SUITABILITY ASSESSMENT OF ALKALI ACTIVATED CLAY FOR APPLICATION IN VEGETABLE OIL REFINING

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ABSTRACT: Production of acid activated clay and its application in vegetable oil refining has reached its limit of optimization. Most acid activated clay often increases the acid value of refined bleached and deodorized (RBD) oil and hence requires further treatment to get the desired quality. In addition, the waste effluent from the treated clay is hazardous to the environment and as a result, this study aimed at investigating the potential application of alkali activated clay for Shea butter bleaching. Nigeria local clay was obtained and activated using sodium hydroxide and potassium hydroxide solutions at varying concentrations. The effectiveness of those clays was measured by determining the percentage color reduction and the final free fatty acid of the RBD Shea oil. The adsorption of colored impurities from the Shea butter was favored by low concentration (0.5m/dm³) for sodium hydroxide activated clays and higher concentration (5m/dm³) for potassium hydroxide activated clays. The percentage free fatty acid of the Shea butter was reduced from 6.836 to 2.74 and 3.2 for potassium hydroxide activated clay and sodium hydroxide activated clays respectively. The XRD patterns of the activated clays revealed that the clay sample consists of mixed layered minerals whose morphology has been changed as a result of the modification. The results of this work will address most shortcomings associated with acid activated clay and hence make alkali activated clay a good candidate for bleaching vegetable oil even at the level of the grass root.

KEYWORDS: Suitability Assessment, Lkali Activated Clay, Vegetable Oil Refining

INTRODUCTION

Utilization of clay in Nigeria is very meager compared to its availability. It is very abundant in the South Western and Northern part of the country and yet little attention is given to these available minerals. The popular areas of application are in the making of local pots, toys and some house hold utensils. Modification of Nigeria clay for various industrial applications deserves research attention most especially utilization of clay in the refining process of vegetable oils. The modified clays that are currently used in this area of refining are either imported from Asia, Europe or America despite its abundance on our land. Those imported clays are usually acid activated clay which after being used left the refined, bleached and deodorized (RBD) oil with residual acid, which reduces the quality of the oil.

LITERATURE

The use of clay and its minerals as adsorbent in vegetable oil refining has been adopted on industrial scale. Natural clay such as fuller's earth and bentonite have commonly being used as bleaching clay to remove colour impurities from both edible and non-edible oil (Gizela et al., 2004). However, research has shown that the adsorptive properties of clay and its minerals can be improved upon activation. Clay activation is the chemical or physical treatment applied to certain types of clay to develop their capacity to adsorb colouring matter and other impurities in oils (Onal et al., 2007). Acid activated clays are the commonly used clay adsorbent for vegetable oil bleaching. Nguetnkam et al. (2008) assessed the bleaching capacity of Cameroonian clays on vegetable oils. The authors discovered that the bleaching capacity of natural clays were poor compared to that of industrial adsorbents. However, with acid activation, the clay adsorption power increases. But washing away of the residual acid from the clays with pure water to have acid free adsorbent is a drawback. This is because apart from time and energy consumption, if such washing is done on a large industrial scale will create an acidic waste streams thereby posing threat to the environment on disposal. Research findings have also shown that employing acid-activated could be detrimental to the bleached oil because such activated clay may increase the levels of free fatty acids and the formation of undesirable 3-Monochloropropane-1-2-diol esters (David et al., 2013; Ramli et al, 2011; Zschau et al., 2000).

Various researchers have carried out activation using mineral acid such as hydrochloric acid and sulphuric acid and tested their adsorptive properties on various vegetable oil (Francisco *et al.*, 2001; Hulya *et al.*, 2006; Salawudeen *et.al* 2007; Foletto *et al.*, 2010; Hulya *et al.*, 2006). The oil treated with acid activated clay can be damaged due to the effect of acid on the constituents of oil, because of this adverse effect, the conventionally practice is to wash the clay after acid activation to remove any excess acid thereby increasing the time and cost of activation. Acid activation of clays usually adds to the acid value of the oil which must be neutralized with alkaline during the refining process thereby adding to the cost of production.

