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Synthesis of Zeolite by Thermal Treatment Using Locally Sourced Ugwaka Clay (Black Clay)

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Authors' contributions

This work was carried out in collaboration between all authors. Authors COA and MAA designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors COA and ACA managed the analyses of the study. Authors ACA and MAA managed the literature searches. All authors read and approved the final manuscript.

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Original Research Article

ABSTRACT

Application of response surface methodology in zeolite synthesis from ugwaka clay has been demonstrated. In this study, optimization of synthetic zeolite production was carried out. Process variables such as reaction time, sodium hydroxide concentration, and calcination temperature were optimized using Box-Behnken design. Raw ugwaka clay was treated with distilled water and sodium hexametaphosphate to remove the impurities usually associated with natural clay and induce sedimentation. The clay undergoes metakaolinization at 700°C for 2hours. 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 specifications for the synthesis of zeolite. The reaction time, sodium hydroxide concentration and calcination temperature were varied between 1.5-2.5 hours, 600-900 $^{\circ}$ C and 1-4M respectively. A quadratic model was developed and was used for the prediction of zeolite yield. Optimization of the process resulted in the reaction time of 2 hours, sodium hydroxide concentration

of 2.5 M, and calcination temperature of 800°C. Optimum conditions were validated at the model desirability of 1. The experimental value of 92.03wt% yield of zeolite with 0.895% error was obtained. Comparison of the zeolite produced with commercially available zeolite showed that it has good properties to be used in water treatment.

Keywords: Ugwaka clay; zeolite; optimization.

1. INTRODUCTION

Zeolites are crystalline silicate materials composed of three-dimensional network of SiO⁴ and $AIO₄$ tetrahedral, which have a highly regular and open microporous structure. Due to their high surface area, fast diffusion characteristics, adjustable porosity, and high mechanical strength over amorphous porous silica, they have potential applications in fields such as catalysis, adsorption, bacterial adhesion and ion exchange [1-3]. Naturally, it can be found or even synthesized. According to the report by Breck and John [1], Antonio de Lucas [2], synthetic zeolites were first utilized commercially as a molecular sieve adsorbent. They are synthesized from a 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 materials and conditions for preparation have an influence on the resulting types and amount of zeolites obtained. Based on available materials and publications, it could be concluded that, zeolites have a great potentials as effective sorbent material for large number of water treatment applications in water softening, ammonia removal, removal of heavy metals (from natural water, acid mines drainages, industrial wastewater etc), dyes, oil spillage treatment and many others [1,4]. The composition of zeolites can be represented by the general formula $M_{x/n}[A(O_2)_x(SiO_2)_y]$.zH₂O, where n is the charge of the cation M and the values of x, y and z depend 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 zoelite, $ZK-5(Na_2Al_2Si_{4-6}O_{12-2})$ $6.6H₂O$), 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.

Since the principal raw materials used to manufacture zeolite are silica and alumina which are among the most abundant mineral component on earth, the potential to supply raw material for zeolite synthesis is virtually unlimited. Clay minerals such as kaolin, illite, smectite, montmorillonite, bentonite, and perlite, have been used frequently for zeolite synthesis due to their high contents of silicon and aluminum, which easily dissolves and form zeolite under alkaline condition [7]. In 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. The hydrated cations within the zeolite pores are bound loosely to the zeolite framework and as such, zeolite can be applied as water softening devices [9,10]. Important of process optimization of process parameters involved in the production of zeolite cannot be overemphasized. The purpose of statistically designing an experiment is to collect common relationship between various factors affecting the process towards finding the most suitable conditions [8,11]. Process optimization was carried out in this work using response surface methodology (RSM). It is a statistical tool mainly used for optimization. RSM is mostly employed to study the effect of independent variables on the response(s). It is also used to study the effects of multiple factors and their interactions. These multiple factors are the independent variables while the response(s) is the dependent variable [11-16]. RSM relates product properties by using regression equations that describe interrelations between input variables and product properties [11,17,18]. The most popular and often used form of RSM is the central composite design (CCD) and Box Behnken design. In this work, Box Behnken design was employed for the process optimization. Box-Behnken design is an independent quadratic design in that it does not contain embedded factorial or fractional design like the Box-Wilson design [8,19]. In this design, the treatment combinations are at the midpoints of edges of the process space and at the center. These designs are rotatable or near rotatable. The factors studied were calcination temperature, reaction time, and NaOH concentration. Therefore, the objectives of this research are to synthesize zeolite from locally sourced material and thereafter, optimize the process parameters using Response surface methodology.

