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Bio/fossil fuels refining Appraisal of the Elemental distributions, SiO_4 /AlO_4 and Si/Al Ratios of Itu Virgin Kaolin

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Abstract: There is some evidence from the literature supporting the abundant deposit of untapped kaolin clay in various locations in Itu, Akwa Ibom State, Nigeria. Due to some established industrial applications of kaolin including catalysis, adsorption, ceramics, paper production, coating, plastic fillers, paint extenders, cement and ion-exchangers among others, the need to explore their presence in a given environment and the grade of kaolin present is necessary. Consequently, the present study is designed to evaluate the composition and implications of this mineral in the stated environment concerning their SiO_4 /AlO_4 and Si/Al ratios and also the elemental distributions in Itu virgin kaolin framework The results from the XRF analysis indicated varying concentrations of SiO_2, Fe_3O_2, K_2O, Al_2O_3, TiO_2 and TiO_2 with O, Al, Si, K, Ti, Fe, and Fe as the major chemical compounds. The calculated molar ratio of SiO_2/Al_2O_3 and Si/Al were found to be 2.244: 2.690 and 3.564:2.052, respectively. Based on these results there high tendency that the samples can be modified to form zeolite for biofuel purification.

Keywords: *Kaolin, calcination, silica (sio_2), alumina (Al_2O_3), zeolite*

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1.0 Introduction

The name kaolin was derived from a hill in China (Kao-ling) where it was mined for centuries (Jamo *et al.*,2014). Kaolin is a significant raw material with widespread application in the industrial arena including water treatment, porcelain, cement and ceramics production (Lima *et al.*, 2017), fillers for polymer, paint and rubber (Kotal *et al.*,2015). Kaolin is also used as a catalyst (Li *et al.*, 2018), decolourization agent (Worasith *et al.*,2011), ceramics, paper coating, plastic fillers, paint extenders, and cement (Shafiq *et al.*,2015). The largest use of kaolin as catalyst substrate is in the catalytic cracking of petroleum. The purity of the kaolin is critical in petroleum cracking operations. It is estimated that over 200,000 tons of kaolin are used annually to produce petroleum-cracking catalysts (Murray, 2007).

Kaolins are characteristically a class of crystalline or amorphous microporous aluminosilicate materials that contain SiO_4 /AlO_4, and Si/Al as major chemical components. The exceptional porous structures, strong Bronsted acidity, molecular-level shape selectivity, exchangeable cations, and high thermal/hydrothermal stability make kaolin suitable for the production of zeolites. Zeolites are widely used as coating materials, catalysts, adsorbents, and ion exchangers in industry. Ubuo *et al.*,2023). The activity, selectivity, stability and durability of zeolites in applications are closely related to their Si/Al ratios and Al distributions in the framework (Jialiang Li *et al.*, 2022). The demand for zeolite globally as of 2012 was projected at USD 12.6 billion and may increase in the coming years. There are numerous untapped kaolin clay deposits scattered in various locations in Itu, Akwa Ibom State, Nigeria. Indigenous innovation and ingenuity in harnessing our natural resources is the key to science and technological development and sustainability (Udo *et al.*, 2020). Also, the quest for a sustainable clean environment and biodegradable chemicals in processing fuels is of high necessity because of environmental concerns (Udo *et al.*, 2020). kaolinite zeolite is green, abundant and cut-rate. Owing to the availability and numerous industrial applications of kaolin in catalysis, adsorbent, ceramics, paper coating, plastic fillers, paint extenders, cement and ion exchangers. Naturally occurring zeolite is important in many industrial processes due to its environmentally benign nature, low cost and its relative abundance compared to deleterious, expensive and imported synthetic zeolite. Nigeria has numerous untapped natural kaolin deposits. Unfortunately, for many years now we have experienced protracted increases in prices of petroleum products especially premium motor spirit (PMS) in Nigeria, with adverse economic consequences. This is because of the malfunctioning of all the local refineries in Nigeria, the importation of all petroleum products which are sometimes adulterated (Udo *et al.*, 2023). Also, the urgent demand for industrial revolution in Nigeria especially the petroleum sub-sector of the economy requires exploration of untapped natural resources. It is therefore necessary to conduct modern research in natural deposits e.g. kaolin in our environments. Past research have been conducted researches in Ikot Ebom (Obotowo *et al.*, 2021), and Ikot Ekwere, Ekim, Obong and Mbak in Itu L.G.A. to determine the chemical, physical and mineralogical properties of kaolin clay (Elueze, *et al.*, 1999) but no research had been conducted in Ikot Uso Akpan and Ikot Ukap clay deposits to determine its SiO_4 /AlO_4 and Si/Al ratios and elemental distributions. It is on this basis that the research "Determination of SiO_4 /AlO_4 and Si/Al ratios and elemental distributions in Itu virgin kaolin framework and their implications in bio and fossil fuels refining was conducted. This research will in addition determine the chemical compounds composition of two virgin kaolin samples and the implications of its chemical constituents in its industrial applications especially as a potential zeolite for the purification of biofuel.

