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Investigations on Indigenous Fuller's Earth and its Evaluation After Acid Activation

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Abstract. Indigenous Fuller's earth from Dera Ghazi Khan district, Pakistan was investigated for its physical characteristics, specific to bleaching palm oil. Properties such as swelling index, surface area and thermal behaviour were determined. The results showed that the studied samples had the desirable large surface area, low swelling index, and consisted of illite and montmorillonite. These were then activated by giving treatment with 4 N hydrochloric acid at 100 °C for 3 h. Raw palm oil was bleached by adding 3% activated earth and the bleaching activity was determined by Lovibond tintometer. Out of the 15 replicate specimens, more than 90% red pigment was bleached in 7 samples, whereas more than 60% red pigment bleaching was noted in 12 samples. However, bleaching of the yellow pigment was not as effective as was observed in the case of red pigment.

Keywords: Fuller's earth, palm oil bleaching, swelling index, illite, montmorillonite

Introduction

The bleaching of edible oils is an important step in their refining for the removal of impurities, such as trace metals, sulphurous compounds, stable pigments, and the pigment breakdown products resulting from raw material damage or oxidation (Hamilton and Bhatti, 1980). The commonly used bleaching agents are activated charcoal and earths of specific nature. Their efficiency in this regard depends on their grade and acid activation treatment. The low cost of the specific-nature earths is an attractive attribute, which makes their use more popular (Gannouni *et al.,* 1999; Brady *et al.,* 1997; Mahatta, 1985). Therefore, Fuller's earth is widely used on account of its cheaper availability, large surface area, and desirable adsorption properties (Worral, 1986). A good number of researchers, due to this reason, have been engaged in studying and activating this type of earths/clays for their use as edible oil bleaching agents.

Two activated clays, one of which was of Brazilian origin, were reported to be equally effective for bleaching purpose (Cardello *et al.,* 1995). Some naturally occurring acid clays of hydrothermal origin, from New Zealand, were evaluated and found to be rich in allophase, halloysite, kaolinite and montmorillonite (Theng and Wells, 1995). These authors reported that decolourizing capacity decreased in the order of halloysite > kaolinite > montmorillonite > allophase. This work also indicated that the clays, severally leached by acids during their formation, were more effective as they required only minor treatment with HCl for optimizing their performance as decolourizing agents. Later on, optimum conditions for the activation of a suitable clay were determined for bleaching olive oil under variable parameters, such as reaction time, temperature, initial concentration of acid, and liquid-solid weight ratio. Good agreement between the anticipated and obtained results was found at the end of this study (Gannouni *et al.,* 1999). Another group of researchers studied the treatment of Ca-montmorillonite with sulphuric acid paying special attention to the layered structure of this type of clay. Such treated clays, when used for the bleaching of cotton seed oil, on elemental analysis, showed that moderate activation had occurred as a result of acid treatment, while linear dependence of bleaching efficiency on the clay surface area and acidity was also observed (Falaras *et al.,* 1999).

Pakistan imports large quantities of bleaching earths for the vegetable oil refining industry. Therefore, efforts have been made in the present study to explore, investigate and activate the indigenously available earths. Bogue (1962) initiated this type of work and explored a small deposit at Thano Bulla Khan in Sindh province of Pakistan. He examined the Fuller's earth, belonging to the same deposit, microscopically, and found that it was locally fossiliferous. He suggested that thorough physicochemical investigations should be done to get maximum benefit through the utilization of indigenous resources of Fuller's earth. The chemical composition of the samples selected from the same deposit indicated significant differences among themselves, except in respect of the Fe_2O_3 content. In addition to this source of sampling, Yousaf *et al.* (1989) studied the earth samples obtained from a huge deposit in Dera Ghazi Khan district in the Punjab province of Pakistan, proposing further de-

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tailed investigations on this source. The present studies were, therefore, conducted to determine the surface area (SA), swelling index (SI) and the mineralogical nature of representative specimens from this deposit, using differential thermal analysis (DTA) and thermogravimetry (TG). Acid activation of this sample of Fuller's earth and its evaluation for the bleaching of palm oil were also carried out.

