A Study on the Viability of Selected Eastern Nigeria Clays as Oil Bleaching Substitute for Foreign Clays (Bentonite)

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ABSTRACT

An investigation into the absorptivity of selected clays:- Ukpor,Nteje (in Anambra State), Inyi,Ekulu (in Enugu State)have been done in June 2017.The result obtained when U.V Spectrophotometer (Spectrum Lab 21A) at 350nm and maximum absorbance of 0.6664 was used show that absorptivity of the Palm Oil by the clays is in the order of: Bentonite > Inyi > Nteje > Ekulu > Ukpor. With Mesh, the clays were sieved into particle sizes of 425µm, 1000µm and 2000µm.It was observed that as the particle size of the clays increased, the absorption capacity decreased. (425µm had higher absorptivity than others) Metal characterization of the clays was also done using Energy Dispersive X-Ray Fluorescence Technique. Measurements were performed using an annular 25 millicurie ^{109}Cd as excitation source, that emits Ag-K X-rays (22.1KeV). As many as twenty eight(28) elements were present in each clay sample. Iron (Fe)had the highest concentration of 6.86%. The average metal concentration as observed is specified thus:Inyi > Nteje > Ekulu > Ukpor Inyi clay is therefore recommended as equivalent clay to Bentonite .Vegetable Oil industries can therefore utilize the four sampled clays for increasing the quality of their Oils which may have been done using other chemical methods which may be hazardous to health

Keywords: Absorbance, Base-Exchange Equivalence, *Bentonite* ***Clay mesh; .***

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1.0 INTRODUCTION :

Hydrated silicates of aluminum which are amphoteric in nature are clays [7]. This means any clay could be acidic or basic depending on the pH of the environment it is found. Certain metals are embedded into the lattice structure of clay but in relative amounts. Such metals add to the properties of a clay. However they could be ionically removed by acid washing of the aqueous suspension of the clay [10].

Clays are found in large deposits in Eastern part of Nigeria. For example deposits of Kaolin are found in Ukpor, Anambra state. Not much characterization has been done on these clays.

It has been [5] suggested that clays are adsorbents on colouring matter from solution. This means they could be employed to decolourize mineral, vegetable and animal oils [9]. The demand for clays in water treatment, paint manufacturing and pottery is very high. This has lead to greater need of clay, in industries and more importantly as an export commodity.

The people of INYI and Nteje in Enugu and Anambra States respectively are well known in pottery business since the 19th century.

This work characterized locally available clays. It is also geared towards improving the qualities of these natural clays as adsorbents and hence create an avenue for them to serve as feedback to local industries.

