APPLICATION OF DOEHLERT DESIGN TO OPTIMISE THE PREPARATION OF A NEW ACTIVATED CARBON

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Introduction

Previous papers1-3 have reported that olive-waste cake is an excellent precursor for the production of activated carbon. Indeed, these activated carbons have proved more effective to adsorb pollutants contained in drinking water and to decolorize sugar syrup than have some commercial activated carbons.

The main objective of the present paper is to obtain activated carbons from olive-waste cakes, which are abundant waste materials in Morocco and Spain, by means of a one-step method, which combines the above two steps (carbonization and activation) in one step, consisting of the pyrolysis of the raw material at high temperature in a steam flow.

Once the activated carbons were obtained, they were characterized, and we investigated the optimal experimental conditions required to prepare activated carbons suitable for use as adsorbents to remove pollutants from water. These results were compared with those obtained for both activated carbons obtained by the two-step method and a commercial activated carbon used by the National Office of Drinking Water (ONEP) in Morocco.

Experimental

Raw material. Olive-waste cakes were obtained from olive oil processing.

Activated carbon preparation. The activation of the raw material was done in a thermolyne silica electric oven. The steam flow was 140 cm³ min⁻¹. The activation temperatures were between 750°C and 850°C and the activation times between 30 and 80 min.

Adsorption tests from aqueous solutions. The adsorption capacities of the carbon samples for methylene blue (Y3) and iodine (Y4) were calculated applying the Langmuir equation.

The methylene blue were dosed spectrophotometrically at 680 nm. The iodine concentrations were determined using the sodium thiosulfate volumetric method.

Response Surface Methodology: The analysis was achieved by response surface methodology, which gave satisfactory results.

Each response (Y) can be described by a second order model adequate to predict responses in all experimental regions:

\[ Y = a_0 + a_1X_1 + a_2X_2 + a_{11}X_1^2 + a_{22}X_2^2 + a_{12}X_1X_2 \]

where \( X_1 \) is the coded variable related to the natural variable \( U_1 \) (activation temperature) and \( X_2 \) is related to the natural variable \( U_2 \) (activation time). Values for the coefficients “a” are chosen so that the model fits the experimental data as closely as possible.

Results and discussion

The responses studied were the total yield in the activated carbon preparation (Y1), the capacity of the activated carbon to adsorb methylene blue (Y3) and iodine (Y4). The choice of these parameters was based on their characteristics. The methylene blue test can be used to predict organic compound adsorption and is a simple method for screening for a specific carbon in water treatment. The iodine adsorption test indicates the total surface area of the carbon and is also a performance indicator for water treatment applications.

Response analysis and interpretation. Following the model established for each response, we can represent graphically the surface of the corresponding responses. The values of the coefficients provide information on the influence of the factors and the curves obtained show the extreme, or at least privileged, directions (zones of interest of the factors).

Total yield (Y1). Analysis of this response (Figure 1) showed that at low activation temperatures, the increase in activation time from 30 to 80 min induces little variation in the total yield. In contrast, at high activation temperatures, the increase in activation time produced a major reduction in yield. These results indicate that the gasification rate of olive-waste cakes with steam is very low at low temperatures (around 750 ºC) and high at high temperatures (around 850 ºC).

Adsorption capacity of methylene blue (Y3) and iodine (Y4). As shown in Figure 2, the capacity of the carbon samples to adsorb methylene blue (Y3) and iodine (Y4) is highly dependent on the activation temperature (X1) and time (X2) used to prepare the carbon samples.
The effect of activation time on these characteristics is noticeable only at high activation temperatures, especially in the case of methylene blue adsorption. Thus, at activation temperatures below 770 °C the activation time did not affect the capacity of the carbon sample to adsorb this compound, whereas at high activation temperatures, a small increase in activation time brings about a major increase in methylene blue adsorption. At high temperatures, the activation reaction of the olive-waste cakes may take place rapidly producing a development of the porosity of the activated carbon obtained, and, therefore, an increase in its capacity to adsorb methylene blue (Figure 2.a) and iodine (Figure 2.b).

Optimization. The main objective of the optimization was to determine the optimal conditions of activated temperature and residence time for the preparation of active carbons from olive waste cakes in one step. Because this material will be used in the process of drinking water treatment, it was necessary to establish domains of variation of each response in relation to the activate carbon characteristics required. From an economical point of view, the total yield of the process (Y1) is a positive parameter. The total yield of 10 - 20% is compares well with the average yield of 8% in the industrial sector.

With respect to quality characteristics (Y2 and Y3), we established a range of variation for these two responses of 180 - 450 mg/g for methylene blue and 900 - 1450 mg/g for iodine.

The optimization of a process depends on a number of constraints. In the present study, the objective was to enhance the yield in the manufacture of an activated carbon of given characteristics. These requirements cannot be differentiated in the interest zones of the factors. Thus, it is difficult to optimise all responses under the same conditions because the interest region of factors is different. Indeed, when Y1 increases, the other two responses (Y2 and Y3) decrease. This situation led us to seek a compromise (domain depicted in Figure 3) between the quality and quantity of the active carbon prepared. It can be observed that there is an extensive range of both temperature and time of activation in which activated carbons with the required characteristics can be obtained.

The optimal point indicated by the model corresponds to a temperature of 785°C and a residence time of 85 min (Figure 3). The response values of the carbon calculated from the model for these experimental conditions are given in Table 3 (Sample AC-1). In order to test the validity of the results, an activated carbon sample (optimal activated carbon) was obtained at these experimental conditions following the one step method (Sample AC-1) and its characteristics (Y1, Y2 and Y3), were experimentally determined (Table 3). The experimental values of these parameters show a good agreement with those calculated from the model.

Table 3 also shows the calculated and experimental response values of the “optimal” activated carbon obtained by two steps (Sample AC-2) and the experimental response values of the activated carbon AC-ONEP. Comparing the responses of these “optimal” activated carbons, it is clear that carbon obtained by the two-step method has a greater capacity to adsorb methylene blue (Y2) and iodine (Y3) than those obtained by the one-step method. Both of these activated carbons showed higher values of Y2 and Y3 than those of the commercial activated carbon AC-ONEP.

Table 3. Calculated and experimental response values corresponding to a compromise between Y1, Y2 and Y3 for the “optimal” activated carbons

<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Responses</th>
<th>Y1 (%)</th>
<th>Y2 (mg g⁻¹)</th>
<th>Y3 (mg g⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>AC-1</td>
<td>Calculated</td>
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<td>288</td>
<td>1116</td>
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<tr>
<td></td>
<td>Experimental</td>
<td>15.1</td>
<td>268</td>
<td>1125</td>
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<tr>
<td>AC-2</td>
<td>Calculated</td>
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<td>1422</td>
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<tr>
<td></td>
<td>Experimental</td>
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<td>426</td>
<td>1390</td>
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<tr>
<td>AC-ONEP</td>
<td>Experimental</td>
<td>250</td>
<td>1100</td>
<td></td>
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REFERENCES