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Optimization of activated carbon from residues of oregano using experimental design method

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Abstract: A series of eight activated carbons were obtained by chemical activation of oregano marc, which is abundant waste in Morocco. The activated carbons responses (capacity of adsorption, and yield) were analyzed as a function of the experimental parameters (temperature, time and chemical agent), using the complete factorial design of 2^3 experiments. Each response has been described by a second order model that was adequate to predict responses in all experimental regions. The experimental values obtained were in good agreement with the values predicted from the models, with relatively small errors between the predicted and the actual values. The optimization of activated carbon, using the function of desirability, was carried out by JMP software. The optimal activated carbon is obtained when using 60 min as activation time, 350°C as activation temperature, and H_3PO_4 as chemical agent.

Keywords: Oregano; activated carbon; capacity of adsorption, yield, experimental design.

Introduction

Morocco has important potentialities in aromatic and medicinal plants. At present, it produces important quantity of oregano. This plant is widely used in industries such as food-processing, pharmaceutical and cosmetic for its antimicrobial and antioxidants properties[1, 2, 3].

However the residues of extraction obtained from oregano, which represent more than 80 % of the weight of the plant, are not exploited enough. This requires a new way of exploitation by transforming the residues of oregano in activated carbon[4, 5] to be exploited in related environment fields[6, 7]. Activated carbon is a substance obtained after several operations such as pyrolysis and activation treatments to make it more porous. Its vast porosity gives it a specific surface area ranging from 500 to 2000 m2/g [8], which contributes to its great power as an adsorbent. Commercially activated carbon is produced from bituminous or lignite coal. The long-term availability of coal, environmental impacts and potentially

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increasing cost has encouraged researchers to find other alternatives, which may be cost effective and equally potential. Activated carbon can be manufactured from any material that has reasonable elemental carbon content. Any lignocellulosic material can be converted to an activated carbon. The literature mentions many precursors for activated carbon such as bagasse, scrap tires, saw dust, almond, pecan, olive stones, black walnut, hazelnut shells, rice husk … etc.

The goal of this work was to optimize the preparation conditions of activated carbon from the residues of oregano. This precursor in its natural state is a poor adsorbent of organic compound. The residues of the oregano must be modified physically and chemically to enhance its adsorptive properties towards organic molecules or metal ions, routinely found in water and wastewater. This is effectively accomplished by converting this precursor to an activated carbon.

In this work, experimental design was applied to reduce the number of experiment trials needed to evaluate multiple parameters (temperature, time and chemical agent) and their interactions on the responses (capacity of adsorption, yield), and to look for optimal operating conditions[9, 10].

Results and Discussion

Univariate analysis

Temperature of activation

The TGA profile obtained under inert gas condition is presented in figure 1. The thermal degradation of lignocellulosic materials under inert atmosphere was well described in the literature[11]. According to this figure, pyrolysis curve of oregano marc follow the usual shape for lignocellulosic materials[12]. Indeed, the following curve show the typical degradation profile with well demarked regions for moisture release, devolatilization and char degradation. The first mass loss region due to moisture release and light volatiles loss occurs between 25°C and 125°C. The apparently higher moisture release from oregano marc could be due to simultaneous moisture and low temperature volatiles release. Then, devolatilisation, which is the main pyrolysis of lignocellulosic materials, starts at proximately 200°C. Between 200 and 400°C there was major weight loss 53% (where the main degradations occurred). During the devolatilization step, two decomposition processes corresponding to the degradation of hemicellulose and cellulose are observed. For the oregano marc, there are two distinct regions of TGA curve. The first region appears at approximately 225°C and the following second region is characterized by peaks with maxima at 325°C. Appearance of these peaks could be generated by the decomposition of hemicellulose and some of the lignin[12]. At the end of this decomposition step, a continuous slight devolatilization is observed. This is attributed to the slow degradation of lignin[13]. Thus, lignin is the first component to decompose at a low temperature and low rate and continues up to 900 °C.

Time of activation

The figure 2 shows that the activated carbon elaborated in 200°C treated during 90min is the one which gives the best capacity of adsorption with regard to the other samples where the capacity of adsorption decreased with the increasing duration of thermal activation. This has allowed defining the experimental domain of activation time between 15min to 90min.

