

## Evaluation of Locally Available Fuller's Earth for the Bleaching of Soybean Oil

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**Abstract.** Locally available Fuller's earth was investigated for bleaching soybean oil. Investigations showed that raw earth samples possessed desirable physical properties and consisted of the clay minerals suitable for bleaching edible oils. The Fuller's earth sample was also activated by refluxing with 4 N hydrochloric acid for 3 h at 100 °C. Fresh volumes of soybean oil were bleached with 3% of the activated earth and its bleachability was determined by Lovibond tintometer. The efficiency of bleachability was compared with that of Tarana Optimum, the standard bleaching earth of German origin for comparison. It was found that bleachability of the activated earth samples and that of Tarana Optimum was quite comparable.

**Keywords:** oil bleachability, Fuller's earth, soybean oil, Fuller's earth activation

### Introduction

Impurities resulting from the raw material breakdown, or oxidation, impart undesirable colouration to edible oils, which is therefore required to be bleached during the refining process, (Hamilton and Bhatti, 1980). Activated charcoal and earths of specific nature are commonly utilized for this purpose. However, the latter being low cost materials are economically very attractive and popular (Brady *et al.*, 1997; Mahatta, 1985). Fuller's earth, the most important among these, is widely used on account of its low cost. In addition to the cost factor, it has large surface area and possesses the desirable adsorptive properties (Worral, 1986). Several researchers, due to this reason, have studied and attempted to activate such type of earths/clays for their optimum utilization as edible oil bleaching agents.

Theng and Wells (1995) investigated naturally occurring acid clays of hydrothermal geological formation from New Zealand and found that these were rich in Allophase, Halloysite, Kaolinite and Montmorillonite. They reported, as a result of their studies, that decolourizing capacity decreased in the order Halloysite > Kaolinite > Montmorillonite > Allophase. They also found that the naturally acid leached clays were more effective and required only minor treatment with HCl for optimizing their performance regarding decolourizing properties. Two activated clays, one imported and the other of Brazilian origin, were studied by Cardello *et al.* (1995), who reported that these were equally effective for bleaching the vegetable oil of *Gossypium hirsutum* (cotton). Similarly, a patent was registered in Germany (Haehn and Eisgruber, 1995) showing the importance of Fuller's earth in view of bleachability of

edible oils. It involved the regeneration of the used oil-containing bleaching clays through different steps, such as, decolourization by extraction with a suitable solvent, thermal treatment at 500-650 °C upto 5 h in oxidizing atmosphere, without disturbing the Montmorillonite contents, and treatment with an aqueous acid solution (15-50%) at acid : clay ratio of 0.2-2 : 100.

As Pakistan imports large quantities of bleaching earths for the vegetable oil refining industry, efforts have been made to explore, investigate and activate the locally available earths that have oil bleachability potential. A preliminary attempt was made to achieve the objective by Bogue under the Soil Survey of Pakistan (GSP-GSU, 1962). He investigated a small deposit at Thano Bulla Khan in the Sindh province of Pakistan and determined its chemical composition. Later on, a huge deposit of Fuller's earth was explored in Dera Ghazi Khan district of the Punjab province of Pakistan. Yousaf *et al.* (1989) investigated the deposit physicochemically upto some extent, and reported it to be promising if studied further and activated properly. This source has been, therefore, further investigated for its utilization for bleaching edible oils, which is reported here.

### Materials and Methods

**Fuller's earth samples.** Sixteen samples, belonging to the Dera Ghazi Khan deposit, obtained from four different sites (four replicate samples from each) were selected for the present investigations.

