

INDIGENOUS BENTONITES FOR REFINING COTTONSEED OIL

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Indigenous bentonites have been studied for refining cottonseed oil. Three different processes, i.e., (i) heat treatment, (ii) acid treatment and (iii) salt treatment have been employed for activation of the bentonites. Semi-refined cottonseed oil of colour index (Lovibond scale) 9.0 yellow units was treated with various activated bentonites. Maximum decolorization of the oil achieved from such a treatment was up to 85%.

In Europe and America bentonite is used in petroleum industry, oils and fats industry for the decolorization of vegetable oils, in foundry work, for wool scouring, soap manufacture, as a base for cosmetics and a substitute for starch in sizing cloth and in dry cell. It can also be employed for de-inking old newspaper, as an absorbent for nitroglycerine in the manufacture of dynamite and in the preparation of surgical dressing and thermal insulating materials.³

Bentonite formed by alteration of volcanic ashes is composed of montmorillonite ($\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$ with substitution of magnesium for part of aluminium) and minor beidmites (hydrous Al Si O_2) with traces of constituents like feldspar, gypsum, quartz, limestone and other minerals.^{3,4} Bentonites may be of varying colours like white, grey, pink or brown, yellowish, green or olive green.

There are two types of bentonites:—

(i) Those that have great swelling power and form suspension in water. They have non-bleaching characteristics and are non-activable by acid treatment;

(ii) Those that have slight swelling power and settle rapidly in thin water dispersion. They can be activated by acid treatment and are analogous to fuller's earth. They can be competitively used as oil clarifier after activation.

The non-swelling type of bentonite is evaluated on the basis of moisture content, particle size and amount of grit. The activated clays are usually several times stronger adsorbent than natural clays. The acid treatment extends considerably the surface of the clay and probably causes some important chemical changes.¹ Acid activated clays retain more oil per unit weight of the clay but the over-all loss through retention is compensated for by their greater activity.

Pakistani Bentonites

A considerable quantity of indigenous bentonites is estimated to be available for various uses. A systematic survey about the production of bentonites has not yet been undertaken. However, a report about the bentonites of Bhimber and Chitti Deri of Azad Kashmir, Ganda, Rohtas, Jogi Tila villages of district Jhelum and other areas in district Gujrat, has been brought out by the Geological Survey of Pakistan. The report states that bentonites are available in large quantity.⁹

In Pakistan, no use has, however, been made of the indigenous bentonites. In view of a large expansion of vanaspati factories there is great scope in making use of our bentonites. At present the demand for bleaching of oils is mainly met with by the imported fuller's earth, which increases to a large extent the cost of the process. As most of the imported earths are of bentonite origin, subsequently activated by acid treatment, it was attempted to utilize the indigenous bentonites accordingly. Bentonites of local origin were, therefore, investigated with respect to their bleaching properties. Their performance after activation was compared with the imported fuller's earth. The following imported samples were employed for comparative studies:—

- (i) I.C.I. Earth. It is an activated fuller's earth produced by I.C.I. Ltd.
- (ii) Fuller's earth 'Tarana', made in Germany.
- (iii) Activated charcoal (Dramstadt, Germany).

Experimental Work

Separation of Gritty Matter from the Bentonites^{3,4,5}.—Fifty g. of the bentonite was taken in 500 ml. beaker. Water was added and the slurry was mechanically stirred. The supernatant suspension containing bentonite proper

was filtered off. The process was repeated with fresh water several times till the supernatant liquid was clear. After drying, the gritty matter with unrecovered bentonite and the bentonite proper were separately weighed and a material balance was made on original weight of the sample. The results are indicated in Table I.

