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Evaluation and Activation of Cambalpur Bentonite for Industrial Utilization

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Abstract. An experimental study of the bentonite clays of Cambalpur (Attock) area of Pakistan, indicated their performance to be comparable with the imported clays and that these can be used as import substitute after activation by hydrochloric acid or sulphuric acid. No reversal of colour or adverse effects were noticed.

Keywords: Cambalpur, bentonite, clays, activation, Pakistan

Introduction

Bentonite is the sub-group of clay mineral smectite, a group of sodium, calcium, magnesium, iron and lithium aluminium dioctahedral 2:1 layered silicates (Kirk-Othmer, 2004). Bentonite clay deposits are dominantly composed of montmorillonite and beidellite. Chemically, the bentonite is an aluminium hydrosilicate in which the ratio of silicic acid to alumina is 4:1 (Phoenix, 2004). Bentonite deposits are formed by alteration of eruptive igneous rocks, usually tuffs and volcanic ash and contain, in addition, varying amounts of cristobalite, zeolites, biotite, quartz, feldspar, zircon etc., (Deer *et al*., 1992).

Bentonite clays are used in the manufacture of bricks, ceramics, drilling mud, paper, paints, rubber and moulding sands. The clays are also used as decolourizing, clarifying, filtering and bleaching agents and as catalysts in hydrogenation and other chemical reactions.

Bleaching properties of clay can be further enhanced by treating it with a suitable mineral acid leading to its activation. The activation of clay is often accompanied by the change in key physical properties e.g., surface acidity, surface area and surface volume etc. Such activated clays are used for decolourizing or bleaching of various oils such as mineral oils, vegetable oils, various fractions of petroleum, especially lubricating oils and purification of melted animal fats and bees wax.

For bleaching of edible oils, desirable properties of clay are as under (Ahmad and Siddiqui, 1992):

i. The clay should be able to bleach the oils to the extent so that these do not revert to the original colour on standing.
ii. The oil should filter easily.
iii. The clay should not impart any odour to the oil.
iv. The quantity of oil retained by the clay should be small.
v. No spontaneous ignition should occur either in the filter press or in the waste pits.

In Pakistan, bentonite deposits occur at a few places in NWFP, Punjab, Sindh and Azad Kashmir. The deposits at Karak (NWFP) were investigated by Engineers Combined Limited in 1976 for the Government of NWFP (Ahmad and Siddiqui, 1992). In Punjab, reasonably big deposits have been found at Dera Ghazi Khan and Cambalpur (Yousaf *et al*., 1989); at Cambalpur, the deposits occur near villages of Dherikot and Dheri Chohan in the vicinity of the left bank of Haro River (a tributary of the Indus) and are easily accessible. According to some non-published estimates, the reserves of the area have been estimated to be around one million tons. The indigenous occurrences of bentonite in appreciable quantities and the high prices of import varieties are the reasons for undertaking the present study for exploring the possibilities of activation of local clays so as to make them suitable for utilization in local industries.

Materials and Methods

The experimental part consisted of the following:

Lumps of clay were dried in air at room tempertutre. The clay was cleaned manually to remove stones and particles with metallic iron materials which are generally dark reddish brown in colour and can be removed easily by colour sorting. The dried and cleaned clay was grounded to pass through British standard sieve (BSS) # 100 and tested for methylene blue value, which indicates its original ion exchange capacity.

Determination of the cation exchange capacity (CEC) of bentonite with methylene blue dye adsorption. ***Preparation of methylene blue dye.*** A sample of crystalline dye was dried at 105 °C and loss in weight was determined which was 12.34%. Crystalline methylene blue (3.00 g) was placed in 1 L flask and 250 mL warm distilled water was added. The flask was shaken and on dissolution of solid, it was cooled and made upto the