**Cation exchange capacity.** Since the cation exchange capacity (CEC) of minerals may vary with several factors, it can be exactly comparable only if the values are obtained by the same

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standard procedure. Therefore, CEC for all the investigated earth samples was determined. The CEC value of these samples was determined by adding 100 ml of 1 N ammonium acetate to 10 g of the earth sample contained in 500 ml beaker, stirred well and allowed to stand overnight at room temperature. The suspension was filtered through Whatman # 44 filter paper, collecting the filtrate in one litre volumetric flask. The procedure was repeated five times. 200 ml aliquot from this extract was evaporated on waterbath, dried on hotplate, and ignited in a muffle furnace at 1000 °C. To the residue was added 50 ml of 0.05 N HCl when cold, warmed gently, and left to stand for 1 h. The excess acid was titrated with 0.05 N sodium hydroxide and the CEC value was calculated in terms of milliequivalents/100 g by applying the specific formula as reported earlier (Yousaf *et al.*, 1989).

**Swelling index.** Samples were dried at 100 °C for one h, pulverized to 100 mesh (USS), and then added to 100 ml Nessler's tubes. Their volumes were noted separately and sufficient volume of distilled water was added upto the fixed mark, contents were shaken well, and allowed to stand at room temperature for 24 h. The expanded volumes (EV) were determined to the nearest millimeter and the swelling index (SI) values were calculated as the ratio between the expanded volumes and initial volumes (IV).

**Differential thermal analysis.** Four representative samples (one from each site) of the unactivated raw earth were finely ground to pass 100 mesh sieve (USS) for differential thermal analysis (DTA). The DTA tests were carried out at the constant heating rate of 10 °C/min within the temperature range 20-1000 °C, on a derivatograph (MOM, Budapest). Calcined Al<sub>2</sub>O<sub>3</sub> was used as the reference material throughout all the investigations.

**Surface area.** Particle size distribution was determined by using Andreasen and Lundberg apparatus. 5% suspension of the earth samples was made up in a 100 ml cylindrical vessel, shook well, and allowed to settle. Samples of the liquid, at the height of 20 cm from the surface, were withdrawn by 10 ml pipette at intervals. These were dried in collecting dishes, on a waterbath, separately, and the obtained powdery residues were weighed accurately. Particle size of the withdrawn fractions of the suspension, was calculated by applying Stokes Law and the surface area was determined by utilizing the accumulated particle size distribution data (Searle and Grimshaw, 1959).

**Activation and bleaching.** 100 g of each earth sample was ground to pass 60 mesh sieve (USS) and refluxed with 400 ml of 4 N hydrochloric acid at 100 °C, for three h. These were then filtered and washed thoroughly with distilled water, 3% activated earth was added alongwith 0.3% carbon to the soybean

oil samples for bleaching purposes. The resulting mixture was stirred on a waterbath for 45 min and the bleached oil was separated by filtration. The same process was repeated on all the fresh oil samples by using Tarana Optimum, the standard bleaching earth of German origin.

**Bleachability determination.** The bleachability was determined by applying the Lovibond tintometer method. The bleached soybean oil samples were filtered for removing any impurities and it was made sure that these were absolutely clear and free of turbidity. The Lovibond tintometer glass cell was dried after cleaning with carbon tetrachloride, filled with the sample and placed in the tintometer. Combinations of red and yellow Lovibond glass slides were then placed along the side of the instrument for matching the colour shade. The shade of oil was keenly observed through the combination of slides and the colour count was calculated in terms of Lovibond units by applying the standard formula (Bhatnagar and Dilgit, 1985). The colour count of the unbleached oil samples was taken as 100 during these calculations. All of the oil samples, bleached by Tarana Optimum, were also tested in the same manner for comparison.

**Statistical analysis.** The data obtained on CEC, SI and bleachability with respect to red pigment (BR) and yellow pigment (BY) were tabulated. These were then subjected to analysis of variance (ANOVA), using completely randomized design (CRD) and comparison of the means was done at 5% level of significance (Steel and Torrie, 1960).

