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OPTIMIZED CONDITIONS FOR SYNTHESIS OF Na-A ZEOLITE FROM COAL FLY ASH BY APPLYING THE RESPONSE SURFACE METHODOLOGY

Abdul Salam Matlob[1,*], Rose Aini Kamarudin[1], Zaemah Jubri[1] and Zainab Ramli[2]

[1]*Department of Engineering Sciences & Mathematic, College of Engineering, Universiti Tenaga Nasional, Km 7 Jalan Kajang-Puchong, 43009 Kajang, Selangor, Malaysia*

[2]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 80990 Skudai, Johor, Malaysia*

**Corresponding Author: abdulsalam@uniten.edu.my*

ABSTRACT

Response Surface Methodology (RSM) was used in this study to determine the optimum conditions for the synthesis of Na-A zeolites from coal fly ash (CFA). Application of this methodology allows a better understanding of the influence of various factors (Si/Al ratio (0.5-1.5), incubation temperature (70-120 °C) and time of incubation (2–4 days)) on the synthesis of zeolites. The Box–Behnken design was applied with different levels of the factors, determining its influence on yield percent in order to obtain contour plots. The silicates and aluminates were extracted from coal fly ash (CFA) with 4M NaOH solution assisted by microwave irradiation (power level 100 watts) for 6 minutes followed by incubation at various temperatures. The products isolated were characterized by their XRD images and found to be Na-A zeolites, sodalite octahydrate and gibbsite. The highest percent yield of product was obtained at 0.5 SiO_2/Al_2O_3 molar ratio, 70 °C incubation temperature for 3 days, the product however, was not a zeolite. It was gibbsite which contains $Al(OH)_3$. Na-A zeolite was formed at SiO_2/Al_2O_3 molar ratio 1-1.5, incubation temperature was 70 – 95 °C and 2-4 days of incubation and the highest yield was observed at $SiO_2\backslash Al_2O_3$ ratio = 1, incubation temperature 70 ^oC for 4 days. The contour plots showed that the yield percent of the product was inversely proportional to the three factors used. The order of effectiveness of the factors on yield percent is: SiO_2/Al_2O_3 molar ratio > incubation temperature > duration of incubation.

Keywords: Na-A zeolites; yield; incubation temperature;

INTRODUCTION

Coal fly ash is one of the solid wastes produced from the combustion of coal in coal fired power stations. Typically fly ash is an agglomerate of hollow spheres with diameter from 1 to 100 μm. These fly ash particles contain silicon and aluminum as the major elements and are composed of an amorphous component with some crystals such as α-quartz, mullite, haematite, and magnetite [1]. It is the amorphous aluminosilicate of CFA which dissolved in alkali solution to form zeolites [2-4].

Zeolites have their aluminosilicate framework structures made from corner sharing tetrahedral SiO_4 and AlO_4 [5]. Zeolites has many uses such as drying agents, shape selective catalyst, shape selective separators and selective ion exchangers [6–8]. Zeolites formed when the supernatant from the fusion of coal fly ash with alkaline solution such as NaOH solution [9 - 14] are incubated. For the formation of Na-A zeolite, a white precipitate, the SiO_2/Al_2O_3 molar ratio needs to be adjusted to a certain value [10]. This is because the natural SiO_2/Al_2O_3 molar ratio in CFA will not induce the production of Na-A zeolites. Certain materials such as a mixture of Na_2SiO_4 and $Al(OH)_3$ [15], ammonium aluminum sulfate hydrate $(NH_4Al(SO_4)_2 \cdot 12H_2O$ [16], NaOH-$NaAlO_2$ solutions [10] and Al_2O_3 [17] can be used as a source of aluminum to adjust the SiO_2/Al_2O_3 molar ratio.

In the last 10 years, heating and driving chemical reactions by microwave energy have been an increasingly popular theme in the scientific community. The microwave-assisted synthesis of zeolites has also been investigated and reported in the literature. It was found that the synthesis duration of zeolites can be greatly shortened by microwave heating as compared to the conventional heating method [18-21].

Recently Response Surface Methodology (RSM) has been applied in the optimization of several processes [22-26]. RSM is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response is influenced by several variables when varying them simultaneously and the objective is to optimize this response [27].

