Light Metals 2012 *Edited by: Carlos E. Suarez*
TMS (The Minerals, Metals & Materials Society), 2012

OPTIMIZATION OF PREPARATION FOR α-ALUMINA BY CALCINATION FROM ALUMNINUM HYDROXIDE USING RESPONSE SURFACE METHODOLOGY

Bin Zhang[1,2], Jinhui Peng[2,*], Libo Zhang[2], Shaohua Ju[2]
[1]Faculty of Science, Kunming University of Science and Technology, Kunming Yunnan 650093, PR China
[2]Faculty of Metallurgy and Energy Engineering, Kunming University of Science and Technology, Kunming Yunnan 650093, PR China

Keywords: Response surface methodology, Aluminum hydroxide, Calcination, α-alumina

Abstract

The conditions of technique to prepare α-alumina by calcination from aluminum hydroxide were optimized using a central composite design (CCD) of response surface methodology (RSM). A quadratic equation model for field was built and effects of main factors and their corresponding relationships were obtained. The statistical analysis of the results showed that in the range studied the field of α-alumina was significantly affected by the calcination temperature and calcination time. According to results from analysis of variance (ANOVA), the value of the determination coefficient (R^2=0.9890) indicates that the model was a good fit that 98.90% of the variation could be explained well by the model. The value of the adjusted determination coefficient (adj.R^2=0.9811) was also very high to advocate for a high significance of the model. The optimized calcination conditions were as follows: the calcination temperature 1206.81℃ and the calcination time 2.06 h respectively. Under these conditions the field of α-alumina was 95.93%. In addition, the sample was characterized by X-ray Diffraction (XRD).

Introduction

α-alumina have been the subject of many investigations because of their commercial importance and scientific interest. α-alumina powder has been used as raw materials for polishing abrasives, catalyst supports for high temperature reactions, cutting tools, and advanced ceramics. Alumina has got some of the special properties such as high hardness, high mechanical strength, high thermal conductivity and good thermal shock resistance, etc [1]. Calcination of the aluminum trihydroxide or gibbsite obtained from the Bayer process has been the principal method for α-alumina powders [2].

Generally, the traditional approach "one variable at a time (OVAT)" is used to analyze the thermal decomposition process of aluminum hydroxide. In OVAT, the effect of each experimental factor is investigated by altering the level of one factor at a time while maintaining the level of the other factors constant. Furthermore, this technique is not only time and work demanding, but completely lacks in representing the effect of interaction between different factors [3]. In order to solve these problems, it is necessary to find a multivariate statistic technique for optimization of preparation processes. Response surface methodology (RSM) might be a useful method to optimize preparation processes. RSM is a collection of mathematical and statistical techniques useful for analyzing the effects of several independent variables [4]. The main advantage of RSM is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions [5]. It can deal with multivariate experimental design strategy, statistical modeling and process optimization [6]. Several previous researchers have proved that RSM was a powerful statistical tool in process optimization, and it has just recently been applied to optimize the process parameters for biosorption of metals [7] or dyes [8] from synthetic solutions. However, as far as known to the authors, there have been very few studies to optimize the preparation of α-alumina from aluminum hydroxide by the RSM approach. The aim of this work was to optimize the thermal decomposition process of aluminum hydroxide parameters with a consideration of response by applying RSM. A quadratic model was derived to describe the effects of calcination temperature and calcination time on the yield of α-alumina. The crystal structure of α-alumina under the optimum condition was also analyzed.

