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Characterization and Modification of Trona and Redearth as a Bleaching Agent for Red Palm Oil

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Abstract: In this work, redearth and trona were analyzed for physico-chemical properties and modified for bleaching of red palm oil. The results showed that redearth gave 30.5% loss on ignition, 0.156g moisture content. 1.91g/cm^3 density and 75% silica content while Trona gave 42.5%, 0.145g. 0.94g/cm^3 and 90% silica content respectively, as their physical properties from the Original samples. The oxides content analysis showed that redearth has 0.59% CaO, 1.50% Fe_2O_3 1.31% Na_2O, 0.71% K_2O, 2.72% Al_2O_3. 0.08% MgO, 0.02% CuO, 0.57% PbO and 5.80% MnO as against 0.25%, 5.73%, 11.5%, 1.08%, 2.25%, 0.008%, 0.002%, 1.42% and 5.80% respectively for Trona. Bleaching performance on red palm oil using the activated Trona, Red-earth and their 1:1 ratio blend gave 28.07% colour reduction, 6.19N iodine absorbance/value and 68% free fatty acid removal for trona, 76.51% colour reduction, 3.05N iodine absorbance/value and 62% free fatty acid removal for redearth, 90.43% colour reduction, 2.79N iodine absorbance/value and 70% free fatty acid removal for the 1:1 ratio blend respectively. It was observed that 1:1 ratio blend gave the best performance.

Key words: Trona · Redearth · Bleaching agent and Red palm oil

INTRODUCTION

Trona is a hydrated sodium bicarbonate ($Na_3H(CO_3)_3.H_2O$), commonly encountered as a saline lake deposit or sedimentary evaporation product and as an efflorescent on soil. It is usually associated with natron, thermonatrite, halite and gypsum [1]. Redearth is a clay mineral ($Al_2O_3.\ 2SiO_3.\ 2H_2O$) which deposits are typically associated with very low energy depositional environment of time by the gradual chemical weathering of rocks, usually silicate-bearing, by the low concentration of carbonic acid and other dilute solvents through upper weathered layer. In addition to the weathering process, some clay minerals are formed by hydrothermal activity [2]. Redearth is also known as red soil whose colour is due to high Fe content [3]. But its Fe content is not higher than that of Trona which is locally obtained as clay. Trona serves as a common source of soda ash and is useful for the manufacture of glass, chemicals, paper, detergents and textiles. It is also used to treat water, remove sulphur from flue gases and lignite coal but most importantly it is use as food additive [4 and 5]. Many researchers have reported the use of Nigeria clay materials as replacement for the hitherto imported fuller's earth for palm oil bleaching. Bleaching is the process of removing the natural colour of textile fibers, yarns, fabrics, paper, red oil and other products such as foodstuffs, by the treatment with chemicals or by exposure to sun or heat. Bleaching performance of selected acid activated Nigerian clays on some common prebleached palm oil feed stocks had been reported [6]. There are many properties that make clay a good bleaching agent for the refining of vegetable oils, animals oils and fats as well as decolorizing of special mineral oils. These properties include high adsorption power of clay materials for colored bodies and impurities. Moreover clay has high moisture content, acidity, apparent bulk density (ABD), particle size distribution, oil retention and filter rate. All these clay properties such as high ion exchange, high acidity and catalytic properties enhance the effectiveness of as bleaching earth, which can be further modify to beef up its adsorption ability [7 and 8]. Some of the modifications include acid treatment otherwise known as acid activation which enhances the ion exchange capability by the formation of Bronsted acids sites as well as creation of change deficiency on the clay structure by

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the leaching of aluminum ions. Activation of substance is required for a substance to be more actively involved in a chemical reaction. Clay is activated by heat or an acid before it is called a bleaching clay or and adsorbent earth. Activated clay is used in the oil industries for absorbing coloring matter from oil. Three types of bleaching clays include fuller's earth, activated clays and activated bauxite recognized in the industries. Raw clay has a very low natural activity but is highly activable when treated with mineral acid. This involves the acid treatment of substances such as Trona and Redearth so as to use them as substitute for the bleaching of red palm oil. Acid treatment enhances the ion exchange capability of the substance by the formation of Bronsted acid sites as well as creation of charge deficiency on the sample structure by the leaching of aluminum ions [9, 10 and 11]. High acidity bleaching clay generates free fatty acid as a result of the contact between acid on the clays surface and the palm oil. As a result, the hydrogen ion (H^+) catalyzes the hydrolysis of the triglyceride (oil) ester linkage forming free fatty acid and other oxidative by-products which impacts odour on the oil. Thermal activation involves the calacination or heating clay at appropriate temperature clay at appropriate temperature for 3 hours, retrieved and allowed to cool [12]. It has been reported that bleaching performance of clay/limestone composite increases with temperature of activation up to a maximum of 900^0C and bleaching temperature of 150^0C. The aim of this work, therefore, was to characterize the physical and chemical properties of Trona and redearth and to activate them at 150^0C and normal atmospheric condition and bleach Red Palm oil with the activated Trona, red earth in the ratio of 1:1 ratio and compare their performance.

