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UTILIZATION OF EXPERIMENTAL DESIGN FOR SPECIFIC SURFACE AREA OPTIMIZATION OF A PILLARED BENTONITE

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Abstract: *Statistically designed experiments were used to study the effects of relevant factors, such as calcination temperature and duration, in obtaining of Al-pillared clays with a high specific surface area. Experiments have been planned by the factorial 3^2 design methods. The optimal conditions to obtain the maximum specific surface area of Al-pillared bentonite were deduced as follows: calcination temperature 326°C and calcination duration 63 min, for a specific surface area of 152.49 m^2/g. The results from BET (Brunauer-Emmett-Teller) method showed that the pillared smectite clay possesses a specific surface area up to 155.65 m^2/g. Besides, chemical treatment of smectite clay by pillaring process produces an adsorbent with optimal porosity and other adsorption properties suitable for many industrial processes.*

Keywords: *calcium bentonite, factorial design, mathematical optimization, pillaring, BET method*

1. Introduction

Pillared Interlayer Clays (PILCs) are an interesting class of 2-dimensional microporous materials. Due to their high surface area and permanent porosity, they are very attractive solids for adsorption and catalysis purposes.
This research was focused on the use of inorganic hydrated polyhydroxocations as pillaring agents. Such pillaring agents, when calcined, dehydrate and dehydroxylate to form a fixed metal oxide pillar with a high thermal stability and high surface area. The use of the Al_{13} polyhydroxocation was chosen as it is extensively researched and easily prepared [1-6].
The concept of pillaring is very straightforward and consists of two main steps: first, small interlamellar cations are exchanged for other, bulky ions. A second step, calcination, converts the inorganic polyoxocation precursors into rigid, stable metal oxide pillars, tightly bonded to clay layers [7].
Mathematical modeling through factorial design procedure was used by now in different domains for optimizing and modeling of different processes such: water depollution using some unconventional procedures, biogas

production, etc. The advantages of this optimization method consist in the fact that not only the individual (simple) effect of each variable is taken into account, but also the interaction and/or their possible synergy effects. This method allows studying the influence of a large number of variables.
The methods of mathematical planning of experiments aimed the obtaining of quantitative relationships of $y = f(x_1, x_2, x_3, ...)$ type, respectively of mathematical models that are associated to the processes, and the systematical, efficiently and economical investigation of significant factors of the process.
The interest of factorial program of k^n type, appears because of the difficulty to establish, by conventional ways, the mathematical relationship between the variables of studied system-process couple [8, 9].
In this study, the procedure for synthesis of Al-pillared clays consists in five steps: clay purification, ionic exchange of clay with Cu^{2+} ions, preparation of pillaring agent, intercalation of ionic exchanged clay with pillaring agent and calcination. The last step is very important, for the conversion in stable pillared clays.
The aim of this paper is to establish an optimal domain for calcination parameters in the case of Al-pillared clays, using an experimental design study. Two factors were varied (calcination temperature and calcination duration) and evolution of specific surface area was achieved as the response function.

2. Experimental

2.1. Materials and devices

The calcium bentonite from Oraşu Nou (Romania) used as raw material in this study, was purified. All chemicals used in this work were supplied by Alfa-Aesar.
The specific surface area (determined by BET technique), was obtained from N_2 adsorption–desorption isotherm at 77 K, measured in a Micromeritics ASAP 2010. The samples were degassed at 473 K, for 16 h.

2.2. Synthesis

2.2.1. Purification

The aim of purification process for Romanian natural calcium bentonite is the obtaining of well-defined granulometric fractions, with particles of less than 2 µm. The purification process consists in dispersion of some quantity of natural calcium bentonite into a volume of distilled water, for obtaining of 0.4 wt % suspension [10]. The suspension was stirred for 3 hours at room temperature, till a complete homogenization.
Montmorillonitic fractions, which were recuperated on the basis of Stokes' law, were centrifuged, and the recovered clay was dried in an oven at 105°C, for 15 h. The purified bentonite was ground and sieved below 63 µm, in order to use only the finer grains.

2.2.2. Ionic exchange with 0.1 M $CuCl_2$

The bentonite samples were copper-exchanged, by its treatment with 0.1 M $CuCl_2$ solution, with a solid:liquid ratio of 1:20, the suspension being stirred at room temperature, for 24 h [11]. This procedure was repeated two times for obtaining a complete copper-exchanged bentonite. Between copper-exchanged operations, the samples were washed with distilled water, until modified montmorillonite was free of chloride anions (0.1 N $AgNO_3$ test). After sample washing, the suspension was centrifuged. Next, the sample was dried in an oven at 80°C for 16 h, ground and sieved in order to obtain particles size less than 63 μm.

