



Optimization of conditions for the preparation of activated carbons from olive-waste cakes

A. Baçaoui^a, A. Yaacoubi^a, A. Dahbi^a, C. Bennouna^a, R. Phan Tan Luu^b,
F.J. Maldonado-Hodar^c, J. Rivera-Utrilla^{c,*}, C. Moreno-Castilla^c

^aDepartment of Chemistry, Faculty of Science-Semlalia, University of Cadi Ayyad, B.P. 2390, Marrakech, Morocco

^bLaboratoire de Méthodologie de la Recherche Expérimentale, Centre Universitaire de Saint Jérôme, Université d'Aix-Marseille III, Avenue Escadrille Normandie Niemen, 13397, Marseille cedex 13, France

^cDepartamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

Received 13 May 1999; accepted 19 May 2000

Abstract

An experimental design (Doehlert matrix) has been drawn up to optimize the experimental conditions of the preparation of activated carbon from olive-waste cakes. A series of activated carbons have been prepared by physical activation with steam. Adsorption of N₂ (77 K), CO₂ (273 K) and mercury porosimetry experiments have been carried out to determine the characteristics of all carbons prepared. Adsorption of iodine and methylene blue was used as a primary indicator of the adsorption capacity of these carbons. The experimental response varied between: 13–27% for the total yield (Y_1), 115–490 mg/g for the adsorption of methylene blue (Y_2), 741–1495 mg/g for the adsorption of iodine (Y_3), 514–1271 m²/g for the BET surface area (Y_4), 0.225–0.377 cm³/g for the micropore volume (Y_5), 0.217–0.557 cm³/g for the volume of pores with a diameter greater than 3.7 nm (Y_6) and 31.3–132 m²/g for the external surface area (Y_7). The results obtained were exploited using response surface methodology. These responses have been represented and studied in all experimental regions of activation time and activation temperature, the most influential factors in activated carbon preparation. Optimization to obtain activated carbons with textural characteristics suitable to use in water treatment has been carried out. The optimal activated carbon is obtained when using 68 min as activation time and 1095 K as activation temperature. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: A. Activated carbon; B. Activation; C. Modeling; D. Porosity, Textures

1. Introduction

Activated carbon is widely used for adsorption of pollutants from gaseous and liquid phases. In Morocco, the production of olive-waste cakes is estimated to exceed 100,000 t/year and these residues are incinerated. In this work, we focus on the preparation of activated carbon from olive-waste cakes. This is carried out via physical activation (carbonization + activation) using the oxidizing capacity of steam at high temperature. This activated carbon could be used in drinking water purification and water treatment.

The preparation of activated carbon is influenced by

many factors. For this reason a preliminary study on the effect of these factors on the preparation was carried out in order to determine the most important ones and their regions of interest. This method has been described in detail elsewhere [1,2]. The most influential factors were found to be activation time (U_1) and activation temperature (U_2). Thus, in the present work, we prepared a series of activated carbons from olive-waste cakes with values of U_1 and U_2 included in the suitable range [1,2]. Different characteristics of these activated carbons were analysed as a function of these two factors. A Doehlert matrix [3] was used to represent the responses of the two factors in all the experimental regions studied. The choice of the Doehlert matrix is justified by a number of advantages such as: (i) the possibility of presenting a uniform distribution of experimental points in the space studied, (ii) ability to explore the whole of the domain, (iii) usefulness of

*Corresponding author. Tel.: +34-958-248-523; fax: +34-958-248-526.

E-mail address: jriversa@goliat.ugr.es (J. Rivera-Utrilla).

interpolating the response, (iv) possibility of adding new factors without altering the quality of the matrix.

Characterization of the activated carbons has been mainly focused on determinations of surface area and pore size distribution. Additional information on their pore size distribution was obtained by comparing the adsorption characteristics for different adsorbates such as methylene blue and iodine. The choice of these molecules is justified by their properties. Thus, the mesopores of carbon are often studied by methylene blue adsorption and this also serves as a model compound for adsorption of organic contaminants from aqueous solution [4]. The iodine molecule gives information on the surface area contributed by pores larger than 1 nm.

