Parametric investigation of indigenous Nigeria mineral clay (Kaolin and Bentonite) as a filler in the Fluid Catalytic Cracking Unit (FCCU) of a petroleum refinery

Angela Mamudu [a,*], **Moses Emetere** [b,e], **Dumebi Okocha** [a], **Simisola Taiwo** [a], **Felix Ishola** [c], **Francis Elehinafe** [a], **Emeka Okoro** [d]

[a] *Department of Chemical Engineering, Covenant University, Ota, Nigeria*
[b] *Department of Physics, Covenant University, Ota, Nigeria*
[c] *Department of Mechanical Engineering, Covenant University, Ota, Nigeria*
[d] *Department of Petroleum Engineering, Covenant University, Ota, Nigeria*
[e] *Department of Mechanical Engineering Science, University of Johannesburg, South Africa*

Abstract The operational effectiveness of a fluid catalytic cracking unit largely depends on its catalyst, which is a mixture of zeolite, binder, matrix and filler. The filler plays an active role as it provides the catalyst with physical strength and integrity and also presents a heat exchange platform where more imperative and costly zeolite component can be incorporated. In Nigeria, foreign kaolin clay is used as fillers because it contains lesser impurities when compared to the one indigenous to the country. In contrast, Nigeria bentonite clay have unique properties that can be processed and used as an alternative. This paper evaluates the suitability of kaolin and sodium bentonite from southern Nigeria as fillers in the Fluid Catalytic Cracking Unit. Initial characterisation with the aid of an XRF analysis confirmed the presence of iron oxide impurity on both the local and foreign crude clay (Bavaria, Germany). Wet beneficiation processes were carried out on all clay samples with different reaction times, temperatures and amounts of reagents to reduce impurities. Reaction time at 8 h proved more effective as 77% of iron oxide were removed from both the local and foreign clays. The product properties of the beneficiated samples also revealed iron oxide impurities that reduce impurities from 5.62% to 1.41% for kaolin clay and from 9.84% to 2.77% for bentonite clay. Samples of crude oil and products were tested to determine their physical properties using an Emmetteller Brunauer, a scanning electron microscope, a viscometer, and a pH meter to reveal the impact of the benefits on compliance with API standards. Aside from the increase or decrease of

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* Corresponding author.
E-mail address: angela.mamudu@covenantuniversity.edu.ng (A. Mamudu).

particulate or grain size, the structural modifications reflect the impact of mineral clay in retaining exchangeable cations (nutrients).

1. Introduction

1.1. Background knowledge

Mineral clays are one of the many materials that have been used by man for centuries. Initially, they were mostly used in the manufacture of ceramics, but recently they are being utilised in other industries. These industries include agriculture, engineering, construction, environmental remediation and the focus of this research paper; catalysis [1]. It should be noted that the term clay should not be mistaken for clay mineral; a clay mineral is a group of hydrous aluminium phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earth and other cations found on or near some planetary surfaces that form in the presence of water [2]. In contrast, clay is a finely-grained soil material that joins at least one earth mineral with conceivable hints of quartz, metal oxides and natural matter [3].

The flexible nature of clay is credited to the occurrence of clay minerals, which convey significant physiochemical properties namely; particle size and shape, ion exchange, hydration/swelling, plasticity, rheological properties, colour and reaction with the organic and inorganic compound. Particle size and shape are properties that are determined by electron micrographs; clay minerals are in principle < 2 μm in size [3]. In terms of ion exchange, clay minerals can assimilate certain cations and anions without influencing the fundamental silicate structure [3].

Clay minerals are prone to absorb water particles on their outer surfaces, or in their interlayer spaces, related with the interlayer cations or with the interior surface [4]. Clay minerals can accommodate relatively large inorganic cations between their layers. Cationic organic molecules, such as pyridines, methylene blue and aromatic amines may replace inorganic exchangeable cations. Some of the clay minerals can be used as catalysts for reactions in which one organic substance is converted to another on the surface of the mineral [3].

1.2. Kaolin and bentonite clay

Kaolin clay ($Al_2Si_2O_5(OH)_4$) is a chalk-like, lightweight, soft sedimentary rock that has an earthy odour and contains 85–95% of the mineral kaolinite. It also contains mica, quartz and less often, anatase, montmorillonite, feldspar, haematite, bauxite, zircon, illite, rutile, kyanite, sillimanite, graphite and halloysite [5]. There are two major ways of processing kaolin clay; the wet and dry process. The wet method is used in situations where impurities containing silica are highly present in the crude kaolin. The latter dry process involves the aeration, grinding, filtering and packaging of crude kaolin, and it is utilised when impurities and silica content in the crude kaolin is low [6].

Bentonite clay ($Al_2H_2O_6Si$) is an aluminium phyllosilicate clay which consists mostly of montmorillonite. The many kinds of bentonite are named according to their governing element; Potassium (K), Aluminium (Al), Sodium (Na) and Calcium (Ca). The significant process used in improving bentonite clay is called beneficiation. Beneficiation removes impurities (mostly iron oxide) that mitigates the desirable properties in the clay, thereby improving its economic value, which constitutes a higher grade and more effective product. The wet method of beneficiation has been considered the more efficient technique of removing impurities from bentonite clay [7].

Kaolin and Bentonite clay are the most commonly used clays in the manufacture of catalysis due to their unique attributes, which include cheaper cost, environmental compatibility, re-usability, high selectivity, acid-activation ability and non-corrosiveness [8,9]. Kaolin clay is averagely valued at $162.79 per ton and Bentonite clay $41.33 per ton [8]. Kaolin and bentonite clays need little to no chemical processing for industrial use. This advantage removes the cause of pollution precautions [9]. Both clays can be recycled and converted to other products by merely drying it out, adding water and storing until the time of reuse [9]. Kaolin and bentonite clays possess extremely high cation selectivity used in multi-site ion-exchange models present in catalysis [9].

Collectively, both clays have been used in paper filling and covering, paint, plastic, glue and ink pigment, ceramic raw materials, reinforcing rubber agents, cosmetics, industrial cleaning agents, drilling muds and sealants [9]. However, they are yet to be implemented in Nigeria as fillers in the manufacture of catalysts for petroleum refineries.

