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RESPONSE SURFACE OPTIMIZATION FOR ACTIVATION OF BENTONITE USING MICROWAVE IRRADIATION

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Abstract—Microwave irradiation as a means for heating bentonites during acid activation has been investigated in the past but it has never been optimized for industrial applications. The purpose of this study was to apply a factorial 2^3 experimental design to a Serbian bentonite in order to determine the influence of microwave heating on the acid-activation process. The effect of acid activation under microwave irradiation on the textural and structural properties of bentonite was studied as a model reaction. A mathematical, second-order response surface model (RSM) was developed with a central composite design that incorporated the relationships among various process parameters (time, acid concentration, and microwave heating power) and the selected process response of specific surface area of the bentonite. The ranges of values for the process parameters chosen were: time, 5–21 min; acid concentration, 2–7 M; and microwave heating power, 63–172 W. The effect of individual variables and their interaction effects on the textural and structural properties of the bentonite were determined. Statistical analysis showed that the duration of microwave irradiation was less significant than the other two factors. The model showed that increasing the time and acid concentration improved the textural properties of bentonites, resulting in increased specific surface area. This model is useful for setting an optimum value of the activation parameters for achieving the maximum specific surface area. An optimum specific surface area of 142 m^2g^{-1} was achieved with an acid concentration of 5.2 M, activation time of 7.4 min, and microwave power of 117 W.

Key Words—Bentonite, Microwave Irradiation, Statistical Design, Specific Surface Area.

INTRODUCTION

The heating of reactive systems using microwave irradiation has been investigated extensively over the past 20 y. Microwave-assisted operations offer a very promising means of applying an electromagnetic field to intensify chemical processes.

The classic publication by Gedye *et al.* (1986) spawned a series of investigations of the effect of microwaves on chemical reactions. Several beneficial effects of microwave heating, *e.g.* increased reaction rate and selectivity for various kinds of reactions, have been reported (Chemat *et al.*, 1998). Microwave effects are obtained as a result of the direct interaction of the microwave field and the irradiated material, thus creating a temperature field around the irradiated media. This effect cannot be obtained by conventional heating, which is caused by convection and conduction and not by dielectric loss, as is the case with microwave heating (Thomas, 1997; Toukoniitty *et al.*, 2005a, 2005b; Zhang *et al.*, 2007). The use of microwave irradiation in the activation of clay offers advantages over conventional methods, including a higher heating rate in a shorter time due to volumetric heating. The microwave technique also provides more uniform heating compared to conventional heating methods. Microwave irradiation can be used not only to reduce the preparation time but also to prepare unique materials (Tyagi *et al.*, 2006; Rivera *et al.*, 2006; Korichi *et al.*, 2009).

Clays are used in a wide range of applications because of their large cation exchange capacity values, porosity, surface areas, and consequent strong adsorption and absorption capacities. Treatment of catalytic supports and adsorbents and the effect of acid attack on clay properties such as surface area, acidity, and bleaching efficiency have received considerable attention (Srasra *et al.*, 1989; Christidis and Kosiari, 2003; Rožić *et al.*, 2009). Treatment of bentonites with mineral acids is a common way to modify the properties listed above and to impart acidity to the clay surface (Komadel *et al.*, 1990; Falaras and Lezou, 1998; Önal and Sarikaya, 2007; Rožić *et al.*, 2010). A number of studies have correlated acid-treatment parameters with the structural modification and surface acidity generated in clays (Rhodes and Brown, 1992; Christidis *et al.*, 1997; Rožić *et al.*, 2010). Few studies, however, have been carried out on the formation of acid-treated clays by methods

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other than conventional hydrothermal acid digestion. Microwave-assisted operations are recognized as very promising techniques for intensification of chemical processes. The microwave-assisted methods are quicker and allow the preparation of more homogeneous and stable materials compared to conventional hydrothermal activation techniques (Stankiewicz, 2006). Present-day industrial applications, however, demand comprehensive theoretical simulations before the design of the industrial-scale process. Traditional design of experiments, using factorial or fractional factorial designs, is commonly used to optimize processes based on empirical models. An example of empirical modeling is 'response surface modeling' (RSM) (Lazić, 2004). In this method, the objective is to maximize performance by finding the best operating point. The operating point of a dynamic system defines its overall state at a given time. The experimental plan adopts the face-centered central composite design (CCD). A second-order response surface model has been used to develop an equation for predicting selected process responses based on the data collected using a statistical design of experiments (Park and Kim, 1992). The analysis of variation (ANOVA) shows that the observed data fit well into the assumed second-order RSM model. The RSM model is useful for process optimization when only limited experimental data are available.