Vegetable oils in their crude form contain impurities such as carotenes, xanthophylls, carotenoid acids, chlorophyll, tocopherols, gossypol, free fatty acids and fatty acid polymer (Falaras *et al*, 1999; Zschau, 2001). In order to make this oil acceptable to consumers, their purification becomes necessary. Bleaching process is a critical unit operation in the refining process of vegetable oils. It is responsible for the removal of the remaining soaps, phosphorus, trace metals and pigments (chlorophyll and carotenoids), and most of the high molecular weight oxidative products (Roberto, 2006).

Refining of vegetable oils such as soya oil, palm kernel oil, palm oil, olive oil, rape seed oil, cotton seed oil and coconut oil have received attention from researchers, only few works have been reported on Shea oil refining. Shea Butter is multi-purpose oil rich in vitamin A derived from the seed of the Shea tree. The cream is extracted and prepared without the use of chemicals. The best Shea Butter for skin use is prepared by cold press methods without use of added chemicals or preservative (ASBI, 2013). Shea butter oil is a soft solid at room temperature and readily melts when exposed to heat. It has a characteristics smell. It is commonly used as body cream because of its healing and high moisturizing effects. The use of Shea oil as cooking oil has not gained much popularity and acceptance in recent times. The basic reasons for this are its odor and taste when it is unrefined. Research has shown that Shea

oil retains its skin healing properties best when it is unaltered (ASBI, 2013). However, its use for domestic purposes such as cooking and in industries such as pharmaceuticals, cosmetics and medicine has to be encouraged through refining in a way that will make Shea butter more acceptable without necessarily distorting its natural quality. In this research, the use of alkaline activated clay will be investigated to address most common shortcomings associated with acid activated clay in the refining of vegetable oil. The effectiveness of the prepared adsorbent will be measured on the physicochemical properties of the final Shea oil.

METHODOLOGY

Materials

The clay sample was obtained at a mining site located outskirt of Awo which falls within latitude 7°45′N and 747 north of the equator and longitude 424E and 425E of greenwich meridian in osun state, Nigeria. This clay is almost whitish in colour and gave high plasticity when mixed with water. Shea butter was obtained from Saki town, Nigeria. NaoH and KOH used were analytical grade, manufactured by Mayer and Baker, Bagenham, England.

Clay activation

The clay obtained was grinded and wet sieved to remove impurities. The purified clay was dried and grinded to very fine particles. A 9 experimental runs was designed using the Central Composite Design (CCD) of the design expert software at varying alkaline concentrations and the activation time. The sieved clay (100g) was dispersed in 60ml of distilled water to form slurry. The slurry was pre heated to 60°C for 5minutes. 100ml of sodium hydroxide was added to the pre heated slurry and the mixture heated to 90°C for a specific experimental run under continuous stirring. This process produced a homogenous mixture of activating alkaline and the clay. The slurry formed was dried conventionally in a drier at 80°C for 4hours (drier specification) to reduce the moisture content to less than 10%. The dried clay was grinded t 100microns (160 mesh) by using electric grinder (Marlex appliances pvt limited). Activation using sodium hydroxide and potassium hydroxide resulted to 18 activated clays.

Clay characterization

The raw and activated clay samples produced were characterized using Empyrean diffractometer DY 674 (2010) with a cupper anode material manufactured by Panalytical, Holland to determine the mineral composition before and after modification. The measurement were made using CuK_{α} radiation = 1.5418Å, tube current was 40mA and the tention was 45VA.

Bleaching Process

Prior to the bleaching, the shea butter was slightly heated to its melting temperature (45°C) since it is semi solid at room temperature. 75g of heated crude shea butter was weighed into a 250ml round buttom rotary evaporator flask (RE-52A, Biochemistry instrument factory, Shanghai) and heated to a temperature of 60°C under constant mixing at 60rmp. 1.5g of activated clay (2% by weight of clay) was added to the preheated oil under vacuum and continous stirring. The clay-oil mixture was heated to a bleaching temperature of 100°C for 20 minutes. This was followed by filtration of the mixture under vacuum (80mmHg) to remove the adsorbent. The bleaching efficiencies of the activated clays were studied by determining the physicochemical properties of the bleached oil and compared to that of virgin shea butter after adsorption process.

