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Process improvement approach to the acid activation of smectite using factorial and orthogonal central composite design methods

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Abstract: The purpose of this study was to determine the effective operating parameters and the optimum operating conditions of an acid activation process within the framework of improvement of the process. Full two-level factorial and orthogonal central composite design methods were used successively. The examined parameters were the main and interaction effects of temperature, leaching time, acid normality, solid-to-liquid ratio and stirring rate. The selected process response was the leaching yield of the MgO content because Mg is the element most readily removed from the octahedral sheet, which affects the tendency for activation. Statistical regression analysis and analysis of variance were applied to the experimental data to develop a predictive model, which revealed that temperature, leaching time and acid normality exert the strongest influence on the specific surface area of smectite, whilst the solid-to-liquid ratio and the stirring rate have a secondary effect. Furthermore, the highest leaching yield of MgO was found to be 41.86 %, which is responsible for the increase in the specific surface area of up to 221 $m^2 g^{-1}$.

Keywords: statistical modeling; acid activated smectite; leaching of MgO; specific surface area.

INTRODUCTION

The major clay minerals in bentonites are smectites, such as montmorillonite, beidellite, saponite, nontronite and hectorite.[1]. Bentonites may also contain other clay minerals and non-clay minerals.[2] Bentonite consists predominately of smectite 2:1, a clay mineral containing an octahedral sheet between two tetrahedral sheets. Smectite crystals are negatively charged due to the substitution of the trivalent aluminum ions by ions such as Mg^{2+} and Fe^{3+} and substitution of the tetrahedral Si^{4+} by Al^{3+}.[3]

In the raw state, the clay material generally shows mediocre performance but acid activation improves its textural and adsorptive characteristics. The important

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physical changes in acid-activated smectite are the increase of the specific surface area and the average pore volume, depending on the acid strength as well as the time and temperature of treatment.[4,5] Some studies have shown that leaching of octahedral Al^{3+}, Fe^{3+} or Mg^{2+} cations by protons and substitution of exchangeable cations Ca^{2+}, Na^{+} or K^{+} by the protons of the mineral acid occur and increase with the time of activation of smectite clays.[6,7] Mg is the most readily removed element of the octahedral sheet during activation.[4]

Experiments performed to determine the effect of the independent variables (factors) on the dependent variable (responses) of the process and the relation between them, as illustrated by a regression model obtained utilizing the experimental data. Statistical design of experiments is a well known efficient experimentation technique[8] and has been applied in a wide range of fields, such as the drug and food industry, chemical and biological processes, *etc*., to enable the production of high quality products, to operate the processes more economically and to ensure more stable and reliable processes.

The aim of this study was to determine the highest leaching of MgO from Serbian smectite clay and derive a model for acid activation using a full factorial design.

EXPERIMENTAL

Design of experiments

Factorial design is widely used in statistical planning of experiments to obtain empirical linear models relating process responses to process factors. The 2^n factorial design, where each variable runs at two levels, is often used to obtain first-order models. If the variance analysis indicates that the overall curvature is significant, auxiliary experiments are performed to develop a second-order model. Among the various second-order designs, the orthogonal central composite design is widely used as it only requires $2n$ additional runs.[8,9]

A full factorial design was selected to study the influence of the five relevant factors (n), *i.e.*, temperature, leaching time, acid normality, solid-to-liquid ratio and stirring rate on the leaching yield of MgO from smectite.

The results of the experimental design were studied and interpreted by Design Expert 6.0.6 statistical software to estimate the response of the dependent variable.

Materials

Smectite from Bogovina, Serbia was used as the raw material.

Natural smectite clay (A) with particle sizes of mostly less than 75 μm (200 mesh, ASTM), dried at 383 K, having an average composition, wt. %: SiO_2, 69.12; Al_2O_3, 14.01; Fe_2O_3, 5.43; CaO, 1.62; MgO, 2.57; Na_2O, 1.33; K_2O, 0.66, TiO_2, 0.57; a loss ignition of 4.69 was used as the starting material. The CEC, 78 meq/100 g, was determined by the standard method using 1.0 M NH_4Cl.[10]

Acid activation

The chemical activation was carried out under atmospheric pressure in a jacketed glass reactor equipped with a reflux condenser, a thermometer and a stirrer. A typical run was performed as follows: specified amounts of hydrochloric acid of known concentration and smectite clay were loaded into the glass reactor. The stirring speed was held constant by means of a digitally controlled stirrer. The suspension was cooled in air and filtered off and then washed several times with hot distilled water to remove excess Cl^- and dried to constant weight at 373 K.

