

The Use of Mozambican Bentonite in Edible Oil Refining: Characterization, Acid Activation and Performance Evaluation

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The suitability of acid-activated Mozambican white bentonite from Boane district as oil bleaching agent was investigated. The focus was given on the performance of the activated clays on colour removal. The clay effectively removed colour pigments when used to bleach neutral soybean oil and, generated oils comparable in terms of colour with those bleached with commercial clays used in the study. The degree of colour removal was found to be closely dependent on the concentration of the acid and the activation temperature. The colour reduction increased from 76.94 % (for natural clay) to 99.24 and 99.99 % for clays modified with HCl and H₂SO₄ as their concentrations and temperatures used for activation varied from 2 to 4 mol/L and 80 to 100 °C.

1. Introduction

Vegetable oils play an important role in the human diet, providing energy, essential fatty acids and liposoluble vitamins. They are also responsible for the flavor and texture of foods (Guliyev et al., 2018). However, before they reach the market for their consumption, vegetable oils go through a refining process. Crude oil refining process aims to remove impurities or undesirable substances such as phospholipids, free fatty acids, gums, trace metals, soaps, etc. Refining process includes degumming, neutralization, bleaching, deodorization, and further refining. However, bleaching is the most critical stage in the refining process (Hatami et al., 2018) as it helps to remove a wide range of impurities mentioned above and also helps to improve the oil appearance, giving a pleasant taste and stability to the final product. Bleaching is an adsorption process that normally utilizes clay (natural or activated), fuller's earth, sulfuric and hydrochloric acid, synthetic silicates, synthetic resins and activated carbons as adsorbents (Guliyev et al., 2018). However, activated clays, in particular, bentonites stand out among several materials used as bleaching adsorbents. Their high adsorption and ion exchange capacity, their technical and economic viability which, combined with their abundance and low cost make clays cheaper adsorbent agents with scientific and industrial attractiveness.

Clay-based adsorbents are normally activated by a mineral acid treatment such as H₂SO₄ and HCl. Such treatment leads to leaching of aluminum, magnesium, and iron cations from the octahedral layer of the clay. Impurities such as calcite are also removed by leaching with an inorganic acid at elevated temperatures. The edges of the platelets are opened, and, as a result of all these changes, the pore diameters and the surface area increase. Acid activation promotes catalytic activities by increasing the number of Bronsted and Lewis acid sites. During bleaching, the acidic properties will increase free fatty acids by splitting triglyceride molecules while the catalytic properties are responsible for the decomposition of peroxides. Important bleaching or adsorption criteria are quantity of activated earth, dosage, time, mixing, temperature, and atmospheric pressure and vacuum (Wiedermann, 1981).

The bleaching of oil in many Mozambican refining factories has been carried out using imported activated bentonites, despite the fact that the country has considerable reserves of this resource. The import of these products has negative impacts for the national industry in the sector because of the high costs involved. Given this scenario, there is a pressing need to find local alternatives that will minimize these impacts. It is in this context that the present research work was proposed.

Mozambique has huge reserves of bentonite. The well-known and investigated bentonite deposit is located in the District of Boane, Maputo Province. Previous studies (Massinga et al., 2010) indicated that Boane bentonite is composed mainly of montmorillonite (MMT) in about 60 wt.%, with cristobalite being the major impurity. The presence of MMT in the clay is of utmost importance as it confers the bleaching power to clay, making this bentonite a potential candidate to be used as adsorbent agent in the bleaching stage. However, it is believed that this potential can be improved through an acid treatment, a procedure still very little known and explored scientifically and technologically at the national level. This was the primary objective of the present study. The work aimed to evaluate the suitability of acid-activated Boane bentonite as oil bleaching agent. For this purpose, several samples of bentonite were treated with acids (hydrochloric or sulfuric). Activation conditions such as type and concentration of acid and temperature of the activation process were evaluated. The bleaching power of the synthesized products was then compared with locally available commercial bleaching clays. However, in this stage of the study the focus was given on mineralogical and physico-chemical analysis of the pristine clay and the performance of the activated clay on colour removal.

