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EFFECT OF ACID ACTIVATION ON STRUCTURAL AND BLEACHING PROPERTIES OF A BENTONITE

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Abstract: *A natural bentonite obtained from Khorasan, Iran, was submitted to acid activation with sulphuric acid. Sample aliquots (5gr)*
were leached with 100 ml H_2SO_4 solutions of various concentrations (2–7N) at 80±2 oC for 2 hours. X–ray diffraction, chemical analysis, infrared spectroscopy and specific surface area measurements were performed in order to evaluate important structural modifications occurring as a result of acid attack. Octahedral sheet was affected by acid activation resulting into the dissolution of cations (Mg^{2+}, Fe^{2+}, Al^{3+}) and consequent decomposition of montmorillonite structure. Bentonite samples were then tested in order to verify their capacity to bleach colza–soybean oil, and their performances were compared to that of a commercial bleaching clay. The bleaching ability of the natural clay was poor when compared with that of the industrial adsorbent. Acid activation of the bentonite sample with 7N sulphuric acid yielded an adsorbent material which was highly efficient in the bleaching of the oil functioned better than the commercial clay product under the same conditions.

Keywords: *Acid activation, Bentonite, Oil bleaching*

1. INTRODUCTION

Clays whose basic clay mineral is smectite are generally called bentonites [1]. Each smectite is a 2:1 layer clay mineral which shares the common feature that two silica tetrahedral sheets sandwich a sheet of octahedrally coordinated aluminum ions. Most of the smectite minerals have extremely defective structure because of the isomorphic substitution of a divalent metal ion for octahedral Al and a trivalent metal ion for tetrahedral Si [2]. These substitutions result in a net negative charge of the lattice which is subsequently compensated by interlayer exchangeable cations (Ca^{2+}, Na^+, K^+, etc). That is the origin of the cation exchange capacity of the smectite clay minerals. This property along with the other physiochemical properties, such as swelling, adsorption capacity and surface acidity give to bentonite many industrial interests and a great variety of applications [3].

Bentonites may be used both naturally and after some physicochemical treatments such as acid activation, ion exchange and heating according to the application area [4,5]. In edible oils refining, bentonite is the most common adsorbent used in the bleaching process. Bleaching primarily removes coloring pigments such as chlorophylls and carotenes but peroxides and other impurities (e.g. soap, trace prooxidant metals and phosphatides) are also important targets of the bleaching process.

In their natural state, bentonites generally show mediocre decolorizing effect. This ability is greatly enhanced by being leached with strong inorganic acids at slightly elevated temperature [6,7]. The acid activation of smectite clays is usually made on calcium-smecties. However, it is shown that the acid activation of sodium-smectites can produce acid activated clays with good decolorizing ability[8,9]. During acid leaching of clay minerals initially interlayer cations are replaced with H^+ ions of the acid with subsequent dissolution of structural cations. This process results in the de–lamination of the structure, thus increasing clay specific surface area and adsorption capacity.

The desired changes in the adsorptive properties of a bentonite occurring as a result of acid activation depend considerably on acid leaching conditions. Several acid activation experiments under different operating conditions have been reported in the

literature, in particular the choice of acid concentration, treating time and temperature [6,7,10,11]. It is also important to take into account the mineral composition of starting materials from various deposits when developing leaching procedure [11]. Thus it seems imperative to find optimal operating conditions specifically for different clays.

The present study is therefore carried out in order to examine the structural properties of an Iranian natural bentonite after acid activation and to evaluate its suitability for decolorization of edible oils.

2. MATERIALS AND EXPERIMENTAL METHODS

2. 1. Materials

A white bentonite clay collected from Khorasan region, Iran, was used as primary material. This bentotite produces mud of high plasticity when mixed with water and is currently used in the preparation of drilling fluids. Studies were performed on the air–dried and sieved (<149 μm) samples. Alkali–refined colza–soybean oil was obtained from an edible oil refinery factory (Nab Company, Iran). In bleaching tests, a commercial bleaching earth that is currently used in some oil refineries was used as standard.

All chemicals used were analytical reagent grade, obtained from Merck Company. Distilled water was utilized in all experiments.

2. 2. Experimental Methods

2. 2. 1. Activation by Acid Leaching

Five–gram aliquots of the clay were mixed with H_2SO_4 solutions (100 ml) of various concentrations in the range of 2–7N. The resulting suspensions were heated at 80±2 °C for 2 hours under continuous stirring. Leaching was performed in a glass flask equipped with a reflux condenser in order to avoid evaporation during the experiments. After acid activation the slurry was filtered under vacuum and the precipitate was washed thoroughly with distilled water till the filtrate was free from sulphate ions (tested by BaC_{l2} solution). The acid–activated samples were dried initially at room temperature followed at 70 °C for 3 hours. The lumps of dried clay were crushed and sieved again to <149 μm particle size. The clay samples thus prepared are designated as B2 to B7, which the numbers indicate the concentration of H_2SO_4 solutions used during the activation process. The raw clay is designated as B0.