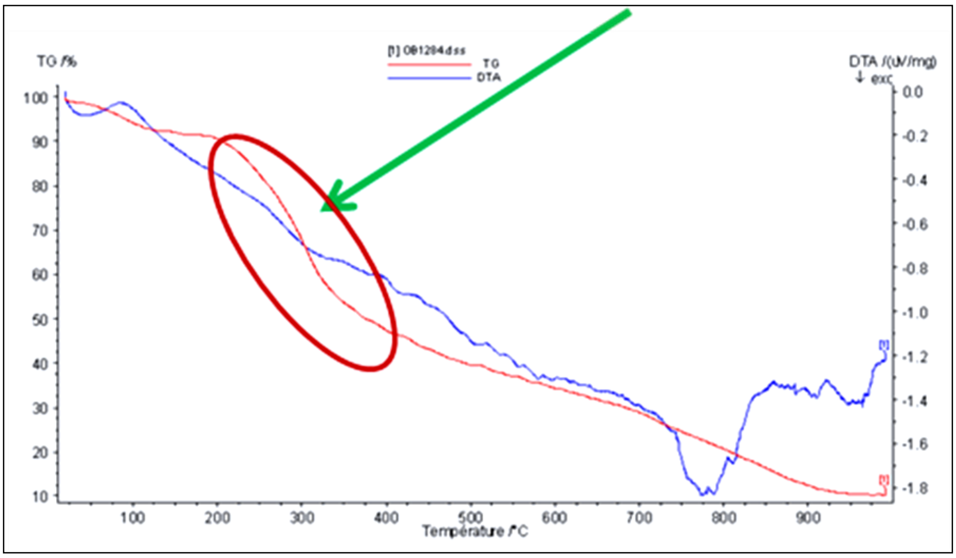


Fig. 1. TGA curve of oregano marc

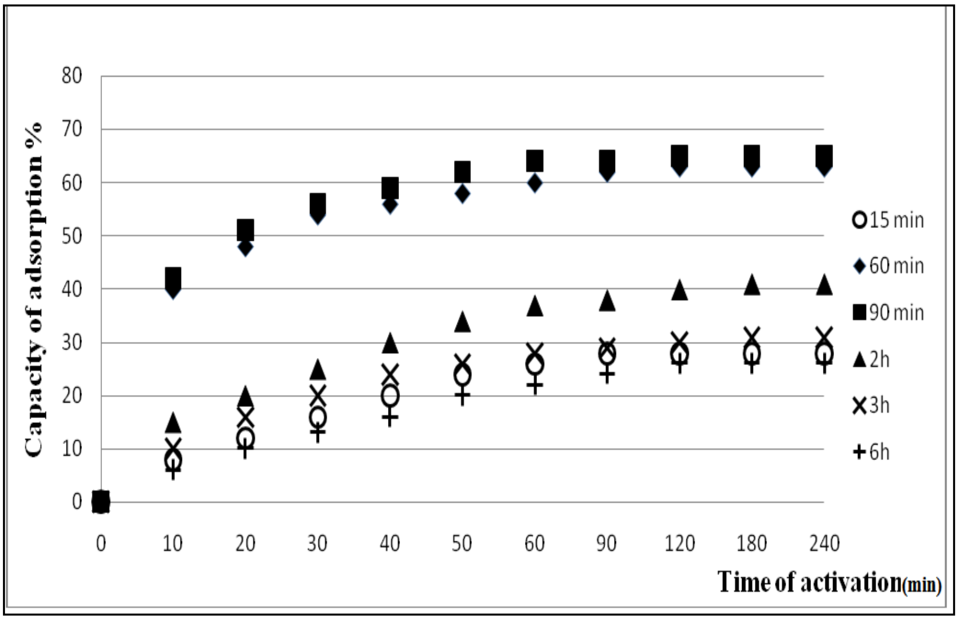


Fig. 2. Kinetic Curves relative to the methylene blue adsorption on the activated carbon elaborated in 200°C

Chemical agent of activation

The figure 3 represents the study of sulphuric and phosphoric acids impact on the mass loss during the activation of the oregano marc.