MATERIALS AND METHODS

Sampling of Trona sample was obtained from Ogbete market in Enugu State, Nigeria, Redearth sample was collected from Awka in Anambra state, Nigeria and red palm oil. AOAC method was used in the analysis of the physical properties; loss on ignition, moisture content, density and silica content of the Redearth and Trona samples. This was done by the following methods:

Loss on Ignition: Weight of empty platinum crucible was weighed and recorded 0.2g of the sample was weighed into and the new weight was noted before heating with Bunsen burner for 1 hr. After 1 hr it was brought down and placed in a desiccator for cooling. The weight of platinum crucible and the sample was noted after heating.

Moisture Content: The weight of petric dish was recorded and 0.2g of the sample was weighed into the dish and weighed again. The set up was placed in an oven and heated to 101^0C until the moisture content of the sample was driven off. The sample was placed in a desiccator for cooling. The weight of platinum crucible and the sample was noted.

Silica Content: 0.2g of the sample was weighed into a platinum crucible and the weight was noted before a drop of Concentrated H_2SO_4 and 2ml of concentrated HF was added with thorough stirring. The mixture was heated until ash colour appeared. The sample was placed in dessicator for cooling. The new weight of platinum crucible and the sample was noted.

Density: Archimedes' principle was used to determine the densities of the samples and they were Redearth = 1.91g/cm^3 and Trona = 0.94g/cm^3

Activation of Sample: The Redearth and Trona samples were ground and sieved to a particle size of 0.15mm. 120g of each was treated with 120ml of concentrated Hydrochloric acid (HCl) in small pot with thorough stirring, the mixtures was heated to dryness for 3 hours on Bunsen burner [13 and 14]. After activation, the filtrate was washed severally and tested with pH meter until the washing indicate an alkaline pH showing complete removal was ash coloured. The residue was taken for further analysis.

Bleaching Sample: 50ml of red palm oil in 250ml beaker was heated to a temperature of 100^0C to evaporate the moisture. To the heated sample was added 5g each of activated redearth and trona obtained (residue). The mixture was heated for 15minutes with continuous stirring. The mixture was separated by filtration and the filtrate was taken for further analysis. The procedure was repeated with a mixture of activated redearth and trona in the ratio of 1:1 [15].

Percent Colour Reduction: 0.5ml of bleached red palm oil obtained from each of the bleaching agents was dissolved in 30ml chloroform and shake vigorously for uniform composition. The sample was introduced into the spectrophotometer for colour reduction and the reading was recorded at the wavelengths of 452nm.

Spectrophotometric Analysis

Digestion of Sample: 0.5g each of the Trona and Redearth samples was digested using Perchloric acid ($HClO_4$), tioxonitrate (v) acid (HNO_3) and hydrogen fluoride (HF) in the ratios of 1:1:2 in a Teflon Crucible. The mixture was heated in an oven at temperature of 150^0C until a clear solution was formed. The clear solution was poured into 250ml volumetric flask and make up to a mark with distilled water. The solution was transferred to a clean plastic bottle and store for further analysis.

AAS Analysis: The stock solution was prepared by known gram of salt in 1L of water based on each of the elements to be determined. The Atomic Absorption Spectrophotometer (Bulk scientific) 210 model was used to determine the levels of Cu, Pb and Mn in the samples of Redearth and Trona and their respective oxide was calculated based on a standard conversion factor.

Spectrophotometric Determination of Percent Colour Reduction: The Campsec spectrophotometer 108 model was used in the analysis of percent colour reduction from the oil bleached with each of the activated Redearth and Trona samples.