2. MATERIALS AND METHODS

The raw ugwaka clay used in this research work was obtained from Otukpo local government area of Benue State, Northern Provence of Nigeria. Distilled water, sodium hexametaphosphate, and sodium hydroxide (NaOH) were purchased from Ogbete main market, Enugu Nigeria. The raw clay was collected with a global positioning system (GPS) device, (Model; Etrex Germin), with latitude; $N05^{\circ}38.216^{\prime}$, , longitude; $E07^{\circ}19.664$, and elevation above sea level; 623ft. The clay was grinded with a laboratory mortar and pestle and sieved to a particle size of 500µm. The grinded clay was stirred with 1liter of
distilled water and 2.5 wt% sodium water and 2.5 wt% sodium

hexametaphosphate and allowed to settle down for 15minutes before the supernatant was separated. The supernatant was then dried in an oven for 6hours at 100°C. The dried supernatant (treated clay) later undergoes metakaoliniazation at 700° C. 1.0g of metakaolin was mixed with 200mil of 2.0M sodium hydroxide (NaOH) at 700°C for 2hours. The resultant suspension was placed in a thermostatic water bath at 100°C and a 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 resultant zeolite was dried at 90°C for 1.5 hours and was stored.

2.1 Sample Characterization

The physical properties of the raw clay and synthetic zeolite were carried out using American Society for Testing and Materials ASTM D7263- 09 [20]. Instrumental characterization 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 raw clay and synthetic zeolite. Fourier transform infrared

Fig. 1. Schematic diagram for the production process of synthetic zeolite from Ugkawa Clay (Black Clay)

Table 1. Factors and levels of independent variables for zeolite production

Table 2. Box-Benken design matrix with response for zeolite production

spectrometer was used to determine the chemical bond and functional groups in the raw clay and synthetic zeolite. Consequently, Scanning Electron Microscopy (SEM) was used to determine the size and morphology of the clay sample and synthetic zeolite. The SEM micro graph was obtained using JOEL scanning electron microscope, model JSM 6400, recording at 15 KV with 8000x magnification.

2.2 Experimental Design

2.2.1 Synthesis of zeolite and optimization of the process parameters

Synthesis of zeolite and optimization of process parameters was done using Box-Behnken experimental design. This design was classically achieved using DOE software called *Design Expert version 11*. Three important factors such as calcination temperature, time and concentration of sodium hydroxide 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. The factors considered included:

(i) Calcination temperature X_1 (${}^{\circ}$ C), (ii) Time X_2 (Hours) and (iii) Strength or concentration of NaOH X_3 (M)

In 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 the analysis.

3. RESULTS AND DISCUSSION

Table 1 shows the parameters used in this investigation, ranges, and level of the independent variables investigated in this work and the results are shown in table 2. For the appraisal of the effects of two or more independent variables on the response(s) (dependent variables), multiple regression analysis was employed. Results of the percentage yield of zeolite generated from experiments were analyzed using multiple regression methods to fit the second-order regression model. The regression model describing the zeolite yield (%Y) as a function of actual values of calcination temperature (X_1) , reaction time (X_2) and sodium hydroxide concentration (X_3) is presented as shown in equation (1) and (2). Physiochemical properties of the raw clay and synthetic zeolite are

presented in table 3. From the table 3, it was observed that most of the properties increased after calcination except carbon and organic matter. The porosity was observed to have increased after metakaolinization owing to increase in bulk density [21]. The Surface area of raw clay was $698.20 \text{m}^2/\text{g}$ but increased to $827.35m²/g$ after metakaolinaization as shown in table 3. The results are in agreement with the report by Ajemba and Onukwuli [16], which states that chemical calcination and thermal treatment of clay increases the surface area and porosity of clay. Also, the surface area and porosity of synthetic zeolite have a close relationship with surface area and porosity of commercially available zeolite (ZeoAqua-25 made by ZEOCEM LTD) as shown in Table 3, which further proved that zeolite produced from local ugwaka clay has the potential for industrial application.