1.3. Fluid Catalytic Cracking Unit

An essential aspect of crude refining process takes place in the Fluid Catalytic Cracking Unit (FCCU) due to its ability to convert high boiling petroleum fraction. These fractions (high value needed transportation fuels) includes gasoline, jet fuels, diesel and olefin gases, which are also used in the petrochemical aspect of the refinery [10,11]. The process produces by-products that contain more carbon–carbon bonds (olefins) which has more financial incentive than products that are thermally cracked [11].

The feed entering the FCCU is heated to a temperature range of 555°F − 850°F at a pressure range of 150 − 3000 psi and then combined with a powdery catalyst. The catalyst breaks down the long-chain particles of high-bubbling hydrocarbon fluids into shorter molecules which are gathered as vapours [12]. The catalyst used in an FCCU comprises of four components, namely zeolite, binder, matrix and filler [14]. The zeolite, which comprises alumina tetrahedral and silica, offers the majority of the activities and remains the primary active component with a range of 15–50 wt% of the catalyst [15]. The matrix consists of amorphous alumina and allows the passage of bigger molecules as opposed to zeolite. This allows the breaking down of higher-boiling, bigger feedstock particles

which are not broken down by the zeolite [13]. The binder, which comes in the form of silica sol, acts as a glue to hold the other three components together [15].

Fillers are particles introduced to materials to reduce the utilisation of a costly binding component or to improve a few properties of the blended materials [16]. Industrially, most utilised fillers include ground calcium carbonate (GCC), sawdust and wood flour for the production of plastics and paper. Nano-particles are also used as fillers for composites [17]. The filler gives the catalyst physical integrity and strength and provides a fluidising and heat exchange medium where more imperative and costly zeolite component can be incorporated [18]. The catalyst is significant because the FCCU's structure and activity are exceptionally dependent on its physical and chemical properties (reactivity, high cation exchange capacity, great firmness to high temperature, large pore sizes and its resistance to attrition) [19].

Presently in Nigeria, about five billion Naira is being budgeted annually for the purchase of FCCU catalyst [20], with the fillers component constituting of 31% of the catalyst imported. The Petroleum Technology Development Fund (PTDF) figured out that if some components of this catalyst were produced locally, it would drastically reduce the total money spent on importation thereby serving as a cost alleviation strategy for the petroleum industry [21]. Although kaolin and bentonite clay have successfully been studied for its application as fillers in other areas due to their unique attributes, its usage as a filler in the preparation of an FCCU zeolite catalyst remains a research gap that has not been met. Some of these previous studies include: Aderiye [22] beneficiated Nigerian Kankara kaolinite clay as particulate filler strengthening material for automobile friction lining development while Aja and Randy [23] successfully proved the suitability of Nigerian Kaolin clay as a filler for soap production. Kirabira et al., [24] also carried out a beneficiation process on kaolin clay sample gotten from Mutaka, South-Western Uganda to improve its quality. Harahap [25] proved that bentonite clay samples from North Sumatra, Indonesia was successfully beneficiated for the reinforcement of HDPE (thermoplastic high-density polyethylene). Ramadhan et al., [26] used organic surfactant to upgrade bentonite sample gotten from Gresik, East Java Indonesia while Singh and Sharma [27] used a mixture of sodium sulphide and oxalic acid in association with a wet beneficiation process to upgrade a sample of Indian bentonite clay for drilling mud application. Bilal et al., [28] also successfully beneficiated samples of Ca-based bentonite clay from Fika formation in north-eastern Nigeria via ion exchange using Na_2-CO_3 as the beneficiating agent

As a country, Nigeria is endowed with indigenous kaolin and bentonite clay, as shown in Fig. 1; displaying the spatial distribution of the two clay types in Nigeria. The specific properties of locally available kaolin, and bentonite which includes: non-corrosive nature, environmental stability, high selectivity, reusability and the acid activation ability, suggested their suitability for both industrial and domestic applications. Despite these, valuable utilisation of these clays had been proportionally low in the country. Therefore, this present study evaluated the suitability of indigenous kaolin and bentonite clays as fillers for the catalyst used in the FCCU. Specifications of FCCU catalyst, according to the American Petroleum Institute standard, as shown in table 1, was used as the benchmark.

2. Materials and methods

2.1. Collection of samples

The kaolin and sodium bentonite clay samples to be used for the analysis were obtained from Bavaria, Germany and Auchi, Edo state, Nigeria.

2.2. Sample preparation

5 kg of the samples (indigenous and foreign) were dried openly for 48 h at room temperature. This was followed by a crushing procedure, which included granulating utilising agate mortar and pestle and a mechanised grinding machine. To evade cross contamination, the grinding machine was adequately cleaned with acetone before each sample was loaded into it. In sieving the samples, a sieve shaker with a 150 μm mesh-mounted was used to acquire the required amount of sieved sample. More than 100 g of each sample were gotten.

2.3. Physical and chemical property tests

The following tests were carried out on all crude clay samples to determine and compare selected physical and chemical properties attributed to standard fillers.

- Particle shape: The particle shape of the clay samples was determined by using a scanning electron microscope (SEM). All images were taken at a pressure of 70pa, accelerating voltage of 15KV (Kilo- Volts), Working distance of 10.4 mm, Lens Magnitude of x6000 and Horizontal field width of 116 μm.
- Specific surface area: The specific surface areas and particle size of the clay samples were determined using the single point N2 BET method, which requires the use of the Autosorb Station1, Quanntachrome to determine the physical adsorption of a gas on the surface of a solid.
- Density: The densities of the clay samples were determined using a weighing balance to weigh a petri dish full of clay and dividing said weight by the volume of the petri dish (g/cm^3).
- Viscosity: The viscosities of the clay samples were determined using a Fann rotational viscometer.
- pH: The pH of the clay samples was determined using a portable soil pH meter.
- Cation exchange capacity: The clay samples were sent to a laboratory to undergo CEC analysis.
- High-temperature reactions: The samples were placed in an oven and subjected to their standard melting points to confirm their threshold under high temperature.

