Recovery of phenolic compounds from multi-component solution by a synthesized activated carbon using resorcinol and formaldehyde

Joana Madureira, Rita Melo, Sandra Cabo Verde, Inês Matos, Maria Bernardo, João P. Noronha, Fernanda M. A. Margaça and Isabel M. Fonseca

ABSTRACT

The adsorption of four phenolic compounds (gallic acid, protocatechuic acid, vanillic acid and syringic acid) is investigated using a synthesized mesoporous carbon on both single and multi-component synthetic solutions. Some correlation of the adsorption capacity of the carbon and the nature of adsorbate could be made, except for gallic acid whose concentration decrease seems to be not exclusively due to adsorption but also to polymerization reaction. In the multi-component mixture, negative effects in the adsorption capacity are observed probably due to competition for the active centers of the adsorbent surface. In desorption studies, ethanol presents better performance than water and acetonitrile. Vanillic acid is the compound with the higher adsorption and interestingly it is then possible to desorb a relatively high amount of it from the adsorbent, which may represent a possibility for a selective recovery of vanillic acid. These results present a potential way to treat the wastewater from the cork industry.

Key words | activated carbon, adsorption, phenolic compounds, selective desorption

INTRODUCTION

In the last decades, cork production and transformation processes have become important sectors of the economic activity in Portugal. The wastewater produced during the cork cooking process represents the main source of wastes from these industries, amounting to approximately 1,500 L per ton of cork. These wastewaters have a high concentration of organic matter and a considerable toxicity (Bernardo et al. 2011). In the literature, the presence of phenolic derivative compounds (Minhalma & Pinho 2001) are reported, which are considered biorecalcitrant. Nowadays, environmental pollution caused due to the release of phenolic derivative compounds from industries such as the cork industry has become widespread in the world, and it has been arousing special attention from the scientific community. Furthermore, the increasingly stringent regulation standards regarding water pollution have boosted the development and improvement of appropriate wastewater treatment technologies (Tasic et al. 2014; Bazrafshan et al. 2016; Teh et al. 2016; He et al. 2017). On the other hand, the potential of these phenolic compounds as antioxidants is well-known (Benitez et al. 2005). In recent studies, the authors observed both a high antioxidant activity for cork industry compounds and their increase with gamma radiation treatment (Madureira et al. 2015, 2017) which could improve the added-value compounds in the cooking water.

Considering these outcomes, the authors considered the possibility of extracting and purifying phenolic derivative compounds from aqueous solutions. Physical, chemical and biological methodologies have been proposed for removing phenolic compounds from wastewaters (Beltrán De Heredia et al. 2004). Adsorption appears to be one of the most suitable methods (Soto et al. 2011) because of the combination of significant efficacy with simplicity of design and operation, as well as its low cost. Activated carbon (AC), a material with a porous structure and large internal surface area, has been proven to be the most adequate adsorbent used for the removal of phenolic compounds from wastewaters because of its high adsorption

In a real situation, wastewater presents multiple compounds that are able to be adsorbed by ACs. Thus, it is important to study the competition effect on the removal efficiency of each compound. For this purpose, the authors have been focused on the identification of the most abundant components in cork cooking water. Lima et al. (Lima et al. 2016) reported gallic acid, protocatechuic acid, vanillic acid and syringic acid as the main compounds present in those wastewaters. Minhalma & Pinho (2001) had already observed the presence of these phenolic acids in cork wastewaters with concentrations ranging between 2 and 35 ppm. With this framework, the authors considered the study of the adsorption capacity of AC, not only on these isolated compounds but also on mixtures of them, to be of great interest. In the literature, works dealing with adsorption studies of these phenolic compounds in multi-component solutions are scarce (García-Araya et al. 2003), which highlights the importance of the present work. In fact, wastewater presents multiple compounds that are able to be adsorbed by ACs. To develop a methodology to adsorb some phenolic compounds from wastewaters, it is necessary to begin from a small scenario where no other molecules can interfere. Thus, it is essential to study the sample as a mixture of the four model compounds for simulating the real situation and for exploring the interactions and the effect of the presence of one compound in the adsorption capacity of other ones.