The purpose of this study was to take these factors into account to develop a theoretical model based on experimental results. Changes to the textural properties of bentonites under microwave irradiation conditions were investigated experimentally using N_2 adsorption-desorption isotherms. Specific surface area was chosen for the process response because the chemical, surface, and structural properties of the activated bentonite determine and limit its potential applications (Srasra *et al.*, 1989). Changes to the structural and textural properties of activated bentonites with variations in relevant factors such as time, acid concentration, and microwave heating power during the process of acid activation are also presented here.

MATERIALS AND METHODS

The bentonite powder from Serbia was used as the starting material. Raw bentonite, with a particle size of <75 μm (200 mesh ASTM), possessed the following chemical composition (wt.%): SiO_2 = 66.58; Al_2O_3 = 15.89; Fe_2O_3 = 5.70; CaO = 2.23; MgO = 2.71; Na_2O = 0.94; K_2O = 1.23; TiO_2 = 0.65; and loss on ignition = 4.69. The XRD patterns (Figure 1) of raw clay demonstrated maximum intensities within the ranges typical of smectite-group minerals. In addition, smectite (Sm), illite (I), feldspar (F), calcite (C), and quartz (Q) were present in the sample. For quantitative purposes, the line broadening of the d_{110} reflection was used to evaluate the mean crystallite size (D).

Acid activation was carried out using a focused microwave reactor (Discover, CEM Corp, Matthews, North Carolina, USA) supplied with a programmed temperature control system, which operated at 2.45 GHz with adjustable power and continuous microwave power output. All experiments were performed in a cylindrical glass cell with a diameter d = 9 mm and height H = 45 mm. To maintain constant microwave irradiation and constant temperature during the process, the cell was thermostated externally. The temperature of the solution was measured with a commercial fiber optic sensor with an accuracy of ±0.5 K. Experiments were performed at a temperature of 358 K. Bentonite (1 g) was added to HCl (10 mL) and the mixture was irradiated using microwaves for 1, 5, 11, 17, and 21 min at a microwave power ranging from 63 to 172 W. After irradiation, the sample was filtered and washed thoroughly with hot distilled water until the filtrate was free of chloride ions. The sample was dried to a constant weight at 383 K.

The chemical compositions of raw and activated bentonites were analyzed using inductively coupled plasma optical spectrometry (ICP OS) using an ICPA 6500 Spectrometer (Thermo Scientific). The crystallite size of the samples was determined by powder X-ray diffraction (XRD) on a Philips PW 1710 diffractometer with CuKα radiation (40 kV, 30 mA, λ = 0.154178 nm) over a scan range of 3−70º2θ. The specific surface area and the pore volumes were determined from the N_2 adsorption-desorption isotherms that were obtained at 77 K with an automatic adsorption apparatus (Sorptomatic 1990 Thermo Finningen). The specific surface area of the samples was calculated by fitting the adsorption data to the linear range of the Brunauer-Emmet-Teller equation (relative to p/p_0, 0.05−0.35) (Gregg and Sing, 1982). The total pore volumes of micro- and mesopores were obtained from N_2 adsorption at p/p_0 = 0.98. Micropore volumes were estimated according to the theory of the micropore volume-filling process and the logarithmic form of the Dubinin-Radushkevich equation (Dubinin, 1975). The pore-size

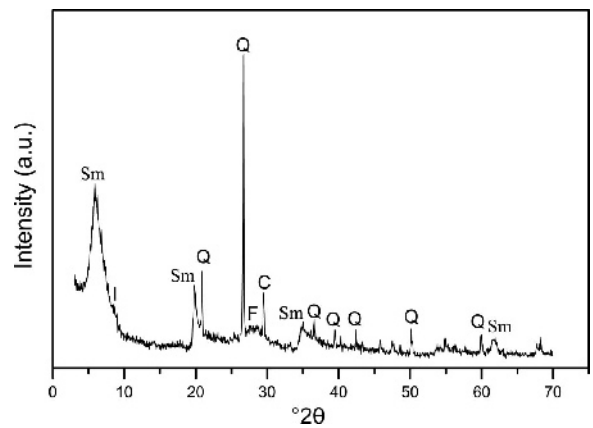


Figure 1. Powder XRD patterns of raw bentonite.

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Table 1. Experimental range and levels of the independent variables.

