Continental J. Applied Sciences
Muhammad et al. (2021) 16 (1): 33 - 44

Research Article

Evaluating the Bleaching Performance of Acid Modified Locally Available Clays from Niger State on Crude Palm Oil

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Abstract

Locally available clay samples collected from Niger State were modified using H_2SO_4 for the purpose of replacing imported clay used for bleaching palm oil and the bleaching performance of the modified local clays on palm oil evaluated. Four different samples of locally available clay and crude palm oil were bleached after it has been degummed and neutralized. The absorbance of crude and bleached palm oil samples was measured and the free fatty acid content determined as a measure of the bleaching performance of the modified clays. UV spectrometer and classical method respectively. The results obtained showed that as the molar concentration of the acid solution was increased, the performance of the modified clays also increased, with different samples showing different optimal bleaching performance for the clay samples. The results obtained also showed that the locally available clay could be a good alternative for the currently imported clays used for bleaching during processing of palm oil.

Keywords: Clay Modification, Adsorbents, Palm oil, Bleaching performance.

Received: 28 May 2021 Accepted: 1 July 2021

Introduction

Nigeria is one of the leading exporters of various agricultural commodities. Recent data puts the contribution of agriculture to the country's GDP at about 19.28 % (National Bureau of Statistics, 2017). Palm oil has the potentials to reduce some of the economic uncertainties associated with petroleum and gas sector (Gharleghi & Yin-Fah, 2013). This can be achieved through diversification, which can shift a dependent

on a monoecomony (i.e petroleum) to diversified economy. The essence is that petroleum has a lifespan and may not be renewable, unlike palm tree that can be cultivated continuously and utilize plant product for both domestic and industrial purposes (Koushki *et al*., 2015). Similarly palm oil consumption has increased globally, as refined products are viable raw materials in most industrial, domestic and pharmaceutical processes. The oil palm tree is highly economical and various fractions such as crude palm oil and crude palm kernel oil are also economically important, with the latter having more industrial and domestic applications.

Crude palm oil (CPO) contains about 1% of minor components, such as phospholipids, metals, phytosterols, carotenes, tocopherols and tocotrienols (Ejikeme *et al.,* 2013), Palm oil is composed basically of fatty acids and glycerol, which is esterified to yield a triglyceride. Oil palm contains an exceptionally high concentration of saturated fat, precisely the 16-carbon saturated fatty acid, palmitic acid, in which it derives its name (Koushki *et al.,* 2015). It also contains monounsaturated oleic acid as a major constituent. Untreated palm oil is a major source of cotrienol (Ahsan et al., 2015). Its high carotenoid content gives the fruit its dark orange color (Pohndorf *et al*; 2016). Palm oil derived from the mesocarp of palm fruit contains approximately 50% fats and 40% unsaturated fats (Ebongue *et al*., 2011). Crude palm oil is an edible vegetable oil extracted from the fleshy part of ripe oil palm fruit (*Elaeis guineensis*). CPO contains impurities such as organic pigments, soaps, oxidation metals and trace metals. These impurities have negative impacts on the taste and smell of the oil as well as on its appearance and shelf life stability which reduces consumer acceptance and marketability, hence the need for removal through refining (Usman *et al*., 2012; Ejikeme *et al*., 2013). In addition, CPO has a very low smoke point, which can be removed if the oil is bleached to remove impurities (Ajemba and Onukwuli, 2013). Red palm oil is rich in carotenes, such as lycopene, α and β carotene which give it a distinctive dark red color. Nevertheless, palm oil that has been treated, deodorized and bleached from crude palm, do not incorporate carotenes after bleaching (Usman *et al*., 2013).