TABLE I.—SEPARATION OF GRITTY MATTER FROM BENTONITE BY ELUTRIATION PROCESS.

| Sample | Wt. of sample g. | Gritty matter and unrecovered bentonite g. | Pure bentonite g. | % of Gritty matter & unrecovered bentonite | % of Recovered bentonite | % Loss by difference |
|---------------|------------------|--|-------------------|--|--------------------------|----------------------|
| 1 Bhimber | 50 | 14.70 | 32.30 | 29.4 | 64.6 | 6.0 |
| 2 Bhimber | 50 | 16.20 | 31.30 | 32.4 | 62.6 | 5.0 |
| 3 Chitti Deri | 50 | 22.40 | 25.60 | 44.8 | 51.2 | 4.0 |
| 4 Sikhim | 50 | 22.60 | 25.40 | 45.2 | 50.8 | 4.0 |
| 5 Jogi Tila | 50 | 22.90 | 24.60 | 48.5 | 49.2 | 5.0 |
| 6 Ganda | 50 | traces | 50 | nil | 100 | nil |
| 7 Bhimber | 50 | 18.30 | 29.70 | 36.6 | 59.4 | 6.0 |

Activation Processes.—The bentonites were first freed of silt by elutriation and its silt contents assessed. Clays so freed from silt were then processed according to the following scheme.

(i) *Activation by Simple Heating*⁵.—The bentonite-clays were heated at different temperatures in a muffle furnace for four hours. The following samples were thus prepared for measuring decolorizing properties:—

By drying the bentonite - clay at room temperature. — 1a
 Heating the clay to 110°C. for four hours — 2a
 Heating the clay to 350°C. for four hours — 3a
 Heating the clay to 500°C. for four hours — 4a

(ii) *Acid Activation*^{5,6}.—The clays were refluxed with 5 N hydrochloric acid for four hours on a sand bath. The acid-clay mixtures were filtered under suction and washed with distilled water till free of the acid. The same procedure was adopted with 4 N sulphuric acid. The acid clays were then heated in a muffle furnace at different temperatures. The following samples were prepared:—

Drying the hydrochloric acid treated clays at room temperature. — 1b

Heating to 110°C. — 2b
 Heating to 350°C. — 3b
 Heating to 500°C. — 4b

Drying the sulphuric acid treated clays at room temperature. — 1c
 Heating to 110°C. — 2c
 Heating to 350°C. — 3c
 Heating to 500°C. — 4c

(iii) *Salt-activation*⁶.—The clays were treated with 1% sodium chloride solution and refluxed for four hours on a sand bath. They were filtered under suction and washed with 5 N hydrochloric acid. They were then washed with distilled water till free of acid. The clays were subsequently heated as follows:—

Drying the salt-treated clay at room temperature. — 1d
 Heating to 110°C. — 2d
 Heating to 350°C. — 3d
 Heating to 500°C. — 4d

In all 112 samples were thus prepared. They were sieved to 100 mesh and tested for their activation on semi-refined cottonseed oil of 9.0 Lovibond yellow units.

Performance of Clays.—One gram of a clay was stirred with 20 g. of the cottonseed oil in a 100 ml. beaker for 45 minutes on a boiling water bath. The oil was filtered hot immediately and the colour index was noted in a Lovibond tintometer. The decrease in colour was calculated on the basis of yellow units removed from the original oil. The results are recorded in Table 2.

Comparison of Activities of Indigenous Bentonites with Imported Fuller's Earths.^{3,4,7}

—Tests were carried out with indigenous bentonites in comparison with well-known foreign brands of bleaching earths. Such a comparison was made selectively with the best acid-activated bentonites only. The activity of a sample of imported fuller's earth was determined first alone and then incorporation with 0.5% carbon. The same procedure had been adopted with the above-mentioned bentonites under identical conditions. The activity of the decolorizing carbon was also carried out separately using 0.5% on the weight of oil. The results are recorded in Table 3.

Chemical Analysis.—The bentonites were analysed by the usual fusion method using sodium carbonate. The quantities of different components were determined according to the usual scheme of analysis.⁸ The results are recorded in Table 4.