Variable (symbol, units)	Coded values				
	−1.682	−1	0	+1	+1.682
Acid concentration (X_1, M)	2	3	4.5	6	7
Time (X_2, min)	1	5	11	17	21
Microwave heating power (X_3, W)	63	85	117	150	172

distribution was calculated from N_2 desorption isotherms according to the Barret-Joyner-Halenda method (Barrett *et al.*, 1951).

Optimization of the textural properties of bentonite by microwave-assisted acid activation was achieved using the response surface methodology. A CCD was used to study the empirical relations between responses (specific surface area of bentonite) and process factors (time, acid concentration, and microwave heating power). The variables were coded according to the following equation:

$$x_i = \frac{X_i - X_0}{\Delta x} \quad (1)$$

where x_i is the dimensionless coded value of each independent variable, X_0 is the value of X_i at the center point, and Δx is the step change value. The behavior of the system is expressed by the following quadratic equation:

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j>1}^{k} b_{ij} X_i X_j + \varepsilon \quad (2)$$

where Y is the predicted response; X_i, X_j, ...X_k are the input variables that affect the response Y; X_i^2, X_j^2,..., X_k^2 are the square effects; X_iX_j, X_iX_k, and X_jX_k are the interaction effects; b_0 is the intercept term; b_i are the linear terms; b_{ii} are the square terms; b_{ij} are the interaction terms; and ε is a random error (Lazić, 2004). The data obtained from the CCD experiments were analyzed using *Design Expert* (Version 8.0.7.1, Stat-Ease, Inc., Minneapolis, Minnesota, USA) software.

RESULTS AND DISCUSSION

The most important parameters that affected the textural properties of bentonites were time, acid concentration, and microwave heating power during the process of acid activation. To study the combined effect of these factors, statistically designed experiments were performed for various combinations of the physical parameters. An orthogonal 2^3 factorial central composite experimental design with six star points and three replicates at the center, with a total of 17 experiments, was used to optimize the process parameters: acid concentration (X_1), time (X_2), and microwave heating power (X_3). Each of the parameters was coded at five levels: −1.682, −1, 0, +1, and +1.682 (Table 1).

The solid/liquid ratio was fixed at 10% (w/v), while the levels of other factors were calculated for each experiment based on the particular operational conditions (Table 2). Significant changes in the specific surface areas of activated samples were observed for all of the combinations, implying that these variables significantly affect the activation processes.

The response plots (Figure 2) provide insights into the effect of each variable. The mean in the plot was calculated by averaging the response over all of the runs for both the high and the low level of the variable studied.

The specific surface areas of activated samples increased with increasing acid concentration, time, or microwave heating power (Figure 2). The activation which proceeded with partial dissolution of smectite was described by pseudo-first-order kinetics and characterized by an initial replacement of the interlayer cations by H^+ followed by dissolution of the tetrahedral and octahedral sheets and subsequent release of the structural cations (Novak and Čičel, 1978; Kaviratna and Pinnavaia, 1994). Indeed, when the acid concentration (or time) was increased, the specific surface area of the

Table 2. Full factorial central composite design matrix of three variables with the observed responses.

Run	X_1	X_2	X_3	S_{BET} (m^2g^{-1})	
				Exp.	Pred.
1	−1	1	−1	119.0	117.7
2	−1	−1	1	127.7	124.8
3	1	1	−1	132.6	128.5
4	−1	−1	1	145.4	145.0
5	1	−1	1	119.5	114.8
6	1	−1	1	122.2	122.0
7	1	1	1	139.1	137.0
8	−1	1	−1	156.5	153.5
9	+α	0	0	120.5	125.5
10	−α	0	0	143.7	145.3
11	0	+α	0	110.8	114.0
12	0	−α	0	145.6	149.1
13	0	0	+α	122.8	125.6
14	0	0	−α	126.5	130.3
15	0	0	0	149.5	149.7
16	0	0	0	151.0	149.7
17	0	0	0	150.0	149.7

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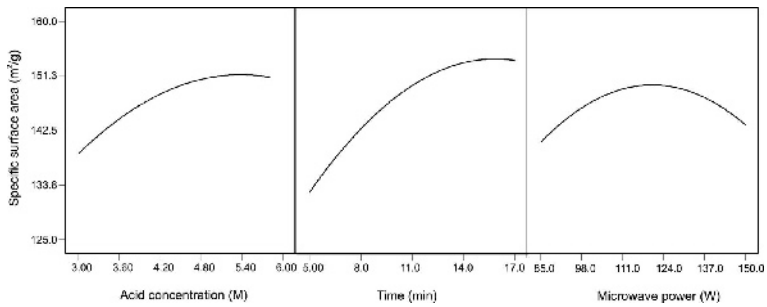