Characterization

The contents of the metal cations in the natural clay and the content of major octahedral cations, Mg^{2+}, total Fe and Al^{3+}, in the activated samples were determined by induced coupled plasma (ICP) spectroscopy using a Spectroflame M-Spectro instrument. The percents of the cations removed from the smectite after acid activation are given in Table I.

TABLE I. Quantities of cations removed from smectite by acid treatment, expressed in terms of oxides

Run	Content of oxides, %		
	MgO	Fe_2O_3	Al_2O_3
1	11.98	1.11	2.19
2	17.23	2.58	5.24
3	32.24	16.02	15.87
4	31.95	14.36	17.99
5	13.44	2.39	5.24
6	19.85	6.63	0.07
7	41.86	29.46	24.57
8	29.03	11.42	11.88
9	39.67	18.97	23.77
10	21.89	6.44	6.51
11	6.88	0.37	0.53
12	0.63	0.92	0.80
13	5.87	0.55	0.93
14	37.93	13.44	14.28
15	30.34	18.42	21.31
16	22.04	22.74	26.49
17	25.24	12.34	9.83
18	25.24	12.34	9.83
19	25.24	12.34	9.83
20	17.05	2.72	7.49
21	34.57	13.12	24.30
22	13.01	2.99	7.25
23	15.92	9.99	8.37
24	24.59	9.44	14.18
25	20.29	4.42	9.69
26	24.22	4.65	11.69
27	20.43	3.27	11.69
28	13.51	3.13	5.71
29	36.17	25.60	26.29

X-Ray diffraction patterns of Serbian smectite were obtained using a Philips PW 1710 diffractometer with CuK_α radiation (40 kV, 30 mA, λ = 0.154178 nm). The diffraction patterns of Serbian smectite before and after activations, for the sample with the highest leaching yield of MgO, are shown in Fig. 1.

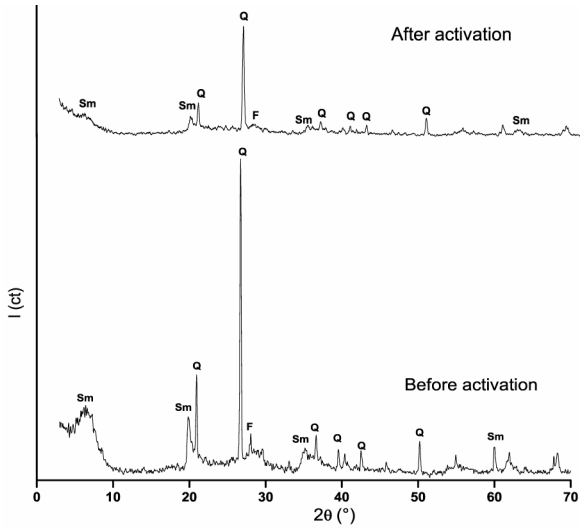

Fig. 1. X-Ray diffraction patterns of natural and acid activated smectite.

Nitrogen adsorption–desorption isotherms were collected on a Sorptomatic 1990 Thermo Finningen surface area and pore size analyzer at 77 K. Prior to adsorption, the samples were outgased overnight at 473 K under a residual pressure of 10^{-2} Pa. The specific surface area was determined by applying the Brunauer–Emmet–Teller (BET) Equation, using 16.3 $Å^2$ for the cross-sectional area of nitrogen.[11] The total pore volumes of the micro pores and meso pores were obtained from the N_2 adsorption at $p/p_0 = 0.98$ expressed in liquid form. The micro-pore volumes were estimated according to the theory of the micro-pore volume filling process and the logarithmic form of the Dubinin–Radushkevich Equation.[12] The pore size distributions were calculated using the Barret–Joyner–Halenda method applied to the parallel pore model.[13] The adsorption branch of the isotherms was taken for the calculation. The desorption branch of the isotherms are not suitable for the determination of the pore size distributions since, during desorption, blocking of nitrogen in the trapped pores occurs.[14]

RESULTS AND DISCUSSION

In order to determine the optimum conditions and derive a model for acid activation of smectite, a full factorial of the type 2^5 was used. The parameters reaction temperature (X_1), hydrochloric acid normality (X_2), stirring speed (X_3), solid-to-liquid ratio (X_4) and reaction time (X_5) were chosen as independent variables and their effect on the leaching yield of MgO from the smectite clay from Serbia was investigated in the light of pre-experiments. The factor levels are shown in Table II.