TABLE 2.—% DECOLORIZATION OF COTTONSEED OIL BY DIFFERENT BENTONITES AFTER ACTIVATION.

| Bentonite Nos. | Origin of Bentonite | I % decolorization | | | | II % decolorization | | | | III % decolorization | | | | IV % decolorization | | | |
|----------------|---------------------|-----------------------|---------|------|------|------------------------|------|------|------|-------------------------|------|------|------|------------------------|------|------|------|
| | | 1a | 2a | 3a | 4a | 1b | 2b | 3b | 4b | 1c | 2c | 3c | 4c | 1d | 2d | 3d | 4d |
| | | 1 | Bhimber | 60.0 | 59.1 | 55.5 | 71.1 | 74.4 | 75.7 | 81.1 | 75.5 | 77.7 | 81.1 | 84.4 | 75.5 | 62.0 | 65.3 |
| 2 | Bhimber | 55.5 | 56.0 | 55.5 | 65.6 | 74.4 | 75.7 | 75.5 | 72.5 | 83.3 | 83.3 | 84.4 | 74.4 | 57.2 | 62.0 | 73.0 | 65.5 |
| 3 | Chitti Deri | 55.5 | 59.5 | 67.7 | 60.0 | 79.7 | 77.7 | 82.2 | 72.2 | 77.7 | 82.2 | 77.7 | 74.4 | 57.7 | 60.0 | 74.4 | 63.2 |
| 4 | Sikhim | 60.0 | 60.0 | 55.5 | 55.5 | 77.7 | 77.7 | 82.2 | 75.7 | 75.5 | 75.5 | 82.2 | 66.6 | 61.2 | 65.0 | 72.5 | 60.0 |
| 5 | Jogi Tila | 66.6 | 65.0 | 66.6 | 66.6 | 77.4 | 73.3 | 74.4 | 72.5 | 55.5 | 72.2 | 76.6 | 77.7 | 66.6 | 68.2 | 72.0 | 66.7 |
| 6 | Ganda | 65.6 | 52.0 | 55.5 | 55.5 | 70.0 | 60.0 | 76.6 | 72.2 | 75.5 | 75.5 | 77.7 | 74.4 | 67.0 | 59.3 | 70.1 | 60.7 |
| 7 | Bhimber | 66.6 | 65.0 | 65.5 | 65.5 | 71.1 | 73.3 | 81.1 | 75.6 | 63.3 | 81.1 | 84.4 | 76.6 | 68.0 | 69.2 | 72.2 | 66.7 |

TABLE 3.—COMPARATIVE STUDIES OF ACID BENTONITES AND IMPORTED FULLERS'S EARTH.
% DECOLORIZATION.

| Charcoal 0.5% | I.C.I. earth | I.C.I. earth +0.5C | Tarana earth | Tarana earth +0.5C | Earth used | Acid used | B _I | B _I + C | B ₂ | B ₂ + C | B ₃ | B ₃ + C | B ₄ | B ₄ + C | B ₅ | B ₅ + C | B ₆ | B ₆ + C | B ₇ | B ₇ + C |
|---------------|--------------|--------------------|--------------|--------------------|------------|--------------------------------|----------------|--------------------|----------------|--------------------|----------------|--------------------|----------------|--------------------|----------------|--------------------|----------------|--------------------|----------------|--------------------|
| 22.2 | 82.3 | 84.7 | 81.2 | 83.3 | Ben- | H ₂ SO ₄ | 84.4 | 89.0 | 84.4 | 89.2 | 77.7 | 84.5 | 82.2 | 85.0 | 76.6 | 84.0 | 77.7 | 85.0 | 84.4 | 89.0 |
| — | — | — | — | — | Ben- | Hcl | 81.1 | 84.4 | 75.5 | 83.3 | 82.2 | 88.2 | 82.2 | 83.2 | 74.4 | 84.4 | 76.6 | 84.0 | 81.1 | 86.7 |