## Results and Discussion

Under the modern concepts of mineralogy, clay minerals are classified under three major groups, namely, Kaolinite group, Montmorillonite group and Illite group. These groups are not only distinguishable by their different chemical compositions, but more particularly by their physical differences as influenced by their respective crystal structures. The Kaolinite group, in this perspective, represents a crystal structure wherein gibbsite sheet is condensed with one silica sheet, whereas the remaining two groups consist of crystal lattice in which gibbsite sheet is enclosed between two silica sheets. Secondly, the important factors influencing CEC indicate that its single value cannot be the characteristic of clay minerals, rather, a range of values characterizes each group of such minerals. The obtained results of CEC determinations are presented in Table 1, which show that five samples: RFE-2, RFE-4 (site A) RFE-5 (site B), RFE-11 (site C), RFE-14 (site D) had CEC values between 30 and 40. The data also indicated that ten samples had CEC values between 20-30. Only one sample (RFE-7; site B) was below 20 in this regard. In brief, all samples, except RFE-7 (site B) with CEC 14.0 fell within the

range 20-40, and were thus non-expanding layered structure clay minerals termed as Illite and Montmorillonite (Worrall, 1986).

The adsorption of water by clays leads to expansion or swelling, the magnitude of which varies widely with the kind of clay minerals present therein. It actually depends upon the extent to which the clay mineral adsorbs water between the individual silicate layers. The SI results are given in Table 1, which indicate that four samples: RFE-2 (site A), RFE-5 (site B), RFE-10 (site C) and RFE-15 (site D) had the values between 2.0-2.5. Eight samples: RFE-1, RFE-3, RFE-4 (site A); RFE-6, RFE-8 (site B); RFE-9 (site C), RFE-13, RFE-16 (site D) were in the range 2.5-3.0 in this regard. Table 1 further shows that four samples: RFE-7 (site B); RFE-11, RFE-12 (site C); RFE-14 (site D), had their respective SI values more than 3, but less than 3.5. Evidently, all of the samples were within the range 2.0-3.5, thereby showing low swelling nature of the investigated earth samples. As earths with higher SI values are undesirable for decolourizing edible oils, these samples were found suitable for bleaching soybean oil.

The activity of a powder is well known to be directly proportional to its surface area, which in turn has linear relationship with the particle size. Therefore, finer the particle size of a powdered material, larger will be its surface area. The surface

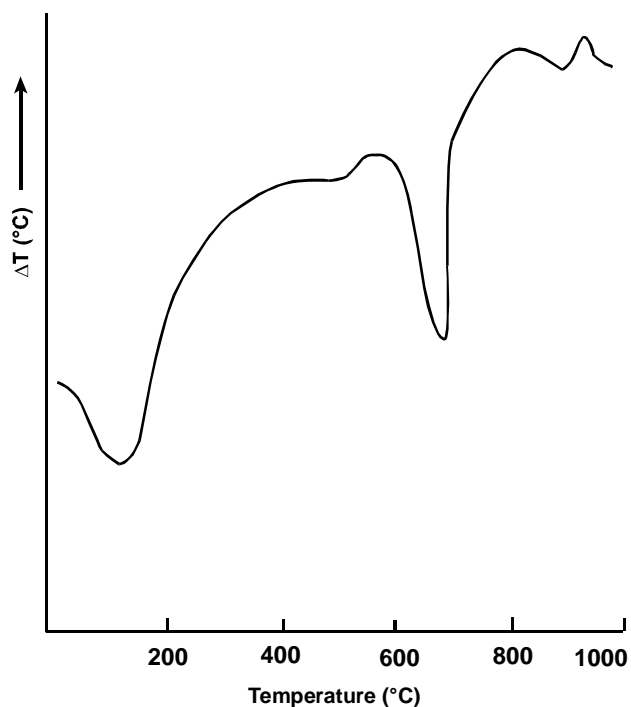
area of the raw earth samples studied was found between 31570-42850 sq cm/g. Hence, their bleachability was expected to be good due to their high surface area. It was so anticipated, as the adsorptive effect of the bleaching earths depended upon surface tension, which is directly proportional to their surface area. It is also notable here that though the unwanted colour of the edible oil is bleachable using chemical methods, foreign materials, nevertheless, continue to remain present in the form of colourless compounds. The adsorption procedure, on the other hand, makes the bleached oil absolutely free from all the foreign/colouring materials (Mahatta, 1985). This aspect is also favourable for the use of Fuller's earth instead of other materials.

