

Production Of 100 Kg/Day of Zeolite a as a Builder for Powdered Detergent from Nigerian Ahoko Kaolin Using Locally Fabricated Mini Zeolite Plant.

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Abstract. This project was aimed at assembling a plant already designed and fabricated, mainly furnace and crystallizer to produce a 100 kg/day of zeolite A. The produced Zeolite A was used to formulate a powdered detergent. The detergent grade Zeolite A was produced via hydrothermal process and used as substitutes for phosphates in the formulation of a powdered detergent. The formulation of the powder detergent was done by mixing and homogenising Sodium sulphate, linear alkyl benzene sulphonate acid (LABSA), Zeolite A, sodium tripolyphosphate (STTP), sodium silicate, and soda ash in a mixing unit. A 100 g of the detergent contains 55 % sodium sulphate (Na_2SO_3), 15 % LABSA, 8 % sodium silicate, 7 % soda ash (Na_2CO_3) and the remaining 15 % is formed by either (100 %) Zeolite A or a Zeolite A:STPP in a 50:50 ratio. In this formulation, aesthetics value additives such as optical brightener, perfumes, preservatives, active enzymes and stabilizer were not used. The Zeolite A produced was characterized using x-ray diffraction and scanning electron microscope. The characterisation shows that the peaks conform with standard Zeolite A, with peaks at 5, 10, 13, 16, 20, 22, 24, 28, 30 and 34 $^\circ$ (2theta) respectively, while the SEM image reveals a particle size of 2.47 μm and a cubical surface morphology. The powdered detergent formulated was characterised and it shows a pH of between 9.8 - 10.2, while 9.5 for commercial detergent, a foam height of 85 - 90 cm, where as commercial detergent has 99 cm, percentage moisture content of 5.1 to 7.2 %, while 8.0 % was for commercial detergent. Therefore, this comparison with a commercial phosphate based detergents and standard organization of Nigeria (SON) standards shows that Zeolite A is a good substitute for phosphates in detergent formulations.

1. Introduction.

As the application of Zeolites which ranges from petroleum refining, to waste treatment increases, the need to increase production at low cost increases (Okoro, 2015). Detergents manufacturers are currently using Zeolites, (Zeolite A) as the builder material which has proved to be a substitute for phosphorus containing additives (Lijalem *et al*, 2016). Despite the remarkable potentials of Zeolite A, being more Eco friendly unlike the phosphates which contribute to eutrophication of aquatic life, its high cost has limited its effective use in detergent industries (Lijalem *et al*, 2016). Since one of the main hindrances in the application of Zeolite A is, its high cost of production, this has necessitated the diversification of more economic or a very low cost ways of producing Zeolite A on a large scale (Okoro, 2015).

Kaolin clay offers a unique and sustainable route toward the manufacturing of Zeolite A. This has ultimately been a factor in an effort to reduce the cost of zeolite A production. Since kaolin clay is a naturally occurring mineral, and it has been found in commercial deposit in many places in Nigeria including Ahoko, kogi state, Nigeria (Tatabu, 2015), this is considered as the most promising local sources of Zeolites in Nigeria (Okoro, 2015). The



total reserve of kaolin in Nigeria as a whole is estimated to be about three billion metric tons in at least 45 known deposits distributed in some state of Nigeria (Alabi and Omojala, 2013).

Although Zeolite A has a wider range of application, the focus of this present work is to produce a detergent grade Zeolite A from Ahoko kaolin clay using the locally fabricated furnace and crystallizer as well as other equipment in order to use cheap route for production and its application in detergent formulation.