TABLE 4.—CHEMICAL ANALYSIS OF THE BENTONITES.

| | Bhimber 1 | Bhimber 2 | Chitti Deri 3 | Sikhim 4 | Jogi Tila 5 | Ganda 6 | Bhimber 7 |
|--------------------------------|-----------|-----------|---------------|----------|-------------|---------|-----------|
| Loss on ignition | .. 20.30% | 19.38% | 18.20% | 18.68% | 15.60% | 17.14% | 18.10% |
| SiO ₂ | .. 50.96% | 51.00% | 55.22% | 51.18% | 53.70% | 50.40% | 50.82% |
| Fe ₂ O ₃ | .. 9.16% | 11.10% | 7.41% | 7.41% | 12.96% | 12.96% | 7.41% |
| Al ₂ O ₃ | .. 12.3 % | 10.98% | 13.00% | 14.37% | 10.44% | 10.44% | 14.19% |
| CaO | .. 3.30% | 3.62% | 3.96% | 4.94% | 3.95% | 4.61% | 5.27% |
| MgO | .. 3.78% | 3.83% | 2.49% | 3.64% | 3.17% | 3.17% | 3.23% |
| Alkalies | .. nil | nil | nil | nil | nil | 1.02% | 0.80% |

Discussion

Table 1 shows that up to 64% of bentonite clay in one sample and more than 50% in other samples is separable from the raw bentonites by simple elutriation. However, small amounts of clay are lost in the gritty matter by this process.

It is evident from Table 2 that the original bentonites have no bleaching action and a simple heat treatment effected no appreciable change in their bleaching properties. Nevertheless, acid treatment activated the clays considerably. Heating of the acid-treated clays further improved their colour removing properties. But temperatures higher than 350°C. seem to have an adverse effect. The optimum temperature of activation can be safely concluded to be 300 - 350°C., at which range the best results were recorded.

The nature of the acid also influenced the activation process. For the same method of treatment and the same temperature of heating, sulphuric acid treated clays were more active than hydrochloric acid ones. But the difficulty in sulphuric acid-treatment is that it imparts to the clays the filtration properties that are undesirable in oil refining.⁵ Moreover in hydrochloric acid treatment, the boiling is conducted for 2 - 3 hours while twice that time is required for sulphuric acid. Bentonites of Bhimber and Chitti Deri were found to be best activated by acid treatment.

It is also evident from Table 3 that the addition of 0.5% activated charcoal enhanced the activation of the bentonites while the decolorization property of the activated charcoal used at such a low percentage was nominal. Furthermore, it is clear from the comparative results that Bhimber (Azad Kashmir) bentonites are not inferior to the I.C.I. and Tarana (Germany) standard bleaching fuller's earths in refining activity.

Chemical analysis reported in Table 4 reveals that five out of the seven bentonites have no alkali contents which conform to their non-swelling properties. These five bentonites are thus quite suitable for activation which is confirmed by experimental studies. Bentonite from Ganda having alkali contents 1.02%, produces gelatinous paste with tap water resembling soft-soap. When it was activated by acid treatment, the swelling

power was considerably decreased. This bentonite has low refining activity and may be used for other purposes.

Conclusions

It can be concluded that Bhimber, Sikhim and Chitti Deri bentonites are fairly comparable in performance with imported fuller's earths. They should be substituted for the imported clays. The economics of the activation process, however, involves consideration to the cost of filtration, reuse of the acid employed for activation, elimination of the wastage of bentonite in the separation of gritty matter and the drying of the earth at the optimum temperature.

It would be safe to conclude that whatever economic considerations, the cost of the activated earth produced should be comparable with that of the imported fuller's earths. Indigenous clays can advantageously replace imported earths. Our clays have not shown any adverse effects on the bleached oils; no reversal of the colour was noticeable after decolorization.

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