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*Author for correspondence; E-mail: shnasreen@yahoo.com mark. As the equivalent weight of anhydrous dye is 319.9 the normality of the solution is calculated as follows:

$$\frac{3}{319.9} \times \frac{100 - 12.34}{100} = 0.0082\ \text{N}$$

Methylene blue adsorption by original clay. The dried and grounded sample of clay was placed in a 2 cz screw-top bottle and 20 mL distilled water was added. The solution was shaken for 1-2 h and left overnight. Contents of the bottle were washed into 100 mL flask and 1 mL of 5N sulphuric acid was added (this improves the end point in some cases). From a 50 mL burette, 0.0082N solution of methylene blue was added (2 mL at a time). Immediately after addition of the dye, the contents of the flask were swirled and a small portion of the suspension on a filter paper (Whatman # 41) was spotted by means of a glass rod. Whilst the dye was being adsorbed by the clay, a sharp boundary on the filter paper between blue clay/dye spot and the accompanying water, radiating from it, appeared. As the end point approached excess dye formed a lighter blue halo around the spot. The CEC in milliequivalent per 100 g dried clay was calculated from the formula:

$$\text{CEC} = 100 \times \frac{\text{volume of methylene blue} \times 0.0082}{\text{weight of clay (dried at 105 °C)}}$$

As the minimum cationic exchange capacity of montmorillonite is 80 milliequivalent (meq/100 g), hence only five samples, having CEC $\geq$60 meq/100 g were selected for chemical analysis and activation studies.

Chemical evaluation. The bentonite samples were analyzed by the fusion method using fusion mixture. The quantities of different components were determined according to the usual scheme of analysis (ASTM, 2009). All chemicals used were A.R. grade from BDH.

Acid treatment for activation of bentonite. Though soil particles of finer size offer greater surface area for activation, the material passing through 100 mesh was found to be satisfactory for activation with respect to both the decolourizing power and the filterability. The clays were refluxed with hydrochloric and sulphuric acids of different normalities i.e., 1-5N, for various time periods (1 h - 5 h) on a heating mantle. The acid clay mixtures were filtered under suction and washed with distilled water till these became free of the acid. The filtered cake was dried at 110 °C, ground to pass through 300 mesh and kept in airtight bottles.

Performance of clay. Bleaching capacity of the activated clay samples was determined by decolourization of methylene blue and cottonseed oil.

Decolourization of methylene blue. Standard methylene blue solution (1 mg/mL) was prepared by dissolving 1 g of dye in distilled water in a 1 L flask and by making the volume upto the mark. Activated clay (1 g) was taken in beaker and methylene blue solution was added from a burette (2 mL at one time), with continuous stirring with a glass rod. Addition of the dye solution was continued till the spot test showed complete adsorption of methylene blue solution (as mentioned above) and then the volume of the dye solution utilized was determined.

Decolourization of cottonseed oil. This test was performed according to the method reported earlier (Ahmad, 1982). About 200 g of crude cotton seed oil was heated to 45 °C on a hot plate and to this 3 mL of 150 °B NaOH was added and stirred for 15 min. After heating upto 65 °C, the oil was filtered through Whatman # 1. This refined cottonseed oil was then reacted with the activated bentonite in order to determine the bleaching ability of the prepared activated clay.

Activated clay (2 g) was added to 100 g of cottonseed oil and heated to 85 °C for 15 min with continuous stirring. The clay was filtered off and decolourization was measured by tintometer. The unit of yellow and red pigment for unbleached oil was taken as 100% colour for the sake of calculation. Decrease in colour was calculated on the basis of yellow and red units removed from the original oil.

The imported clay variety terrana was also subjected to similar test for the sake of comparison with indigenous activated clay.

Results and Discussion

Before undertaking the activation studies, the catinionic exchange capacity (CEC) of original clay samples was determined by methylene blue method. The results showed that five samples had CEC value of more than 60, (Table 1) which indicated absence of non-expanding three layer illites that have CEC between 20 and 40 (Ahmad, 1982).

