

Optimization and Statistical Modeling of Catalytic Cyclohexene Epoxidation with H₂O₂ over Vanadium-Based Polyoxometalates Supported On Montmorillonite as a Green Catalyst

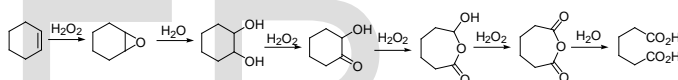
Souheyla Boudjema, Mostapha Zerrouki, Abderrahim Choukchou-Braham

Abstract— This work was designed to study the optimization of the process of cyclohexene epoxidation with hydrogen peroxide in the presence of acid activated montmorillonite clay supported on 11-molybdovanado-phosphoric acid, with the Keggin structure H₄[PVMo₁₁O₄₀].13H₂O (PVMo) as catalyst. This process has been investigated by applying statistical methods for experimental design. The influence of main process parameters on the conversion of hydroperoxides, selectivity of transformation to epoxy compounds with regard to cyclohexene conversion, and selectivity of transformation to epoxy compounds and cyclohexane-1,2-diol, has been described using regression equations in the form of first-order polynomials. Analysis of the obtained regression equations allowed us to optimize the experimental parameters of the cyclohexene oxidation reaction with hydrogen peroxide; these parameters are as follows: catalyst weight = 0.05 g, temperature = 70 °C, reaction time = 9 h, with 20 % PVMo/Hmont used as catalyst, and hydrogen peroxide as oxidant.

Keywords— Cyclohexene epoxidation, Experimental design, Hydrogen peroxide, Process optimization, Polyoxometalates, Montmorillonite.

1 INTRODUCTION

Catalytic oxidation is a key technique for converting petroleum-based feedstocks to useful chemicals such as diols, epoxides, alcohols, and carbonyl compounds [1-6]. Cyclohexene oxidation has been the subject of extensive studies in the last few years, as the products obtained are important synthetic intermediates for the production of fine chemicals; they can also be utilized in the synthesis of polyether polymers. However, in the epoxidation of alkenes, several side reactions can take place, i.e. oxidation of alkenes at the allylic positions, ring-opening of epoxides by hydrolysis or solvolysis, epoxide rearrangement or even total breakdown of the C=C double bond. Cyclohexene is one of the most difficult cases, as the first two situations, namely allylic oxidation and epoxide ring-opening, can occur extensively [7, 8]. Thus, the heterogeneous oxidation of cyclohexene, in the presence of hydroperoxides, has numerous advantages in the field of synthetic chemistry [9]. The development of green practical procedures for the oxidation of six-carbon feedstock is highly desirable, particularly for medium and large-scale synthesis of various intermediates and fine chemicals [10].



Scheme 1 Reaction pathway for the oxidation of cyclohexene to adipic acid

The choice of oxidants determines the practicability and efficiency of the oxidation reactions. While a large number of oxidants have extensively been investigated for catalytic liquid-phase oxidation processes, some of them still produce toxic and environmentally, politically, and economically unacceptable by-products. In addition, the active oxygen contents of most oxidants are low ($\leq 30\%$). In these contexts, H₂O₂ is the most attractive oxidant (after dioxygen) because of its high content of active oxygen species, with co-production of water only (no co-products in some cases); this oxidant is quite cheap and easy to handle. Moreover, in oxidation mechanisms using hydrogen peroxide, it has been suggested that H₂O₂ can be involved in the peroxometal formation (metal coming from the catalyst) which is expected to give, stoichiometrically, oxygen atoms to the substrate [11]. On the other hand, it was observed that peroxometal active oxidant species are favored when the metal of catalyst is in its highest oxidation state, and is both a Lewis acid and a weak oxidant, like the transition metal ions with d⁰ or d¹ electronic configurations (Mo(VI), W(VI), V(V), Nb(V)) [12].

Several research groups have reported that the cyclohexene oxidation reaction can be influenced by several parameters, like the catalyst weight, type of oxidant, temperature, heating mode, support, percentage of active phase to be deposited on the support (x % /support), and molar ratio of cyclohexene to

- Souheyla Boudjema is assistant professor at Kasdi Merbah University - Faculty of hydrocarbons, renewable energy, earth sciences and universe, Ouargla 30000, Algeria. And researcher at Laboratory of Catalysis and Synthesis in Organic Chemistry, Faculty of Sciences, University of Tlemcen, Algeria. E-mail: boudjema.souhila@gmail.com
- Mostapha Zerrouki is Phd-Student at Laboratory of Catalysis and Synthesis in Organic Chemistry, Faculty of Sciences, University of Tlemcen, Algeria.
- Abderrahim Choukchou-Braham is professor researcher at Laboratory of Catalysis and Synthesis in Organic Chemistry, Faculty of Sciences, University of Tlemcen, Algeria.

the oxidant, with various ranges [13-19]. The usefulness of polyoxometalates as oxidation catalysts has been well established in the literature. However, polyoxometalates-based heterogeneous catalysts give a good activity in cyclohexene epoxidation [20]. M. Fraile et al. [21] investigated the cyclohexene epoxidation using hydrogen peroxide as oxidant. The effect of slow addition of H_2O_2 and the hydrophobic character of the support were also studied. The epoxidation of cyclohexene, catalyzed by Keggin-type heteropoly compounds (HPAs), was investigated using anhydrous urea-hydrogen peroxide adduct (UHP) [22]. The effects of various reaction factors, such as the oxidizing reagents, solvent, HPAs and other catalysts containing tungsten, temperature, time, molar ratio of cyclohexene to the oxidant, and the catalyst weight have previously been studied. The optimized conditions were obtained for 3 mmol of cyclohexene, 0.75 mmol of UHP, 0.015 mmol of catalyst $(\text{CPB})_3[\text{PW}_{12}\text{O}_{40}]$ (0.5 mol %), 3 ml of acetonitrile, 1.89 mmol of bromobenzene as an internal standard. Z. Wang et al. [23] used the heteropolyanion $[\text{PMo}_4\text{O}_{24}]^{3-}$ (PMo) which was immobilized on the quaternary-ammonium poly(phthalazinone ether sulfone ketone) as catalyst for cyclohexene oxidation. The effects of various reaction factors, such as the solvent, purity of H_2O_2 and catalyst used, were studied. The optimized conditions were found for 20 mmol and 30 % H_2O_2 in acetonitrile (10 mL), for a time period of 4 h. The reaction conditions were optimized by Z. Karimi [24] in the presence of SBA/HMPAW ($\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot n[\text{C}_6\text{H}_{18}\text{N}_3\text{OP}]$) as a model for other synthesized POMs containing heterogeneous catalysts, while the effects of solvent, catalyst weight, temperature, and oxidant were still taken into consideration. The optimized conditions were reached for 0.025 g catalyst, 1 mmol cyclohexene, 2 mL H_2O_2 , 1 mL CH_2Cl_2 , and 0.1 mmol n-dodecane, under reflux. Each group of researchers proposed some specific operating conditions for the reaction. Actually, the objective is to attain the same operating conditions. Every process needs to be optimized for good yields, and the process shown in Scheme 1 is no exception. On optimizing this process at a small scale (laboratory-and pilot-scale process), industrial production could be achieved to obtain pure products and generate less waste. As suggested by Adams [25], more systematic work is needed in order "to build up the base of knowledge necessary for predictive reasoning."