2. Materials and Methods

2.1. Materials

Natural calcium-bentonite from Boane deposit, exhibiting a white colour was kindly supplied by the Industrial Minerals of Mozambique Lda (MIMOC). For comparison purposes, locally available commercial clays were used namely, Tonsil and Zakuro that were supplied by Southern Refineries and Ginwala factories. The inorganic acids namely sulfuric and hydrochloric, with a purity of 98 % and 32 %, were obtained from Tecnotraguas (Mozambique). The soybean oil used in the clarification tests (previously neutralized) was supplied by Southern Refineries factory.

2.2 Methods

The typical procedure for the acid activation process was as follow: 100 g of natural bentonite (<75 μm fraction) was dispersed in a solution of one of the chosen acids (H_2SO_4 or HCl) at one of the pre-defined concentrations in a proportion of 1.5 g/10 mL under magnetic stirring at 1,500 rpm for 5 min. Then, the suspension was heated to one of the pre-defined temperatures for 2 h under stirring. After this period, the container was closed and the suspension left to rest. The supernatant solution was removed and the resulting material was filtered and washed with distilled water to remove excess acid until the washing water had a pH of around 3 to 4 (List G.R., 2009). The resulting material was finally dried and then milled to a powder for clarification tests and further analysis. For the activation process, 3 variables were chosen, namely the activation temperature, the type of acid and its concentration. For each acid 3 different concentrations were fixed (2, 3 and 4 mol/L of solution) and in turn, for each concentration 3 different temperatures were also fixed (80, 90 and 100 $^\circ\text{C}$), implying a total of 9 samples for each acid. In turn, a typical procedure for the oil bleaching process was as follows: In a 500 mL beaker, 100 mL of neutral oil was placed and heated to a temperature of 100 $^\circ\text{C}$ to remove the water, a process carried out under magnetic stirring for 20 min. After this, 3 wt.% of activated bentonite sample to be tested was added to the hot oil keeping the oil/bentonite mixture for 20 min at a constant speed and temperature of 800 rpm and 100 $^\circ\text{C}$. After the stipulated period, the oil was finally filtered using a vacuum pump. The clarified oils as well as the neutral oil had their chlorophyll contents determined.

2.3 Sample characterization and analysis

X-Ray diffraction (XRD) was used to characterize the natural bentonite (NB). The sample was analyzed as a powder using a PANalytical X'Pert Pro Multi-Purpose with $\text{Cu K}\alpha$ radiation ($\lambda=1,5418 \text{ \AA}$) in the 2θ range from 2° to 60° at a scan rate of $2.0^\circ/\text{min}$. Elemental composition (determined only for NB) was determined by X-ray fluorescence (XRF), using a Philips PW2400 spectrometer. For major element analysis the milled sample (<75 μm fraction) was roasted at 1,000 $^\circ\text{C}$ for at least 3 h to oxidize Fe^{2+} and S and to determine the loss on ignition (LOI). Glass disks were prepared by fusing 1g roasted sample and 9.5 g flux consisting of 70.689 % $\text{Li}_2\text{B}_4\text{O}_7$, 19.786 % LiBO_2 and 0.50 % LiI at 950 $^\circ\text{C}$. The glass disks and wax pellets was analyzed on a Philips brand, model PW 2400. The Cation Exchange Capacity (CEC) of NB was determined by Atomic Absorption Spectrometry (AAS), according to PR-CRI-106. FT-IR spectra were recorded on a SHIMADZU spectrometer; model IR Prestige-21 from 400 – 4,000 cm^{-1} , using an average of 32 scans and a resolution of 2 cm^{-1} . Approximately 1.5 mg of dry sample of NB was mixed with 300 mg of spectroscopic-grade KBr and milled to a powder. The spectra were obtained with respect to a background which was previously corrected using a pure KBr pellet. The surface morphology of the NB was examined by scanning electron microscopy (SEM), using a JSM-6390 Scanning Electron Microscope. An Energy Dispersive X-Ray analyzer, coupled to the microscope, was used for local chemical analyses of the samples. The powder samples were coated five times with gold.