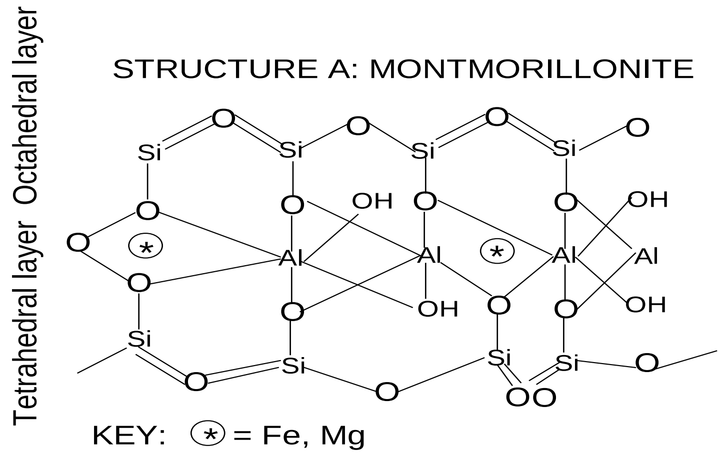


Figure 1: Structure of Montorillonite

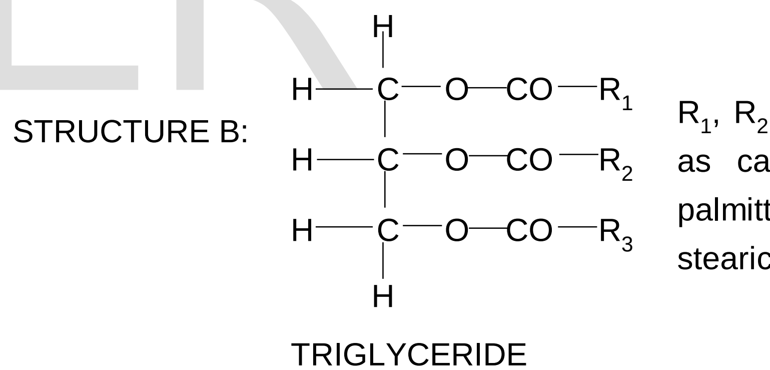


Figure:2 Structure of Palm Oil

1.1 PROCESS CHART/FLOW

Figure: 3 Process/Flow Chart for Bleaching of Palm Oil using Activated Clays

2.0 Experimental:

2.1.1 Preparation of reagents:

The reagents used were prepared as follows:

2.1.2 *0.1M NaOH:*

40g of NaOH pellet was accurately weighed and dissolved in $100cm^3$ of distilled H_2O to get 0.1M NaOH. This was used to titrate against the activated clays at different particle sizes to determine the Base Exchange Equivalence.

2.1.3 0.1M Na_2CO_3:

20g of anhydrous Na_2CO_3 was heated to about 102^oC. This may have driven away some water of crystallization. Then 10.6g of this pure Na_2CO_3 was weighed out using a chemical balance and dissolved in $1000cm^3$ of distilled H_2O.

2.1.4 0.1M HCl :

A 0.15MHCl was prepared and diluted to 0.1MHCl by titration with Na_2CO_3. To get this 0.15MHCl, 12.53ml of the commercial acid was diluted in $1000cm^3$ of distilled water.

$$\text{Vol. (ml)} = \frac{\text{Molarity x mol.wt x100}}{\text{\% purity x Density}}$$

$$\text{Vol. (ml)} = \frac{0.15 \times 100 \times 36.46}{37 \times 1.18} \quad 12.53\text{mls}$$

Equation (1)

This was diluted in $1000cm^3$ of distilled H_20 and titration against $0.1MNa_2CO_3$ the average value was $41.00cm^3$ of the acid. The actual molar concentration of 0.1MHCl was obtained from the relationship.

$$\frac{C_AV_A}{C_BV_B} \quad \frac{n_A}{n_B} \quad \frac{C_A \times 41.00}{0.1 \times 20.00} = \frac{2}{1} \quad C_A = 0$$

Equation (2)

2.1.5 60mg/dm^3 $K_2Cr_2O_7$:

This reagent and 0.005M H_2SO_4 were prepared and used to standardize the spectrophotometer. About 100mg of potassium heptaoxodichromate (vi) was weighed using triple beam balance. It was dried in an oven at a temperature of 90^oC for three hours and cooled in a desiccators. 60mg portion was used to prepare a standard solution, diluted to $1dm^3$.A standard $0.005MH_2SO_4$ was prepared in a similar way as described for 0.1MHCl and used to standardize the $K_2Cr_2O_7$. Methyl orange was prepared by dissolving 1g of the solute in $500cm^3$ of distilled H_2O. $2cm^3$ portion of this $60mg/dm^3$ standardized $K_2Cr_2O_7$ was put in the sample cell of the UV spectrophotometer. Repeated measurements of its absorbance spectrum between 345 to 355nm [within the wavelength range of maximum absorbance] were carried out. This is to ensure performance efficiency of the instrument as well as defensibility of data generated from sample analysis. A maximum absorbance of 0.664 at wavelength of 350nm was recorded. This agreed with literature [4] and proved that the instrument is effective.