Although adsorption of phenolic compounds onto ACs is relatively simple, the process of regenerating the adsorbent and recovering the adsorbate is still a challenge. Besides other techniques such as thermal regeneration or regeneration under supercritical conditions, ultrasound has been widely studied as an improvement for desorption processes (Breitbach & Bathen 2001; Juang et al. 2006), since it could be possible to regenerate the adsorbent without the degradation of the compounds.

In this work, kinetic and adsorption equilibrium liquid-phase studies of the main phenolic derivative compounds present in cork wastewaters, gallic acid, protocatechuic acid, vanillic acid and syringic acid, are reported. The adsorption experiments were carried out using a synthesized mesoporous carbon. The obtained adsorbent was characterized regarding its textural and chemical properties: specific surface area, total pore volume, micropore volume and pore size distribution as well as elemental analysis and pH at the point of zero charge. The adsorption capacity of the different phenolic compounds on the produced carbon was investigated for single and multi-component solutions. Desorption of the adsorbed compounds from the quaternary mixture solution was investigated with different solvents using an ultrasonic bath and the recovery efficiency was evaluated. To our knowledge, there are no studies in the literature concerning the adsorption of the studied phenolic compounds onto this type of synthesized carbon.

### EXPERIMENTAL SECTION

#### Reagents and materials

Gallic acid, protocatechuic acid and syringic acid were purchased from Sigma (St Louis, USA). Vanillic acid was obtained from Fluka (Buchs, Switzerland). Acetonitrile (HPLC grade) was purchased from Sigma (St Louis, USA) and formic acid and absolute ethanol were obtained from Panreac Química SA (Barcelona, Spain). Water was treated in a Milli-Q water purification system (Merck Millipore, USA).

The adsorbates used in this work were four phenolic compounds: gallic acid (3,4,5-Trihydroxybenzoic acid, GA), protocatechuic acid (3,4-Dihydroxybenzoic acid, PA), vanillic acid (4-Hydroxy-3-methoxybenzoic acid, VA) and syringic acid (4-Hydroxy-3,5-dimethoxybenzoic acid, SA). Its main characteristics are presented in Table 1.

All the solutions were prepared with ultrapure water, with adjustment of pH (pH 4.5) with sodium hydroxide 1 M.

#### AC preparation

The AC was synthesized using resorcinol (ca. 15 g) in 18 mL of distilled water and 20 mL of formaldehyde. After the mixing step, the mixture was adjusted to pH = 6.0 with 2 M NaOH. The gelation step was made at 85 °C over 3 days and the sample was put into an oven over 4 days (60 °C on the first day, 80 °C on the second day, 100 °C on the third day and 120 °C in fourth day). Four grams of sample were subjected to thermal treatment performed in a tubular quartz reactor placed in a vertical furnace. The sample was heated to 700 °C, at 2 °C min⁻¹, and kept for 3 h under a N₂ flow of 100 cm³ min⁻¹. After cooling under N₂ flow, the AC was ground and sieved with calibrated MESH (35, 45 and 80). The fraction sifted through 80 (which corresponds to 177 μm) was stored. The adsorbent was named AC-S.
Physical characterization

The textural characterization of the carbon was performed by nitrogen adsorption-desorption isotherms at −196 °C (Thommes et al. 2015) in an ASAP 2010 Pore Structure Analyzer (Micromeritics, USA). Samples were previously degassed at 120 °C for 12 hours. The textural parameters include specific surface area, total pore volume, micropore and mesopore volume. The specific surface area (S\text{BET}) was calculated using the Brunauer–Emmett–Teller (BET) method. Total pore volume (V\text{p}) was determined by the amount of nitrogen adsorbed at P/P\text{o} = 0.99. The mesoporous volume (V\text{meso}) was obtained by BJH (Barrett–Joyner–Halenda) method and microporous volume (V\text{micro}) was determined through the t-method, taking as reference the isotherm proposed by Gregg & Sing (1982).

Chemical characterization

Elemental analysis (C, H, N and S) was carried out using a CHNS Elemental Analyser (Thermo Finnigan – CE Instruments, model Flash EA 1112 CHNS series) on the basis of sample combustion dynamics. The quantity of oxygen was determined by difference.