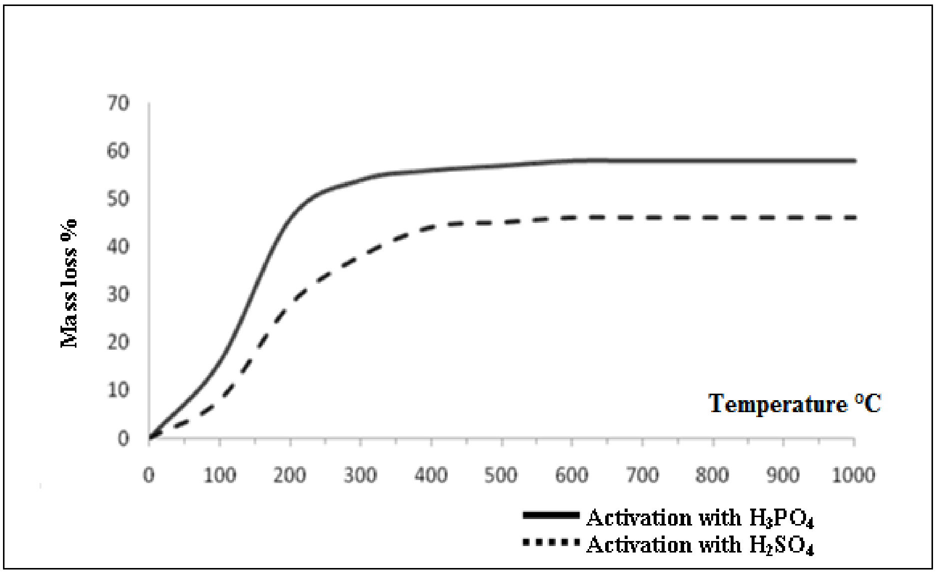


Fig. 3.

Degree of mass loss of the oregano marc impregnated with phosphoric and sulphuric acids

As we can see, both acids allow having a maximum yield in activated carbon between 200°C and 400°C, with a mass loss about 50 % for the sample impregnated with phosphoric acid and about 45 % for the sample impregnated with sulphuric acid.

Optimization of activated carbon by the experimental design method

Development of regression model equations

The values obtained experimentally for the responses studied, capacity of adsorption (Y1) and carbon yield (Y2), of the carbon samples are given in table 1. The experiments were carried out in a random order to minimize the effect of systematic errors[14].

Table 1. Matrix of experimental responses

N°.exp.	X1(°C)	X2 (min)	X3	Y1(%)	Y2 (%)
1	200	15	H_3PO_4	43	90
2	400	15	H_3PO_4	50	70
3	200	90	H_3PO_4	39	62
4	400	90	H_3PO_4	55	80
5	200	15	H_2SO_4	17	85
6	400	15	H_2SO_4	28	55
7	200	90	H_2SO_4	19	58
8	400	90	H_2SO_4	37	49

The complete factorial design was used to develop correlation between the capacity of adsorption and carbon yield. According to the sequential model sum of squares, the models were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased.

For each response, the coefficients of the postulated model, calculated on the basis of the experimental responses, drawn in the experimental region, were used to interpret the results. The determination of influent factors based on screening analysis varies the values of chosen factors in parallel, so it uncovers not just the main effects of each variable but also the interactions between factors. The treatment of experimental results by the statistical software allowed determining the values of the regression coefficients, their standard errors, t-ratios and p-values (table 2). The p-value of 0.05 is the threshold of check indicating that the coefficient is not null and it is consequently significant.

Table 2. Mathematical model coefficients

		Capacity of adsorption			
Term	**Regression coefficient**	**Standard error**	**t-ratios**	**p-value**	**judgment**
Constant	35.875	0.171796	208.82	0.001	Significant
T	6.625	0.171796	38.56	0.004	Significant
t	1.875	0.171796	10.91	0.0009	Significant
Acid [L1]	10.875	0.171796	63.30	0.0008	Significant
T*t	2.125	0.171796	12.37	0.0005	Significant
T* Acid [L1]	-0.875	0.171796	-5.09	0.0007	Significant
t* Acide [L1]	-1.125	0.171796	-6.55	0.0001	Significant

		Yield			
Term	**Regression coefficient**	**Standard error**	**t-ratios**	**p-value**	**judgment**
Constant	68.125	0.727677	93.62	0.0002	Significant
T	-5.125	0.727677	-7.04	0.0006	Significant
t	-6.375	0.727677	-8.76	0.0003	Significant
Acid [L1]	6.875	0.727677	9.45	0.0007	Significant
T*t	7.375	0.727677	10.13	0.0009	Significant
T* Acid [L1]	4.625	0.727677	6.36	0.0001	Significant
t* Acid [L1]	1.875	0.727677	2.58	0.0299	Significant