The objectives of this study are to apply RSM to firstly, determine under what reaction conditions will produce Na-A zeolite and other products if any, thus leading to the optimum conditions for Na-A zeolite synthesis. The three variables used in the synthesis process are: SiO_2/Al_2O_3 ratio (0.5-1.5) with the alumina content adjusted by adding aluminum foil, incubation temperature (70–120 °C) and duration of incubation (2-4 days). Secondly, to study the influence of the three variables on the zeolites yield percent and to find the optimum conditions to maximize the yield.

EXPERIMENTAL DETAILS

Materials

The Coal fly ash (CFA) used in this study was obtained from Kapar Power Station which belongs to the National Electricity Board of Malaysia. It was dried in an oven at 100 °C and sieved before use. Sodium hydroxide of analytical grade from Merck was used without further purification. The chemical composition of CFA is shown in table 1.

The extraction of silica and alumina from the coal fly ash

Four grams of sieved, dried CFA were added to 50 ml 4M sodium hydroxide solution in a conical flask. The slurry was stirred at room temperature for fifteen minutes. The resulting material was exposed continuously to microwave irradiation at 100 Watts power level for 6 minutes period using a household microwave oven under ambient condition. This was followed by aging overnight at room temperature with stirring. The resulting material was filtered and the clear filtrate was collected and diluted with distilled water up to 45 ml volume.

Table 1: Chemical composition of as received CFA

Oxide	Weight %
SiO_2	65.7 ± 0.02
Al_2O_3	15.5 ± 0.01
Fe_2O_3	15.7 ± 0.01
K_2O	1.43 ± 0.01
CaO	1.16 ± 0.01
TiO_2	0.34 ± 0.01
MnO	0.09 ± 0.01
Na_2OO	0.03 ± 0.01

Hydrothermal treatment on the extracted silica and alumina from CFA

Different amounts of aluminum foil were added to the clear solution obtained from 2.2, with stirring to adjust the SiO_2/Al_2O_3 molar ratio to be 0.5, 1 and 1.5. The resulting suspension was filtered and the clear filtrate placed in a 250 ml PTFE bottle and incubated at different temperatures (70, 95 and 120 °C) for different duration (2, 3 and 4 days). White solid formed was collected by filtration and washed several times with distilled water until the pH of the washings reached 10. The product was dried at 100 ^oC and weighed.

Characterization

X-ray diffraction (XRD) patterns of the products were recorded on an automatic Rigaku Geiger-Flex diffractometer using CuK_α radiation (30 kV, 20mA) for 2θ angles from 0-60 degrees.

Table 2**:** Levels of independent variables

Levels	Low	Medium	High
Coding	-1	0	+1
SiO_2/Al_2O_3 molar ratio	0.5	1	1.5
Temperature of incubation/ °C	70	95	120
Time of incubation/days	2	3	4

Response Surface Methodology (RSM)
The effects of the three variables (SiO_2/Al_2O_3 molar ratio, incubation temperature, and incubation time) on the products isolated and on the yield percent were studied by using RSM. The Box-Behnken experimental design was used. According to this design, the total number of experiments is $N = 2k\,(k - 1) + c_p$ where k is the number of factors and (c_p) is the number of the central points. So the number of experiments that have been carried out was fifteen. All factor levels have to be adjusted only at three levels (−1, 0, +1) with equally spaced intervals between these levels. The range and the levels of the variables investigated in this study are given in Table 2.

Second order model was postulated in obtaining the relationship between the yield percent and the independent variables, and it was expressed by the following second-degree polynomial equation [28]:

$$Y = B_o + \sum_{i=1}^{n} B_i x_i + \sum_{ij} B_{ij} x_i x_j + \sum_{j=1}^{n} B_{jj} x_j^2 \qquad (1)$$

Where Y is the predicted response, three variables are involved and hence n takes 3 in this study. Thus by substituting the value 3 for n, the equation (1) becomes:

$$Y = B_o + B_1 x_1 + B_2 x_2 + B_3 x_3 + B_{12} x_1 x_2 + B_{13} x_1 x_3 + B_{23} x_2 x_3 + B_{11} x_1^2 + B_{22} x_2^2 + B_{33} x_3^2 \qquad (2)$$

Where x_1, x_2 and x_3 are input variables; $B_o$is a constant; B_1, B_2 and B_3 are linear coefficients; B_{12}, B_{13} and B_{23} are interaction coefficients; B_{11}, B_{22} and B_{33} are quadratic coefficients. The coefficients have been estimated from the experimental results. The MINITAB release 14 software is used for regression analysis of the experimental data and the response. The quality of the multiple regression model fit are expressed by the coefficient of regression R^2 and F-test which used for checking its statistical significance. The significance of the regression coefficient was tested by a Student's t-test. The confidence levels of the experimental values are 95%.