2.4. Initial characterization

The chemical compositions of the clays were probed to establish the mineralogical compositions of the clay using an X-ray fluorescence (XRF) machine, Philips Spectrophotometer. This invariably helps to determine the appropriate method of beneficiation (wet or dry) to be used on the clay samples. The XRF results showed that there was a higher percentage of sil-
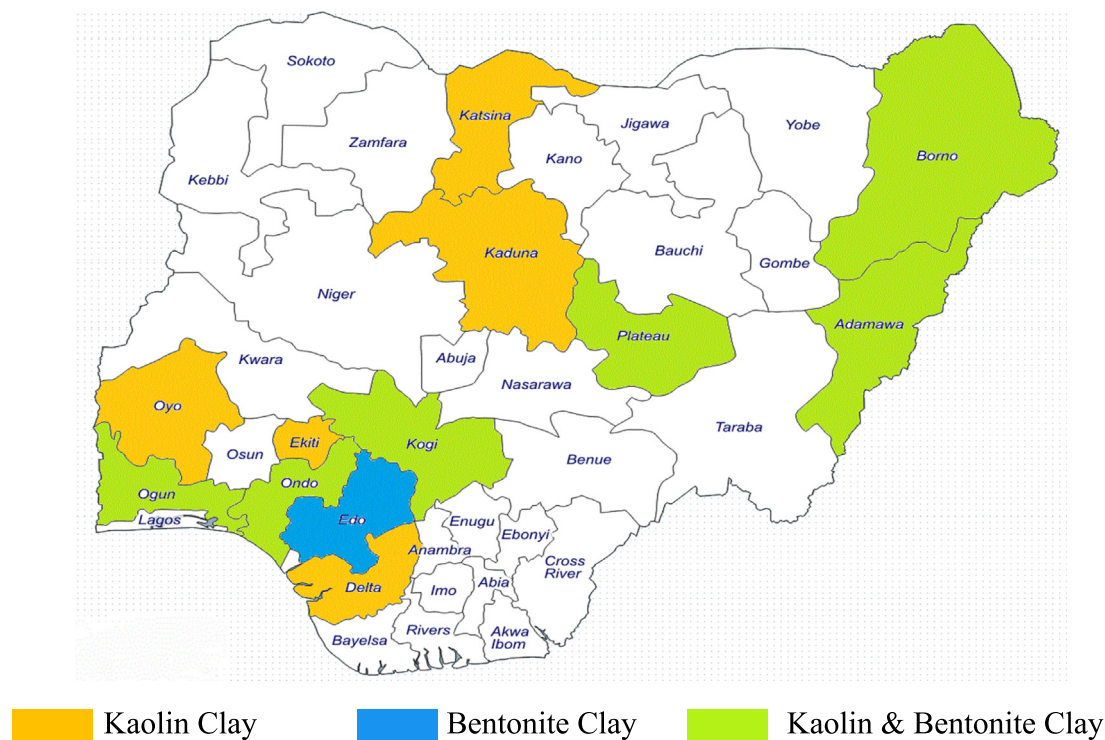
Fig. 1 Nigerian Map Showing Kaolin and Bentonite Clay Deposits.

Table 1 Physical and Chemical Properties – Raw and Beneficiated Clay.

Property	Raw Clay				Beneficiated Clay				API Standard [15]
	Kaolin		Sodium		Kaolin		Sodium		
	Indigenous	Foreign	Indigenous	Foreign	Indigenous	Foreign	Indigenous	Foreign	
Density (g/cm³)	2.76	2.74	2.66	2.68	2.64	2.65	2.49	2.5	2.5–2.63
Viscosity (cP)	4.0	4.3	4.5	4.8	5.7	5.9	5.8	6.0	5.0–6.0
pH	5.4	4.8	5.4	5.8	7.8	8.6	8.9	8.56	3–8.9
Melting Point (°C)	746	750	879	900	1050	950	1189	1200	> 750
Particle Size (μm)	0.74	0.87	1.74	0.86	0.65	0.72	1.25	0.62	0.18–7.3
Specific Surface Area (m²/g)	61.2	58.7	0.67	0.57	63.3	64.5	0.76	0.79	0.8–65
CEC (cmol$_c$/100 g)	11.0	9.7	38.0	55.0	19.8	12.0	78.9	88.0	2–10
Particle Shape	Flake	Flake	Disk Like	Disk Like	Flake	Flake	Disk Like	Disk Like	Flake, Tubular and Disk Like

g-gram, cm-centimeters, μ-micrometer, cP-centipoise, meq- milli-equivalents and °C-celsius.

ica content in the clay samples, and the presence of the iron oxide impurity was also established. Therefore, the wet beneficiation method was used to efficiently remove the iron oxide impurity

Generally, iron oxide removal is carried out to prevent catalyst deactivation, fouling on the catalyst active sites and pore plugging [29,30]. Coke formation and the attendant fouling is an unfortunate side reaction of catalytic cracking which results in the formation of coke or remains in a non-coke form, but effectively blocks the active sites of the catalyst [31]. Gougazeh [32], also emphasised that the presence of iron oxides has a deleterious effect on the colour of the clay,

which limits its use in the production of paper, paints and plastics.

2.5. Beneficiation process

A wet beneficiation process was carried out on the kaolin and sodium bentonite clay samples. The procedure used is similar to the previous works done in Mutaka, South-Western Uganda [24] and Gujarat, India [27]. Reaction time, temperature and reagent dosage were varied during the process to determine the most effective parameters for the removal of iron oxide impurity.

2.5.1. Kaolin clay beneficiation process

A clay suspension with a 20% (w/v) pulp density was utilised. The suspension was leached with oxalic acid of varying concentrations from 0.2 to1.0 with increments of 0.2 at each stage. The resulting suspensions were stirred at room temperature for 30 min. The mixtures were refluxed at different temperatures for different hours. After which, they were filtered and dried at 110 °C for 4 h and then finally heated at 425 °C for 4 h. The filtrate was collected for each suspension, and iron oxide was estimated using absorption spectroscopy (AAS). The clay samples were then collected and packaged for physiochemical analysis.