Experimental

Calcination Experiments

The calcination experiments were carried out at the different calcination temperatures, calcination times and masses of sample. Initially, the Muffle furnace was preheated with a speed of 10 $℃\cdot min^{-1}$ until the desired temperature was reached. Then the aluminum hydroxide was weighed and placed inside the ceramic crucible which was located in the center of the conventional Muffle furnace. During the reaction, the temperature was monitored by a temperature controller system, namely the PID (proportional integral derivative) controller. Several cycles of experiment were repeated. For each cycle, a reaction was performed for a fixed duration, once the fixed duration is over, the experiment was stopped immediately. The product was moved out from the Muffle furnace and put into the drier rapidly. They were naturally cooled to the room temperature. The final weight (m) of sample was weighted subsequently. The content of α-alumina of product was obtained through the method in accordance with the recommended methods of Nonferrous Metals Industry Standard of the People's Republic of China (YS/T). The field was calculated based on the following equation:

$$Y = \frac{m \times w_t}{m_0 \times 0.97 \times 0.6538} \times 100\% \quad (1)$$

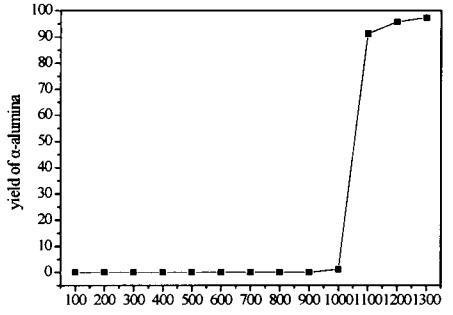
where m and m_0 are final weight and initial weight of sample, respectively; w_t is the content of α-alumina of product, 0.97 is the content of aluminum hydroxide, 0.6538 means theory value of α-alumina obtained from 1 g aluminum hydroxide, Y is yield of α-alumina.

Single Factor Experiments

The major factors and the rough ranks of calcination process were obtained through single factor experiments.

Fig. 1 shows the effect of the calcination temperature on yield of α-alumina. From Fig. 1, it can be found that the yield of α-

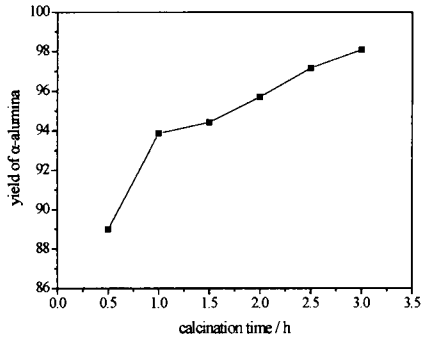
alumina was effect significantly by calcination temperature. When the calcination temperature was raised to 1000℃, the yield of α-alumina is increased along with the increasing of the calcination temperature. When the calcination temperature reaches 1200℃, the yield of α-alumina is 95.7%, which meets the requirements of Nonferrous Metals Industry Standard of the People's Republic of China (YS/T 89—1995).



t=2 h, m=50 g

Fig. 1 Effect of the calcination temperature on yield of α-alumina

Fig. 2 shows the effect of the calcination time on yield of α-alumina. From Fig. 2, it can be found that the yield of α-alumina was effect significantly by calcination time. When the calcination time was extended, the yield of α-alumina was increased. When the calcination time reaches 2 h, the yield of α-alumina is 95.7%, which meets the requirements of Nonferrous Metals Industry Standard of the People's Republic of China (YS/T 89—1995).

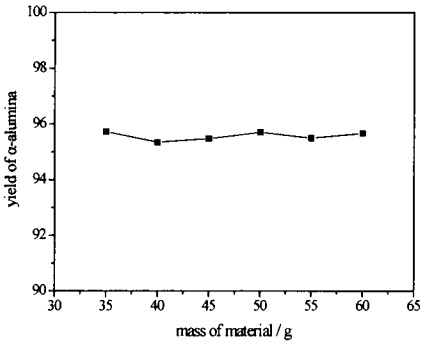


T=1200℃,m=50 g

Fig. 2 Effect of the calcination time on yield of α-alumina

Fig. 3 shows the effect of the mass of material on yield of α-alumina. From Fig. 3, it can be found that the yield of α-alumina was almost no impacted by mass of material. So, the mass of material is not major factors of the calcination process.