Crude oil refining is a process in which moisture, insoluble impurities, free fatty acids and oxidation product are reduced from an oil sample. There are four processes in palm oil refining, these includes degumming, neutralization and adsorptive bleaching (Mustapha *et al.,* 2013). In all refining processes bleaching is the only process studied due to its ability to remove contaminants such as carotenes and their derivatives, free fatty acids and other contaminants (Hassenein *et al*., 2011). The adsorptive removal of these substances is important because these impurities have negative impacts on the taste and smell of the oil as well as on its appearance and shelf life stability which reduces consumer acceptance and marketability (Usman *et al*., 2012, Ejikeme *et al*., 2013). Oil bleaching is usually done to improve colour, remove impurities and improve taste (Okolo and Adejumo, 2014). Bleaching is an adsorption process which

ISSN: 1597 – 9928. Science and Education Development Inst., Nigeria

requires the use of an adsorbent in removing impurities from oil (Afshar *et al*., 2014; Bello *et al*., 2011). It is based on the ability of the adsorbent to preferentially concentrate on specific substance from solutions unto their surface (Nwabanne *et al*., 2018). Crude palm oil bleaching using acid activated clay has been reviewed by many studies (Okolo and Adejumo, 2014; Mustapha *et al*., 2013; Nwabanne and Ekwu, 2013; Usman *et al.,* 2013; Usman *et al.,* 2012; Bello *et al.,* 2011; Gunawan *et al.,* 2010; Mukasa-Tebandeke *et al*., 2016; Udonne *et al.,* 2016; Uzoh *et al*., 2014) whose studies have shown that Nigerian clays are competent for adsorptive bleaching and have high performance when compared to fullers earth. The quality of bleached palm oil can be obtained by determining parameters of oil such as peroxide value, iodine value, carotene value, refractive index, specific gravity, color and/or absorbance, free fatty acid (FFA) content and other properties of oil (Ismail *et al.,* 2016). Where FFA is the most used criterion in determining oil quality and it must not exceed 5% when expressed as palmitic acid (Ebongue *et al.,* 2011). The presence of high FFA in oil is an indication of deterioration of oil quality (Ekwenye, 2010).

The recent ban placed by the Federal Government of Nigeria on the importation of commercial bleaching earths (fuller earth) and edible oils poses an obvious demand in the production of a high quality alternative. Therefore, it is paramount to generate modern methods and means of improving the quality of vegetable oil by producing cheaper sorbent materials which could be employed for the adsorptive bleaching of edible oils. This work was undertaken to investigate the potential use of acid activated clay for adsorptive bleaching of palm oil to enhance the appearance of the oil.

Materials and Methods

Clay samples were obtained from selected local government areas in Niger State, Nigeria. Clay sample LR was obtained from Lapai, PR was obtained from Paikoro, BB was obtained from Bosso and CG was obtained from Chanchanga. The crude palm oil was purchased from Enugu state, Nigeria.

Sample Purification

The sample was purified by method reported by Mustapha *et al.,* 2013 and modified as follows; each of the clay samples was pulverized using mortar and pestle, the powdered sample was transferred to a beaker and then agitated repeatedly with distilled water to give a solution. The solution was then allowed to stand for 5 minutes for the impurities to settle. The slurry above was decanted leaving behind impurities such as sand, grits and stones at the base. The decanted slurry was allowed to stand for 24 hours, the surface water decanted off and the clay was air dried for several days. The clay samples were again pulverized filtered through a 0.2 mm sieve and stored in an air tight container for analysis.

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Acid Activation of Clay

The clay was activated by method described by Usman *et al.,* (2013) and modified as follows. Approximately 7g of the pre-treated clay sample was mixed with 70 ml of 1.0 M sulphuric acid (SIGMA-ALDRICH, Riedel-de Haen) and the mixture heated at 100 °C under reflux for 3 hours. The obtained samples were then cooled, washed repeatedly with distilled water until the waste water tested neutral as indicated by a litmus test. The washed samples were dried in an oven at 105 °C for 2 hours. The acid activated clay was crushed, filtered through a 0.2 mm sieve and stored in polyethylene bags. The procedure was repeated using five concentrations of sulphuric acid (SIGMA-ALDRICH, Riedel-de Haen) 1.0 M, 2.0 M, 3.0 M, 4.0 M and 5.0 M.