RESULTS AND DISCUSSION

When a suspension of CFA and NaOH were subjected to microwave irradiation, a viscous solution was obtained. The microwave irradiation enhances the extraction of SiO_2 and Al_2O_3 from the CFA. The aluminium foil when added to the above solution to adjust the molar ratio between silica and alumina, reacted vigorously with gas and heat released during the process. Upon filtration a viscous liquid was collected leaving a gray colored waste on the filter paper. White colored product crystallized upon incubating the viscous liquid after a few days at different temperature.

Products isolated
The Box–Behnken design matrix and products isolated from the fifteen experiments are given in Table 3.

Table 3: Box-Behnken design matrix and Products

Experiment	SiO_2/Al_2O_3	Temperature/° C.	Time/da y	Product*
1	0.5	120	3	Sodalite
2	0.5	95	4	Gibbsite
3	0.5	95	2	Gibbsite
4	0.5	70	3	Gibbsite
5	1	70	4	ZeoliteNa-A
6	1	70	2	ZeoliteNa-A
7	1	95	3	ZeoliteNa-A
8	1	95	3	ZeoliteNa-A
9	1	95	3	ZeoliteNa-A
10	1	120	2	Sodalite
11	1	120	4	Sodalite
12	1.5	120	3	Sodalite
13	1.5	95	2	ZeoliteNa-A
14	1.5	95	4	ZeoliteNa-A
15	1.5	70	3	ZeoliteNa-A

*All products are characterized based on their XRD images

From the fifteen experiments mentioned above, three types of products isolated: Na-A zeolites, gibbsite which contains $Al(OH)_3$ and sodalite octahydrate. These products were characterized based on their XRD patterns. In the hydrothermal fusion stage, the supernatant containing silicates and aluminates from CFA for all 15 experiments were extracted using the same conditions i.e. 4M NaOH, 100 Watts microwave power for 6 min.

From Table 3, it is observed that the product isolated from reactions 5-9 and 13-15 was Na-A zeolite. When the SiO_2/Al_2O_3 molar ratio is 1 and the incubation temperature is 70 or 95°C, the product is Na-A zeolite regardless of the time of incubation. This is also observed at 1.5 SiO_2/Al_2O_3 molar ratio and 70 or 95 ^oC incubation temperature. At 120 ^oC, for all SiO_2/Al_2O_3 molar ratios and duration of incubation only sodalite octahydrate was observed (reactions 1, 10-12). This implied that SiO_2/Al_2O_3 molar ratio and time of incubation has no effect on the formation of sodalite octahydrate when the temperature of incubation is 120 $^\circ C$. At high temperature (120^oC) only sodalite octahydrate, more stable with small pore size, formed. Consequently at this high temperature, at whatever SiO_2/Al_2O_3 molar ratio and duration of incubation, there is no formation of Na-A zeolite observed. As the large pore size leads to less stable zeolite Na-A, cannot bear the high temperature so it will decompose and the more stable sodalite octahydrate will form instead. This result indicate that sodalite octahydrate, has low industrial application, was more stable than Na-A zeolite during the hydrothermal crystallization process, and the temperature of incubation has the crucial role in controlling the product. The third product, which is not a zeolitic material, gibbsite contains $Al(OH)_3$ was isolated from reactions 2-4. These three reactions at 70 and 95 °C with SiO_2/Al_2O_3 molar ratio of 0.5 showed only gibbsite formed. This is expected because at this ratio, there is a large quantity of Al^{3+} and OH^- in the solution, so the formation of $Al(OH)_3$ will predominate. $SiO_2\backslash Al_2O_3$ ratio is the product controlling factor when it was less than unity, which leads to the formation of the gibbsite. Then Na-A zeolite cannot form at elevated temperature 120 °C and at $SiO_2\backslash Al_2O_3$ less than unity.

X-ray diffraction patterns

From Figure 1, XRD pattern of Na-A zeolites from reaction 7, the high intensity of the peaks observed indicates the high crystallinity of the zeolite. The peaks appeared at 2-theta were 7.18, 10.17, 12.46, 16.09, 21.64, 23.99, 27.09, 29.94, 34.149 representing planes [200], [220], [222], [420], [442], [622], [642], [644] and [664] respectively. The XRD pattern observed is similar to those that have been published [5]. The XRD pattern of the product isolated from reaction 12 was that of sodalite octahydrate and it is shown in Fig. 2. The peaks appeared at 2-theta were 14.16, 24.65, 31.99, 35.13 and 43.99 representing planes [110], [211], [310], [222] and [330] respectively. The XRD pattern observed is similar to that of sodalite octahydrate from reference [5]. Fig. 3 shows the XRD image of the product isolated from reaction 4 and was found to be a non-zeolite. The product from reaction 4 was identified to be gibbsite which contains $Al(OH)_3$. All the 3 products obtained from the reactions 1-15 are known hence there is no need for further elaboration of their XRD images.

