

Synthesis of Zeolite by thermal treatment using locally sourced Ugwaka Clay (Black clay)

Christian O, Asadu¹, Mark A ,Abuh² and , Nonyelum L, Eneh³

¹-Department of Chemical Engineering, Enugu State University of Science and Technology, P.M.B. 01660, Enugu, Nigeria

aasadu@yahoo.com

²- Department of material and energy technology, Projects Development Institute (PRODA) federal ministry of science and technology, Emene Industrial layout, Enugu Nigeria.

Markabuh1@gmail.com

³-Department of Engineering Material Research, Nigeria Building and Road Research Institute, Nnewi, Anambra State Nigeria

nonyelumilouno@yahoo.com

ABSTRACT

Application of response surface methodology in production of synthetic zeolite from Ugwaka clay has been demonstrated. In this study, optimization of synthetic zeolite production was carried out, in which the process variables such as reaction time (hours), Sodium hydroxide (NaOH) concentration and calcinations temperature were optimized using Box-Behnken design. X-ray Florescence (XRF), Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM) were used in sample characterization. XRF analysis of raw Ugwaka clay gave silica-alumina ratio of 1.705 which falls within the specification for the synthesis of synthetic zeolite. The reaction time, NaOH concentration and calcinations temperature were varied between 1.5-2.5 hours, 600-900°C and 1-4 M respectively. A quadratic model was developed and was used for the prediction of zeolite yield. Optimization of the process resulted in reaction time of 2hours, NaOH concentration of 2.5 M, and calcinations temperature of 800°C. Optimum conditions were validated at model desirability of 1. Experimental value of 92.03wt% yield of synthetic zeolite with 0.895% error was obtained.

Key words: Ugwaka clay, Synthetic Zeolite, Optimization

INTRODUCTION

The material called Zeolites are hydrated aluminosilicate fashioned under hydrothermal setting. Naturally it can be found or even synthesized. According to the report in the work done by [1], Synthetic zeolites were first utilized commercially as molecular sieve adsorbent [1]. They are synthesized from solution of sodium silicate and sodium aluminates. Raw materials such as natural and synthetic glasses, aluminosilicate gels and clay materials such as

kaolin can also be used in Zeolite Synthesis [2-3]. Information from prior research showed that the starting material and conditions for preparation have influence on the resulting types and amount of zeolites obtained. Based on available materials and publications, it could be concluded that due to their unique properties, zeolites have a great potentials as effective sorbent material for large number of water treatment applications such as water softening ammonia removal (from municipal sewage, animal farms, fertilizer factory waste water, fish breeding pond, swimming pools etc), removal of heavy metals (from natural water acid mines drainages, industrial wastewater etc), phosphates removal of dissolved organic compounds and dyes, oil spillage treatment and many others.

They belong to the class of minerals known as 'Tectosilicate' and consist of three dimensional frameworks of $[\text{SiO}_4]^{4-}$ And $[\text{AlO}_4]^{-5}$ tetrahedral. The aluminum ion is small enough to occupy the position in the centre of the tetrahedral four oxygen atoms and the isomorphous replacement of Si_4^{+} by Al^{3+} produces a negative charge in the lattice. The negative charge is balanced by the exchangeable cation (sodium, potassium, or cadmium). These cations are exchangeable with certain solution such as lead, Cadmium, zinc and manganese [4, 1].

The composition of zeolites can be represented by the general formula $\text{M}_{x/n}[\text{A}(\text{O}_2)_x(\text{SiO}_2)_y] \cdot z\text{H}_2\text{O}$, where n is the charge of the cation M and the values of x, y and z depends on the type of zeolite [5]. Synthetic zeolites are generally produced by alkali treatment of silica and alumina-bearing raw materials of synthetic, natural or waste origin. The first synthetic zeolite, ZK-5 ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 6\text{H}_2\text{O}$), unknown as natural mineral, was obtained in the late 1940s by Richard Barrer who investigated the conversion of minerals under the action of strong salt solutions at high temperatures. Later, Milton pioneered the use of more reactive starting materials, enabling milder reaction conditions and leading to the discovery of zeolite A [6], which has become the most important synthetic zeolite, commercially used as a water softener in detergent industry, in radioactive waste treatment, and in the purification of industrial wastewaters. Typical

Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral component on earth, the potential to supply raw material for zeolites synthesis is virtually unlimited. Clay minerals such as kaolin, illite, Smectite, montmorillonite, bentonite, perlite, have been used frequently for zeolite synthesis, due to their high contents of silicon and aluminum, which easily dissolve and form zeolite under alkaline condition [7]. Several important reactions involving organic molecules, Zeolites are extremely useful as catalysts [8]. Most of the reactions are cracking, isomerisation and hydrocarbon synthesis. Catalytic reactions including acid-base and metal induced reactions can be promoted by Zeolite. The reactions can take place within the pores of the zeolite - which allows a greater degree of product control. Sequel to the fact that the hydrated cations within the zeolite pores are bound loosely to the zeolite framework, and can readily exchange with other cations when in aqueous media, zeolite can be applied as water

softening devices [9,10]. This research is aimed at optimizing the synthesis of zeolite from Ugwaka clay (Black clay) using Response surface methodology.