Palm Oil Refining

Degumming

This was achieved using method described by (Udonne *et al.*, 2016) with slight modification. Hot water of about 90 ^{o}C was added to the oil. The mixture was agitated slowly for about 20 minutes and the aqueous layer removed. The mixture was allowed to stand for several minutes in a separating funnel until a clear layer of oil and water was visible. The oil layer (degummed oil) was then collected for further treatment.

Neutralization

Neutralization was done by adding 100ml of 1 M sodium hydroxide solution to the degummed oil sample under slow agitation until formation of emulsions. The mixture was heated at a regulated temperature of 80 ^{o}C for 15 minutes to dissolve the emulsion formed by the alkali. The neutralized sample was treated using a centrifuge (SEARCHTECH) at 3000 rpm for 10 minutes to separate the oil and soap. After centrifuging two layers were formed, oil and soap. The oil was decanted, and stored for bleaching purpose and other studies.

Adsorptive Bleaching

Adsorptive bleaching was achieved by adding 70 ml of the neutralized palm oil along with 0.7g of sized activated clay sample into a 100 mL beaker (1 % v/w bleaching process). The mixture was heated and agitated repeatedly via a magnetic stirrer on a reflux and regulated at 120 ^{o}C for 30 minutes. The mixture was allowed to cool, and filtered under vacuum before measuring the absorbance.

Clay Characterization

Clay materials have already been characterized in previous work (Onyema *et al.,* 2019). This study is to monitor the effect of the activated clay sample on their bleaching performance using crude palm oil.

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Analysis of the Final Product

Absorbance of Crude and Bleached Palm Oil

The bleaching performance of the activated clay samples was carried out by measuring the absorbance of the bleached oil using a UV-Visible spectrometer (Biochrom UV2800). The oil sample was first diluted in acetone (KERMEL) and the maximum absorbance was read at 450 nm wavelength using acetone as reference. The percentage colour reduction used to express the performance of the clay sample.

Free fatty acid determination

This was determined by adding 0.5 g of the melted oil into 12.5 ml of ethanol-ether solution, one drop of the phenolphthalein indicator was added and the mixture stirred properly. The content was titrated against the standard 0.1 M KOH solution. The mixture was stirred constantly until a pink colour which persists for about 30 seconds was obtained.

Results and Discussion

Free Fatty Acids

Table 1 present free acid content of CPO and DPO. Free fatty acids are natural constituents of palm oil and it concentration in an index for estimating rancidity and shelf life of the oil (Ekoo *et al*., 2007; Eddy and Ekop, 2007).

The results obtained (Table 1) reveals the existent of strong correlation between bleaching performance and FFA content with the trend that indicates increase in bleaching capacity with reducing FFA. This can be clearly observed in the indicated CG series, which indicated that sample CG4 with the highest bleaching potential had the least value of FFA. Similar trend was observed for the other clay samples, which confirm that FFA is also a good index for analyzing the quality of palm oil. This information is also confirmed by the trend in the observed plot (Fig. 1) for the variation of percentage bleaching performance with FFA content of the oil.

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Table 1: FFA content of CPO and BPO

Clay sample	FFA content in CPO	FFA content in BPO
LR0	28.671	27.600
LR1	28.671	21.245
LR2	28.671	20.282
LR3	28.671	17.263
LR4	28.671	20.245
LR5	28.671	21.160
BB0	28.671	25.245
BB1	28.671	23.282
BB2	28.671	22.916
BB3	28.671	20.757
BB4	28.671	19.160
BB5	28.671	18.611
PR0	28.671	21.599
PR1	28.671	18.233
PR2	28.671	19.635
PR3	28.671	24.684
PR4	28.671	24.401
PR5	28.671	19.916
CG0	28.671	23.562
CG1	28.671	20.794
CG2	28.671	18.074
CG3	28.671	17.038
CG4	28.671	13.074
CG5	28.671	20.477

Fig. 1: Bleaching performance of BB samples

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Fig. 1 shows the result on the bleaching performance of BB series (acid activated and neutral) on neutralized palm oil. The effectiveness of these adsorbents were investigated and observed to be low with increase in bleaching performance from 9.62 % to 50.43 % as acid concentration increases. The maximum observed at 50.43 % for sample BB5 makes it the least performing clay in this study. Though this sample has shown low bleaching performance but its low values are also an indication that the clay showed some activity. This result conforms to the low values obtained by Usman *et al.,* (2012) for 3M HCl activated clay that was used in bleaching.