Determination of Physicochemical Properties of Oil

The major properties considered for determining the efficiency of the activated clays produced are percentage color reduction, acid value, % free fatty acid and oil density.

Percentage colour reduction

The percentage colour reduction was determined using colorimeter (Uniscope colorimeter SM-3004). A full absorbance spectrum was carried out over the entire wavwlenghts, the wave length that gave the highest absorbance (480nm) for the unbleached oil was chosen for the absorbance test. The absorbance was determined by diluting the oil with n-hexane in a 5ml cuvette. The percentage colour reduction was calculated using the following relation:

Where Ao and A are absorbance of crude and bleached oil respectively.

Acid value and free fatty acid

The oil acid value was determined using titrimetric method (ISO Method 660, 2009). The melted shea oil was dissolved in ethyl alchohol (99%) and heated for about 2minutes before titrated while still hot against 0.1M NaOH using phenolphthalein as indicator. The acid value was then calculated equation 2.2:

$$Acid value = \frac{56.11 \times V \times N}{M} - - - (2.2)$$

Where, V is the volume of Potassium hydroxide used in ml N is the exact normality M is the mass in g of oil sample.

% free fatty acid (%FFA) =
$$0.503 \times \text{acid value}$$
 $---$ (2.3)

Oil density

The density was determined using pyscnometry method using water as a working liquid of known density. An analytical weighing balance (OAUS pioneer analytical weighing balance, Ohaus Corporation) was used throughout the experiment and the density was calculated following the relation below:

$$S.G = \frac{W_2 - W_1}{W^3 - W^1} \qquad --- (2.5)$$

$$\rho_{oil} = S.G \times \rho_{water}$$

Where,

S.G is the specific gravity of oil,

 W_1 is the weight of the empty pycnometer,

 W_2 is the weight pycnometer + oil sample,

W₃ is the weight distilled water +pycnometer,

 ρ_{water} is 1000g/cm^3 .

RESULTS AND DISCUSSION

Mineralogical composition

Both the raw and activated clay samples were analyzed using XRD to determine the mineral composition before and after activation. The XRD patterns showing the mineral compositions of the raw and activated clay samples are shown in figures 1, 2, 3, 4 and 5. The x-ray diffraction results revealed that the clay samples contain mixed layered minerals. Mixed layered minerals are minerals whose chemical compositions are not in the same domain, that is they have different chemical composition which can be determined by studying the peak (Alain, 2005).

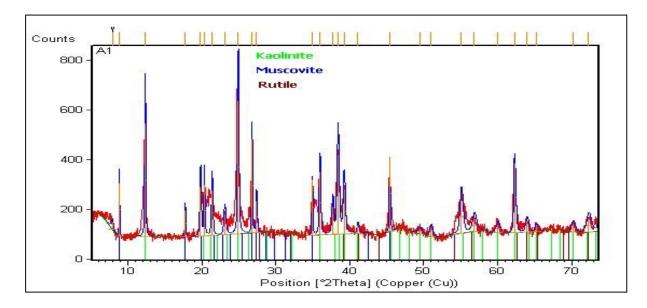


Figure 1: XRD pattern of raw clay sample

Figure 1 shows the XRD pattern of the raw clay sample with the number of counts (intensity) on the vertical axis and the corresponding 2-thetal angle on the abscissa. The mixed layered minerals present are kaolinite (aluminum silicate hydrate), muscovite (potassium aluminium silicate hydroxide), and rutile (titanium oxide) with muscovite showing highest peak indicating its dominance in the clay sample. Kaolinite and muscovite are clay minerals while rutile is an ore (impurity in the clay mineral). Muscovite has its highest peak at 2θ angle of about 27° and x-ray count (intensity) above 800.