The pH at the point of zero charge (pH\text{PZC}) was determined using a modified version of a direct pH measurement method (Moreno-Castilla et al. 2000). Briefly, 0.1 g of AC was added to 1 mL of ultrapure water and stored in constant stirring at room temperature during 24 h. The final pH of the mixture was registered.

The Fourier transform infrared spectroscopy (FT-IR) spectrum of the AC was obtained on a Nicolet™ iS™ 50 FT-IR spectrophotometer (Thermo Scientific, USA). About 1 mg of carbon was used on a 200 mg KBr pellet. The pellet was analyzed immediately after preparation by compression in a hydraulic press. The spectrum of a pure KBr pellet was used as background.

Electrospray ionization mass spectrometry (ESI-MS)

This analytical technique was performed using a Bruker HCT quadrupole ion trap mass spectrometer. Sample solutions in acetonitrile were introduced into the ESI source via a syringe pump at a flow rate of 150 mL min⁻¹. The

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular structure</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>Solubility in water [mg L⁻¹] (Noubigh et al. 2007)</th>
<th>λ\text{max} [nm]</th>
<th>pK\text{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallic acid (GA)</td>
<td></td>
<td>C₇H₆O₅</td>
<td>170.12</td>
<td>11,570 (25 °C)</td>
<td>271</td>
<td>4.16</td>
</tr>
<tr>
<td>Protocatechuic acid (PA)</td>
<td></td>
<td>C₇H₆O₄</td>
<td>154.12</td>
<td>18,730 (25 °C)</td>
<td>260</td>
<td>4.22</td>
</tr>
<tr>
<td>Vanillic acid (VA)</td>
<td></td>
<td>C₈H₈O₄</td>
<td>168.14</td>
<td>1,530 (25 °C)</td>
<td>261</td>
<td>4.16</td>
</tr>
<tr>
<td>Syringic acid (SA)</td>
<td></td>
<td>C₉H₁₀O₅</td>
<td>198.17</td>
<td>5,750 (25 °C)</td>
<td>274</td>
<td>4.34</td>
</tr>
</tbody>
</table>

Table 1 | Chemical characteristics of studied phenolic derivative compounds
heated capillary temperature was set to 209 °C and the cover inert gas to a flow rate of 2 L min⁻¹. For MS² experiments, the precursor ion of interest was first isolated by applying an appropriate waveform across the end-cap electrodes on the ion trap. The isolated ions were then subjected to a supplementary AC signal to resonantly excite them and therefore cause collision-induced dissociation.

**Adsorption studies**

To study the adsorption kinetics, 15 mL of phenolic compounds (single and in quaternary mixture) solution (500 mg L⁻¹) was mixed with 150 mg of AC into glass flasks. The quaternary mixture solution was prepared so that each phenolic compound concentration was 500 mg L⁻¹ ensuring a 25% w/w ratio.

As mentioned above, all the solutions used were prepared at pH 4.5. The flasks were placed in a water bath at 25 °C, stirred in an agitation plate (Kottermann, Germany) and aliquots of 1 mL were collected at different time steps. After collection, the samples were filtered (DISMIC 25, 0.45 μm, Specanalitica, Portugal), diluted if needed, and the compounds concentration was measured by High Performance Liquid Chromatography (HPLC) (Prominence CBM 20-A, Shimadzu, Japan) with UV-DAD detector. The HPLC column was a Merck Purospher STAR RP-18e (5 μm, 250 mm, 4.0 mm) and the detection was made at 280 nm. The mobile phase used was: A (90% (v/v) ultrapure water with 0.1% formic acid) and B (10% acetonitrile 0.1% H₂O) with pump flow rate of 1 mL min⁻¹ ensuring a 25% w/w ratio.

For quantification purposes, a calibration plot was performed under the experimental conditions used. The amount of phenolic compound adsorbed on the AC was calculated by the difference between the initial concentration and the equilibrium concentration.

