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ACTIVATION OF CLAY SAMPLE FROM ZARIA L.G.A. OF KADUNA STATE AND TESTING ITS BLEACHING PERFORMANCE ON GROUNDNUT OIL, PALM OIL AND COTTENSEED OIL

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ABSTRACT

Clay samples from Zaria L.G.A. of Kaduna state was acid activated using hydrochloric acid in the concentration range of 5%, 10%, to 30% (v/v), at 90°C ± 2°C for 3 hours, and heat activated at 145°C for 30 minutes. The raw, acid and heat activated clay were tested on groundnut, palm and cottonseed oils. The per cent colour reduction was monitored spectrophotometrically. There was improvement in the decolourizing performance of the clay sample when acid or heat activated towards the three oil samples, but acid activation is more suitable for groundnut oil, while for palm and cottonseed oils the results obtained were similar for both methods.

Keywords: Clay, Kaolinite, Bleaching, Zaria, Oil

INTRODUCTION

Clay is a group of hydrous aluminium silicate minerals with particles that are ether < 2 μm or < 5 μm in nominal spherical diameter. The actual size may be 100 μm in one dimension and very much less than 1 μm in another (Raftery, 2005).

Commercial clays, or clays utilized as raw material in manufacturing, are among the most important non-metallic mineral resources. The value of clays is related to their mineralogical and chemical composition, particularly the clay mineral constituents, kaolinite, montmorillonite, illite, chlorite and attapulgite (McGraw-Hill Encyclopidia, 1987).

Because of their extremely small particle size, clay and humus have a large surface area per unit weight. Also, they exhibit surface charges that attract negative and positive ions and water. The attraction (adsorption) of ions such as Ca^{2+}, Mg^{2+} and K^{+} on the surface of colloidal clay and humus is not as exciting as the exchange of these ions for other ions in the soil solution. The intimate contact between soil solution ions and adsorbed ions make such exchange possible (Brady, 2002).

Fats and fatty oils, commonly called triglycerides, are constituted of triesters of glycerols, and include minor amounts of fatty acids. Triglycerides are distributed in nature. Some triglycerides are edible while others are not. Many are derived directly from vegetable, animal and marine sources. Others are obtained as by-products, in the production of fibre from vegetable matter in the production of protein from vegetable, animal, or marine matter (Shaked, *et al*., 1998).

In vegetable oil refining, the gold of bleaching clays is the elimination of series of contaminants that can be grouped into: primary, secondary and tertiary. The primary contaminants are oil soluble components originated from vegetable organisms: proteins, sterols, tocoferols, hydrocarbons and natural pigments (chlorophyll, carotenoids-carotene, lutein, gossipol, or xantophyll). The secondary contaminants are organic compounds formed inside the oil seeds by chemical degradation during their storage: free fatty acids, peroxides, ketones, aldehydes, pigments and non-hydrolysable phosphatides (Velenzuela-Diaz and Santos, 2001). The tertiary contaminants are chemicals compounds left or aggregated during the growth, development and processing of the oil seed; those coming from the deterioration of the equipment used in the process or by thermal degradation, solvents, biocides, free fatty acids, soaps, heavy metals, (as Fe^{3+} and Cu^{2+}), phosphoric acids and others (Velenzuela-Diaz and Santos, 2001).

The adsorption of neutral organic molecules on phyllosilicates has been studied extensively (Bradley, 1945; Mac-Ewan, 1948). Neutral molecules penetrate into the interlayer space of clays when the energy released in the adsorption process is sufficient to overcome the attraction between layers (Newman, 1987).

Possible adsorption sites in clay structure are firstly, the exchangeable metal ions with which sorbate molecules may form coordination compounds and, secondly, the surface oxygens of the tetrahedral sheets which may act as proton acceptors for the formation of H-bonds with molecules containing –OH or –NH groups. Both adsorption mechanisms may act simultaneously, but their relative contribution to the adsorption process will depend on the nature of the sorbate molecules and on the kind of exchangeable cations presents in the clay (Newman, 1987).

The best property of bleaching earth is its high adsorption capacity, which can be enhanced by acid treatment. The increased in specific surface area and pore volume improve the adsorption capacity of metals impurities, phosphatides and colour bodies (Velenzuela-Diaz and Santos, 2001).

EXPERIMENTAL

Chemicals of analytical grade purity and distilled/de-ionized water were used in the preparation of reagents. Clay sample was collected from Zaria local government, Kaduna state at the depth of 1 to 2 meters, using plastic hand shovel. The sample was air-dried by spreading out thinly in a dry, warm and highly ventilated room at room temperature. The sample was grinded using porcelain mortar and pestle and sieved through 65 mesh sieve. The soil sample was sealed in a polythene bag and stored (Agbenin, 1995).

The clay sample was acid activated with HCl (at variables concentrations; 5%, 10%, 15%, 20%, 25% and 30%), ratio 1:4 (w/v), at temperature of 90°C ± 2°C, and treatment time of 3 hours. Filtered and washed (pH = 3.5/4.5), dried 105°C/110°C and reground finer than 65 mesh sieve (Velenzuela-Diaz and Santos, 2001). The clay sample was heat activated at 145°C for 30 minutes (Hall *et al*., 1980).

10 cm^3 each of the oil samples (groundnut, palm and cottonseed oil) were placed separately in four 250 cm^3 beakers, then 0.5, 1.0, 1.5 and 2.0% (clay : oil) of the raw clay sample was added separately and the content of the beakers placed in an oven, set to a temperature of 90°C ± 2°C, for a contact time of 30 minutes. This process was repeated using 5%, 10%, 15%, 20%, 25% and 30% of the acid activated clay sample, and heat activated clay samples (Velenzuela-Diaz and Santos, 2001).