2.0 Materials and Methods

The study areas were located at Ikot Uso Akpan Itam and Ekim Itam, Itu Local Government Area, Akwa Ibom State, Nigeria. The study locations have large untapped kaolin deposits. Villages in Itu e.g. Ikot Ebom Itam and Ikot Ekwere Itam communities have a longstanding history of pottery activities that has opened up the locality for its clay potential (Obotowo *et al.,* 2021). Itu Local Government Area is bounded in the North and North-East by Odukpani in Cross River State and Arochukwu in Abia State, in the West by Ibiono Ibom and Ikono L.G.A, in the South and South-east by Uyo and Uruan L.G.A respectively. Itu is located in the tropical rainforest belt of West Africa and lies within a Latitude of 5.203624(5°12'13.05°N) and a longitude of 7.968822(7°58'7.76°E) and altitude of 94 m above the sea level. It has a total land area of about 606.10 square meters (Bassey *et al.,* 2020, Udo *et al.,* 2023)

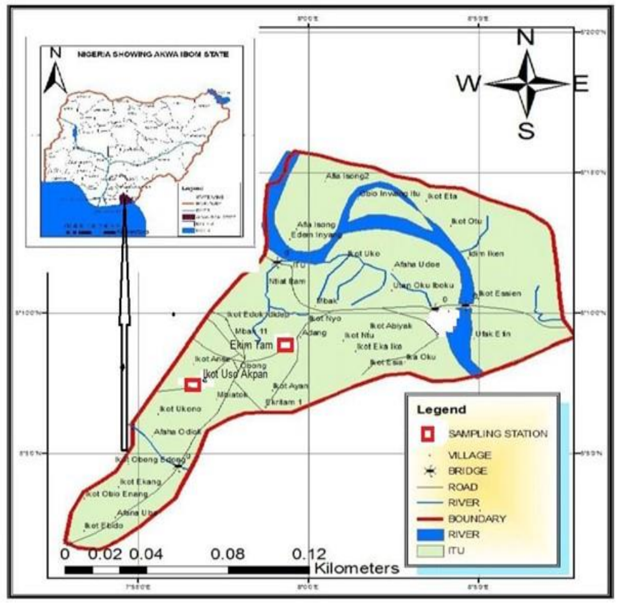

Fig. 1: Map of the study area showing sampling locations

Fig 2. kaolin Clay Sample of Ekim Itam

Fig 3. Kaolin Clay Sample of Ikot Uso Akpan

2.1 Calcination of the acidified kaolin

The acidified -kaolin was oven-dried at 120^{O}C for one (1) hour and calcined at 550^{O}C for two (2) hours in a muffle furnace and later cooled. The calcined kaolin was stored in a lid-tight container and properly labelled. The heating process drives off water from the mineral kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), the main constituent of kaolin clay, and collapses the material structure, resulting in an amorphous aluminosilicate ($Al_2O_3 \cdot 2SiO_2$), metakaolinite. The process is known as dehydroxylation $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O\uparrow$.

2.2 Characterization untreated and calcined kaolin

A unique Ux-30 XRF spectrophotometer was used in analyzing individual elementals and chemical compounds present in the studied materials. The chemical composition of the zeolitic material using XRF is of fundamental importance to determine the SiO_2/Al_2O_3 ratio of materials (Klunk et al, 2020). XRF has been generally applied to determine the Si/Al ratios of zeolites. This is because of the analytical features of XRF investigation which include accuracy, rapidity, multi-element capacity, and non-destructiveness (Pilar *et al*., 2022,; Zhu *et al*., 2022 and Zhang *et al*., 2022 ;Aniedi *et al*., 2020).