Materials and Methods

Thirty representative specimens, obtained from different sites of the Dera Ghazi Khan Fuller's earth deposit were pulverized to 100 mesh (USS) and dried at 110 °C for 1 h. These samples were then studied as replicate samples for determining their swelling index (SI) and efficiency for oil bleachability.

Swelling index (SI). Each sample (10 g) was transferred to 100 ml Nessler's tube (calibrated in mm with 2 cm internal dia). Their volumes were noted after tapping gently. Sufficient volume of distilled water was added upto the mark and contents were shaken well. These were allowed to stand at room temperature for 24 h and the expanded volumes were noted to the nearest mm. The SI values were calculated as the ratio between the expanded volume and the initial volume (Yousaf *et al.,* 1989).

Differential thermal analysis (DTA). Three representative specimens of the raw (inactivated) Fuller's earth samples were ground separately to pass 100 mesh (USS) and marked. DTA was carried out on Derivatograph (MOM, Budapest, Hungary) at the heating rate of 10 °C/min within the temperature range from 20-1000 °C. Thermogravimetric (TG) test was also run alongwith DTA on the same instrument. The reference material used throughout all these experiments was calcined Al_2O_3 (Yousaf *et al.,* 1989).

Surface area. Particle size distribution was determined by using Andreasen and Lundberg apparatus. The Fuller's earth samples were made up as 5% suspension in a 100 ml cylinder, shook well and allowed to settle. Samples of the liquid, at a distance of 20 cm from the surface, were withdrawn using 10 ml pipettes. These were dried in collecting dishes on a waterbath, separately, and the obtained powdery residue was weighed accurately. Grain size of the particles, in the withdrawn fractions of the suspension, was calculated by applying Stokes Law and the surface area of the particles was determined by utilizing the accumulated grain size distribution data (Searle and Grimshaw, 1959).

Activation and bleaching. Earth samples (100 g) were refluxed with 400 ml of 4 N HCl at 100 °C for 3 h. These were removed from the acid and washed thoroughly with distilled water till free of chloride ions. Bleaching was performed by adding 3% activated earth to the palm oil samples. The resulting mixtures were continuously stirred on a waterbath for 45 min and separated by filtration. This process was repeated on all the oil specimens by using Tarana Optimum, the standard bleaching earth of German origin.

Bleachibility determination. Tintometer glass cell was dried after thorough washing with carbon tetrachloride, filled with the sample and placed at appropriate position in the tintometer. Combinations of red and yellow Lovibond glass slides were then placed along side the tintometer for matching the colour shades. The shades of bleached oil were observed through 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 the oil samples bleached by Tarana Optimum were also tested using similar procedure.

Statistical analysis. The data obtained on SI and bleachibility with respect to red (BR) and yellow pigments (BY) were properly tabulated. These were then subjected to analysis of variance (ANOVA) using completely randomized design (CRD) and a comparison of mean values was done at 5% level of significance (Steel and Torrie, 1960).

Results and Discussion

The modern concept of mineralogy recognizes clay minerals to comprise of three major groups, namely, kaolinite group, montmorillonite group, and illite group. These groups are not

Table 1. Swelling index values of the raw Fuller's earth samples from Dera Ghazi Khan district, Pakistan

Sample	Swelling index (mean ± SD)
1	3.08 ± 0.02
2	3.63 ± 0.03
3	3.07 ± 0.07
4	3.82 ± 0.19
5	3.01 ± 0.70
6	2.34 ± 0.14
7	3.35 ± 0.20
8	2.78 ± 0.05
9	2.34 ± 0.08
10	2.92 ± 0.09
11	2.46 ± 0.17
12	2.51 ± 0.13
13	3.85 ± 0.21
14	2.66 ± 0.07
15	2.40 ± 0.02

SD = standard deviation

only distinguished by their varying chemical compositions but particularly so by their physical differences as influenced by their crystal structures. The kaolinite group, in this perspective, represents a crystal structure in which gibsite sheet is condensed with one silica sheet, whereas the remaining two groups consist of crystal lattice in which gibsite sheet is enclosed between two silica sheets. The adsorption of water in clays leads to expansion or swelling, the magnitude of which varies widely with the kind of clay minerals present in them. This depends on the extent to which the clay mineral adsorbs water between the individual silicate layers. The swelling index observations on the presently studied Fuller's earth samples are given in Table 1, which show that the majority of samples (all, except 2, 4 and 13) lie within the range 2 -3.5, thus indicating their low swelling nature. Since the Fuller's earths having higher swelling index values are undesirable for the purpose of bleaching edible oils, the studied samples were found to be suitable for the bleaching of palm oil.