2.1.6 Sample collection: Palm oil: a freshly fruit extract of Elaesis guineesis was milled and collected from Umuocham Ntu Village in Ngor-Okpala L.G.A of Imo State.

2.1.7 Clays: Clays from Ukpor, Ekulu, Nteje, Inyi and Bentonite were collected from designated points.

2.1.8 *Treatment of the samples:* The clays were sun dried, grounded and sieved into particle sizes of 425µm, 1000µm and 2000µm using mesh [3]. Each of the samples was activated with dil. 0.1MHCl and by heating. In acid activation, ion-exchange mechanism as well as adsorption are involved. 200cm^3 of 0.1MHCl was added to 20g of each clay sample. Dispersion, vigorous and continuous stirring was done with a magnetic stirrer for one hour and the mixture left over night. Repeated washing was done with distilled H_20 followed by decantation after settling. After single washing, the pH of the solution was noted and this continued until a stable pH was noted. Finally, the settle clay was dried at 100^{o}C in an oven (Gallen Kamp, Volts 220/249AC), and kept as an acid clay. Also 10g of each clay sample was heated at 350^{o}C in an electric furnace for 40 minutes and sieved. This is also kept as calcinated clay.

2.1.9 Bleaching of palm oil: 10.0g of bleaching clay was added to 30.0g of oil in a beaker. Heating was carried out in an oil bath at temperature of 120-130^{o}C after suspending a Thermometer for temperature reading. This mixture was stirred continuously for one hour. Filtration, centrifugation were done.

2.2 *Extent of bleaching determination:* Both the activated and un-activated forms of each clay at specific particle size were used to bleach the palm oil. 8g, 6g, 4g, 2g of each clay were used to bleach 100ml of palm oil. Their absorbance were read with U.V spectrophotometer (spectrum Lab 21A) and the effect of concentration on adsorption determined.

2.2.1 Determination of Base Exchange Equivalence: 2.0g of each acid clay and of particle sizes (425µm, 1000µm and 2000µm) were dispersed in 10cm^3 of distilled H_2O. 0.1MNaOH was added gradually in the order of 1cm^3, 2cm^3, 3 cm^3, 4 cm^3 etc. and the pH value for each addition was noted. This potentiometric titration continued until pH rose sharply, indicating the end point. The volume of NaOH consumed at end point indicated the base-exchange equivalence for each type of clay.

2.2.2 Characterization of clay using EDXRF: Each clay was characterized for elemental composition as well as their respective concentration. The samples were ground with an agate mortar and pestle to grain size of 125µm. Pellets of 19mm diameter were prepared from 0.3-0.5g powder mixed with (3) drops of organic binder and pressed afterward with a hydraulic press. Energy Dispersive X-Ray florescence (EXDRF) that emits Ag-K X-rays (22.1KeV) using 25millicullies ^{109} Cd as excitation source was used for measurement. The spectra were then evaluated using Axil-QUAS programme [1] Quantitative analysis of the samples was carried out using the "Emission-Transmission Method [2], [6], [4]. As many as twenty-eight (28) metals were found in each clay.

3.0 RESULT AND DISCUSSION:

The result of the investigation are shown in tables 1- 5

TABLE 1: VARIATION OF PH OF ACID-ACTIVATED CLAYS AFTER WASHING WITH DISTILLED WATER:

	pH				
NO. OF WASHING	INYI CLAY	UKPOR CLAY	UKPOR CLAY	EKULU CLAY	BENTONITE CLAY
0	4.9	4.8	5.0	4.9	4.8
1	5.0	5.1	5.0	5.0	5.0
2	5.2	5.2	5.3	5.2	5.3
3	5.4	5.5	5.6	5.5	5.7
4	5.7	5.9	6.0	5.9	6.1
5	6.2	6.3	6.2	6.2	6.3
6	6.5	6.6	6.6	6.5	6.6
7	6.8	6.7	6.9	6.8	6.7
8	6.9	6.8	7.1	7.0	7.1
9	7.1	7.1	7.1	7.1	7.1
10	7.1	7.1	7.1	7.1	7.1

Table 1 shows the pH of the clays after several washing with distilled water. The clays were acidic at their normal state. Such clays when used directly for sequestration of metal ions or bleaching have the ability to interact with oil molecules and therefore may not be good. Washing has the ability of reducing the pH as indicated from the pH values obtained after ten washings. The results obtained indicated that as the number of washing increased, the pH moved from acidity to neutral.