The DTA method is a widely used technique, based on graphic recording of the changes occurring in the tested samples as a function of time, which are manifested by heat-related effects. The information obtained through this technique can be utilized for the identification of clay minerals. The data accumulated with DTA have been shown as curves given in Fig. 1-3. It is evident from these curves that the first endothermic peak in all the samples occurred around 140 °C, indicating the possibility of both Montmorillonite and Illite. However, peaks of the same nature appeared around 600 °C in the case of sample RFE-15 from site D (Fig. 3). Their comparison, with the standard DTA cards, showed that this sample

**Table 1.** Cation exchange capacity (CEC) and swelling index

Site	Sample*	CEC	Swelling index (milliequiv/g)
<b>A</b>	RFE-1	29.00	2.56
	RFE-2	31.00	2.38
	RFE-3	29.00	2.57
	RFE-4	32.60	2.92
<b>B</b>	RFE-5	30.00	2.50
	RFE-6	24.00	2.78
	RFE-7	14.00	3.12
	RFE-8	22.80	2.99
<b>C</b>	RFE-9	27.60	2.80
	RFE-10	23.80	2.26
	RFE-11	33.20	3.08
	RFE-12	20.00	3.21
<b>D</b>	RFE-13	29.66	3.00
	RFE-14	30.30	3.50
	RFE-15	24.00	2.40
	RFE-16	26.30	2.62

\* = raw samples of Fuller's earth investigated before their acid activation



**Fig. 1.** Differential thermal analysis (DTA) curve of sample RFE-3, site A.

**Table 2.** Bleachability (%) of soybean oil by different activated Fuller's earth samples

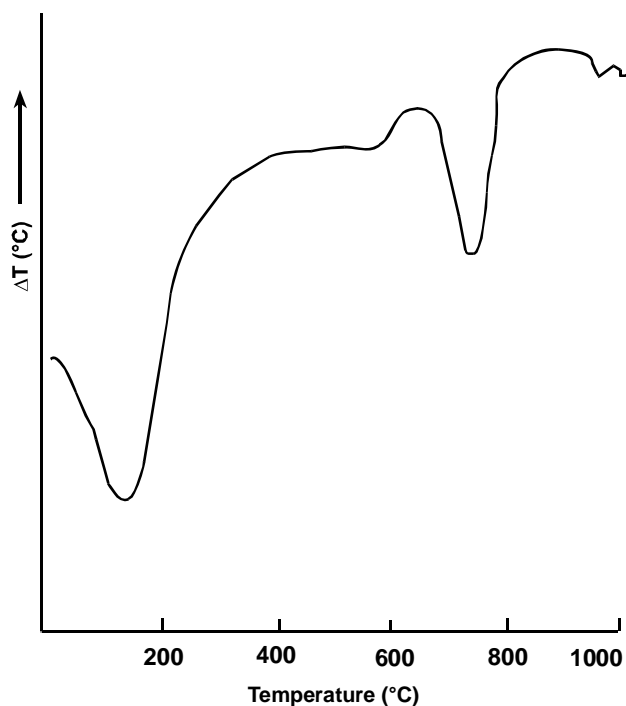
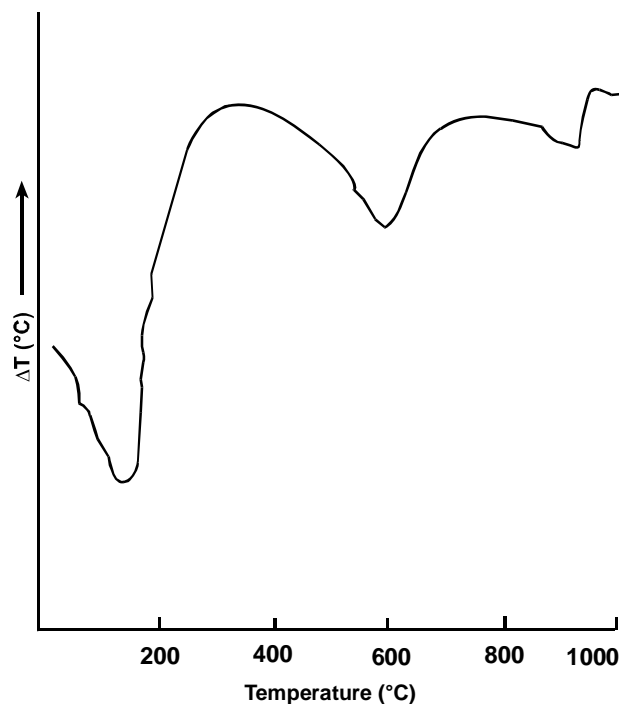
Site	Sample*	Yellow	Red
<b>A</b>	AFE-1	94.2	96.6
	AFE-2	93.8	96.5
	AFE-3	95.5	96.4
	AFE-4	93.8	96.3
<b>B</b>	AFE-5	93.5	96.6
	AFE-6	92.1	93.3
	AFE-7	93.5	96.5
	AFE-8	93.8	96.4
<b>C</b>	AFE-9	95.2	96.5
	AFE-10	93.5	96.5
	AFE-11	91.4	93.3
	AFE-12	94.2	96.4
<b>D</b>	AFE-13	95.5	96.5
	AFE-14	95.2	96.4
	AFE-15	94.5	96.5
	AFE-16	94.8	96.4