The images of the surfaces were generated with magnification of 1,000 times and with energy of 15 kV. Thermal behavior of the neat clay was analyzed by thermogravimetric analysis (TGA). The TGA was performed using the dynamic method on a SHIMADZU Simultaneous DTA-TG Aparatus, model DTG-60. About 10 mg of the sample (clay or polymer) was placed in open 150 μ L alumina pans. Temperature was scanned from 25 $^{\circ}$ C to 1,000 $^{\circ}$ C at a rate of 10 $^{\circ}$ C/min with air flowing at a rate of 50 mL/min. The chlorophyll concentration in the crude and in the clarified oils was determined using AOCS Official Method Cc 13d-55 and AOCS Official Method Cc 13i-96. AOCS Official Method Cc 13d-55 is used to determine mg/kg (ppm) of chlorophyll-related pigments (predominantly pheophytin a) in oil from spectrophotometric absorption measurements at 630, 670 e 710 nm. The chlorophyll concentration is then calculated using Eq(1) given below.

$$C(\text{ppm}) = \frac{A_{670} - (A_{630} + A_{710})/2}{F \times L} \quad (1)$$

where C is the chlorophyll pigments concentration in mg/kg (ppm), A is absorbance, L is cuvette length in cm and F is a factor specific to each spectrophotometer. In turn, AOCS Official Method Cc 13i-96 is used to determine the total chlorophyll pigments expressed as mg of pheophytin a in 1 kg of crude vegetable oil. The content of chlorophyll pigments is then calculated using Eq(2) given below.

$$C = 345.3 \times \frac{A_{670} - 0.5 \times A_{630} - 0.5 \times A_{710}}{L} \quad (2)$$

where C is the chlorophyll pigments content as mg of pheophytin a in 1 kg of oil, A is absorbance at the respective wavelength in nm and L is a light the spectrophotometer cell in mm.

3. Results and discussion

3.1 X-Ray diffraction (XRD) and scanning electron microscopy (SEM)

XRD investigations (Figure 1a) showed that the white bentonite from Boane deposit, Mozambique is a co-mixture of smectite and cristobalite. Previous Rietveld Quantitative Analysis of the XRD carried out by Massinga et al. (2010) indicated that the crude Boane bentonite contain 60.3 wt.% MMT, 35.7 wt.% cristobalite and 4 wt.% quartz. This is the sample, which was purified and modified with soda ash.

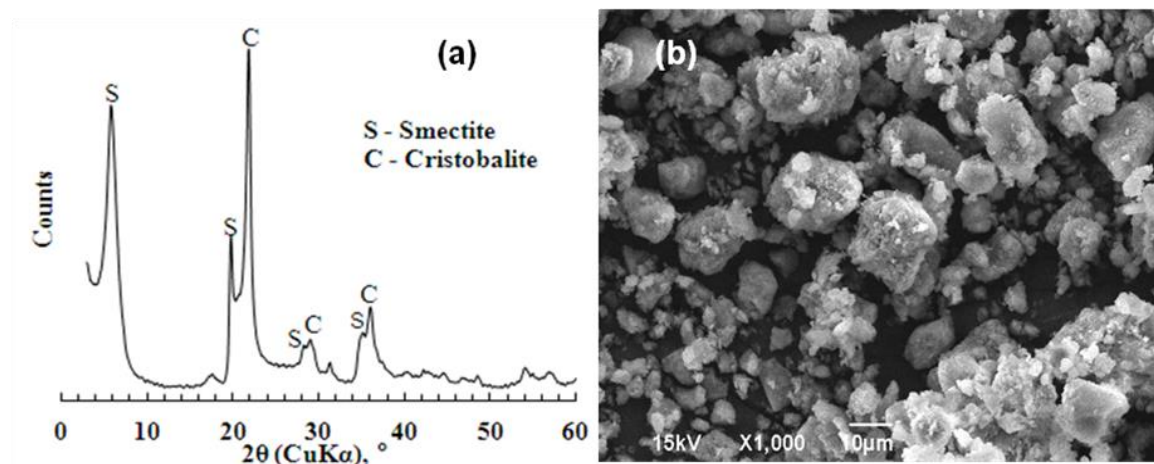


Figure 1: XRD patterns (a) and SEM micrograph (b) of natural bentonite (NB)