From above analysis, we can concluded that the calcination temperature and calcination time are major factors of the calcination process, and the rough better reaction conditions are the calcination temperature 1200℃ and the calcination time 2 h respectively (the higher the calcination temperature and the longer the calcination time, the bigger the average crystal size of α-alumina).



T=1200℃, t=2 h

Fig. 3 Effect of the mass of material on yield of α-alumina

Designing Experiment Using Response Surface Methodology

On the basis of rough decomposition results and analysis of single factor experiments, RSM was employed to optimize the calcination conditions in order to obtain a qualified α-alumina, and CCD was employed to design the experiments. This method helps to optimize the effective parameters with a minimum number of experiments and also analyze the interaction between the parameters and results [9]. In this study, the effects of two independent variables, x_a (calcination temperature), and x_b (calcination time), at five level were investigated using central composite design. The rank of values associated with the variables: calcination temperature (℃) was 1100 and 1300, and calcination time (h) ranged between 1.5 and 2.5 (Table 1). Generally, a second-order polynomial model with main, quadratic and interaction terms can be developed to fit the experimental data obtained from the experimental runs conducted on the basis of CCD. The experimental data obtained from the designed experiment were analyzed by the response surface regression procedure using the following second-order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i \chi_i + \sum_{i=1}^{n} \beta_{ii} \chi_i^2 + \sum_{i<j} \beta_{ij} \chi_i \chi_j \qquad (2)$$

where Y is the predicated response, β_0 is a constant, β_i is the ith linear coefficient, β_{ii} is the ith quadratic coefficient, β_{ij} is ijth interaction coefficient, x_i, x_j are the coded values of independent variables, and the terms $x_i x_j$ and x_i^2 represent the interaction and quadratic terms, respectively.

Table 1 Independent variables and their levels for central composite rotatable design

Variables	Symbol	Range and levels				
		-1.41421	-1	0	1	1.41421
calcination temperature /℃	x_a	1058.58	1100	1200	1300	1341.42
calcination time / h	x_b	1.29289	1.5	2	2.5	2.70711

XRD Analysis

The X-ray diffraction analysis of the final solid product under optimization conditions were carried out using D/max-2200 Diffractometer (Japan) with Ni-filtered CuKa radiation under air

atmospheres. The identification of the completeness of the α-alumina was made by comparing the diffraction peaks of each compound in the sample with the ones of the standard α-alumina. If the diffraction pattern of the final solid product satisfactorily matched with that of the standard α-alumina, it means that the decomposition of aluminum hydroxide is complete.

Results And Discussion

Data Analysis And Evaluation Of the Model By RSM

The experiments were conducted based on the design matrix under the defined conditions and the responses obtained from the experimental runs are shown in Table 2.

Table 2 Experimental design matrix and results

Run	Calcination variables		Yield of α-alumina, Y_1 / %	Average crystal size of α-alumina Y_2 / nm
	Calcination temperature, x_a / ℃	Calcination time, x_b / h		
1	1100(-1)	1.5(-1)	90.52	66.5
2	1300(+1)	1.5(-1)	96.34	95.2
3	1100(-1)	2.5(+1)	92.24	69.8
4	1300(+1)	2.5(+1)	98.45	110.9
5	1058.58(-1.41421)	2.0(0)	88.47	64.7
6	1341.42(+1.41421)	2.0(0)	98.67	120.6
7	1200(0)	1.29(-1.41421)	94.52	68.9
8	1200(0)	2.71(+1.41421)	97.27	85.3
9	1200(0)	2.0(0)	95.67	70.5
10	1200(0)	2.0(0)	95.70	70.8
11	1200(0)	2.0(0)	95.82	71.1
12	1200(0)	2.0(0)	95.26	69.2
13	1200(0)	2.0(0)	95.46	69.3