In the present study, the optimal experimental conditions required to obtain adequate activated carbons with a suitable porosity for use as adsorbents in aqueous solutions are determined. Thus, a modelling technique is applied to relate the experimental conditions of the activated process with properties of activated carbons.

2. Experimental

A series of seven activated carbons were prepared for the experiment. The preparation procedure, characterization and methodology of experimental design are described below.

2.1. Raw material

Olive-waste cakes were obtained from olive oil processing. This residue was extracted a second time by hexane in order to eliminate the remaining oil. Because of the nature of the separation process of the olive-waste cakes (traditional method), this raw material contained a mixture between pulp and olive stone, with a particle size between 0.1 and 10 mm.

2.2. Carbonization/activation

Carbonization was carried out in a 125-cm³ Prolabo stainless steel autoclave. A known amount of olive-waste cakes (40 g) was introduced into the reactor which was then heated to the desired temperature (673 K) and maintained for 1 h at the final temperature in a nitrogen flow.

The activation processes were carried out in a thermolyne silica electric oven with a temperature control device linked to a thermocouple; a silicon reactor and a steam generator were placed at the entrance of the reactor. Details of this unit and the operating procedure are described elsewhere [2]. The activation times were between 30 and 70 min and the activation temperatures were between 1023 and 1123 K. The domains of variation of

these factors are defined on the basis of preliminary results [2].

After activation, the activated carbons were boiled for 30 min in distilled water, dried, ground and sifted to obtain a powder with a particle size smaller than 45 µm. This powder was then dried at 383 K until constant weight and kept in a hermetic bottle for future tests.

2.3. Characterization

In order to characterize the activated carbons the following experiments were carried out.

2.3.1. Adsorption tests from aqueous solutions

The adsorption isotherms of methylene blue (C₁₆H₁₈ClN₃S) and iodine on the activated carbon samples were obtained by adding 0.2 g of carbon to flasks containing 100 cm³ of aqueous solutions with different initial known concentrations of either methylene blue or iodine. These flasks were kept in a thermostat shaker bath at 293 K. When the equilibrium time (determined by kinetic tests; 2 h for iodine and 4 h for methylene blue) was reached, the suspensions were filtered and the equilibrium concentrations were determined. In the case of methylene blue, the concentrations were determined spectrophotometrically at the maximum absorbance wavelength (680 nm). The iodine concentrations were determined using the sodium thiosulfate volumetric method. The adsorption capacities of the carbon samples for methylene blue (Y₂) and iodine (Y₃) were calculated by applying the Langmuir equation [5].

2.3.2. Gas adsorption test

The samples were characterized by N₂ and CO₂ adsorption at 77 and 273 K, respectively. The BET equation was applied to the N₂ adsorption isotherms, from which the nitrogen surface area (Y₄) was obtained using a value of 0.162 nm² for the molecular area of N₂ at 77 K. The Dubinin–Raduskevich equation was applied to the CO₂ adsorption isotherms to obtain the micropore volume (Y₅). Details of the experimental method and calculation are given elsewhere [6].

2.3.3. Mercury porosimetry test

These experiments were carried out with a Quantachrome, Autoscan 60, equipment up to a final pressure of 4200 kg cm⁻², obtaining the pore volume of pores with a diameter greater than 3.7 nm (Y₆) and the external surface area (Y₇).

2.4. Methodology of experimental design

Using the response surface methodology [7–10], it is possible to systematically study many processes. This is a single-factor-at-a-time method which studies the phenomenon by varying one factor while keeping all other

Table 1
Doehlert's experimental matrix and the corresponding experimental conditions

No. exp.	Time (X_1)	Temperature (X_2)	Time (U_1) (min)	Temperature (U_2) (K)
1	+1	0	70	1073
2	-1	0	30	1073
3	0.5	0.866	60	1123
4	-0.5	-0.866	40	1023
5	0.5	-0.866	60	1023
6	-0.5	0.866	40	1123
7	0	0	50	1073

conditions constant. However, the effect of each factor is not necessarily additive. It is, therefore, necessary to take into account the influence of each factor and the interaction between these factors which may be synergistic or antagonistic [7].

