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Template Recycling and Reuse in Mobil Crystalline Material 41 (MCM-41) Synthesis: Statistical Study

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Abstract

The recycle and reuse of template in MCM-41 synthesis were analysed using 2^3 full factorial design in order to study the effect of the template extraction parameters on the mass of MCM-41 powder produced. Four consecutive MCM-41 synthesis cycles utilizing the recycled template were studied with three factors that are ethanol fraction (A), amount of ion exchange agent (B) and the type of ion exchange agent (C). The significant effects contributed by the factors A, B and C and their interactions were identified through the half-normal probability plot and normal probability plot of the residuals. F-test and t-test were carried out to test the contribution of regression coefficients for synthesis cycles of MCM-41 synthesis models. AB interaction showed that larger mass of MCM-41 powder was obtained at high ethanol volume fraction and high quantity of ion exchange agent when either type of ion exchange agent was used.

Keywords: *MCM-41 synthesis DOE, statistical analysis, surfactant template*

1. Introduction

Mesoporous material is a material with pore diameters that are ranging from 2 to 50 nm according to International Union of Pure and Applied Chemistry (IUPAC) definition [1]. Mesoporous silica materials are materials which have great potential as adsorbents and catalysts in many chemical industry applications because of their high specific surface area, high pore volume and thermal stability [2]. MCM-41 is a synthesized mesoporous silica material available in M41S family that has hexagonal mesophase with ordered cylindrical pore channels [3]. The synthesis of MCM-41 was carried out using liquid templating method. The surfactant template was initially self-assembled to form an array of micellar rod and the silica source was condensed onto the micellar rods of surfactant template to form silica walls through polymerisation [4]. The as-synthesized MCM-41 was then obtained through the mixing of silica source and the surfactant template. After the synthesis is completed, the template was eventually removed from the pores of the synthesized MCM-41 to form structured mesopores. The removal of surfactant template was performed by solvent extraction at 70°C under reflux for 4 h. The extracted surfactant molecules in the mother liquor was recovered and reused for the next MCM-41 synthesis. The purpose of recycling the surfactant template was in order to maintain the hexagonal mesopores structure of MCM-41 and to utilize the surfactant template for repeating synthesis cycle.

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The statistical analysis of MCM-41 synthesis was conducted using Design of Experiment (DOE). DOE is fundamentally important in engineering design process by manipulating the process system input variables and examines the changes in response output in order to improve existing processes or to develop new products [5]. Statistical DOE is a scientific methodology using statistical method to conduct statistical experiment specification layout [6]. The type of design model is initially selected and then the design model that is preferable to the output response is being developed based on the input variables provided for process improvement [7].

Factorial design, the experimental design which involves two or multiple factors could be performed using this type of design model. A complete experiment trial for all possible factor levels combination is investigated. The changes in response produced by the change in different levels of factors with or without the interaction between factors are examined in the factorial design [8]. The response surface method (RSM) designs are used to identify the settings of the factors which produce optimum response [9]. The optimum response can be either minimum when process disturbance that influenced the process flow is investigated or maximum value if product yield is being determined [10]. In RSM, the expected response that represents the “surface” is determined in order to study the linear relationship between the response and the factors which influenced the response [10]. The factors used in these three design models can be either qualitative or quantitative [11, 12].

The approach of “one-factor-at-a-time” was reported mostly on studying the effects of varying synthesis parameters such as composition of reaction mixture, silica source, surfactant, pH, temperature and time [13]. “One-factor-at-a-time” is a design that involves the changes of one factor while setting all other factors constant without investigating the interaction between synthesis parameters and MCM-41 product characteristics [14]. In the current study, the effects of the interaction of significant factors are studied simultaneously using the factorial design.

The main objective of this work was to study the significance of ethanol volume fraction, ion exchange agent quantity and ion exchange agent type effects on MCM-41 yield produced in four consecutive synthesis cycles using DOE statistical study. Another objective was to conduct factorial design to investigate the effects of each significant factor and their interaction effects for the yield of MCM-41 product produced in four MCM-41 synthesis cycles.

In this current study, a 2^3 factorial design is chosen to perform the experimental design of MCM-41 synthesis in order to investigate whether the adjustment of the three factors that are the ethanol volume fraction, the quantity of ion exchange agent used and type of ion exchange agent at two levels would influence the significant mass of MCM-41 powder that would be produced in four consecutive cycles of MCM-41 synthesis. The analysis of variance (ANOVA) models would be used to execute the statistical data analysis of the MCM-41 synthesis experimental design by partitioning the variability of total experimental data sets into components which assign to independent variables and interaction between independent variables [15].

2. Methodology

2.1. Materials

Tetraethylorthosilicate (TEOS, $C_8H_{20}O_4Si$, 98%, Sigma-Aldrich) and hexadecyltrimethyl ammonium bromide powder (CTAB, $C_{19}H_{42}BrN$, R&M) were used as silica source and template for the MCM-41 synthesis. Nitric acid (HNO_3, 65%, Fisher) was used as catalyst for silica hydrolysis and pH adjustment whereas ethanol (C_2H_5OH, 95%, HMBG) was used as solvent. Ammonium nitrate (NH_4NO_3, R&M) and 1-butyl-3-methylimidazolium chloride (BMlmCl, $C_8H_{15}ClN_2$, $\geq$ 98%, Sigma-Aldrich) were used as ion exchange agents to enhance the removal of surfactant template from the as-synthesized material by ion exchange.