2. 2. 2. Characterization

The chemical composition was determined by X–ray fluorescence (XRF), using a Philips PW 2400 XRF spectrometer. Before chemical analysis, each sample was heated at 1000 °C for 2 hours, and the decrease in mass was taken as the loss on ignition (LOI). X–ray diffraction (XRD) patterns were recorded with a Philips PW 3710 powder difractometer with Cu–Kα ($\lambda = 1.5405$ Å) radiation and a Ni filter. FT–IR spectra were obtained using a Shimadzu 8400 S spectrometer, with samples prepared by the conventional KBr disc method. The specific surface area was measured at 77 °K by BET method with a Micromeritics Gemini 2360 instrument using N_2 gas.

2. 2. 3. Bleaching Test

The bleaching experiments were carried out in a rotary evaporator instrument (Laborota 4001) under vacuum. The bleaching procedure involved placing of alkali–refined colza–soybean oil into a round–bottom rotary evaporator flask of 250 ml. The flask was evacuated and heated with stirring at 60 rmp to 65 ºC. Vacuum was then released and clay was added. Bleaching apparatus was again evacuated and heated further to the reaction temperature (90 ºC) and kept at the temperature for 10 min. A clay/oil ratio equal to 2% was used for all tests. At the end of the experiments, the suspension was filtered using a filter paper. The bleaching capacity of the activated clays was then determined by measuring the color of bleached oils using a UV–Vis spectrophotometer (Shimadzu UV mini 1240) at 421.0, 444.5 and 472.5 nm. During the measurements of the absorbance, the filtered oil was diluted by adding hexane. In this study bleaching capacity is defined by the following expression:

$$\text{Bleaching capacity (\%)} = (T_a - T_0/T_s - T_0) \times 100 \qquad (1)$$

Where T_0, T_a and T_s are the sum of the transparence values at three wavelengths mentioned above for the unbleached oil, oil bleached with the activated sample and with the standard one, respectively. A commercial bleaching clay was used as standard. For comparison, experiments were also performed with unleached natural clay sample.

3. RESULTS AND DISCUSSION

3. 1. Mineralogical Composition

The XRD patterns of the natural and acid–activated samples are given in Fig. 1. The natural bentonite contains a sodium–rich montmorillonite (NaM) with the d(001)–value of 1.25 nm as the dominant clay mineral [12]. Montmorillonite seems well crystallized in the sample. Other accessory minerals were found to be quartz, cristobalite, calcite, gypsum and feldspar.

Leaching of the sample with sulphuric acid produces important mineralogical changes as can be seen from XRD patterns. The most pronounced modification occurs in the montmorillonite d(001) peak (the first peak appearing at 2θ angle about 7°) which shows reduction in intensity as a result of acid attack. The reduction in intensity and increase in width of the 001 peak indicate that the crystallinity of the NaM is considerably affected by acid activation. This means that the process favors the production of amorphous phase by decomposing montmorillonite structure. On the other hand, since the montmorillonite peak is still present after acid treatment, we may assume that the structure has been partially destroyed. That balance between acid attack and structural preservation may hold the key for the establishment of optimal bleaching parameters.

It can be also observed that the characteristic peaks corresponding to gypsum and calcite minerals disappear after acid activation under relatively mild conditions, whereas feldspar is not destroyed even by activation with the maximum acid concentration of 7N, indicating that feldspar is resistant to acid attack.

3. 2. Chemical Composition

Table 1 shows the changes of the chemical composition and specific surface area of the bentonite clay as a function of acid concentration. As is evident from the changes in chemical composition, acid activation modifies the bentonite chemistry. The process results in a material with greater silica content and lower abundance of metal oxides.