3.1 X-ray Fluorescence (XRF) Analysis Results of the Raw Clay and Synthetic Zeolite

XRF analysis was performed to determine the chemical composition of minerals that are

present in the natural ugwaka clay and synthetic zeolite. The results of the analysis are presented in table 4. It was observed that ugwaka clay contained a high silicon oxide content of 57.41wt%. The results are in agreement with the report by Kang et al. [7], Asadu et al. [22] which states that clay with high concentration of silicon oxide is a precursor for the production of floor tiles. The raw clay had alumina (Al_2O_3) content of 33.67wt % and silica-alumina ratio of 1.705, which is greater than 1. This agrees with the report by Breck and John [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.

It was observed that synthetic zeolite had an increased silicon oxide content of 65.25 wt% against 57.41wt% earlier observed in raw clay as shown in Table 4, signifying a 7.84 wt%

Samples	рH	Surface area (m 2 /g)	Bulk density (g/cm ³)	(%)	Carbon Organic matter $(\%)$	Particle density ($g/cm3$)	Total porosity
Raw clay	6.01	698.30	1.62	2.43	7.01	2.48	21.80
Synthetic Zeolite	7.52	827.25	1.98	1.32	2.53	3.92	44.96
Commercial zeolite	7.77	996.32	2.37	1.56	1.97	5.62	52.54

 Table 3. Physio-chemical properties of raw clay and synthetic zeolite

increase. The increase in silicon oxide could be attributed to the effect of thermal treatment during metakaolinization. The treatment of clay with concentrated sodium hydroxide also resulted in the removal of some fraction of alumina content as observed from Table 4 with synthetic zeolite alumina content (17.89 wt %) against (33.67 wt %) present in raw clay. The percentage composition of silica and alumina in synthetic zeolite has a close comparison with silica and alumina composition in commercial zeolite as shown in Table 4.

3.2 Results of Scanning Electron Microscope (SEM)

The SEM analysis of raw clay and synthetic zeolite were presented as shown in Figs. 2a-b. Fig 2a shows a coarse and loosely packs with some well formed flakes, irregular and hexagonal edges (Kaolinites). Chlorites appeared as interrelating platy particles with well defined subangular borders. Vermiculite manifested that the reference clay micrographs in the form of an aggregate of very small particles with curled edges. Although the preliminary study by Vicente et al. [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 2a, the image showed moderately ordered flakes, with poorly developed hexagonal outlines. Pseudo-hexagonal 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 Barrer [4]. From Fig 2b, it was observed that larger pores of different shapes appeared on the

surface of synthetic zeolite after scanning. This could be attributed to the effect of chemical and thermal 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 during metakaolinization. This buttresses the report by Igbokwe et al. [14] which states that metakaolinization increases the porosity of clay.

3.3 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 the 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 Figs. 3a and b respectively. It was seen that there was a strongly structural modification on the clay sample during matakaolinization which resulted in steepness of peak disappearance in Fig. 3b at peak level between 1250 and 1000 when compared with Fig. 3a. The transmission level bands for both natural clay and metakaolin are dissimilar. Comparing results, it is clear that, there were structural modifications on the clay sample after metakaolinization as a result of the removal of some impurities. This result agrees with the findings reported by Ajemba and Onukwuli [16].

Fig. 2a. SEM analysis of ugwaka clay at 30 µm Fig. 2b. SEM analysis of synthetic zeolite at 200 µm

3.4 Statistical Analysis of the Results for the 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 5, a significance level 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_2^2 , X_3^2 , are significant as shown in Table 5, The model F-value of 7.01 implies that the model is significant which is validated by the P-values been less than 0.05 (< 0.05).

The final model equations are shown in equation 1:

Yield of zeolite (Y%) = $43.00 + 0.3750X_1 0.1250X_2 + X_3 - 0.500X_1X_2 - 0.250X_1X_3 0.2500X_2X_3-0.500X_1^2-1.0X_2^2-1.0X_3^2$ (1)

Moreover, equation (2) shows the polynomial equation after the removal of the insignificant model terms.

Yield of zeolite (Y%) = $43.00 + 0.3750X_1$ – $0.1250X_2 + X_3 - 0.500X_1X_2 - 0.250X_1X_3 0.2500X_2X_3 - 1.0X_2^2 - 1.0X_3^2$ (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 variable 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 in a decrease in the response. Hence an increase in temperature, NaOH concentration and calcination temperature will cause an increase in the percentage yield. Calcination temperature will have a more significant effect on the increment of the response since the coefficients are higher. The test of the adequacy of the regression models, the significance of individuals of model 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 variables

Statistical analysis obtained from the analysis of variance (ANOVA) for the response surface quadratic model is shown in table 5. The value of "Prob > F" indicates that the model is significant which is desirable as it indicated that the terms in the model have a significant effect on the response. Generally, P-value lower than 0.05 indicated that the model is considered to be statistically significant at the 95% confidence level [5].