2.2. Synthesis of MCM-41

Total volume of 5 mL TEOS was initially added into 15 mL of distilled water and stirred for 15 minutes by referring the solution as Solution 1 (S1). While, the solution named Solution 2 (S2) has total amount of 3.17 g CTAB dissolved in the ethanol contained different ethanol fraction such as either 0.3 or 0.5 under stirring for 5 minutes. S1 and S2 were then mixed and stirred vigorously for 20 minutes. After mixing, the mixture named Mix-1 was tested by ultraviolet-visible (UV-vis) spectroscopy using PerkinElmer LAMBDA 35 UV/Vis spectrophotometer to measure the concentration of surfactant and hence the mixture was kept for homogenization for 1.5 h. Next, 2 mL of HNO_3 was added drop wise into the mixture to adjust the pH of mixture to the desired pH value of 0.5. The mixing was continued for an hour following the pH adjustment. After the mixing is completed, the pH was monitored and the mixture was kept for 48 h without mixing for gel formation.

The resulting gel is filtered when the synthesis reaction was completed to separate the white powder (as-synthesized MCM-41) and the mother liquor (filtrate). After the filtration, 1 g of NH_4NO_3 or BMlmCl was dissolved in total volume of 30 mL distilled water and added to the as-synthesized MCM-41 powder and in order to perform the ion exchange between the surfactant template and the ion exchange agent under vigorous stirring for 1 h. The mixture was named Mix-2 and further undergoes second filtration to separate the as-synthesized MCM-41 powder and the ion exchange agent solution. The as-synthesized MCM-41 powder was further extracted at 70°C under reflux for 4 h by using mother liquor as extracting solution. Water addition was carried out when necessary for the duration of extraction and after the extraction in order to maintain the volume of extracting solution for every synthesis cycle. When the extraction was completed, the mother liquor was again tested for UV-vis spectroscopy to evaluate the concentration of CTAB. The mother liquor was then reused for the 2nd synthesis cycle by adding 5 mL TEOS. The synthesis procedure continued till no significant gel or powder was produced. The synthesis of MCM-41 and surfactant template recycling experiment was repeated by using 2 g of NH_4NO_3 and 2 g of BMlmCl. A complete synthesis and surfactant template reuse cycle is illustrated in Figure 1.

3. Design of Experiment

A 2^3 full factorial design was used to carry out the analysis of MCM-41 synthesis using Design-Expert (version 6.0) software, in order to study the effect of the three factors namely volume fraction of ethanol (A), amount of ion exchange agent (B) and type of ion exchange agent (C). Each factor was tested at two levels with low denoted as (−1) and high denoted as (+1). The indicating low level and high level for the respective factor A, factor B and factor C were outlined in Table 1. Each MCM-41 synthesis contained four cycles with total of 64 runs conducted for the factorial design. A complete randomized experiment was hence performed with random order of experiment runs presented in Table 2.

The statistical analysis of the 2nd, 3rd and 4th MCM-41 synthesis cycles utilizing recycled surfactant template were conducted to study the effects of the synthesis factors on the amount of calcined MCM-41 produced. The half normal probability of effects and normal probability of residuals were plotted and analysed to identify the significant effects of the synthesis factors. The Analysis of Variance (ANOVA) was used to analyse and interpret the significant main effects and the interaction of the effects on the particular synthesis cycle. Both F-test and t-test were used to test the hypothesis and the significant contribution of regression coefficient such as AB, AC and BC to the statistical predicting models. The values of calculated F_{calc} and t_{calc} were compared to the obtained statistical F_{stat} and t_{stat} using standard normal probability distribution.

4. Result and Discussion

4.1. Statistical analysis of 2nd MCM-41 synthesis cycle

The plots of half-normal probability of effects and normal probability of residuals for the 2nd cycle of MCM-41 synthesis are shown in Figure 2 (a) and (b). Straight line in Figure 2 (a) indicates the insignificant effects pointed toward the origin and the points were assembled approximately close to the reference line from the origin as illustrated in Figure 2 (b). It can be concluded that factors A, B, C and the AB interaction are significant statistical model factors. Random pattern was illustrated in the plot of the residuals versus the predicted mass of MCM-41 powder in the 2nd synthesis cycle that was obtained from MCM-41 synthesis experiment in Figure 3. This indicates that the linear regression model is appropriated for the data. Thus, the residual plot for the model of 2nd MCM-41 synthesis cycle is considered satisfactory. The ANOVA for the 2nd cycle of MCM-41 synthesis model is shown in Table 3. The ANOVA shows that the linear regression model is insignificant for the mass of MCM-41 powder produced in the 2nd synthesis cycle by obtaining probability value of individual factor greater than conventional significance level of probability value such as 0.05. In Table 3, the probability value for ethanol volume fraction, quantity of ion exchange agent and type of ion exchange agent are 0.13, 0.20 and 0.61 respectively. The investigated probabilities indicate that the ethanol volume fraction levels, levels of ion exchange agent quantity and type of ion exchange agent levels are not correlated with the varying MCM-41 powder yield in the 2nd synthesis cycle. The probability value for the AB interaction is 0.07 which is approaching the conventional probability value of 0.05. The probability value for the AB interaction indicates that the relationship between the quantity of ion exchange agent and the mass of MCM-41 powder produced in the 2nd synthesis cycle are independent of the volume fraction of ethanol. The R^2 value for the 2nd cycle of MCM-41 synthesis model is found to be 0.84 indicating the level of variability in the mass of the MCM-41 powder produced in the 2nd synthesis cycle. The statistical model for predicting the mass of MCM-41 powder produced in the 2nd synthesis cycle in terms of the coded factors is shown in Equation (1).