Optimization problems in chemistry often involve the adjustment of large numbers of variables in order to obtain the ideal set of experimental conditions that produce the most desirable results [26]. An important issue in catalytic experimentation concerns the way to design experiments in order to explore and optimize the multidimensional parameter space, by minimizing the number of trials required to achieve a unique solution. This problem is so complex that classical analysis of this reaction would be very time consuming, but the experimental design offers an interesting alternative for identifying the experimental factors that affect the catalytic

activity and selectivity. The experimental design, a well known tool in several scientific and industrial areas, has seldom been used in the field of heterogeneous catalysis. Approaches for experimental design include techniques like factorial designs [27-29], deterministic optimization algorithms, such as the holographic search [30], and *split & pool* methods [31, 32]. Stochastic procedures, like the simulated annealing and genetic algorithms (GAs), have already been used to optimize several processes.

The aim of the present work is to identify the highest number of factors that control the oxidation of cyclohexene. For this multi-factor optimization, the traditional method of "changing one factor at a time" could have been applied, but was avoided because it is tedious and does not guarantee to attain the optimum set of parameters. Instead, the "full factorial design" method was preferred here. Based on a mathematical model that combines the effects of the processing factors, this approach was found to be much more reliable.

In our previous works, 11-molybdovanado-phosphoric acid, which was introduced into the mesoporous silica structure [33] and supported on acid activated montmorillonite clay [34], showed high oxidation activity for the oxidation of cyclohexene, in the presence of H_2O_2 (60 %). Furthermore, a series of modified clay materials, known as metal pillared clays, were prepared in our laboratory [35-37]. These porous materials, with a controlled pore structure, are great selective catalysts for the cyclohexene oxidation.

2 EXPERIMENTAL

2.1 Catalytic Experiments

The catalytic epoxidation of cyclohexene, with hydrogen peroxide 30 % H_2O_2 as oxidant, was carried out in a two-neck, round-bottom glass flask, equipped with a magnetic stirrer and a reflux condenser. Unless otherwise specified, all oxidation reactions were carried out at atmospheric pressure, under reflux, with 30 mmol of cyclohexene. A quantity of 30 % H_2O_2 (30 mmol) was used as oxidant and was slowly added (during 3 h) with a syringe pump, in addition to 10 mL of acetonitrile as solvent, 1 mL of 1,2-dimethoxyethane as internal standard for product quantification, and 25 mg of catalyst PVMo/Hmont (the catalyst was prepared and characterized in our previous work [34]). The reaction mixture was stirred at 70 °C. The catalytic reactions were monitored by means of a gas chromatograph (Agilent Technologies 7890A GC System) equipped with a Phenomenex Zebron-HT-5 Inferno column (30 m x 0.25 mm x 0.25 mm) column; a flame ionization detector (FID) was also used.

2.2 Experimental Design and Statistical Analysis

Cyclohexene oxidation was investigated and optimized using a combination of the factorial design and stepwise regression methods. Based on previous research work, the factors or in-

dependent variables, that may influence the conversion efficiency of cyclohexene and the selectivity of each product of the cyclohexene oxidation reaction, include the reaction temperature, molar ratio of cyclohexene to H₂O₂, reaction time, weight and loading of the catalyst used. They were assumed as the main factors in changing the results of cyclohexene catalytic oxidation process. In this study, the response variables are the conversion of cyclohexene (Y₁ %) and the combined selectivity of cyclohexene oxide and cyclohexane-1, 2 diol (Y₂ %).

To examine the effects of interactions, as well as the main effects of our parameters, on the conversion evolution and product selectivity, a factorial design with two levels and five factors (2⁵) was used. By applying this method, the reaction conditions could be optimized by doing just 32 runs for the above-mentioned mentioned variables. The coded and uncoded factors, with their levels, are listed in Table 1. These levels were coded as (+1) and (-1), for high and low levels, respectively, and 0 for the center point. The transformation of the independent factors from natural to coded form was performed by applying a linear transformation of the variables, as given in Eq. (1):

$$x_i = (X_i - X_{i0}) / \Delta X_i \quad \text{Eq. (1)}$$

Where x_i is the coded value of the variable at a certain point of the experimental design (i = 1, ..., k), X_i is the natural value of the variable at the same point of the experimental design (i = 1, ..., k), X_{i0} is the natural value of the variable at the central point of the experimental design (i = 1, ..., k), and ΔX_i is the step value along the X_i axis (natural).

The behavior of the system is explained by the following polynomial equation as a function of independent variables involving their interactions.

$$Y = b_0 + \sum b_i x_i + \sum b_{ij} x_i x_j + e \quad \text{Eq. (2)}$$

Where Y is the dependent variable (one of the response functions Y₁-Y₂); b₀, b_i, and b_{ij} are the coefficients of the regression equations (i, j = 1, ..., k); x_i and x_j are the independent factors in a coded (dimensionless) form (i, j = 1, ..., k); and k is the number of factors of the experimental design (k = 5).

For each experiment, parameters such as the conversion of cyclohexene (Y₁) and the combined selectivity of cyclohexene oxide and cyclohexane-1, 2 diol (Y₂ %) were calculated.

Analysis of the experimental design results was conducted with SPSS 22. The significance of the main effects, and their interactions, on the responses were evaluated using a variance analysis (ANOVA), where the P values were generated to prove the null hypothesis with a 95 % confidence level (α=0.05).

TABLE 1
Level of examined factors

| Factor value in coded form | | Factor value in natural form | | | | |
|----------------------------|-------|------------------------------|----------------------|---------------------|--|--------------------|
| | | Catalyst weight (m) | Catalyst loading (C) | Temperature (T) | % of H ₂ O ₂ (P) | Reaction time (t) |
| x _i | Level | X ₁ (g) | X ₂ (%) | X ₃ (°C) | X ₄ (%) | X ₅ (h) |
| Low | -1 | 0.025 | 10 | 70 | 30 | 6 |
| High | +1 | 0.05 | 20 | 80 | 60 | 9 |

3 RESULTS AND DISCUSSION

3.1 Overall Analysis of Test Results

Thirty-two (32) experiments were carried out, under the given experimental conditions, and the values of the responses (conversion of cyclohexene and combined selectivity of cyclohexene oxide + cyclohexane diol), are given in Table 2.