\* = activated Fuller's earth samples obtained after investigations on the raw earth sample; bleachability of Tarana Optimum (standard/control) was 94.2% for yellow and 94.9% for red pigment

consisted of Illite. While in the case of the curves for samples RFE-3 from site A (Fig. 1) and RFE-11 from site C (Fig. 2), the second endothermic peak occurred at 700 °C, instead of 600 °C. This indicated the presence of Montmorillonite. However, the last endothermic peak, which appeared in all the curves near 920 °C shows the possibility of both the Illite and Montmorillonite. These observations collectively indicate that the investigated samples consisted mainly of Illite and Montmorillonite.

Tarana Optimum bleached 94.2% yellow and 94.9% red pigment of soybean oil. The results obtained for the bleachability potential of the activated Fuller's earth samples are shown in Table 2. It is obvious from the given data that bleachability of most of the samples regarding yellow colouration was comparable with Tarana Optimum. However, the sample AFE-6 and AFE-11 were slightly on the lower side. Table 2 further reveals that sample AFE-3, AFE-9, AFE-13 and AFE-14 even excelled the standard earth sample. Fourteen samples, in view of bleaching red colouration, also excelled the Tarana Optimum, while the remaining two samples, AFE-6 and AFE-11, were fairly comparable.

So far as the bleaching phenomenon is concerned, it seemed to be due to physical adsorption of the colouring material on the activated earth powder. In fact, acid treatment of the raw

**Fig. 2.** Differential thermal analysis (DTA) curve of sample RFE-11, site C.**Fig. 3.** Differential thermal analysis (DTA) curve of sample RFE-15, site D.