Table 1. Levels of interest for experimental design factors

Factor	**Type of factor**	**Low level (−1)**	**High level (+1)**
A (volume fraction of ethanol)	Numerical	0.3 volume fraction	0.5 volume fraction
B (amount of ion exchange agent)	Numerical	1 g	2 g
C (type of ion exchange agent)	Categorical	C1-BMlmCl	C2-NH_4NO_3

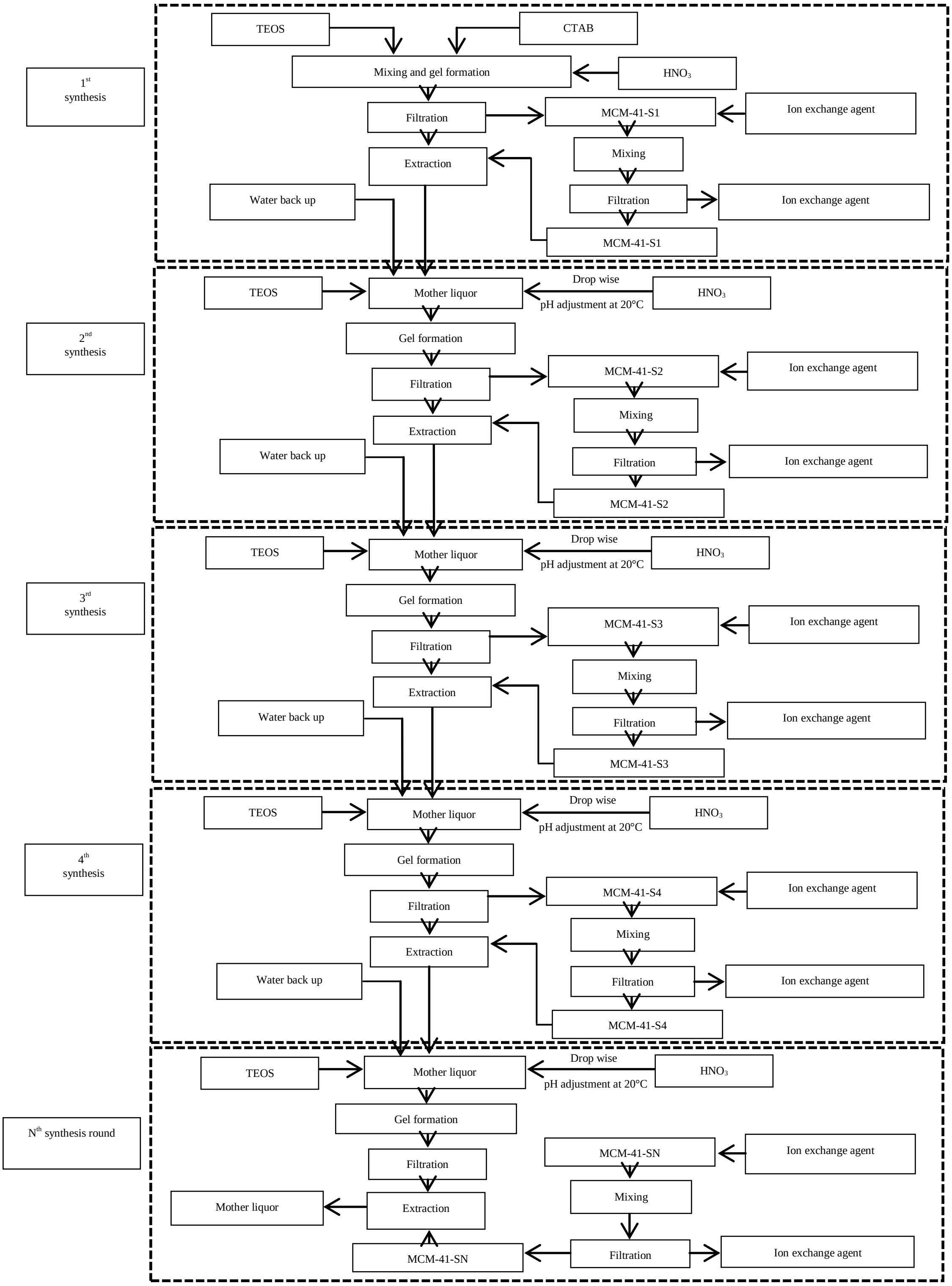
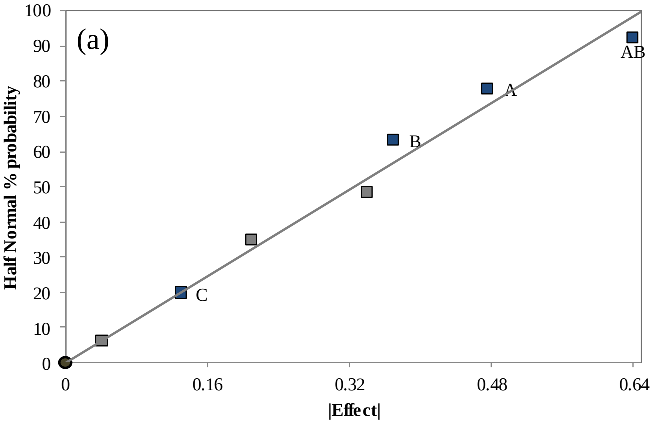


Figure 1. Schematic diagram for MCM-41 synthesis and surfactant template reuse cycles experiment.



