Purification and activation of the Iraqi bentonite for edible oil Production

Hameed R D Alamery¹,* and Saad A Ahmed²

¹ University of AL- Muthannia, College of Engineering Chemical Engineering Department.
² University of Baghdad ,College of Education for Pure Science Ibn Al-Haitham.

*Corresponding author Email: hameed_hrd@mu.edu.iq

Abstract Samples of Iraqi bentonitic sediments, representing local montmorillonite brought from Traifawi region near the Syrian border. Mineralogical the samples were characterized as low grade of Ca-smectite, particle size, chemical analysis, XRD, and BET surface area analyses of the samples were carried out to examine the structure of bentonite before and after acid activation. The goal is to prepare a bleaching earth for edible oil production. Iraqi Bentonite was beneficiated and activated by series of physical and chemical steps, using 4N & 6N concentration of hydrochloric acid and at a temperature of 70-80 °C. Surface area and pore volume of the samples were determined to assess the bleaching power of the activated bentonite. The chemical composition of the bentonite improve after remove Calcite phase was disappeared, reduced Iron oxide percentage with Increasing the concentration of hydrochloric acid and the treatment time lead to the growth of Smectite phase and change the structural of bentonite which noticed by improve of surface area from 58.93 to 206.62 m² g⁻¹.

Keywords: Bentonite; Beneficiation, Smectite; bleaching earth; Acid Activation.

1. Introduction:
Bentonite is term that was first used to designate particular, highly colloidal, plastic clay exist near Fort Benton in the Cretaceous beds of Wyoming, USA. It is characterized by unique properties like swelling to several times its original volume when placed in water and that forms thixotropic gels with water even whit small amount of bentonite. montmorillonite is the dominant content of smectite minerals, named after the deposits in Montmorillon, a region, in central-western, France [1].

Beneficiation of bentonite clay stone has been studied by various methods, including dispersion studied dispersion sedimentation. [2,3] hydro cyclone separation process. [4-6].
Bentonite is usually activated to be suitable for such uses, and to enhance its properties. Chemical activation using sulfuric acid to enhance adsorption of methylene blue. [7] Activated bleaching earths, for the vegetable oil industry. Where the fuller’s earth has been replaced by acid activated clays, which are sulfuric or hydrochloric acid treated bentonites [8,9]

Bentonite structure is affected by using hydrochloric acid or sulfuric acid as the concentration of aid increase the surface area increased. [10-12]

Bleaching of edible oil is one of the important stages in the production of edible oils. It is used to reduce the impurities which affects color and removes oxidation products namely hydro peroxides. Removal of these substances is essential in the refining of oils as it improves the stability and the quality of the oils. Color enhancement is achieved by the adsorption of colored organic pigments such as carotenoids, xanthophylls, chlorophyll, pheophytin, gossypol, and their degradation products, that impart undesirable color to the oils [9-13].

The goal of this work is to prepare acid activated bentonite from locally occurred raw materials. The second goal is to study the efficiency of the prepared material in bleaching color of sunflower seed oil produced in Iraqi edible oil factories by compare them with the commercial bleaching earth.

2. Materials and Methods
Bentonite mineral: brought from “Traifawi” a region near Syrian border, obtained from the General Company for Geological Survey and Mining in Baghdad, Iraq. Chemical analysis of raw materials and produced samples are done in the same company. Laser diffraction particle size analyzer (SALD 2101 from Shimadzu) was used for the particle size distribution measurement. The median size for particles was $6.748 \, \mu m$ as shown in figure (1).

Hydrochloric acid was used at a concentration of 37%, $d = 1.165 \, g/cm^3$) supplied by GFS Chemicals Germany of Leaching and activation process.

![Particle size distribution of raw material.](image)
The method of processing is shown in the block diagram presented in figure (2), the raw material is processed in physical and chemical steps to reach the activated bentonite (bleaching earth).

2.1 Beneficiation
The sample was crushed to particle size < 75 \( \mu \text{m} \) (-200 mesh), the crushed material is subjected to attrition scrubbing, process conditions are 50% solid content and mixing for 1 hr. to remove the gangue materials. Then a physical separation step to remove Calcite after sieving on 45 \( \mu \text{m} \) (325 mesh). The size (+325 mesh), was washed and dried at 60 °C and then washing by 0.5N hydrochloric acid to remove the remained calcite.

2.2 Activation
In this process, bentonite is activated by treating it with hydrochloric acid at different concentrations (4N, 6N) for different times (3hr, 4hr, 6 hrs.) and with a weight ratio of bentonite / acid (5:1) and at a temperature of 70-80 °C, then it is washed with hot water until reaching the PH = 7 followed by drying.

3. Results and discussion
3.1 Diagnosis of the phases
X-ray diffraction examination of raw bentonite revealed the presence of calcite, smectite, kaolin and quartz phases as shown in figure (3), as well the figure (4) shown the phases of XRD test for the commercial active bentonite.
Figure 3. X-ray diffraction of raw Iraqi bentonite

Figure 4. X-ray diffraction of commercial active bentonite

Figure 5. X-ray diffraction of active Iraqi bentonite with 4N3hr.
**Figure 6.** X-ray diffraction of active Iraqi bentonite with 4N6hr.