As indicated in the Introduction, the most influential factors on the characteristics of activated carbons are activation time (U_1) and activation temperature (U_2). A Doehlert matrix [3] was used to represent the responses studied in all experimental regions of these two factors. The factors are given in the form of coded variables (X_i) with no units in order to permit comparison of factors of different natures. The transformation of natural variables (U_i) into coded corresponding variables (X_i) is made on the basis of the following equation:

$$X_{ij} = \frac{U_{ij} - U_j^0}{\Delta U_j}$$

where X_{ij} is the value of coded variable j in experiment i ; U_{ij} is the value of natural variable j in experiment i ; U_j is the value of natural variable j in the center of the domain of interest; it corresponds to $X_j = 0$; ΔU_j is the variation of the natural variable j corresponding to a variation of the coded variable j equal to +1.

Doehlert's experimental matrix and the corresponding experimental conditions (factors) are given in Table 1.

Table 2
Experimental responses^a

No. exp.	Conditions	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_7
1	70/1073	18	373	1261	1201	0.298	0.557	132.0
2	30/1073	27	115	796	514	0.249	0.238	31.3
3	60/1123	13	490	1495	1271	0.377	0.456	117.0
4	40/1023	27	121	741	687	0.225	0.217	51.3
5	60/1023	23	197	996	700	0.272	0.303	59.8
6	40/1123	15	364	1017	1127	0.317	0.389	102.0
7	50/1073	24	285	930	1025	0.229	0.294	73.4

^a Y_1 , total yield (%); Y_2 , methylene blue adsorption capacity (mg/g); Y_3 , iodine adsorption capacity (mg/g); Y_4 , BET surface area (m²/g); Y_5 , micropore volume (cm³/g); Y_6 , volume obtained by mercury porosimetry ($\phi > 3.7$ nm) (cm³/g); Y_7 , external surface area (m²/g). Conditions: activation time/activation temperature (min/K).

This combination is chosen in such a way that the factors are not correlated with each other and that modelling can be done with uniform accuracy over the whole parameter space [10]. This analysis was achieved by response surface methodology which gave satisfactory results [11,12]. Each response (Y) can be described by a second order model adequate for predicting the 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 time); X_2 is related to U_2 (activation temperature); a_0 is the intercept term, a constant that corresponds to the response when X_i is zero for each factor; a_1 determines the influence of activation time; a_2 determines the influence of activation temperature; a_{12} is the interaction effect between the activation time and activation temperature; a_{11} and a_{22} can be regarded as a curve 'shape' parameter.

For each response (Y_i), the coefficients (a_i, a_{ij}) of the postulated model were calculated on the basis of the experimental responses by least squares regression using the NEMROD [13] software (New Efficient Methodology for Research using Optimal Design). The Doehlert matrix consists of N experiments with $N = K^2 + K + 1$, where K is the number of variables studied. In this case $K = 2$ and, therefore, the matrix was comprised of seven experiments (Table 2). These seven points are scattered uniformly in the space of the coded variables (X_i) and are located in the corners of a hexagonal polyhedron.

3. Results and discussion

The experimental responses studied were: total yield (Y_1), adsorption of methylene blue (Y_2), adsorption of iodine (Y_3), surface area (Y_4), micropore volume (Y_5), volume of pores with diameter greater than 3.7 nm (Y_6) and external surface area (Y_7). The values obtained experimentally for these parameters of the carbon samples

are given in Table 2. The experiments were carried out in a random order to minimise the effect of systematic errors.

3.1. Response analysis and interpretation

For each response, the coefficients of the postulated model, calculated on the basis of the experimental responses (Table 2) and the isoresponse curves, drawn in the experimental region, were used to interpret the results [14].

3.1.1. Total yield (Y_1)

The total yield is calculated according to the equation: $R_t = R_c \cdot R_a$, where R_c is the carbonization yield and R_a is the activation yield.

