Development and Characterization of Zeolite-A from Elefun Kaolin

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Abstract-
Zeolites are important industrial materials of unique chemical structure that are utilized in various industrial plants as adsorbent for gases, liquid, solids or even as catalysts. The use of synthetic chemicals as starting materials for commercial production of Zeolite-A is cost intensive. However, low-cost raw materials such as clay minerals, coal ashes, natural zeolites, municipal solid wastes and industrial sludge have been widely used. In this study, the synthesis and characterization of Zeolite-A from natural raw Kaolin (Elefun) clay using hydrothermal treatment technique was investigated. The raw and beneficiated kaolin were experimentally studied and comparison was made based on material characterization and application. Metakaolinization was achieved by thermal activation of the beneficiated kaolin at 850 °C for 2 hours. Thereafter, Sodium Aluminosilicate gel was prepared with the molar ratio SiO₂/Al₂O₃ = 2.6, Na₂O/SiO₂ = 3.0, and H₂O/Na₂O = 40 by mixing calculated amounts of metakaolin with sodium hydroxide solution of analytical grade. The gelled samples were aged for 24 hours at ambient temperature and subsequently crystallized for 24 hours at 100 °C. The starting kaolin, beneficiated kaolin, calcined kaolin and final product were characterized using X- Ray Fluorescence (XRF) and results were corroborated by X-Ray Diffractometer (XRD) and Scanning Electronic Microscope (SEM). The results showed that Zeolite-A can be synthesized from Elefun kaolin by ageing at room temperature for 24 hours and crystallization at 100 °C for 24 hours.

Key words: Beneficiation; Calcination; Kaolin clay; Metakaolin; Aging; Zeolite-A

1. Introduction
Zeolites or molecular sieves contain porous aluminosilicate earth metal minerals which are highly crystalline. This crystalline structure arises from a three-dimensional network of tetrahedral [SiO₄]⁴⁻ and [Al₄]⁵⁻ whose framework has cations located within the pores of the material material’s pores [1]. Zeolite-A is a recognized type of zeolite among all synthetic and natural zeolites due to its wide range industrial application in Catalytic and molecular sieving capacities, detergent formulation / manufacturing, water softening etc. most importantly its large ion exchange capacity makes it most suitable for use as an adsorbent and ion exchanger. Increased research into the use of Kaolinite materials in the synthesis of Zeolite compounds has increased over the last decade. This is due to the increased need for a cheap source and environmentally conducive material [2]. In addition, these traditional approach for the synthesis of Zeolite compounds have undesirable effect on the environment and hence not viable [2]. The orthodox approach to zeolite synthesis makes use of pure sodium silicate and sodium aluminate which are costly, with undesirable effect on the environment when related with Kaolinite based Zeolites synthesis [3]. Ayele et al. (2018) [4] synthesized Zeolite-A for removal of Chromium (III) from tannery waste water. It was observed that 99.8 % removal of Chromium (III) was achieved and
similar results were also reported by other researchers [5, 6]. This significant outcome is attributed to the high adsorptive power of modified Zeolite-A. However, the unstructured surfaces of pure Zeolite which has not been chemically modified shows very low affinity for anions [6]. They can be modified to contain water molecules and metals such as alkaline and alkali earth metals in their structure, tailored towards the adsorption of contaminants in water [7]. Studies carried out by other researchers have revealed that modification of Zeolites with some characteristic surfactants have produced adsorbents that have unusual affinity for several anions [8]. Kaolin is a clay mineral which is a product of the weathering of silicate rocks and contains kaolinite as the main mineral phase [9]. Nigeria has a projected reserve of approximately 800 million tons of Kaolin deposit scattered in diverse parts of the country including Ogun, Edo, Plateau, Anambra, Akwa Ibom and Nasarawa states [10, 11, 15, 16]. Zeolite synthesis involves the treatment of the Kaolin clay with sodium hydroxide solution in an autoclave at elevated temperatures. The essential factors or process variables controlling Zeolite-kind synthesis are the silica-alumina ratio, reaction time, hydrodynamics, temperature and pH (alkalinity) [12]. In spite of the wide usage of Kaolin for the synthesis of Zeolite-A, no attempt has been made previously to develop Zeolite-A from Elefun clay under various operating conditions. In this research work, full characterization of Nigerian Kaolin clay from Elefun deposit is presented along with its beneficiation and calcination process. Furthermore, Zeolite-A was hydrothermally synthesized from raw Elefun kaolin. The synthesized products were characterized by X-ray diffraction (XRD), XRF and scanning electron microscopy (SEM).

2. Methodology

2.1. Materials

The raw Elefun Kaolin used in this research was obtained from Abeokuta located in Ogun state, Nigeria. The analytical grade Sodium hydroxide pellets (Sigma-Aldrich, Lobal Chemie, ≥98 %) was used in the synthesis.