On the threshold of the new millennium, the attention of the detergent industry is focused on delivering against four challenges Economics Safety and Environment Technology Consumer Requirements The pressure of increasing costs and competition is forcing manufacturers to seek favourably priced raw materials and production processes. Laws and regulations with respect to environment and safety, as well as voluntary agreements, have already been affecting various detergent ingredients for years (example, phosphates and surfactants) it has also impacted upon packaging. New measures include a monitored self-regulation by detergent manufacturers (AISE: Code of Good Environmental Practice), and the introduction of an Eco - label for detergents. Both measures are having a direct impact on the composition and technology of detergents. In particular, efforts to save energy and to reduce detergent consumption have had an impact on the technological development of both detergents and washing machines. The crucial factor, however, remains the consumer. Although washing habits differ from country to country, there is a trend towards easier handling (compact powders, tablets). First and foremost, however, the consumer continues to demand a clean wash combined with maximum protection of the items laundered. The resulting requirement to continuously improve the performance of detergents is leading to the use of new or optimized raw materials. (Zeodet, 2000). To a large degree, the aforementioned challenges dominated the development of detergents in the 1980s and 90s. Zeolite, originally designed as a phosphate substitute for purely ecological reasons, increasingly had to meet the demands imposed by modified detergent composition and production technologies. In particular, the trend towards compact detergents increased the demand for builder systems with a high adsorption capacity for liquid components, especially for surfactants. Zeolite A, introduced approximately 20 years ago, proved to be a good carrier for surfactants and in the 90s advanced to become the builder leading to compact and super compact detergents. Nevertheless, the market demanded further improvements (Zeodet, 2000). The manufacturers of detergent Zeolites responded to the demand for higher standards of performance and processing by developing new grades of Zeolite. These include the Zeolites of types P, X and AX, which have all recently been introduced into the market. (Zeodet, 2000).

2. Material and methods

Purification (Pre-treatment) of Raw Kaolin

Beneficiation Process.

Beneficiation process is the first stage in the experiment; it involves beneficiation of the raw material (kaolin), which is the removal of debris, pebbles, clay particles and some inorganic matter (Kovo and Edoga, 2005). To start up this process the raw kaolin sample was collected from Ahoko village in Kogi state, Nigeria, mechanical methods such as separation and sedimentation was carried out to remove mainly quartz and other suspensions (Lijalem, *et al*, 2016). Two Hundred kilograms (200 kg) of raw kaolin clay

was crushed and was soaked in deionized water (in batches) of 25 kg per batch, for four days during which it was vigorously mixed using stirrer (Kovo and Edoga, 2005). The Kaolin suspension was then transferred into sedimentation apparatus (10,000 ml) measuring cylinders and was allowed to settle out, on settling, the coarse component remained at the bottom, while the supernatant (Kaolin) settled on top (Kovo, 2010). The supernatant after ward was decanted into measuring cylinders and was allowed to settle for 24 hr, the recovered clay was then dried in an electric oven at 45 °C for 48 hr.

Calcination Process

One hundred kilogram (100 kg) of the beneficiated clay was calcined in batches of 10 kg per batch in the first unit, the locally fabricated pilot plant (Dehydroxylated furnace) at a temperature of 650 °C for 10 minutes. The metakaolin obtained was kept aside for further processing into Zeolite A. The calcination process was done by putting weighted quantity of the beneficiated clay in the rotating drum of the furnace, thereby subjecting it to a high temperature of 650 °C for the time range of 10 minutes. This process is meant to prepare the beneficiated clay to a more reactive form, before Zeolite A formation process.