3.0 Results and Discussion

The results of the analysis of untreated (raw) kaolin and the calcined kaolin from the study areas (Ikot Uso Akpan Itam and Ekim Itam) are as presented in Tables 1 to 4.

Table 1: Results of X-ray Fluorescence analysis of oxide compositions of kaolin from Ikot Uso Akpan Itam

Untreated			Calcined		
Oxide	**C (mg cm^{-2})**	**Mole %**	**Oxide**	**C (mg cm^{-2})**	**Mole %**
SiO_2	62.898	73.537	SiO_2	63.001	71.832
V_2O_5	0.116	0.045	V_2O_5	0.106	0.041
Cr_2O_3	0.032	0.015	Cr_2O_3	0.069	0.032
MnO	0.027	0.027	MnO	0.013	0.013
Fe_2O_3	1.996	0.878	Fe_2O_3	1.850	0.820
Co_3O_4	0.010	0.003	Co_3O_4	0.005	0.002
NiO	0.010	0.010	NiO	0.007	0.006
CuO	0.041	0.037	CuO	0.028	0.025
Nb_2O_3	0.013	0.004	Nb_2O_3	0.010	0.003
MoO_3	0.001	0.000	MoO_3	0.002	0.001
WO_3	0.000	0.000	WO_3	0.000	0.000
P_2O_5	0.000	0.000	P_2O_5	0.000	0.000
SO_3	0.131	0.115	SO_3	0.198	0.175
CaO	0.310	0.388	CaO	0.336	0.423
MgO	0.000	0.000	MgO	0.000	0.000
K_2O	2.270	1.693	K_2O	2.163	1.624
BaO	0.173	0.079	BaO	0.113	0.052
Al_2O_3	28.764	19.817	Al_2O_3	31.017	21.523
Ta_2O_5	0.027	0.004	Ta_2O_5	0.027	0.004
TiO_2	2.437	2.143	TiO_2	2.220	1.967
ZnO	0.018	0.015	ZnO	0.010	0.009

Ag_2O	0.008	0.002	Ag_2O	0.007	0.002
Cl	0.551	1.092	Cl	0.686	1.369
ZrO_2	0.166	0.095	ZrO_2	0.131	0.075
SnO_2	0.000	0.000	SnO_2	0.000	0.000

Table 2: Result of elemental composition of the kaolin samples from Ikot Uso Akpan Itam.

Untreated		Calcined	
Element	**C (mg cm^{-2})**	**Element**	**C (mg cm^{-2})**
O	49.319	O	49.250
Mg	0.000	Mg	0.000
Al	15.224	Al	16.416
Si	29.401	Si	28.515
P	0.000	P	0.000
S	0.053	S	0.079
Cl	0.551	Cl	0.686
K	1.885	K	1.795
Ca	0.222	Ca	0.240
Ti	1.461	Ti	1.331
V	0.065	V	0.060
Cr	0.022	Cr	0.048
Mn	0.021	Mn	0.010
Fe	1.396	Fe	1.294
Co	0.007	Co	0.004
Ni	0.008	Ni	0.005
Cu	0.033	Cu	0.022
Zn	0.014	Zn	0.008
Zr	0.123	Zr	0.097
Nb	0.011	Nb	0.008
Mo	0.000	Mo	0.001
Ag	0.007	Ag	0.006
Sn	0.000	Sn	0.000
Ba	0.155	Ba	0.101
Ta	0.022	Ta	0.022
W	0.000	W	0.000

Table 3: Results of chemical compounds of the kaolin from Ekim Itam.