2.2. Beneficiation of Elefun Clay

4kg of the Elefun kaolinite clay was measured using an analytical balance and soaked in 10 liters of distilled water for 24 hours. During the soaking period, the clay was masticated at intervals to break into small lumps. Floating dirt was also removed by discarding the water on top and adding fresh water afterwards. After 24 hours, the mixture was decanted several times to get rid of the sand, stony particles, heavy impurities and soluble salts present. The resulting mixture was allowed to soak for seven days with intermittent stirring at predetermined intervals. On the seven day, the mixture was thoroughly stirred and sieved using a 150-micron mesh. The filtrate was then allowed to settle and the column of water decanted. The clay part was allowed to stand in the sieve to remove excessive water from it. After dewatering, the Kaolin clay was sun/air dried (while spreading it on a polythene material in form of a small size lump) for 2 days. The clay material was then put in an oven to be dried further at 150 °C for 3 hrs. After drying, the lumped Kaolin clay was crushed using a mechanical crusher after which the sample was sieved using 75 micron sieve in a digital Sieve shaker thereby giving an extra fine texture in readiness for calcination. The mass of the resulting sample was recorded and part was packaged for XRF analysis.

2.3 Calcination of Elefun Clay
The beneficiated kaolin clay was transformed into metakaolin via a thermal treatment using an electric furnace with a temperature of 850 °C for 2 hrs using ceramic crucible as container. The calcined sample was cool in a desiccator, prior to characterization and usage. The essence is to dehydroxylate the beneficiated Kaolin to form an activated amorphous material called metakaolin. The metakaolin was then transferred to an airtight plastic bottle/containers and sample was subjected to XRF analysis and in preparation for synthesis.

2.4 Hydrothermal Synthesis of Zeolite-A

The gel (Sodium aluminosilicate) was prepared with the molar ratio SiO$_2$/Al$_2$O$_3$ = 2.6, Na$_2$O/SiO$_2$ = 3.0, and H$_2$O/Na$_2$O = 40 by mixing calculated amounts of metakaolin with sodium hydroxide solution. The ratio of silica to alumina is as obtained from the compositional analysis of the calcined sample (Metakaolin), the mass of sodium hydroxide as well as volume of water required for the gel formation of 50 g metakaolin was calculated. The alkaline treatment of metakaolin was done by mixing 50 g of metakaolin with calculated amount of 3M NaOH at 50 °C for 1 hr under 500 RPM for gel formation similar to the method used by Ayele et al. (2016). Thorough mixing was done using electrically powered stirrer to achieve homogeneity. The gel was then aged at room temperature in static conditions for 24 hrs. Crystallization is carried out in laboratory oven under static condition for 24 hrs at 100 °C. At the end of the synthesis, the reaction was stopped by quenching the bottles in cold water. The reaction mixtures were filtered and washed in distilled water until the pH of the filtrate was below 10 after which the samples was oven dried overnight at 80 °C before material characterization.

2.5 Characterization of Kaolin and Zeolite-A

The crystal structure and the relative crystallinity of the starting Kaolin as well as the synthesised Zeolite-A was analysed using X-ray diffraction (XRD) and patterns were recorded on an X-ray diffraction machine (Cubic 3 Cement PAN analytical) using Cu-ka radiation with a wavelength of 1.540598. The morphological study of the samples was performed by the scanning electron micrograph (SEM) Phenom Pro-X SEM. Chemical composition of Kaolin was analysed by X-ray Fluorescence machine (Axios Pan analytical).

3. Result and discussions

3.1. Elefun Kaolinite Clay Particle and Synthesized Zeolite-A Characterization

The chemical composition, crystalline phase and morphology characteristics of the Elefun Kaolinite clay samples were analyzed using XRF/XRD/SEM machine. Table 3.1 shows compositional analysis conducted on the raw, beneficiated and calcined Elefun kaolin. The results show that Elefun kaolin contains some oxides of Iron (Fe), Magnesium (Mg), Calcium (Ca), Potassium (K), Titanium (Ti) etc. however, the main constituents are silica and alumina as shown in Table 3.1. It also indicates the effect of beneficiation on the treated raw kaolin as value of SiO$_2$ reduced from 57.50 % to 56.80 % due to removal of free silica (quartz) from raw kaolin. Table 3.1 also indicates that Elefun kaolin is ferric in nature due to its high content of iron oxide as compared with that of potassium. Similarly, the white colour of the raw and beneficiated Elefun Kaolin can be attributed to the significant content of TiO$_2$. Pure raw kaolinite clay is expected to have silica/alumina ratio of between1 to 2 (Ajayi et al., 2010). Table 3.1 shows that the SiO$_2$/Al$_2$O$_3$ ratio...
of 2.37, 2.01 and 1.54 for the raw, beneficiated and calcined Kaolin respectively is within theoretical value.

