., Bhatti, I.A., Ahmad, N., Zahid, M., 2016. Response surface methodology
  application in optimization of cadmium adsorption by shoe waste: A good option of
  waste mitigation by waste. Ecol. Eng. 88, 265–275.
  https://doi.org/10.1016/j.ecoleng.2015.12.041
- Iqbal, M.J., Farooq, S., 2007. Effect of doping of divalent and trivalent metal ions on the
  structural and electrical properties of magnesium aluminate. Mater. Sci. Eng. B SolidState Mater. Adv. Technol. 136, 140–147. https://doi.org/10.1016/j.mseb.2006.09.009
- Jain, A., Tripathi, S.K., 2014. Almond shell-based activated nanoporous carbon electrode for
   EDLCs. https://doi.org/10.1007/s11581-014-1282-1
- Jasielec, J.J., 2021. Electrodiffusion Phenomena in Neuroscience and the Nernst–Planck–
  Poisson Equations. Electrochem 2, 197–215.
  https://doi.org/10.3390/electrochem2020014
- Jiao, Y., Hu, Y., Han, L., Zhou, M., 2020. Activated Carbon Derived from Rice Husk as

- Efficient Oxygen Reduction Catalyst in Microbial Fuel Cell. Electroanalysis 32, 2969–
  2975. https://doi.org/10.1002/elan.202060409
- Jodra, Y., Mijangos, F., 2003. Phenol adsorption in immobilized activated carbon with
  alginate gels phenol adsorption in immobilized activated. Sep. Sci. Technol. 37–41.
  https://doi.org/10.1081/SS-120019412
- 665 Khan, A.S., Ibrahim, T.H., Khamis, M.I., Nancarrow, P., Iqbal, J., AlNashef, I., Jabbar, N.A.,

Hassan, M.F., Mjalli, F.S., 2021. Preparation of sustainable activated carbon-alginate

- beads impregnated with ionic liquid for phenol decontamination. J. Clean. Prod. 128899.
  https://doi.org/10.1016/j.jclepro.2021.128899
- Krishna, M. S., Raju, G. J., & Rao, C. V., 1966. Mass Transfer in Packed Beds in Annuli
  Electrolytic Redox Reactions. Period. Polytech. Chem. Eng. 11, 95–102.
- Li, D., Qu, Y., Liu, J., He, W., Wang, H., Feng, Y., 2014. Using ammonium bicarbonate as
  pore former in activated carbon catalyst layer to enhance performance of air cathode
  microbial fuel cell. J. Power Sources 272, 909–914.
  https://doi.org/10.1016/j.jpowsour.2014.09.053
- Li, Y., Zhang, C., Jiang, Y., Wang, T., Wang, H., 2016. Effects of the hydration ratio on the
  electrosorption selectivity of ions during capacitive deionization. Desalination 399, 171–
  177. https://doi.org/10.1016/j.desal.2016.09.011
- Lissaneddine, A., Mandi, L., Achaby, M. El, Mousset, E., Eldon, R., Ouazzani, N., Pons, M.,
- Aziz, F., 2021a. Performance and dynamic modeling of a continuously operated pomace
- olive packed bed for olive mill wastewater treatment and phenol recovery. Chemosphere
- 681 130797. https://doi.org/10.1016/j.chemosphere.2021.130797
- Lissaneddine, A., Pons, M.-N., Aziz, F., Ouazzani, N., Mandi, L., Mousset, E., 2021b. A

critical review on the electrosorption of organic compounds in aqueous effluent –
Influencing factors and engineering considerations. Environ. Res. J. Under revision.

Liu, B., Zhong, F., Yokoyama, W., Huang, D., Zhu, S., Li, Y., 2020. Interactions in starch co-685 686 gelatinized with phenolic compound systems: effect of complexity of phenolic compounds and amylose content starch. Carbohydr. Polym. 116667. 687 of https://doi.org/10.1016/j.carbpol.2020.116667 688

689 Macías-garcía, A., Carrasco-amador, J.P., Encinas-sánchez, V., Díaz-díez, M.A., 2019. Preparation of activated carbon from kenaf by activation with H 3 PO 4. Kinetic study 690 of the adsorption / electroadsorption using a system of supports designed in 3D, for 691 Environ. 7, 692 environmental applications. J. Chem. Eng. 103196. https://doi.org/10.1016/j.jece.2019.103196 693

- Mi, F., Sung, H., Shyu, S., 2002. Drug release from chitosan ± alginate complex beads
  reinforced by a naturally occurring cross-linking agent. Carbohydr. Polym. 48, 61–72.
- Miller, A., Singh, L., Wang, L., Liu, H., 2019. Linking internal resistance with design and
  operation decisions in microbial electrolysis cells. Environ. Int. 126, 611–618.
  https://doi.org/10.1016/j.envint.2019.02.056
- Miomandre, F., Sadki, S., Audebert, P., Méallet-Renault, R., 2005. Electrochimie Des
  concepts aux applications. Dunod, Paris. (in French), Paris.
- Mousset, E., 2020. Unprecedented reactive electro-mixing reactor: Towards synergy between
  micro- and macro-reactors? Electrochem. commun. 118, 106787.
  https://doi.org/10.1016/j.elecom.2020.106787
- Mousset, E., Frunzo, L., Esposito, G., van Hullebusch, E.D., Oturan, N., Oturan, M.A., 2016a.
  A complete phenol oxidation pathway obtained during electro-Fenton treatment and

validated by a kinetic model study. Appl. Catal. B Environ. 180, 189–198.
https://doi.org/10.1016/j.apcatb.2015.06.014