Table 2 shows the total number of 13 experiments as per CCD method. The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. Five experiments were repeated in order to estimate the experimental error. According to the sequential model, the sum of squares can be obtained, and the models were selected based on the highest order polynomial where the additional terms were significant and the models were not aliased [10]. The responses of field and average crystal size of α-alumina were considered in studying the effect of process variables. The responses of field and average crystal size of α-alumina and the independent variables were used to develop two empirical models, which is presented by Eq. (3) and Eq. (4):

$$Y = 95.58 + 3.31\chi_a + 0.96\chi_b + 0.098\chi_a\chi_b - 1.09\chi_a^2 + 0.070\chi_b^2 \quad (3)$$

$$Y = 70.18 + 18.61\chi_a + 5.27\chi_b + 3.10\chi_a\chi_b + 11.42\chi_a^2 + 3.64\chi_b^2 \quad (4)$$

The quality of the two models developed was evaluated based on the correlation coefficient value [11] (Table 3 and Table 4). The R^2 value for Eq. (3) was 0.9890 and for Eq. (4) was 0.9957, which indicated that 98.90% variability of the total variation in the field was attributed to the experimental variables studied and 99.57% variability of the total variation in the average crystal size was attributed to the experimental variables studied. The closer the R^2 value to unity, the better the model will be as it will give predicted values which are closer to the actual values for the response. The R^2 of 0.9890 for Eq. (3) was considered relatively high, indicating that there was a good agreement between the experimental field of α-alumina and the predicted one from this model. The R^2 of 0.9957 for Eq. (4) was considered relatively high, indicating that there was a good agreement between the experimental average crystal size of α-alumina and the predicted one from this model.

Table 3 Analysis of variance (ANOVA) for response surface quadraticmodel for the yield of α-alumina

Source	Sum of squares	D_f	Mean square	F-value	Prob>F
Model	103.59	5	20.72	125.85	<0.0001
Residual	1.15	7	0.16		
Lack of fit	0.96	3	0.32	6.47	0.0515
Pure error	0.20	4	0.049		
Cor total	104.74	12			

R^2=0.9890; R^2adj=0.9811; adequate precision=37.035(>4)

Table 4 Analysis of variance (ANOVA) for response surface quadratic model for the average crystal size of α-alumina

Source	Sum of squares	D_f	Mean square	F-value	Prob>F
Model	3970.11	5	794.02	326.51	<0.0001
Residual	17.02	7	2.43		
Lack of fit	13.95	3	4.65	6.06	0.0571
Pure error	3.07	4	0.77		
Cor total	3987.13	12			

R^2=0.9957; R^2adj=0.9927; adequate precision=51.792(>4)

Furthermore, analysis of variance (ANOVA, also a part of RSM) was further carried out to justify the adequacy of the model. The ANOVA for the quadratic model for field and average crystal size are presented in Table 3 and Table 4. The model's adequacy was tested through the lack of fit F-test, in which the residual error was compared to the pure error. According to the software analysis, "Lack of fit F-values" of 6.47 and 6.06 imply that the lack of fit was not significant relative to the pure error due to noise. The "Model F-values" of 125.85 and 326.51 imply that the two models were significant. Value of "Prob > F" less than 0.05 indicates that the two models terms are significant [12], whereas the values greater than 0.1000 are not significant.

Response Surface Analysis

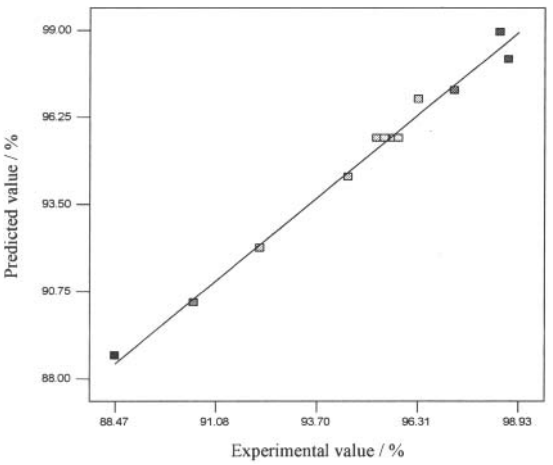


Fig. 4 Comparison of model prediction with the experimental data for yield of α-alumina

