Pakistan J. Sci. Ind. Res., Vol. 31, No. 4, April 1988

STUDIES ON INDIGENOUS FULLER'S EARTH

M. Arshad Ali Beg, T.H. Usmani and Tamoor Wahab

PCSIR Laboratories, Karachi-39

(Received December 21, 1985; revised April 21, 1988)

Fuller's earth deposits discovered recently at Nooriabad (Distt. Dadu) can be activated by leaching the earth with 25 to 45 % sulphuric acid. The process of activation with 30 % sulphuric acid reduces the iron content from 12.7 % to 10.8 %, raises the silica-alumina ratio to 1:5.06, yields a product having improved colour and easy filterability. Activity of clay has been determined against crude soyabean oil and it has been found that product achieves maximum activity at a concentration of 5 % as compared with 7-8 % for other products.

Key words: Indigenous fuller's earth, Activation, Soyabean oil.

INTRODUCTION

The term Fuller's earth is applied to clays which have adequate decolorizing and purifying capacity for commercial use in oil refining without chemical treatment [1]. Fuller's earth contains hydrous silicates of aluminium, magnesium, calcium and contains small amounts of iron, sodium, potassium etc. These clays can deodorize, dehydrate and neutralize. Besides these functions they are generally used to decolorise oils.

The earths for bleaching edible oils are used in natural state or prepared to enhance their bleaching power [2]. They vary from green, yellow to grey in colour and occur in layers of variable thickness. The appropriate clay stratum is seldom contaminated with sand or limestone. The layers are of variable quality lie at different depths, under 2 to 20 metre overburden [3]. The deposits at Nooriabad were discovered through LANDSAT Imageries by the American Counterparts of M/s. Sui Pakistan Ltd. [4].

Fuller's earth for high bleaching power is activated by treatment with sulphuric or hydrochloric acid or some other suitable chemicals. Such chemically treated earths are more efficient when compared with naturally occuring ones.

The present studies have been carried out (a) to know the nature of the Nooriabad based clay and (b) to develop an activation method to obtain the desired bleaching power by acid treatment.

The process involves preparation of a smooth paste with water [5], adding an economical mineral acid, such as sulphuric acid, which is easy to handle and activating by using live steam. Activation with acid reduces the iron content whose excess can drastically reduce the adsorbing characteristics of a Fuller's earth [6]. Other activation chemicals mentioned in literature are hydrochloric acid, acetic acid, oxalic acid, phosphoric acid, hydrofluoric acid and zinc chloride etc. Their use on commercial scale pose difficulties and are not practicable.

EXPERIMENTAL

For the present studies, samples of Fuller's earth from Nooriabad (Distt. Dadu) were used. The iron content of this earth was 12.7 %.

The crushed raw earth was first ground to retain a maximum of only 10 % on a 170 mesh sieve and one kg sample was used for each experiments. The sample was treated with 4 litres of sulphuric acid of 15 to 40 % strength. The mixture was then treated at 100-105° with live steam for 6 hours in a glass lined vessel with refluxing to reduce evaporation losses. Samples drawn after definite intervals of time were treated and washed with fresh water by decantation and finally under vacuum until it was free from acid. The samples were oven dried at 100-150° to an appropriate moisture content. The conglomerates were again ground to a fineness of 10 % retained on 170 mesh sieve.

The chemical analysis were carried out by standard analytical methods [7].

The effect of varying concentration of acid on bleaching power of earths was determined to optimize the reaction conditions [8]. The bleached soyabean oils were then compared by means of a Lovibond Tintometer through a 1 inch thickness of oil.

The relation between time and temperature of treatment on clarifying properties of Fuller's earths were

determined by the method described in the literature.

The presumptive loss of oil by different Fuller's earths have been determined by Standard Method [9]. The filtration rate of different earths were compared under reported working conditions [10].