Chemical analysis. Chemical analysis reveals little about the mineralogical composition of the clay because of the isomorphous replacement of elements and the possibility of the occurrence of more than one clay mineral in the same clay deposit. Analysis of montmorillonite frequently shows high

Table 1. Testing of activated bentonite with methylene blue dye

Sample (1 g)	Methylene blue (1 mL-1 mg) decolourized
1	88.00
2	90.00
3	93.00
4	92.00
5	93.00
Terrana (German bentonite)	115.00

value of H_2O, SiO_2: R_2O_3 ratio (4: 1or more) and low K_2O. About 20 percent Fe_2O_3 is indicative of pure nontronite and less than 1 percent MgO, while 10% Fe_2O_3 is indicative of biedelite (Makenzie, 1957). Illite or hydrous mica contains appreciable amount of potash, approximately 6% as K_2O. In attapulgite-sepiolite series, magnesium is predominant. In attapulgite, Al_2O_3 and MgO are in equal proportion, whereas, sepiolite is the magnesium end member and contains little alumina (Robertson *et al.*, 1954).

Chemical analysis (Table 2) revealed that the clay is montmorillonite type as the ratio of silica (SiO_2: R_2O_3) is equal or near to 4 in all samples. Presence of high magnesium indicates that the clay may contain some saponite. Average specific gravity of the clay was found to be 1.90. Presence of alakalies in all samples confirms their swelling characteristic. Higher concentration of alumina and low content of iron indicate that the clay is aluminous in nature rather than ferroaluminous.

Since the clays containing minerals of montmorillonite subgroup give better results on activation, acid activation seems to be the most appropriate activation method for the clay under study.

Activation. Activation by partial leaching with mineral acid appears to be a very simple process but in practice, it requires an extreme degree of control of process variables in order to obtain a product of requisite bleaching power. A variety of processes have been patented but very little information is available on the actual industrial processes except those given in the classical article by Burghardt (1931) and thereafter by Rich (1960).

As activation is dependent on various factors such as strength of acid, temperature and heating time and washing of clay, one of the five samples was treated under varying conditions to ascertain the parameters. The activation was initiated with an acid of lower strength of 1N and progressively raised upto the strength of 5N (Fig. 1) and likewise time period of heating was raised from 1 h to 5 h (Fig. 2). It is clear from Fig. 1 that the activity of clay increased with the increase in acid concentration and reached the maximum at the strength of the acid 4N, while Fig. 2 indicates that activity increased steadily with time and attained maximum value in 3 h. It also shows no significant effect on the activity of clay on further heating. It is evident from Fig. 1 and 2, that both the hydrochloric acid (HC1) and the sulphuric acid (H_2SO_4) are capable of activating the clay to a level conducive for industrial utilization but H_2SO_4 proves to be a comparatively better activating agent. Thus rest of the samples were activated by treating with 4N H_2SO_4 for 3 h.

Table 2. Chemical analysis of Attock bentonite

Chemical composition	Sample no.				
	1	2	3	4	5
SiO_2	52.49	58.60	52.10	52.20	57.14
Al_2O_3	17.17	12.17	15.85	16.77	13.98
Fe_2O_3	2.02	4.36	3.07	3.13	2.49
TiO_2	0.30	0.72	0.70	0.49	0.60
MnO	Trace	Nil	0.20	0.11	0.10
P_2O_5	Nil	0.064	0.09	Trace	0.02
CaO	3.65	1.59	3.12	3.97	4.10
MgO	3.2	2.15	1.10	3.85	1.61
Na_2O	1.00	0.20	3.90	1.98	3.99
K_2O	0.47	0.55	2.20	1.44	2.10
Loss on ignition	18.66	19.45	17.99	16.37	14.10

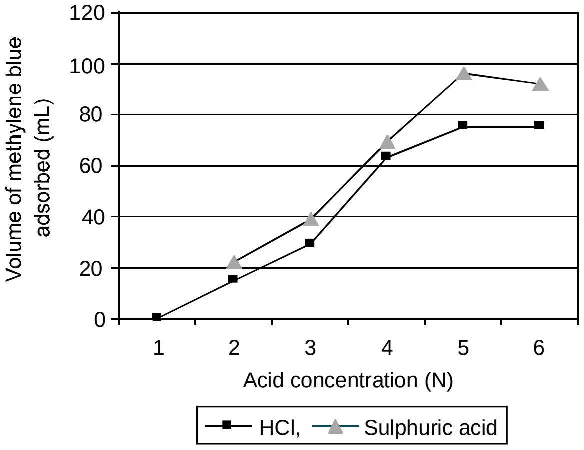

Fig. 1. Effect of acid concentration on activity of the clay.