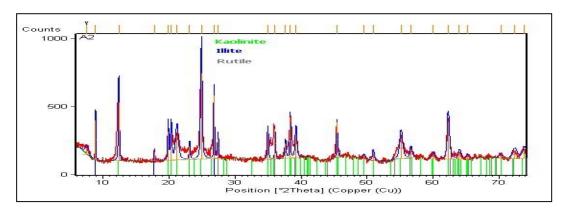


Figure 2: XRD pattern of clay sample activated with 0.5M NaOH

Figure 2 is the XRD pattern of the local clay activated with 0.5M sodium hydroxide. The mixed layered minerals present are kaolinite, illite and rutile. It was evident from the diffraction pattern that alkaline activation of the clay has resulted in changes in mineral composition of the sample by Illite replacing muscovite. Illite (potassium aluminum silicate hydroxide hydrate) is a low temperature equivalent of muscovite (Alain, 2005). It can also be observed that the highest peak was at its corresponding 2θ angle was recorded at higher x-ray count, above 1000 when compared to that of raw clay which is 800 (Figure 1). The presence of this clay mineral could be as a result of the hygroscopic nature of the activating agent (sodium hydroxide.) The chemical formula is (K,H₃₀) Al₂ (Si₃Al) O₁₀ (OH)₂.xH₂O showing the presence of hydrated water.

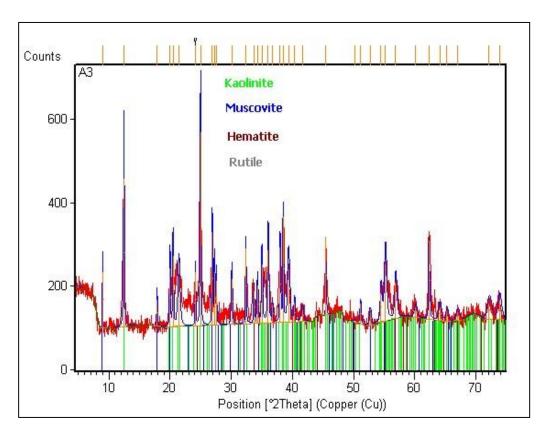


Figure 3: XRD pattern of clay sample activated with 5M NaOH

Figure 3 shows the XRD pattern of local clay activated with 5M sodium hydroxide. The XRD pattern is still mixed layer but a new mineral, hematite (iron oxide) has been detected. Kaolinite has been considered not to display isomorphic substitution that is, the replacement of one ion by the other. However, the presence of Fe³⁺ has been systematically detected due to some weathering condition (Balan, et al 1999). The presence of ore minerals (hematite and rutile) has reduced the quantity of the muscovite in the clay sample which may in turn reduce the adsorption capacity of the clay. Hill et al., (2002), reported that additional components in the clay sample should not be greater than 10% for its effective used in vegetable adsorption. It can be seen from the XRD pattern that the x-ray count has reduced to 600 indicating the chemical changes that has occurred in the transformation of the clay to activated clay.

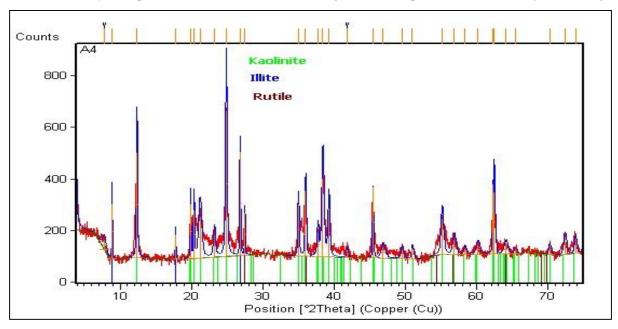


Figure 4: XRD pattern of clay sample activated with 0.5M KOH

Figure 4 shows the XRD pattern of clay sample activated with 0.5M potassium hydroxide. Muscovite has been replaced by Illite when the pattern is compared with that of raw clay sample (Fig. 1). This is also traceable to the hygroscopic nature of the activating agent. It was also discovered that the x-ray count was not affected when compared to raw clay pattern.