Dissolution (%) of the cations from the

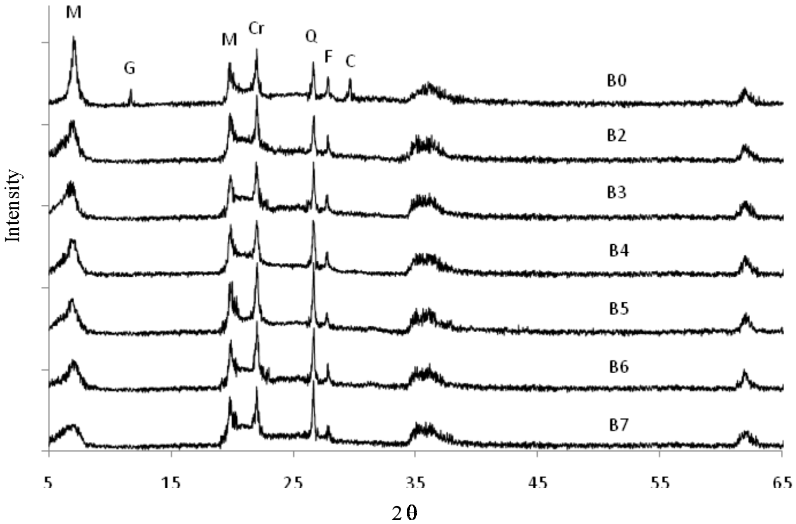

Fig. 1. X-ray diffraction patterns of the natural and acid activated bentonite samples (M = montmorillonite; G = gypsum; Cr = cristobalite; Q = quartz; F = feldspar; C = calcite).

Table 1. Chemical analysis and specific surface area (SBET) of the natural and acid activated bentonite samples

	(mass%)								
Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	LOI	$S_{BET}(m^2/g)$
B0	56.41	13.95	3.59	3.59	3.70	5.76	0.30	12.40	23
B2	65.72	12.66	2.79	2.58	1.71	2.76	0.20	11.21	102
B3	66.75	12.20	2.72	2.50	1.70	2.76	0.20	10.98	119
B4	67.26	11.90	2.66	2.47	1.65	2.75	0.19	10.87	127
B5	68.50	11.68	2.50	2.23	1.68	2.68	0.19	10.19	153
B6	69.39	11.38	2.45	2.19	1.63	2.72	0.19	9.83	171
B7	69.61	11.13	2.41	2.13	1.70	2.66	0.19	9.86	163

bentonite structure is calculated and shown in Fig. 2. Here, two groups of cations can be easily distinguished. First group contains; Ca^{2+}, Na^{+} and K^{+} which a significant amount of them is removed after leaching with 2N acid concentration. Dissolution of these cations remains almost constant by continuing the activation process with higher acid concentrations. The amount of Ca^{2+}, Na^{+} and K^{+} removal by acid treatment corresponds to the exchangeable cations which are located out of the montmorillonite lattice (between layers), so that they dissolve easily under mild condition (removal of Ca is partly related to calcite since a slight proportion of the Ca is present as the acid soluble carbonate). However a considerable amount of these elements is still found in the activated clays due to the presence of impurities, mainly, feldspar that has calcium, sodium and potassium, and is resistant to acid attack [10,13] or alternatively, they may precipitate as a new amorphous phase from the leachate. Fe^{2+}, Mg^{2+} and Al^{3+} are included in second group which belong to the octahedral sheet. As can be seen in Fig. 2, dissolution of these cations is less than exchangeable cations especially in low acid concentrations and they need stronger condition to be removed from montmorillonite structure. In contrast to interlayer exchangeable cations, octahedral cations removal from bentonite increases as the acid concentration increases between 2–7N. This increasing trend, however, is not similar for these three cations. Dissolution of Al^{3+} cation increases regularly by increasing acid concentration, whereas for Mg^{2+} and Fe^{2+} cations a rather sharp rise can be observed by switching acid concentration from 4N to 5N. The cations dissolution trend also shows higher leaching of MgO (41%) than Fe_2O_3 (33%) after activation with 7N acid concentration. It clearly shows that Mg^{2+} ions are more prone to acid attack.

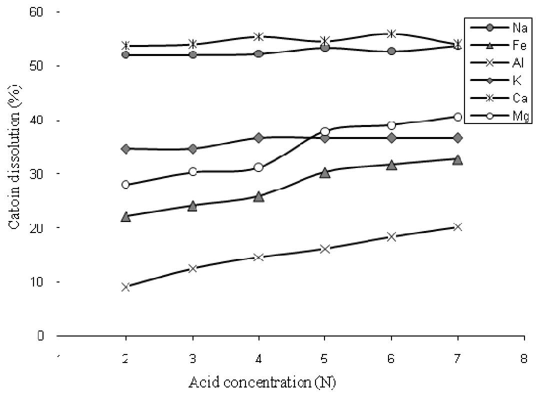

Fig. 2. Dissolution of the cations after acid activation as a function of acid concentration.