Mousset, E., Loh, W.H., Lim, W.S., Jarry, L., Wang, Z., Lefebvre, O., 2021. Cost comparison
of advanced oxidation processes for wastewater treatment using accumulated oxygenequivalent criteria. Water Res. 200, 117234.
https://doi.org/https://doi.org/10.1016/j.electacta.2021.138466

Mousset, E., Pontvianne, S., Pons, M.-N., 2018a. Fate of inorganic nitrogen species under
homogeneous Fenton combined with electro-oxidation/reduction treatments in synthetic
solutions and reclaimed municipal wastewater. Chemosphere 201, 6–12.
https://doi.org/10.1016/j.chemosphere.2018.02.142

Mousset, E., Puce, M., Pons, M.N., 2019. Advanced electro-oxidation with boron-doped diamond for acetaminophen removal from real wastewater in a microfluidic reactor:
Kinetics and mass-transfer studies. ChemElectroChem 6, 2908–2916.
https://doi.org/10.1002/celc.201900182

Mousset, E., Quackenbush, L., Schondek, C., Gerardin-Vergne, A., Pontvianne, S., Kmiotek,
S., Pons, M.N., 2020. Effect of homogeneous Fenton combined with electron transfer on
the fate of inorganic chlorinated species in synthetic and reclaimed municipal
wastewater. Electrochim. Acta 334, 135608.
https://doi.org/10.1016/j.electacta.2019.135608

Mousset, E., Wang, Z., Hammaker, J., Lefebvre, O., 2017. Electrocatalytic phenol
degradation by a novel nanostructured carbon fiber brush cathode coated with graphene
ink. Electrochim. Acta 258, 607–617. https://doi.org/10.1016/j.electacta.2017.11.104

Mousset, E., Wang, Z., Hammaker, J., Lefebvre, O., 2016b. Physico-chemical properties of
 pristine graphene and its performance as electrode material for electro-Fenton treatment

# 730 of wastewater. Electrochim. Acta 214, 217–230. 731 https://doi.org/10.1016/j.electacta.2016.08.002 </

- Mousset, E., Wang, Z., Olvera-Vargas, H., Lefebvre, O., 2018b. Advanced electrocatalytic
  pre-treatment to improve the biodegradability of real wastewater from the electronics
  industry A detailed investigation study. J. Hazard. Mater. 360, 552–559.
  https://doi.org/10.1016/j.jhazmat.2018.08.023
- Parida, K.M., Pradhan, A.C., 2010. Removal of phenolic compounds from aqueous solutions
  by adsorption onto manganese nodule leached residue. J. Hazard. Mater. 173, 758–764.
  https://doi.org/10.1016/j.jhazmat.2009.09.003
- Sahin, E.M., Tongur, T., Ayranci, E., 2020. Removal of azo dyes from aqueous solutions by
  adsorption and electrosorption as monitored with in-situ UV-visible spectroscopy. Sep.
  Sci. Technol. 55, 3287–3298. https://doi.org/10.1080/01496395.2019.1676786
- Selman, J.R., Tobias, C.W., 1978. Mass-transfer measurements by the limiting-current
  technique. Adv. Chem. Eng. 10, 211–318.
- Sharma, M., Jain, P., Varanasi, J.L., Lal, B., Rodríguez, J., Lema, J.M., Sarma, P.M., 2013.
- Enhanced performance of sulfate reducing bacteria based biocathode using stainless steel
  mesh on activated carbon fabric electrode. Bioresour. Technol. 150, 172–180.
  https://doi.org/10.1016/j.biortech.2013.09.069
- Singleton, V. L., & Rossi, J.A., 1965. Colorimetry of total phenolic substances. US Am.
  Chem. Soc. Symp. Ser. 26, 47–70.
- Situmorang, R.S., Seri, O., Kawai, H., 2020. Estimation of exchange current density for
  hydrogen evolution reaction of copper electrode by using the differentiating polarization
  method. Appl. Surf. Sci. 505, 144300. https://doi.org/10.1016/j.apsusc.2019.144300

