Chemical Investigation of Kankara Kaolin for its Pharmaceutical Applications

Abstract
Kaolin samples from Kankara in Kastina, North-West Nigeria was analysed to investigate its suitability for use as raw materials to pharmaceutical industries. The samples were analysed using Instrumental Neutron Activation Analysis (INAA) with Near Infra-Red analytical techniques. The result showed that Kankara kaolin with Fe$_2$O$_3$ content of 2.4 x 10$^{-3}$, K$_2$O content of 0.061%, Na$_2$O content of 0.6%, TiO$_2$ (BDL) and Ba$^{2+}$ (BDL) meets the specification for use in pharmaceutical industries. Its Al$_2$O$_3$ content of 35.28% was above the threshold for pharmaceutical applications except if subjected to further chemical treatment. The Kankara kaolin was found to be reasonably good for use in drug formulation.

Keywords: Kankara; Kaolin; Ceramics; Clay; Oxides

Introduction
Research on clay minerals has received considerable attention in recent times owing to their numerous industrial applications. Deposits of this important raw material are widely distributed in Africa, especially, Nigeria [1-8]. Inspite of the extensive use and the demand for clay in industrial processes, chemical investigation of this mineral for their pharmaceutical applications has received lesser attention. This is important, in order to add value to the clay as an industrial raw material for the production of pharmaceuticals.

Kaolin has the approximate chemical formula of H$_4$Al$_2$Si$_4$O$_{10}$(H$_2$O) and is a white or yellow-white powder that has a slightly oily feel. It is an environmentally benign aluminosilicate mineral [9] that is insoluble in water [10]. Light kaolin is the preferred material for use in pharmaceutical preparations. The finely divided particles yield a very large surface area that adsorbs a wide variety of compounds [11].

Kaolin, a clay mineral with a variegated range of physical, chemical and physicochemical properties, clay minerals has an undisputable role in pharmaceutical industries. It is widely used in the pharmaceutical industry as excipients in pharmaceutical preparations to enhance its organoleptic characteristics, such as flavor and color, improve their physicochemical properties, such as viscosity of the active ingredients (emulsifying, thickening and anticaking agents), facilitate their elaboration (lubricants, diluents, binders, isotonic agents) or conservation (desiccants, opacifiers) and facilitate liberation of the active ingredient within the organism [12].

Clay minerals with very fine, thin particles and high adsorbent properties are quite useful for the antibiotics sorption. Kim et al. studied the sorption of oxytetracycline on clay minerals especially in acidic soils with high organic matter content [13]. The adsorption of four widely used drugs, carbamazepine, diclofenac, ibuprofen and ketoprofen, was investigated onto a porous silica under varied ionic strengths, and with different anions, divalent cations (Ca$^{2+}$ and Mg$^{2+}$), trivalent cations (Al$^{3+}$ and Fe$^{3+}$) and natural organic matter. The studies demonstrated that at a given pH the adsorption was most affected by ionic strength, trivalent cations and properties of pharmaceuticals.

Clay minerals sorption activity is the most suitable application in veterinary science. Kaolins and smectites are most commonly used in animal nutrition as growth promoters and supplements for the treatment of gastrointestinal disturbances, particularly diarrhea [14].

Because metal oxide content of kaolin clay has profound influence on its chemical properties and by extension its pharmacological utility, it has become necessary to investigate their concentration in Kankara Kaolin clay in order to ascertain its suitability for pharmaceutical applications. The industrial chemical specification for quality kaolin clay for pharmaceutical application is shown in Table 1.

Table 1: Percentage chemical composition of clay minerals commonly used in pharmacy and cosmetics.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Range in Percentage (%)</th>
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</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>38.1–39.5</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.1–0.2</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0–0.1</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0–0.2</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0–1.4</td>
</tr>
<tr>
<td>Ba$^{2+}$ (ppm)</td>
<td>low</td>
</tr>
</tbody>
</table>

Materials and Method

Sample collection

Kankara lies at Latitude 11° 55 and Longitude 7° 25 North-west Nigeria (Figure 1). 100 samples were collected from the site. The vegetation in the selected site was cleared with a machete and the top soil which normally contained a lot of organic matter removed. Equipment and machines for drilling and mining had not been installed in any of the sites, therefore the Kolin’s were dug out manually with holes, diggers and shovels from well-like boreholes, sometimes diverting into underground tunnels.

Figure 1: Location map of Kankara Kaolin Deposit Oyeka [18].

Packaging of samples

In order to avoid contamination, samples were kept in vessels appropriate for the type of irradiation to be performed. Samples requiring smaller time (<20 minutes) were each packaged and sealed in 7cm² rabbit capsules. For elements leading to long lived activation products, samples were wrapped in polyethylene films and packed in a stack inside the 7cm² rabbit capsule and sealed for irradiation [19].