Examination of the total yield isoresponse curves given in Fig. 1a shows that the total yield in carbon (R_t or Y_1) varies between 13 and 26%. These high values are due, to a large extent, to the nature of olive-waste cakes that are very rich in lignin (36% lignin, 19% hemi-celluloses and 18% of cellulose) [2], which favors the production of carbon during carbonization to the detriment of gas and condensate. The total yield in carbon (Y_1) can be described as follows:

$$Y_1 = 22.50 - 4.00X_1 - 6.35X_2 - 4.00X_2^2 + 1.15X_1X_2.$$

The correlation between the theoretical and experimental responses, calculated by the model, is satisfactory ($r^2 = 0.969$) and the accuracy, given by the model, of 2.2%. Analysis of the results shows, as expected, that the activation temperature (X_2) has a highly negative influence ($a_2 = -6.35$) on yield (Y_1), compared with other factors. Indeed, the increase in temperature (X_2 increase) quickens the gasification reactions of carbon and, therefore, the attack of the amorphous components which obstruct the pores, bringing about a decrease in the total carbon yield (R_t) (Fig. 1b). The activation time (X_1) also has a negative influence ($a_1 = -4.00$). A maximum yield is obtained at low activation time and temperature (Fig. 1a).

3.1.2. Adsorption of methylene blue (Y_2)

The validity of the model chosen is justified by the coefficient of correlation between the maximum capacities of adsorption calculated by the model and those which are experimentally determined. The coefficient (r^2) obtained in this case is 0.991, and the accuracy, given by the model, is 5.8%

$$Y_2 = 302.50 + 119.7X_1 + 154.7X_2 - 58.5X_1^2 + 6.8X_2^2 + 28.9X_1X_2.$$

The effects of the activation temperature ($a_2 = 154.7$) and the activation time ($a_1 = 119.7$) are more important than their interaction ($a_{12} = 28.9$). The increase in temperature (X_2 increase) entails an opening and enlargement of the pores, which enhances the adsorption of methylene blue (Y_2) (Fig. 2b). Indeed the methylene blue molecule has a minimum molecular cross-section of about 0.8 nm, and it has been estimated that the minimum pore diameter it can enter is 1.3 nm [15]. Therefore, it can only enter the largest micropores, but most of it is likely to be adsorbed in mesopores [16]. Thus, the methylene blue test can be used to predict organic compound adsorption (microcystin, olive waste, color bodies, etc.) and to provide a simple method for screening for a specific carbon in water application. In Morocco, the minimum required (for any activated carbon used in drinking water treatment) is 180 mg g⁻¹. Therefore, higher values than the conditions of U_1 and U_2 described by the response curve number 3 in Fig. 2a are required.

3.1.3. Adsorption of iodine (Y_3)

The iodine molecule, compared with methylene blue, is greatly adsorbed due to its smaller size permitting its penetration into micropores. The coefficient of correlation (r^2) between the maximum capacities of adsorption calculated by the model and those determined experimentally in this case is 0.970, with an accuracy of 2.1%

$$Y_3 = 950.0 + 277.2 X_1 + 223.7X_2 + 78.5X_1^2 + 123.5X_2^2 + 128.7X_1X_2.$$

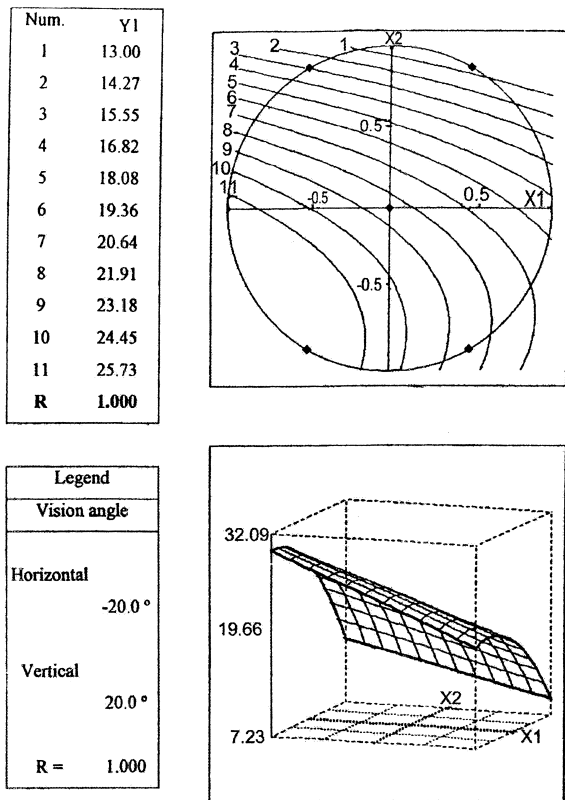


Fig. 1. Variation of total yield (Y_1) versus (X_1, X_2).