The equilibrium adsorption studies were carried out at 25 °C varying the adsorbate concentrations (25–500 mg L⁻¹). The equilibrium was reached after stirring for 6 h. The concentration of phenolic compounds remaining in solution at equilibrium (Cₑ) was determined by HPLC analysis and the uptake (qₑ) was calculated using the Equation (1).

\[ qₑ = \frac{(Cₑ - C₀) V}{W} \]  

where qₑ is the amount (mg g⁻¹) of phenolic compound adsorbed at equilibrium, C₀ is the compound initial concentration (mg L⁻¹), Cₑ is the compound concentration at equilibrium (mg L⁻¹), V is the volume (L) of the adsorbate solution and W is the weight (g) of dried carbon. All adsorption assays were made in triplicate.

**Desorption studies**

Desorption experiments were performed accordingly to the method described by Chakma & Moholkar (2011) with some modifications. The first step of the experiments is to saturate the adsorbent with the model compounds. For this purpose, 600 mg of AC was added to 80 mL of phenolic compounds solution (quaternary mixture) with the concentration of 500 mg L⁻¹ (pH = 4.5), and the mixture was stored with constant stirring at room temperature during 24 h to reach the equilibrium state. Initial and residual phenolic concentration was analyzed by HPLC at the same conditions as above. Then the adsorbent was filtered and dried at 60 °C and used in the desorption experiments. For that, 100 mg of saturated adsorbent was added to 15 mL of desired solvent (ultrapure water and ethanol) and the flask was placed inside the ultrasonic bath (47 kHz). After 4 h, the samples were filtered to remove the solids, the solvent was evaporated and the concentrate was redisolved in 15 mL of ultrapure water. Then the concentration of phenolic compounds was measured by HPLC according to the method described in section 2.6.

Preliminary tests for the desorption assays were made with 2 h and 4 h of contact time, and the results showed almost no difference in the obtained desorption efficiency after 2 h. Nevertheless, to ensure maximum desorption, 4 h of contact time was used in the subsequent tests.

**RESULTS AND DISCUSSION**

**Characterization of the adsorbent**

The N₂ adsorption-desorption isotherms (data not shown) of the carbon belong to type IV in the IUPAC classification (Thommes et al. 2015), characterized by its hysteresis loop, which is associated with capillary condensation taking place in mesopores and the limiting uptake over a range of high relative pressure. The mesoporous nature of this carbon sample is confirmed by its high mesopore volume (Table 2), which accounts for more than 70% of the overall pore volume. The AC possesses a large internal surface area.
Regarding surface chemistry, the value of pH_{PZC} revealed the carbon’s basic nature. The high carbon content of the sample should be highlighted.

The FT-IR spectrum of the synthesized AC is illustrated in Figure 1.

In the absorption region between 3,600 cm\(^{-1}\) and 3,200 cm\(^{-1}\), the present band can be attributed to the hydroxyl groups present on the surface of the carbon but also to water adsorbed by the material (Moreno-Castilla et al. 2000). In the range of 3,000–2,800 cm\(^{-1}\), small peaks due to vibration of the C-H bonds are visible. The peak around 800 cm\(^{-1}\) can be representative of the deformation vibrations of the out-of-plane C-H bonds of the aromatic ring. In the region between 1,750–1,600 cm\(^{-1}\), peaks at 1,700 cm\(^{-1}\) and 1,630 cm\(^{-1}\) are usually associated with the stretching of the C=O bonds, and may represent the presence of quinones, ketones, aldehydes or carboxylic acid groups. Also, in the region between 1,300–1,000 cm\(^{-1}\), a pronounced band is observed that can be assigned to C-O bonds of acids, alcohols, phenols, esters and/or ester groups (Rivera-Utrilla et al. 2011; Yakout & Sharaf El-Deen 2016). Although this carbon presents a low amount of oxygen and a basic character, the FT-IR results reveal the presence of significant oxygenated functional groups in its surface.

### Adsorption studies

#### Single component adsorption

The rate of adsorption is studied by measuring the concentration changes as a function of time, keeping constant the initial concentration and the mass of adsorbent.

Adsorption kinetic data of single components of the AC sample are presented in Figure 2.