The "Pred R-Squared" of 0.9882 is in reasonable agreement with the "Adj R-Squared" of 0.9849; i.e. the difference is less than 0.2. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 43.481 indicates an adequate signal. This model can be used to navigate the design space. The ANOVA results were valid because of the normal distribution of the experimental data as could be seen in Fig 4. Normal plot of residuals was used to indicate whether the residuals follow a normal distribution. Therefore, the values of the response predicted from the model are in line with the observed values over the range of the selected operating variables of calcination temperature, reaction time and sodium hydroxide concentration with a relatively high coefficient of determination($R^2 = 99.25\%$). The fitted model in equation (2) gave a reasonable estimate to the experimental condition.

3.5 Influence of Interaction of Factors

The interaction effect of calcination temperature (X_1) , reaction time (X_2) and sodium hydroxide concentration (X_3) were plotted in Figs. 5(a-c). From the graphs, it was observed that the interaction of these factors had a significant effect on the response (zeolite yield). This means that an increase or decrease in any of the factors will have an effect on the responses.

Contour plots and 3D response surfaces were used to show the effect of process parameters

Normal Plot of Residuals

Fig. 4. Normal plot of residuals for zeolite production

Fig. 5. Contour plots and response surface plots for (a) effects of time and calcination temperature, (b) effect of sodium hydroxide concentration and calcination temperature and (c) effect of time and sodium hydroxide concentration

on the yield of zeolite. In order to develop 3D response surface plots and contour plots, the linear, quadratic and interaction terms of the model were applied. Each contour represents a certain value for the height of the surface above the plane defined for the combination of the levels of the independent variable [8,11]. From Fig 5a, it can be seen that increase in interaction of time and calcination temperature improved zeolite yield and quality. The increase in zeolite yield could be attributed to increase in surface area of the treated clay due to thermal treatment as shown in Table 3. The effect of time and calcination temperature can further be proved as shown in Table 5 with the p-value less than 0.05 (P<0.05). Fig 5b shows the contour plot and response surface plot for the effect of sodium hydroxide concentration and calcination temperature on zeolite yield. It can be seen from Fig 5b, that the zeolite yield increased with increase in the interaction of the factors. The increase in zeolite yield could be attributed to the removal of impurities from raw clay after treatment with concentrated sodium hydroxide as shown in Table 5b, which showed that the concentration of most of the compounds decreased in zeolite produced when compared with the concentration in raw clay and as such, the quality of zeolite was increased by the increase in surface area. Pvalue of the interaction of sodium hydroxide concentration and calcination temperature is less than 0.05 as shown in Table 5 which proved that interaction of the factors

strongly influenced the yield of zeoilte from Ugwaka clay. Similar reasons could be attributing to the effect of interactions between sodium hydroxide concentration and time as shown in Fig. 5c.

3.6 Process Optimization

In synthetic zeolite production from an indigenous alluminosilicate (ugwaka clay) using response surface methodology, optimization was done using design expert software version 11. 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 results showed an improvement in the production of zeolite when compared with the work reported by Franus et al. [23], where 90 wt% yield of zeolite was recorded at concentration of 5M sodium hydroxide, temperature of 95 \degree C after 24 hours.

The optimum conditions predicted for the 92.925.49% yield of zeolite were as follows: calcination temperature $800 °C$, reaction time 2.0 hours and sodium hydroxide concentration 2.5M. This value is in close agreement with the experimental value of 92.03%, performed at the same optimum values of the process variables.

Table 6. Validation of optimum conditions

4. CONCLUSION

A quadratic model was developed, and diagnostics of the model revealed a strong correlation between the prediction and observed response values. The optimum conditions for the zolite synthesis were 2.0 hours, 800°C and 2.5M for time, temperature and sodium hydroxide concentration. The silica to alumina ratio obtained after XRF analysis of zeolite produced showed that ugwaka clay is a good source of zeolite. FTIR results of the synthetic zeolite revealed that, some peaks disappeared after clay treatment. Results of the characterization of zeolite produced were compared with commercially available zeolite and observation showed that it has the potential to be used in commercial water softening and purification and also, as a sorbent in adsorption of gases.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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