Figure 2. Main effects of the parameters influencing specific surface area.

activated bentonite increased. Therefore, the relative contents of the insoluble cations in bentonite increased in the order: Ca^{2+}< Na^{+}< Mg^{2+}< $Fe^{2+/3+}$ < Al^{+3} < K^{+}< Si^{4+}<Ti^{4+} (Table 3). The K^{+} cations and the Si^{4+} cations at the tetrahedral sites of smectite did not dissolve during the acid activation (Önal and Sarikaya, 2007). The increase in relative content of these cations depended on the dissolution of other cations during the activation. In particular, the decrease in CaO from 1.62% to <0.2% probably corresponded to the dissolution of calcite in acid conditions rather than smectite surface-exchange reactions. The presence of calcite appears to be confirmed by the 3.03 Å reflection (peak labeled C in Figure 1).

Furthermore, the dissolution of octahedral cations was most effective when the acid concentration was ⩾ 4.5 M. At high acidity, more octahedral cations were dissolved into the liquid phase, thus favoring the structural and textural modification of the smectite. The increase in the microwave heating power improved the textural properties of the activated samples (Table 4).

These factors had an influence on the textural properties of the activated samples. All of the samples yielded type IV isotherms (Gregg and Sing, 1982), which indicate mesoporous materials. The general shape of the isotherms did not change after activation with microwave irradiation; however, a slight decrease in the amount of nitrogen adsorbed was observed. All of the isotherms were reversible at a low equilibrium pressure. Under high pressure, however, an H3 hysteresis loop was observed (Gregg and Sing, 1982), indicating that the pores were shaped as slits or ink-bottles (pores with narrow necks and wide bodies). A comparison of the results (Table 4) showed that the specific surface area and the total pore volume increased as the values of process parameters increased. The values of the micropore volume of the activated samples showed a very similar behavior to that of the total pore volume. Besides, the mesopore diameter, particularly the average mesopore diameter, did not change appreciably, whereas the number of mesopores increased considerably with microwave-assisted acid activation. These changes in the

Table 3. Chemical analyses (wt.% oxides) for raw and activated bentonite samples.

Run	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	TiO_2	Na_2O	K_2O
1	70.65	14.54	0.17	2.44	5.34	0.72	0.22	1.20
2	70.59	14.52	0.10	2.47	5.44	0.73	0.23	1.23
3	70.00	15.28	0.15	2.54	5.45	0.74	0.21	1.17
4	70.16	14.78	0.19	2.56	5.49	0.73	0.23	1.23
5	69.73	15.20	0.16	2.57	5.50	0.73	0.21	1.21
6	70.91	15.19	0.01	2.65	5.64	0.72	0.21	1.14
7	69.25	15.54	0.17	2.56	5.68	0.73	0.22	1.21
8	69.64	15.07	0.10	2.56	5.52	0.75	0.20	1.16
9	71.14	14.39	0.14	2.44	5.36	0.70	0.22	1.18
10	68.65	15.85	0.22	2.63	5.58	0.73	0.38	1.26
11	69.53	15.56	0.06	2.63	5.66	0.76	0.20	1.19
12	70.27	15.14	0.13	2.56	5.46	0.72	0.22	1.20
13	69.28	15.42	0.11	2.60	5.61	0.75	0.33	1.21
14	68.90	15.44	0.12	2.66	5.65	0.74	0.20	1.22
15	69.87	15.46	0.02	2.52	5.45	0.76	0.20	1.16
16	68.74	15.87	0.15	2.70	5.67	0.75	o.21	1.22
17	70.23	15.30	0.03	2.49	5.30	0.78	0.20	1.14
Raw bentonite	66.58	15.89	1.62	2.71	5.70	0.65	0.94	1.23

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Table 4. Structural and textural properties of microwave-assisted, acid-activated bentonites.