Kinetic curves have an initial stage where the uptake adsorption is fast, followed by a second step where the uptake steadily increases up to equilibrium concentrations, with the exception of gallic acid. Textural properties of the adsorbent seem to have an important role in the initial adsorption rate. The higher mesoporous volume of the carbon sample justifies the initial fast uptake, as they function as transport pores to the microporous sites where adsorption takes place.

Even though the difference between the adsorption curves is not very accentuated, some observations can be made. It seems that the effect of carbon surface chemistry cannot be excluded. Considering the pKa values of these phenolic acids, at the working pH of 4.5 the deprotonation of carboxylate groups may occur, generating mono-ionic species. This suggests that the interactions with the carbon
surface may also be of an electrostatic nature, favoring the adsorption. As such, not only the nature of the carbon surface groups, but also the chemical structure of the molecules will influence the adsorption behavior. The different natures of the substituents in the aromatic ring will determine different electron distribution as the ring is more or less activated. These differences could affect the way the compounds interact with the carbon surface groups. The adsorption behavior seems to follow the order of deactivation of the aromatic ring, being higher for syringic acid (Michailof et al. 2008), excluding gallic acid.

The complete adsorption of gallic acid by the adsorbent is also not in agreement with that observed by García-Araya (García-Araya et al. 2003). These authors reported that the higher the solubility in water the lower the adsorption capacity, and that syringic acid was more strongly adsorbed onto AC than gallic acid. A conceivable explanation for the difference in behavior for the gallic acid is the possibility that the polymerization of this compound is occurring under these experimental conditions. The consumption of gallic acid observed is not exclusively due to an adsorption process but also due to the polymerization reaction affording the formation of a new compound that may or may not be adsorbed to the surface of the AC (Vidic et al. 1997; Michailof et al. 2008; Giannakopoulos & Deligiannakis 2011). Actually, other authors have reported the possibility of polymerization of phenolic compounds occurring if oxygen is present in solution (Vidic et al. 1997). In the present work, this hypothesis is supported by the appearance of unknown peaks in the HPLC spectra during the course of the experiment using gallic acid. Posterior studies of the solutions by ESI-MS (see Figure S2, available with the online version of this paper) revealed the presence of dimers, resulting from the oligomerization of the gallic acid. For this reason, the consumption of gallic acid was not considered in the mathematical treatment of the kinetic results, because it is very likely that adsorption is not the predominant occurring phenomenon.

It was possible to adjust the kinetic data obtained for carbon AC-S to a pseudo-first and a pseudo-second order kinetic model as described by Ho (2006). The fittings were done using the linear form of the expressions. The obtained fitting using the pseudo-first order model, using Equation (2), revealed that this model was not adequate to describe the results as it presented lower determination coefficient values. On the other hand, the pseudo-second order kinetic model (Equation (3)) gives good fitting to the experimental data with high determination coefficients ($R > 0.994$). Also, with this model the estimated values obtained for $q_e$ are very similar to the experimental ones.

The following expressions were used:

$$\ln(q_e - q_t) = \ln(q_e) - k_1t$$  \hspace{1cm} (2)

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \left(\frac{1}{q_e}\right)t$$  \hspace{1cm} (3)

where $k_1$ is the pseudo-first order constant (h$^{-1}$), $k_2$ is the pseudo-second order rate constant (g mg$^{-1}$ min$^{-1}$), and $q_e$ and $q_t$ are the adsorbate uptake (mg g$^{-1}$) at equilibrium and at time $t$, respectively. Here, the product $k_2q_e^2$ represents the initial adsorption rate. The different parameters found are presented in Table 3.

The $q_e$ values obtained for protocatechuic acid and syringic acid are very similar; however, the kinetic parameters reflect a better behavior for the syringic acid, which presents a higher estimated value for the kinetic rate constant, probably as a consequence of its lower solubility.

Vanillic acid is the least soluble of the three compounds, justifying the higher kinetic rate constant.

**Quaternary mixture adsorption**

An important and innovative study is the adsorption behavior of these systems in a multi-component environment. As mention before, wastewater presents multiple compounds that are able to be adsorbed by ACs. Thus, it is essential to study the sample as a mixture of the four model compounds for simulating the real situation and for exploring the interactions and the effect of the presence of one compound on the adsorption capacity of other ones.