Measurement in neutron activation

The packaged samples were placed near the core of the nuclear research reactor where the neutrons emitted by the reactor interacted with the nuclei of the element’s atoms causing them to become radioactive. The short regime capsules were sent in for irradiation in turn in an outer irradiation channel, B4, the neutron section of low to moderate flux densities. The long irradiation regime rabbit capsules were placed in the inner irradiation section (i.e. A1, B1, B2, B3) to take advantage of the maximum value of thermal neutron flux in the inner channels and were irradiated for six hours. The stability of the neutron flux throughout the period was checked by monitoring the neutron flux reading of a fission chamber connected to a microcomputer control system. Radioactivity measurement of the induced radionuclide was performed by the PC base gamma-ray spectrometry [19].

Identification and quantification

Elemental radioisotopes formed through this interaction subsequently decays by emitting gamma rays (γ-rays) that is unique in half-life and energy. The distinct energy signature created by each element is unique to the element and was identified and quantified using the high purity detector (HPGE) which has a relative efficiency of 10% at 1332.5K, gamma ray line and the gamma ray analysis software 2004 version for data processing and analysis [19].

Counting

After the irradiation process, the samples were allowed to decay and counted using a detector for the resultant γ -rays emitted from the irradiation process. For the short irradiation regime, the first round of counting was performed for 10mins (SI) after a waiting time of 2 to 15 minutes. The samples were placed on a flexi glass sample holder designated as “H2” which corresponds to source –detector geometry of 5cm. The second round of counting was also carried out for 10 minutes following the short irradiation regime (i.e. S2) after a waiting period of 3 hours, samples were counted on a flexi-glass holder designated as “HI” corresponding to a source geometry of 1cm. For the long irradiation regime, the first round of counting was carried out for 30 minutes using the holding “H” after a waiting period of 4-5 days. The second round of counting was performed for 60 minutes (i.e. L2) after a cooling time of 10-15 days. Samples were counted using the flexi-glass holder “H”. The choice of cooling time and sample detector geometry is such that detectors dead time is controlled to less than 10% [19].

Standard for INAA determination

Verifying the accuracy and quantification result of the INAA procedure is as important as with any viable analytical techniques, while in theory it is feasible to calculate target atoms mathematically, it is generally not acceptable since there can be significant uncertainties in value available for various nuclear parameters. Equally important is the fact that the neutron energy spectrum and flux densities of the reactor are not always constant and can vary during different irradiation periods. For these reasons, standard certified reference material of the Chinese geo-chemical rock standard GSD -11 and GSR -5 were used as standard for analytical quality control to validate the procedure of the analysis of interest in the sample. Results of the analysed kaolin samples from the site are as presented in the Table 2.

Table 2: Percentage metal oxide content of the analysed kaolin Sample.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>0.6%</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.061%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>35.28%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.4 x 10⁻⁵%</td>
</tr>
<tr>
<td>TiO₂</td>
<td>BDL</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>BDL</td>
</tr>
</tbody>
</table>

BDL: Below Detection Limit

Results and Discussions

Aluminum oxide has many uses in pharmaceutical industry. It is used as an adsorbent, desiccating agent, and catalyst, and
in the manufacture of dental cements. It is also available for use in hemodialysis. The \( \text{Al}_2\text{O}_3 \) content of 35.28% in Kankara clay is below the minimum specification as shown in Table 1. Thus, increasing the \( \text{Al}_2\text{O}_3 \) value will increase the quality of the clay for these uses.

The \( \text{Fe}_2\text{O}_3 \) content of kaolin accounts for its application as pigment in pharmaceutical capsules. The concentration of this oxide (2.4 x 10^{-3}) in Kankara clay is far below the maximum value of 0.7%.

The pharmaceutical application of kaolin clay as adsorbent is largely attributed to its sodium and potassium oxide content which form part of the prominent cations found on the clay surface. The low amount of these oxides in kaolin implies it could be a good raw material for use in this regard.

Titanium dioxide (\( \text{TiO}_2 \)) is primarily used as a pigment in pharmaceutical products because of its brightness, high refractive index, and resistance to discoloration. It also possesses antimicrobial properties. The Titanium oxide BDL concentration of Kankara kaolin makes it a good source of raw material for use by pharmaceutical industries.

Barium in clay is poisonous and toxic if ingested. It is an irritant for inhalation and skin contact. Excessive amounts can cause violent diarrhea, convulsive tremors, and muscular paralysis. Barium is known to affect the heart and nervous system. The barium content of Kankara kaolin was found to be BDL, enhancing its suitability for use in drug formulation.

**Conclusion**

The results of the chemical investigation of the Kankara kaolin have shown that it has vast potential for use as raw material to pharmaceutical industries. It is wished that the findings of this research would be of immense help to Industrialists and academic researchers locally and internationally.

**Acknowledgment**

The authors would like to extend their sincere appreciation to the Department of Chemistry, Faculty of Physical Sciences, Ahmadu Bello University Zaria, Nigeria for supporting this research.

**Conflicts of Interest**

The authors declare no conflict of interest.

**References**