TABLE 2: RELATIONSHIP BETWEEN PARTICLE SIZES, BASE-EXCHANGE EQUIVALENCE OF THE CLAYS AT DIFFERENT pH RANGES

.

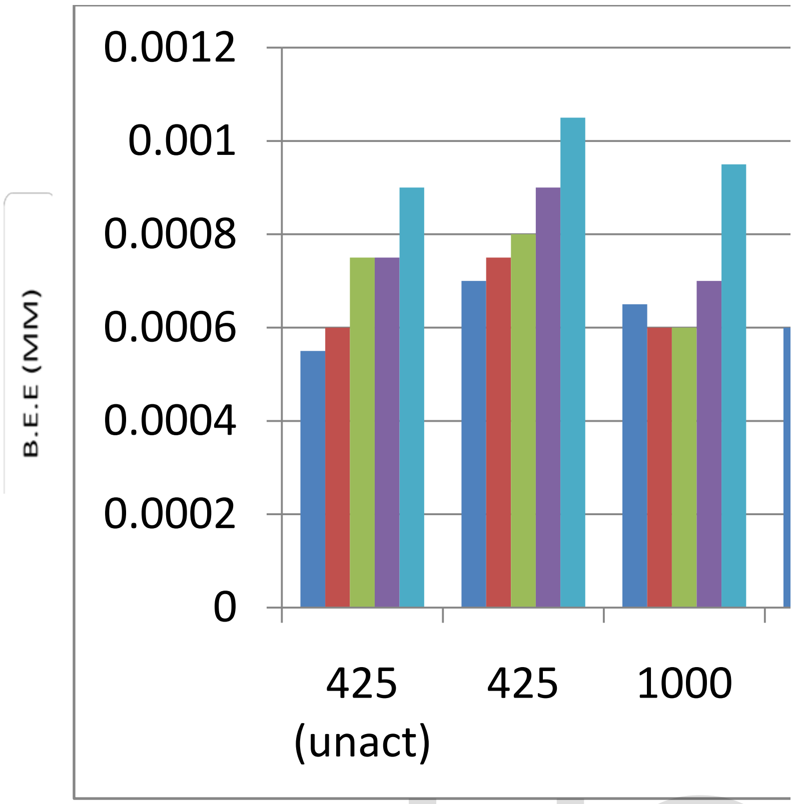
	INYI		NTEJE		UKPOR	
SIZE (µM)	B.E.E (MM)	pH	B.E.E (MM)	pH	B.E.E (MM)	pH
425	0.0009	5.4-9.1	0.0008	5.6-8.7	0.0007	5.5-9.6
1000	0.0007	4.9-7.8	0.0006	4.2-7.6	0.00065	5.3-7.7
2000	0.00065	4.9-8.1	0.0006	4.4-4.7	0.0006	5.2-7.7
425 (unact.)	0.00075	5.3-8.2	0.00075	5.4-8.2	0.00055	5.0-7.8

Table 2 Shows an inverse relationship between Particle size and Base-Exchange Equivalence

Table 3: Percentage Bleaching Performance of Acid and Heat Activated Clay Samples at Different Particle Sizes.

PARTICLE SIZE (µM)	INYI		NTEJE		UKPOR	
	ACID	HEAT	ACID	HEAT	ACID	HE
425	92.68	99.04	91.25	96.55	85.7	80.
1000	77.6	97.5	75.6	75.6	74.97	64.
2000	72.9	96.8	72.9	72.4	71.8	34.