Residual colour measurements were carried out on the bleached and unbleached oil using the absorbance method (1:1.4, oil : hexane). The absorbance measurements were carried out using UV spectrophotometer (Cecil CE 7400) at a wavelength of 490.5, 706.0 and 910.5 nm for groundnut oil, palm oil and cottonseed oil respectively, using n-hexane as reference. The bleaching power of the adsorbent was determined as illustrated by Njiribeako and Nwanya (2000)

$$\%\, colour\ reduction = [\ 1 - \ A_{\downarrow}f / A_{\downarrow}i\ \ ]$$

Where; A_f = absorbance of the bleaching oil and A_i = absorbance of the unbleached oil.

RESULTS AND DISCUSSION

The bleaching performance of the bleaching agent with respect to colour reduction is shown in Tables 1 to 3.

The raw clay samples generally showed very low decolourizing ability, with the respective highest bleaching power of 25.1% at 1.5%, 10.0% at 1.5% and 25.0% at 2.0% against groundnut, palm and cottonseed oil. It was observed that the acid activated sample, the highest bleaching power for the three oil samples was 84.5% by 5% HCl at 0.5% for groundnut oil, 81.1% by 20% HCl at 1.5% for palm oil and 72.5% by 20% HCl at 0.5% for cottonseed oil.

In the case of the heat activated clay sample, the highest bleaching power was at 46.5% at 1.0% for groundnut oil, 71.2% also at 1.0% for palm oil and 49.6% at 0.5% when applied to cottonseed oil.

The low decolourizing power for the heat activated clay sample when applied to groundnut oil may be attributed to statement; while chlorophyll-rich oils such as soybean oil require a low pH for optimum adsorptive capacity, for other vegetable oils such as palm oil which are either low in chlorophyll or completely deficient, the clay's pH evidently is not as critical. And is the same reason for the heat activated clay sample being effective on palm oil despite its relatively high pH (Atu and Victor, 2008).

The high bleaching performance of the acid activated clay sample when applied to groundnut oil is due to the fact that the pH of the clay was lowered as a result of the acid activation to 3.5-4.5. For the same reason the acid activated sample showed average improvement in the bleaching ability of cottonseed oil. This is also in accordance with the fact that chlorophyll-rich oils require a low pH for optimum adsorptive capacity.

Bleaching clays are usually not equally efficient at removing colour impurities from different oils. Furthermore, there are seasonal variations in the content of colour impurities in many vegetable oils (Brooks *et al*., 1991). This may be another reason for the acid activated sample being effective on groundnut and palm oil, and both acid and heat activated sample showing average improvement when applied to cottonseed oil. For these reasons, processors of oils must inventory various bleaching clays and select from these a clay which meets the current needs of the processor (Brooks *et al*., 1991).

The observed increased in colour reduction with the quantity of bleaching agent is probably due to the availability of more adsorption sites until saturation point is attained, or could also be as a result of an increase in the collision frequency between the molecules of the colouring matter and the particles of the bleaching agent. The decrease in colour reduction, beyond this point, could be due to the increased adsorption of the oil molecules in preference to the molecules of the colouring matter. It could also be as result of the formation of new colours by fixation (non-respond to adsorption) of some of the existing colour pigments also by oxidation (Atu and Victor, 2008).

In summary, there was generally high improvement in the bleaching performance of the clay samples when acid activated compared with the raw clay sample for groundnut and palm oils, but is not much for cottonseed oil. For the heat activation only bleaching of palm oil observed a drastic improvement, whereas, for groundnut and cottonseed the improvement was not much.

Table 1: Percentage colour reduction of the bleached groundnut oil using raw, acid and heat activated clay sample

Weight of clay (%)	0.5	1.0	1.5	2.0
5%	84.5	83.8	83.8	82.3
10%	81.9	77.5	82.7	81.9
15%	83.0	81.5	81.9	82.3
20%	81.9	79.0	71.6	68.3
25%	81.9	80.1	80.4	81.9
30%	83.4	83.4	82.7	83.4
Heat Activated	44.3	46.5	46.1	43.5
Raw Clay	20.7	16.6	25.1	8.4

Table 2: Percentage colour reduction of the bleached palm oil using raw, acid and heat activated clay sample

Weight of clay (%)	0.5	1.0	1.5	2.0
5%	2.6	62.4	14.4	42.5
10%	77.4	39.1	61.9	70.7
15%	50.5	56.2	73.8	62.8
20%	62.4	51.2	81.1	67.5
25%	77.2	70.3	71.4	69.8
30%	72.3	57.8	73.3	73.7
Heat Activated	57.2	71.2	42.9	59.0
Raw Clay	5.0	7.5	10.0	10.0

Table 3: Percentage colour reduction of the bleached cottonseed oil using raw, acid and heat activated clay sample

Weight of clay (%)	0.5	1.0	1.5	2.0
5%	31.9	42.4	46.0	43.8
10%	43.8	42.0	43.8	42.8
15%	41.3	42.4	42.3	42.4
20%	72.5	42.8	40.6	39.1
25%	41.3	42.4	37.3	41.3
30%	36.2	34.1	35.9	36.2
Heat Activated	49.6	39.1	35.1	41.3
Raw Clay	14.9	19.9	23.5	25.0

In conclusion acid activation is appropriate for the bleaching of groundnut oil, whereas heat activation is not effective. For palm oil and cottonseed oil both acid and heat activation showed similar improvement in bleaching performance, but the improvement is better with palm oil than with cottonseed oil.

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