Titrimetric Determination of Iodine Value/Absorbance, Free Fatty Acid Content and Percent Fatty Acid Removal: A blank of 8.80cm^3 solution containing iodine was prepared. 0.5ml of the bleached red palm oil each of the bleaching agents (redearth, trona and 1:1 blend) was dissolved in 15ml of chloroform and 25ml of Wiji's solution. The mixture was thoroughly stirred, stored in an airtight bottle and kept in the dark for 30minutes. 20ml of 10% Kl and 150ml of distilled was added to the sample after 30minutes and the mixture was titrated with 0.1N sodium thiosulphate until reddish colour separation. 5ml of 1% starch was added before the end point, which was marked by change of colour. The procedure was repeated for the unbleached palm oil.

RESULTS

Table 1 presents the physical and chemical parameters of the investigated Redearth and Trona samples.

Table 2 presents levels of elements and their corresponding oxides in the investigated Redearth and Trona

Table 3 presents the percentage of oxide of metals in the investigated Redearth and Trona

Table 4 present the bleaching performance of the investigated Redearth and Trona and their ratio blend on palm oil

Table 5 presents the oil iodine value / Absorbance, Free Fatty acid Removal and the efficiency of Redearth and Trona and their 1:1 ratio blend

Table 1: Physical and Chemical Properties of Redearth and Trona

Sample	Redearth	Trona
Loss of ignition	30.5%	42.5%
Moisture content	0.156g	0.129g
Density	1.91g/cm^3	0.94g/cm^3
Silica content	75%	90%

Table 2: Concentrations of Elements and their Oxides in Redearth and Trona from AAS

Sample	Redearth			Trona		
Elements	Cu	Pb	Mn	Cu	Pb	Mn
Absorbance	0.058	0.024	0.040	0.005	0.063	0.039
Concentration from graph	0.000006	0.00085	0.0148	0.0000005	0.0021	0.0144
Conversion factors for oxide	6.258	1.08	6.258	6.258	1.08	1.29
% oxide concentration	0.02	0.57	5.80	0.002	1.42	5.80

Table 3: Percentage oxide concentration of metals in Redearth and Trona

	% Oxide Concentration								
Sample	CaO	Fe_2O_3	Na_2O	K_2O	Al_2O_3	MgO	CuO	PbO	MnO
Redearth	0.59	1.50	1.30	0.71	2.72	0.08	0.02	0.57	5.80
Trona	0.25	5.78	11.57	1.08	2.25	0.008	0.002	1.42	5.80

Table 4: Bleaching performance of Redearth, Trona and their ratio blend on Red Palm oil.

Bleached Palm Oil				
	Bleaching agents	Activated trona	Activated Redearth	1:1 ratio blend
1	Colour of the bleached oil with the bleaching agents	Yellow (not bright)	Yellow (bright)	Light-yellow
2	Absorbance	2.165	0.707	0.288
3	% Colour reduction	28.07	76.51	90.42
UNBLEACHED PALM OIL				
Colour		Absorbance		% colour reduction
Red		3.010		

Table 5: Red Palm oil iodine value / Absorbance, FFA Removal Efficiency of Redearth, Trona and their 1:1 ratio blend.

BLEACHED PALM OIL				
s/n	Bleaching agents	Activated trona	Activated Redearth	1:1 ratio blend
1	Iodinevalue/Absorbance (N)	6.19	3.05	2.79
2	FFA (cm^3)	1.40	1.70	1.30
3	FFA content	1.60	1.90	1.50
4	FFA removal	68	62	70
UNBLEACHED PALM OIL				
Iodine value / absorbance		FFA (cm^3)	FFA content (N)	FFA removal
8.63		4.550	5.0	-