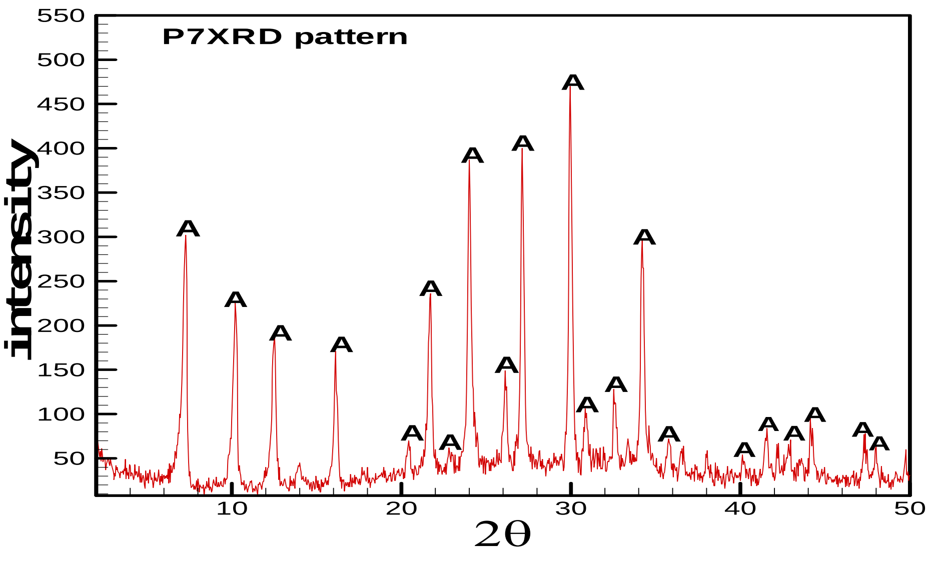

Figure 1: XRD pattern of zeolite Na-A from experiment 7, A = Na-A zeolite

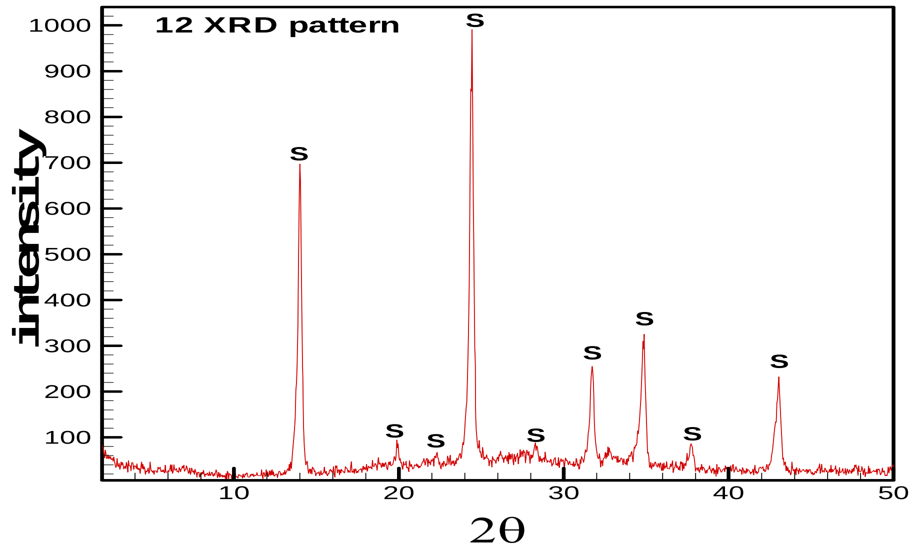

Figure 2: XRD pattern of sodalite octahydrate from experiment 12, S = sodalite octahydrate