Differential thermal analysis (DTA) is a widely used technique, which is based on graphic recording of the changes occurring in the tested sample as a function of time, which are manifested by heat related effects. The information obtained through this procedure is utilized for the identification of clay minerals. Data regarding DTA of the clay samples have been shown in Fig.1. The first endothermic peak in all the samples occurred around 140 °C indicating the possibility of both montmorillonite and illite. However, this uniformity was not observed regarding the second peak as of the same nature. This peak appeared around 600 °C in the case of samples 8 and 9 (Fig. 1b and Fig.1c, respectively). Comparison with standard DTA cards showed that these samples consisted of illite. On the other hand, the second endothermic peak of samples 2 and 12 occurred at 700 °C (Fig. 1a and Fig. 1d, respectively), instead of 600 °C as was noted for samples 8 and 9. This indicated the presence of montmorillonite. The last endothermic peak, for all the samples occurred near 920 °C, which shows the possibility of both the illite and montmorillonite. It is evident, in view of these observations, that the investigated samples, consisted mainly of illite and montmorillonite clay minerals.

The thermogravimatric observations have been shown in Fig. 2, from which it is obvious that the first loss in weight occurred around 140 °C indicating the evaporation of moisture, whereas the second major loss was observed at 600-700 °C, which was due to the removal of structural water. Evidently, the differential thermal analysis and the thermogravimetric results are consistent with each another.

It is well known that the activity of any powder is 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 Fuller's earth samples studied was found to be between 31570-42850 cm^2/g. Hence, their bleachibility was expected to be good due to high surface area. It is also expected that the adsorptive effect of the bleaching

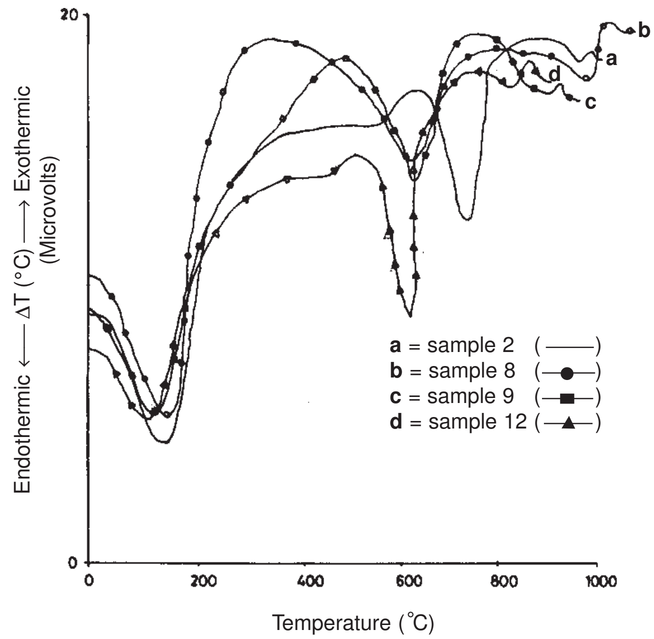

Fig. 1. Differential thermal analysis (DTA) curves of samples 2, 8, 9 and 12 of the Fuller's earth samples from the deposits at Dera Ghazi Khan district, Pakistan.