2.2.3. Al-pillaring solution preparation

The dilute Al-pillaring solution was prepared by drop-wise addition of a 0.2 M NaOH solution to a 0.2 M $AlCl_3$ solution, at room temperature with vigorous stirring, till the (OH/Al) molar ratio was 2, for obtaining the maximum content of Keggin cation (Al_{13}) [2]. The pillaring agent was kept at room temperature, for 48 h.

2.2.4. Intercalation of Cu-clay with Al-pillaring agent

Cu-montmorillonite was dispersed in distilled water (2 wt % slurry) and the suspension was stirred for 1 h, at room temperature. Further, this slurry was mixed with the pillaring solution at room temperature, until the molar ratio was 10 mmoles Al/g clay. The clay was then washed with distilled water for the removal of chloride ions, and centrifuged. The pillared clays were then dried at 80°C for 15 h, and then hand-ground into a mortar.

2.2.5. Calcination

The calcination of intercalated samples was realized using a device with a tubular furnace under nitrogen. The nitrogen flow was maintained at 100 mL N_2/min, at a heating rate of 2°C/min. The calcination temperatures were varied from 300°C, 400°C to 500°C for 1, 2 and 3 h.

2.3. Factorial design

The most often used experimental programs are K^n factorial design type, where K is the variation number of parameters level, and n is the number of parameters [9, 12].
In this study, it was investigated the influence of two parameters for the preparation of Al-pillared bentonites, which are expressed in terms of calcination temperature (X_1) and calcination duration (X_2) upon one response function, the specific surface area, in the variation ranges summarized in Table 1.

Table 1.
Parameters that influence pillaring process and their variation domain

Parameters (X_i)	**Reduced variable**	**Minimal level (X_i^{min})**	**Median level (X_i^{med})**	**Maximal level (X_i^{max})**	**ΔX_i**
Calcination duration [min]	x_1	60	120	180	60
Calcination temperature [°C]	x_2	300	400	500	100

3. Results and Discussion

The response function was the specific surface area of Al-pillared bentonites that is presented in table 2. In parenthesis are noted the reduced values of the variables.

Table 2.

Factorial 3^2 experiment design and response function for specific surface area of Al-pillared bentonites

Run	Calcination duration [min]	Calcination temperature [^oC]	Specific surface area (S_{BET}) [m^2/g]
	x_1	x_2	Y
1	60 (-1)	300 (-1)	**155.65**
2		400 (0)	141.67
3		500 (+1)	122.51
4	120 (0)	300 (-1)	143.21
5		400 (0)	140.98
6		500 (+1)	125.58
7	180 (+1)	300 (-1)	133.12
8		400 (0)	128.51
9		500 (+1)	96.36

To calculate the significance of the program, three other tests in the central point of the domain (0, 0) were also realized; the obtained values are shown in the table 3.

Table 3.

Values in the central point of the domain

y_k^0	y_1^0	y_2^0	y_3^0
Value for specific surface area [m^2/g]	141.32	140.78	142.18

3.1. Elaboration of the mathematical model

The particular form of response function for factorial program of type 3^2 is presented in equation (1). In table 4 are presented the coefficients values of polynomial mathematical model. These were calculated according to the literature specifications [8, 9, 12].

$$Y = a_o + a_1 \cdot x_1 + a_2 \cdot x_2 + a_{12} \cdot x_1 \cdot x_2 + a_{11} \cdot x_1^2 + a_{22} \cdot x_2^2 \qquad (1)$$

Table 4.

Values of the polynomial coefficients

Coefficient	Value	Coefficient	Value
a_0	141.689	a_{12}	-0.905
a_1	-14.588	a_{11}	-7.648
a_2	-10.307	a_{22}	-6.953

According to the polynomial coefficients, the mathematical model which describes the response function of the optimizing criteria is:

$$Y = 141.689 - 14.588 \cdot x_1 - 10.307 \cdot x_2 - 0.905 \cdot x_1 \cdot x_2 - 7.648 \cdot x_1^2 - 6.953 \cdot x_2^2 \qquad (2)$$

3.2. Determination of the coefficients significance

In order to determine the significance of the polynomial coefficients it was used the *t - student test.* For this, it is necessary first to calculate the average value of the three response functions and of the average value of the measurement errors according to the algorithm presented in the literature [7, 10]. The t-student test results are used to determine the insignificant coefficients (Table 5).

It will be calculated the average specific surface area in the central point of the domain (0, 0):

$$y^0_{med} = \frac{\sum_{i=1}^{3} y^0_i}{3} = 141.427 \quad (3)$$

The average error square is calculated, knowing that the control samples number, *n*, is 3, using the equation:

$$\varepsilon^2 = \sum_{i=1}^{n} \frac{\left(y^0_i - y^0_{med}\right)^2}{n-1} = 0.499 \quad (4)$$

It will be calculated the error for control samples:

$$\varepsilon = 0.706 \quad (5)$$

The calculation of coefficients significance, *S*, is realized with the equation (6), knowing that the number of experiments, *N*, is 9:

$$S = \frac{\varepsilon}{\sqrt{N}} = 0.235 \quad (6)$$

The significance of the coefficients will be tested using student t-test, with the equation:

$$t_j = \left|a_j\right| / S \quad (7)$$

The t-student test values for each coefficient are presented in Table 5. The t-student test results show that the term that can be eliminated is x_{12}.