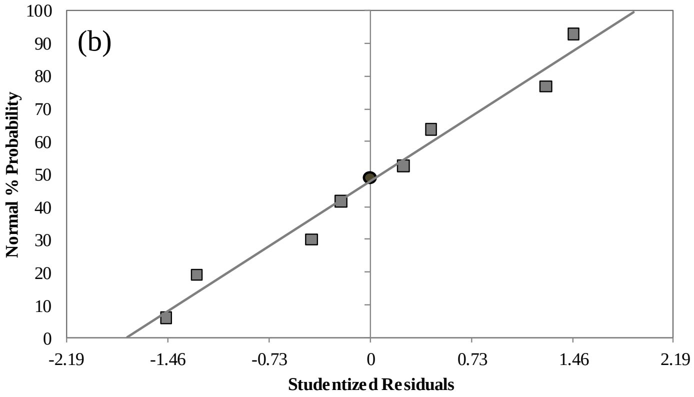


Figure 2. (a) Half-normal probability plot of the effects and (b) normal probability plot of the residuals for the mass of MCM-41 powder produced in the 2nd synthesis cycle.

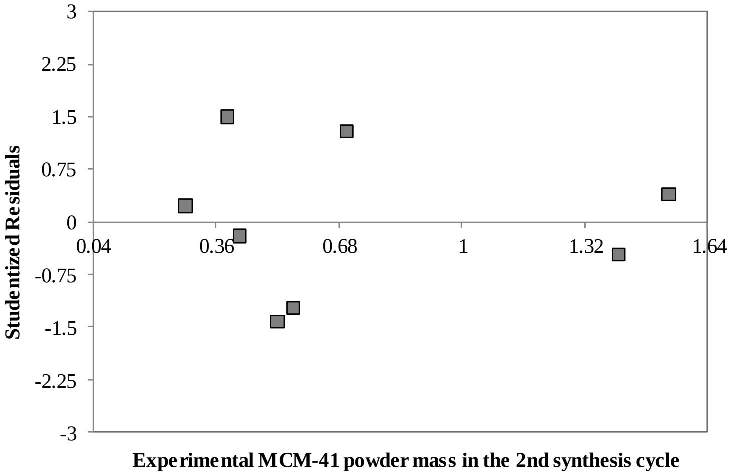


Figure 3. Plot of residuals versus experimental MCM-41 powder mass in the 2nd synthesis cycle.

Table 2. 2^3 factorial designs data of MCM-41 synthesis

Run	Factor A	Factor B	Factor C	Response			
				Mass of MCM-41 powder (g)			
				1st cycle	2nd cycle	3rd cycle	4th cycle
1	-1	1	C2	0.94	0.33	0.37	0.51
2	-1	-1	C2	0.66	0.31	1.21	0.27
3	1	1	C2	1.59	1.32	1.38	0.51
4	1	-1	C2	0.78	0.68	1.06	0.77
5	-1	1	C1	1.49	0.37	0.60	1.31
6	-1	-1	C1	0.93	0.94	0.22	0.41
7	1	1	C1	1.42	1.62	0.08	1.62
8	1	-1	C1	0.52	0.23	0.72	1.04

$$\text{Mass of MCM-41 (2}^{\text{nd}}\text{ cycle)} = 0.73 + 0.24A + 0.19B - 0.065C + 0.32AB \tag{1}$$

Partial F-test was used to perform the hypothesis testing to the statistical model of 2nd MCM-41 synthesis cycle in order to investigate the significance of regression coefficient AC and BC to the particular model. The hypotheses that would be tested are H_0: AC and BC = 0 and H_1: AC and BC $\neq$ 0. Two rules are reported in the partial F-test. First hypothesis is H_0 would be accepted when F_{calc} is smaller than the F_{stat} obtained that falls in the right-tail of the probability distribution ($F_{\alpha,r,n-p}$) where α, r and n-p is defined as the probability, degree of freedom for the tested variable and the degree of freedom for the residual. Second hypothesis states H_0 would be rejected if F_{calc} is greater than or equal to $F_{\alpha,r,n-p}$ [16]. The ANOVA table for the full model and the statistics for t-test are shown in Table 4. The ANOVA table for the reduced model is tabulated in Table 3.