RESULTS AND DISCUSSION

Upgradation of Fuller's earth can be carried out by treatment with different chemicals such as zinc chloride or by acids like hydrochloric acid, acetic acid, phosphoric acid, sulphuric acid, oxalic acid and hydrofluoric acid. Among these hydrochloric acid and sulphuric acid are most commonly used for activation. However, the use of hydrochloric acid is not economically feasible because of its high cost. The use of sulphuric acid on the other hand does not pose these problems and can activate the indigenous earth to the desired level. Accordingly the method described here can be developed for the production of activated Fuller's earth from Nooriabad deposits. The unactivated earth is subjected to treatment with acid of varying concentration. The reaction yields Fuller's earth of favourable $SiO_2:Al_2O_3$ ratio [11] and compared with the raw material.

Table 1 shows the detailed analysis before and after activation using different acid concentrations. It may be

Table 1. Analysis of indigenous fuller's earth on activation with different concentrations of acid.

Sr. No.	Constituent	Concentration of sulphuric acid used for activation 25 %	30 %	35 %	40 %	45 %
1.	Moisture	10.09	10.38	10.40	10.12	10.26
2.	Loss on Ignition	5.61	5.73	5.57	5.92	5.80
3.	SiO_2	57.33	59.00	58.21	58.75	58.85
4.	Fe_2O_3	8.91	8.87	8.62	9.07	8.98
5.	Al_2O_3	12.27	11.66	11.92	11.82	11.75
6.	CaO	1.61	1.02	1.12	1.05	1.11
7.	MgO	2.75	2.25	2.51	2.42	2.35

observed that the $Al_2O_3:SiO_2$ ratio of 1:5.06 is achieved on activation with 30 % sulphuric acid. The ratio gradually decreases with increase in concentration of acid, possibly due to loss of combined water which would yield silica rather than hydrated silicic acid.

Table 2 shows detailed analysis of Fuller's earths of different origin. It may be noted that silica content of the earth "A" increases after acid activation while that of alumina and iron decreases. The decrease in the soluble constituents perhaps increases the specific surface area of

Table 2. Analysis of fuller's earths of different origins*

Sr. No.	Constituent	A (%)	B (%)	C (%)	D (%)	E (%)
1.	Moisture Content	10.93	10.38	10.36	13.37	10.10
2.	Loss on ignition	9.94	5.73	5.64	10.64	9.80
3.	SiO_2	51.29	59.00	69.12	62.11	62.24
4.	Fe_2O_3	12.77	8.87	4.38	1.69	6.18
5.	Al_2O_3	11.86	11.66	10.62	11.19	11.10
6.	CaO	1.70	1.02	0.79	0.74	0.60
7.	MgO	2.26	2.25	0.90	1.57	1.24

*A: Unactivated (Nooriabad); B: Activated (Nooriabad); C: China; D: Kashmir; E: German (Terrana).

the earth by formation of a network of pores, thus increasing the activation capacity. It may also be seen that treatment with mineral acid raises the $SiO_2:Al_2O_3$ ratio from the original 1:4.3 in unactivated earth A to 1:5.06 in activated earth B which closely resembles that of D and E which is 1:5.55 and 1:5.6 respectively.

The results showing different levels of activation with different concentrations of sulphuric acid are shown in (Table 3).

Fig. 1 shows that optimum activation was achieved by using 30 % concentration of sulphuric acid, and also observed that earth A activated shows better activity at lower percentage. It also attains maximum adsorptive power at 5 % concentration whereas in other cases this is achieved at 7 or 8 % concentration hence conforming the results of Table 1, of A washed with 30 % acid giving maximum $SiO_2:Al_2O_3$ ratio. Earth A activated was used in subsequent experiments.

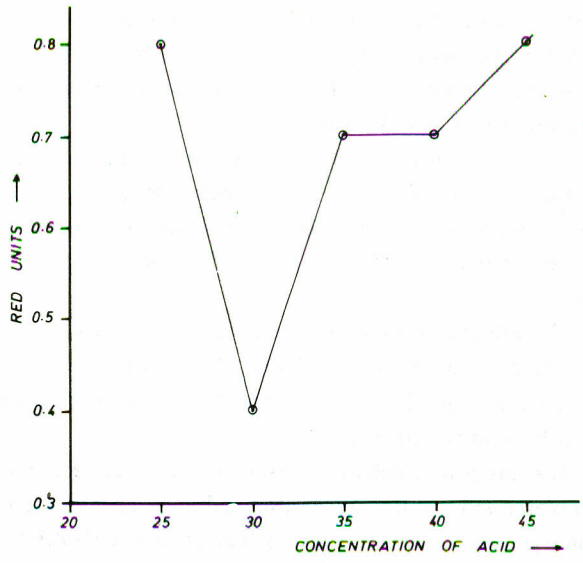

Fig. 1. Effect of concentration of acid on activity of indigenous fuller's earth.