DISCUSSIONS

Table 1 shows that the percentage of loss of ignition was higher in Trona than in Redearth. This is because the moisture content of Trona was lower than Redearth. In addition, thermal decomposition of bicarbonate yields carbonate / carbon (iv) oxide and water and this contribute to the loss on ignition [16]. It was observed that Trona contains less moisture content (0.149g) than Redearth (0.156g). This shows that high loss on ignition leads to less moisture content and the higher the loss on ignition, the more beneficial for moisture content [16]. Also it was observed that Trona has high silica content (90%) than Redearth (75%). This means that Trona is acidic and the silica content is due to the catalyst effect, which could be acid. Again, the Redearth has high density while Trona has low density. Table 2 shows that the percentage of CuO and PbO were 0.02% and 0.57% in Redearth and 0.002%, 1.42% in Trona respectively. Both Redearth and Trona was observed to have 5.80% MnO. Table 3 shows that the is percentage oxide which was observed in Trona to have 5.78% Fe_2O_3, 11.57% Na_2O, 1.08% K_2O, 0.25%CaO, 2.25% Al_2O_3, 0.0085% MgO. Hence high concentrations of oxides of Fe, Na, Al, Pb and K and low concentrations of Ca, Mg and Cu were observed in Trona. Also from Table 3 the percentages of have Fe_2O_3, Na_2O, K_2O, CaO, Al_2O_3 and MgO were to be 1.50%, 1.30%,0.71%, 0.59%, 2.72% and 0.08% respectively in Redearth. Hence, high concentrations oxides were the oxides Al, Fe and Na while low concentration oxides were the oxides of Ca, K and Mg. Trona has relatively high percentage concentration oxides (> 1.0%) of Fe, Na and Pb which implies that Trona can be called potash (because of high potassium content); soda ash (because of high sodium content); clay (because of high silica content) and relatively low percentage concentration oxides of Ca, Mg and average concentration of oxide of Al content implies that trona cannot be called a soil. On the other hand, Redearth has high percentage concentration oxide of Al, Mn and Fe implies that Redearth can be called clay. The low percentage concentration oxides of Ca, K, Cu and Pb show that Redearth cannot be called potash [17]. Equal concentration of percentage of oxide of Mn shows that they contain transition or volatile metal that contributed to the loss on ignition.

Table 4 shows that the bleaching agents have different percent colour. The bleeding performance of 1:1 ratio blend, activated Redearth and Trona gave 90.42%, 76.51% and 28.07% respectively. The 1:1 ratio blend has high colour reduction when compared with activated Redearth and trona. This means that it has high colour reduction and could be as a result of an increase in the

collision frequency between the molecules of the coloring matter and the particle of it. Also activated Trona has poor bleaching performance, which could be as a result of the formation of new colours by oxidation or fixation (non-response to adsorption) of some by oxidation or fixation (non-response to adsorption) of some of the existing colour pigments also by oxidation [18]. Table 5 revealed that 1:1 ratio blend gave 70 % FFA removal and 2.79N iodine value, activated Redearth gave 62% and 3.05N and activated Trona gave 68%, 6.19N respectively. The activated Redearth absorbed more iodine which implies more degree of instauration of oil while activated Trona absorbed less iodine which shows less degree of instauration of oil. Also the FFA content of the unbleached Red palm oil was observed to be at the moderate level (i.e not high or low which shows that the tendency of getting rancid is low). Also, the hydrogen ions cause some hydrolysis of the oil glycerides to form FFA and glycerine. Therefore, 1:1 ratio behaved more or less as a base and its FFA removal is believed to be at moderate level, followed by activated Trona and activated Redearth which shows the least [16 and 19].

CONCLUSION

The result of physical properties showed that Redearth has 30.5% loss on ignition, 0.156g moisture content, 1.91g/cm^3 density and 75% silica content while Trona has 42.6%, 0.149g, 0.94g/cm^3 and 90% silica constant respectively. Also the result of chemical properties showed that Redearth has 0.59% Fe_2O_3, 1.30%Na_2O, 0.17%K Q, 2.72% Al O_2, $_3$0.08% MgO, 0.02%CuO, 0.57% PbO and 5.80% MnO while Trona has 0.25%, 5.73%, 11.57%, 1.08%, 2.25%, 0.008%, 0.002%, 1.42% and 5.80% MnO respectively. Also bleaching Performance (modification) in term of percentage colour reduction, iodine value / absorbance, free fatty acid removal showed that 1:1 ratio blend gave the best bleaching performance followed by the activated Redearth which gave 76.51% colour reduction, 3.05N iodine values / absorbance and 62% free fatty acid removal while activated Trona gave 28.67% colour reduction, 6.19N iodine value / absorbance and 68% free fatty acid removal. Also apart from the 1:1 ratio blend, activated redearth is the best in terms of bleaching performance than activated trona. The comparism between Trona and Redearth (activated) showed that activated redearth can serves as a substitute for imported fuller's earth in the market. Based on the finding of this work, the 1:1 ratio blend of Trona and Redearth is recommended as a best substitute for imported fuller's earth as bleaching agent for red palm oil since its performance as found from this work in red oil bleaching is similar to that of fuller's earth.

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