Table 3. ANOVA of the mass of MCM-41 powder obtained in the 2nd synthesis cycle (reduced model)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Coefficient Estimate	Standard Error	95% CI* Low	95% CI High
Model	1.59	4	0.40	3.83	0.15	-	-	-	-
Intercept	-	1	-	-	-	0.73	0.11	0.36	1.09
A	0.45	1	0.45	4.34	0.13	0.24	0.11	−0.13	0.60
B	0.27	1	0.27	2.64	0.20	0.19	0.11	−0.18	0.55
C	0.03	1	0.03	0.33	0.61	−0.07	0.11	−0.43	0.30
AB	0.83	1	0.83	8.01	0.07	0.32	0.11	−0.04	0.69
Residual	0.31	3	0.10						
Cor Total	1.90	7							
R^2	0.84								

*CI = Confidence Interval

Table 4. ANOVA and t_{stat} for full model of 2nd MCM-41 synthesis cycle

Source	**Sum of Squares**	**DF**	**Mean Square**	**Coefficient Estimate**	**Standard Error**	**t_{calc} (DF = 1)**	**α**	**α/2**
Model	1.68	6	0.28	-	-	-	-	-
Intercept	-	1	-	0.73	0.17	4.29	0.15	0.073
A	0.45	1	0.45	0.24	0.17	1.41	0.39	0.20
B	0.27	1	0.27	0.19	0.17	1.12	0.46	0.23
C	0.034	1	0.034	−0.065	0.17	−0.38	0.77	0.38
AB	0.83	1	0.83	0.32	0.17	1.88	0.31	0.16
AC	0.084	1	0.084	0.10	0.17	0.59	0.66	0.33
BC	0.0032	1	0.0032	−0.020	0.17	−0.12	0.92	0.46
Residual	0.22	1	0.22					
Cor Total	1.90	7						

Initially, the extra sum of squares due to the coefficient AC and BC interactions are calculated by subtracting the sum of square of reduced model from sum of squares of full model. The extra sum of squares obtained is 0.09. Hence, the F-value can be obtained through the division of extra mean square value with the mean square of residual of full model to test for the hypothesis of H_0. The value of F_{calc} calculated from the partial F-test is 0.41 with the right-tail probability distribution of F_{stat} obtained equal to 0.64. In comparison to $F_{0.5,1,1}$, which used the probability of 0.50 has the value of 1.00 and is greater than F_{calc}. As a result, the hypothesis H_0 is accepted and explained that both variables of coefficient AC and BC are insignificant to the 2nd cycle of MCM-41 synthesis model.

An alternative approach, t-test was used to test the contribution of regression coefficient AC and BC to the corresponding model of 2nd MCM-41 synthesis cycle. The hypotheses that would be tested for the coefficient AC and BC are H_i: AC = 0, H_{ii}: AC ≠ 0, H_{iii}: BC = 0 and H_{iv}: BC ≠ 0. Two rules applied in the t-test. These are the hypothesis of H_i and H_{iii} would be accepted for $t_{calc} < t_{stat}$ obtained from the normal probability distribution ($t_{\alpha/2,n-k-1}$) where k represents the degree of freedom for the residual or both hypothesis H_i and H_{iii} would be rejected for $t_{calc} \geq t_{\alpha/2,n-k-1}$ [16].

The t_{stat} for each factor in the full model of 2nd MCM-41 synthesis cycle was evaluated and the probability of t_{stat} with either right-tail or left-tail probability distribution are obtained and compared [17]. The value of t_{calc} for the coefficient AC ($t_{calc,AC}$) and BC ($t_{calc,BC}$) resulted from the t-test are 0.59 and −0.12 while the probability of $t_{calc,AC}$ and $t_{calc,BC}$ distributed in two-tails are 0.66 and 0.92 respectively. It was found that the corresponding probability for ($t_{calc,AC}$) with either value of −0.59 or 0.59 are 0.33 whereas the probability of $t_{calc,BC}$ which falls in the left-tail probability distribution is 0.46. Comparing $t_{calc,AC}$ to $(t_{calc,AC})_{stat}$, the t-statistics for $t_{0.3,1}$ ($(t_{calc,\ AC})_{stat}$) with two-tails probability distribution using the probability, 2α of 0.60 for probability in right-tail probability distribution, α of 0.30 and degree of freedom (DF) of 1 is 0.73. This is greater than the $t_{calc,AC}$ resulted from t-test (shown in Table 4) with α of 0.66 at 0.59. This means that the hypothesis of H_i is accepted. Other than that, the value obtained for t_{stat} of coefficient BC which falls in the left-tail probability distribution with the probability of 0.60 ($t_{0.6,1}$) is 0.32. The resulting $t_{0.6,1}$ is greater than $t_{calc,BC}$ which concluded that the hypothesis for H_{iii}: BC = 0 is accepted. Therefore, as shown in the t-test, both AB and BC coefficients are insignificant to the model of 2nd MCM-41 synthesis cycle. As a result, similar conclusion was obtained through both the partial F-test and t-test.

The graph of AB interaction is plotted in Figure 4. The lines which indicate the low quantity of ion exchange agent (B = −1) and high quantity of ion exchange agent (B = +1) used are not parallel to each other. This shows that an interaction occurred between the two factors. The volume fraction of ethanol has large effect when the quantity of ion exchange agent was at the high level while the effect of ethanol volume fraction was small when the quantity of ion exchange agent was at the low level. The difference in the mass of MCM-41 powder produced in the 2nd synthesis cycle at low and high level of ethanol volume fraction using low quantity of ion exchange agent are the same when either C1 or C2 was used as the ion exchange agent. Therefore, this can be concluded that maximum yield of MCM-41 powder would be obtained when both ethanol volume fraction and quantity of ion exchange agent used are at high level using both extraction agents C1 and C2.