2.5.2. Sodium bentonite clay beneficiation process

Beneficiation of sodium bentonite clay was done by sodium sulphide-oxalic acid method. A clay suspension with a 20% (w/v) pulp density was utilised. However, to determine the optimum dosage of sodium sulphide to oxalic acid, their composition ratio was varied from 0.2 to 1.0 with an increment of 0.2 at each stage. The amount of oxalic acid was fixed at 10%, whereas the sodium sulphide was varied in each case. The resulting suspensions were stirred at room temperature for 30 min, and a varying concentration of sodium sulphide-oxalic acid solution was added to each sample with vigorous stirring. The pH of the suspensions was maintained at about 7.50–8.50 employing 10% (w/v) NaOH.

The resulting mixtures were refluxed at different temperatures for different hours. About 25 ml of 0.1 M HCl was added to accelerate the leaching of iron. The suspension was cooled, filtered and washed to free excess sodium sulphide-oxalic acid and chloride ions. The clay residue was dried in an air oven at 120 °C for 4 h and then finally heated at 425 °C for 4 h. The filtrate was collected for each suspension, and iron oxide was estimated using atomic absorption spectroscopy (AAS). The clay samples were then collected and packaged for physiochemical analysis.

2.6. Physical and chemical property tests

Various tests as highlighted in Section 2.3 were also carried out on the beneficiated clay to compare selected physical properties attributed to fillers.

3. Results and discussion

3.1. Physical and chemical properties tests on crude mineral clay

The physical and chemical property tests conducted on both indigenous and foreign clay samples (Kaolin and Bentonite) include particle shape, density, viscosity, melting point, pH, particle size, specific surface area, cation exchange capacity and high-temperature reactions. For particle shape, comparison between both samples was made using a scanning electron microscope (SEM). Fig. 2A and B compares the SEM image for both foreign and local kaolin clays respectively and reveals a clear kaolin clay particle with a flake shape labelled (3.) and (1.) Fig. 2C which represents the local bentonite sample reveals a blurry disk-like particle shape labelled (5.) while 2D reveals a clear disk-like particle shaped labelled (7.)

Fig. 2, in general, reveals that all raw clays have particle shapes and suits the American Petroleum Institute standard for fillers, as highlighted in table 1. From Table 1, it is also observed that indigenous and foreign kaolin and bentonite clays possess other similar physical properties ranging from density to specific surface area. The same is for their chemical properties

3.2. X-ray fluorescence (XRF) analysis on indigenous and foreign clay samples

The XRF analysis on the indigenous and foreign kaolin and sodium bentonite clay samples are shown in Table 2. From the table, it is observed that foreign and indigenous (kaolin and bentonite) clays possess similar chemical constituents with their weight % varying slightly.

Based on the results obtained from the physical and chemical property tests and the XRF analysis, it can be concluded that indigenous kaolin and bentonite clay can serve as a substitute for foreign clay in its use as a filler for the catalyst in the FCCU. However, the similarity in physiochemical properties and mineralogical compositions is not enough to back up this claim. According to literature, the presence of iron oxide in clays hinders its usability in the industry. As seen in Table 2, the results show the presence of iron oxides (5.62%. 2.03%) and (9.84%, 9.43%) in both the kaolin and sodium bentonite clay samples. Hence, the need for the removal of the iron oxide impurity through the more efficient wet beneficiation process for further analysis to be conducted. The table also indicates that the raw clay sample is ferric in nature due to the high presence of iron oxide compared with that of potassium

3.3. Results of wet beneficiation process

For the wet beneficiation process, three parameters; reaction time, temperature and reagent dosage were varied to determine the most effective method to use while trying to rid indigenous and foreign sodium bentonite and kaolin clay samples of their iron oxide impurities.

3.3.1. Effect of reaction time

The effect of reaction time on the removal of iron oxide from the indigenous kaolin and sodium bentonite clay samples is shown in Fig. 3. For kaolin clay, a reflux treatment method was used. About 74% removal of iron oxide was noticed at 8 h reaction time. Further increase in reaction time did not affect iron oxide removal. For sodium bentonite clay, a treatment of sodium sulphide and oxalic acid was used. This resulted in about 72% removal of iron oxide at 6 h reaction time. Further increase in the reaction time had no effect on the removal of iron.

The effect of reaction time on the removal of iron oxide from the foreign kaolin samples by reflux treatment and sodium bentonite samples by treatment of sodium sulphide and oxalic acid is presented in also presented in Fig. 3. About 80% removal of iron oxide was noticed at 8 h reaction time for kaolin clay. Further increase in reaction time did not affect the removal of iron oxide. For sodium bentonite clay, the effect of reaction time on the removal of iron oxide was about 79% at 8 h reaction time. Further increase in the reaction time did not affect the removal of iron oxide.
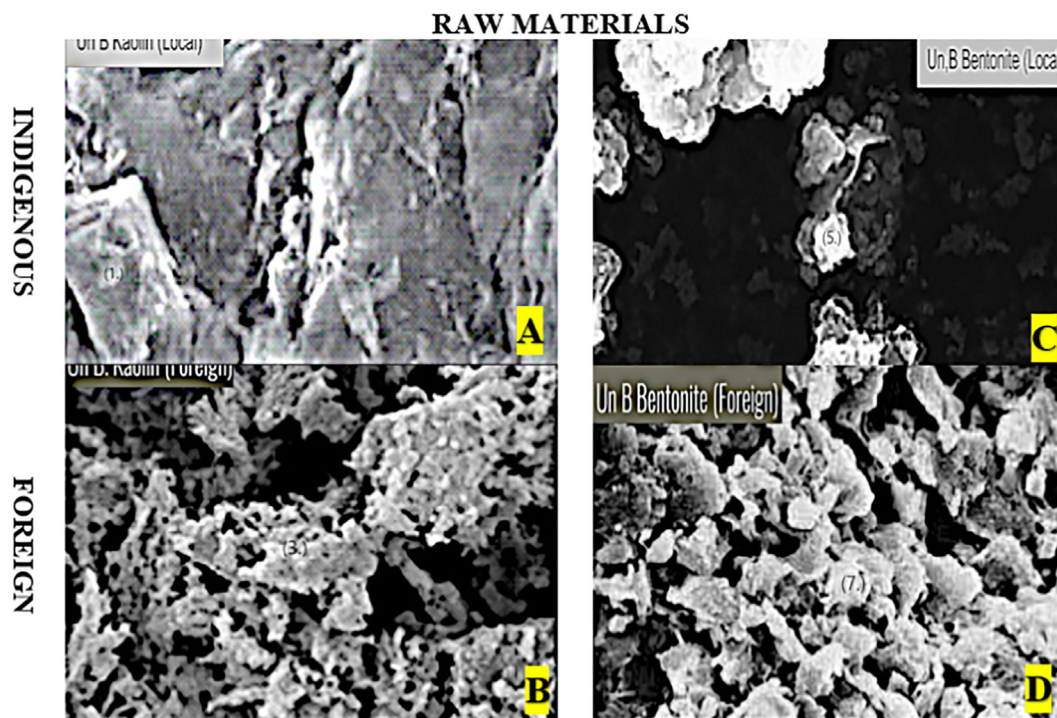
Fig. 2 SEM Images of Crude Mineral Clay. A: Indigenous Kaolin (Un-beneficiated), B: Foreign Kaolin (Un-beneficiated), C: Indigenous Bentonite (Un-beneficiated) and D: Foreign Bentonite (Un-beneficiated).