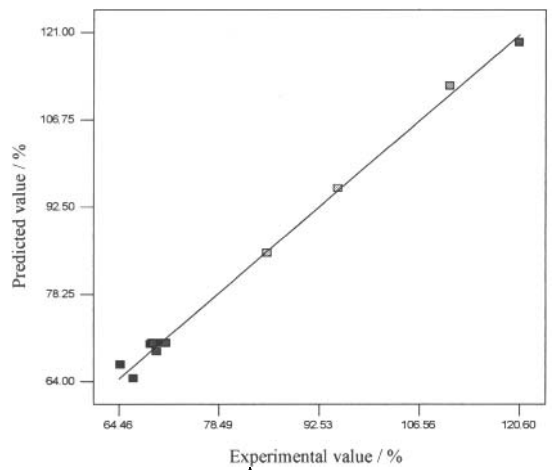


Fig. 5 Comparison of model prediction with the experimental data for average crystal size of α-alumina

Fig. 4 and Fig 5 show the predicted values versus the experimental values for field and average crystal size of α-alumina. Actual response values were measured for a particular run, and the predicted values were evaluated from the model and generated by using the approximating equations. As can be seen, the predicted values obtained were quite close to the experimental values, indicating that the two models developed were reasonable. The best way to visualize the influence of the independent variables on the response is to draw surface response plots of the model [14]. The three-dimensional response surfaces which were constructed to show the effects of the calcination of aluminum hydroxide variables on field and average crystal size of α-alumina using the fitted quadratic polynomial equations obtained from regression analysis was shown in Fig. 6 and Fig. 7.

Fig. 6 shows the effect of calcination temperature and calcination time on field of α-alumina at the fixed mass of sample of 50 g. It was observed that the field significantly increased with increasing calcination temperature. Increasing the calcination temperature up to 1300℃ gave an enhanced effect on the field, as the maximum predicated value of 98.45% was achieved. The figure reveals that the effect of the calcination temperature on the field was more significant than calcination time.

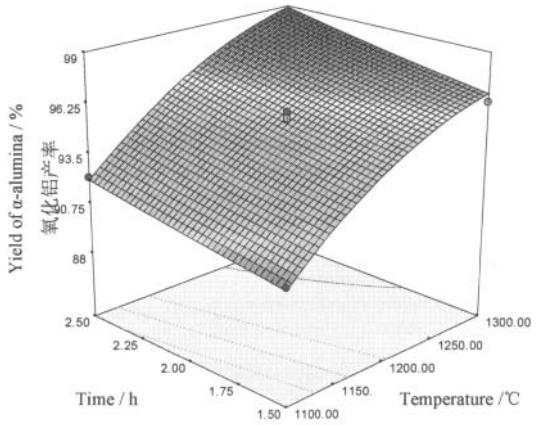


Fig. 6 Effect of calcination temperature and holding time on the yield of α-alumina

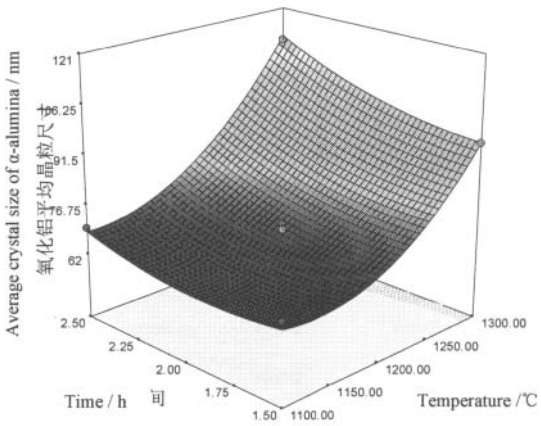


Fig. 7 Effect of calcination temperature and holding time on the averagecrystal size of α-alumina