Table 5.

T-student test results

t_j	t_0	t_1	t_2	t_{12}	t_{11}	t_{22}
Value	602.019	61.984	43.792	3.845	32.497	29.544

The mathematical model that describes the response function of optimization criterion, after the removal of insignificant term using t-student test, is:

$$Y = 141.689 - 14.588 \cdot x_1 - 10.307 \cdot x_2 - 7.648 \cdot x_1^2 - 6.953 \cdot x_2^2 \quad (8)$$

Forward, it will be discussed the effects of parameters. The a_o value (141.689) indicates that the optimal specific surface area is close to this value.

Because the coefficients a_1 and a_2 are negative, the variables x_1 and x_2 have an unfavorable individual action on the pillaring process. The individual effect of the x_{12} term that was determined with t-student test, was insignificant, it will not be discussed.

Analyzing the quadratic coefficients a_{11} and a_{22}, which values are negative, thus the response function is characterized by a maximum in relation with the variables x_1 and x_2.

For response function obtained after the insignificant terms elimination, using t-student test, the partial derivatives of first order will be calculated, in rapport with each variable:

$$\frac{\partial y}{\partial x_1} = -14.588 - 2 \cdot 7.648 \cdot x_1$$
$$\frac{\partial y}{\partial x_2} = -10.307 - 2 \cdot 6.953 \cdot x_2 \qquad (9)$$

By equating the partial derivatives of first order with 0, the linear system resulted will be resolved.

The optimal point searched, represented in dimensionless coordinates, is (-0.953; -0.741). As it can be seen, the optimal values for x_1 and x_2 are within the limits of the domain (-1, 1) that were initially supposed.

Knowing the range of variation of calcination temperature and calcination duration, it can be obtained the real values of the optimal point using the following equations:

$$X_1 = \Delta X_1 \cdot x_1 + X_1^{med}$$
$$X_2 = \Delta X_2 \cdot x_2 + X_2^{med} \qquad (10)$$

where:

X_1, X_2 – real values of optimum;

x_1, x_2 – dimensionless values of optimum;

ΔX_1, ΔX_2 – step of each variation domain;

X_1^{med}, X_2^{med} – real average value of parameters.

$$X_1 = 62.82 \ \text{min}$$
$$X_2 = 325.9^o C \qquad (11)$$

In this study, the specific surface area dependence was established according to the two factors, temperature and duration calcination in order to obtain the Al-pillared clays. This dependence can be illustrated using the curve shown in the diagram presented in figure 1.

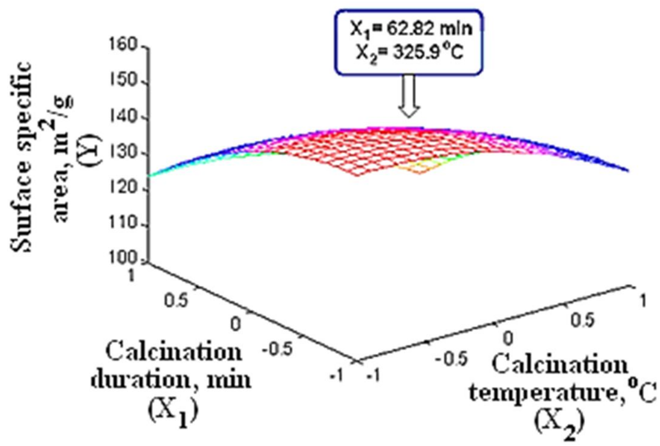

Figure 1. *Influence of calcination duration (X_1) and calcination temperature (X_2) on specific surface area (Y)*

As long as both coefficients of quadratic terms have negative signs, the quadratic terms determine a maximum and the response surface (figure 1), which corresponds to the model is concave.

The optimal value of specific surface area obtained by factorial planned experiments was 152.49 m^2/g.

4. Conclusions

From 3D representation of concave shape, it can be distinguished the roundness of area and the maximum due to the quadratic coefficients effects. This representation evidences the obtained results of experimental design. The real optimal values of varied parameters are:

- 325.9^{o}C for the optimal calcination temperature;
- 62.82 minutes as the optimal calcination duration,

and give an optimal specific surface area value of 152.49 m^2/g.

This optimal specific surface area value could be still increased by the application of experimental design to the other steps for Al-pillared clays obtaining, like: purification, ionic exchange and intercalation.

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