The bleaching power of an earth greatly depends upon its physical characteristics. Removal of absorbed water from any bleaching earth, improves bleaching properties. If heating removes the water of composition, it may lose its activity altogether. The effect of combined/free water on bleaching power of all earths was determined by heating them to a temperature of 100° and 600° (Table 4). Heating at a temperature of 600° remarkably decreases the bleaching power, due to the transformation of hydrated silicic acid into the anhydrous form [12].

Attempts were made to find a general relationship between temperature and time of treatment [13]. A comparative results of effect of time on bleaching of B with A, C, D and E are presented in (Table 5).

Figure 2 indicates that the time of treatment at 160° increases the red units of soyabean oil gradually in all activated earths except earth A.

A comparative study of the effect of temperature on bleaching power of different earths has been carried out Table 6 (Fig. 3), showing that oil bleaching action of the

Table 3. Effect of concentration of acid on activity of indigenous fuller's earth
lovibond reading of untreateds soyabean oil at 160°C $\frac{R}{3.1}$ $\frac{Y}{14}$

Sr. No.	Percentage of earth 'A' used	25 %		30 %		35 %		40 %		45 %	
		R	Y	R	Y	R	Y	R	Y	R	Y
1.	1	2.1	11	1.1	10.4	2	11.2	2.2	12	2.3	12.5
2.	2	1.6	8	1	10	1.5	10	1.7	11	2	10.4
3.	3	1.2	7.8	0.9	8	1.3	10	1.1	10	1.6	8
4.	4	0.8	4.4	0.7	7	1	8	1	8	1.2	7
5.	5	0.8	4.2	0.4	5	0.7	6	0.7	6	0.8	7
6.	6	0.7	4.2	0.4	4	0.6	5	0.6	6	0.6	5
7.	7	0.5	4.0	0.4	4	0.5	4	0.5	5	0.5	4
8.	8	0.5	4.0	0.4	4	0.4	4	0.4	4	0.3	4

Table 4. Effect of combined/free water on earths.

Sr. No.	Temperature to which earth has been heated	A		B		C		D		E	
		R	Y	R	Y	R	Y	R	Y	R	Y
1.	100°C	0.5	12	0.4	11	1.3	13	1.0	11	1.0	14
2.	600°C	1.0	14	0.9	10	1.4	14	1.3	12	1.3	15

Table 5. Effect of time on bleaching of soyabean oil at 160° of earths of various origin
lovibond reading of untreated soyabean oil at 160° $\frac{R}{3.1}$ $\frac{Y}{14}$
Percentage of earth used = 5 %

Sr. No.	Time of treatment (min.)	A		B		C		D		E	
		R	Y	R	Y	R	Y	R	Y	R	Y
1.	10	1.5	11	0.9	9	1	7	0.8	9	0.6	7
2.	20	1.4	11	1	11	1.1	11	0.9	11	0.7	10
3.	30	1.4	11.5	1.1	11.5	1.2	10	1.1	11	0.9	11
4.	40	1.3	12	1.2	12	1.3	13	1.2	12	1	12
5.	50	1.2	11	1.3	13	1.4	13	1.3	13	1.1	12

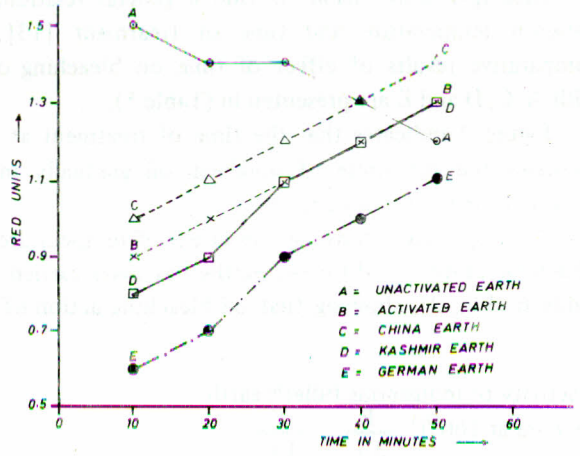

Fig. 2. Effect of time on activity of earths at 160°C.