Run	S_{BET} (m^2g^{-1})	$\Sigma V_{0.98}$ (cm^3g^{-1})	V_{mic} (cm^3g^{-1})	d (nm)	D (nm)
1	149.5	0.131	0.067	3.94	19.21
2	122.2	0.119	0.054	3.68	17.34
3	139.1	0.122	0.063	3.68	18.38
4	127.7	0.115	0.058	3.92	16.76
5	150.0	0.141	0.054	3.82	17.54
6	110.8	0.170	0.050	3.74	18.00
7	119.0	0.110	0.054	3.94	15.54
8	145.6	0.116	0.061	3.91	17.77
9	126.5	0.107	0.057	3.87	17.91
10	120.5	0.108	0.055	3.91	17.39
11	143.7	0.120	0.064	3.90	17.39
12	122.8	0.103	0.076	3.92	18.91
13	132.6	0.120	0.063	3.92	16.36
14	119.5	0.108	0.054	3.95	15.26
15	145.4	0.121	0.066	3.91	16.52
16	126.9	0.112	0.058	3.89	17.54
17	156.5	0.130	0.071	3.88	17.56
Raw bentonite	63.4	0.028	0.071	4.10	21.49

S_{BET} – specific surface area of the samples
$\Sigma V_{0.98}$ – total pore volume of micro- and mesopores obtained from N_2 adsorption at $p/p_0 = 0.98$
V_{mic} – micropore volumes
d – pore size diameter
D – crystallite size

pore structure were the result of the combined effects of the three factors relevant to this process.

The full width at half maximum (FWHM) of the main reflection peak in the X-ray powder diffraction patterns of the raw and acid-activated samples (Figure not shown) can be used to determine the crystallite size of the smectite particles using Scherer's equation (Table 4). The XRD patterns of the activated samples indicated that microwave power in the range 63–172 W did not affect the structure of the components to any noticeable extent. The results calculated indicated that the crystallite size varied from 15.3 nm to 19.2 nm. The changes in the crystallite size are caused by significant changes in Al_2O_3 content *vs*. structural changes in the smectite layer. A more likely explanation may be the degree of disorder among layers.

A regression model relating the response (Y) to the variables (X) for the microwave-assisted acid activation of bentonite was developed using the experimental results, and the relationship is given in the following quadratic polynomial equation:

$$Y = 149.76 + 5.90X_1 + 10.58X_2 + 1.39X_3 + 2.35X_1X_2 + 2.83X_2X_3 - 5.06X_1^2 - 6.54X_2^2 - 7.75X_3^2 \quad (3)$$

Apart from the linear effect of the parameters on the response, the RSM also gives insight into the quadratic and interaction effects of the parameters. Analysis of the various effects of the parameters was done by means of the Fisher 'F' test and the Student 't' test. The 'F' test was used to determine the significance of the interaction among the variables, which in turn may indicate the patterns of the interactions among the variables. Generally, the larger the magnitude of the value of F and the smaller the probability (P), the more significant was the corresponding coefficient term. The regression coefficients and the F and P values for all the linear, quadratic, and interaction effects of the parameters were calculated (Table 5).

The values obtained showed that the coefficients for the linear effect of time and acid concentration were highly significant ($P = 0.0001$ and 0.0008, respectively). All square terms such as (acid concentration)^2, (time)^2, and (microwave heating power)^2 were significant ($P = 0.0034$, 0.0008, and 0.0002, respectively). Furthermore,

Table 5. Analysis of variance values for the fitted quadratic polynomial model of microwave-assisted acid activation of bentonite.

Source of variance	Sum of squares	Degress of freedom	Mean of squares	F-test	Probability > F
X_1	475.89	1	475.89	27.79	0.0008
X_2	1517.76	1	1517.76	88.62	<0.0001
X_3	26.47	1	26.47	1.55	0.2490
X_1X_2	44.18	1	44.18	2.58	0.1469
$X_2\ X_3$	63.90	1	63.90	3.73	0.0895
X_1^2	290.08	1	290.08	16.94	0.0034
X_2^2	469.14	1	469.14	27.39	0.0008
X_3^2	671.60	1	671.60	39.21	0.0002
Model	3056.29	8	382.04	22.31	<0.0001
Residual	137.01	8	17.13		
Lack of fit	135.85	6	22.64	38.81	<0.0253
Pure error	1.17	2	0.58		
Total	3193.30	16			