3.2 Mathematical and Graphical Analysis of Test Results

Fig. 1 is the Length plot, which shows the significance of each process factor and its interaction with the response variable (Y₁), which represents the conversion of cyclohexene.

Briefly, the main factors, such as X₁, X₂, X₃, X₅, the two-way interactions like X₁X₂, X₁X₃, X₁X₅, X₂X₄, X₂X₅, X₃X₄, and the three-way interactions like X₁X₃X₄, X₂X₃X₄, X₂X₃X₅ were found to be statistically significant (Table 3). Consequently, these parameters with a statistical significance should be considered in the predicted model. The multiple regression equations, i.e. (3) and (4), for coded and uncoded variables were, consequently, obtained from the full factorial design (FFD). In particular, the model derived from coded variables is known to be more widely used in predicting the response, because of the dimensionless independent variables used.

Coded levels (-1, +1):

$$\hat{Y}_1 = 63.323 + 4.514 X_1 + 3.227 X_2 - 9.098 X_3 + 4.786 X_5 - 2.586 X_1 X_2 - 6.236 X_1 X_3 - 1.147 X_1 X_5 - 1.683 X_2 X_4 + 1.195 X_2 X_5 - 2.963 X_3 X_4 + 3.165 X_1 X_3 X_4 - 2.623 X_2 X_3 X_4 - 1.309 X_2 X_3 X_5 \quad \text{Eq. (3)}$$

Uncoded levels:

$$\text{Conversion} = 63.323 + 4.514 m + 3.227 C - 9.098 T + 4.786 t - 2.586 mC - 6.236 mT - 1.147 mt - 1.683 CP + 1.195 Ct - 2.963 Tt + 3.165 mTP - 2.623 CTP - 1.309 CTt \quad \text{Eq. (4)}$$

To properly interpret the predicted coded model, represented by Eq. (3), the coefficient of determination (R²) and the adjusted coefficient of determination (R²_{adj}), for the linear model, were evaluated. They were found equal to 0.979 and 0.965, respectively.

TABLE 2
Design matrix and experimental results

TABLE 1
Level of examined factors

| Run | X ₁ | X ₂ | X ₃ | X ₄ | X ₅ | Catalyst weight (m) | Catalyst loading (C) | Factor values in natural form | | | | |
|-----|----------------|----------------|----------------|----------------|----------------|---------------------|----------------------|-------------------------------|------------------------------------|---------------|----------------|----------------|
| | | | | | | | | Temperature | % of H ₂ O ₂ | Reaction time | Y ₁ | Y ₂ |
| | | | | | | | | (T) | (P) | (t) | Conversion | Selectivity |
| 1 | -1 | -1 | -1 | -1 | -1 | 25 | 10 % | 70 | 30 % | 6 | 48 | 82 |
| 2 | 1 | -1 | -1 | -1 | -1 | 50 | 10 % | 70 | 30 % | 6 | 85 | 64 |
| 3 | -1 | 1 | -1 | -1 | -1 | 25 | 20 % | 70 | 30 % | 6 | 48 | 88 |
| 4 | 1 | 1 | -1 | -1 | -1 | 50 | 20 % | 70 | 30 % | 6 | 77 | 75 |
| 5 | -1 | -1 | 1 | -1 | -1 | 25 | 10 % | 80 | 30 % | 6 | 44 | 52 |
| 6 | 1 | -1 | 1 | -1 | -1 | 50 | 10 % | 80 | 30 % | 6 | 44 | 62 |
| 7 | -1 | 1 | 1 | -1 | -1 | 25 | 20 % | 80 | 30 % | 6 | 69 | 57 |
| 8 | 1 | 1 | 1 | -1 | -1 | 50 | 20 % | 80 | 30 % | 6 | 57 | 70 |
| 9 | -1 | -1 | -1 | 1 | -1 | 25 | 10 % | 70 | 60 % | 6 | 56 | 63 |
| 10 | 1 | -1 | -1 | 1 | -1 | 50 | 10 % | 70 | 60 % | 6 | 80 | 78 |
| 11 | -1 | 1 | -1 | 1 | -1 | 25 | 20 % | 70 | 60 % | 6 | 66 | 85 |
| 12 | 1 | 1 | -1 | 1 | -1 | 50 | 20 % | 70 | 60 % | 6 | 76 | 95 |
| 13 | -1 | -1 | 1 | 1 | -1 | 25 | 10 % | 80 | 60 % | 6 | 44 | 61 |
| 14 | 1 | -1 | 1 | 1 | -1 | 50 | 10 % | 80 | 60 % | 6 | 51 | 49 |
| 15 | -1 | 1 | 1 | 1 | -1 | 25 | 20 % | 80 | 60 % | 6 | 47 | 90 |
| 16 | 1 | 1 | 1 | 1 | -1 | 50 | 20 % | 80 | 60 % | 6 | 44 | 78 |
| 17 | -1 | -1 | -1 | -1 | 1 | 25 | 10 % | 70 | 30 % | 9 | 53 | 85 |
| 18 | 1 | -1 | -1 | -1 | 1 | 50 | 10 % | 70 | 30 % | 9 | 86 | 80 |
| 19 | -1 | 1 | -1 | -1 | 1 | 25 | 20 % | 70 | 30 % | 9 | 70 | 93 |
| 20 | 1 | 1 | -1 | -1 | 1 | 50 | 20 % | 70 | 30 % | 9 | 88 | 80 |
| 21 | -1 | -1 | 1 | -1 | 1 | 25 | 10 % | 80 | 30 % | 9 | 56 | 59 |
| 22 | 1 | -1 | 1 | -1 | 1 | 50 | 10 % | 80 | 30 % | 9 | 50 | 74 |
| 23 | 1 | 1 | 1 | -1 | 1 | 25 | 20 % | 80 | 30 % | 9 | 76 | 73 |
| 24 | 1 | 1 | 1 | -1 | 1 | 50 | 20 % | 80 | 30 % | 9 | 59 | 77 |
| 25 | -1 | -1 | -1 | 1 | 1 | 25 | 10 % | 70 | 60 % | 9 | 71 | 54 |
| 26 | 1 | -1 | -1 | 1 | 1 | 50 | 10 % | 70 | 60 % | 9 | 82 | 71 |
| 27 | -1 | 1 | -1 | 1 | 1 | 25 | 20 % | 70 | 60 % | 9 | 81 | 95 |
| 28 | 1 | 1 | -1 | 1 | 1 | 50 | 20 % | 70 | 60 % | 9 | 91 | 96 |
| 29 | -1 | -1 | 1 | 1 | 1 | 25 | 10 % | 80 | 60 % | 9 | 51 | 77 |
| 30 | 1 | -1 | 1 | 1 | 1 | 50 | 10 % | 80 | 60 % | 9 | 60 | 53 |
| 31 | -1 | 1 | 1 | 1 | 1 | 25 | 20 % | 80 | 60 % | 9 | 60 | 95 |
| 32 | 1 | 1 | 1 | 1 | 1 | 50 | 20 % | 80 | 60 % | 9 | 55 | 90 |