As we can see, all the coefficients as their interactions have a significant effect on both responses. In this case the final empirical models in terms of coded factors for capacity of adsorption (Y1) and carbon yield (Y2) are shown respectively by the following:

$$\mathbf{Y1 = 35{,}875 + 6{,}625\, x_1 + 1{,}875\, x_2 + 10{,}875\, x_3 + 2{,}125\, x_1x_2 - 0{,}875\, x_1x_3 - 1{,}125\, x_2x_3}$$

$$\mathbf{Y2 = 68{,}125 - 5{,}125\, x_1 - 6{,}375\, x_2 + 6{,}875\, x_3 + 7{,}375\, x_1x_2 + 4{,}625\, x_1x_3 + 1{,}875\, x_2x_3}$$

Variance Analysis

The results of the analysis of variance (Table 3) shows that the experimental value of Scnedecor (Fexp), which is the ratio between the square of the model and the average square of the residue, is largely higher than the critical value [$F_{0.001\,(6)} = 5.95$, $F_{0.001\,(9)} = 4.78$] of the F distribution at a 99.9 % level of confidence with 6 and 9 degrees of freedom. Consequently, the regression is thus very significant and the models are considered corresponding.

Table 3. Analysis of the variance of the postulated models

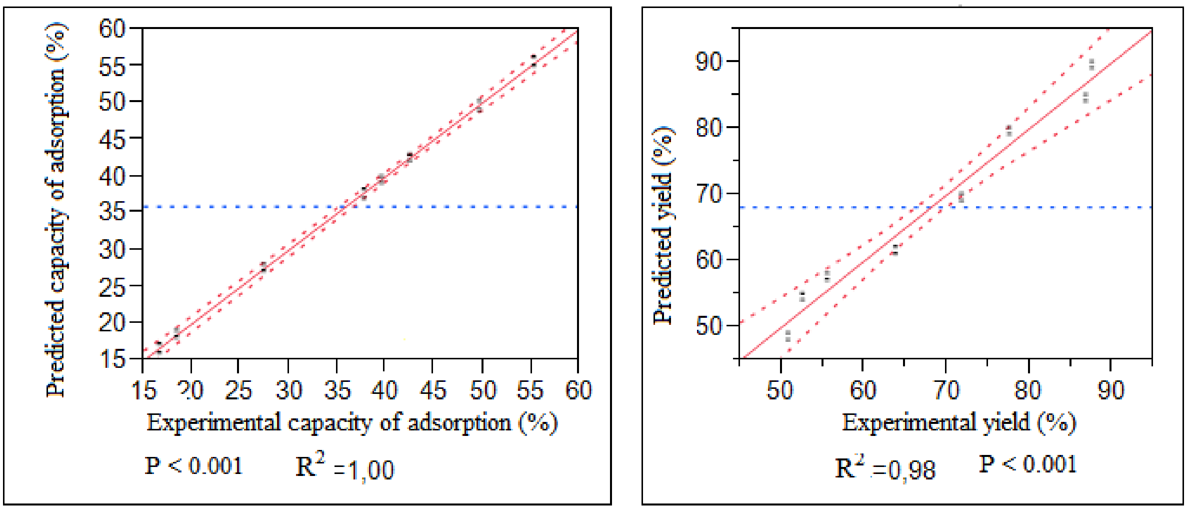
		Capacity of adsorption			
Source	**Degree of freedom**	**Sum of squares**	**Average square**	**F_{exp}**	**p-value**
Model	6	2755.50	459.25	972.53	<0.001
Residue	9	4.25	0.47		
Total	15	2759.75			
		Yield			
Model	6	3095.50	515.92	60.89	<0.001
Residue	9	76.25	8.47		
Total	15	3171.75			

Validity of the mathematical models

From the statistical results obtained, it was shown that the above models were adequate to predict the capacity of adsorption and the carbon yield within the range of variables studied. Figure 4 shows the predicted values versus the experimental values for capacity of adsorption and carbon yield, respectively. These results confirm that the models of regression explain well the experimental results. Therefore, these models have a good adjustment for both responses and they can be used for optimization.