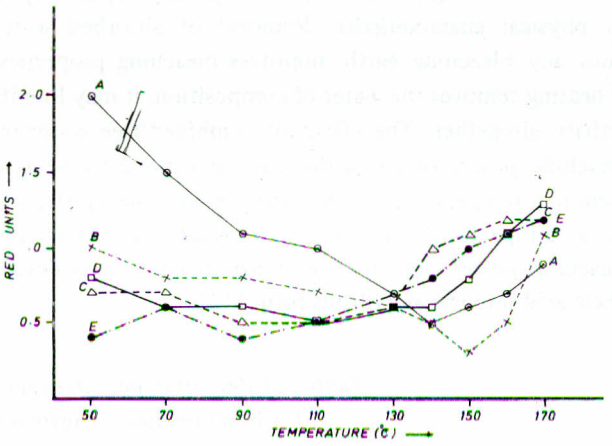

Fig. 3. Effect of temp on activity earth in 30 minutes.

Table 6. Effect of temperature on bleaching of soyabean oil of earths of various origin Time of treatment = 30 minutes

Lovibond reading of untreated soyabean oil at 160°C $\frac{R}{3.1}$ $\frac{Y}{14}$

percentage of earth used - 5 %

Sr. No.	Temperature of treatment °C	A		B		C		D		E	
		R	Y	R	Y	R	Y	R	Y	R	Y
1.	50	2	14	1.0	13	0.7	9	0.8	9	0.4	4
2.	70	1.5	12	0.8	10	0.7	6	0.6	5	0.6	5
3.	90	1.1	10	0.8	7	0.5	5	0.6	4	0.4	5
4.	110	1	7	0.7	8	0.5	5	0.5	6	0.5	6
5.	130	0.7	6	0.6	6	0.6	6	0.6	7	0.7	9
6.	140	0.5	4	0.5	5	1.0	7	0.6	9	0.8	10
7.	150	0.6	5	0.3	5	1.1	7	0.8	9	1.0	11
8.	160	0.7	7	0.5	7	1.2	8	1.1	10	1.1	11
9.	170	0.9	10	1.1	8	1.2	9	1.3	14	1.2	12

Table 7. Comparison of bleaching power of different fuller's earths at 160°

lovibond reading of untreated soyabean oil at 160°C $\frac{R}{3.1}$ $\frac{Y}{14}$

Sr. No.	Percentage of fuller's earth used	A		B		C		D		E	
		R	Y	R	Y	R	Y	R	Y	R	Y
1.	1	1.5	14	1.1	13	1.6	14	1.5	14	1.5	13
2.	2	1.3	12	1	11	1.5	12	1.4	13	1.3	12
3.	3	1.2	10	0.7	6	1.4	11	1.4	12	1.3	12
4.	4	1	8	0.5	4	1.2	10	1.2	11	1.2	10
5.	5	0.8	7	0.4	4	1.2	8	1.1	10	1.1	8
6.	6	0.6	5	0.3	3	1.1	7	1	8	1	6
7.	7	0.5	5	0.3	2	1	7	0.9	7	0.9	6
8.	8	0.5	4	0.3	2	1	5	0.9	5	0.8	5