<table>
<thead>
<tr>
<th>Pseudo-first order</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Protocatechuic acid (PA)</td>
<td>0.296</td>
<td>0.965</td>
<td>15.503</td>
<td>36.060</td>
</tr>
<tr>
<td>Vanillic acid (VA)</td>
<td>0.385</td>
<td>0.938</td>
<td>8.963</td>
<td>28.800</td>
</tr>
<tr>
<td>Syringic acid (SA)</td>
<td>0.401</td>
<td>0.960</td>
<td>13.142</td>
<td>35.600</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pseudo-second order</th>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Protocatechuic acid (PA)</td>
<td>0.095</td>
<td>0.994</td>
<td>36.100</td>
<td>36.060</td>
</tr>
<tr>
<td>Vanillic acid (VA)</td>
<td>0.290</td>
<td>0.997</td>
<td>28.200</td>
<td>28.800</td>
</tr>
<tr>
<td>Syringic acid (SA)</td>
<td>0.150</td>
<td>0.998</td>
<td>35.700</td>
<td>35.600</td>
</tr>
</tbody>
</table>

$q_e$, calc – compound remaining in solution at equilibrium calculated by the pseudo-second order kinetic model; $q_e$, exp – value obtained directly from the experimental data.

Note: Gallic acid data not included due to the occurrence of polymerization.
Adsorption kinetic data of the phenolic compounds with the AC sample from the quaternary mixture solution are presented in Figure 3.

The kinetic adsorption behavior of the AC changed when dealing with a quaternary mixture. In fact, except for gallic acid, the capacity adsorption is higher in single solutions than in the quaternary mixture, in particular for protocatechuic and syringic acids. This negative effect on the adsorptive capacity for syringic acid was also observed by García-Araya et al. (2003) and can be due to the competition between the four phenolic compounds for the active centers of the adsorbent surface when they are in the mixture.

For the quaternary mixture, the kinetic parameters estimated using the pseudo-second order kinetic model (which presented the best fitting) also support this conclusion. The estimated values are presented in Table 4.

Syringic acid presents the most improved kinetic parameters when compared to the single solution, but the adsorption uptake does not vary accordingly, suggesting the presence of a more complex structural effect.

The removal efficiencies of phenolic compounds obtained in the equilibrium conditions by the studied adsorbent are presented in Table 5. Considering that the polymerization of gallic acid is occurring instead of simple adsorption, the behavior of this compound will not be further discussed.

Removal efficiency is calculated by Equation (4).

\[
re = \frac{C_0 - q_{e,calc}}{C_0} \times 100
\] (4)

with these results, the competition between the compounds for the active centers of the AC surface when the phenolic acids are in mixture can be noticed, which causes the reduction of the removal efficiency in comparison to the single solutes.

Interestingly, the vanillic acid adsorption was not hindered. In fact, its uptake seems to be slightly raised. This preferential adsorption is probably a combination of two effects: its lower solubility in water and a smaller dimension when compared with syringic acid (see Figure S1, available with the online version of this paper). This feature may constitute an advantage for selective adsorption of this compound.

### Adsorption equilibrium isotherms

The isotherms were obtained using a lower solid/liquid ratio (5 mg mL\(^{-1}\)) in order to guarantee that there would not be a total removal of the compounds from solution, which would prevent a valid curve being obtained.

The isotherms are displayed in Figure 4.

As stated before, due to the occurrence of polymerization, the obtained adsorption isotherm for gallic acid could not be compared or correlated to the other compounds, and for that reason it is not presented. As individual compounds, the difference between the curves is very small. It seems that the behavior observed is related to the nature of the carbon rather than to differences between molecules. When the...

