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Modeling and optimization of Al-pillaring process using experimental design procedure

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Abstract

Calcium bentonite from Orasu Nou deposit (Romania) has been used in order to obtain Al-pillared bentonites, which are microporous materials with special properties. The pillaring process consists in the following steps: bentonite purification, ionic exchange of bentonite, preparation of pillaring agent, intercalation of the exchanged bentonite with pillaring agent and calcination. The pillared clays present a rigid structure, a high termic stability given by the oxido-metallic pillars formed after calcination. This paper presents the application of the k^n experiment design procedure for simulation and optimization of the Al(III)-pillaring process. There were performed 9 experiments according to the experimental design procedure. The input variables were calcination temperature (x_1) and calcination duration (x_2) and the output variable was the basal spacing, d_{001} (Y). The optimal conditions for Al-pillared bentonites synthesis were obtained for a calcination duration of 114 min and a calcination temperature of 457°C. The material with these optimal calcination parameters will be used in liquid effluents remediation.

Keywords: calcium bentonite, pillaring process, calcination, basal spacing, modeling, optimization

1. Introduction

Pillared InterLayered Clays (PILCs) have been widely used in recent researches, these solids being obtained from smectite clay minerals. Montmorillonite belongs to smectite clay mineral group, with a double-layered structure (2:1), it being the most used clay in pillaring process. The synthesis of different metal oxide PILCs led to the obtaining of microporous materials with special properties, the most used metal oxides as pillars being Al, Fe, Cr, Ni, Zr, Mg, Bi, Ti, Cu, Ga, Mo [1-5].

These materials are obtained with the following steps synthesis procedure: polymerization of a multivalent cation; intercalation of these polycations into the interlayer space of smectite clays and calcination at moderate temperatures.

The latter step transforms the polycations into stable oxi-hydroxide phases named pillars, the materials obtained being called pillared clays.

Factorial programs allow better organization of experimental tests that accompany a scientific study. By factorial plans, quantitative relationships of $y = f(x_1, x_2, x_3, \ldots)$ type can quickly and efficiently be obtained, which correspond to mathematical models associated to processes [6, 7].

Factorial designed experiments consist in simultaneous variation after a certain plan of all parameters which are considered that influence the process [8, 9]. 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 [7, 9].

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In this paper, Al-PILCs were synthesized under various experimental conditions, using Romanian calcium bentonite as raw material. The aim of this research is to establish an optimal domain for calcination parameters in the case of Al-PILCs, using the experimental design procedure. The varied parameters were calcination temperature and calcination duration and the response function was the basal spacing of Al-PILCs obtained.

2. Materials and Methods

2.1. Materials and devices

In this paper, Romanian calcium bentonite was used as raw material, which was supplied from SC Bentonita SA. All chemical reagents were supplied by Alfa-Aesar. The calcium bentonite from Orașu Nou (Romania) was used as raw material in this study. All chemicals were used without further purification and were supplied by Alfa-Aesar ($AlCl_3 \cdot 6H_2O$) and Merck ($CuCl_2 \cdot 2H_2O$, $AgNO_3$, NaOH, pellets).

The basal spacing (d_{001}) of clay samples was determined using the diffractometer Bruker D8 Advance, which works on monochromatic k_{a1} radiation of Cu ($kCuK_{a1}$ = 1.54 Å). X-ray diffraction spectra are recorded in the angular range of 2θ = 2 – 40°, the step size being 0.0197°.

2.2. Synthesis

The procedure for synthesis of pillared clays consists in the following 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 [10, 11].

The aim of bentonite purification is the obtaining of well defined granulometric fractions, with particles < 2 μm. This procedure was detailed in a previous paper [5]. The purified bentonite was copper-exchanged, by using the experimental protocol described in a previous work [10]. Al-pillaring solution preparation, intercalation of ionic exchanged bentonite with pillaring agent and calcination were realized according to the protocol reported in our previous work [12].

2.3. Factorial design

In this paper, it was investigated the influence of two parameters for the preparation of Al-pillared bentonites, which are expressed in terms of calcination duration (X_1) and calcination temperature (X_2) upon the response function, which was the basal spacing (Y). The variation ranges are summarized in Table 1.

Table 1. Parameters that influence Al-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 Discussions

The response function was the basal spacing of Al-pillared bentonites which values are presented in Table 2. The reduced values of the variables are presented in parenthesis.

Three other tests were also realized in the central point of the domain (0, 0) to calculate the significance of the program; the obtained values are shown in the Table 2.

3.1. Elaboration of the mathematical model

The particular form of response function for factorial program of 3^2 types is:

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

In Table 3 are presented the coefficients values of polynomial mathematical model, which were calculated according to the literature specifications [5].