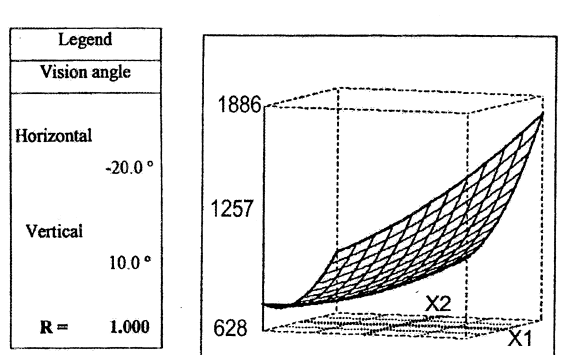
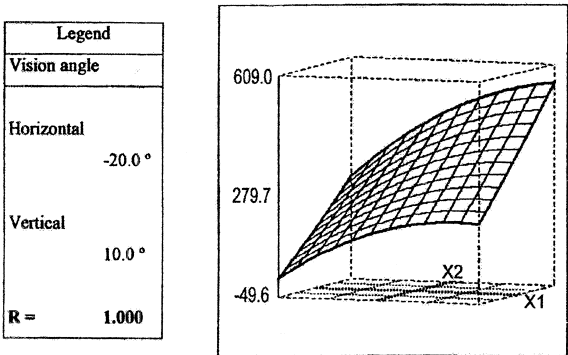
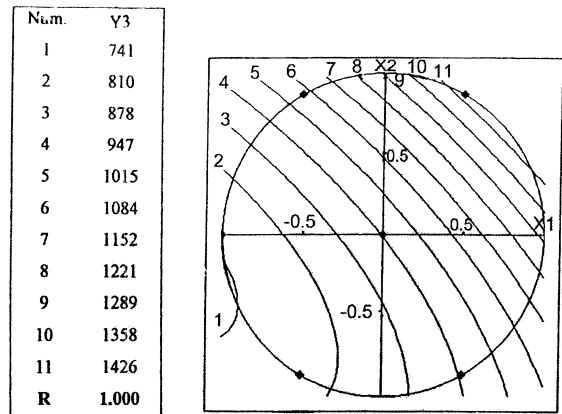
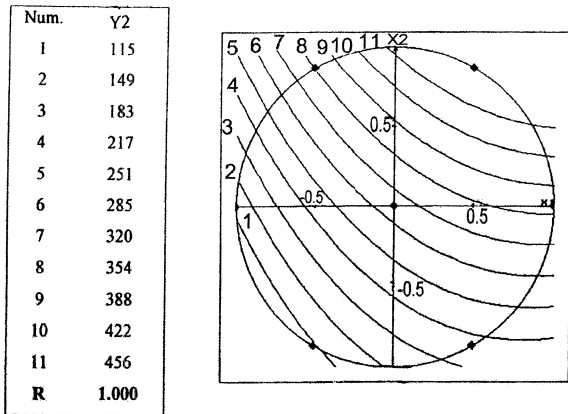


Fig. 2. Variation of the methylene blue adsorption capacity (Y_2) versus (X_1, X_2).

Fig. 3. Variation of the iodine adsorption capacity (Y_3) versus (X_1, X_2).

As in the case of response Y_2 , it is clear that the activation temperature ($a_2 = 223.7$) and activation time ($a_1 = 277.2$) have a strong impact on development of the porous texture during activation and can, therefore, influence the adsorption behavior of carbons. It seems that more micropores are being opened with the increased activation temperature (X_2 increase) and activation time (X_1 increase) without any decrease in the adsorption of iodine in the domain studied (Fig. 3b).

The iodine adsorption test is also a performance indicator for water treatment applications. The minimum iodine number required for carbons to be used as adsorbents in aqueous solutions is 900 mg g^{-1} . Therefore, to obtain this kind of carbon, conditions beyond those corresponding to isoresponse curve number 4 in Fig. 3a are required.