Fig. 7 shows the effect of calcination temperature and calcination time on average crystal size of α-alumina at the fixed mass of sample of 50 g. It was observed that the average crystal size significantly increased with increasing calcination temperature. Increasing the calcination temperature up to 1300℃ gave an enhanced effect on the average crystal size, as the maximum predicated value of 110.9 nm (obtained by the Scherrer formula) was achieved. The figure reveals that the effect of the calcination temperature on the average crystal size was more significant than calcination time.

Fig. 8 shows the effect of calcination temperature and calcination time on field (the higher, the better) and average crystal size (the smaller, the better) of α-alumina at the fixed mass of sample of 50 g. It was observed that the optimal condition for field and average crystal size was at 1206.81℃, and 2.06 h and the field was 95.93%, the average crystal size was 72.25 nm.

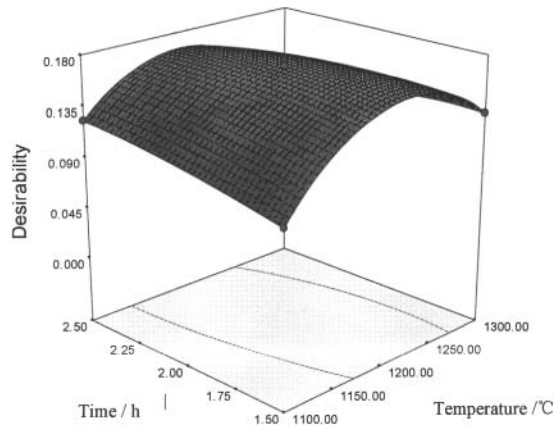


Fig. 8 Effect of calcination temperature and holding time on the comprehensive performance of α-alumina

Optimal Conditions And Verification Of The Model

Thus, based on the above model, the optimal condition for field was at 1206.81℃, and 2.06 h. In order to confirm the optimized conditions, the accuracy of the model was validated with experiments under conditions of optimum. An experiment was carried out with parameters as suggested by the model. The conditions used in the confirmatory experiment were as follows: calcination temperature 1207℃ and calcination time 2 h, the giving a field of 96.18% and average crystal size of 72.34 nm(Table 5), which concurred with the model prediction. The two models, therefore, were considered to fit the experimental data very well in these experimental conditions. Therefore, the two models are acceptably valid.

Table 5 Optimum calcination conditions with model validation

Calcination temperature, x_a / ℃	Calcination time, x_b / h	Yield of α-alumina Y_1 / %		Average crystal size of α-alumina Y_2 / nm	
		Predicted	Experimental	Predicted	Experimental
1207	2	95.9251	96.18	72.2455	72.34

XRD Analysis

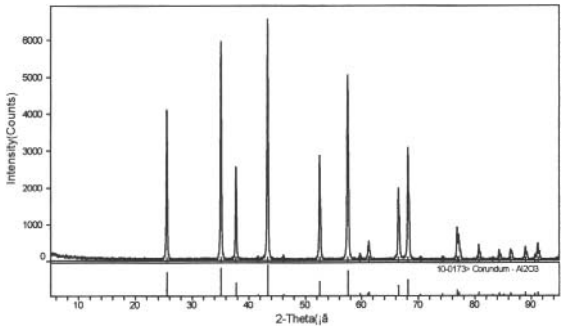


Fig. 9 The XRD pattern for the decomposition final solid products under the optimization conditions

Results of X-ray diffraction studies of the products on optimization conditions are shown in Fig. 9. The results show that α-alumina was the most solid product identified in which diffraction patterns satisfactorily matched with that of α-alumina and few decomposition products or reaction intermediates were identified in the XRD studies. Furthermore, it indicated that it is feasible to prepare α-alumina by calcination from aluminum hydroxide under optimum conditions.