The matrix for five variables was varied at two levels (+1 and –1). The higher level of variable was designated as "+1" and the lower level as "–1". Initially, a half replicate of the full 2^5 factorial design was used to obtain the first-order model with interaction terms.

As usual, the experiments were performed in random order to avoid systematic error. In addition, three central replicates were added to the experimental

plan to calculate the experimental error. The design of the experimental matrix of smectite acid activation and leaching yield of MgO, both the experimental and the predicted values, calculated by Eq. (2), are presented in Table III.

TABLE II. Factor levels used in the experiments

Factor	Physical quantity	Low level (–)	Medium level (0)	High level (+)
X_1	Temperature, K	343	353	363
X_2	HCl concentration, mol dm^{-3}	3.0	4.5	6.0
X_3	Stirring speed, rpm	300	450	600
X_4	Solid/liquid ratio	1:3	1:4	1:6
X_5	Time, h	1	2	3

TABLE III. Experimental design and leaching yields of MgO

Run	X_1	X_2	X_3	X_4	X_5	MgO content, %	
						Experimental	Predicted
1	–1	1	–1	1	1	6.88	7.34
2	–1	–1	1	1	1	11.98	11.28
3	1	1	–1	1	–1	29.03	29.41
4	–1	–1	1	–1	–1	37.93	37.91
5	1	–1	1	1	–1	21.89	21.11
6	1	–1	1	–1	1	30.34	30.55
7	1	1	1	1	1	41.86	41.18
8	–1	1	–1	–1	–1	0.63	1.77
9	1	1	1	–1	–1	31.95	33.20
10	1	1	–1	–1	1	39.67	41.04
11	–1	1	1	–1	1	5.87	6.10
12	–1	1	1	1	–1	19.85	20.35
13	–1	–1	–1	1	–1	20.00	19.33
14	1	–1	–1	1	1	32.24	30.40
15	–1	–1	–1	–1	1	13.44	12.51
16	1	–1	–1	–1	–1	17.23	17.32
17	0	0	0	0	0	25.24	22.97
18	0	0	0	0	0	25.24	22.97
19	0	0	0	0	0	25.24	22.97

The response was expressed as mass % leaching yield of MgO, calculated as $((c_0–c)/c_0)\times100$ where c_0 is the initial concentration of MgO and c is the final concentration of MgO. Initially, a first order model with interaction terms was chosen to fit the experimental data:

$$y = b_0 + \sum_{i=1}^{5} b_i x_i + \sum_{i=1}^{5} \sum_{j\geq1}^{5} b_{ij} x_i x_j \quad (1)$$

The first-order model obtained by variance analysis conducted at the 95 % confidence level is:

$$y_{\mathrm{MgO}} = 22.55 + 7.98X_1 + 2.66X_3 + 5.68X_1X_2 - 1.68X_1X_3 + 5.27X_1X_5 + 2.02X_2X_4 + 1.37X_2X_5 - 1.73X_3X_4 - 2.93X_3X_5 \quad (2)$$

Analysis of the variance detected a curvature effect. Since the analysis of variance revealed that quadratic terms were effective, the orthogonal central composite design was applied to separately estimate the quadratic terms. With $F = 16$ (the number of experimental design), $m_0 = 3$ (the number of central replicates) and $n = 5$ (the number of factors), β was calculated as 1.6644 according to relation:[11]

$$\beta = \left(\frac{QF}{4}\right)^{0.25}; \quad Q = \left(N^{0.5} - F^{0.5}\right)^2; \quad N = 2n + F + m_0 \quad (3)$$

and the new factor levels ($-\beta$,$+\beta$) are given in Table IV, where some variable levels were rounded based on the sensitivity of the equipment employed.

TABLE IV. Auxiliary factor levels used in the central composite design

Factor	Physical quantity	Low level ($-\beta$)	Medium level (0)	High level ($+\beta$)
X_1	Temperature, K	336	353	370
X_2	HCl concentration, mol dm^{-3}	2.0	4.5	7.0
X_3	Stirring speed, rpm	200	450	700
X_4	Solid/liquid ratio	1:2.3	1:4	1:7.3
X_5	Time, h	0.336	2	3.66

The design matrix and the results of the auxiliary experiments carried out to calculate the second order model parameters are given in Table V. The second-order model is defined in its usual form as:

$$y = b_0' + \sum_{i=1}^{5} b_i x_i + \sum_{i=1}^{5} b_{ii} x_i^2 + \sum_{i=1}^{5} \sum_{j>1}^{5} b_{ij} x_i x_j \quad (4)$$

where $b_0' = b_0 - \sum_{i=1}^{5} b_{ij} \bar{x}_i^2$, and $\bar{x}_i^2 = \frac{1}{N} \sum_{i=1}^{n} x_i^2 = \frac{F + 2\beta^2}{N}$.