^aReaction conditions: catalyst: x % PVMo/Hmont, 30 mmol cyclohexene, 30 mmol H₂O₂, 10 mL CH₃CN

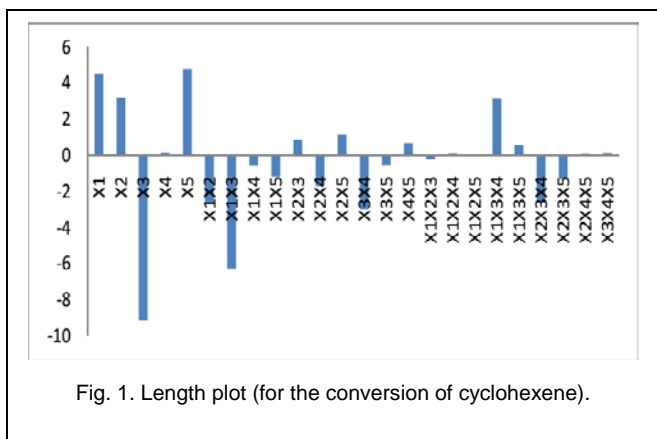


Fig. 1. Length plot (for the conversion of cyclohexene).

Alternatively, the R-squared statistics indicates that the well fitted model could suitably explain 97.9 % of the variability in the conversion efficiency. Likewise, the adjusted R-squared (R²) was found equal to 96.5 %. The standard error of the mean (SE of the mean) estimated the standard deviation of the residuals to be equal to 2.83269.

The experimental values of the response Y₂ are given in Table 2. The results and statistical analyses, using the t-test, are reported in Table 3, where the coefficients b₁, b₂, b₃, b₄ and b₅ are the weights and their associated factors X₁, X₂, X₃, X₄ and X₅, respectively (b₀ is the intercept), and b_{ij} are the different

interactions. The values of these coefficients are represented on an effects plot, where the magnitude and sign of each coefficient are shown (Fig. 2).

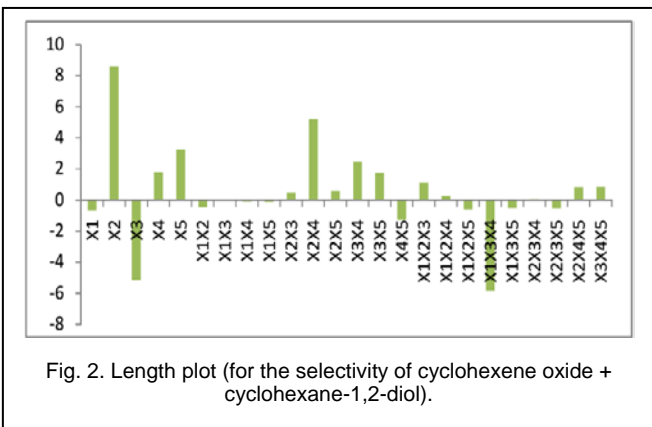


Fig. 2. Length plot (for the selectivity of cyclohexene oxide + cyclohexane-1,2-diol).

The regression coefficients are used to predict the response of each factor assisted by the linear regression equation as follows:

Coded levels (-1, +1):

$$\hat{Y}_2 = 74.979 - 0.646 X_1 + 8.603 X_2 - 5.134 X_3 + 1.814 X_4 + 3.259 X_5 - 0.445 X_1 X_2 - 0.050 X_1 X_3 - 0.078 X_1 X_4 - 0.106 X_1 X_5 + 0.459 X_2 X_3 + 5.186 X_2 X_4 + 0.598 X_2 X_5 + 2.463 X_3 X_4 + 1.733 X_3 X_5 - 1.270 X_4 X_5 + 1.137 X_1 X_2 X_3 + 0.247 X_1 X_2 X_4 - 0.593 X_1 X_2 X_5 - 5.830 X_1 X_3 X_4 - 0.515 X_1 X_3 X_5 + 0.074 X_2 X_3 X_4 - 0.543 X_2 X_3 X_5 + 0.845 X_2 X_4 X_5 + 0.870 X_3 X_4 X_5$$

Eq. (5)

In order to determine the statistical significance of different parameters in Eq. (5), the null hypothesis for each parameter needs to be rejected. The null hypothesis states that a parameter has no influence on the model and is rejected if the calculated *t*-value for a parameter is smaller than the critical *t*-value extracted using the experiment confidence level. Another easier method is to use the *p*-value of the *t*-test. If the *p*-value is less than that of the specific confidence level, the null hypothesis is rejected. In other words, the *p*-value of the null hypothesis indicates the error in rejecting the null hypothesis. In this model, the confidence level of 95 % was used, as it leads to the critical *p*-value of 0.05. The parameters with *p*-value less than 0.05 are statistically significant. The coefficients of X_2 and X_5 were found positive, which shows that they have synergic effects on Y_2 , %. Nevertheless, the coefficient of X_3 turned out to be negative, indicating an antagonistic effect on Y_2 , %. The interactions such as X_2X_4 , X_3X_4 and $X_1X_3X_4$ were statistically significant.

In the new model, if the *t*-value of a low-order parameter is lower than the critical *t*-value but the higher-order *t*-value of the same parameter is larger than the critical *t*-value, the lower order parameter is kept in the equation. For example, the R^2 coefficient in the initial model was equal to 0.961 while the

modified coefficient is 0.928 which show that 93 % of the variation was covered by the initial model. In order to investigate the correctness of the model, ANOVA analysis was carried out and the results are shown in Table 4. The *p*-value for the *F*-test at the confidence level of 95 % is 0.05. Therefore, parameters with confidence levels lower than 95 % (*p*-value = 0.05) were eliminated from the initial model and the new model was analyzed. This new model is presented in Eq. (6):

$$\hat{Y}_2 = 74.979 - 0.646 X_1 - 5.134 X_3 + 3.259 X_5 + 5.186 X_2 X_4 + 0.598 X_2 X_5 + 2.463 X_3 X_4 - 5.830 X_1 X_3 X_4$$

Eq. (6)

The results obtained in both experimental designs were statistically treated; they permitted the validation of empirical coded models in terms of weight and loading of catalyst, temperature, % of H_2O_2 and reaction time. The effects of different variables could be assessed on the basis of *p*-values (significance) and *t*-student tests, as described in Table 3. Table 4 displays the statistical test of the models obtained through the Fisher test for the analysis of variance. The coefficients of determination ($R^2 = 0.979$ and $R^2_{adj} = 0.965$) and the correlation coefficient ($R = 0.995$) were used to check the model's reliability. These values imply that the cyclohexene conversion (Y_1) and selectivity on cyclohexene oxide + cyclohexane-1,2-diol (Y_2) can accurately be described by Eqs. (3) and (6).

