

## RECLAMATION AND RE-ACTIVATION OF SPENT BLEACHING CLAYS USED IN THE CLARIFICATION OF EDIBLE AND NON-EDIBLE FATS AND OILS

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**Abstract:** Bleaching clays (Fuller's earth) are special types of 3-layered clays used in bleaching both edible and non-edible fats and oils of animal and vegetable origin. Reclamation of the spent Fuller's earth was achieved by solvent extraction using non-polar or weakly polar solvents such as light petroleum ether and diethylether. Petroleum ether extraction appears to be more efficient than extraction with diethylether. Reclaimed bleaching clays were activated thermally by drying in an oven at various temperatures and best results were obtained at 80°C. Chemical activation was effected by introducing into the clay lattice some trivalent and divalent cations, by soaking the reclaimed clays overnight in a 10% aqueous solution of the respective cations. The results of our study reveal that chemically activated clays had improved bleaching properties.

**Key words:** Bleaching clay, fats, oils.

### INTRODUCTION

Bleaching clays, in particular Fuller's earth, are used extensively in bleaching edible and non-edible oils. These clays are essentially aluminium silicates (80-90%),<sup>1</sup> containing a small percentage of other minerals, mainly calcium and magnesium. Fuller's earth is a three layered, expandable clay.

Bleaching clays are imported by Nigeria and most other third world countries, for refining vegetable oils, in particular palm oil and animal fats (e.g. tallow) by the edible oils and soap industries. The lipochromes<sup>2</sup> present in these oils and fats are predominantly carotenes and the bleaching action of these clays is attributed mainly to surface adsorption and to a lesser extent to zeolitic action.<sup>3</sup>

Nigeria imports Fuller's earth, since it is not available locally. About 2-4% by weight of the clays is used for every ton of oil bleached and the spent clay is discarded

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after each use, though it retains about 30% (by weight) of oil, which constitutes a waste. With the modern practice of continuous process, rather than batch process, an average industry would use approximately 60 tons of oil per day. Thus simple computation reveals that (36-72) tons of bleaching clays are used and discarded every month and 11-22 tons of oil entrapped in them. Hence reclamation of the spent bleaching clay and the recovery of the oil entrapped in them constitutes an economically viable process.

## METHODS AND MATERIALS

The spent Fullers earth used was obtained from Lever Brothers (Nigeria) Ltd., Aba, Imo State, Nigeria. The palm oil used was crude palm oil readily available in the local markets in Imo State, Nigeria. Chemicals and solvents used in this study were all reagent grade, purified by recrystallization or distillation as appropriate. Soxhlet extractions of the spent Fuller's earth were carried out using a conventional extractor.

**Soxhlet extraction of spent Fuller's earth:** Spent Fuller's earth (100.0g) was extracted with dry diethyl ether or petroleum ether (40-60°C, 250cm<sup>3</sup>) using a soxhlet extractor until the extract was colourless (i.e. no more colour could be extracted). The extract was evaporated using a rotary evaporator.

**Thermal activation:** The soxhlet residue was dried in an oven at temperatures ranging from 80°C to 120°C for periods of approximately 15 h.

**Chemical activation:** This was carried out on the clays (both recovered and virgin clays) by soaking about 2.0g of the earth in 10% aqueous solution (20cm<sup>3</sup>) of each of the cations. Either the chlorides or sulphates of these cations were used. The clays were soaked overnight and filtered. The residue was washed free of chloride or sulphate as appropriate. The washed clay was then dried in an oven at 80°C for 15 h.

**Bleaching of crude palm oil:** The activated clay (2.0g) was transferred into a beaker (25cm<sup>3</sup>) and crude palm oil (5 cm<sup>3</sup>) was added. The mixture was stirred well with a glass rod and heated carefully for five minutes at a temperature of 210-215°C, care being taken to avoid charring of the oil.

**Preparation of colour standards:** Crude palm oil (1cm<sup>3</sup>) was made up to 10cm<sup>3</sup> in CCl<sub>4</sub>, giving a 0.1 dilution. A known volume of this solution (1cm<sup>3</sup>) was withdrawn using a grade A pipette and made up to 10cm<sup>3</sup> with CCl<sub>4</sub>. The same pipette was used throughout the study for consistency. This gave a 0.01 dilution. A series of solutions of crude palm oil in CCl<sub>4</sub>, varying in the intensity of their colours were produced by appropriate serial dilution, to cover the range of colours produced in the bleaching operation.

## RESULTS AND DISCUSSION

Reclamation of spent bleaching clays was carried out using a soxhlet extractor, with either diethyl-ether or light petroleum ether 40-60° C as the solvent. Our studies reveal that light petroleum ether is a better solvent for such extractions than diethyl ether since extraction with the former took 5-6 h while with the latter it took about 9h.

The recovered oil solidified at room temperature. This was not unexpected because tallow and palm kernel oils were used by Lever Brothers (Nigeria) and these are solids at ambient temperature.

