

ACTIVATION OF FULLER'S EARTH OF D.G. KHAN WITH SULPHURIC ACID

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A huge deposit of fuller's earth essentially montmorillonitic has been identified in D.G. Khan. An investigation on its activation with sulphuric acid was made to make it suitable for cleansing and decolourising edible oils. However, special attention was paid to the comprehensive study of (i) concentration of acid (ii) time of activation and (iii) solid contents of the slurry, for activating the clay to a maximum possible degree so as to make it commercially acceptable.

Key words: Activation, Montmorillonite, Clay, Sulphuric acid.

Introduction

Fuller's earth is an important industrial clay mineral with the ability to absorb oil, grease or colouring matter. It is differentiated from the large volume clay mineral products like kaolin, ball clay, fire clay and refractory clay etc in terms of being commercially rare. [1, 2]

A huge deposit of about 10 million metric tons of montmorillonitic fuller's earth has been identified in Dera Ghazi Khan [3, 4]. The activation studies of this clay have been undertaken to ensure optimum utilization of the reserve to make it suitable for bleaching and refining edible oils.

The refining of vegetable oils for human consumption involves the removal of a number of impurities phosphatides, fatty acids and trace metals etc, followed by decolourisation and finally deodorisation. The purification and decolourisation stage of refining process employs activated bleaching earth which is later removed from the oils by filtration.

An acid activated clay has proved an efficient decoloriser due to its large surface area produced by the corrosion of the lattice [5]. The cations of the clay absorb colouring matter and impurities onto the surface thus enhancing the bleaching activity. Hence, it was decided that this particular mon-tmorillonitic clay be activated with inorganic acid as it serves three purposes: (i) dissolves impurities such as calcite, (ii) replaces exchangeable divalent calcium ions with monovalent hydrogen ions and (iii) dissolves some aluminium ions contained in the tetrahedral layer and some Fe^{+++} , Fe^{++} , Al^{+++} and Mg^{++} ions from the octahedral layer. In tetrahedral layers, some Si^{++++} ions are replaced by Fe^{+++} , Fe^{++} , Ca^{++} and Mg^{++} ions.

Sulphuric acid has been selected because of some advantages over hydrochloric acid; (i) it causes less corrosion problems with mild steel vessels and (ii) produces less fumes, hazardous to health, at activated temperature. The

investigations involve comprehensive studies of parameters: (i) concentration of acid (ii) contact time and (iii) clay acid composition, to confirm the suitability of finished product and its comparability to those of the imported ones available in the market.

At present, the oil industry of our country is relying upon the import of activated clay to meet the rapidly increasing requirements, therefore, a successful attempt on the activation of D.G. Khan deposits of fuller's earth can pave the way for our country to become self sufficient in the activated clay.

Experimental

The experimentation was confined to washing of the clay, its activation and finally the bleaching behaviour of the activated clay toward soybean oil [4].

Washing. The crude clay from the reserve was washed with water in plastic tubs using gravity separating techniques to eliminate small indispersible fraction, called gangue, not suitable for activation. The gangue carried away undissolved impurities and heavy particles settled down. The upper dispersed layer was decanted off, passed through 80 mesh screen in the settling tanks. It was then allowed to stand still until a supernatant water layer separated out which was poured leaving behind washed mud. The mud was spread on clean ground to dry in the sun for further experimentation. The gangue and other impurities were found to be 6.35%.

Activation. The activation of the washed clay was carried out with sulphuric acid according to Table 1. The contents i.e., weighed quantities of acid, clay and water were refluxed in a round bottom flask fitted with water condenser for a specified duration of time. At the end of the reaction, the hot mixture of acid, clay and water was poured down into a plastic tub containing sufficient cold water to stop the reaction. The activated clay was washed with water till the

pH of the mixture was around 4. It was then rapidly filtered, dried at $100 \pm 5^\circ\text{C}$ in an air oven and ground to pass through 100 mesh sieve [6].

Bleaching. 0.25 g of activated clay was added to 25 g of soybean oil and heated in an oil bath at $90 \pm 5^\circ\text{C}$ with constant stirring for 30 min. The oil was then rapidly filtered and the colour of the bleached oil was measured on a livibond tintometer. (Tables 2-5) [7].