TABLE V. Experimental design for the second-order model and the leaching yields of MgO

Run	X_1	X_2	X_3	X_4	X_5	MgO content, %.	
						Experimental	Predicted
20	+1.664	0	0	0	0	17.05	14.85
21	–1.664	0	0	0	0	34.57	38.76
22	0	+1.664	0	0	0	13.01	15.96
23	0	–1.664	0	0	0	15.92	14.96
24	0	0	+1.664	0	0	24.59	20.86
25	0	0	–1.664	0	0	20.29	26.01
26	0	0	0	+1.664	0	24.22	23.13
27	0	0	0	–1.644	0	20.43	23.50
28	0	0	0	0	+1.664	13.51	22.79
29	0	0	0	0	–1.664	36.17	28.88

The second-order model tested at the 95 % confidence level is as follows:

$$y_{\mathrm{MgO}} = 23.56 + 7.18X_1 - 0.30X_2 + 1.55X_3 + 0.11X_4 + \\ +1.83X_5 + 1.10X_1^2 - 3.00X_2^2 + 0.75X_5^2 + 5.81X_1X_2 + \\ +5.39X_1X_5 + 1.89X_2X_4 + 1.49X_2X_5 - 1.86X_3X_4 \quad (5)$$

From the statistical analysis, the temperature, stirring rate, liquid/solid ratio and time have positive effects, whereas the HCl concentration has a negative effect on the leaching yield of MgO, as can be seen from Eq. (5). Also, the interaction effects between temperature and HCl concentration, temperature and time, HCl concentration and liquid/solid ratio, HCl concentration and time, stirring rate and liquid/solid ratio, were found to be significant.

Residual analysis is a valuable tool to detect the existence of systematic errors. The normalized residual is defined as:

ε = (experimental value – model value)/standard deviation

For a well-established model, systematic errors are absent and the normalized residuals result from experimental error which exhibit a normal distribution according to a widely accepted statistical convention.[9]

The test graphics are shown in Fig. 2, which supports the reliability of the model, Eq. (5).

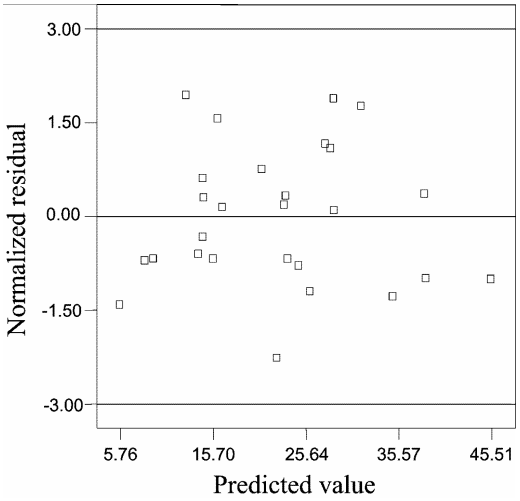

Fig. 2. Test graphics.

Also, the graphs of the residuals *vs*. the individual factors are presented in Fig. 3. The residual plot shows an equal scatter of the residual data above and below the *x*-axis for all the individual factors (temperature, HCl concentration, stirring rate, liquid/solid ratio and time), which indicates that the data are dependent on the model.