MATERIALS AND METHODS

Source of raw materials

The indigenous aluminosilicate used in this research work was obtained from Otukpo local government of Benue State, Northern Province of Nigeria. Distilled water and sodium hydroxide (NaOH) used was purchased from Ogbete main market, Enugu, Enugu State Nigeria. The raw clay was collected with a Global Positioning System (GPS) Device, (Model; Etrex Germin), with Latitude; N05° 38.216', Longitude; E07°19.664', and elevation above sea level; 623ft. The clay was grinded with a laboratory mortar and pestle and sieved to a particle size of 500µm. 1.0g of clay was mixed with 200ml of 2.0M Sodium hydroxide (NaOH) for 2 hours at 700°C. The resultant suspension was placed in thermostatic water bath at 100°C and rotation Speed of 200rpm at a particular time. After cooling, the clay was filtered and washed Several times with distilled water until neutral pH of 7 was obtained. The experiment was repeated with temperatures between 600°C and 900°C and other factors as shown in table 1. The Clay was dried at 90°C for 1.5 hours and was stored.

Physical Characterization

The physical properties of the raw clay and synthetic zeolite were carried out using American Society for Testing and Materials ASTM D7263-09 [17]. Instrumental of the samples was done using X-Ray Fluorescence (XRF) which is controlled by a PC running the dedicated Mini-Pal analytical software. The Mini-Pal 4 version used was PW 4030 X-ray Spectrometer running with voltage (30KV maximum) and a current (1mA maximum) to determine the mineral composition of the aluminosilicate. Fourier transform infrared spectrometer was used to determine the chemical bond and functional groups in the aluminosilicate and synthetic zeolite. Consequently, Scanning Electron Microscopy (SEM) was used to determine the size and morphology of the aluminosilicate and synthetic zeolite. The SEM micro graph was obtained using JOEL scanning electron microscope model JSM 6400 Scanning electron microscopy recording at 15 KV with 8000x magnification

Experimental Design

Production and Optimization of Synthetic Zeolite Using Box-Behnken Design

The optimization and production of Zeolite was done using Box-Behnken experimental design method. This design was classically achieved using DOE software called ***Design Expert 9.0.2.0***. Three important factors such as calcinations temperature, time and concentration of base were considered as independent variables in which their effects respectively and collectively were studied. The Box-Behnken experimental design method contains all possible combinations of a set of factors. Experimental runs were performed at every combination of the factor level:

- i. Calcination temperature (°C) X_1
- ii. Time (Hours) X_2
- iii. Strength or concentration of NaOH (M) X_3

Based on this research, two levels (-1, +1) and null experimental point (0) were essential to reduce noise and systematic error in the experiment. These provided for near accuracy of analysis.

Table 1: Factors and Levels of Independent variables for synthetic zeolite production

Parameter	Low Level (-1.000)	Null Point (0.000)	High Level (+1.000)
X_1	1.5	2.0	2.5
X_2	1	2.5	4
X_3	600	750	900

Table 2: Box-Benken Design matrix with response for synthetic zeolite production

Std	Run	Factor 1	Factor 2	Factor 3	Response
		X ₁	X ₂	X ₃	Percentage yield
5	1	-1.000	0.000	-1.000	86.52
1	2	-1.000	-1.000	0.000	86.86
7	3	-1.000	0.000	1.000	86.76
14	4	0.000	0.000	0.000	91.97
17	5	0.000	0.000	0.000	91.96
2	6	1.000	-1.000	0.000	87.97
8	7	1.000	0.000	1.000	90.01
6	8	1.000	0.000	-1.000	89.32
9	9	0.000	-1.000	-1.000	88.26
11	10	0.000	-1.000	1.000	85.68
12	11	0.000	1.000	1.000	88.36
4	12	1.000	1.000	0.000	90.66
3	13	-1.000	1.000	0.000	86.41
16	14	0.000	0.000	0.000	92.02
13	15	0.000	0.000	0.000	91.95
15	16	0.000	0.000	0.000	92.03
10	17	0.000	1.000	-1.000	86.44

Results and Discussion

Physico-chemical properties of the raw clay and synthetic zeolite are presented in Table 3. From the table, it was observed that most of the properties increased after calcination except carbon and organic matter. The porosity was observed to have increased after calcination owing to increase in bulk density [18]. The Surface area of raw clay was 698.20m²/g but increased to 827.35m²/g after calcinations as shown in table 3. The results are in agreement with the report by [16], that chemical calcinations of clay increase the surface area and porosity.