The main smectite phase reflection d_{001} was found at 15.18 \AA , a value which is in agreement with the theoretical value of the Ca^{2+} saturated smectites. The interlayer spacing of 15.18 \AA suggests characterizing this smectite as the one having a mixture of monovalent/divalent exchangeable cations (Inglethorpe et al., 1993). SEM image of NB is shown in Figure 2b. The clay featured some crystalline pseudo-hexagonal edges and semi-rounded micro-sized particles on the surface of the clay mineral particles. However, some irregularly shaped aggregates are also observed. Similar results were observed by Massinga et al. (2010). Most of the particles were much smaller than 10 μ m in size and are arranged in face-to-face patterns. Elemental analysis

made by SEM-EDX (not shown here) confirmed the predominant character of the smectite clay mineral, since the natural clay presented in its composition Si, Al and O, consistent with the X-ray data.

3.2 X-Ray fluorescence (XRF) and Cation Exchange Capacity (CEC)

XRF measurements indicated the following chemical composition: 71.3 wt.% SiO₂, 10.8 wt.% Al₂O₃, 3.08 wt.% Fe₂O₃, 0.39 wt.% CaO, 0.23 wt.% K₂O, 1.05 wt.% Na₂O, 2.57 wt.% MgO, 0.01 wt.% MnO, 0.19 wt.% TiO₂, 0.02 wt.% P₂O₅, and 10.41 wt.% LOI. The high silica and low contents in Al₂O₃ and MgO, when compared to typical bentonites with Al₂O₃ (16 - 20 wt.%) and MgO (3 - 6 wt.%) are features that are strictly related to the parent rocks of dominantly rhyolitic composition. Mg, Ca, K and Na are located in the galleries of the clay mineral and are the main bearers of ion-exchange properties (Dos Muchangos 2006). The cristobalite phase, present as a major impurity in this clay is the responsible for the higher content of silica. As expected, Fe₂O₃ and TiO₂ contents displayed low values due to the white colour of the sample. The lowest K₂O percentage is a clear indication that the bentonite is free of K-feldspar, a non-clay mineral (Falode et al., 2008).

CEC measurements for NB indicated 67.53 meq/100 g, a value that lies within the range presented by typical commercial grade bentonite (40 to 120 meq/100 g) and also within the range predicted by (Cíleck, 1989) for Boane bentonite. The exchangeable cation pool for CEC was found to be 24.06 meq/100 g for Mg²⁺, 31.90 meq/100 g for Na⁺, 11.0 meq/100 g for Ca²⁺ and finally 0.57 meq/100 g for K⁺. From exchangeable cation pool values the ratio of Na₂O to CaO is 2.90, a value greater than 1 and indicative of the presence of a swelling bentonite (Wu et al., 2006).

3.3 Thermogravimetric and Differential thermal analysis (TGA and DTA)

Figure 2 shows the TGA (a) and DTA (b) curves in air environment of NB sample. Initial mass loss between 20 °C and about 300 °C is observed, characteristic of smectite clays. Two endo-exothermic bands (see DTA curves) were observed in which the endothermic band at about 60 °C is due to residual water and the exothermic band with a maximum at about 185 °C which can be related to the initial decomposition of organic matter likely to be present in NB. In the range of approximately 400 °C and 750 °C there was also a loss of mass with a very broad endothermic band that can be associated with aluminosilicate dehydroxylation. Above 750 °C there is an exothermic band, with the maximum at about 80 °C that can be related with the destruction of the crystal lattice (formation of new crystalline phases of the clay).