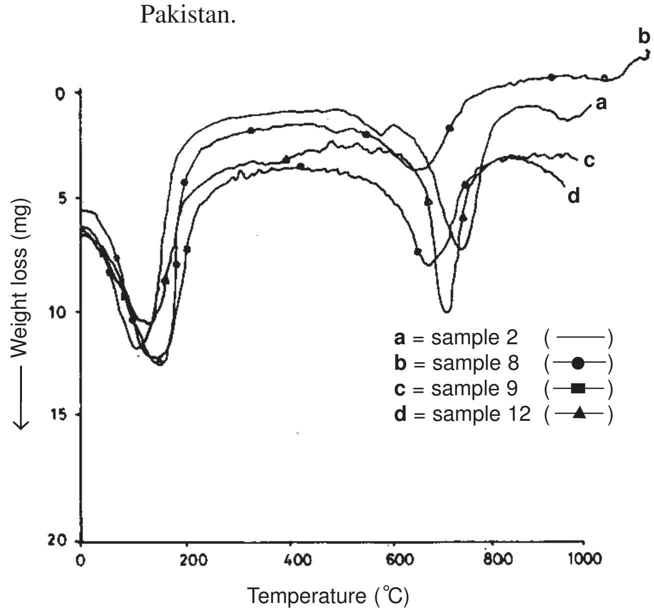

Fig. 2. Differential thermogravimetric (DTG) curves of samples 2, 8, 9 and 12 of the Fuller's earth samples from the deposits at Dera Ghazi Khan district, Pakistan.

earths depends upon their surface tension, which is directly proportional to their surface area. It is relevant to note that though chemical treatments bleach the undesirable colour, these do not remove colourless materials present in the edible oil as impurities. The physical adsorption procedure, on the other hand, renders the bleached oil absolutely free from all foreign materials and the colouring agents (Mahatta, 1985). This aspect is a positive attribute for the utilization of Fuller's earth instead of other materials and chemical treatments.

Tarana Optimum, the standard bleaching earth of German origin, bleached yellow and red pigments of palm oil, respectively, 60.0% and 95.8%. The efficiency of the presently investigated activated Fuller's earth samples to bleach palm oil have been given in Table 2, from which it is obvious that two samples, namely, 2 and 9 approached the Tarana Optimum in bleaching red pigment from the palm oil. Four other samples, namely, 8, 10, 13 and 15 though bleached this pigment less than samples 2 and 9, yet were able to bleach the red pigment more than 90%. Sample 1 bleached the red pigment even greater than Tarana Optimum. The yellow pigment was bleached fairly by most of the samples, but the bleaching was not as effective when compared with the Tarana Optimum. It is notable, however, that bleaching of red pigment of the edible oil is of greater significance, whereas the presence of the less bleached yellow pigment is tolerable. It is also important to note that red pigment was bleached more than 60% (minimum bleachibility percentage) by twelve samples in the total of 15 samples studied.

Table 2. Bleachibility of red and yellow colours of palm oil (%) by activated Fuller's earth from Dera Ghazi Khan district, Pakistan

Sample	*BY (mean ± SD)	**BR (mean ± SD)
1	51.8 ± 2.54	96.3 ± 0.78
2	40.3 ± 2.75	94.7 ± 0.36
3	32.7 ± 2.68	85.9 ± 3.08
4	46.15 ± 5.44	77.1 ± 1.13
5	44.2 ± 2.68	85.0 ± 0.92
6	17.3 ± 2.68	63.3 ± 2.58
7	13.5 ± 2.68	63.8 ± 0.70
8	7.7 ± 0.00	92.2 ± 0.56
9	40.3 ± 0.00	95.4 ±1.55
10	28.9 ± 2.68	92.8 ± 2.96
11	36.5 ± 2.68	43.3 ± 1.00
12	0.0 ± 0.00	27.8 ± 1.00
13	5.8 ± 2.68	93.3 ± 0.84
14	7.7 ± 0.00	58.7 ± 2.90
15	36.5 ± 2.68	93.7 ± 2.53

*BY = bleachibility with respect to yellow pigment; **BR = bleachibility with respect to red pigment; SD = standard deviation

The observed bleachibility of the activated Fuller's earth seemed to be due to physical adsorption of the colouring matter on account of the active centres created by its acid treatment. Such a treatment removes the foreign matter contained in the capillary tubes of the raw Fuller's earth, and thus made it extremely porous with enhanced surface area, the specific property which plays the most vital role regarding its bleachibility attributes.

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