3.1.4. Surface area (Y_4)

This response is described by the following equation:

$$Y_4 = 942.0 + 255.2X_1 + 291.9X_2 - 84.5X_1^2 + 33.8X_2^2 + 75.6 X_1X_2$$

with a coefficient of correlation (r^2) of 0.885. The accuracy

given by the model is 6.0%. Analysis of this response shows that the direct effects of activation time ($a_1 = 255.2$) and activation temperature ($a_2 = 291.9$) are positive and are more important than their interaction ($a_{12} = 75.6$). The apparent surface area (Y_4) increased with increases in both X_1 and X_2 (Fig. 4b) due to the fact that both micropores and larger pores are developed, presumably by widening of micropores to mesopores, while more micropores are being opened [17].

3.1.5. Micropore volumes (Y_5)

For this response, the coefficient of correlation (r^2) is 0.892. The accuracy given by the model is 4.0%

$$Y_5 = 0.255 + 0.034X_1 + 0.057X_2 + 0.019X_1^2 + 0.051X_2^2 + 0.008X_1X_2.$$

Temperature has a strong positive effect ($a_2 = 0.057$) in this response. Activation time also has a positive effect ($a_1 = 0.034$). The increase in activation temperature from 1023 to 1123 K and the activation time from 30 to 70 min increases the micropore development.

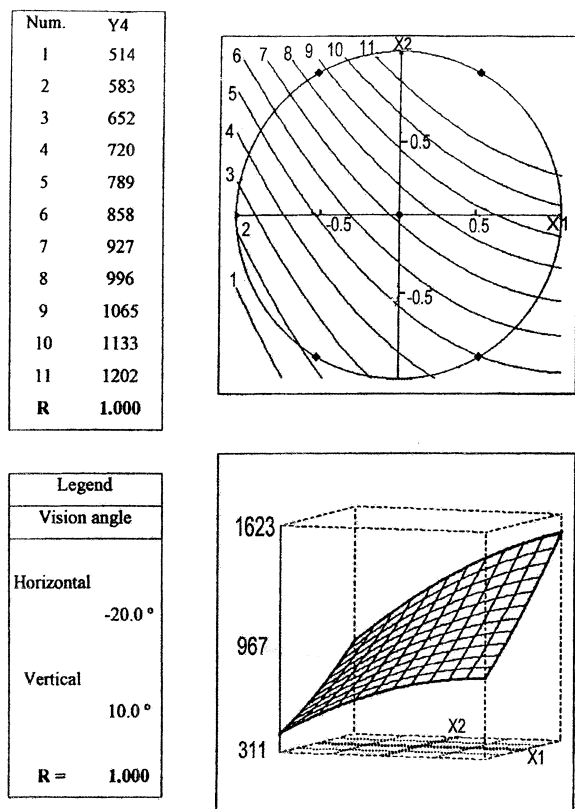


Fig. 4. Variation of BET surface area (Y_4) versus (X_1, X_2).

3.1.6. Pore volume obtained by mercury porosimetry (Y_6)

This response represents addition of the volumes corresponding to the fraction of mesopores ($\phi > 3.7$ nm) and macropores. It is described by the following equation:

$$Y_6 = 0.286 + 0.131X_1 + 0.094X_2 + 0.112X_1^2 + 0.037X_2^2 - 0.011X_1X_2$$

with a coefficient of correlation (r^2) of 0.951 and an accuracy, given by the model, of 9.6%. In general, a continuous increase in meso- and macropore volume with the increase in activation temperature and activation time was detected. This results from the conversion of micropores. Steam was found to produce a wide range of pore size distribution with a large development of mesoporosity and macroporosity, both of which are useful for adsorption transport routes to the micropores [18].

3.1.7. External surface area (Y_7)

The response function corresponding to the external surface area (surface area corresponding to pores with a diameter greater than 3.7 nm) is described by the following equation:

$$Y_7 = 68.4 + 37.5X_1 + 31.2X_2 + 13.3X_1^2 + 14.4X_2^2 + 3.8X_1X_2$$

with a coefficient of correlation (r^2) of 0.877 and an accuracy given by the model of 17%. The increase in activation temperature ($a_2 > 0$) and activation time ($a_1 > 0$) increases the external surface area (all the activated carbons prepared present a burnt-off between 60 and 87%, which favors an important external surface area).