Table 2 XRF Analysis – Indigenous and Foreign Kaolin and Sodium Bentonite Clay Samples.

Chemical Constituents (Wt. %)	Kaolin Clay		Bentonite Clay	
	Indigenous	Foreign	Indigenous	Foreign
SiO_2	58.50	57.01	48.67	50.34
Al_2O_3	16.62	30.7	16.56	18.80
Fe_2O_3	5.62	2.03	9.84	9.43
TiO_2	0.90	1.27	0.90	0.60
CaO	1.14	0.03	1.04	0.12
P_2O_5	0.10	0.08	1.06	1.09
K_2O	1.50	3.65	2.58	0.04
MnO	0.01	0.08	0.01	0.03
MgO	2.09	0.55	2.75	1.14
Na_2O	1.07	0.30	1.23	1.21
LOI	12.35	4.11	14.32	15.20
TOTAL	99.9	99.81	98.96	98.0

3.3.2. Effect of temperature

The effect of temperature on the removal of iron oxide from the indigenous kaolin samples by reflux treatment and sodium bentonite samples by treatment of sodium sulphide and oxalic acid is shown in Fig. 4. For kaolin, the temperatures were varied in a water bath at 30, 50, 70, 90, 110 °C. About 72% removal of iron oxide was noticed at 110 °C at a constant 8-hour reaction time. For sodium bentonite clay, other variables were kept constant (reaction time 8 h and 0.8:1.0 ratio of sodium sulphide to oxalic acid) and the experiment was conducted at different temperatures of 30, 50, 70, 90 and 110 °C. It was observed that at approximately 90 °C, 60% of iron oxide was removed from the samples, and there was no drastic change beyond that temperature.

The effect of temperature on the removal of iron oxide from the foreign kaolin samples by reflux treatment varying the temperatures in a water bath at 30, 50, 70 90 and 110 °C is also presented in Fig. 4. About 82% removal of iron oxide was noticed at 90 °C at a constant 8-hour reaction time. The effect of temperature on the removal of iron oxide from the foreign bentonite samples by treatment of sodium sulphide and oxalic acid is also shown in Fig. 4. Keeping other variables constant (reaction time 8 h and 0.8:1.0 ratio of sodium sulphide to oxalic acid) the experiment was conducted at different temperatures of 30, 50, 70, 90 and 110 °C. It was observed that at approximately 92 °C, 75% of iron oxide was removed from the samples, and there was no drastic change beyond that temperature.Comparing the results obtained for kaolin clay, the
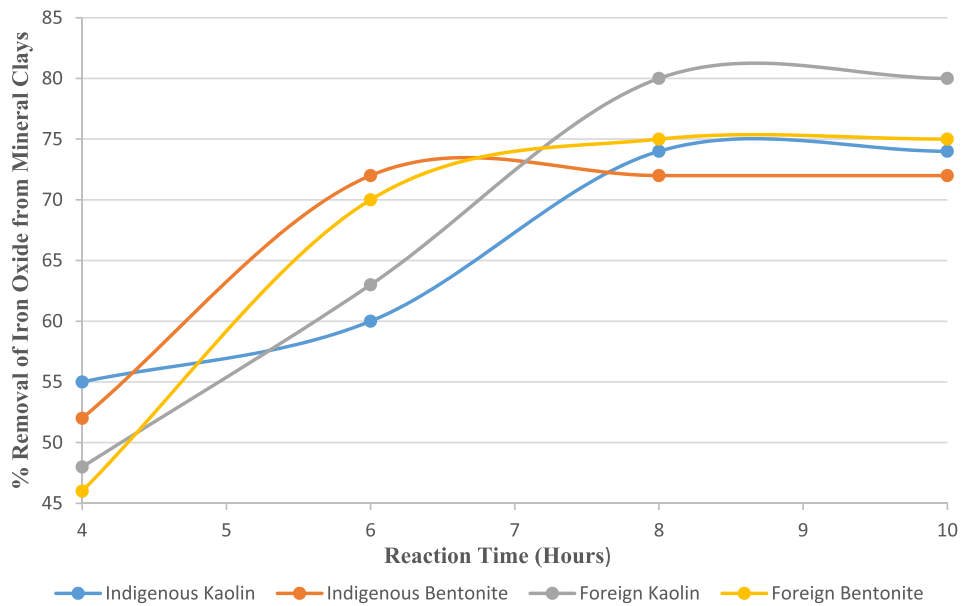
Fig. 3 Effects of Reaction Time on Raw and Beneficiated Clays.
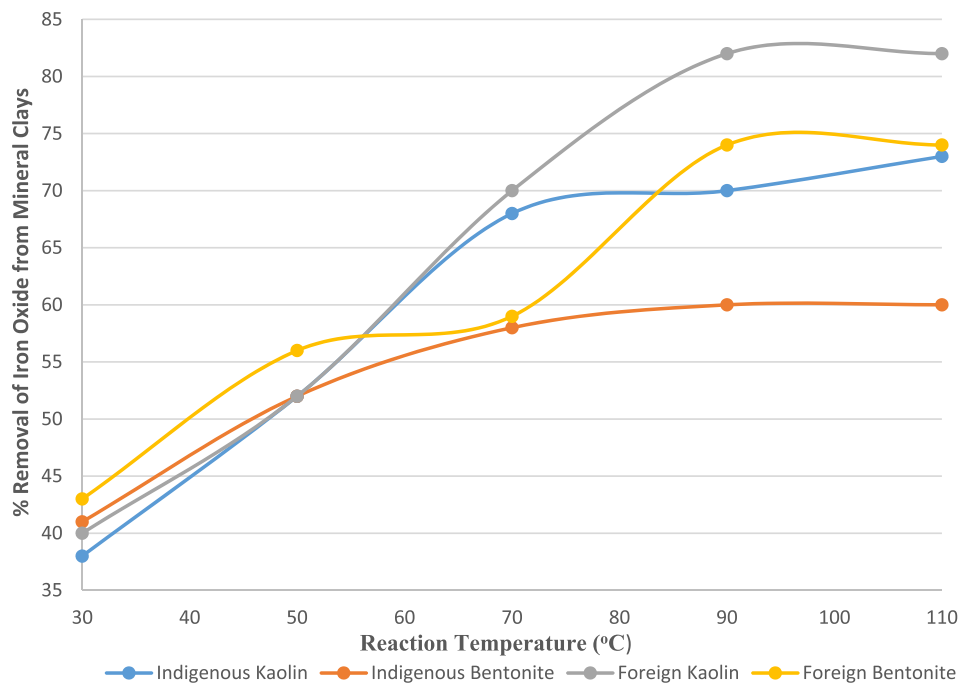