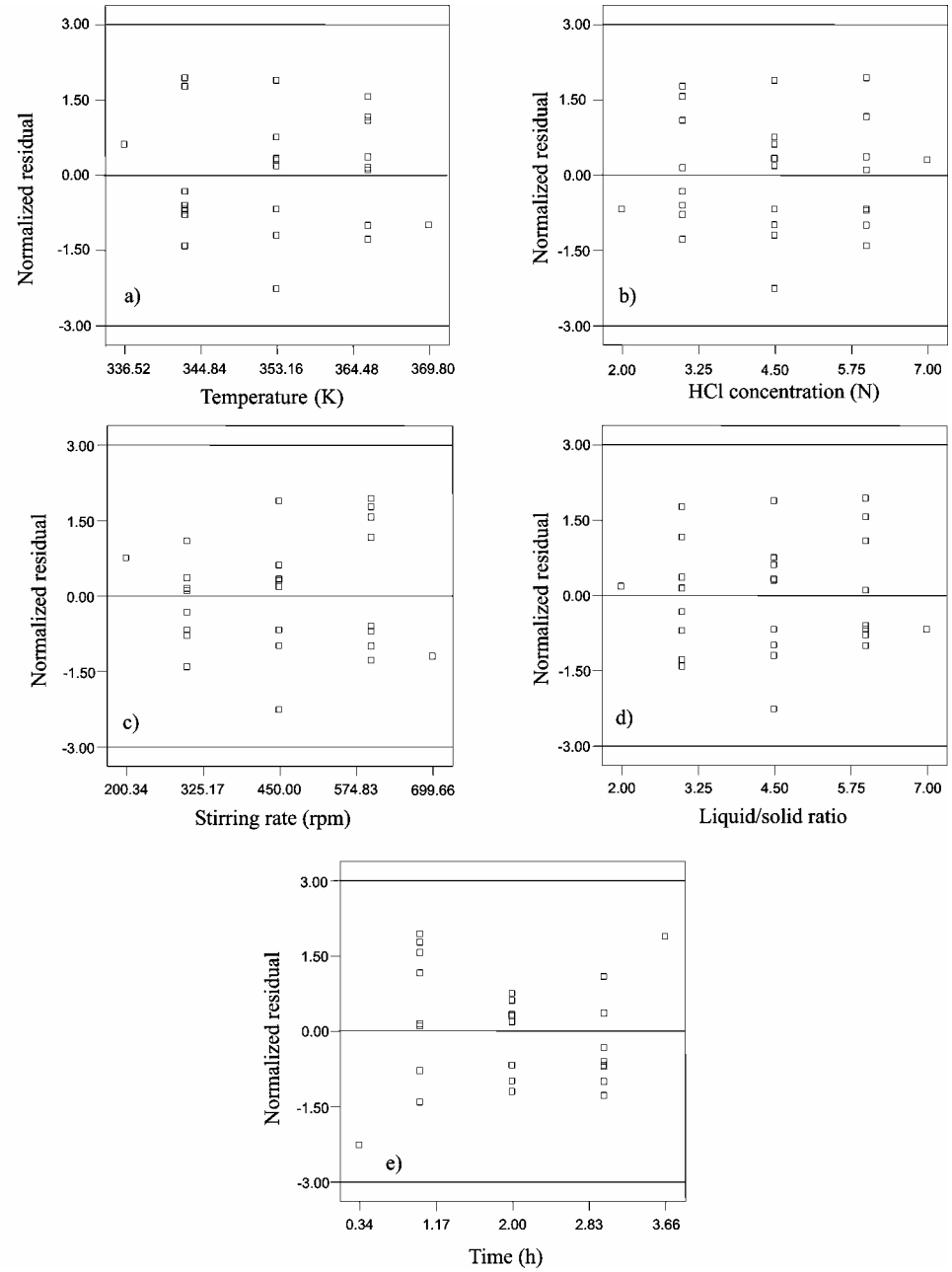

Fig. 3. The graphs of the residuals *vs*. the individual factors.

The highest leaching yield of MgO was obtained at 363 K, 6.0 M HCl, 600 rpm, a solid-to-liquid ratio of 1:6 and a process duration of 3 h. The lowest leaching

yield of MgO was obtained at 343 K, 6.0 M HCl, 300 rpm, a solid-to-liquid ratio of 1:3 and a process duration of 1 h. When the second order model, Eq. (5), and the first order model, Eq. (2), are compared, it can be seen that X_2 (acid concentration), X_4 (solid to liquid ratio) and X_5 (time) are significant in the second order model. For the first order model, the low level of acid concentration, the solid to liquid ratio and the reaction time are 3.0 M, 1:3 and 1 h, respectively, while for the second order model, they are 2.0 M, 1:2.3 and 0.336 h, respectively.

It appears that the leaching yield is significantly dependent on the acid concentration of 2.0 M HCl and the reaction time, especially during the first twenty min.

Natural smectite has a relatively underdeveloped micro pore volume, total porosity and specific surface area, as measured by nitrogen adsorption (Table VI).