Table 3: Physio-chemical characterization of the raw clay and synthetic zeolite

Sample	pH	Surface Area (m ² /g)	Bulk Density (g cm ⁻³)	Carbon (%)	Organic Matter (%)	Particle Density (g cm ⁻³)	Total Porosity (%)
Raw Clay	6.01	698.20	1.62	2.43	7.01	2.48	21.80
Synthetic zeolite	7.52	827.35	1.98	1.32	2.53	3.92	44.96

X-ray Florescence (XRF) analysis results of the raw clay and Synthetic zeolite

XRF analysis was performed to determine the chemical composition and combination of minerals that are present in the natural Ugwaka clay and synthetic zeolite. The results of the analysis are presented as shown in table 4a and 4b. It was observed that Ugwaka clay contained high silicon Oxide content of 57.41wt%. The results agree with the report by [7] which states that clay with high concentration of silicon oxide can be used as a source of silica for the production of floor tiles. The aluminosilicate had Alumina (Al₂O₃) content of 33.67wt % and silica-alumina ratio of 1.705, which is greater than 1. This is in agreement with the report by [1] on the quality of clays that can be used for zeolite synthesis and as such, implies that Ugwaka clay can be used in Zeolite synthesis. Other major oxides in the clay are Ferrous and Titanium Oxide though in varying compositions. There were also traces of other Oxides such as Calcium, Zinc, Nickel and Copper among others in very small quantities. Oxides of Manganese, Vanadium, Zinc, Chromium, Nickel and Copper were in minute quantity.

Table 4a Results of XRF analysis of Ugwaka clay

Chemical Compounds	Composition (%)
SiO ₂	57.41
Fe ₂ O ₃	6.90
Al ₂ O ₃	33.67
CaO	0.81
MgO	0.53
K ₂ O	0.03

TiO ₂	4.05
CaO	0.08
MnO	0.072
V ₂ O ₅	0.23
Cr ₂ O ₃	0.051
ZnO	0.001
NiO	0.003
CuO	0.008
<i>Si/Al</i>	1.705

Table 4b Chemical Composition of synthetic zeolite

Chemical composition	Percentage composition
SiO ₂	65.25
Fe ₂ O ₃	4.77
Al ₂ O ₃	17.89
CaO	0.92
MgO	0.44
K ₂ O	0.04
TiO ₂	3.02
CaO	0.09
MnO	0.041
V ₂ O ₅	0.11
Cr ₂ O ₃	0.064
ZnO	0.002
NiO	0.004
CuO	0.006
Na ₂ O	0.745
<i>Si/Al</i>	3.647

It was observed from table 4b that synthetic zeolite had an increased Silicon Oxide content of 65.25wt% against 57.41wt% earlier observed in raw clay as shown in table 4a, indicating a 7.84wt% increase. The increase in silicon oxide could be attributed to the effect of chemical treatment. The chemical treatment also resulted in removal of some fraction of the alumina content as observed from table 4b with alumina content (17.89 wt %) against (33.67 wt %) present in raw clay as shown in table 4a.

Scanning Electron Microscope (SEM)

The SEM analysis of the clay indicates coarse and loosely packs with some well formed flakes and irregular and hexagonal edges (Kaolinites). Others appear as plates of variable thickness and size with relatively well defined edges (Illites) or showing some elements of curling layers in the particles (Smectite). Chlorites appeared as inter-relating platy particles with well defined sub-angular borders. Vermiculite manifested that the reference clay micrographs in the form of aggregate of very small particles with curled edges.

Although the preliminary study by [13] suggested that clay minerals could be characterized and identified by exploiting their morphological features (using as many as possible clay minerals as standards to cover a range of morphological features). As shown in fig 1a, the image showed moderately ordered flakes, with poorly developed hexagonal outlines. Psuedohexagonal morphology is suggested, hence the edges of the particles are beveled, somewhat ragged and irregular which is very similar to an observation earlier reported by [4]. From fig 1b, it was observed that larger pores of different shapes appeared for scanning electron microscope of synthetic zeolite. This could be attributed to the effect of the chemical treatment that caused a serious morphological change and did enormous harm to the surface of clay by removing some of the inorganic elements and therefore, increases the surface area and porosity of clay. This buttresses the report by [14] which states that chemical treatment increases the porosity of clay.