As mentioned above, the parameter a_{12} represents an indication of the interactions between activation time and activation temperature. In practice, the observed response is not necessarily additive, in that not all factors are independent. In this study, however, we find that a_{12} is much smaller than a_1 and a_2 suggesting that within the region of variability studied there is very little interaction between these factors.

3.2. Optimization

Finally, because the main objective of this paper is to determine the experimental time and activation temperature required to prepare activated carbons from olive-waste cakes, suitable for their efficient employment as adsorbents to remove pollutants from water, the first step was to establish the values of yield and the textural characteristics of an ideal activated carbon for adsorption from aqueous solutions. Then, using the above methodology for experimental design, the ranges of activation time and activation temperature required to obtain this ideal carbon were determined. Thus, this activated carbon should have a high total yield (10–20%) for economical viability, and a large surface area (1000–1300 m² g⁻¹). Since the micropores are inaccessible to most water pollutants, in order for a large fraction of the surface area to be accessible to the pollutant molecules, its micropore volume must not be too large (0.250–0.400 cm³ g⁻¹), on the contrary, this ideal carbon should have a high meso- and macropore volume (pore volume with diameter greater than 3.7 nm) in between 0.400 and 0.600 cm³ g⁻¹ and a large external surface area (90–150 m² g⁻¹). Values of methylene blue and iodine adsorption should be those required in the market to activate carbons used in the water treatment field (180–500 and 900–1500 mg g⁻¹, respectively). According to the calculation method used, to obtain this ideal carbon with the above characteristics, the activation process should be carried out in the domain delimited in Fig. 5.

To optimize all responses under the same conditions is difficult because the interest region of factors are different, thus, when Y_1 increases all the other responses decrease; therefore, in order to find a compromise, we have resorted to the 'function of desirability' using the software NEMROD. The optimal point indicated by the model corresponds to an activation time of 68 min and an activation temperature of 1095 K. In order to test the validity of this method, we have prepared an activated carbon sample under the above

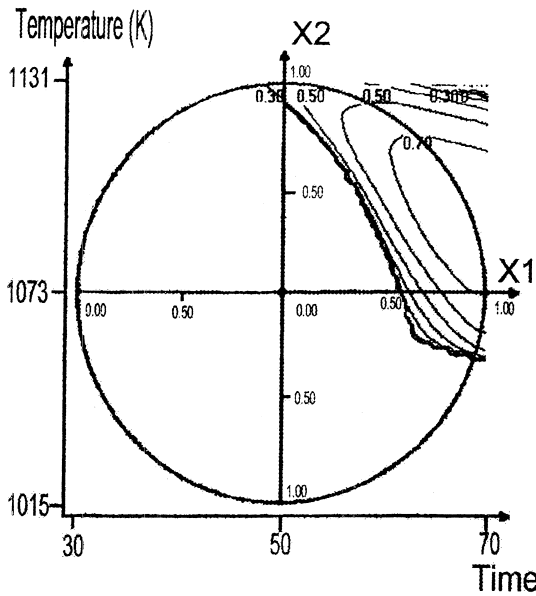


Fig. 5. Variation of the function of desirability as a function of both activation temperature and activation time.

experimental conditions. The characteristics of this sample are shown in Table 3 together with those calculated from the model. It is important to note the good agreement found between the experimental values and those calculated from the model.

Comparing the textural characteristics of the activated carbons obtained from olive-waste cakes, studied in the present paper, with those of activated carbons obtained from other agricultural by-products (olive stones, almond shells, peach stones) studied in previous papers [6,19], it is observed that they have similar values. Nevertheless, the activation time required in the case of olive-waste cakes is much lower.

4. Conclusions

Olive-waste cakes are a good precursor for the production of activated carbons with interesting characteristics (great adsorption capacity and high surface area).

The response surface methodology using Doehlert's matrix is an appropriate tool to study optimization of the

activation process to prepare activated carbons to be used in a given technological process.

In the present paper, this optimization was carried out to obtain activated carbons from olive-waste cakes with textural characteristics suitable for use in water treatments. The experimental parameters analyzed were activation time and activation temperature and the optimal values obtained were 68 min and 1095 K, respectively.