Fig. 4 Effects of Reaction Temperature on Raw and Beneficiated Clays.

indigenous clay had 72% removal of iron oxide at 110 °C while the foreign kaolin clay, 82% removal also at 110 °C.

3.3.3. Effect of reagent dosage

The effect of reagent dose (ratio of sodium sulphide to oxalic acid) on the removal of iron oxide from both the indigenous and foreign sodium bentonite samples is shown in Fig. 5. Different amounts have been tested where it is observed that the maximum removal of iron oxide was obtained at a ratio of 0.8:1.0 of sodium sulphide to oxalic acid for the indigenous clay. Removal of approximately 69% was obtained. The

beneficiation of kaolin clay does not require any reagents. Hence, the absence of its representation in Fig. 5.

For the foreign sodium bentonite samples, it is observed that the maximum removal of iron oxide was obtained at a ratio of 0.8:1.0. Removal of approximately 80% was obtained. It should be noted from previous studies that sudden stagnation in iron oxide impurities during the beneficiation process is not new. Singh and Sharma [27] noticed a static phase after 70% and 72% of iron oxide impurity was removed from low-grade Indian bentonite clay at 7 h and 100 °C respectively. In terms of the ratio of sodium sulfide to oxalic acid, 0.8:1.0
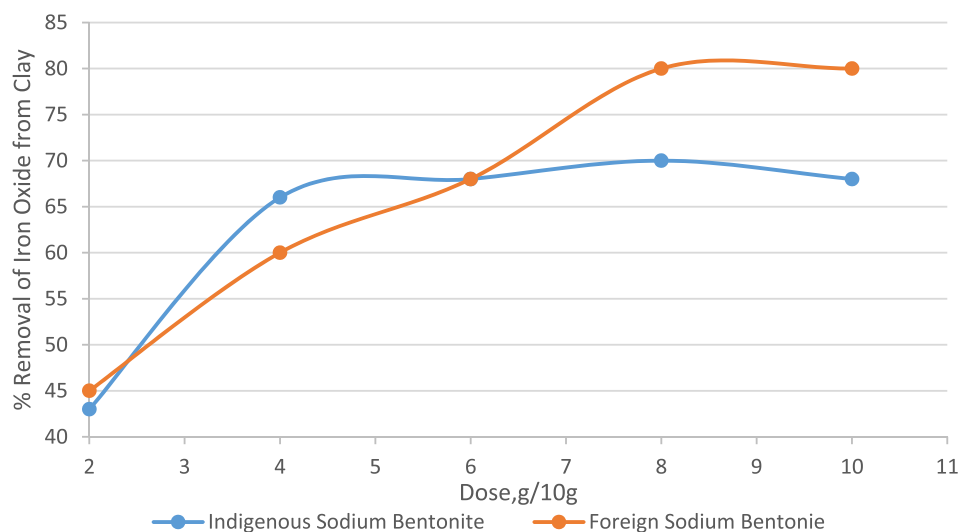
Fig. 5 Effects of Reagent Dosage on Indigenous and Foreign Sodium Bentonite Clays.

seemed capable as it recorded a peak value of 60% iron oxide removal. Gougazeh [32] also achieved a 94% iron oxide removal from Jordanian kaolin clay using sodium dithionite while Hernandez et al., [33] successfully removed 80% iron oxide from kaolin clay using an oxalic acid solution.