Fig 1a SEM analysis of ugwaka clay at 30 μ m

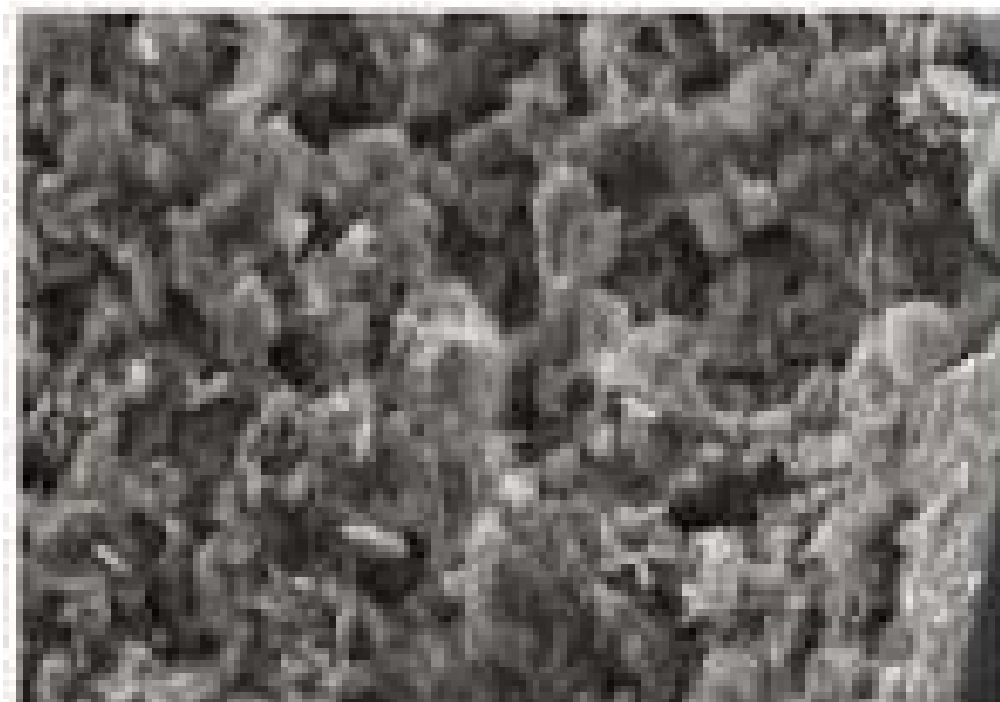


Fig 1b SEM analysis of synthetic zeolite at 200μm

Fourier Transform Infrared (FTIR) analysis results

The chemical structure of the zeolite is of vital importance in understanding its application. The FTIR technique is an important tool to identify the characteristic functional groups, which are instrumental in removal of aromatic compounds. FTIR studies of the zeolite help in the identification of various forms of the minerals present in the clay. The coupled vibrations are appreciable due to the availability of various constituents [15].

The result of the FTIR spectrum for ugwaka clay and synthetic Zeolite is shown in Fig 2a and 2b respectively. It was seen that there were strongly structural modification on the clay sample that was calcined with sodium hydroxide which resulted to steepness of peak disappearance in fig. 2b between 1250 to 1000 when compared with Fig. 2a is different from the raw clay as can be seen from the figures.

The transmission level bands for both natural and Calcined clays are dissimilar. Comparing results, it is clear there were structural modifications on the clay sample after calcinations as a result of the removal of some impurities. This result is in agreement with the findings reported by [16]