	Untreated			Calcined	
Oxide	**C (mg cm^{-2})**	**Mole %**	**Oxide**	**C (mg cm^{-2})**	**Mole %**
SiO_2	60.572	71.533	SiO_2	60.761	71.336
V_2O_5	0.165	0.064	V_2O_5	0.119	0.046
Cr_2O_3	0.033	0.016	Cr_2O_3	0.070	0.033
MnO	0.039	0.039	MnO	0.020	0.020
Fe_2O_3	2.575	1.144	Fe_2O_3	2.356	1.048
Co_3O_4	0.012	0.003	Co_3O_4	0.005	0.002
NiO	0.008	0.007	NiO	0.007	0.007
CuO	0.038	0.034	CuO	0.034	0.031
Nb_2O_3	0.017	0.005	Nb_2O_3	0.017	0.005
MoO_3	0.000	0.000	MoO_3	0.003	0.002
WO_3	0.000	0.000	WO_3	0.000	0.000
P_2O_5	0.000	0.000	P_2O_5	0.065	0.032
SO_3	0.123	0.109	SO_3	0.116	0.103
CaO	0.273	0.345	CaO	0.621	0.786
MgO	0.134	0.237	MgO	0.000	0.000
K_2O	1.999	1.506	K_2O	2.037	1.536
BaO	0.165	0.076	BaO	0.132	0.061
Al_2O_3	30.148	20.980	Al_2O_3	30.579	21.296
Ta_2O_5	0.021	0.003	Ta_2O_5	0.033	0.005
TiO_2	2.859	2.540	TiO_2	2.657	2.363
ZnO	0.022	0.019	ZnO	0.014	0.012
Ag_2O	0.010	0.003	Ag_2O	0.006	0.002
Cl	0.618	1.237	Cl	0.592	1.185
ZrO_2	0.167	0.096	ZrO_2	0.155	0.090
SnO_2	0.000	0.000	SnO_2	0.000	0.000

The results of analysis of untreated (raw) kaolin from the two study locations indicated varying concentrations (mg cm^{-2}) of: SiO_2(62.898), Fe_3O_2(1.996), K_2O(2.270), Al_2O_3(28.764), TiO_2(2.437) and SiO_2(60.572), Fe_3O_2(2.575), K2O(1.999), Al2O3(30.148), TiO2(2.859) as the major chemical compounds Tables 1 and 2. The concentrations (mg cm^{-2}) of major individual chemical elements compositions in untreated (raw) kaolin from the two study locations were O(49.319), Al(15.229), Si(29.401), K(1.885), Ti(1.461), Fe(1.396) and O(49.019), Al(15.956), Si(28.401), K(1.885), Ti(1.660), Fe(1.801) respectively Table 2 and Table 4. Udochukwu *et al.*, 2019 reported that an

alumina content of 28.52% is a potential source of alumina (aluminium)

Also, the concentrations of major chemical compounds in calcined kaolin sample from Ikot Uso Akpan Itam and Ekim Itam were SiO_2(63.001), Fe_3O_2(1.850), K_2O(2.163), Al_2O_3(30.579), TiO_2(2.220) and SiO_2(60.761), Fe_3O_2(2.356), K_2O(2.037), Al_2O_3(31.017), TiO_2(2.657) as shown in Tables 1 and 2 respectively However, the elemental concentrations of CK from Ikot Uso Akpan and Ekim Itam were O(49.250), Al(16.416), Si(28.515), K(1.795), Ti(1.461), Fe(1.331), Fe(1.294) and O(49.099), Al(16.184), Si(28.215), K(1.795), Ti(1.593), Fe(1.294) respectively Table 2 and Table 4. The analysis also indicated a slight increase in concentrations of to SiO_2, Fe_2O_3, Al_2O_3, TiO_2 in the calcined kaolin when compared with untreated kaolin samples Tables 2 and 4

Table 4: Results of chemical compounds of the kaolin from Ekim Itam

	Untreated		**Calcined**
Element	**C (mg cm^{-2})**	**Element**	**C (mg cm^{-2})**
O	49.091	O	49.099
Mg	0.081	Mg	0.000
Al	15.956	Al	16.184
Si	28.314	Si	28.215
P	0.000	P	0.000
S	0.049	S	0.047
Cl	0.618	Cl	0.592
K	1.660	K	1.795
Ca	0.195	Ca	0.240
Ti	1.714	Ti	1.593
V	0.093	V	0.060
Cr	0.023	Cr	0.048
Mn	0.030	Mn	0.010
Fe	1.801	Fe	1.294
Co	0.008	Co	0.004
Ni	0.006	Ni	0.005
Cu	0.030	Cu	0.022
Zn	0.017	Zn	0.008
Zr	0.124	Zr	0.097
Nb	0.013	Nb	0.008
Mo	0.000	Mo	0.001
Ag	0.010	Ag	0.006
Sn	0.000	Sn	0.000
Ba	0.148	Ba	0.101
Ta	0.017	Ta	0.022
W	0.000	W	0.000