Optimization

In the production of commercial activated carbons, relatively high product yields are expected for economical feasibility and the most important property of activated carbon is its adsorption capacity. Therefore, the activated carbon produced should have a high carbon yield and also a high adsorption capacity for economical viability. However, to optimize both these responses under the same condition is difficult because the interest region of factors is different. When Y1 increases, Y2 will decrease and vice versa. Therefore, in order to compromise between these two responses, the function of desirability was applied by prediction profiler using JMP software (figure 5).



a **b**

Fig. 4. Graphs of applied model adequacy for (a) capacity of adsorption and (b) yield

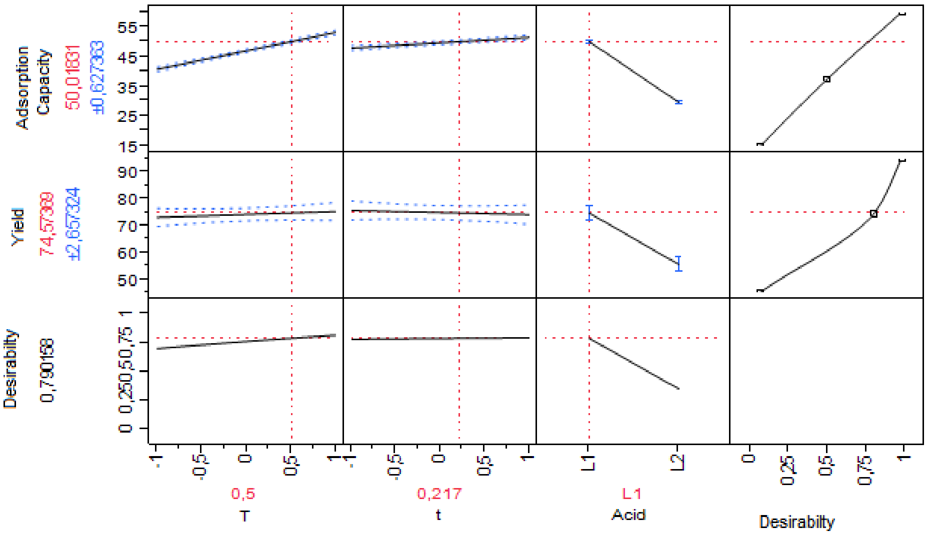


Fig. 5. Prediction profiler

The experimental conditions with the highest desirability were selected to be verified. The activated carbon was prepared under the experimental conditions given in figure 5, together with the predicted and experimental values for capacity of adsorption and carbon yield. The optimal activated carbon was obtained using preparation condition as: 350°C activation temperature (0.5 in coded value), 60min activation time (0.217 in coded value) and phosphoric acid as chemical agent of activation, which resulted in 52.8% of adsorption capacity and 78.2% of carbon yield. It was observed that the experimental values obtained were in good agreement with the values predicted from the models, with relatively small errors between the predicted and the actual values, which was only 5% and 4.64%, respectively for capacity of adsorption and carbon yield.

Under these operating conditions, the phosphoric acid intervenes as a catalyst of the dehydration and a promoter of separation between cellulose and lignin and reacts with the hydroxyl functions of the precursor in order to finally create surfaces groupings which will inhibit oxidation of the carbon while protecting the carbon skeleton.

Conclusion

The optimization method of activated carbon from residues of oregano by experimental design process allowed reducing number and cost of experiments.

Univariate analysis was conducted to study the effect of three factors, separately, on the elaboration process of activated carbon namely the activation temperature between 200 and 400°C, activation time between 15 and 90min and the chemical agent (phosphoric and sulphuric acids). In these conditions and by taking steps of 50°C and 15min for activation, the exhaustive classic experimental design will be constituted of 5x6x2; that is 60 independent experiences to reproduce.

Experimental Section

Univariate analysis

Univariate analysis is the first step of analysis of process variables (temperature, time chemical agent). The analysis is carried out with the description of a single variable and its attributes of the applicable unit of analysis. This step was used in the first stages of research, in analyzing the data at hand, before being supplemented by multivariate analysis using experimental design.

Temperature of activation

The weight loss behavior of the oregano marc was measured by using a thermobalance (TGA - Pyrolyseur Netzsch STA 409). The sample was heated up to final temperature of 1000°C at a heating of 25°C/min under N_2 flow.

Time of activation

The analysis of activation time effect was defined using adsorption test of cationic dye, the methylene blue (MB), on the activated carbon elaborated at an activation temperature of 200°C. Exactly 100 ml of MB solution of known initial concentration (200mg/l) was mixed with a required dose of adsorbent (5.0g/l), the mixtures were then subjected to agitation using shaker incubator at 180 rpm. In all cases, the working pH was that of solution and was not controlled. Mixtures were taken from the shaker at appropriate time intervals (15min, 60min, 90min, 2h, 3h and 6h) and the concentration of MB in the aqueous solution was determined at λmax of 660 nm using UV-visible spectrophotometer (Perkin Elmer).