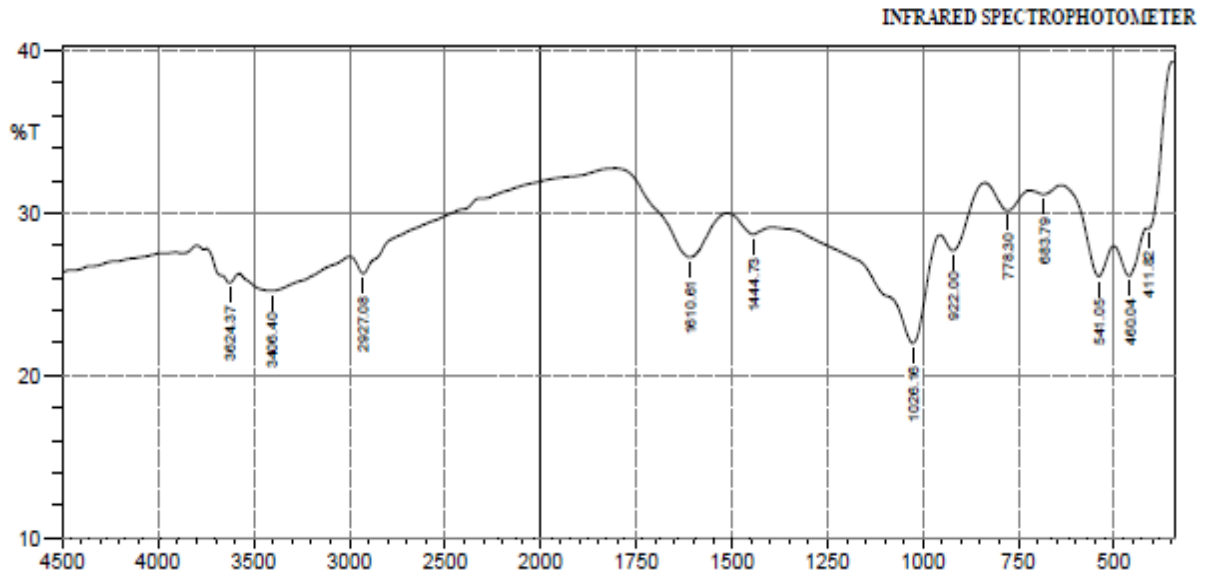


Fig 2a FTIR Spectrum of Ugwaka clay @30μm

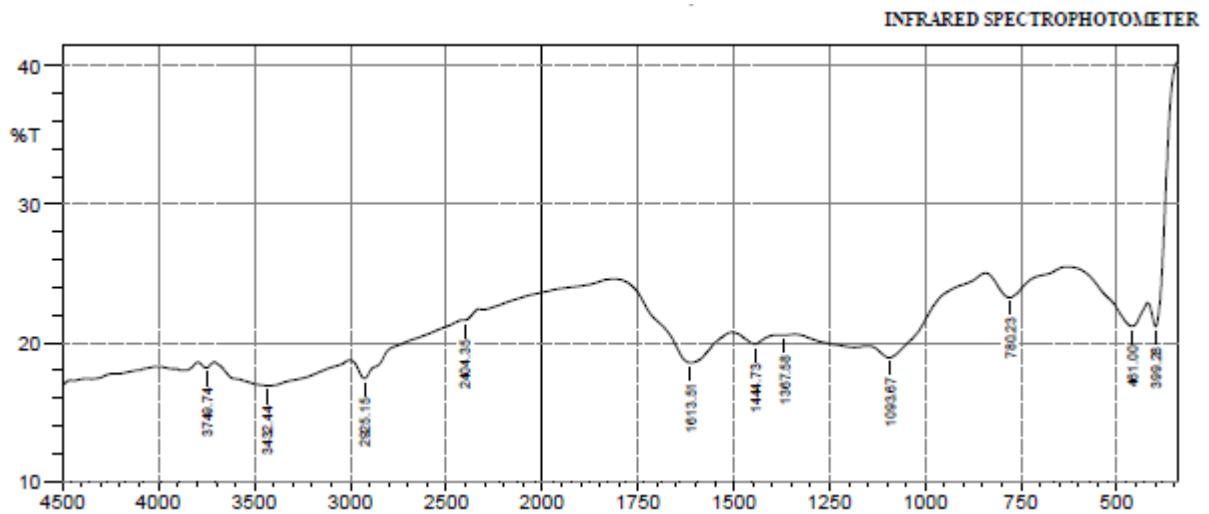


Fig 2b: FTIR Spectrum of Synthetic Zeolite @30μm

Statistical analysis of the results for the synthetic zeolite production

The variables studied using Box-Benken experimental design were time (hours), sodium hydroxide concentration (M) and calcination temperature (°C).

The ANOVA table is given in table 6, A significance of 5% was used, hence all terms whose P-value are less than 0.05 are considered significant. Therefore X_1 , X_2 , X_3 , X_1^2 , X_2^2 , are significant as shown in table 5, the regression F-value of 36.55 implies that the model is significant which is validated by the P-values been less than 0.0001 (<0.0001).

The final model equation in terms of coded factors is shown in equation 1:

$$\text{Yield of Synthetic zeolite(\%)} = 84.83 + 2.41X_1 + 7.57X_2 + 4.88X_3 + 1.39X_1X_3 - 1.14X_1^2 - 1.80X_2^2 \quad (1)$$

The final model equation in terms of the actual factor is shown in equation 2:

$$\text{Yield of synthetic zeolite (\%)} = 19.00804 - 0.98393\text{reaction time} + 19.84554 + \text{sodium hydroxide concentration} + 0.013562 \text{ calcination temperature} + 0.027750 \text{ reaction time , calcination temperature} - 2.12500\text{E} - 003 \text{ sodium hydroxide concentration*calcination temperature} - 4.54286 \text{ reaction time}^2 - 1.79821\text{sodium hydroxide concentration}^2 \quad (2)$$

The coefficient with one factor represent the effect of the particular factor, while the coefficients with two factors and those with second order terms represent the interaction between two factors and quadratic effect respectively [12].

In a regression equation, when an independent variables has a positive sign, it means that an increase in the variable will cause an increase in the response, while a negative sign will result a decrease in the response. Hence an increase in temperature, NaOH concentration and calcination temperature will cause an increase in the percentage adsorbed. NaOH concentration and calcination temperature will have more significant effect in the increment of the response since their coefficient were higher.

The test of adequacy of the regression models, significance of individuals of models coefficients and the lack of fit test were performed using the same statistical package.

The P-values were used as a tool to check the significance of each of the coefficients, which in turn are necessary to understand the pattern of the mutual interactions between the process variable

Table 5: Analysis of Variance (ANOVA)

Source	Sum of squares	df	Mean square	F-Value	P-Value
Model	1619.44	7	231.34	36.55	<0.0001
X ₁ - Reaction time	102.64	1	102.64	16.21	0.0014
X ₂ -NaOH Concentration	923.38	1	923.38	145.87	<0.0001
X ₃ -Calcination Temperature	393.23	1	393.23	62.12	<0.0001
X ₁ X ₃	16.20	1	16.20	2.56	0.1185
X ₂ X ₃	0.46	1	0.46	0.073	0.8012

X_1^2	33.35	1	33.35	5.27	0.0280
X_2^2	87.31	1	87.31	13.79	0.0019
Residual	64.36	12	6.33	-	-
Lack of fit	54.30	7	7.76	3.50	0.0935
Pure error	11.09	5	2.22	-	-
Cor total	1575.03	19		-	-

Statistical analysis obtained from the analysis of variance (ANOVA) for response surface quadratic model is shown in table 5. The value of “Prob>F” indicated that the model is significant which is desirable as it indicated that the terms in the model have a significant effect on the response. The P-value of 0.0001 indicated that there is only a 0.01% chance that a “model F – value” this large could occur due to noise.