**Figure 7.** X-ray diffraction of active Iraqi bentonite with 6N3hr.

**Figure 8.** X-ray diffraction of active Iraqi bentonite with 6N6hr.
After the activation process with hydrochloric acid and concentrations of 4 & 6N with time 3& 6 hrs for each concentration, the disappearance of calcite and kaolin phases was observed, as shown in figures (5 to 8) due to reaction and decomposition. Table No. (1) Confirms that the percentage of calcite in activated models decreased to less than 1% due to the effectiveness of beneficiation and activation processes. The growth of smectite phase was also observed in the activated samples (Nos. 5 to 8) compared to the crude sample. It indicates an attainment of the required characteristic of bentonite. Regarding the silica phase, a noticed growth the activated samples observed at the expense of the decreasing the other oxides content.

3.2 Chemical analysis
Table No. (1) Show the chemical analysis of raw material and the activated samples with hydrochloric acid at concentrations 4N and 6N, as follows:

A- The percentage of calcite in the raw material is 5.6% and upon activation with hydrochloric acid it decreases to less than 1%.

B- The percentage of iron oxide (Fe₂O₃) in the ore is 5.02%, and upon activation by increasing the acid concentration and the treatment time, the iron oxide content decreases. The maximum removal was investigated at the concentration of 6N and the time of 6 hours, reaching 2.42%.

C- Other oxides: It was observed that the percentage of MgO, Na₂O, and K₂O decreased by increasing concentration and treatment time (7).

| Sample No. | SiO₂ | Fe₂O₃ | Al₂O₃ | TiO₂ | CaO | Na₂O | MgO | K₂O | L.O.I |
|------------|------|-------|-------|------|-----|------|-----|-----|------|
| Raw        | 54.84| 5.02  | 15.58 | 0.71 | 5.6 | 0.95 | 3.9 | 0.42 | 11.71 |
| Commercial | 60.88| 2.88  | 9.11  | 0.78 | 5.88| 0.15 | 9.4 | 0.42 | 8.9   |
| 4N3HR      | 61.26| 4.98  | 16.76 | 0.89 | 0.84| 0.21 | 2.75| 3.6  | 11.44 |
| 4N4HR      | 62.3 | 4.88  | 15.81 | 0.84 | 0.84| 0.17 | 2.7 | 3.7  | 11.99 |
| 4N6HR      | 65.18| 3.26  | 15.34 | 0.84 | 0.56| 0.16 | 2.55| 0.38 | 11.2  |
| 6N3HR      | 65.12| 2.7   | 16.05 | 0.41 | 0.84| 0.14 | 2.7 | 0.36 | 11.7  |
| 6N4HR      | 64.18| 2.58  | 16.37 | 0.74 | 0.84| 0.19 | 2.65| 0.32 | 10.99 |
| 6N6HR      | 65.22| 2.42  | 16.76 | 0.55 | 0.56| 0.15 | 2.7 | 0.36 | 10.72 |

3.3. Surface area
Brunauer, Emmett and Teller (BET): the specific surface area and pore size distribution had been carried out in the petroleum research and development center, Baghdad.

This information is used to predict the dissolution rate, as this rate is proportional to the specific surface area. Thus, the surface area can be used to predict bioavailability. Further it is useful in evaluation of product performance and manufacturing consistency.

Table No. (2) Shows the surface area and pore size of the raw and activated samples with hydrochloric acid concentrations of 4N and 6N. It is clearly observed that there is a significant increase in the surface area of the activated samples when compared with the raw and commercial samples. Surface area and porosity increased in the same manner with the increase in acid concentration and the treatment time. The highest value of the surface area was 206 m²/g for 6N acid treatment and of (6 hrs.) time. The porosity is increased to 0.1712 cc/g.
Table 2. Surface area and pore volume of the raw and activated samples

| Sample Type | Surface Area (m²/G) | Pore Volume (Cc/G) |
|-------------|---------------------|--------------------|
| Raw         | 58.93               | 0.069              |
| commercial  | 69.29               | 0.107              |
| 4N3HR       | 142.78              | 0.111              |
| 4N6HR       | 180.37              | 0.140              |
| 6N3HR       | 193.39              | 0.147              |
| 6N6HR       | 206.62              | 0.171              |

3.4. Bleaching

The bleaching test: The pH-value (acidity) of the aqueous suspensions for hydrochloric acid leached bentonite samples, as well as the red and yellow colors index of the oil bleached by these adsorbents change depending on the weight fraction and bleaching time. Bleaching test for the prepared samples gives good results with the sunflower oil as shown in table (3).

Table 3. Show the results of bleaching test and PH values

| No. | Sample | Time (hrs) | Colour Index Before Bleaching | Colour Index After Bleaching | Value Of PH |
|-----|--------|------------|------------------------------|-----------------------------|-------------|
| 1   | 4N HCl | 3          | 9.9 R - 73.5 Y               | 5.7 R - 25.7 Y              | 2.7         |
|     |        | 6 hr       |                              |                             | 3           |
| 2   | 6N HCl | 3 hrs      | 9.9 R - 73.5 Y               | 5.8 R - 20.8 Y              | 2.7         |
|     |        | 6 hrs      |                              | 1.5 R - 7 Y                 | 3.4         |

4. Conclusions

The following conclusions can be drawn based on the results obtained in the current study.

1- Calcite phase was disappeared with the hydrochloric acid treatment.

2- Increasing the concentration of hydrochloric acid and the treatment time lead to the growth of Smectite phase.

3- Iron oxide percentage decreases with increasing hydrochloric acid concentration and treatment time.

4- The surface area increases with increasing hydrochloric acid concentration and treatment time.

5- The size of the porosity increases with increasing the concentration of hydrochloric acid and the treatment time.

6- The process steps involved in the purification and activation processes lead to superior bentonite specifications related to the commercial samples by assessing the surface area and growth of the Smectite phase.
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