3.4. Product characterisation

The absence of the iron oxide impurity in the clays led to the clay possessing different physiochemical properties. The results of the analysis are also highlighted in Table 1, where it is observed that the physical and chemical properties of the clays improved. After beneficiation, an XRF analysis was also conducted on the beneficiated clay samples. The results show that the iron oxide present in the indigenous and foreign clays were reduced to (1.41%, 0.42%) for kaolin clay and (2.77%, 2.84%) for bentonite clay respectively. The beneficiation helped reduce the density and particle size while an increase in viscosity, melting points, specific surface area and the cation exchange capacity of the clays were observed.
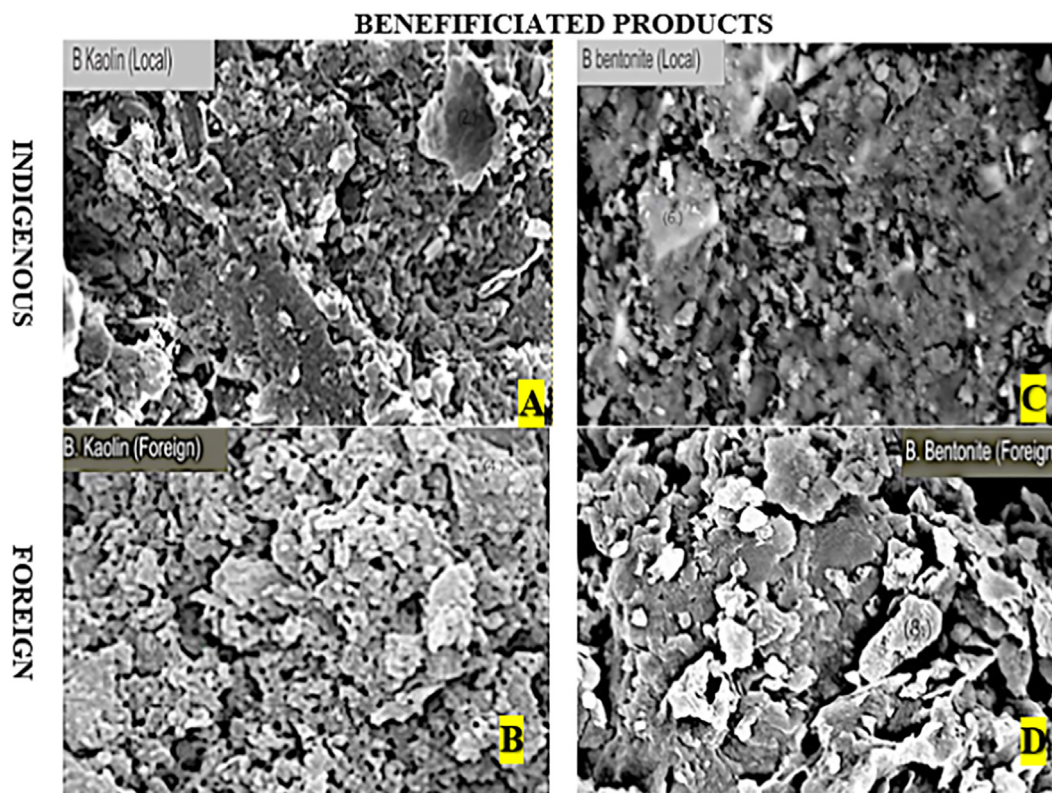

Fig. 6 SEM Images of Crude Mineral Clay. A: Indigenous Kaolin (Beneficiated), B: Foreign Kaolin (Beneficiated), C: Indigenous Bentonite (Beneficiated) and D: Foreign Bentonite (Beneficiated).
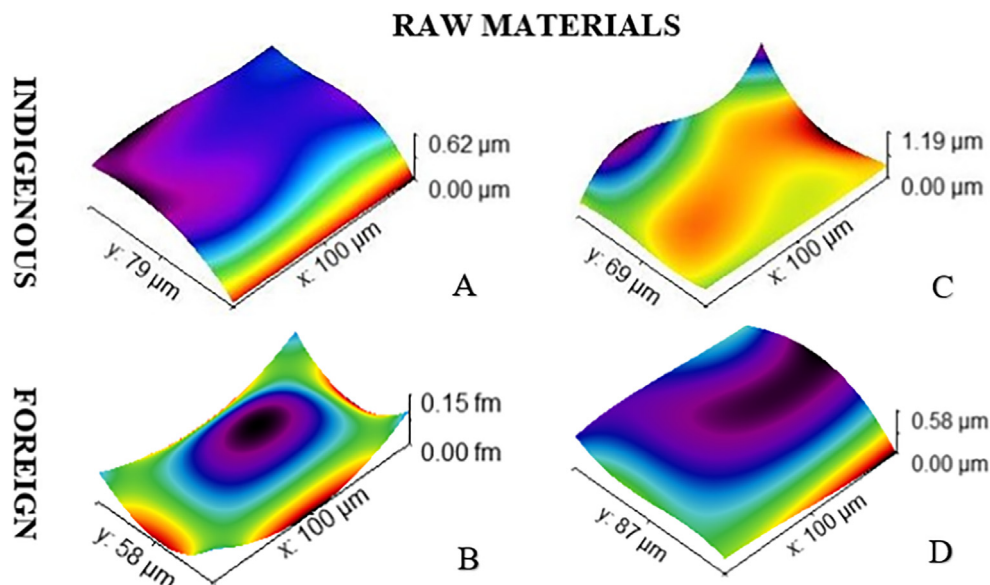
Fig. 7 Structural Analysis of Raw Mineral Clays. A: Indigenous Kaolin (Un-beneficiated), B: Foreign Kaolin (Un-beneficiated), C: Indigenous Bentonite (Un-beneficiated) and D: Foreign Bentonite (Un-beneficiated).

The particle shape of the kaolin and bentonite clay also improved. Fig. 6A is the SEM image of the beneficiated indigenous kaolin clay sample. It reveals a clear kaolin clay particle with a flake shape. The particles, although the same shape appear smaller and more defined, which is owing to the beneficiation process. The same observation applies for the foreign kaolin clay, as seen in Fig. 6B. Fig. 6C is the SEM image of the beneficiated indigenous bentonite clay sample. It reveals a clear disk-like particle shape labelled (6.) which appears clearer than the clay samples that were not beneficiated. A similar observation applies for the foreign bentonite clay sample, as seen in Fig. 6D.

Also, in comparison with the API standards for fillers in the petroleum industry as given in Table 1, it is seen that after the beneficiation process, like foreign clay, indigenous clay meets all the standards.

3.5. Structural analysis of raw and beneficiated product

In this section, the structural effect of the beneficiated process on indigenous kaolin and bentonite was carried out. This was done using computational processing of the scanning electron microscopy images. Fig. 7 shows the 3D structural display of the background content of un-beneficiated mineral clays. The process involves generating the fits data of the SEM image by a polynomial of the given order and subtracts this polynomial to give the background of the SEM image. The fitted polynomial is gotten through equation (1)

$$\sum_{j}^{m} \sum_{k}^{n} a_{j,k} x^{j} y^{k} \tag{1}$$

where a is the projected area of the SEM image, m and n are the selected horizontal and vertical polynomial degrees, x and y are the dimensions of the image, j and k are the directions.