The desirability is approximately 1 for all four experiment criteria (i) low ethanol volume fraction and low quantity of ion exchange agent used, (ii) high ethanol volume fraction and low quantity of ion exchange agent used, (iii) low ethanol volume fraction and high quantity of ion exchange agent used and (iv) high ethanol volume fraction and high quantity of ion exchange agent. Hence, the predicted mass of MCM-41 powder produced in 2nd synthesis cycle at four different criteria using either C1 or C2 are desirable. Figure 5 (a) and (b) shows the response contour plot when the type of ion exchange agent used is C1 or C2. The contours are curved lines as shown in both Figure 5 (a) and (b) which indicate that the model of 2nd MCM-41 synthesis cycle contains an interaction term. The relative yield of MCM-41 powder increases when both the ethanol volume fraction and the quantity of ion exchange agent used increase. Similar conclusion is obtained from the contour plots of AB interaction as same as the AB interaction graph. These two contour plots show that the model of 2nd MCM-41 synthesis cycle is desirable to obtain an approximate relative mass of MCM-41 powder of 0.79 g when ion exchange agent, C1 is used and 0.67 g when ion exchange agent, C2 is used. The feasible predicted mass of MCM-41 powder that would be obtained from the 2nd synthesis cycle at four different experiment criteria as observed from the overlay plot are listed in Table 5.

Table 5. Predicted mass of MCM-41 powder from overlay plot

Type of ion exchange agent	**Experiment criterion no.**	**Experiment Factor**		**Predicted mass of MCM-41 powder (g)**
		A (volume fraction of ethanol)	**B (amount of ion exchange agent)**	
C1	(i)	−1	−1	0.69
	(ii)	+1	−1	0.52
	(iii)	−1	+1	0.42
	(iv)	+1	+1	1.54
C2	(i)	−1	−1	0.56
	(ii)	+1	−1	0.40
	(iii)	−1	+1	0.29
	(iv)	+1	+1	1.40

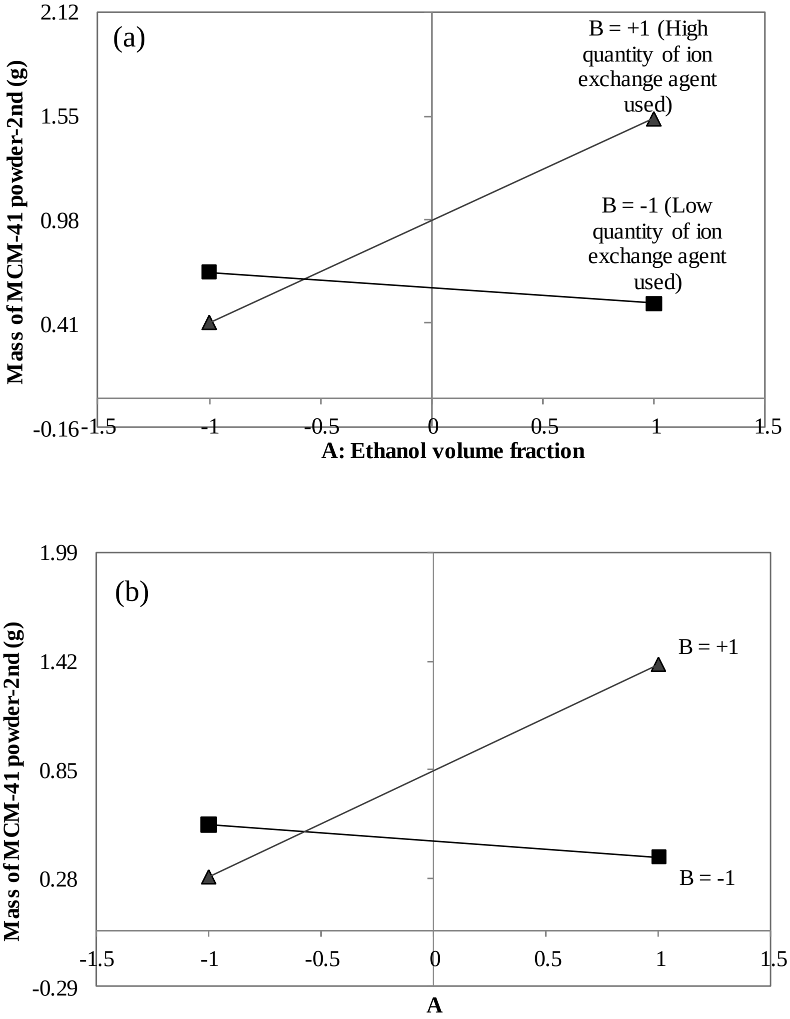


Figure 4. AB interaction graph with ion exchange agent (a) C1 and (b) C2.