Generally P – value lower than 0.01 indicated that the model is considered to be statistically significant at the 99% confidence level [5]. Values of “Prob>F” less than 0.0500 indicated the model terms are significant. In this case, X_1 , X_2 , X_3 , X_1^2 , X_2^2 are significant model terms.

The quality of the model developed was further assessed using residual plots. Residual is the difference between the experimental value and value predicted by the model. Some of the residual plots used were: plot of residual vs. predicted values which tests the assumption of constant variance, plot of residuals vs. run which checks for lurking variables that may have influenced the response during the experiment, normal plot of residuals which indicates whether the residuals follow a normal distribution, and plot of predicted vs. Actual response values which helps to detect a value, group of values that are not easily predicted by the model. The residual plots are shown in Fig. 4 to 7

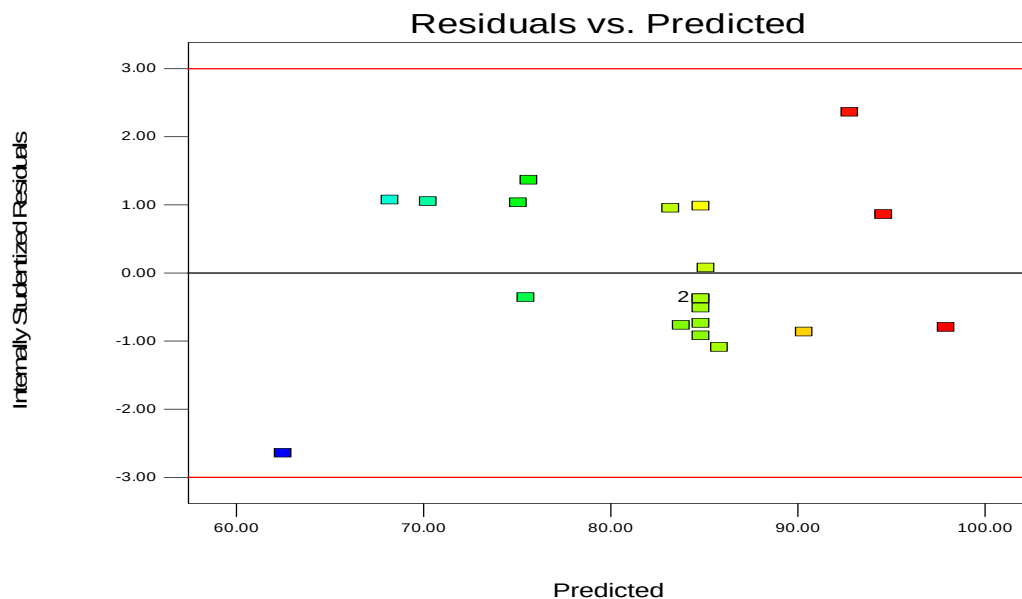


Fig 4: Plot of residual vs predicted for zeolite production

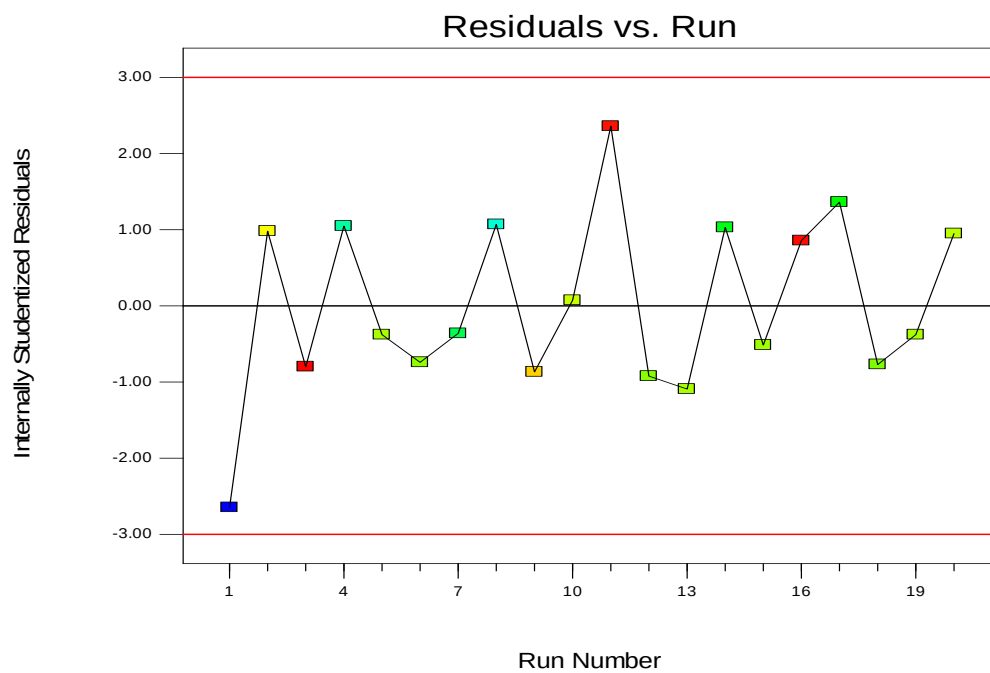


Fig 5: Plot of residuals vs experimental run for zeolite production

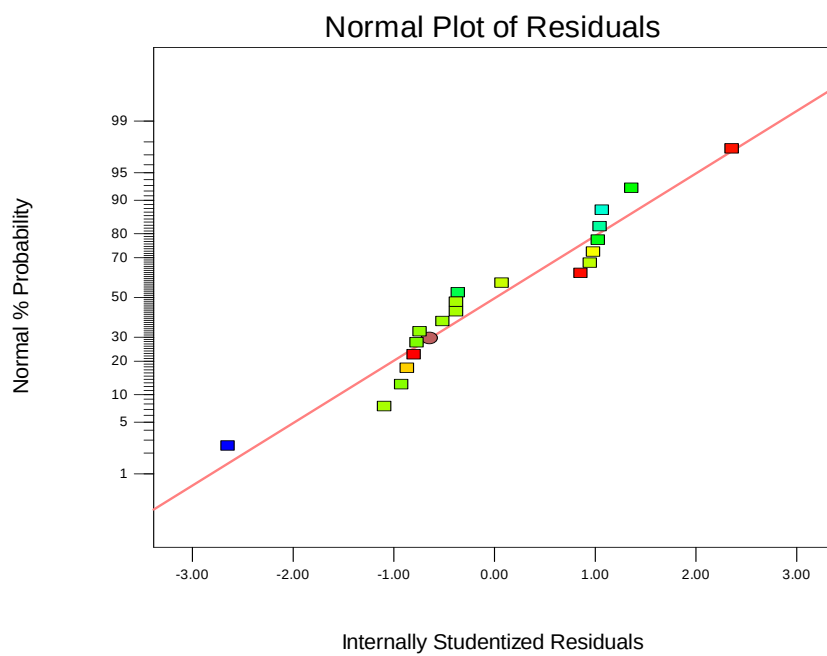


Fig 6: Normal plot of residuals for zeolite production

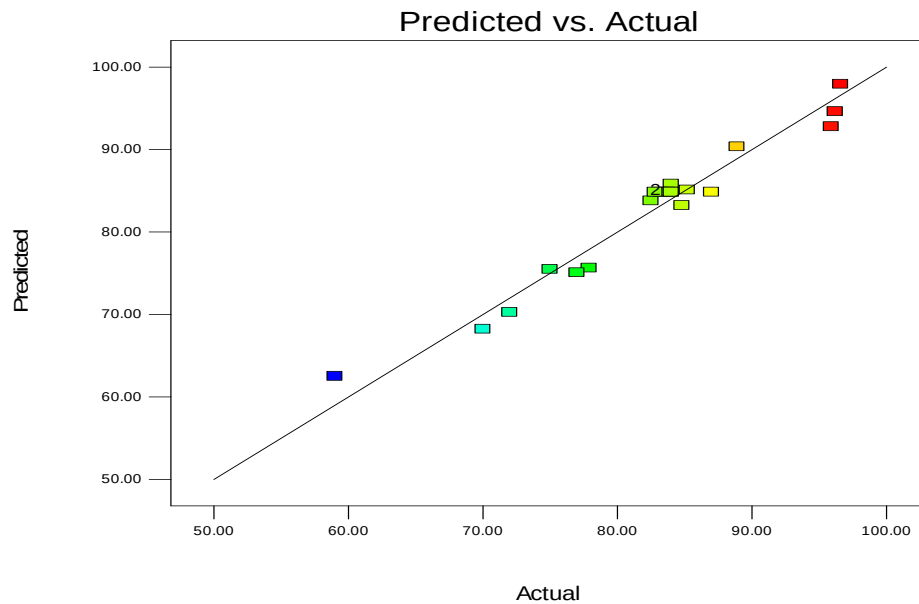


Fig 7: Plot of actual response vs predicted response for zeolite production

Influence of individual factors

The individual effect of Reaction time (X_1), NaOH Concentration (X_2), and Calcination temperature (X_3) were plotted in figs. 8(a-c) from the graph it showed that Reaction time (X_1), NaOH Concentration (X_2), and Calcination temperature (X_3) had effect on the response. This meant that any increase or decrease on the factor will have an effect on the response.