Results and Discussion

For the determination of optimum parameters for maximum activation, the significant factors i. e. concentration of acid, solid contents of the slurry and duration of acid treatment were taken into account. Clay contents of the slurry were varied from 17 to 29 %, concentration of the acid from 2 to 8N and duration of activation lasted from 1 to 24 hrs. Detailed study of the variation of these parameters was necessary because the acid activation of such clays is a very delicate and important matter. The clay lattice was corroded by the reaction of acid to a suitable extent to impart maximum possible bleaching power to the resulting activated clay. Activation was brought about by

heating the fuller's earth in suspension with a mineral acid at about 100°C .

The acid penetrated the fine, suspended fuller's earth particles until it reaches the individual crystals whose edges were probably attacked in preference to the surfaces. Ions of aluminium, magnesium and iron got extracted from the octahedral layer and passed into the solution as salts of the mineral acid used for activation. More or less simultaneously, the exchangeable calcium, sodium and potassium ions lying in the intracrystalline space were replaced by cations present in the activating solution predominantly as hydrogen. Cations extracted from the octahedral layer were also replaced by hydrogen ions while auxiliary minerals such as calcite, limonite and iron pyrites etc simultaneously decomposed and passed into the solution. On washing the clay with water, the dissolved salts were separated. As a result of acid activation, the exposed surface of clay assumed the reactive properties of solid and the surface available for absorption also increased considerably.

The aim of this investigation was to activate the clay to a maximum possible degree using a minimum amount of acid in the shortest possible time.

TABLE 1. PLAN OF WORK.

% Content of slurry	Normality of acid	Time in hours							
		4	5	6	7	8	9	10	11 12
16.7	2.16	4	5	6	7	8	9	10	11 12
	2.88	4	5	6	7	8	9	10	11 12
	3.60	2	3	4	5	6	7	8	
	4.32	2	2-1/2	3	3-1/2	4			
	5.76	1	1-1/2	2	2-1/2	3	3	3-1/2	
	7.20	1	1-1/2	2	2-1/2	3	3-1/2		
20	2.16	4	6	8	10	12	14	16	1.
	2.88	4	6	8	10	12	14	16	18
	3.60	3	4	5	6	7	8	9	10
	4.32	2	2-1/2	3	3-1/2	4	5	6	
	5.76	1-1/2	2	2-1/2	4	3-1/2	4		
	7.20	1	1-1/2	2	2-1/2	3	3-1/2		
24.24	2.16	6	8	10	12	14	16	18	20
	2.88	6	8	10	12	14	16	18	20
	3.60	6	8	10	12	14	16		
	4.32	2	3	4	5	6			
	5.76	1-1/2	2	2-1/2	3	3-1/2	4		
	7.20	1-1/2	2	2-1/2	3	3-1/2			
28.57	2.16	6	8	10	12	14	16	18	20
	2.88	6	8	10	12	14	16		
	4.32	2	3	4	5	6			
	5.76	1-1/2	2	2-1/2	3	3-1/2	4		
	7.20	2	2-1/2	3	3-1/2	4			

The results relating to the bleaching efficiency produced during these activation experiments are represented in Tables 2-5. These results indicate that an increase in the acid strength, while other parameters were kept constant, increased the bleaching power upto a limit of optimum corrosion of the lattice. After that the bleaching efficiency decreased with the increase in the acid strength.

TABLE 2.

Clay content (%)	Duration of reaction (hrs)	% Bleachability at acid normality					
		2.16N	2.88N	3.60N	4.32N	5.76N	7.20N
16.7	1	-	-	-	-	-	66.00
	1-1/2	-	-	-	-	77.57	72.00
	2	-	-	76.66	78.00	78.18	70.00
	2-1/2	-	-	-	74.00	78.63	68.00
	3	-	-	76.66	74.00	81.81	64.00
	3-1/2	-	-	-	68.00	77.72	-
	4	40.00	71.66	80.00	66.00	77.27	-
	5	55.00	71.66	80.00	-	-	-
	6	55.00	71.66	80.00	-	-	-
	7	55.00	70.00	80.00	-	-	-
	8	60.00	70.00	80.00	-	-	-
	9	60.00	70.00	-	-	-	-
10	70.00	70.00	-	-	-	-	
11	70.00	70.00	-	-	-	-	
12	71.66	70.00	-	-	-	-	
Bleaching of standard clay		86.66	86.66	80.00	80.00	86.36	80.00

TABLE 3.