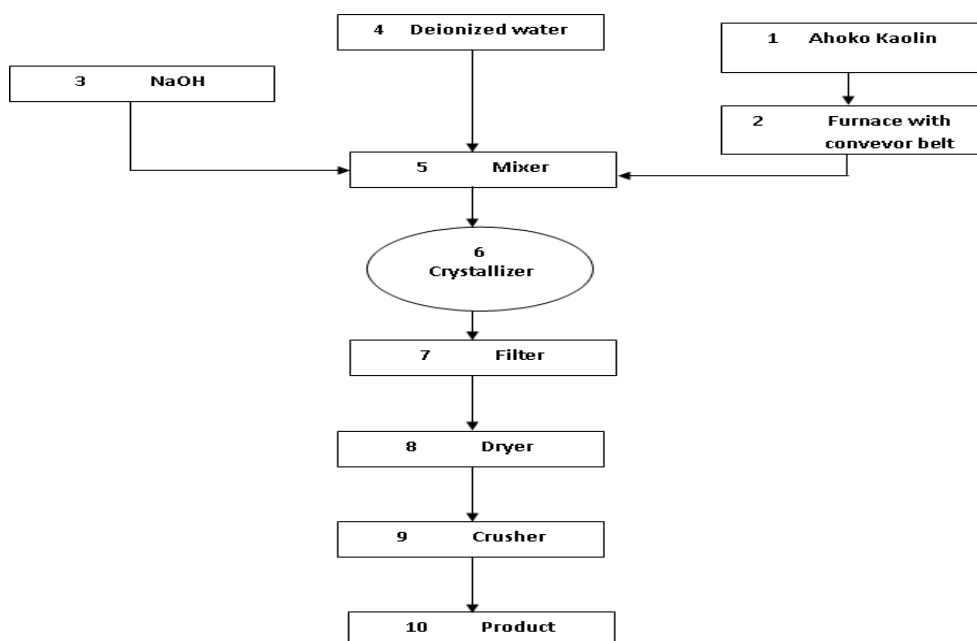


Figure 1: Step wise procedure for Zeolite A production

Zeolite A production procedure

Zeolite A production was carried out using Kaolin conversion process. The Kaolin conversion process makes use of the Meta Kaolin produced earlier, sodium hydroxide (pellets) and deionized water, as starting raw materials (Tatabu, 2015). Conventional hydrothermal procedure reported by (Kovo, 2011) was chosen due to its uniqueness in rapid achievement of the zeolite-A product. In the conventional hydrothermal process, the activation of chemically inert kaolin was performed by taking 10 kg each of purified kaolin separately and calcining it at 650 °C for 10 minutes in the locally fabricated furnace. Then the alkaline treatment was done in a mixer using NaOH (0.832 g:12 g:0.693 g) of (NaOH:deionized water:Mata kaolin respectively), with stirring (500 rpm) at 50 °C for 1 h

for the complete homogenization of the reaction mixture. The gel formed undergoes ageing at room temperature under static conditions. (Lijalem *et al*, 2016). The molar gel composition was:



Crystallization was carried out using hydrothermal method in the second unit of the locally fabricated pilot plant (autoclave crystallizer) for 3 hr at 100 °C. Once the time was attained, the reaction mixtures were filtered and washed with deionized water to remove excess alkali until the pH of the filtrate is below 10. Then, the samples were oven dried overnight at 80 °C.



Plate 1: Locally Fabricated mini Zeolite Plant

Formulation of powdered detergent

Formulation of the powder detergent was done by mixing and homogenizing Sodium sulphate, linear alkyl benzene sulphonate acid (LABSA), zeolite A, sodium tripolyphosphate (STTP), sodium silicate, and soda ash in a mixing unit. The formulation of 100 g of detergent contains 55 % sodium sulphate (Na_2SO_3), 15% LABSA, 8% sodium silicate, 7% soda ash (Na_2CO_3) and the remaining 15% is formed by either 100 % Zeolite or a zeolite A:STTP in a 50:50 ratio. For this particular formulation (research work), aesthetic value additives such as optical brightener, perfumes, preservatives, active enzymes and stabilizer were not used. In addition, a commercial powder detergent having sodium tripolyphosphate as a builder was characterised for comparison. The Zeolite A sample synthesized from Ahoko kaolin were compared with commercial Zeolite A. In this study we have tried to substitute STTP from 50 % to 100 % with Zeolite A in the detergent formulation and composition. (Lijalem, *et al*, 2016)

3. Result and discussions

Characterization of Zeolite A samples

The characterization of detergent grade Zeolite A samples was carried out using X-ray diffraction (XRD) and scanning electron microscope (SEM). Figure 2 below shows the XRD of the synthesized Zeolite A, while figure 3 shows the SEM image. The XRD image shows that the peaks conform with standard, with peaks at 5, 10, 13, 16, 20, 22, 24, 28, 30 and 34 °(2theta) respectively, while the SEM image reveals a particle size of 2.47 µm and a cubical surface morphology. The XRD peaks were indexed with a reference to commercial Zeolite A sample obtained from Treacy and Higgins, 2001.