Conclusions

This study showed that response surface methodology was a suitable approach to optimize conditions for achieving qualified yield and average crystal size of α-alumina. The experimental and predicted values were very close, which reflected the correctness and applicability of RSM. Using RSM to optimize experiments, the optimal condition was found to be at 1206.81℃ and 2.06 h, respectively. Under these conditions, the predicted value of yield of 95.9251% and average crystal size of 72.2455 nm were in good agreement with the actual experimental values (96.18% and 72.34 nm). The α-alumina prepared under the optimum conditions was characterized by XRD, from which the diffraction pattern satisfactorily matched with that of the standard α-alumina.

Acknowledgements

Financial support for this work from the National Natural Science Foundation Council of China (50734007) and Analysis and Testing Foundation of Kunming University of Science and Technology (2010-284) are gratefully acknowledged.

References

1 Pratima, Mishra. Low-temperature synthesis of α-alumina from aluminum salt and urea [J]. Materials Letters, 2002, 55(6):425-429

2 Youn Sug Yoo, Kyun Young Park, Kyeong Youl Jung and Sung Baek Cho. Preparation of α-alumina nanoparticles via vapor-phase hydrolysis of $AlCl_3$ [J]. Materials Letters, 63(21):1844-1846

3 Bingguo Liu, Jinhui Peng, Libo Zhang, Rundong Wan, Shenghui Guo, Liexing Zhou. Optimization of preparation for Co_3O_4 by calcination from cobalt oxalate using response surface methodology [J]. Chemical Engineering Research and Design, 2010, 88(8):971-976

4 Myers, R.H. and Montgomery, D.C. Response Surface Methodology. (John Wiley & Sons, Inc, USA). 2002

5 Ming-Ju Chen, Kun-Nan Chen, Chin-Wen Lin. Optimization on response surface models for the optimal manufacturing conditions of dairy tofu [J]. Journal of Food Engineering, 2005, 68(4):471-480

6 Jianfeng Fu, Yaqian Zhao, Qiuli Wu. Optimising photoelectrocatalytic oxidation of fulvic acid using response surface methodology [J]. Journal of Hazardous Materials, 2007, 144(1-2):499-505

7 Bala Kiran, Anubha Kaushik, C.P. Kaushik. Response surface methodological approach for optimizing removal of Cr(VI) from

aqueous solution using immobilized cyanobacterium [J]. Chemical Engineering Journal, 2007, 126(2-3):147-153

8 Sarayu Mohana, Shalini Shrivastava, Jyoti Divecha, Datta Madamwar. Response surface methodology for optimization of medium for decolorization of textile dye Direct Black 22 by a novel bacterial consortium [J]. Bioresource Technology, 2008, 99(3):562-569

9 R. Azargohar, A.K. Dalai. Production of activated carbon from Luscar char: Experimental and modeling studies [J]. Microporous and Mesoporous Materials, 2005, 85(3):219-225

10 I.A.W. Tan, A.L. Ahmad, B.H. Hameed. Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology [J]. Chemical Engineering Journal, 2008, 137(3):462-470

11 Hill, W.J. and Hunter, W.G. A review of response surface methodology: a literature review [J]. Tecimometrics, 1966, 8:571-590

12 A.L. Ahmad, S.C. Low, S.R. Abd Shukor, A. Ismail. Optimization of membrane performance by thermal-mechanical stretching process using responses surface methodology (RSM) [J]. Separation and Purification Technology, 2009, 66(1):177-186

13 Bahadir K. Körbahti, Muhammad A. Rauf. Determination of optimum operating conditions of carmine decoloration by UV/H_2O_2 using response surface methodology [J]. Journal of Hazardous Materials, 2009, 161(1):281-286

14 Raymond, H., Myers, Andre, I., Khuti, Walter, H. and Carter. Response surface methodology [J]. Tecimometrics, 1989, 312:432-438