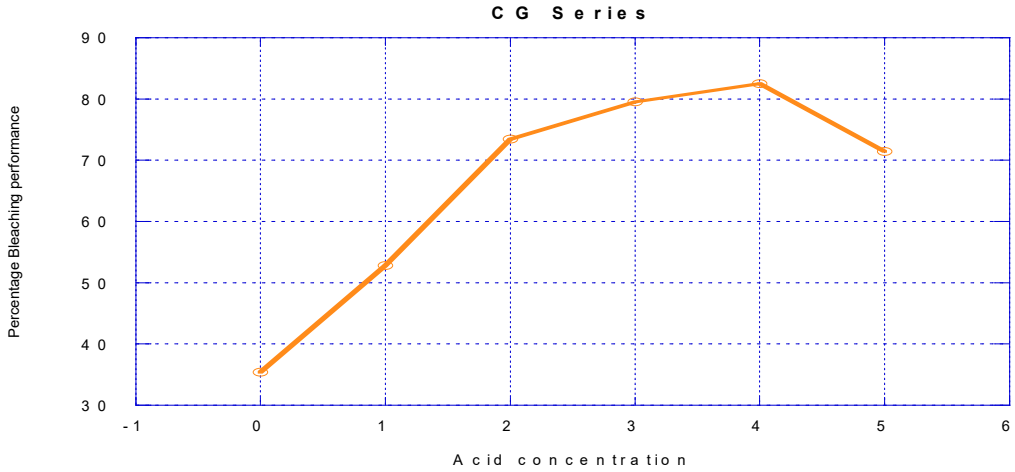

Fig. 2: Bleaching performance of CG samples

Fig. 2 showed the bleaching performance of the inactivated sample (CG0) at 35.79 % and indicates that clay sample CG in its natural state is a good adsorbent. A steady increase in bleaching performance was observed as acid concentration increases up to a maximum bleaching performance of 82.49 % CG4 and for CG5. A similar trend observed by LR series. The optimal bleaching performance of 82.49 % for the clay sample CG is the highest and may be due to the high solubility of Mg, Ca and Fe sulphates contents of the clay materials. Other impurities such as Fe_2O_3, CaO, MgO etc. which covers part of the active sites might have been removed (Salawudeen *et al.*, 2007).

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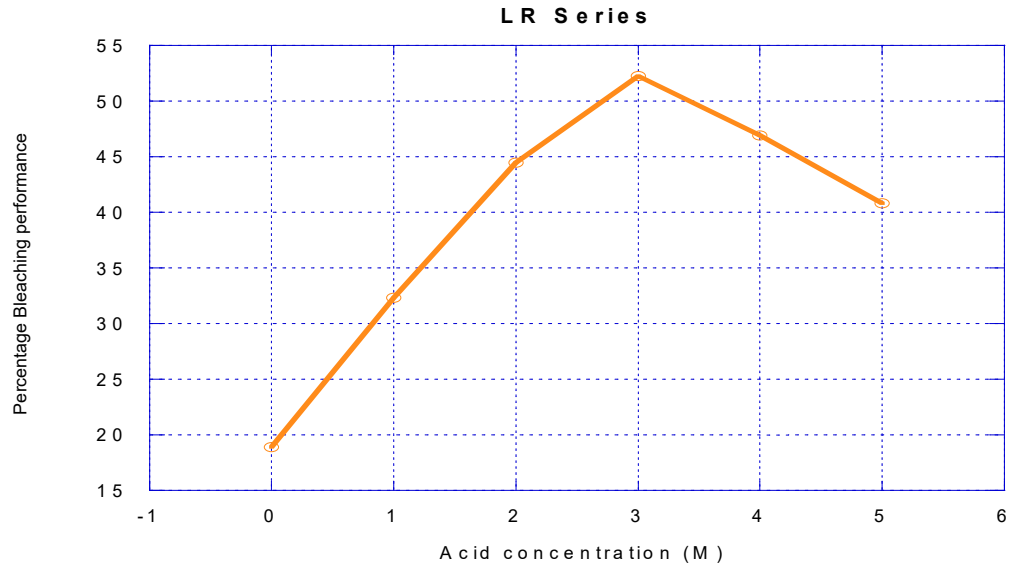