Acknowledgements

The authors wish to acknowledge Agencia Española de Cooperación Internacional and Universidad de Granada for financial support.

References

- [1] Baçaoui A, Yaacoubi A, Dahbi A, Bennouna C, Ayele J, Mazet M. Characterization and utilisation of a new activated carbon obtained from Moroccan olive wastes. *J Water SRT-Aqua* 1998;47(2):68–75.
- [2] Baçaoui A, Yaacoubi A, Dahbi A, Bennouna C, Ayele J, Mazet M. Activated carbon production from moroccan olive wastes. Influence of some factors. *Environ Technol* 1998;19:1203–12.
- [3] Doehlert DH. Uniform shell design. *Appl Statist* 1970;19(3):231–9.
- [4] Lussier MG, Shull JC, Miller DJ. Activated carbon from cherry stones. *Carbon* 1994;32(8):1493–8.
- [5] Stumm W, Morgan JJ. In: 2nd ed, *Aquatic chemistry*, New York: Wiley, Inter-Science, 1981.
- [6] Rivera-Utrilla J, Utrera-Hidalgo E, Ferro-Garcia MA, Moreno-Castilla C. Comparison of activated carbons prepared from agricultural raw materials and Spanish lignites when removing chlorophenols from aqueous solutions. *Carbon* 1991;29:613–9.
- [7] Box GEP, Hunter WG, Hunter JS. In: *Statistics for experimenters, an introduction to design, data analysis and model building*, New York: Wiley, 1978, pp. 306–604.
- [8] Lange T, Köpsel R, Kuchling T, Klose E. Hydrogenation behaviour of a German brown coal. 1. Influence of pressure, temperature and reaction time. *Fuel* 1989;68:361–5.
- [9] Bennoua C, Salhi N, Bitar H, Sergent M, Phantan Luu R. Pyrolysis optimization of tarfaya (Morocco) oil shale. *Química Analítica* 1997;16:67–73.
- [10] Wächter R, Cordery A. Response surface methodology modeling of diamond-like carbon film deposition. *Carbon* 1999;37:1529–37.

Table 3

Calculated and experimental responses corresponding to the optimal activated carbon

Response	Y_1 (%)	Y_2 (mg/g)	Y_3 (mg/g)	Y_4 (m ² /g)	Y_5 (cm ³ /g)	Y_6 (cm ³ /g)	Y_7 (m ² /g)
Calculated	16.2	433	1422	1249	0.334	0.540	130
Experimental	15.8	426	1390	1145	0.311	0.512	125

- [11] Herath B, Albano C. Optimization of a mechanical peat dewatering process by using multivariate data analysis. *Fuel* 1989;68:354–60.
- [12] Mathieu D. Contribution de la methodologie de la recherche experimentale a l'etude des relations structure-activite, France: Université D'aix-Marseille, 1981, Ph.D. thesis.
- [13] Mathieu D, Phan Tan Luu R. Software NEMROD, France: Université d'Aix-Marseille III, 1980.
- [14] Dumenil G, Mattei G, Sergent M, Bertrand JC, Laget M, Phan Tan Luu R. Application of a Doehlert experimental design to the optimization of microbial degradation of crude oil in sea water by continuous culture. *Appl Microbiol Biotechnol* 1988;27:405–9.
- [15] Barton SS. The adsorption of methylene blue by active carbon. *Carbon* 1987;25:343–50.
- [16] Warhurst AM, McConnachie GL, Pollard SJT. Characterization and application of activated carbon produced from moringa oleifera seed husks by single-step steam pyrolysis. *Water Res* 1997;31(4):759–66.
- [17] Wigmans A. Industrial aspects of production and use of activated carbons. *Carbon* 1989;27:13–22.
- [18] Warhurst AM, McConnachie GL, Pollard SJT. The production of activated carbon for water treatment in Malawi from the waste seed husks of moringa oleifera. *Water Sci Technol* 1996;34(11):177–84.
- [19] Ferro-García MA, Rivera-Utrilla J, Rodríguez-Gordillo J, Bautista-Toledo I. Adsorption of zinc, cadmium and copper on activated carbons obtained from agricultural by-products. *Carbon* 1988;26:363–73.