**Table 3.** Means ( $\bar{x}$ ) and standard deviations (SD) regarding CEC, SI, BR and BY\*

Site	CEC (mean $\pm$ SD)	SI (mean $\pm$ SD)	BR (mean $\pm$ SD)	BY (mean $\pm$ SD)
A	29.06 $\pm$ 1.06 <sup>a</sup>	27.1 $\pm$ 0.23 <sup>a</sup>	96.55 $\pm$ 0.057 <sup>a</sup>	94.6 $\pm$ 0.92 <sup>a</sup>
B	27.27 $\pm$ 3.90 <sup>a</sup>	2.73 $\pm$ 0.55 <sup>a</sup>	95.67 $\pm$ 1.58 <sup>a</sup>	93.65 $\pm$ 1.27 <sup>ab</sup>
C	25.05 $\pm$ 8.27 <sup>a</sup>	2.79 $\pm$ 0.36 <sup>a</sup>	95.67 $\pm$ 1.58 <sup>a</sup>	93.72 $\pm$ 1.75 <sup>ab</sup>
D	25.42 $\pm$ 5.43 <sup>a</sup>	2.93 $\pm$ 0.24 <sup>a</sup>	96.37 $\pm$ 0.05 <sup>a</sup>	94.15 $\pm$ 0.47 <sup>b</sup>

\* = the values with same superscript are non-significant at 5% level of significance; CEC = cation exchange capacity; SI = swelling index; BR = red pigment; BY = yellow pigment

earth removed the foreign matter contained in its capillary tubes and thus made it extremely porous. This, in turn, enhanced the surface area of the so treated earth, the factor which played a vital role to bleach the colouring matter of soybean oil.

The results of statistical analysis have been shown in Table 3. All of the RFE (raw Fuller's earth) samples belonging to sites A, B, C and D indicated non-significant difference for the CEC and SI values. So far as AFE (activated Fuller's earth) samples are concerned, these also showed similar results with respect to bleachability, except those belonging to site A and site D, which indicated significant difference regarding yellow pigment only.

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### References

- Bhatnagar, A.P., Dilgit, S. 1985. *Edible Oil Technology*, pp. 192-198, Small Business Publications, New Delhi, India.
- Brady, G.S., Clauser, H.R., Vaccari, J.A. 1997. *Materials Handbook*, pp. 387-391, 14<sup>th</sup> edition, McGraw-Hill Book Co., New York, USA.
- Cardello, H.M.A.B., Borghi, A.B.M.P., Vila, M.M.D.C., Goncalves, L.A.G. 1995. Conventional bleaching procedure for cotton seed oil (*Gossypium hirsutum*). *Aliment. Nutr.* **6**: 77-87.
- GSP-GSU. 1962. *Fuller's Earth Deposit Near Thano Bulla Khan*, Technical Report, pp. 1-10, Geological Survey of Pakistan, Quetta, Pakistan.
- Haehn, R., Eisgruber, M. 1995. Regeneration of Used Oil-Containing Bleaching Clays by Extraction and Thermal Treatment, German Patent No. D.E. 4, 330, 274.
- Hamilton, R.J., Bhatti, A. 1980. *Fats and Oils, Chemistry and Technology*, pp. 144-146, Applied Science Publishers, London, UK.
- Mahatta, T.I. 1985. *Technology and Refining of Oils and Fats*, pp. 208-209, Small Business Publications, New Delhi, India.
- Searle, A.B., Grimshaw, R.W. 1959. *The Chemistry and Physics of Clays and Other Ceramic Raw Materials*, pp. 382-385, 3<sup>rd</sup> edition, Earnest Benn Ltd., London, UK.
- Steel, R.G.D., Torrie, J.H. 1960. *Principles and Procedures of Statistics*, pp. 7-30, McGraw-Hill, London, UK.
- Theng, B.K.G., Wells, N. 1995. Assessing the capacity of some New Zealand clays for decolourizing vegetable oils. *Appl. Clays Sci.* **9**: 321-326.
- Worral, W.E. 1986. *Clays and Ceramics Raw Materials*, 2<sup>nd</sup> edition, Elsevier Applied Science Publishers, New York, USA.
- Yousaf, M., Mian, M., Iqbal, M., Rafiq, M., Ayoub, M. 1989. Characterization of Fuller's earth from D.G. Khan. *Pak. J. Sci. Ind. Res.* **32**: 798-804.