Heat activation increased the bleaching performance of clays more than acid activation method.



Particle size (µm)

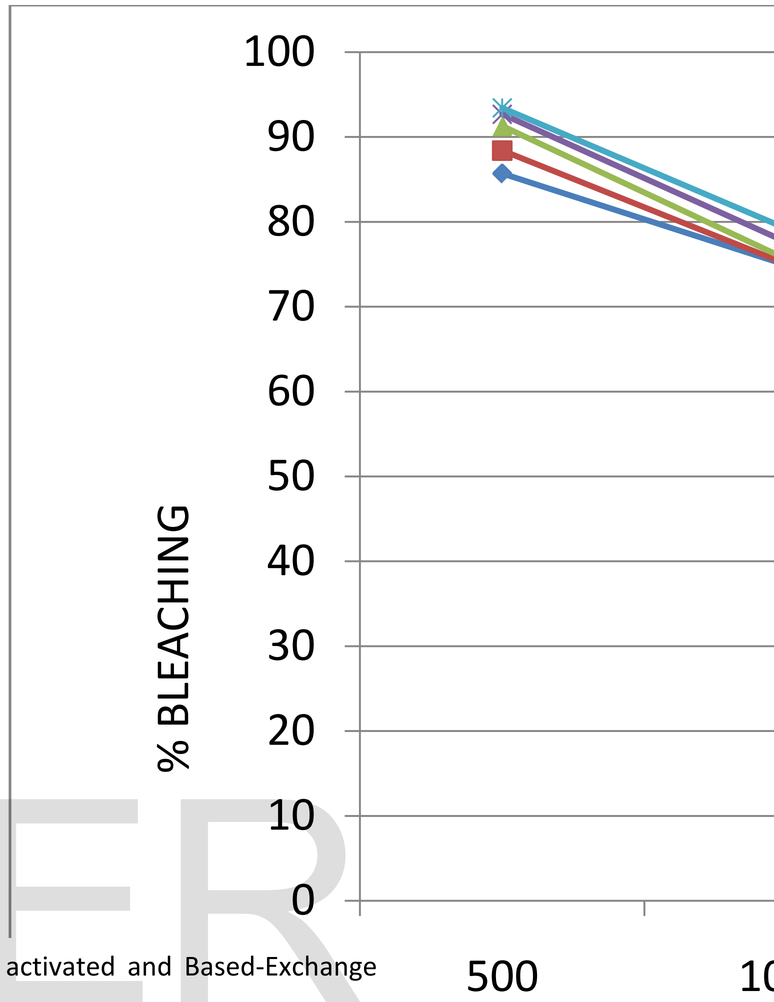


Figure 4 indicated that among the local clays, INYI is the most activated and Based-Exchange Equivalence increased as particle size decreases.

Figure 5 shows that as particle size increases, the bleaching performance increases.

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Table 4: Variation of Concentration, Absorbance and Percentage Bleaching of Clay Samples. (ABS of unbleached oil, Co = 1.886)

YPE OF CLAY	MASS OF CLAY USED C(g)	MASS OF OIL M(g)	ABS OF BLEACHED OIL C_r	EXTENT OF BLEACHING $Co-C_r$	% BLEACHING
YI	2	100	0.190	1.696	89.90
	4	100	0.185	1.701	90.20
	6	100	0.136	1.750	92.80
	8	100	0.126	1.760	93.30
TEJE	2	100	0.697	1.189	63.00
	4	100	0.365	1.511	80.10
	6	100	0.355	1.531	81.20
	8	100	0.202	1.684	89.30
KPOR	2	100	1.095	0.791	41.90
	4	100	1.071	0.815	43.20
	6	100	1.021	0.865	45.86
	8	100	0.368	1.518	80.50
KULU	2	100	0.850	1.036	54.90
	4	100	0.720	1.166	61.80
	6	100	0.375	1.511	80.10
	8	100	0.320	1.566	83.00
ENTONITE	2	100	0.143	1.783	92.40
	4	100	0.138	1.748	92.70
	6	100	0.121	1.765	93.60
	8	100	0.115	1.771	93.90