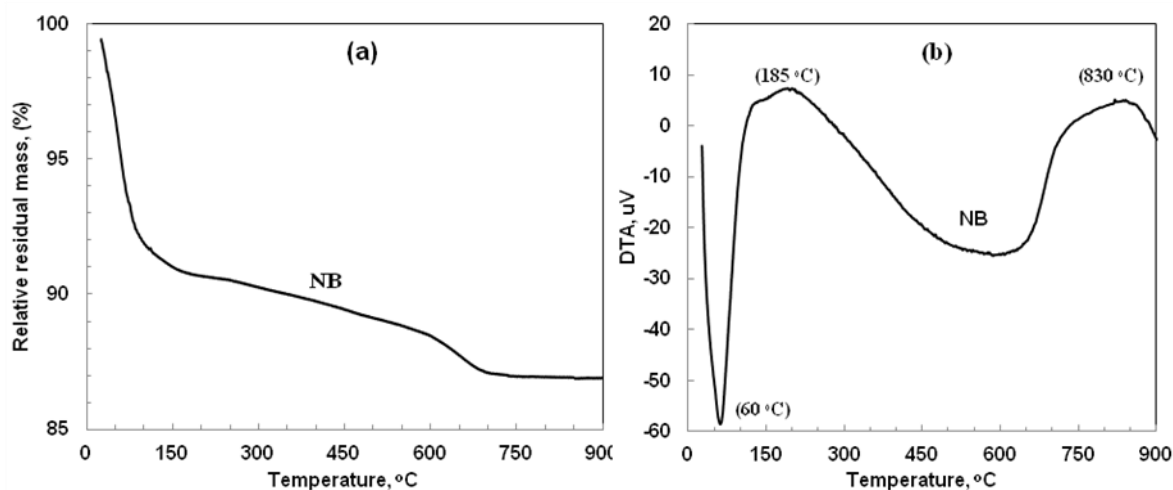


Figure 2: TGA (a) and DTA (b) curves in air environment of the natural bentonite

3.4 FT-IR analysis

The spectrum absorption bands of NB in the IV region are shown in Figure 3. NB shows peaks in wavelengths characteristic of the smectite group. The little pronounced peak present at 3,618 cm⁻¹ and the peak present at approximately 1,636 cm⁻¹ can be attributed to the stretching vibrations of the free and/or combined OH group of the bentonite clay. The interlayer and adsorbed water into the bentonite provide bands of approximately 3,418 cm⁻¹ and 1,636 cm⁻¹, corresponding to the stretching of HOH bonds for the first case and HOH deformation for the second. The bands present at approximately 1,034 and 1,096 cm⁻¹ are characteristic of the stretching of the Si-O bonds present in the smectite's crystal lattice.

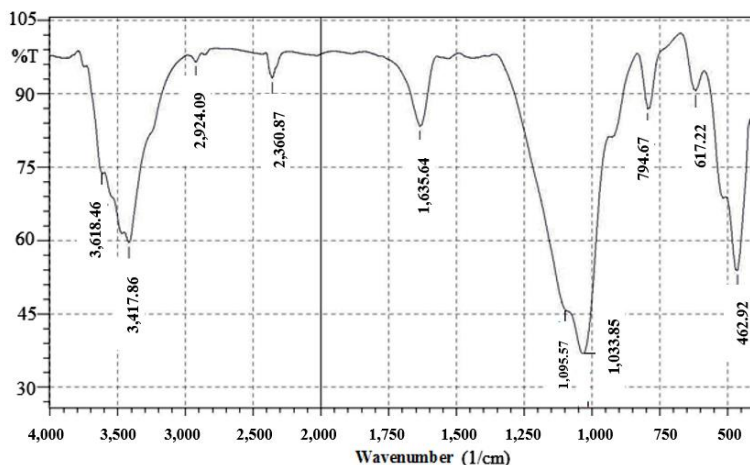


Figure 3: FTIR spectra of natural bentonite.

The bands present at 617 cm^{-1} and approximately 795 cm^{-1} refer to the octahedral layers (Al-O bonds). The band present at approximately 463 cm^{-1} can be attributed to the vibrations of Si-O-Si.