The XRF analysis results for the synthesized Zeolite-A from the local Kaolinite clay (Elefun clay) is shown in Table 3.2. The chemical compositions ranged 37.3% for SiO₂, 26.9% for Al₂O₃, 1.6% for Fe₂O₃, and 15.4% for Na₂O. This also reveals the presence of Al, Si, O, Na and Fe in their elemental states which were also present in the structure of the synthesized Zeolite-A and in agreement with the results obtained from XRF, as given in the table 3.1. Therefore, from the increased purity of the synthesized Zeolite-A, and its similarity with numerous global deposits of significant commercial value gives the Zeolite-A from Elefun clay high prospective for use in waste water treatment. The chemical data show that the ratio of Silica to Alumina (Si/Al) content is 1.4 which is similar to what is obtainable for universally for Zeolite-A compounds. The major element presents in the distribution replicates the mineral composition of the Zeolite-A compound. Comparatively, the chemical compositions of the synthesized Zeolite-A was found to be comparable with other Zeolite-A compositions. This implies that the Zeolite-A synthesized from the local Kaolinite clay (Elefun Clay is encouraging for application in industrial and environmental purposes). This is especially the case for the removal of heavy metals from industrial and waste water.

**Table 3.1: XRF results of the Raw, Beneficiated and Calcined Elefun kaolin**

| S/N | Composition (%) | Raw Kaolin(Rk) | Beneficiated Kaolin (Bk) | Calcined Kaolin (Ck) |
|-----|----------------|----------------|-------------------------|---------------------|
| 1   | SiO₂           | 57.50          | 56.80                   | 57.40               |
| 2   | Al₂O₃          | 24.30          | 28.20                   | 37.32               |
| 3   | SO₃            | 0.34           | 0.12                    | 0.10                |
| 4   | K₂O            | 0.13           | **ND**                  | **ND**              |
| 5   | Na₂O           | 0.01           | **ND**                  | **ND**              |
| 6   | CaO            | 0.14           | 0.11                    | 0.08                |
| 7   | MgO            | 0.006          | **ND**                  | **ND**              |
| 8   | TiO₂           | 2.06           | 1.06                    | 0.13                |
| 9   | MnO            | 0.016          | 0.001                   | **ND**              |
| 10  | Fe₂O₃          | 2.214          | 1.74                    | 1.06                |
| 11  | CuO            | 0.021          | 0.15                    | 0.02                |
| 12  | As₂O₃          | 0.005          | 0.002                   | **ND**              |
| 13  | ZrO₂           | 0.072          | 0.25                    | 0.02                |
| 14  | BaO            | 0.12           | 0.001                   | 0.046               |
| 15  | HfO₂           | 0.014          | 0.015                   | 0.002               |
| 16  | PbO            | 0.001          | 0.005                   | 0.02                |
| 17  | L.O.I          | 13.00          | 11.78                   | 3.20                |

* L.O.I - Loss on Ignition  **ND - Not detected

**Table 3.2: XRF analysis of the Synthesized Zeolite A**

| %      | SiO₂ | Al₂O₃ | Na₂O | Fe₂O₃ | Si/Al |
|--------|------|-------|------|-------|-------|
| Composition | 37.3 | 26.9  | 15.4 | 1.6   | 1.4   |

3.2. X-Ray Diffraction Studies
Figure 3.1 below is the result of X-ray diffraction (XRD) pattern for the raw Elefun Kaolin, which has a layered structure conforming to that kaolinite. It indicated two peaks corresponding to the kaolinite and quartz present in the material. A study of the peaks shows a sharp peak with medium intensity at $2\Theta = 12.4083^\circ$ (d = 76.36) and another sharp peak with high intensity at $2\Theta = 24.9341^\circ$. This is the main peak used in identification of kaolinite clay (Ramirez, 2007). In addition, the peak obtained at position corresponding to $2\Theta = 26.6748^\circ$ indicated the presence of large quantities of quartz. Kaolinite and quartz are predominant characteristics of natural kaolin (Tracy and Higgins, 2001, Evamako et al., 2001). However, the quartz content of Elefun kaolin needs to be reduced to minimum before its usage in zeolites development.

![X-ray Diffraction pattern for Raw Elefun Kaolin](image)

**Figure 3.1: X-ray Diffraction pattern for Raw Elefun Kaolin**

### 3.3. Scanning Electron Micrographs

Results of Scanning Electron Micrographs (SEM) are shown in Figures 3.2 – 3.3. The micrograph of the raw Elefun clay shows a plate like layer structure and hexagonal outlines with cavities as seen in figure 3.2. In accordance with the results of other analytical methods quartz can be identified even by SEM in the sample (see Table 3.1). Cubic crystalline structures with well-defined edges are observed on the micrographs of the Zeolite-A samples as shown in Figure 3.3. This is in line with the work of other researchers [13, 14].
Figure 3.2: SEM Micrograph of Raw Elefun Kaolin at 500x magnification
4. Conclusion
The work presents the development and characterization of Zeolite-A from Kaolin using Elefun clay in Western Nigeria. The synthesis of the Zeolite-A from natural raw Kaolin (Elefun) clay using hydrothermal treatment technique. The raw and beneficiated Kaolin were compared using material characterization technique such as XRF/XRD and SEM. The prepared Zeolite-A showed good materials properties with traditional synthesized Zeolite-A samples from other sources. The implication of this is the vast reserves of Kaolinite deposits in Nigeria can be harnessed for the production and development of Zeolite-A compounds. However, this study is in the process of evaluating the adsorbent characteristics of the prepared Zeolite-A samples for waste water treatment. The focus of this subsequent study is in the removal of heavy metals from industrial effluents.

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