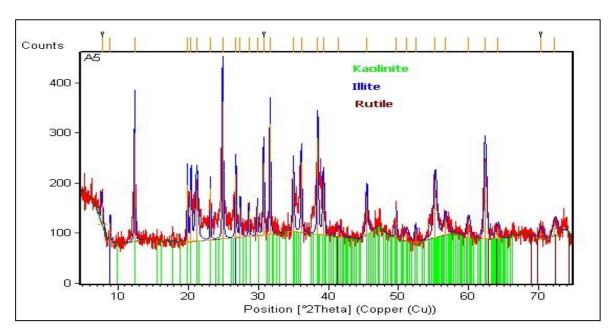


Figure 5: XRD pattern of clay sample activated with 5M KOH

Figure 5 shows the XRD pattern for clay activated with 5M potassium hydroxide. Clay modification at higher alkaline concentration had effect on the crystal structure of the clay as shown in Figure 5. Illite showed the highest peak at 2θ angle 25° but the x-ray count has been reduced from 800 to 400. Also, the colour indicating the presence of Kaolinite (green) appeared

more in Figure 5. This is an indication that more Kaolinite has been synthesized in the clay sample as a result of the modification with higher concentration.

Bleaching Efficiency of the Activated Clay Samples

The bleaching efficiency of the activated clay were measured by studying the effect of activating parameters (alkaline concentration and activation time) on the physicochemical properties [percentage color reduction (%CR), percentage free fatty acid (%FFA) and density] of the shea oil before and after bleaching. Tables 1 and 2 presents the clay activation parameters (in coded form) and physicochemical properties of oil bleached with sodium hydroxide activated clays (NaOHAC) and potassium hydroxide activated clays (KOHAC) respectively. The results, compared to that of crude Shea oil showed a sharp decrease in percentage free fatty acid content (%FFA) and increase in percentage colour reduction (%CR). This is attributed to an increase in the clay active sites due to activation and this enhances the mass movement of colloids and other particulate matters from the bulk mixture to the surface of the clay.

Table 1: Physicochemical Properties of shea butter bleached with Sodium hydroxide activated clays

	Factors		Responses		
	Alkaline				
	conc	Activation			Density
Run	(mol/dm ³)	time (min)	%CR	%FFA	(g/cm^3)
1	1	-1	13.5	3.3	893.02
2	1.41	0	8	3.1	893.89
3	0	1.41	29.8	3.4	894.77
4	1	1	13.7	3.2	892.13
5	-1	1	30.2	4	892.17
6	-1	-1	30.2	4.7	895.63
7	0	-1.41	29.8	3.9	895.21
8	-1.41	0	28.8	4.9	892.67
9	0	0	30.2	3.7	893.6

Table 2: Physicochemical Properties of shea butter bleached with Potassium hydroxide activated clays

	Factor		Responses		
Run	Alkaline Conc (mol/dm³)	Activation time (min)	%CR	%FFA	Density (g/cm³)
1	1	1		2.74	890.34
2	0	-1.41	20.5	3.95	887.33
3	1	-1	24.9	2.53	889.3
4	-1.41	0	14	5.12	891.1
5	1.41	0	28	2.45	896.1
6	-1	1	17.4	5.08	899.18
7	-1	-1	16.6	4.74	893.09
8	0	0	20	3.91	893.41
9	0	1.41	20.6	4.06	888.96

Note: Code '1' = 5mol/dm^3

Code '-1' = 0.5mol/dm^3

Code '1.41' = 5.93mol/dm^3

Code '-1.41' = 0.43mol/dm^3

Code '0' = 2.75mol/dm^3

Code '1' = 80minutes

Code -1 = 55.86minutes

Code 1.14' = 60 minutes

Code '-1.14' = 84.14 minutes

Code '0' = 70 minutes

Effect of activation on Percentage colour reduction of oil bleached with NaOHAC and KOHAC

It can be observed in Table 1 that reduction in NaOH concentration has resulted to a better color enhancement. The least %CR (8%) was recorded at the highest concentration (5.93M). As the alkaline concentration reduces to 2.75mole/dm³, there was significant increase in the %CR up to 29.8% and reaches its peak when the alkaline concentration was 0.5mole/dm³ with 30.2% color reduction recorded. These changes were not really affected by the activation time even though the activation time was varied. This was indicative from the results of experimental runs 1 and 4 where alkaline concentrations were the same but at different activation time (60 and 84minutes respectively). Similarly, runs 5 and 6 were both activated with 0.5M at 60 and 80minutes respectively and the %CR were both 30.2%.