A graphical representation of the observed responses (cyclohexene conversion, Y_1 and the selectivity of cyclohexene oxide + cyclohexane-1,2 diol, Y_2) for the experiments, plotted against the responses predicted by the models, is shown in Fig. 3. The coefficients of correlation between the predicted and observed values, for the conversion and selectivity, were found equal to 0.979 and 0.916, respectively. The points are nearly randomly distributed around the line; this represents a perfect match and thus a good prediction of the model.

3.3 Optimization

To find the experimental conditions for maximizing the cyclohexene conversion and the selectivity of epoxide and cyclohexane-1,2 diol, the influence of each interaction is to be analyzed (Figs. 4 and 5).

a. *Catalyst weight- Catalyst loading (X_1 - X_2)*

If $X_1 = 0.025$ g, then the concentration of catalyst has a strong influence on the response. For $X_1 = 0.05$, the response increases slowly with increasing catalyst loading. The maximum value is obtained for $X_1 = 0.05$ g and $X_2 = 20$ % PVMo/Hmont (Fig. 4a).

b. *Catalyst weight - Temperature (X_1 - X_3)*

TABLE 3
 Design matrix and experimental results*

| Variable | Name | Coefficient | | Standard deviation | | t value | | Significance | |
|--|--------------------|-------------|----------|--------------------|----------|----------|----------|--------------|--------------------|
| | | Design A | Design B | Design A | Design B | Design A | Design B | Design A | Design B |
| Intercept | b ₀ | 63.323 | 74.979 | 0.547 | 1.048 | 115.738 | 71.551 | 0.000 | 0.000 ^a |
| X₁ | b ₁ | 4.514 | -0.646 | 0.547 | 1.048 | 8.250 | -0.616 | 0.000 | 0.557 |
| X₂ | b ₂ | 3.227 | 8.603 | 0.547 | 1.048 | 5.898 | 8.210 | 0.001 | 0.000 ^a |
| X₃ | b ₃ | -9.098 | -5.134 | 0.547 | 1.048 | -16.628 | -4.899 | 0.000 | 0.002 ^a |
| X₄ | b ₄ | 0.170 | 1.814 | 0.547 | 1.048 | 0.311 | 1.731 | 0.765 | 0.127 |
| X₅ | b ₅ | 4.786 | 3.259 | 0.547 | 1.048 | 8.747 | 3.110 | 0.000 | 0.017 ^a |
| X₁X₂ | b ₁₋₂ | -2.586 | -0.445 | 0.547 | 1.048 | -4.726 | -0.425 | 0.002 | 0.684 |
| X₁X₃ | b ₁₋₃ | -6.236 | -0.050 | 0.547 | 1.048 | -11.398 | -0.048 | 0.000 | 0.963 |
| X₁X₄ | b ₁₋₄ | -0.553 | -0.078 | 0.547 | 1.048 | -1.010 | -0.075 | 0.346 | 0.942 |
| X₁X₅ | b ₁₋₅ | -1.147 | -0.106 | 0.547 | 1.048 | -2.097 | -0.101 | 0.074 | 0.922 |
| X₂X₃ | b ₂₋₃ | 0.892 | 0.459 | 0.547 | 1.048 | 1.631 | 0.438 | 0.147 | 0.675 |
| X₂X₄ | b ₂₋₄ | -1.683 | 5.186 | 0.547 | 1.048 | -3.077 | 4.949 | 0.018 | 0.002 ^a |
| X₂X₅ | b ₂₋₅ | 1.195 | 0.598 | 0.547 | 1.048 | 2.184 | 0.571 | 0.065 | 0.586 |
| X₃X₄ | b ₃₋₄ | -2.963 | 2.463 | 0.547 | 1.048 | -5.416 | 2.351 | 0.001 | 0.051 |
| X₃X₅ | b ₃₋₅ | -0.537 | 1.733 | 0.547 | 1.048 | -0.981 | 1.654 | 0.359 | 0.142 ^a |
| X₄X₅ | b ₄₋₅ | 0.713 | -1.270 | 0.547 | 1.048 | 1.303 | -1.212 | 0.234 | 0.265 |
| X₁X₂X₃ | b ₁₋₂₋₃ | -0.205 | 1.137 | 0.547 | 1.048 | -0.374 | 1.085 | 0.719 | 0.314 |
| X₁X₂X₄ | b ₁₋₂₋₄ | 0.147 | 0.247 | 0.547 | 1.048 | 0.269 | 0.236 | 0.796 | 0.820 |
| X₁X₂X₅ | b ₁₋₂₋₅ | 0.030 | -0.593 | 0.547 | 1.048 | 0.055 | -0.566 | 0.957 | 0.589 |
| X₁X₃X₄ | b ₁₋₃₋₄ | 3.165 | -5.830 | 0.547 | 1.048 | 5.784 | -5.564 | 0.001 | 0.001 ^a |
| X₁X₃X₅ | b ₁₋₃₋₅ | 0.619 | -0.515 | 0.547 | 1.048 | 1.131 | -0.492 | 0.295 | 0.638 |
| X₂X₃X₄ | b ₂₋₃₋₄ | -2.623 | 0.074 | 0.547 | 1.048 | -4.795 | 0.071 | 0.002 | 0.946 |
| X₂X₃X₅ | b ₂₋₃₋₅ | -1.309 | -0.543 | 0.547 | 1.048 | -2.393 | -0.519 | 0.048 | 0.620 |
| X₂X₄X₅ | b ₂₋₄₋₅ | 0.132 | 0.845 | 0.547 | 1.048 | 0.240 | 0.806 | 0.817 | 0.447 |
| X₃X₄X₅ | b ₃₋₄₋₅ | 0.163 | 0,870 | 0.547 | 1,048 | 0.298 | 0.830 | 0.775 | 0.434 |

^a Statistically significant at 95 % confidence level.

*Design A: conversion of cyclohexene and Design B: selectivity of cyclohexene oxide + cyclohexane-1,2- diol.

The maximum value was obtained at X₃ = 70 °C; the catalyst weight has a weak influence at that temperature. The optimum is reached when X₁ = 0.05 g and X₃ = 70 °C (Fig. 4b).

TABLE 4

Variance analysis for the validation of mathematical models at 95 % confidence level (After stepwise regression)

| | Factor | Sum of squares | Degrees of freedom | Mean square | F | Sig. |
|-------------------|------------|----------------|--------------------|-------------|--------|-------|
| Design A* | Regression | 6880.366 | 13 | 529.259 | 65.958 | 0.000 |
| | Residuals | 144.435 | 18 | 8.024 | | |
| | Total | 7024.801 | 31 | | | |
| Design B** | Regression | 5895.996 | 8 | 736.999 | 37.190 | 0.000 |
| | Residuals | 455.789 | 23 | 19.817 | | |
| | Total | 6351.793 | 31 | | | |

* $R^2 = 0.990$ and $R^2_{adj} = 0.958$, before stepwise regression.