- Sun, D., Chen, Y., 2016. Electrode kinetics of CO<sub>2</sub> electroreduction.
  https://doi.org/10.1201/b20177-4
- Sun, X.-F., Guo, B.-B., He, L., Xia, P.-F., Shu-Guang Wang, 2016. Electrically accelerated
  removal of organic pollutants by a three-dimensional graphene aerogel. AIChE J. 59,
  215–228. https://doi.org/10.1002/aic
- Taylor, P., Ji, M., Jiang, X., Wang, F., 2015. Desalination and water treatment a mechanistic
  approach and response surface optimization of the removal of oil and grease from
  restaurant wastewater by electrocoagulation and electroflotation. Desalin. water Treat.
- 761 37–41. https://doi.org/10.1080/19443994.2014.929034
- Thakur, S., 2018. Synthesis, characterization and adsorption studies of an acrylic acid-grafted
   sodium nanocomposite. https://doi.org/10.1177/0263617417700636
- Tian, X., Bao, S., Zhang, Y., 2020. Adsorption properties of V(IV) on the resin-activated
  carbon composite electrodes in capacitive deionization. Int. J. Miner. Metall. Mater.
- Tiwari, A., Soni, A., Bajpai, A.K., 2012. Nanoparticles loaded alginate beads as potential
  adsorbent for removal of phenol from aqueous solution. Synth. React. Inorganic, Met.
  Nano-Metal Chem. 42, 1158–1166. https://doi.org/10.1080/15533174.2012.682835
- Tundis, R., Conidi, C., Loizzo, M.R., Sicari, V., Cassano, A., 2020. Olive Mill Wastewater
  Polyphenol-Enriched Fractions by Integrated Membrane Process : A Promising Source
  of Antioxidant , Hypolipidemic and Hypoglycaemic Compounds 1–15.
- Ververi, M., Goula, A.M., 2019. Pomegranate peel and orange juice by-product as new
  biosorbents of phenolic compounds from olive mill wastewaters. Chem. Eng. Process.
  Process Intensif. 138, 86–96. https://doi.org/10.1016/j.cep.2019.03.010
- Wadhawan, S., Jain, A., Nayyar, J., Kumar, S., 2020. Role of nanomaterials as adsorbents in

- heavy metal ion removal from waste water: a review. J. water Process Eng. 33, 101038.
  https://doi.org/10.1016/j.jwpe.2019.101038
- Wang, Y., Cui, C., Zhang, G., Xin, Y., Wang, S., 2021. Electrocatalytic hydrodechlorination
  of pentachlorophenol on Pd-supported magnetic biochar particle electrodes. Sep. Purif.

780 Technol. 258, 118017. https://doi.org/10.1016/j.seppur.2020.118017

- Wang, Y., Sheng, Z.M., Yang, H., Jiang, S.P., Li, C.M., 2010. Electrocatalysis of carbon
  black- or activated carbon nanotubes-supported Pd-Ag towards methanol oxidation in
  alkaline media. Int. J. Hydrogen Energy 35, 10087–10093.
  https://doi.org/10.1016/j.ijhydene.2010.07.172
- Xu, S., Jin, Y., Li, R., Shan, M., Zhang, Y., 2021. Amidoxime modified polymers of intrinsic
   microporosity/alginate composite hydrogel beads for efficient adsorption of cationic dyes
   from aqueous solution. J. Colloid Interface Sci. https://doi.org/10.1016/j.jcis.2021.08.157
- Yang, W., Zhou, M., Ma, L., 2021. A continuous flow-through system with integration of
  electrosorption and peroxi-coagulation for efficient removal of organics. Chemosphere
  274, 129983. https://doi.org/10.1016/j.chemosphere.2021.129983
- Yue, F., Zhang, Q., Xu, L., Zheng, Y., Yao, C., Jia, J., Leng, W., Hou, S., 2019a. Porous
  reduced graphene oxide/single-walled carbon nanotube film as freestanding and flexible
  electrode materials for electrosorption of organic dye. ACS Appl. nano Mater. 2, 6258–
  6267. https://doi.org/10.1021/acsanm.9b01236
- Yue, F., Zhang, Q., Xu, L., Zheng, Y., Yao, C., Jia, J., Leng, W., Hou, S., 2019b. Porous
  reduced graphene oxide/single-walled carbon nanotube film as freestanding and flexible
  electrode materials for electrosorption of organic dye. ACS Appl. Nano Mater. 2, 6258–
  6267. https://doi.org/10.1021/acsanm.9b01236

799	Zhang, X., Li, K., Yan, P., Liu, Z., Pu, L., 2015. N-type Cu <sub>2</sub> O doped activated carbon as
800	catalyst for improving power generation of air cathode microbial fuel cells. Bioresour.
801	Technol. 187, 299–304. https://doi.org/10.1016/j.biortech.2015.03.131
802	Zhu, P., Zhao, Y., 2019. Cyclic voltammetry measurements of electroactive surface area of
803	porous nickel: Peak current and peak charge methods and diffusion layer effect. Mater.
804	Chem. Phys. 233, 60–67. https://doi.org/10.1016/j.matchemphys.2019.05.034
805	Ziati, M., Hazourli, S., 2019. Experimental investigation of activated carbon prepared from
806	date stones adsorbent electrode for electrosorption of lead from aqueous solution.
807	Microchem. J. 146, 164–169. https://doi.org/10.1016/j.microc.2018.12.041
808	
809	
810	