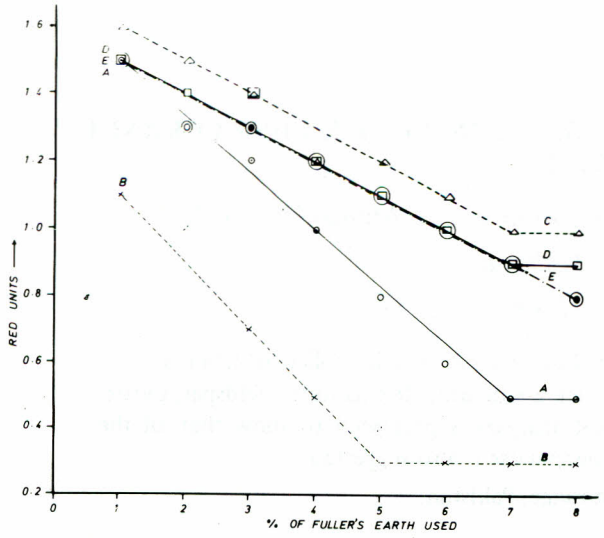

Fig. 4. Comparison of bleaching power of different fuller's earth.

earth increases with a rise of temperature upto 100-110° in Fuller's earth samples C,D and E, but in case of A and B the maximum activity is achieved at temperature of 140-160°.

The bleaching power of different earths was compared using 1-8 % of the earths with well refined soyabean oil. The results are shown in Table 7 (Fig. 4), indicating that earths A and B show better activity at higher temperatures (160°), whereas samples C,D and E show lower activity at this temperature.

Absorption of oil by different earths is recorded in (Table 8). The standard German earth (TERRANA), E is known to cause 19 % loss of oil due to absorption. The presumptive losses in other earths have been calculated on the basis of this value (Table 8). This study indicates that a maximum presumptive loss occurs in earth E which incidently has the maximum activity. The results shown in (Table 8) support the results of Table 5, indicating a relationship between activity and the resultant presumptive loss in different earths. It may be seen that increase in the activity of the earths results in loss of oil due to absorption.

Table 8. Loss of oil due to absorption of different fuller's earths.

Sr. No.	Brand of fuller's earth used	Oil absorbed (%)	Presumptive loss (%)
1.	A	44.83	13.54
2.	B	59.08	17.84
3.	C	50.24	15.17
4.	D	60.47	18.26
5.	E	62.89	19.0

The relative filtration rates of different earths have been measured (Table 9) showing that the filtration rate of earth B alongwith C and D has remarkably improved when compared to the unactivated earth A and are better than those of earth B.

Table 9. Comparison of filtration rates of different fuller's earths.

Sr. No.	Brand of fuller's earth used	Time of filtration (Minutes)
1.	A	Very poor (more than 8 hr.)
2.	B	11.0
3.	C	3.03
4.	D	2.48
5.	E	3.9

The data presented suggest that for removal of odorous substances and colouring matter from vegetable oils, earth B can be used in the activated form.

REFERENCES

1. R.E. Kirk and D.F. Othmer, *Encyclopedia of Chemical Technology* (Interscience Publishers, New York, 1964) Vol. 5, p.577.
2. T.G. Richert, Ind. Eng. Chem., **9**, 599 (1917).
3. O. Burghardt, Ind. Eng. Chem., **23**, 800 (1931).
4. A. Baig, Personal Communications.
5. J.F. Thorpes and M.A. Whiteley, *Thorpe's Dictionary of Applied Chemistry* (Longman's Green & Co., London, New York, 1944), Vol. **4**, p.248.
6. P.G. Nutting, J. Oil Gas, **31**, 14 (1933).
7. R.E. Kirk and D.F. Othmer, *Encyclopedia of Chemical Technology* (Interscience Publishers, New York, 1964), Vol. **4**, p.55.
8. D. Snell and L.S. Ettre, *Encyclopedia of Industrial Chemical Analysis* (Interscience Publishers N.Y., 1970), Vol. 10, p.111.
9. B.S. Kulkarni and S.K.K. Jatkar, J. Ind. Inst., **23**, 227 (1941).
10. T.G. Richert, Ind. Eng. Chem., **9**, 599 (1917).
11. A.B. Cummins and L.E. Weymouth, Ind. Eng. Chem., **34**, 392 (1942).
12. C.W. Davis and L.R. Messer, U.S. Tech. Publication No. 207 (1929).
13. A.W. Putland, Cotton Oil Press, **6**, 34 (1922).
14. Seiichi U-eno, Ind. Eng. Chem., **7**, 597 (1915).