** $R^2 = 0.961$ and $R^2_{adj} = 0.829$, before stepwise regression.

c. Catalyst weight - Reaction time (X_1 - X_5)

The conversion of cyclohexene does not vary with the catalyst weight when $X_5 = 9$ h, but it increases for $X_5 = 6$ h. The response is maximal for $X_1 = 0.05$ g and $X_5 = 9$ h (Fig. 4c).

d. Catalyst loading - % of H_2O_2 (X_2 - X_4)

The conversion of cyclohexene does not change with the variation of catalyst loading and the purity of hydrogen peroxide. The maximum value is obtained for $X_2 = 20$ % PVMo/Hmont and $X_4 = 30$ or 60 % H_2O_2 (Fig. 4d).

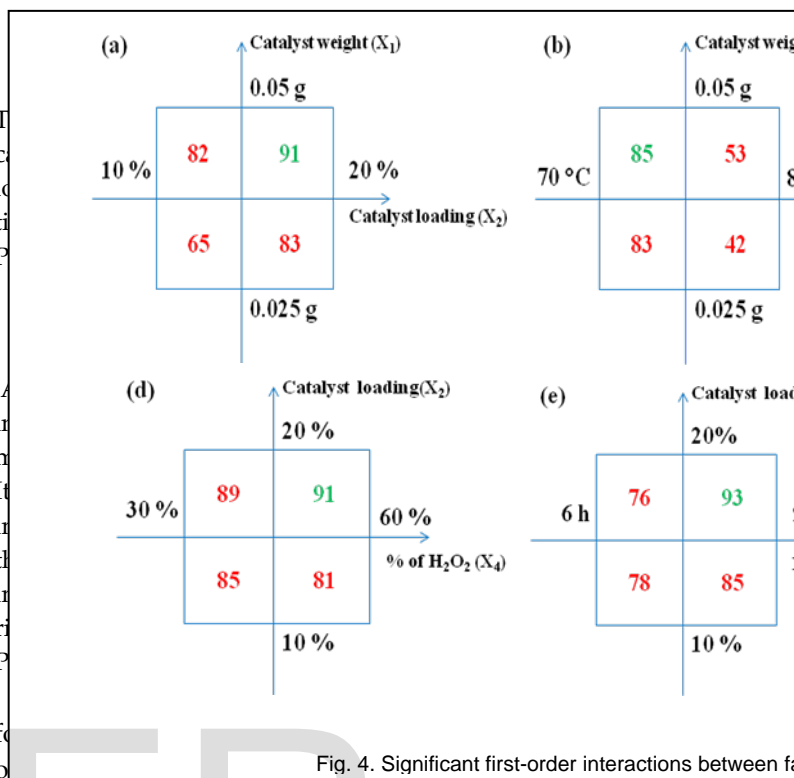


Fig. 4. Significant first-order interactions between factors.

Figure 5 shows the most significant interaction and indicates that a synergistic effect exists between the factors. It can be concluded from these results that the maximum selectivity (100 %) can be achieved with $X_1 = 0.05$ g, $X_2 = 20$ % PVMo/Hmont, $X_3 = 70$ °C or 80 °C, $X_4 = 60$ % H_2O_2 and $X_5 = 9$ h, which are considered as the best experimental conditions.

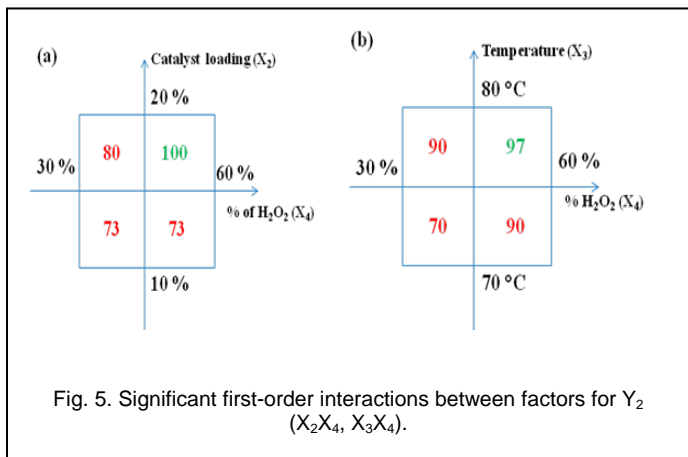


Fig. 5. Significant first-order interactions between factors for Y₂ (X₂X₄, X₃X₄).

Every process needs to be optimized to achieve good yields. In the present work, specific attention was focused on five selected factors. This experimental program provided the opportunity to analyze the influence of a pertinent selection of experimental parameters on the yield of cyclohexane 1,2 diol + cyclohexene oxide; this yield is defined as a novel response (Y₃).

In this modeling procedure, this yield was chosen, for its simplicity, to represent the influence of each factor through a linear variation. By analyzing the results quantitatively, and based on this assumption, it can clearly be seen that the correlation between the resulting response (Y₃) and the 5 selected factors (X₁, X₂, X₃, X₄, X₅) can be represented by the following polynomial model (Fig. 6):

$$\hat{Y}_3 = 48.000 + 3.248 X_1 + 7.744 X_2 - 10.062 X_3 + 1.547 X_4 + 5.693 X_5 - 1.932 X_1 X_2 - 4.885 X_1 X_3 + 2.243 X_2 X_4 + 2.022 X_2 X_5 - 2.294 X_2 X_3 X_4 \quad \text{Eq. (7)}$$

The sign of each coefficient shows how the related factor influences the response. If the coefficient is positive, the response is increased (synergistic effect) as the factor moves from a low level to a higher level; the opposite situation is obtained (inverse relationship/antagonist effect) if the coefficient is negative [38].

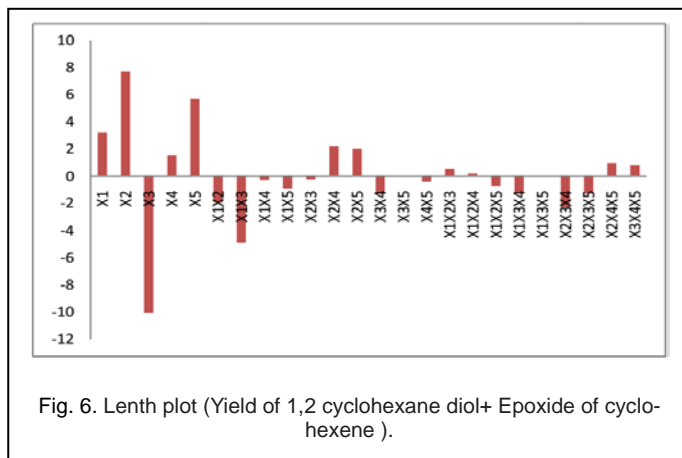


Fig. 6. Lenth plot (Yield of 1,2 cyclohexane diol+ Epoxide of cyclohexene).