Table 4 shows that the higher the concentration the lower the absorption value and the higher the bleaching performance. This obeys Freundlich's isotherm equation. $V=KP^{1/n}$ ([8]

% BLEACHING = (Co-Cr/Co) x 100/1 Equation 3

Table 5: Concentration of Metals in Clay Samples

ELEMENT	% CONCENTRATION			
	INYI	NTEJE	UKPOR	EKULU
K	1.68	1.58	1.27	1.49
Sn	0.128	0.130	0.133	0.130
Ca	0.727	0.850	0.722	0.757
Sc	0.422	0.455	0.394	0.457
Ti	1.13	0.650	2.86	1.37
V	0.110	0.107	0.143	0.108
Cr	0.0708	0.0796	0.0696	0.115
Mn	0.0879	0.0826	0.0469	0.0766
Fe	6.87	6.25	2.92	5.6
Co	0.0307	0.0376	0.0279	0.0328
Ni	0.0198	0.0176	0.0146	0.0312
Cu	0.0151	0.0140	0.0126	0.0143
Zn	0.0126	0.0111	0.00772	0.00876
Ta	0.0265	0.0336	0.0241	0.0251
W	0.0222	0.0304	0.0197	0.0194
Ga	0.0108	0.00767	0.00781	0.00821
As	0.00893	0.00742	0.00649	0.00685
Se	0.00352	0.00443	0.00329	0.00379
Pb	0.0129	0.0106	0.00938	0.0100
Br	0.00333	0.00293	0.00254	0.00266
Rh	0.00840	0.00387	0.00233	0.00822
Sr	0.0114	0.0127	0.0135	0.0216
Th	0.00361	0.00334	0.00494	0.00371
Y	0.00555	0.00169	0.00378	0.00414
U	0.00303	0.00266	0.0448	0.00311
Zr	0.00320	0.0187	0.100	0.0699
Nb	0.00347	0.00321	0.00797	0.00291
Mo	0.00128	0.00116	0.00143	0.00147
Average metal concentration	0.40828	0.37182	0.31691	0.37078

Table 5 revealed that the average metal concentration as observed is specified thus: INYI>NTEJE>EKULU>UKPOR

CONCLUSION AND RECOMMENDATION:

Characterization of the clays by particle size analysis showed that the smaller the particle size, the better the base exchanged equivalence and the better the bleaching performance of all clays analyzed.

Both acid activation and calcinations improved the bleaching performance of the clays. This was because acid activation leads to displacement of some elements, creating vacant sites for adsorption. Calcination a better activation method tends to open pore sizes of clay, thus increasing the surface area of contact. This leads to increase in frequency of collision, reaction and adsorption. The bleaching capacity of the sampled clays is of the order Bentonite>INYI>NTEJKE>EKULU>UKPOR. The average metal concentration is specified, thus INYI>NTEJE>EKUL:U>UKPOR. This may have led to high degree of cationic-exchange and hence increase in activation and B.E.E in that order [3]. Nteje clay is the richest in calcium with concentration of 0.85%; while Fe is the most abundant of all elements (except in Nteje). This may be the reason why Nteje clay is widely sold and consumed in Eastern part of Nigeria. It is a source of mineral recommended for pregnant women in treatment of malformation of bones and teeth.

From aforementioned results, INYI clay is recommended as equivalent substitute to Bentonite (foreign clay). Vegetable oil industries can now utilize the sampled clays to improve quality of their oil.

The funds meant for importation of Bentonite could now be channeled to solve other problems in the society.

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