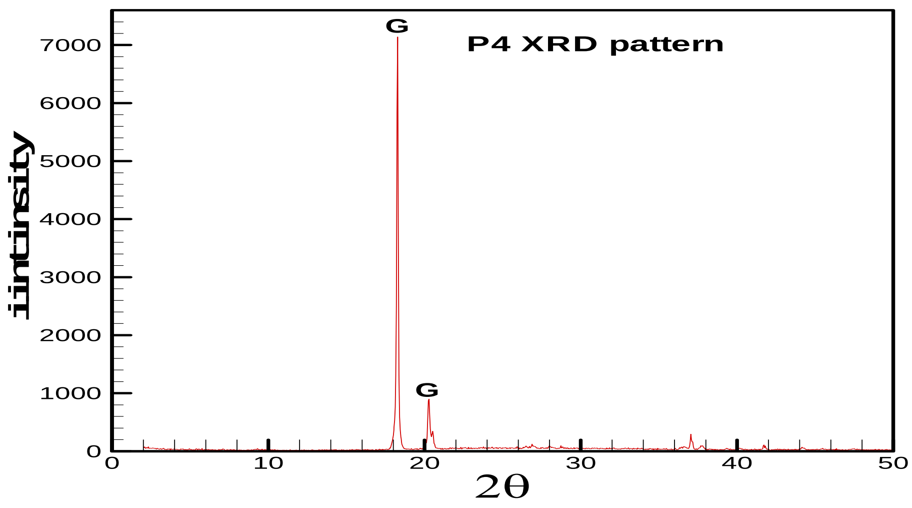

Figure 3: XRD pattern of gibbsite from experiment 4, G = Gibbsite containing $Al(OH)_3$

Validation of response surface model

The relationship between independent variables and response was described by second-order polynomial equation. The regression equation coefficients were calculated and data was fitted to a second-order polynomial equation for product yield. Statistical testing of the model was performed with *F*-test to obtain the mathematical relationship

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between response and process variables. To ensure a good model, the test for significance of regression model was performed and applying the analysis of variance (ANOVA). Table 4 showed the results of ANOVA for zeolite yield percent. The non-significant lack-of-fit 0.075, more than 0.05 for the 95% confidence level, showed that quadratic model is valid for present study. Non-significant lack-of-fit is good for data fitness in the model. The R^2 value (multiple correlation coefficient) closer to 1, in this case the value of R^2 = 0.991, denotes better correlation between the observed and predicted values.

Table 4: Analysis of Variance for Yield%

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	3420.71	3420.71	380.078	59.20	0.000
Linear	3	2096.73	1235.32	411.774	64.13	0.000
Square	3	964.65	964.65	321.550	50.08	0.000
Interaction	3	359.33	359.33	119.775	18.66	0.004
Residual Error	5	32.10	32.10	6.420		
Lack- of -Fit	3	30.47	30.47	10.156	12.42	0.075
Pure Error	2	1.64	1.64	0.818		
Total	14	3452.81				

Hence the values of the response determined by means of the empirical models were compared to the experimental data as shown in Figure 4. As can be seen the experimental and predicted yields are much closed.

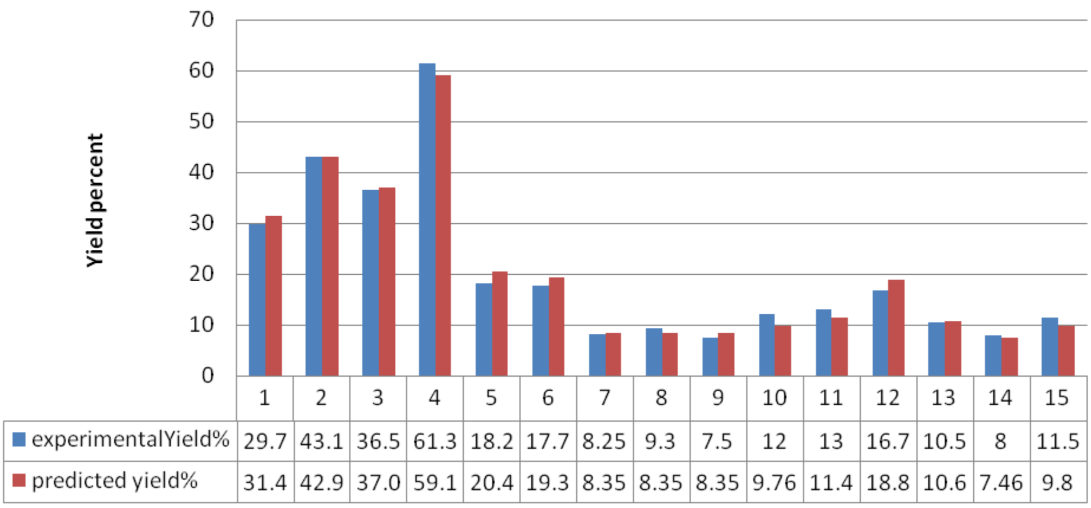

Figure 4: Experimental and predicted yields of product for the 15 experiments

This means the response model shows good fit to the experimental data. Therefore, the second order model that has been used can be considered adequate for prediction and optimization. As a result, the mathematical equation was given by:

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Zeolites %Yield = 269.421 - 210.245 Si\Al - 2.792 Temp.\°C - 0.025 Time\day + 61.500 Si\Al*Si\Al + 0.010 Temp.\C*Temp.\°C + 0.800 Time\day*Time\day + 0.736 Si\Al*Temp.\°C - 4.550 Si\Al*Time\day + 0.005 Temp.\°C*Time\day

The order of the coefficients by absolute value indicates the relative importance of each factor to the response; the factor with the biggest coefficient has the greatest impact. The equation shows that Si\Al ratio has the greatest importance followed by temperature and the time importance was the lowest. The equation also shows that the yield percent increases with decrease in Si/Al molar ratio, temperature of incubation and time of incubation.

Contour plots for yield percent
The proposed model shows the contour plots, Figure 5-7, which can be usefully employed to study the influence of the variables on the response and determine the optimum conditions. Since the significance of the three variables from the model equation is in the sequence SiO_2/Al_2O_3 molar ratio > the incubation temperature > incubation time, hence only the first two factors which are significant will be discussed by the contour plots while keeping the incubation time constant. Figures 5-7 shows the influence of SiO_2/Al_2O_3 ratio and the temperature versus the yield percent at the different incubation times. From these three figures, it is observed that for all three incubation times (2, 3 and 4 days) the yield percent increases with decreasing the SiO_2/Al_2O_3 ratio and the incubation temperature. In other words there is an inversely proportional relationship between the response and the two variables (SiO_2/Al_2O_3 ratio and the temperature). This observation is compatible with results obtained from the model equation. Consequently, the time of incubation has very small effect on the response, which will be explained later. Hence the maximum yield of zeolites product is obtained by decreasing the SiO_2/Al_2O_3 ratio and the incubation temperature.

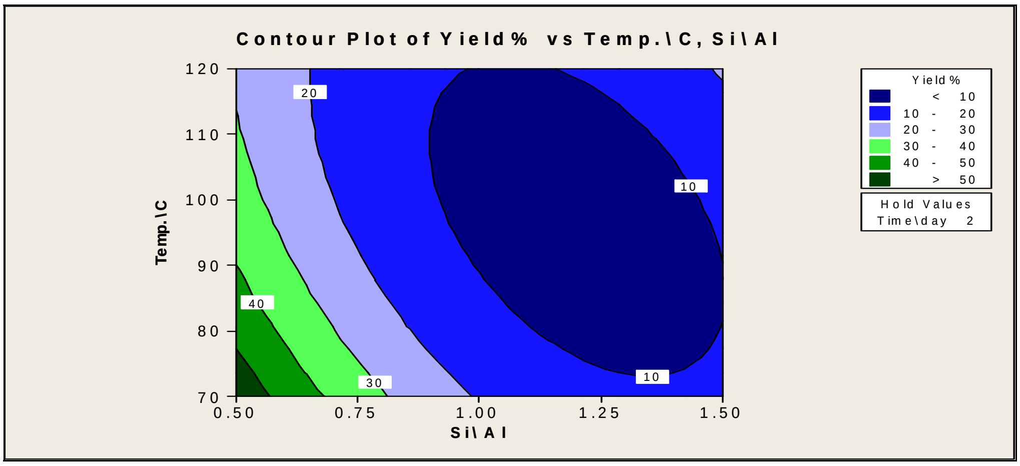

Figure 5: Contour plot of yield percent versus SiO_2/Al_2O_3 ratio and incubation temperature after 2 days incubation