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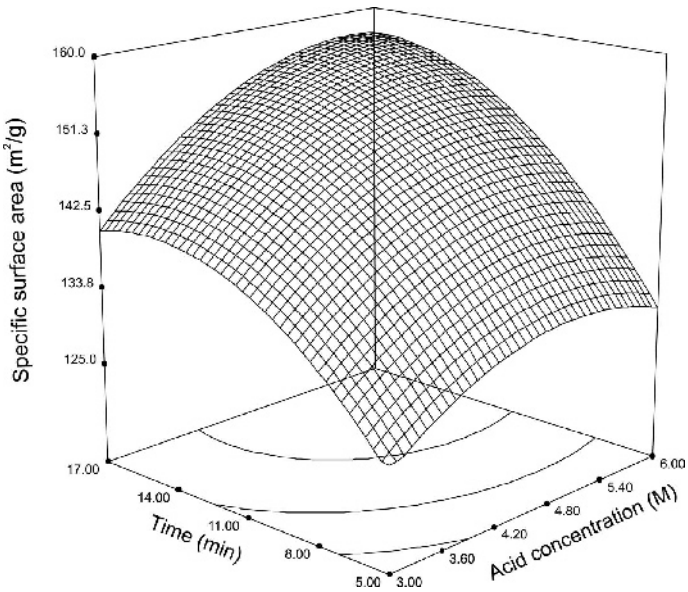


Figure 3. Response surface plot showing the effect of time and acid concentration on the specific surface area of bentonite.

high values of R^2 (0.957) and R^2 (adjusted) (0.914) indicated a high dependence and correlation between the observed and the predicted values of the response. These high values also indicated that ~96% of the result of the total variation can be explained by this model.

The 3D response surfaces and the 2D contour plot are generally the graphical representation of the regression equation. This representation shows the relative effects of any two variables when the remaining variables were kept constant. Response surface plots to estimate the specific surface area of bentonites activated with microwave heating against the independent variables (Figures 3) revealed that the interaction between time and acid concentration at constant microwave power (117 W) was not significant (*P* value = 0.1469).

Increasing the time and acid concentration promoted partial dissolution of octahedral cations and improved the textural properties, resulting in an increase in the specific surface area.

The response surface plot as a function of time *vs.* the microwave power at a constant acid concentration of 4.5 M (Figure 4) clearly showed that the specific surface

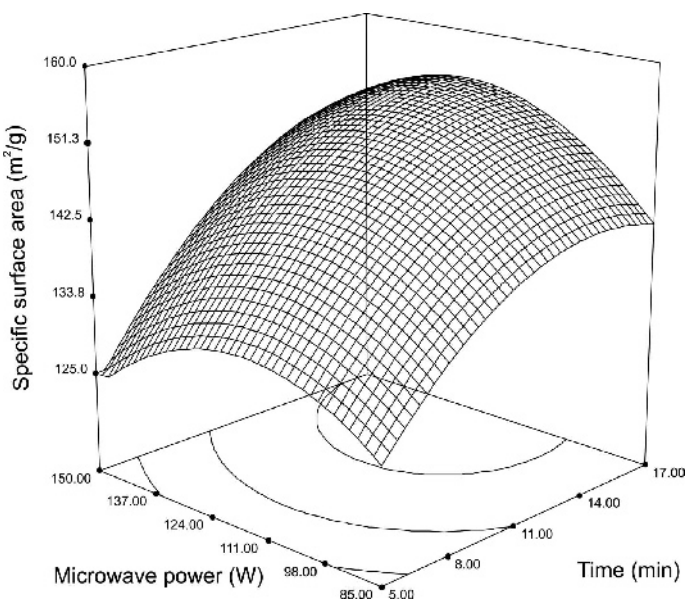


Figure 4. Response surface plot showing the effect of time and microwave power on the specific surface area of bentonite.

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area increased with increasing time. Clearly, the effect of time on improving the textural properties of bentonite is quite significant.

The optimum conditions to obtain the maximum specific surface area for microwave-assisted acid-activated bentonite were determined to be: acid concentration = 5.2 M, time = 7.4 min, and microwave power = 117 W. The time required for preparing acid-activated bentonite by the microwave heating method is less (and, therefore, more economical) than the time required for the conventional thermal activation method, as discussed previously (Novaković *et al.*, 2008; Rožić *et al.*, 2010).

CONCLUSIONS

The statistical design of experiments and the response surface methodology proved to be powerful tools for planning and analyzing experiments to ascertain the influence of acid concentration, time, and microwave power on the textural properties of bentonite. The calculated regression models were statistically significant at the required range and presented little variability. Increasing the time and acid concentration promoted partial dissolution of octahedral cations and improved the textural properties, resulting in an increase in the specific surface area. The optimum conditions to obtain the maximum specific surface area for microwave-assisted acid-activated bentonite were determined to be as follows: acid concentration = 5.2 M, time = 7.4 min, and microwave power = 117 W. Acid activation of bentonite was faster with microwave irradiation than with conventional heating. Microwave-assisted processes, therefore, have the potential to develop into a cost-efficient method for acid activation of bentonite.

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