3.5 Performance on chlorophyll pigments removal

The neutral and dehydrated soybean oil used in the clarification tests showed an initial chlorophyll content of 0.03156 ppm. After clarification with NB, the residual chlorophyll content in the oil was 0.00754 ppm, which is equivalent to a performance (% percentage of chlorophyll removed) of 76.94 %. All activated samples by either HCl or H_2SO_4 , showed better chlorophyll removal power compared to the natural sample as can be seen in Table 1. Table 1 also show that the performance in removing chlorophyll pigments increases with increasing acid concentration. For instance, the colour reduction increased from 76.94 % to 99.24 and 99.99 %, for clays modified with HCl and H_2SO_4 as their concentrations used for activation varied from 2 to 4 mol/L. On the other hand, for the same concentration, the performance increases with increasing temperature, a scenario that is more prominent for samples activated with sulfuric acid. The type of acid used in the activation of the clay seems to have influenced the performance, with samples modified with sulfuric acid being those that performed slightly better in removing chlorophyll. This was expected since sulfate ions in aqueous solution react easily with interlamellar cations than chlorides ions given the greater strength of H_2SO_4 when compared to HCl. The residual chlorophyll contents after clarification with commercial clays were 0.00089 and 0.00024 ppm, which is equivalent to the performances of 97.18 and 99.24 % for Tonsil and Zakuro clays. These values are comparable to those obtained from activated clays.

Table 1: Performance on chlorophyll pigments removal of the activated clays

Concentration (mol/L)	Temperature ($^{\circ}\text{C}$)	Chlorophyll removal (%), HCl	Chlorophyll removal (%), H_2SO_4
0	-	76.94 ± 0.03	76.94 ± 0.03
2	80	95.25 ± 0.10	98.09 ± 0.10
2	90	96.12 ± 1.22	98.77 ± 0.01
2	100	97.04 ± 0.70	99.50 ± 0.21
3	80	99.17 ± 1.15	98.42 ± 0.07
3	90	99.11 ± 0.05	99.05 ± 0.00
3	100	99.20 ± 0.01	99.64 ± 0.01
4	80	98.92 ± 0.19	99.16 ± 0.01
4	90	97.84 ± 1.56	99.47 ± 0.43
4	100	99.24 ± 0.84	99.99 ± 0.20

Figure 4 makes a visual comparison of the clarifying effect between NB, the two commercial clays (Tonsil and Zakuro) and the two activated clays that showed the best performance (1004HCl and 1004 H_2SO_4).

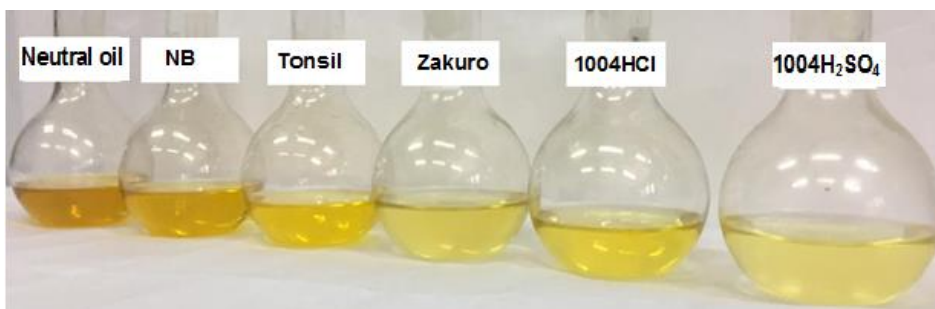


Figure 4: Visual comparison of the clarifying effect between NB, the two commercial clays (Tonsil and Zakuro) and the two activated clays that showed the best performance. Key: 1004HCl = Clay activated with HCl at a concentration of 4 mol/L and temperature of 100 °C, 1004H₂SO₄ = Clay activated with H₂SO₄ at a concentration of 4 mol/L and temperature of 100 °C.

4. Conclusions

XRD, SEM, EDS, XRF and AAS analysis confirmed the presence of MMT in Boane Bentonite. All activated samples showed better chlorophyll removal power compared to the natural sample. The colour reduction increased from 76.94 % (for NB) to 99.24 and 99.99 % for clays modified with HCl and H₂SO₄ as their concentrations and activation temperatures varied from 2 to 4 mol/L and 80 to 100 °C. The degree of colour removal was found to be dependent on the concentration of the acid and the activation temperature as well as on the type of acid. In conclusion, acid-activated Mozambican bentonite from Boane deposit effectively removed colour pigments when used to bleach neutral soybean oil, and generated oils comparable in terms of colour with those bleached with commercial clays used in the present study. The study has shown that Boane bentonite clay is a viable source of adsorbent agent for vegetable oil bleaching and the activated products can be a viable alternative to imported commercial bleaching earth. A feasibility study for its exploitation is hereby recommended.

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