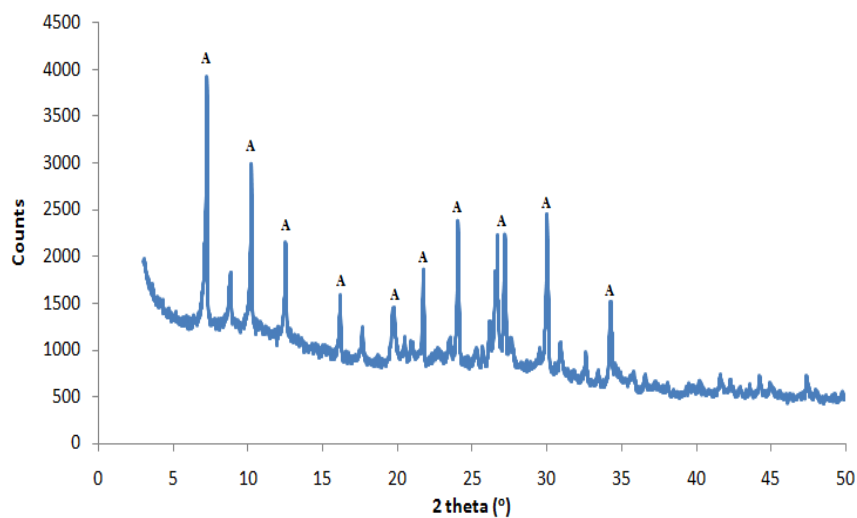


Figure 2: XRD pattern of Zeolite A synthesized from Ahoko kaolin

Figure 3 below shows the SEM image of the Zeolite A produced in this present work showing cubical morphology at 3h of crystallization which typical of Zeolite A.