Fig. 3: Bleaching performance of LR sample

It can be seen from Fig. 3 that the percentage bleaching capacity of the inactivated clay sample was 18.91 %, a steady increase in the bleaching performance of the clay on acid activation was also observed as the bleaching capacity of the acid activated clay sample increased from 32.33 % for sample LR1 to 44.47 % to sample LR2. The optimum bleaching performance of LR series was ~~at~~ 52.26 % for sample LR3. However, a steady decline in bleaching performance was observed as the concentration of the acid increases from 3 M and above. This may due to passivation of some of the surfaces of the clay and the subsequent formation of a protective layer in the clay (Cristidis *et al.*, 1997).

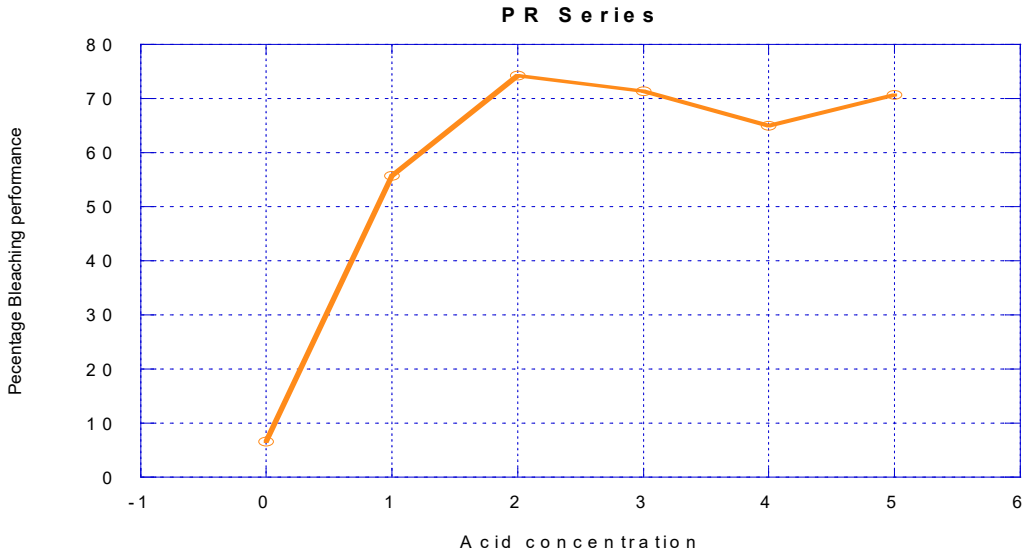

Fig 4: Bleaching performance of PR samples

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From Fig. 4, acid treatment was observed to modify the structure of the activated clay as indicated by incremental changes in the absorption of color pigments from the activated clay which was more than the extent observed in the raw clay. Consequently, the performance was raised from 6.61 % to 74.26 %. The bleaching performance witnessed initial increase with increase in the concentration of the acid up to 2 M which was succeeded by a steady decrease in bleaching performance for the CG and LR series. However, subsequent increase in the bleaching performance of LR5 was attributed to passivation by the rest of the clay, which protects the clay layers from further acid attack. A similar trend was also observed by Ujeneza (2012) for both raw and activated bentonite clay minerals activated at different acid concentrations.

Conclusion

Acid activation was found to increases the bleaching power of local clays obtained in Nigeria, with the bleaching efficiency increasing with concentration of acid. Hence, the utilization of locally sourced clays as a low-cost alternative adsorbent for the adsorptive bleaching of crude palm oil has revealed that samples activated with acid showed more bleaching capacity than the inactivated samples.

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ISSN: 1597 – 9928. Science and Education Development Inst., Nigeria