The 3D structural display of the background content describes the tendencies of the cation exchange capacity of the material clay with its grain size. Due to the smaller grain size of un-beneficiated foreign bentonite (table 3, Fig. 7D), it has a compact arrangement of its particulates within a thickness of 0.58 μm. This means there are fewer gaps in its structural formation. In the other hand, the indigenous un-beneficiated bentonite has larger grain size and full thickness of 1.19 μm. This means that there are more significant gaps in the structural formations of the indigenous un-beneficiated bentonite (Fig. 7C).

It is observed that unlike the structural information in bentonite, the un-beneficiated kaolin has more unique features. The indigenous un-beneficiated kaolin (Fig. 7A) has a smaller grain size. However, it occupies a higher thickness of 0.62 μm while the foreign un-beneficiated kaolin has a larger grain size but are arranged within a low thickness of 0.15 fm. Hence, the particulates in the foreign un-beneficiated kaolin are compact (Fig. 7B). However, comparing the results with Table 1, it is observed that the determination of the cation exchange capacity is not determined by the compact nature of the material structure but on the grain size of the material.

Table 3 Grain Size Variation for the Different Mineral Clays.

| Mineral Clay	Grain size (nm)	Mineral Clay	Grain size (nm)
Un-beneficiated Indigenous Kaolin	194.463	Beneficiated Indigenous Kaolin	232.359
Un-beneficiated Foreign Kaolin	333.766	Beneficiated Foreign Kaolin	212.590
Un-beneficiated Indigenous Bentonite	286.204	Beneficiated Indigenous Bentonite	205.793
Un-beneficiated Foreign Bentonite	269.459	Beneficiated Foreign Bentonite	263.458

BENEFICIATED PRODUCTS
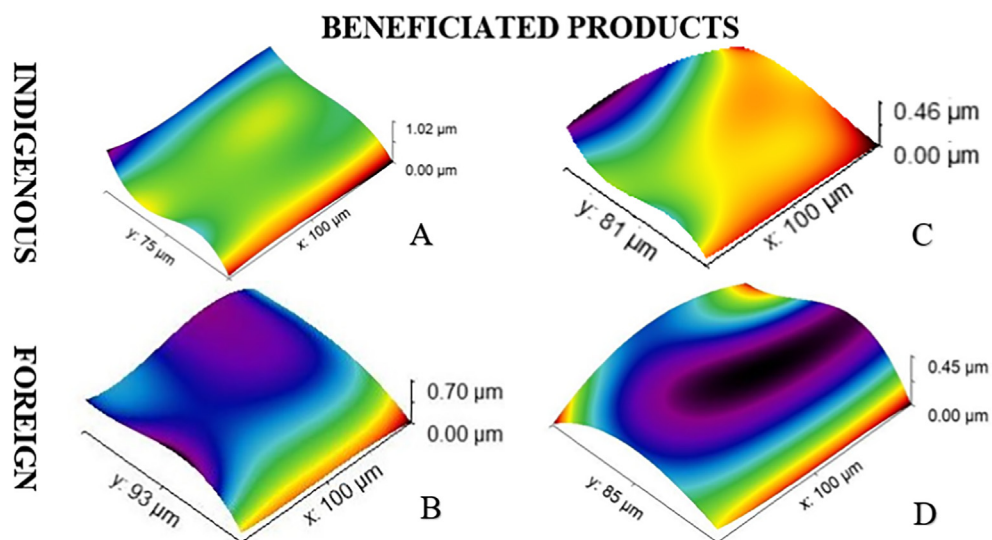
Fig. 8 Structural Analysis of Beneficiated Mineral Clays A: Indigenous Kaolin (Beneficiated), B: Foreign Kaolin (Beneficiated), C: Indigenous Bentonite (Beneficiated) and D: Foreign Bentonite (Beneficiated).

It is also observed that the beneficiated processes do affect not only the grain size of the product but also its structural content. For example, the beneficiated kaolin is presented in Fig. 8A and B.

It is observed that while the grain size of the foreign beneficiated kaolin significantly decreased, the indigenous beneficiated kaolin grain wise increased significantly (Table 3). However, the salient question is: what is the impact of structural arrangement in determining the quality of the product? First, it is observed that while the thickness of beneficiated kaolin increased, the foreign beneficiated kaolin had a significant increase in its thickness. This means that the structural arrangements of the particulates are significantly affected (Fig. 8A and B). For example, the beneficiated processes increased the grain size of indigenous kaolin by 16.3% with a significant 44.4% increase in the cation exchange capacity. On the other hand, the beneficiated processes decreased the grain size of foreign kaolin by 36.3% with a significant 20% increase in the cation exchange capacity. Hence, it is clear, that aside from the magnitude of the particulate grain size, the structural formation has a significant effect on the product quality.

The 3D display of the background content of beneficiated foreign and indigenous bentonite is presented in Fig. 8B and 8C. It is observed that the beneficiated process did not significantly affect the structure of foreign bentonite. However, the beneficiated process significantly influenced the particulate distribution and grain size of the indigenous bentonite. Lastly, it is observed that though the indigenous beneficiated bentonite increased by 51.8%, structural modifications have significant influence like the increase or decrease of particulate grain size on the product.

4. Conclusion

This study shows that sodium bentonite and kaolin clay from Auchi Edo state Nigeria can be improved on for FCCU fillers application. Although potassium and magnesium oxides exist in the crude mineral clay, Fe_2O_3 contributed the most substantial amount of impurities for both local and foreign clay. Reaction time at 8 h seems to be the most effective parameter for the wet beneficiation process as a reduction of iron oxide impurities from (5.62%, 2.03%) to (1.42%, 0.42%) for local and foreign kaolin clay was recorded. Simultaneously, Fe_2O_3 was also reduced from (9.84%, 9.43%) to (2.77%, 2.84%) for local and foreign-based bentonite clay. The beneficiation process also helped in reducing the density, particle size for the crude clay while viscosity, melting point, specific area and cation exchange capacity were increased. A clearer disk-like particle shaped was also observed at the final SEM evaluation. All properties conformed to the API standard for filler preparation. It was observed that, aside from the increase or decrease of particulate grain size, the structural modifications also have a significant influence on the product.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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