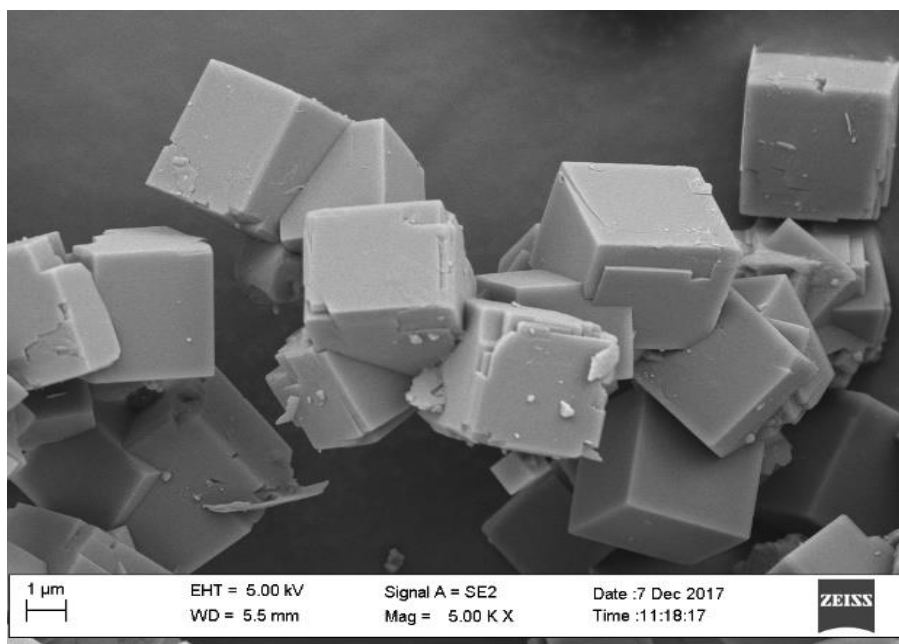


Figure 3: SEM image of the ZeoliteA produced

Characterization of the formulated detergent powder

The formulated detergent sample was then tested using various physiochemical parameters such as the moisture content, foam height, pH value, alcohol and water insolubility, which are adapted from the Nigerian Standards for Soaps and Detergent. The same tests were also conducted on the known commercial powder detergent brand and the results of their comparative evaluation are presented. Foam height measurement was done by preparing 1 % detergent solution. 1 g of the detergent is dissolved in 99 ml of real hard water having moderate hardness (120 mg CaCO_3 per l). Then 10 ml of the prepared solution was taken in a 100 ml measuring cylinder with a glass stopper and shaken very well until the detergent is completely dissolved and forms foam. The foam height was measured after 10 minutes of stability of the foam. The pH of the 1 % detergent solution was measured using a pH meter at 25°C following the calibration of the instrument. For the moisture and volatile content, 5 g of detergent sample was weighed, and dried to constant mass in an oven at $105 \pm 2^\circ\text{C}$. This was done until constant mass is attained when successive heating for one-hour period shows less than 5 mg difference. The percentage (%) moisture content was calculated using the following equation:

Error! Reference source not found. (2)

In this scenario insoluble matter in alcohol refers to inorganic salts, such as phosphates, sulphates, silicates and carbonates, which are usually present in non-soapy detergent preparations. This was done by weighing 5 g of the detergent into a beaker and digested with 50 ml of ethanol, followed by heating on a steam bath for about 2 minutes. Any hard lump was broken down with a glass rod flattened at one end. The solid matter was then allowed to settle and decanted through a sintered glass filter funnel. The alcoholic digestion was repeated in a similar manner with five further consecutive 30 ml portions of boiling ethanol. Each extract was filtered in turn through the same sintered glass funnel and the residue was washed several times with hot ethanol to remove all the alcohol soluble matter. Finally, the sintered glass funnel was dried with the residue at a temperature of $105 \pm 2^\circ\text{C}$ until a constant weight is obtained. The insoluble matter in alcohol is determined using an equation:

Error! Reference source not found. (3)

For water insoluble matter analysis, 5 g of detergent sample was weighed and digested with 200 ml of freshly boiled water until the sample is completely dissolved. Then, the solution was filtered through the filter paper, dried at $105 \pm 1^\circ\text{C}$ and mass recorded. The residue was washed several times with hot water. The filtrate and the residue were dried for 3 h at $105 \pm 2^\circ\text{C}$.

Finally, the water insoluble matter was calculated using the equation below;

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The same characterisations were also carried out on a popular brand commercial powder detergent and results of their comparative evaluation are presented. Two (2) compositions were characterised: 50 % substitution of STTP by Zeolite A then followed by 100 % substitution of Zeolite A in the formulation. The results obtained are shown in tables 1 to 5.

Table 1 PH value

Detergent type	PH value
Detergent (50 % Zeolite: 50 % STTP)	9.8
Detergent (100 % Zeolite: 0 % STTP)	10.2
Commercial detergent (100 % STTP)	9.5
SON standard	9 - 11 maximum

* SON Standard, the pH of requirement for 1 % aqueous solution of industrial detergent determined at 25 °C shall not be less than 9 and more than 11.

Therefore, the value measured for the powder detergent formulated with the synthetic Zeolite A is in good standing order with the specification range and also with the commercial detergent.

Table 2 Foam height analysis (Lather formation)

Detergent type	Foam height (cm)
Detergent (50 % Zeolite: 50 % STTP)	90
Detergent (100 % Zeolite: 0 % STTP)	85
Commercial detergent (100 % STTP)	99
SON standard	80 minimum

From table 2 above is the result for foam height, it shows that the 50 % Zeolite substitution exhibited almost the same foam height with 100 % substitution by Zeolite A. The foam height result is comparable with the foam height of commercial powder detergent which is a very good development. The standard is 80 cm minimum.