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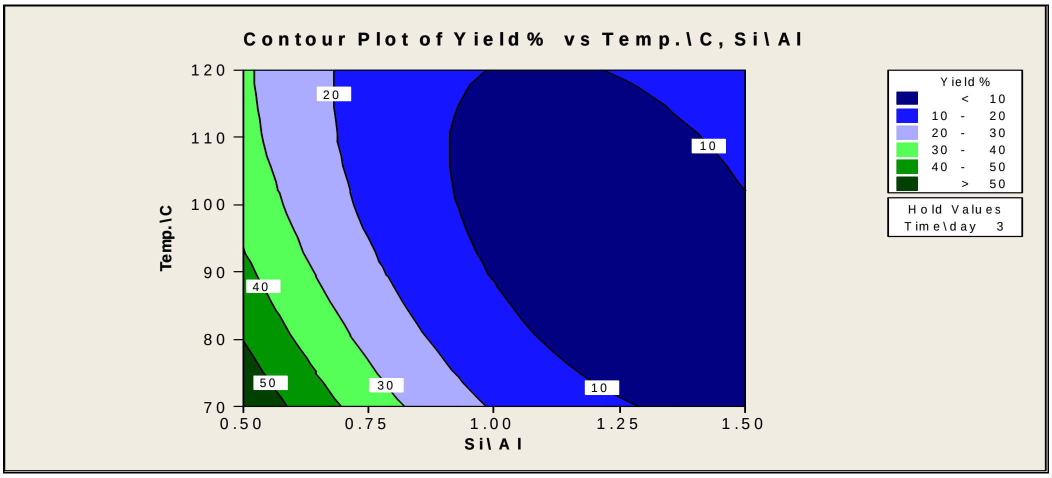

Figure 6: Contour plot of yield percent versus SiO_2/Al_2O_3 ratio and incubation temperature after 3 days incubation

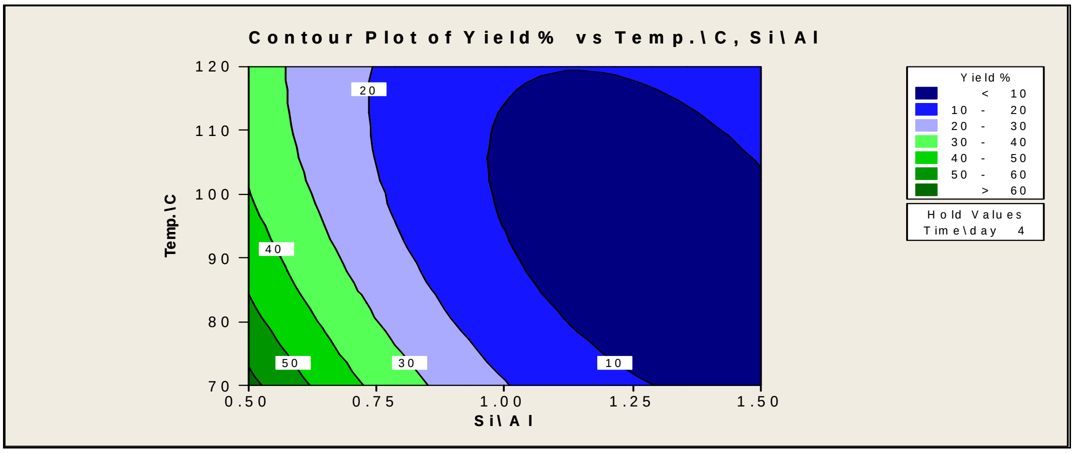

Figure7: Contour plot of yield percent versus SiO_2/Al_2O_3 ratio and incubation temperature after 4 days incubation

Main effects of the three factors

As shown in Figure 8 which represents the plot of zeolites % yield versus the 3 factors namely SiO_2/Al_2O_3 molar ratio, incubation temperature and time, it can be seen that the first factor has the most significant effect on the yield percent of the zeolite followed by the incubation temperature. Decreasing the level of these factors (x-axis) tends to increase the yield percent of the product in all 3 plots especially when going from medium to low level value. This result was compatible with the coefficient of SiO_2/Al_2O_3 ratio in the model equation and the contour plots shown.