The kaolin samples contained mostly kaolinite minerals and quartz (silica). Calcination at varying temperatures collapses the crystalline nature of kaolin (Udochukwu *et al*, 2019). Calcination increases the reactivity of kaolinite (Adamu *et al.*, 2022). Metakaolin (anhydrous alumino-silicate) is the final product of calcination. The amorphous structure of metakaolin gives it enormous reactive possibilities when it is activated in an alkali solution Elimbi 2011. The results of the

investigation of kaolin presented that SiO_2 and Al_2O_3 were the major chemical components in both untreated and calcined with a small amount of other chemical compounds in both untreated and calcined kaolin. The mole ratio of SiO_2: Al_2O_3 and Si: Al in the calcined kaolin were 2.244: 2.690 and 3.564: 2.052 respectively. And Si/Al for UNTK for the samples was 2.18 and 2.01. The Si/Al ratio of 2 was recorded for the two CK samples. There was an increase in Si/Al after calcination. This implies that the dealumination had taken place during calcination at 600 ^oC. Dealumination (deduction of aluminium) concentration in Y-zeolite will produce ultra-stable Y-zeolite with higher hydrothermal stability and good catalytic performance in fluid catalytic cracking (FCC) Jialiang Li *et al.*, 2022. Zeolites can be categorized concerning the Si: Al and SiO_2:Al_2O_3 ratio. Low silica zeolite occurs if Si:Al mole ratio = 1:2 and SiO_2:Al_2O_3 mass ratio = 1.18: 2.35 Cheng et al, 2019. In Y-zeolite, high-silica" corresponds to Si/Al ratios of >3, "Al-rich" corresponds to Si/Al ratios of <3 but >1.5, which is a criterion for X and Y zeolites (Gua *et al.*, 2022). From related works, (Jialiang Li *et al.*,), 2022, (Oleksiak et al, 2017), (Meng *et al.,* 2021) and Cheng et al, 2019, the studied kaolin samples are Al-rich which corresponds to Si/Al ratio < 3. The concentrations of SiO_2 and Al_2O_3 must be the major chemical components for a good zeolite (Musyoka *et al.*, 2009), (Klunk *et al.*, 2020). The corresponding molar ratio of SiO_2/Al_2O_3 and Si/Al in the studied kaolin infers that the kaolin sample may produce a better Y-zeolite and X-zeolite with higher activity, selectivity, stability, durability of zeolites with higher surface area after careful modifications. Zeolites can be categorized concerning the Si/Al ratio. The calcination process collapses the material structure, resulting in amorphous aluminosilicate ($Al_2O_3.SiO_2$) to produce Metakaolinite. According to (Cheng *et al.*, 2022) amount of acid, time of treatment, and temperature could effectively affect the SiO_2/Al_2O_3 ratio of natural zeolite. Clay samples from southern Nigeria are mostly kaolinite clay, leaching with acid and calcination can improve the mineral composition and quality of the clay.

4.0 Conclusion

The results of the investigation presented that SiO_2, Al_2O_3, Si and Al were the major chemical components detected by XRF in both untreated and calcined samples from the study areas. The mole ratio of SiO_2/Al_2O_3 and Si/Al in untreated and calcined kaolin samples indicated the studied kaolin samples were Al-rich kaolin. Also, the molar ratio of SiO_2/Al_2O_3 and Si/Al in the studied kaolin indicates that with proper dealumination, the investigated kaolin sample can produce an excellent zeolite with higher activity, selectivity, stability and higher surface area. Furthermore, the molar ratio of SiO_2/Al_2O_3 (2.244: 2.690) and Si/Al (3.564:2.052) as revealed in this investigation implies the investigated kaolin can be used as low silica zeolite with high hydrophilicity and relatively stronger interaction with polar molecules like water. But with proper dealumination, a high hydrophobicity zeolite can be obtained with relatively stronger interaction with nonpolar molecules, higher hydrothermal stability and good catalytic performance.

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All data used in this study will be readily available to the public.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data public.

Competing interests

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