Clay content (%)	Duration of reaction (hrs)	% Bleachability at acid normality					
		2.16N	2.88N	3.60N	4.32N	5.76N	7.20N
20.00	1	-	-	-	-	81.81	81.81
	1-1/2	-	-	-	-	82.00	81.81
	2	-	-	-	81.81	82.00	81.81
	2-1/2	-	-	-	81.81	82.00	81.81
	3	-	-	76.66	80.75	82.00	81.20
	3-1/2	-	-	-	80.45	81.81	81.06
	4	70.00	73.33	76.66	80.00	81.06	-
	5	-	-	80.00	77.27	-	-
	6	70.00	80.00	80.00	77.12	-	-
	7	-	-	83.33	-	-	-
	8	71.66	83.33	76.66	-	-	-
	9	-	-	76.66	-	-	-
	10	76.66	80.00	76.00	-	-	-
	11	-	-	-	-	-	-
	12	80.00	80.00	-	-	-	-
	13	-	-	-	-	-	-
	14	74.66	80.00	-	-	-	-
	15	-	-	-	-	-	-
16	73.33	76.66	-	-	-	-	
17	-	-	-	-	-	-	
18	73.33	76.66	-	-	-	-	
Bleachability of standard clay		86.66	86.66	86.66	86.36	86.36	86.36

The laboratory investigations revealed that maximum activation of the clay was achieved by various combinations of the activation parameters. The acid strength between

TABLE 4.

Clay content (%)	Duration of reaction (hrs)	% Bleachability at acid normality					
		2.16N	2.88N	3.60N	4.32N	5.76N	7.20N
24.24	1	-	-	-	-	-	-
	1-1/2	-	-	-	-	77.27	75.75
	2	-	-	-	76.81	78.03	75.60
	2-1/2	-	-	-	-	77.27	76.66
	3	-	-	-	77.27	76.51	76.36
	3-1/2	-	-	-	-	76.51	76.06
	4	-	-	-	77.27	76.51	-
	5	-	-	-	75.75	-	-
	6	80.00	70.00	70.00	75.00	-	-
	7	-	-	-	-	-	-
	8	76.66	76.66	70.00	-	-	-
	9	-	-	-	-	-	-
	10	73.33	73.33	71.66	-	-	-
	11	-	-	-	-	-	-
	12	70.00	70.00	71.66	-	-	-
	13	-	-	-	-	-	-
	14	70.00	70.00	70.00	-	-	-
	15	-	-	-	-	-	-
	16	70.00	70.00	70.00	-	-	-
	17	-	-	-	-	-	-
18	70.00	70.00	-	-	-	-	
19	-	-	-	-	-	-	
20	70.00	70.00	-	-	-	-	
Bleachability of standard clay		86.66	86.66	83.33	86.36	86.36	86.36

TABLE 5.

Clay content (%)	Duration of reaction (hrs)	% Bleachability at acid normality					
		2.16N	2.88N	3.60N	4.32N	5.76N	7.20N
28.57	1	-	-	-	-	-	-
	1-1/2	-	-	-	-	-	-
	2	-	-	-	70.00	46.66	76.93
	2-1/2	-	-	-	-	53.33	75.80
	3	-	-	-	70.00	63.33	75.00
	3-1/2	-	-	-	-	53.33	74.19
	4	-	-	-	73.33	53.33	74.00
	5	-	-	-	73.33	-	-
	6	61.66	70.00	66.66	66.66	-	-
	7	-	-	-	-	-	-
	8	63.33	70.00	70.00	-	-	-
	9	-	-	-	-	-	-
	10	70.00	70.00	70.00	-	-	-
	11	-	-	-	-	-	-
	12	70.00	70.00	70.00	-	-	-
	13	-	-	-	-	-	-
	14	70.00	66.66	71.66	-	-	-
	15	-	-	-	-	-	-
	16	70.00	66.66	70.00	-	-	-
	17	-	-	-	-	-	-
18	71.66	66.66	70.00	-	-	-	
19	-	-	-	-	-	-	
20	71.66	66.00	-	-	-	-	
Bleachability of standard clay		83.33	83.33	83.33	86.66	86.66	79.35

4 and 5 seemed to be suitable which required a reaction time of 2-4 hr. The amount of the slurry solids found suitable, was 20-25 per cent.

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