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**Table 4** | Pseudo-second order adsorption parameters for the different phenolic acids with AC-S in the quaternary mixture solution

<table>
<thead>
<tr>
<th></th>
<th>(k_2)</th>
<th>(R^2)</th>
<th>(q_e^{calc})</th>
<th>(q_e^{calc})</th>
<th>(q_e^{exp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protocatechuic acid (PA)</td>
<td>0.119</td>
<td>0.988</td>
<td>85</td>
<td>26.600</td>
<td>26.500</td>
</tr>
<tr>
<td>Vanillic acid (VA)</td>
<td>0.210</td>
<td>0.999</td>
<td>357</td>
<td>40.800</td>
<td>40.800</td>
</tr>
<tr>
<td>Syringic acid (SA)</td>
<td>0.350</td>
<td>0.999</td>
<td>526</td>
<td>38.700</td>
<td>38.800</td>
</tr>
</tbody>
</table>

Note: Gallic acid data not included due to the occurrence of polymerization.

**Table 5** | Removal efficiencies of studied phenolic compounds in single solutes and quaternary mixture onto activated carbon AC-S

<table>
<thead>
<tr>
<th></th>
<th>Single solutes</th>
<th>Quaternary mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protocatechuic acid (PA)</td>
<td>76</td>
<td>49</td>
</tr>
<tr>
<td>Vanillic acid (VA)</td>
<td>73</td>
<td>80</td>
</tr>
<tr>
<td>Syringic acid (SA)</td>
<td>81</td>
<td>67</td>
</tr>
</tbody>
</table>

Note: Gallic acid data not included due to the occurrence of polymerization.
adsorption occurs in a mixture of the four compounds, significant differences are observed. The value for the adsorption capacity reduces and the behavior is different for each compound. Clearly, the vanillic acid is the best adsorbed, the syringic acid seems to reach its adsorption capacity quite fast, and the protocatechuic acid exhibits a strange behavior probably due to a competition effect for the adsorption sites.

Two-parameter isotherm models, Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906), were applied to the experimental data. Among the various models available these are the most widely used.

The estimated values for equilibrium isotherm parameters with both models are presented in Table 6. The fitting of the models were made by nonlinear approach, using the solver tool in Excel®, and the fitting error was evaluated by the standard deviation parameter, $SE$ (Equation (5)):

$$SE = \sqrt{\frac{\sum (q_e - q_t)^2}{N}}$$

where $N$ is the number of experimental points, $q_e$ is the experimental adsorption capacity and $q_t$ is the theoretical adsorption capacity given by the model.

The fitting of the models revealed that it is difficult to establish which model better describes the isotherms’ behavior either as individual compounds or in a mixture solution. Although better determination values of $R^2$ are always obtained for the fitting of the Freundlich model, the difference in $R^2$ values between model fittings is not very big. This may suggest that these compounds present a mix behavior from mono to multi-layer formation during the adsorption process.

In any case, both models revealed some effect of the mixture adsorption. Comparing the theoretical monolayer adsorption capacity value obtained for the Langmuir model ($q_m$) in single and mixture solutions, all compounds show a decrease in this value, reflecting the competition effect for the adsorption sites. From the Freundlich computed values a competition effect is also observed; the $n$ value that conveys

Table 6 | Langmuir and Freundlich isotherm parameters for the adsorption of phenolic compounds with AC-S

<table>
<thead>
<tr>
<th>Compound</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single</td>
<td>Mixture</td>
</tr>
<tr>
<td>Protocatechuic acid (PA)</td>
<td>$K_L$ 0.034 0.013</td>
<td>$K_F$ 8.71 4.85</td>
</tr>
<tr>
<td>Vanillic acid (VA)</td>
<td>$K_L$ 0.026 0.035</td>
<td>$K_F$ 14.10 8.93</td>
</tr>
<tr>
<td>Syringic acid (SA)</td>
<td>$K_L$ 0.029 0.214</td>
<td>$K_F$ 8.67 15.61</td>
</tr>
</tbody>
</table>

Note: Gallic acid data not included due to the occurrence of polymerization.
a measure of the heterogeneity of the adsorption surface is higher for all the compounds in the mixture, suggesting that a decrease in adsorption affinity takes place.

**Desorption studies**

As mentioned before, wastewater presents multiple compounds to be adsorbed by ACs. Taking this into account, desorption studies were performed only with the quaternary mixture solution, in order to predict the behavior in a real situation.