Chemical agent of activation

Several works in the literature were based on the production of the activated carbon by impregnation of lignocellulosic material with the phosphoric acid[15]. We have introduced in this experimentation the sulphuric acid as the second qualitative factor for its cheaper price. The study of the impact of these two acids in the activation of oregano marc was carried out using thermogravimetric Analysis (TGA).

Preparation of activated carbon

Oregano marc is milled in the hammer mill “CONDUX D 6451” to reduce the size. A series of eight activated carbons are prepared, four samples are impregnated with the same mass of 80% phosphoric acid (H_3PO_4) and the other samples impregnated with the same mass of concentrated sulphuric acid (H_2SO_4). Every blend is mixed for half an hour in the ambient temperature. The obtained pastas are carried in the temperature of 120°C for 24 hours. The obtained materials underwent the reaction of activation in a leading electric thermolyne oven to self-regulation provided with a programmer of temperature, connected with the oven by a thermocouple and a special steel reactor. The system was then purged with 100 ml/min of N_2 for 15 min to ensure inert conditions. The reactor was heated at a rate of 25°C/min until the desired temperature was reached. The domains of variation of temperature and time activation were defined on the univariate analysis. After activation, the activation carbons are washed with distilled water until all acid was eliminated, dried, ground and sifted to obtain a powder with a particle size between 100 and 400µm.

Activated carbon yield

The activated carbon yield was calculated based on Eq. (1).

$$\text{Yield (\%)} = \frac{Wc}{Wo} \qquad (1)$$

Where W_C is the dry weight (g) of final activated carbon and W_O is the dry weight (g) of precursor.

Adsorption capacity of activated carbon

In a set of eight Erlenmeyer flasks (250ml) 100 ml of MB solution of known initial concentration (200mg/L) was mixed with a required dose of adsorbents (5.0g/L). The flasks were placed in a shaker incubator at 180 rpm and 30 ± 1°C. The clarified supernatant solutions (1 mL each) were taken after 6h then analyzed with UV-visible spectrophotometer (Perkin Elmer) at 668 nm.

The capacity of adsorption (%) was calculated based on Eq. (2).

$$\text{Capacity of adsorption (\%)} = \frac{Co - Ce}{Co} \qquad (2)$$

where Co and Ce are the initial and final dye concentrations (mg/L) respectively.

Methodology of experimental design

In the present work, the effects of three independent variables, including two numerical variables (i.e., temperature of activation (X1) and time of activation (X2), both at two levels (-1 and +1), and one categorical variable X3 (i.e., the use of H3PO4 or H2SO4 as the chemicals agents (X3) were investigated using complete factorial design of 2^3 experiments following the experiment matrix according to theYates method (tableau 4) [16,17].

Table 4. Matrix of full factorial experimental design for the production of activated carbons

N°.exp.	Temperature X1(°C)	Time X2(min)	Chemical agent X3
1	-1	-1	H_3PO_4
2	+1	-1	H_3PO_4
3	-1	+1	H_3PO_4
4	+1	+1	H_3PO_4
5	-1	-1	H_2SO_4
6	+1	-1	H_2SO_4
7	-1	+1	H_2SO_4
8	+1	+1	H_2SO_4

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:

$$X_{ij} = \frac{U_{ij} - U^0_j}{\Delta U_j} \qquad (3)$$

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 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.

The capacity of adsorption (Y1) and carbon yield (Y2) of the resulting adsorbents were taken as the two responses of the designed experiments. Each response (Y_i) can be described by a first order model adequate for predicting the responses in all experimental regions:

$$\mathbf{Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}XX_3 + a_{23}X_2X_3 + a_{123}x_1X_2X_3} \qquad (4)$$

where X_1 is the coded variable related to the natural variable U (activation temperature), X is related to U (activation time), X3 is related to U (chemical agent), a_0 is the intercept term, a constant that corresponds to the response when X is zero for each factor, a_1 determines the influence of activation temperature, a_2 determines the influence of activation time, a_{12} is the interaction effect between the activation temperature and activation time, a_{13} the interaction effect between the activation temperature and chemical agent, a_{23} the interaction effect between the activation time and chemical agent and a_{123} the interaction effect between temperature, time activation and chemical agent.

For each response (Yi), all the coefficients of the postulated model were calculated by least squares regression using the JMP (statistical software) [14].

The study of prediction profiler can predict the operating conditions necessary to elaborate activated carbon with the optimal responses.

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