Table 5 presents the statistical test of the models performed by Fisher's statistical test for the analysis of variance. The coefficients of determination ($R^2 = 0.958$ and $R^2_{adj} = 0.938$) and correlation coefficient ($R = 0.979$) were used to check the model's reliability. These values imply that the yield of cyclohexane-1,2 diol+ epoxide of cyclohexene (Y₃) can be accurately explained

TABLE 5

Analysis of variance for the validation of mathematical models at 95 % confidence level

| Factor | Sum of squares | Degrees of freedom | Mean square | F | Sig. |
|------------|----------------|--------------------|-------------|--------|-------|
| Regression | 7953.506 | 10 | 795.351 | 48.153 | 0.000 |
| Residuals | 346.862 | 21 | 16.517 | | |
| Total | 8300.367 | 31 | | | |

by Eq.7. Fig. 7 exhibits the prediction capacity of the developed model for the yield of cyclohexane-1,2 diol+ epoxide of cyclohexene versus the experimental yield, which confirms the good prediction ability of the model.

The analysis of all factors and their significant interactions were carried out to find the experimental conditions maximizing the response Y₃. The results indicate that the maximum yield was achieved with the following optimum experimental conditions, i.e. X₁ = 0.05 g, X₂ = 20 % PVMo/Hmont, X₃ = 70 °C or 80 °C, X₄ = 60 % H₂O₂ and X₅ = 9 h.

The maximum values of the response functions, which were calculated using regression functions, agree well with the values determined experimentally (for the same values of the independent factors), and within the limit of experimental errors (Table 6). The values of the multidimensional correlation coefficient R, ranging from 0.96 to 0.98, for the investigated response functions, confirm that the experimental data

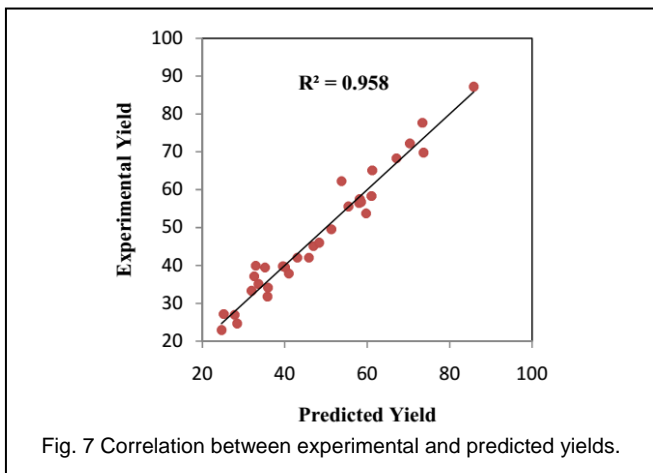


Fig. 7 Correlation between experimental and predicted yields.

TABLE 6
Reaction parameters giving an optimal response

| Function n | Maximum value | | Optimum parameters of the response functions | | | | |
|---------------|---------------|-------|--|--------------------|---------------------|--------------------|--------------------|
| | Expt. | Calc. | X ₁ (g) | X ₂ (%) | X ₃ (°C) | X ₄ (%) | X ₅ (h) |
| \hat{Y}_1 | 91 | 90.7 | 0.05 | 20 | 70 | 60 | 9 |
| \hat{Y}_2 | 96 | 100.6 | 0.05 | 20 | 70 | 60 | 9 |
| \hat{Y}_3 | 87 | 91 | 0.05 | 20 | 70 | 60 | 9 |

are in good agreement with the values calculated from the regression equations.

The catalytic activities of different samples were evaluated for the epoxidation of cyclohexene. All the catalytic systems proved to be highly active and selective towards diol. Similar oxidation reactions were also carried out with an acid-activated montmorillonite support; only a negligible catalytic activity was evidenced, and no by-products were detected. The obtained results clearly indicate that polyoxometalates (POMs) are responsible for the high oxidation activity of these heterogeneous catalysts. Besides, the large pores of the HMont support permit the diffusion of a relatively large quantity of cyclohexene and the oxidation proceeds selectively inside the pores of the support [34]. Generally, the reaction is believed to proceed through the mechanism postulated from the Keggin-type POMs. Monomeric, dimeric, and tetrameric peroxo species are generated when polyoxometalates react with hydrogen peroxide, and the peroxo species are supposed to be the active species for the epoxidation of olefins within a POM/H₂O₂ system [23, 39, 40]. It has been postulated that the epoxidation reaction rate and epoxide yield, for the same type of catalytic species, can be determined by the catalyst's acid strength [41, 42]. However the high diol selectivity, with 20% PVMo/HMont, is clearly justified considering the acidity of the support. The catalytic performance of the heterogeneous catalysts is also due to the fine dispersion of the active catalytic species within the supports. Here, the acid Brønsted sites of PVMo, acid Lewis sites of support and redox properties of PVMo are shown to have a crucial effect on the oxidation process [34].

4 CONCLUSIONS

Through the optimization process, acid activated montmorillonite clay supported on 11-molybdovanado-phosphoric acid catalysts, with enhanced cyclohexene epoxidation activity and selectivity have been found. The strategy for the experimental design made it possible to explore the multidimensional space and optimize the areas exhibiting the highest epoxidation performances. A full factorial experimental design

was adopted, based on the analysis of the experimental data. All five parameters, namely temperature, weight and loading of catalyst, purity of hydrogen peroxide and reaction time, were effective in cyclohexene conversion and selectivity of cyclohexane-1,2 diol. Temperature had the most significant effect among all independent variables. In this study, the reaction time and the two-way interaction between temperature and the catalyst weight were most significant. These optimum conditions were achieved at (1) catalyst weight of 0.05 g, (2) catalyst loading of 20 wt.% PVMo/Hmont, (3) reaction temperature of 70 °C, (4) purity of hydrogen peroxide of 60 % H₂O₂, and (5) reaction time of 9 h. Lewis acid sites from montmorillonite, Brønsted acid sites from polyoxometalates and peroxo species, could be used to catalyze the cyclohexene epoxidation to attain a high conversion efficiency (91 %), and a high selectivity to cyclohexane-1,2 diol (100 %).