Table 2. Varied parameters and response function for basal spacing of Al-pillared bentonites

Run	Calcination duration, min	Calcination temperature, °C	Basal spacing, nm
	x_1	x_2	Y
1	60 (-1)	300 (-1)	1.704
2	120 (0)	300 (-1)	1.685
3	180 (+1)	300 (-1)	1.660
4	60 (-1)	400 (0)	1.618
5	120 (0)	400 (0)	1.612 (1.620; 1.612; 1.618)
6	180 (+1)	400 (0)	1.572
7	60 (-1)	500 (+1)	1.572
8	120 (0)	500 (+1)	1.636
9	180 (+1)	500 (+1)	1.583

Table 3. Values of the polynomial coefficients

Coefficients	Coefficient value
a_0	1.618
a_1	-0.013
a_2	-0.043
a_{12}	0.014
a_{11}	-0.026
a_{22}	0.039

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

$$Y = 1.618 - 0.013 \cdot x_1 - 0.043 \cdot x_2 + 0.014 \cdot x_1 \cdot x_2 - 0.026 \cdot x_1^2 + 0.039 \cdot x_2^2 \quad (2)$$

3.2. Determination of the coefficients significance

The *t - student test* was used in order to determine the significance of the polynomial coefficients. First it is necessary to calculate the average value of the response function and the average value of the measurement errors according to the algorithm presented in the literature [7, 8, 10]. The *t-student* test results (Table 4) indicate that no term have to be eliminated.

Table 4. T-student test results

t_j	t_0	t_1	t_2	t_{12}	t_{11}	t_{22}
Value	$1.166 \cdot 10^{-3}$	9.488	30.985	9.908	18.855	28.343

The effects simulation of the optimization study consists in discussing the absolute value and the sign of each coefficient separately. The a_o value indicates that the optimal basal spacing is close to 1.618 nm.

The individual coefficients (a_1 and a_2) are negative, so the x_1 and x_2 variables have an unfavorable individual effect on the pillaring process. The interaction term (a_{12}) being positive, it has a favorable action on Al-pillaring process. Analyzing the quadratic term coefficients (a_{11} and a_{22}) which values are negative, respectively positive, it can be said that the response function is characterized by a maximum in relation to variable x_1 and by a minimum in relation to variable x_2.

For response function obtained, the partial derivatives of first order will be calculated, in rapport with each variable.

By equating the partial derivatives of first order with 0, the linear system resulted was resolved. The optimal point searched is (-0.096; 0,57), represented in dimensionless coordinates. It can be seen, that the optimal values for x_1 and x_2 are within the limits of the domain (-1, 1) which initially were supposed.

The real values of the optimal conditions for Al-pillared bentonites synthesis were obtained for a calcination duration of 114 min and a calcination temperature of 457°C.

In this study, the basal spacing dependence was established according to the two factors, duration and temperature calcination in order to obtain the Al-pillared bentonites, dependence that can be illustrated using the curve presented in Figure 1. Figure 1 shows a saddle-shape response surface determined by the different signs of quadratic terms coefficients.

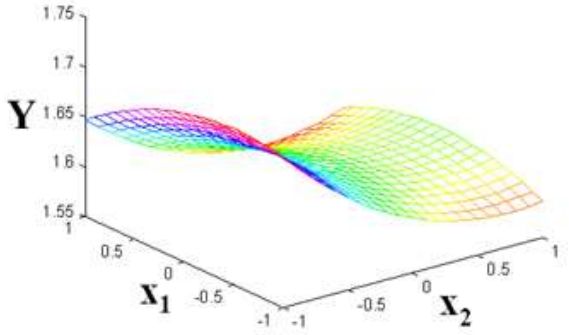

Figure 1. Influence of calcination duration (X_1) and calcination temperature (X_2) on basal spacing (Y)

4. Conclusions

The design experiments utilization in order to modeling and to optimize the Al-pillaring process, demonstrate the viability of this analysis technique of experimental data. The factorial experimentation makes possible the estimation of decisive parameters effects of calcination process of intercalated clays with polyhydroxocations. Based on experimental data, an equation was elaborated by experimental programming, which is the expression of basal spacing of Al-pillared clays, as a polynomial where the coefficients attached to the independent variables can be determined by regression analysis.

The optimal conditions for Al-pillared bentonites synthesis were obtained for a calcination duration of 114 min and calcination temperature of 457^{o}C. The optimal value of nanomaterial basal spacing obtained by factorial planned experiments was 1.63 nm.

The optimized values obtained from the experimental design are in agreement with the values of parameters initially explored. The material with the optimum calcination parameters will be chosen in the aim of its using in liquid effluents remediation.

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Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human / or animal subjects (if exist) respect the specific regulation and standards.

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