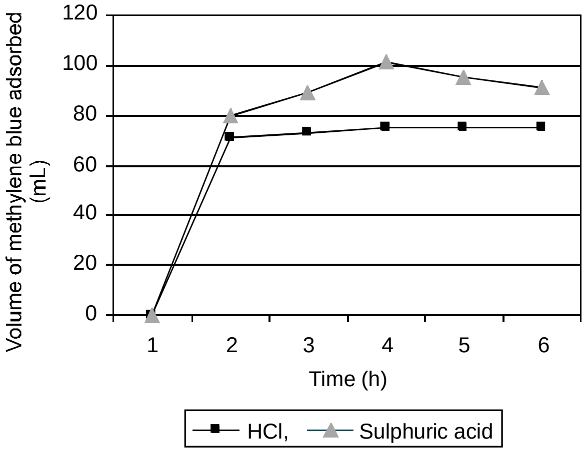

Fig. 2. Effect of time on activity of the clay.

Activity tests. Tests were conducted for comparing the activated bentonite with well-known German brand of bleaching earth (Terrana), under similar conditions (Table 1 and 3). The

Table 3. Optimised sulphuric acid activation tests (oil bleaching) (tintometric results); Reference oil: naturalized cottonseed oil with colour content (Yellow unit: 30 and Red unit: 3.7)

Sample no.	Percentage of clay in oil clay mixture	Colour retained		Percentage of colour bleached	
		Yellow unit	Red unit	Yellow unit	Red unit
1	2	8.10	0.80	73.00	78.38
2	2	7.90	0.71	73.66	80.81
3	2	8.10	0.68	73.00	81.62
4	2	7.80	0.69	74.00	81.35
5	2	8.00	0.70	73.33	81.08
Terrana (Imported German)	2	4.10	0.50	86.48	86.33

five samples of clay subjected to activation, collected from different locations of the deposit, showed varying extent of activation. This depicts the changes in chemical and mineralogical compositions of the clay with variation in locations. Results of bleaching activity indicates that absorption of methylene blue dye by the indigenous clay varies from 88 to 93 mg/g, which is comparable to 115 mg/g of imported variety i.e., Terrana (Table 1). Similarly the results of decolourization of oil by indigenous and imported clays are much the same (Table 3). The activated Cambalpur clay refines the cottonseed oil upto 81% while the same value for the imported clay is 86%. The results indicate that the bleaching properties of the clay activated with sulphuric acid also compare favourably with those of the imported German variety (Terrana).

Conclusion

The activation studies carried out for the clay deposit of Attock area, show that the clay is dominantly composed of montmorillonite and allied members of clay group. It responds actively to treatment with hydrochloric acid and sulphuric acid, both. However, the response to sulphuric acid is better than to hydrochloric acid. All samples of Cambalpur (Attock) clay were found to acquire optimum activation when treated with 4N sulphuric acid for 3 h. This indicates second to complete homogeneity of mineralogical composition throughout the deposit. The results of cottonseed oil bleaching (Table 3) revealed that the performance of activated Cambalpur bentonite is fairly comparable with that of the imported German variety (Terrana). Further the clay did not show any adverse effect on the oil and no reversal of colour was noticed after decolourization. The economics of the activation process, however, involves consideration of the wastage of bentonite in separation of gritty matter and that during filtration.

The demand of activated bentonite has gone up with the expansion of vegetable ghee industry in Pakistan. Presently most of the national requirements are met through imports mainly from Germany, UK, China etc. The indigenous Cambalpur bentonite can be substituted for the imported clay and this could be a source of saving the valuable foreign exchange. Although bleaching power of the indigenous clay is somewhat lower than the imported clay but the low cost of production will have a balancing effect. Abundant availability of raw materials at a low price is likely to make such a venture commercially viable.

The indigenous petro-chemical and edible oil/ghee industries use a variety of imported clays (activated) for bleaching/ decolourization of products. These activated clays can be produced by simple treatment of locally available clays.

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