ACKNOWLEDGMENT

The authors would like to thank the General Directorate for Scientific Research and Technological Development (DGRST) for the financial support. The authors acknowledge the facilities and the scientific and technical assistance of members of *Departamento de Química Orgánica, Instituto de Síntesis Química y Catálisis Homogénea, Facultad de Ciencias, Universidad de Zaragoza-CSIC, Pedro Cerbuna, 12, E- 50009 Zaragoza, Spain.*

REFERENCES

- [1] L.I. Simándi, T.M. Simándi, Z. May, G. Besenyi, *Coord. Chem. Rev.*, 245 (2003) 85-93.
- [2] J.-E. Bäckvall, *Modern oxidation methods*, John Wiley & Sons, (2011).
- [3] F. Meyer, C. Limberg, *Organometallic oxidation catalysis*, Springer, (2007).
- [4] N. Mizuno, *Modern heterogeneous oxidation catalysis: design, reactions and characterization*, John Wiley & Sons, (2009).
- [5] T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.*, 105 (2005) 2329-2364.
- [6] F. Cavani, J.H. Teles, *Chem. Sus. Chem.*, 2 (2009) 508-534.
- [7] S. El-Korso, I. Khaldi, S. Bedrane, A. Choukchou-Braham, F. Thibault-Starzyk, R. Bachir, *J. Mol. Catal. A: Chem.*, 394 (2014) 89-96.
- [8] J.M. Fraile, J.I. García, J.A. Mayoral, L. Salvatella, E. Vispe, D.R. Brown, G. Fuller, *J. Phys. Chem. B*, 107 (2003) 519-526.
- [9] G. Lapisardi, F. Chiker, F. Launay, J. Nogier, J. Bonardet, *Micro. and Meso. Mater.*, 78 (2005) 289-295.
- [10] C.-Y. Cheng, K.-J. Lin, M.R. Prasad, S.-J. Fu, S.-Y. Chang, S.-G. Shyu, H.-S. Sheu, C.-H. Chen, C.-H. Chuang, M.-T. Lin, *Catal. Commun.*, 8 (2007) 1060-1064.
- [11] R.H. Ingle, N.K. Raj, P. Manikandan, *J. Mol. Catal. A: Chem.*, 262 (2007) 52-58.
- [12] M. Ziolk, *Catal. Today*, 90 (2004) 145-150.
- [13] N.K. Kala Raj, S.S. Deshpande, R. Ingle, T. Raja, P. Manikandan, *Catal Lett*, 98 (2004) 217-224.

- [14] K. Youngjin, K. Hyungrok, L. Jungho, S. Kyuseon, H. Yohan, P. Hangnam, *Appl. Catal. A*, 155 (1997) 15.
- [15] H. Kameyama, F. Narumi, T. Hattori, H. Kameyama, *J. Mol. Catal. A: Chem.*, 258 (2006) 172-177.
- [16] S. Mukherjee, S. Samanta, A. Bhaumik, B.C. Ray, *Appl. Catal. B*, 68 (2006) 12-20.
- [17] N.V. Maksimchuk, M.N. Timofeeva, M.S. Melgunov, A.N. Shmakov, Y.A. Chesalov, D.N. Dybtsev, V.P. Fedin, O.A. Kholdeeva, *J. Catal.*, 257 (2008) 315-323.
- [18] S. Tangestaninejad, V. Mirkhani, M. Moghadam, I. Mohammadpoor-Baltork, E. Shams, H. Salavati, *Ultrason. Sonochem.*, 15 (2008) 438-447.
- [19] G. Lewandowski, E. Milchert, *Ind. Eng. Chem. Res.*, 40 (2001) 2402-2408.
- [20] A.C. Kalita, C. Roch-Marchal, R. Murugavel, *Dalt. Trans.*, 42 (2013) 9755-9763.
- [21] J.M. Fraile, J.I. García, J.A. Mayoral, E. Vispe, *Appl. Catal. A*, 245 (2003) 363-376.
- [22] Y. Ding, Q. Gao, G. Li, H. Zhang, J. Wang, L. Yan, J. Suo, *J. Mol. Catal. A: Chem.*, 218 (2004) 161-170.
- [23] Z. Weng, J. Wang, S. Zhang, C. Yan, X. Jian, *Appl. Catal. A*, 339 (2008) 145-150.
- [24] Z. Karimi, A.R. Mahjoub, S.M. Harati, *Inorganica Chimica Acta*, 376 (2011) 1-9.
- [25] J.M. Adams, *Appl. Clay Sci.*, 2 (1987) 309-342.
- [26] S.A. Hosseini, A. Niaei, D. Salari, R.K. Vieira, S. Sadigov, S.R. Nabavi, *Journal of Industrial and Engineering Chemistry*, 19 (2013) 166-171.
- [27] D. Montgomery, C. Design, in *Analysis of Experiments*, Wiley, New York, (2001).
- [28] P. Sriprom, C. Lin, A. Neramittagapong, S. Neramittagapong, in *Investigation of Important Parameters for Lignin Degradation Using Fenton-Like Reaction via Cu Doped on Bagasses-MCM-41*, A.I. Parinov, S.-H. Chang, Y.V. Topolov Eds., pp. 115-127, Springer International Publishing, Cham (2016).
- [29] T.-H. Đặng, B.-H. Chen, *Fuel. Proc. Tech.*, 109 (2013) 7-12.
- [30] L. Végvári, A. Tompos, S. Góbbölös, J. Margitfalvi, *Catal. Today*, 81 (2003) 517-527.
- [31] J. Klein, T. Zech, J.M. Newsam, S.A. Schunk, *Appl. Catal. A*, 254 (2003) 121-131.
- [32] M.a.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, F.J. Romero, F.J. Urbano, *J. Catal.*, 209 (2002) 413-416.
- [33] S. Boudjema, A. Choukchou-Braham, R. Bachir, *Adv. Mater. Res.*, 1064 (2015) 71-76.
- [34] S. Boudjema, E. Vispe, A. Choukchou-Braham, J.A. Mayoral, R. Bachir, *J.M. Fraile, RSC Advances*, 5 (2015) 6853-6863.
- [35] N. Belaidi, S. Bedrane, A. Choukchou-Braham, R. Bachir, *Appl. Clay Sci.*, 107 (2015) 14-20.
- [36] A. Dali, I. Rekkab-Hammoumraoui, A. Choukchou-Braham, R. Bachir, *RSC Advances*, 5 (2015) 29167-29178.
- [37] S. Brahimi, S. Boudjema, I. Rekkab, A. Choukchou-Braham, R. Bachir, *RJPBCS*, 6 (2015) 63-76.
- [38] R.K. Deshmukh, J.B. Naik, *J. Pharma. Innov*, 8 (2013) 276-287.
- [39] N.K.K. Raj, A. Ramaswamy, P. Manikandan, *J. Mol. Catal. A*, 227 (2005) 37-45.
- [40] C. Swalus, B. Farin, F. Gillard, M. Devillers, E.M. Gaigneaux, *Catal. Commun.*, 37 (2013) 80-84.
- [41] Z. Karimi, A.R. Mahjoub, *Appl. Surf. Sci.*, 256 (2010) 4473-4479.
- [42] J.M. Fraile, J.I. García, J.A. Mayoral, E. Vispe, *J. Catal.*, 233 (2005) 90-99.