The obtained results for desorption of each compound with three different solvents (ethanol, acetonitrile and water) are presented in Table 7. The values presented here correspond to a single extraction step, no successive steps were tested.

From these results, it seems that the used solvents cannot entirely remove the solutes from the adsorbent. Nevertheless, pure ethanol shows the best performance to recovery phenolic compounds in these conditions, with recovery percentages of almost 50%.

Solvent polarity plays a significant role in the desorption/recovery of the phenolic compounds from the AC sample. Ethanol polarity is the lowest among the three solvents (the dipole moment of ethanol is 1.69 D vs 1.85 D for water and 3.92 D for acetonitrile), and this property determines ethanol exhibiting the best performance. Galanakis et al. (2013) also observed that this group of phenolics have a solubility preference to solvents with intermediate polarity like ethanol rather than more polar solvents, which was related to the lower activity coefficient data of the compounds in ethanol. The solubility tendency can be explained by the stereochemistry of phenols (the polar and the non-polar fragment inside their molecules) and the intermolecular forces (mainly hydrogen bonds) that occurred between them and the solvents. The preference of phenols for ethanol can be attributed to their non-polar part and the aliphatic fragment of ethanol.

The recovery of protocatechuic acid seems to be difficult in these conditions for all the solvents (the values are very low compared with those of vanillic acid and syringic acid) but it was slightly better with water due to the high water solubility of this compound. Also, gallic acid is not desorbed with ethanol, which corroborates the hypothesis that a polymerization reaction occurs instead of adsorption.

As mentioned before, in the mixture solution vanillic acid presents the higher adsorption performance with removal efficiencies of 80%. Interestingly, the desorption results demonstrate that is possible to desorb a relatively high amount (43%) of vanillic acid from the adsorbent. This scenario may represent a possibility for selective recovery of vanillic acid. This outcome may afford an interesting contribution to the valorization of the wastewater from the cork industry using low-cost technologies. Thinking of the possibility of the extraction of phenolic compounds and their antioxidant potential, these compounds could be used to replace synthetic antioxidants in other industries that crave for antioxidants, like food or cosmetic industries.

**CONCLUSIONS**

Single and competitive liquid-phase adsorption studies of four phenolic derivative compounds frequently present in cork wastewaters were carried out using a synthesized mesoporous carbon as adsorbent.

The results evidenced the competition for the active centers of the AC by the four phenolic compounds with a marked influence on the adsorption capacities. The capacity for adsorption is higher in single solutions than in the quaternary mixture, particularly for protocatechuic and syringic acids. In addition, it was hypothesized that the polymerization of gallic acid is occurring under these experimental conditions and the decrease in compound concentration was not exclusively due to an adsorption process but also due to the polymerization reaction. In single component aqueous solution, the adsorption trend was found to be syringic acid > protocatechuic acid > vanillic acid. Nevertheless, the achieved removal efficiencies for protocatechuic acid, vanillic acid and syringic acid in the quaternary mixture solution were 49%, 80% and 67%, respectively. Concerning the desorption experiments, from the three solvents tested, ethanol presented the best performance in the recovery of the studied phenolic compounds, particularly for vanillic and syringic acid.

The global adsorption-desorption results become relevant thinking in the treatment of cork wastewaters, since the adsorption of phenolic acids on AC can be an alternative technology to reduce the presence of these recalcitrant compounds. Nevertheless, the conditions for desorption experiments should be

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Table 7 | Desorption of phenolic compounds from AC-S using different solvents

<table>
<thead>
<tr>
<th>Desorption [%]</th>
<th>Ethanol</th>
<th>Water</th>
<th>Acetonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallic acid (GA)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Protocatechuic acid (PA)</td>
<td>13</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Vanillic acid (VA)</td>
<td>43</td>
<td>8</td>
<td>38</td>
</tr>
<tr>
<td>Syringic acid (SA)</td>
<td>49</td>
<td>10</td>
<td>45</td>
</tr>
</tbody>
</table>
studied, in order to improve the extractable compounds. The possibility of using the extractable compounds obtained from natural and biorenewable resources to replace synthetic antioxidants is an important issue to valorize the wastewater from the cork industry and its economy.

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