Unlike NaOHAC bleached Shea oil, it is evident from Table 2 that higher KOH concentration favored %CR, thus, the higher the KOH concentration the higher the %CR for KOHAC. The highest percentage colour reduction recorded was 28% when KOH concentration was 5.93mole/dm³ and around 25% when the concentration was 5mole/dm³. Also at a very low KOH concentration of 0.43mole/dm³, the %CR was 14%. It can therefore be inferred from the results that NaOH is a better activating agent since less concentration will be required to achieve optimum result compared to KOH.

Effect of Activation on % FFA of shea oil bleached with NaOHAC and KOHAC

As shown in Table 1 and 2, the bleaching process resulted in the removal of free fatty acid from the oil. The %FFA has being reduced from 6.84% (raw shea oil) to as low as 2.45% when KOHAC was used and 3.10% when NaOHAC was used. %FFA decreased with increasing alkaline concentration for both adsorbents produced. This may be attributed to the fact that both adsorption and neutralization cum soap formation occurred during bleaching. It is also indicative that higher activation time favors FFA reduction simply because as activation time increases more FFA are been converted to soap through neutralization. Both neutralization and adsorption process simultaneously reduces oil density and these are indicative in Table 1 and 2.

Summary of the Effect of Activation on Physicochemical properties of crude Shea butter

Crude Shea butter is a semi solid at room temperature; therefore all experiment and analysis were carried out at the melting temperature of the Shea oil (45°C). Table 3 shows the physicochemical properties of the crude Shea oil, oil bleached with sodium hydroxide activated clay (0.5m/dm³) and oil bleached with potassium hydroxide activated clay (5m/dm³). The unbleached Shea oil had a density close to that of most vegetable oils (0.907g/cm³) and relatively high free fatty acid content (6.83%). It is darkly colored when in molten form. It can be seen from the table that the acid value, percentage free fatty and color of the oil improved after the adsorption bleaching using the best alkali activated clay. All these have led to a decrease in the density of the final bleached oil. That is 0.892 and 0.890g/cm³ respectively for NaOH and KOH activated clay.

Table 3: physicochemical properties of crude and Refined Shea butter

Properties	Crude Oil	Refined (0.5m/dm ³)	Refined (5m/dm³)
Specific gravity (g/cm ³)	0.907	0.8921	0.8903
viscosity (mpas)	876	875.60	875.9
Solidification point (°C)	25	25.00	25
Melting point (°C)	45	45.00	45
Acid value	13.456	6.365	5.447
FFA (%)	6.836	3.20	2.74
CR (%)	-	30.20	27.5

IMPLICATION TO RESEARCH AND PRACTICE

This work has shown an alternative way of vegetable oil refining using alkali activated clay instead of conventional acid activated clay which has been reported to be detrimental to the bleached oil (David *et al.*, 2013). The alkali activated clay here is serving a dual purpose i) it acted as adsorbent and ii) FFA reducer. This has not been thoroughly investigated in the previous research and hence has not been put to practice.

CONCLUSION

Alkaline activation of a Nigeria clay with muscovite as the major clay mineral resulted in significant structural modification. This modification resulted in synthesis of other clay minerals such as Illite which improved the bleaching efficiency of the activated clay. Bleaching

efficiency was favored by lower concentration (0.5mole/dm³) for sodium hydroxide and higher concentration (5mole/dm³) for potassium hydroxide. However, this research has shown that muscovite/illite based clay minerals can be an effective adsorbent in vegetable oil refining upon modification. The presence of Kaolinite in all the samples is an indication that the activation process did not destroy the clay structure but rather improved the kaolinite grade by reducing the composition of the gang minerals. Hence, the best results of 30.20 and 27.50% color reduction and 46.81 and 40.08% FFA reduction was achieved for both NaOH and KOH activated clay respectively. Base on these findings, it can be concluded that alkali activated clay will serve as a good candidate for vegetable oil refining in contrast to acid activation as reported in literatures due to its ability to reduce FFA in addition to its high bleaching efficiency.

FUTURE RESEARCH

To further research in this area, optimization of process parameters in the refining of vegetable oil using alkali activated clay will be investigated and the process will be extended to other vegetable oils apart from Shea oil.

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