Table 3 Percentage (%) moisture content analysis

Detergent type	Moisture content (%)
Detergent (50 % Zeolite: 50 % STTP)	7.2
Detergent (100 % Zeolite: 0 % STTP)	5.1
Commercial detergent (100 % STTP)	8.0
SON standard	13.0 maximum

The table 3 above, shows % moisture content test results on the detergents shows 7.2 %, 5.1%, 8.0 % percentage moisture on 50 % zeolite, 100 % zeolite, and commercial (100 % STTP) detergents respectively. The maximum moisture and volatile component content requirement of any commercial synthetic detergent is 13 % by mass.

Table 4 Percentage (%) matter insoluble in water

Detergent type	Matter insoluble in water (%)
Detergent (50 % Zeolite: 50 % STTP)	7.0
Detergent (100 % Zeolite: 0 % STTP)	5.0
Commercial detergent (100 % STTP)	6.0
SON standard	5.0 - 10.0 maximum

The above results (table 4) are in good agreement with commercial detergent and indicate the possibility of zeolite A to be used for detergent formulation. The appropriate solubility of detergent in water is one of the requirements in washing. The maximum insoluble matter in water should not exceed more than 5 – 10% by mass.

Table 5 Percentage (%) matter insoluble in alcohol

Detergent type	Matter insoluble in alcohol (%)
Detergent (50 % Zeolite: 50 % STTP)	71.0
Detergent (100 % Zeolite: 0 % STTP)	75.0
Commercial detergent (100 % STTP)	69.0
SON standard	80.0 maximum

Although 50% and 100% detergents show a higher values than the commercial detergent, all are still in the range of the standard, which is 80% maximum.

The summaries of tables 1 to 5 shown on table 6

Table 6 Summary of characterisations on 50 % Zeolite, 100 % Zeolite, and commercial powder 100 % (STTP) detergents

Detergent type	B	C	D	E	F
50 % Zeolite Detergent.	7.2	90	9.8	7.0	71.0
100 % Zeolite Detergent.	5.1	85	10.2	5.0	75.0
Commercial Detergent.	8.0	99	9.5	6.0	69.0
SON standard	13 %	80 min.	9-11 max.	5-10 max.	80.0 % max.

Key:

B- Moisture content (%)

C- Foam height (cm³)

D- pH Value

E- Matter insoluble in water (%)

F- Matter insoluble in alcohol (%)

min - minimum

max - maximum

The detergency of the formulated powdered detergent

The formulated detergents both 50 % and 100 % has a high detergency or cleansing power as shown by the formation of foam in water as shown in table 2 which is actually the ability of the detergents to form lather when dissolve in water, and this makes the detergents very efficient in washing / cleaning.

4. Conclusions

The following conclusions were drawn;

1. A mini Zeolite plant was assembled from a locally fabricated units mainly furnace and auto clave crystallizer, Zeolite A was produced from Ahoko kaolin via the procedure reported by Kovo (2011) for 10 minutes calcination time, at a temperature of 650 °C using the assembled mini plant.
2. The X-ray diffraction (XRD) image of the Zeolite produced shows conformity with standard Zeolite A, with peaks at 5, 10, 13, 16, 20, 22, 24, 28, 30, and 34 °(2theta) respectively, while the scanning Electron Microscope (SEM) image reveals a particle size of 2.47 µm and a cubical surface morphology. Also the result of the XRD of the meta kaolin using the fabricated furnace acted as a guide to develop a new route for the production of meta kaolin with the main aim of reducing the time of exposure taken to obtain the amorphous material.
3. The Zeolite A produced was efficiently used as a builder in detergent formulation by substituting the environmentally unfriendly phosphate based builder sodium tripolyphosphate (STTP), This was done by formulating powder detergent using the Zeolite-A as substitute to STTP with 50 % and 100 % zeolite A. The result shows that the zeolite-A based detergent performs almost similar to a very popular brand of commercial powder detergent composed of sodium tripolyphosphate (STTP) detergent builder.
4. The powder detergent formulated was characterized and compared with commercially available phosphate based detergents and standards and the results shows that Zeolite-A is a better substitute for phosphates in detergent formulations.

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