TABLE VI. Pore structure parameters for natural and acid-activated smectite

Run	S_{BET} / m^2 g^{-1}	$\Sigma V_{0.98}$ / cm^3 g^{-1}	d / nm	V_{mic} / cm^3 g^{-1}
1	138	0.125	3.8	0.061
2	159	0.143	2.4	0.066
3	218	0.255	3.6	0.090
4	154	0.136	2.2	0.066
5	121	0.110	4.0	0.053
6	125	0.128	3.8	0.054
7	222	0.207	3.6	0.096
8	162	0.163	3.8	0.068
9	210	0.272	1.8	0.085
10	113	0.138	1.9	0.055
11	117	0.131	2.0	0.051
12	73	0.092	1.8	0.033
13	110	0.128	3.8	0.052
14	54	0.069	3.8	0.024
15	177	0.212	3.6	0.076
16	62	0.075	3.8	0.029
17	153	0.158	2.3	0.065
18	153	0.158	2.3	0.065
19	153	0.158	2.3	0.065
20	69	0.078	3.9	0.033
21	157	0.182	3.6	0.068
22	87	0.087	3.8	0.042
23	121	0.131	3.7	0.056
24	142	0.133	3.8	0.060
25	127	0.124	3.7	0.054
26	148	0.144	3.7	0.062
27	143	0.136	3.7	0.059
28	104	0.101	3.9	0.048
29	192	0.212	3.6	0.077
Natural smectite	63	0.071	4.1	0.028

Acid treatment of the samples contributed to their adsorption capacity. As can be seen in the Table VI, the specific surface area and the textural properties of the acid activated smectite were strongly affected by the processes parameters.

The specific surface area, total pore volume and micro pore volume attained a maximum for sample 7. This indicates that the observed chemical and structural changes after treatment with 6.0 M HCl, at 363 K during 3 h caused an alteration of the morphology and, consequently, of the adsorption properties of the smectite samples. The pore size analysis showed that the natural clay had a wide pore size distribution with a mean pore diameter of 4.1 nm. The acid-activated samples had a greater increase of the pore volume of the micro- and meso-pores and this resulted in a lower value of the average pore diameter, compared to that of natural clay (Table VI). These changes of the pore structure are a result of removal of exchangeable cations and impurities from the clay by HCl.

CONCLUSIONS

The process improvement approach to the acid activation of smectite clay from Serbia was investigated by means of the full factorial design. The recovery of the Mg content from natural smectite, as a process response, was determined with respect to temperature, leaching time, acid normality, solid-to-liquid ratio and stirring rate. Initially, the 2^5 full factorial design was used to obtain a first-order model with interaction terms. Based on the results of the analysis of the variance, it was necessary to conduct auxiliary experiments using an orthogonal central composite design to obtain a second-order model relating the MgO leaching yield to the experimental variables.

The highest leaching yields of MgO were obtained at 363 K, 6.0 M HCl, 600 rpm, solid-to-liquid ratio 1:6 and a process duration of 3 h.

The specific surface area and the textural properties of acid activated smectite were strongly affected by the processes parameters. Pore size analysis showed that the acid-activated samples had a greater increase of the pore volume of the micro- and meso-pores, which resulted in a lower value of the average pore diameter, compared to that of natural clay. These changes of the pore structure are the result of removal of exchangeable cations and impurities from the clay by HCl.

The obtained results may provide a background for pilot and industrial scale applications.

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И З В О Д

ФАКТОРИЈАЛНИ И ОРТОГОНАЛНО ЦЕНТРАЛНО КОМПОЗИТНИ ПЛАН ЕКСПЕРИМЕНТА КИСЕЛИНСКЕ АКТИВАЦИЈЕ СМЕКТИТА

ЉИЉАНА РОЖИЋ, ТАТЈАНА НОВАКОВИЋ и СРЂАН ПЕТРОВИЋ

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Сврха овог рада била је одређивање ефективних процесних параметара и оптималних процесних услова киселинске активације смектита из Србије. Успешно су коришћене две методе математичког моделовања: пун факторијални и ортогонални централни композитни план

експеримента. При оптималном планирању експеримента истовремено се мењају сви параметри који утичу на процес, што нам омогућава одређивање њиховог међусобног утицаја и смањење укупног броја експеримената. Током планирања експеримената разматран је утицај следећих релевантних параметара: температуре, времена активације, концентрације киселине, односа течно/чврсто и броја обртаја мешалице, на степен издвајања магнезијум-оксида. Резултати оптимизације параметара киселинске активације смектита, на бази статистичких планова експеримента, показали су да концентрација киселине, температура и време активације имају најјачи утицај на промену специфичне површине смектита, док однос течно/чврсто и број обртаја мешалице имају секундарни ефекат. Максимални степен издвајања магнезијум-оксида од 41,86 % узрокује и највећи пораст специфичне површине до 221 $m^2 g^{-1}$.

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