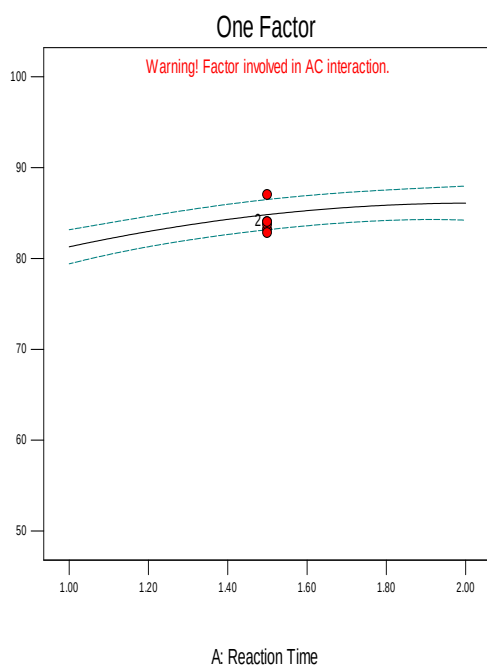


Fig 8a; Effect of reaction time

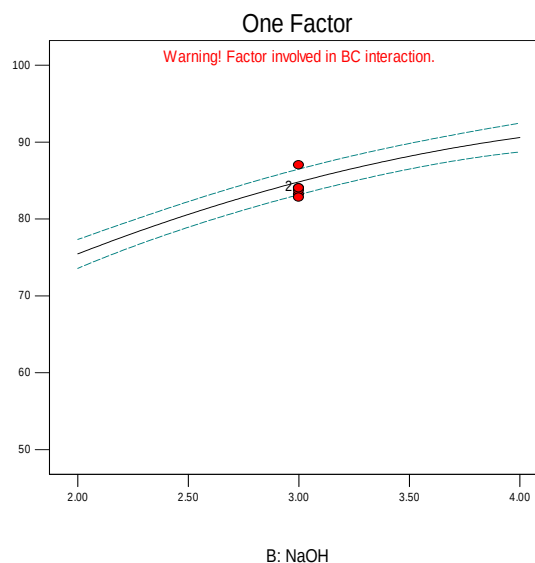


Fig 8b; Effect of NaOH Concentration

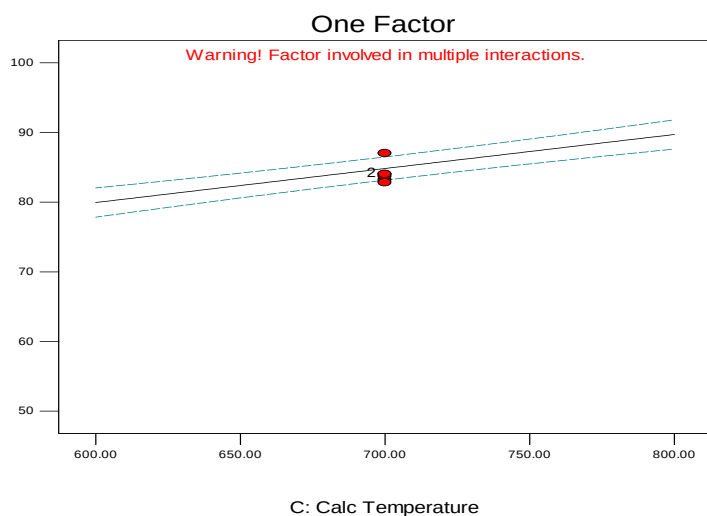


Fig 8c; Effect of Calcination temperature

From the selected optimum condition, the optimum time for the yield of zeolite was 2 hours. Time has a significant effect on the yield of zeolite as indicated in the interaction with other factors as shown in fig 8a. This was buttressed by the p-value been less than 0.05 as shown in table 5 hence, increase in time between 0 to 2 hours increases the yield of synthetic zeolite. Increase in concentration of sodium hydroxide increases the yield of synthetic zeolite as indicated in fig 8b. The effect of increase in concentration of sodium hydroxide was significant

as shown by the p-value (< 0.05) in table 5. Temperature has effective interactions with other factors as shown in fig 8c, however the interaction of temperature with other factors are not significant but the individual effect are significant as shown in table 5 (p-value < 0.05) which showed that increase in temperature has a positive effect on the yield of synthetic zeolite.

Process Optimization

In synthetic zeolite production from an indigenous alluminosilicate using response Surface Methodology, optimization was done using Design expert software **9.0.2.0** version. With the aim of maximizing the response, the condition that gave the highest desirability of 1 was selected. The Optimal yield of 92.03wt% was obtained using Reaction time of 2 hours, Calcination Temperature of 800°C and Sodium hydroxide concentration of 2.5M. These result showed an improvement in the production of synthetic zeolite when compared with the work reported by [19], where 90wt% yield of zeolite was recorded at concentration of 5M sodium hydroxide, temperature of 95°C after 24hours.

Table 6: Validation of Optimum Conditions

Model desirability	Reaction Time (hrs)	Calcination Temperature (°C)	NaOH Concentration (M)	Percentage Yield		
				Predicted	Experimental	% error
1.0	2.0	800	2.5	92.925	92.03	0.895

Conclusion

A quadratic model was developed, and diagnostics of the model revealed a strong correlation between the prediction and observed response values. The important factors that significantly affected the yield of zeolite from natural clay were temperature, time and concentration of sodium hydroxide. The optimum parameters for the zeolite synthesis were 2.0 hours, 800°C and 2.5M for time, temperature and sodium hydroxide concentration. Silica to Alumina ratio obtained after XRF analysis of Zeolite produced showed that Ugwaka clay is a good source of synthetic zeolite. Also, increase in calcination temperature and concentration of sodium hydroxide had a significant effect on the yield of synthetic zeolite. FTIR results of the synthetic zeolite showed some peaks disappeared after clay treatment.

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