4.2. Statistical analysis for 3rd and 4th MCM-41 synthesis cycles

The ANOVA for the respective 3rd and 4th MCM-41 synthesis cycles are listed in Table 6 and Table 7. Both 3rd and 4th cycles of MCM-41 models were found insignificant for the response in the mass of MCM-41 powder produced. From Table 6, the interaction of AB has the largest probability with the value of 0.93. It can be said that the relationship between the quantity of ion exchange agent and mass of MCM-41 powder is independent of the volume fraction of ethanol. In the 4th cycle of MCM-41 synthesis model with ANOVA table tabulated in Table 7, the F-value probability of factor C has the smaller value of 0.084. This indicates that the factor of the type of ion exchange agent is slightly correlated with the amount of MCM-41 powder that would be produced during the 4th cycle of MCM-41 synthesis. The corresponding t_{stat} for the respective models of 3rd and 4th MCM-41 synthesis cycles are shown in Table 8 and Table 9. The hypotheses in section 3.1 (H_0, H_1, H_i, H_{ii}, H_{iii} and H_{iv}) are used to perform the partial F-test and t-test in order to test for the significance of regression coefficient AC and BC to the 3rd and 4th cycles of MCM-41 synthesis models. The extra sum of squares due to the coefficient AC and BC obtained is 0.10. The value of F_{calc} calculated from the partial F-test is 0.17 with the probability in the right-tail probability distribution obtained is 0.75. As compared to $F_{0.7,1,1}$ using the probability of 0.70, $F_{0.7,1,1}$ has the value of 0.26 that is greater than F_{calc}. Other than that, the value of $t_{calc,AC}$ and $t_{calc,BC}$ from the t-test are 0.41 and −0.12 with individual probability of 0.38 and 0.46. When compared to $t_{0.3,1}$ and $t_{0.6,1}$, the statistics of $t_{0.3,1}$ that falls in two-tails probability distribution with the probability of 0.60 and the statistics of $t_{0.6,1}$ that falls in the left-tail probability distribution with the probability of 0.60 are 0.73 and 0.32 respectively which indicate that the resulting value of $t_{0.3,1}$ and $t_{0.6,1}$ are greater than $t_{calc,AC}$ and $t_{calc,BC}$. Therefore, the hypotheses of H_0, H_i and H_{iii} are accepted and the variables of x_{AC} and x_{BC} are insignificant to the 3rd cycle of MCM-41 synthesis model.

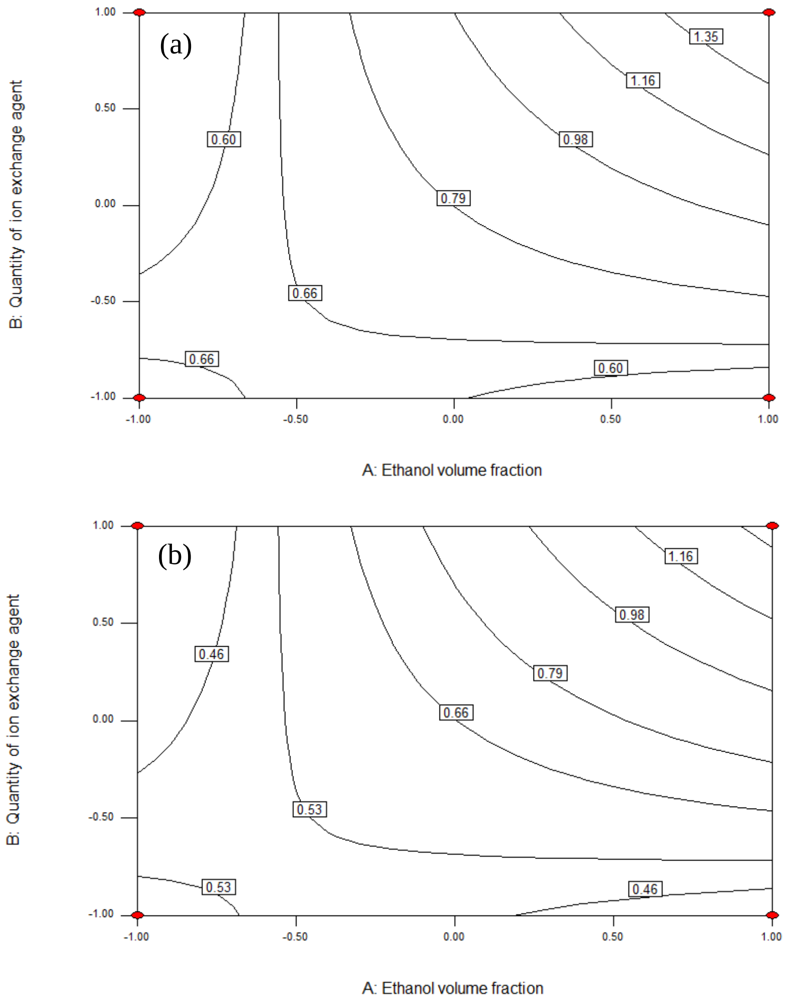


Figure 5. Contour plot of MCM-41 powder mass in the 2nd MCM-41 synthesis cycle with ion exchange agent (a) C1 and (b) C2.

Table 6. ANOVA of the mass of MCM-41 obtained in the 3rd synthesis cycle (reduced model)

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	**Coefficient Estimate**	**Standard Error**	**95% CI Low**	**95% CI High**
Model	0.89	4	0.22	0.95	0.54	-	-	-	-
Intercept	-	1	-	-	-	0.70	0.17	0.16	1.25
A	0.087	1	0.087	0.37	0.58	0.10	0.17	−0.44	0.65
B	0.077	1	0.077	0.33	0.61	−0.098	0.17	−0.64	0.45
C	0.72	1	0.72	3.09	0.18	0.30	0.17	−0.24	0.84
AB	0.0023	1	0.0023	0.0099	0.93	0.017	0.17	−0.53	0.56
Residual	0.70	3	0.23						
Cor Total	1.59	7							

Table 7. ANOVA of the mass of MCM-41 obtained in the 4th synthesis cycle (reduced model)

Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Prob > F**	**Coefficient Estimate**	**Standard Error**	**95% CI Low**	**95% CI High**
Model	1.28	4	0.32	3.11	0.19	-	-	-	-
Intercept	-	1	-	-	-	0.81	0.11	0.44	1.17
A	0.26	1	0.26	2.51	0.21	0.18	0.11	−0.18	0.54
B	0.27	1	0.27	2.58	0.21	0.18	0.11	−0.18	0.54
C	0.67	1	0.67	6.52	0.084	−0.29	0.11	−0.65	0.071
AB	0.084	1	0.084	0.81	0.43	−0.10	0.11	−0.46	0.26
Residual	0.31	3	0.10						
Cor Total	1.59	7							

Table 8. ANOVA and t_{stat} for full model of 3rd MCM-41 synthesis cycle

Source	**Sum of Squares**	**DF**	**Mean Square**	**Coefficient Estimate**	**Standard Error**	**t_{calc} (DF = 1)**	**α**	**$\alpha/2$**
Model	0.99	6	0.17	-	-	-	-	-
Intercept	-	1	-	0.70	0.27	2.59	0.23	0.12
A	0.087	1	0.087	0.10	0.27	0.37	0.77	0.39
B	0.077	1	0.077	−0.098	0.27	−0.36	0.78	0.39
C	0.72	1	0.72	0.30	0.27	1.11	0.47	0.23
AB	0.0023	1	0.0023	0.017	0.27	0.063	0.96	0.48
AC	0.098	1	0.098	0.11	0.27	0.41	0.75	0.38
BC	0.0082	1	0.0082	−0.032	0.27	−0.12	0.92	0.46
Residual	0.60	1	0.60					
Cor Total	1.59	7						

As for the 4th cycle of MCM-41 synthesis model, the extra sum of square calculated is 0.31 and hence F_{calc} has the value of 76.54 with probability of 0.07. The probability of 0.05 is used to calculate

$F_{0.05,1,1}$ by obtaining the value of 161.45. As a result, F_{calc} value is smaller than F_{stat} ($F_{0.05,1,1}$) where the hypothesis H_0 is accepted with insignificant coefficient of AC and BC. For the t-test, $t_{calc,AC}$ and $t_{calc,BC}$ with the value of −2.39 and −8.26 have the individual probability distributed in left-tail probability distribution are 0.13 and 0.04. The resulting $t_{0.2,1}$ and $t_{0.05,1}$ that fall in the left-tail probability distribution using the probability of 0.20 and 0.05 are −1.38 and −6.31 respectively. The value of $t_{calc,AC}$ and $t_{calc,BC}$ resulted are smaller than $t_{0.2,1}$ and $t_{0.05,1}$. Therefore, the hypothesis for H_i: AC = 0 and H_{iii}: BC = 0 are accepted and explained that the variables of x_{AC} and x_{BC} contributed insignificantly to the model of 4th MCM-41 synthesis cycle.

Table 9. ANOVA and t_{stat} for full model of 4th MCM-41 synthesis cycle

Source	**Sum of Squares**	**DF**	**Mean Square**	**Coefficient Estimate**	**Standard Error**	**t_{calc} (DF = 1)**	**α**	**α/2**
Model	1.59	6	0.26	-	-	-	-	-
Intercept	-	1	-	0.81	0.023	35.22	0.018	0.009
A	0.26	1	0.26	0.18	0.023	7.83	0.081	0.040
B	0.27	1	0.27	0.18	0.023	7.83	0.081	0.040
C	0.67	1	0.67	−0.29	0.023	−12.61	0.050	0.025
AB	0.084	1	0.084	−0.10	0.023	−4.35	0.14	0.072
AC	0.024	1	0.024	−0.055	0.023	−2.39	0.25	0.13
BC	0.28	1	0.28	−0.19	0.023	−8.26	0.077	0.038
Residual	0.0041	1	0.0041					
Cor Total	1.59	7						

5. Conclusions

In this work, the statistical analysis of the 2nd cycle of MCM-41 synthesis model determined that the significant effects of this model are contributed from factor A, B and C and the interaction of AB. The residual plot illustrates a random pattern which show that the data fit well to the linear regression model. The model of 2nd MCM-41 synthesis cycle explained that the variability in the mass of the MCM-41 powder produced in the 2nd synthesis cycle is about 83.62%. Other than that, both results of partial F-test and t-test have proven that the regression coefficient AC and BC are insignificantly to the 2nd cycle of MCM-41 synthesis model through smaller F_{calc} value, $F_{calc\ [0.41]} < F_{0.5,1,1\ [1.00]}$, $t_{calc,AC\ [0.59]} < t_{0.3,1\ [0.73]}$ and $t_{calc,BC\ [-0.12]} < t_{0.6,1\ [0.32]}$. Moreover, the graphs of AB interaction using the type of ion exchange agent either C1 or C2 indicated that the mass of MCM-41 powder would be maximized at both high level of ethanol volume fraction and quantity of ion exchange agent used. Similar conclusion in the AB interaction graphs was also obtained from the contour plots with the use of either C1 or C2. The feasible higher MCM-41 powder mass could be obtained at both high level of ethanol volume fraction and quantity of ion exchange agent used are 1.54 g when using C1 as ion exchange agent and 1.40 g when using C2. Coefficient AC and BC to the models of 3rd and 4th MCM-41 synthesis cycles have insignificant contribution as concluded by the partial F-test and t-test with the values of $F_{\alpha,r,n-p}$ and $t_{\alpha/2,n-k-1}$ greater than the value of F_{calc} and t_{calc}.

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