The recovered clays were re-activated by drying in an oven at 80°, 100° and 120°C respectively. It has been established that the presence of a certain critical amount of water (6.62% by wt) <sup>4</sup> in the earth is necessary for optimum bleaching. This critical water level can only be achieved by adequate control of temperature (and time) of the thermal reactivation of the earth. Thermally reactivated clays were used in bleaching crude palm oil, care being exercised to avoid charring of the oil. The bleaching effects of the activated clays were determined by comparing the colour of the bleached palm oil against colour standards prepared by serial dilution of crude palm oil in CCl<sub>4</sub>. The results of such studies are represented in Table-1 and reveal that the recovered clays activated at 80°C exhibited better bleaching properties than those dried at higher temperatures.

**Table 1 : Colour match of regenerated and thermally activated Fuller's Earth**

Earth:Oil	Colour match ( $\times 10^{-3}$ )		
	80°C*	100°C*	120°C*
1. 1:1	1.5	1.5	2.0
2. 1:2	1.5	1.5	2.5
3. 1:3	2.0	2.0	3.0
4. 1:4	2.0	3.0	3.0
5. 1:5	2.5	4.0	4.5

(\* Drying temperature)

It has been reported that drying of clays improves the bleaching properties, but completely dehydrated samples lose their bleaching effect. Best results are obtained when the water content is between 5-10%. However, heating clays such as Fuller's earth to temperatures up to 300-800°C causes no serious structural changes of the clays.<sup>5,6</sup> The only effect, therefore, will be on the volatile materials, in particular, water.

Chemical activation of reclaimed clays was carried out by soaking the clays in a 10% aqueous solution of the cations such as  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Mg^{2+}$  and  $Co^{2+}$  respectively. Either the chlorides or sulphates of these cations were used.

The chemically activated clays were dried at  $80^{\circ}C$  for 5 h and the bleaching effects of the activated clays were determined in a manner exactly similar to those used for thermally activated clays.

**Table 2: Colour matching results for regenerated and chemically activated Fuller's Earth**

Cation	Colour match ( $\times 10^{-3}$ )	
	Virgin Fuller's earth	Reclaimed Fuller's earth
1. $Al^{3+}$	0.4	0.4
2. $Fe^{3+}$	0.5	0.4
3. $Ni^{2+}$	0.8	1.2
4. $Co^{2+}$	1.5	1.5
5. $Mg^{2+}$	1.5	1.5
6. $Mn^{2+}$	2.0	3.0
7. (*)	2.5	3.0

(\*Only thermal activation)

It is quite clear from the results presented in Tables 1 and 2 that chemically activated clays, both virgin and reclaimed, have better bleaching properties than the unactivated ones (i.e. both virgin and reclaimed clays). It is also apparent that the bleaching effects of chemically activated clays differ considerably, depending on the type of cations used. Among the cations studied, trivalent cations such as  $Al^{3+}$  gave better results than divalent cations. Although  $Al^{3+}$  and  $Fe^{3+}$  have the same ionic charge, the former cation gave better results than the latter, indicating that not only the ionic charge is relevant, but also the size of the ions concerned. The charge to size ratio of ions used in this study are presented in Table 3. It is pertinent to point out that chemical activation of the reclaimed clays was carried out using aqueous solutions of the respective cations and hence the ionic radii of hydrated cations would have been more relevant in determining the charge to size ratio. However, such data are not available in the literature but the limiting ionic mobilities in aqueous solutions of these cations are reported<sup>7</sup> and these values are directly related to the hydrated cationic radii. However, these follow generally the same order as the unhydrated cationic radii.

**Table 3: Charge to size ratio of cations used in the study**

Cation	Ionic Radius (nm)	Charge/size
1. Al <sup>3+</sup>	0.051	58.82
2. Fe <sup>3+</sup>	0.064	46.89
3. Ni <sup>2+</sup>	0.069	28.99
4. Co <sup>2+</sup>	0.072	27.78
5. Mg <sup>2+</sup>	0.066	30.30
6. Mn <sup>2+</sup>	0.080	25.00

It can be seen (Table 3) that Al<sup>3+</sup> has the highest charge to size ratio and that for Fuller's earth, the bleaching effect increases with increase in charge/size ratio. The bleaching action of clays is predominantly due to adsorption of carotenes. Both the carotenes and the oil are potential substrates which compete for adsorption on the available sites in the clay. Carotenes will be preferentially adsorbed because of the higher number of double bonds present in them, compared to those in the oil. Thus, more or less selective adsorption of carotenes takes place. With ions of similar or identical size, the higher the ionic charge, the greater the adsorption of carotenes (i.e. bleaching action of clays increases with the ionic charge of the cation).

Work is in progress to determine the effect of other variable parameters such as the concentration of salt solution, length of soaking time etc., on the bleaching effect.

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