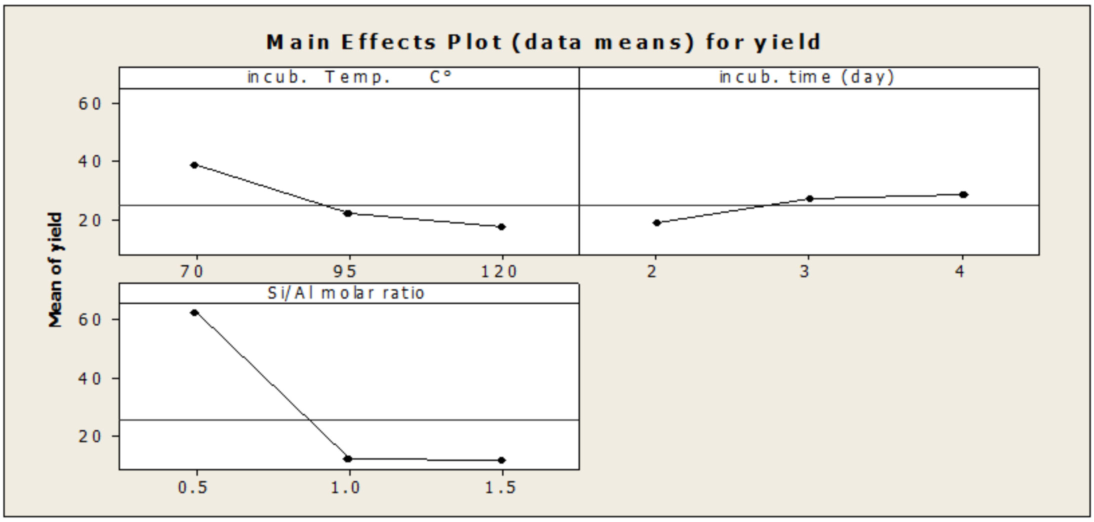

Figure 8: Main effects plot for yield percent

Variables significance
The significance level (*p*-value) which obtained in Table 5, estimated regression coefficients, used to identify the significance of variables on the response. The significance level (*p*-value) adopted was 0.05 for confidence level 95% [29]. As shown in Table 5, Estimated Regression Coefficients, the p-value for the SiO_2/Al_2O_3 ratio and the temperature of incubation was 0.000 and 0.001. This implied that these two factors are significant and important in the process. The table of Estimated Regression Coefficients also shows small p-values for the square of SiO_2/Al_2O_3 (p = 0.000), temperature squared (p = 0.006) and SiO_2/Al_2O_3 ratio by temperature interaction (p = 0.001) suggesting these effects may be important. The variables Si\Al, Temp.\ °C and Time\day have negative relationship in the zeolite yield production.

Table 5: Estimated Regression Coefficients for Yield%

Term	Coef	SE Coef	T	p
Constant	269.421	30.2595	8.904	0.000
Si\Al	-210.245	16.2787	-12.915	0.000
Temp.\ °C	-2.792	0.4420	-6.316	0.001
Time\day	-0.025	9.6437	-0.003	0.998
Si\Al* Si\Al	61.500	5.2747	11.659	0.000
Temp.\ C* Temp.\ °C	0.010	0.0021	4.626	0.006
Time\day* Time\day	0.800	1.3187	0.607	0.571
Si\Al* Temp.\ °C	0.607	0.1014	7.262	0.001
Si\Al* Time\day	-4.550	2.5339	-1.796	0.132
Temp.\ °C* Time\day	0.005	0.0507	0.099	0.925

S = 2.534   R-Sq = 99.1%   R-Sq(adj) = 97.4%

CONCLUSION

The products isolated from the 15 experiments were Na-A zeolite, sodalite octahydrate and gibbsite, which were characterized by their XRD patterns. Zeolite Na-A was formed at 1 to 1.5 SiO_2/Al_2O_3 molar ratio provided the incubation temperature range is 70 or 95 °C regardless of the incubation time. No Na-A zeolite was observed at 0.5 SiO_2/Al_2O_3 ratio and incubation temperature 120 °C. Incubation time has no effect on Na-A zeolite formation. The second product, sodalite octahydrate, was observed when the incubation temperature was 120 °C regardless of SiO_2/Al_2O_3 molar ratio and time of incubation. The third product was gibbsite. It contains $Al(OH)_3$ and is not a zeolitic material. Gibbsite is formed only when the SiO_2/Al_2O_3 molar ratio is less than 1 and the incubation temperature less than 120 °C. The optimum conditions for maximum yield percent of product were: 0.5 SiO_2/Al_2O_3 molar ratio, 70 °C incubation temperature for 3 days. And the optimum conditions for Na-A zeolite synthesis were: 1 SiO_2/Al_2O_3 molar ratio, 95 °C incubation temperature and 4 days of incubation. The yield percent is inversely proportional to the factors that have been used, and the order of effectiveness of the factors on the yield percent was: SiO_2/Al_2O_3 molar ratio > incubation temperature > time of incubation. The contour plots showed that the yield percent increases with decreasing SiO_2/Al_2O_3 molar ratio and incubation temperature. The duration of incubation has no significant effect on the yield percent.

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