The Si^{4+} cations at tetrahedral sites of smectite are not dissolved by acid activation. The increase in relative content of these cations occurs as a result of depletion of the cations from the interlayer and octahedral sheets of the montmorillonite. In the 2:1 clay minerals, the tetrahedral cations are generally the most resistant to acid attack, followed by the octahedral cations, with the exchangeable cations the most vulnerable.

3. 3. Specific Surface Area

Table 1 shows that the surface area can be increased upon acid treatment. As the activation progresses, surface area increases rapidly at first, reach a maximum and decreases again. An approximately seven–fold increase in the specific surface area of the bentonite results from acid treatment, producing maximum surface area in sample B6.

At first the rise in specific surface area is a result of the unoccupied octahedron spaces remaining from the Mg^{2+}, Fe^{2+}, and Al^{3+} ions that have left the 2:1 layers. Then as the activation progresses the empty spaces grow larger and the micropores are transformed into mesopores and finally, because of the decomposition of the crystal structure at some locations, some of the mesopores disappear, leading to a drop in specific surface area [14].

3. 4. FT–IR Spectroscopy

Fig. 3 shows the FT–IR spectra of the raw and acid activated samples in the wave number range of 4000–500 cm^{-1}. The spectrum of the original clay exhibits absorption bands at 3423 and 1639 cm^{-1} assigned to the stretching and bending vibrations of the OH groups for the water molecules adsorbed on the clay surface, and a band at 3624 cm^{-1} representing the stretching vibration of the hydroxyl groups coordinated to octahedral Al^{3+} cations [15]. The Si–O bands are strongly evident in the silicate structure of the original clay and can be easily recognized in the infrared spectrum by very strong absorption bands in the 1100–1000 cm^{-1} region. The most intensive band at 1040 cm^{-1} is attributed to Si–O in–plane stretching and the shoulder at 1090 cm^{-1} is due to Si–O out–of–plane stretching vibration [16]. The bands at 519 and 466 cm^{-1} correspond to Si–O–Al (octahedral) and Si–O–Si bending vibrations respectively [17]. The raw clay spectrum also contains a band at 794 cm^{-1} which is attributed to cristobalite [15,16]. The bands at 915, 875 and 836 cm^{-1} arise from the bending modes of the hydroxyl groups AlAlOH, AlFeOH and AlMgOH, respectively [18,19].

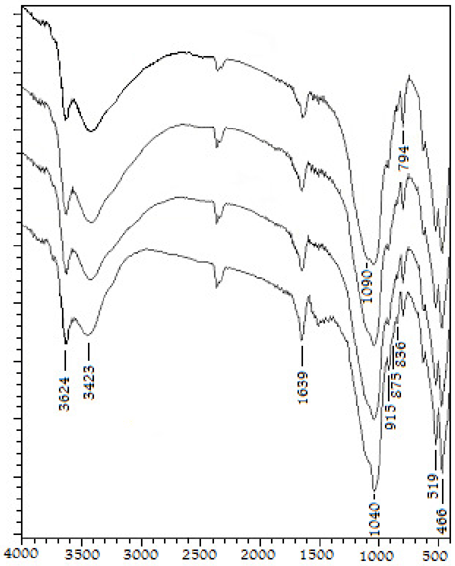

Fig. 3. FT–IR spectra of the natural and some acid activated samples.

The FT–IR spectra of the natural and acid activated clay samples reflect the structural modification which takes place due to acid activation. Leaching causes the intensity of the absorption bands at 915, 875 and 836 cm^{-1} to decrease. This results suggests the partial depletion of Al, Mg and Fe from the clay structure, in accordance with the changes in chemical composition. The intensity of the bands at 3423 and 1639 cm^{-1} for water of hydration and the hydroxyl stretching band at 3624 cm^{-1} also show significant decrease after acid activation. It is due to the removal of octahedral cations, causing the loss of water and hydroxyl groups coordinated to them. After acid leaching, the intensity of the band at 1090 cm^{-1} increases due to the formation of three–dimensional networks of amorphous Si–O–Si units. However the persistence of a weak band at 1040 cm-1 indicates that the layer structure of the original clay is not fully destroyed, in agreement with the XRD result s. The band at 794 cm^{-1} associated with cristobalite not only survives the acid leaching but increase in intensity during the process.

3. 5. Bleaching Efficiency

The results of the bleaching runs for colza–soybean oil using natural and activated clays are presented quantitatively in Table 2 and illustrated in Fig. 4. As can be seen in Fig. 4 the adsorption spectrum for the unbleached oil shows three maxima at 421.0, 444.5 and 472.5 nm, the intensities of which reduce slightly after bleaching with the natural sample. However the

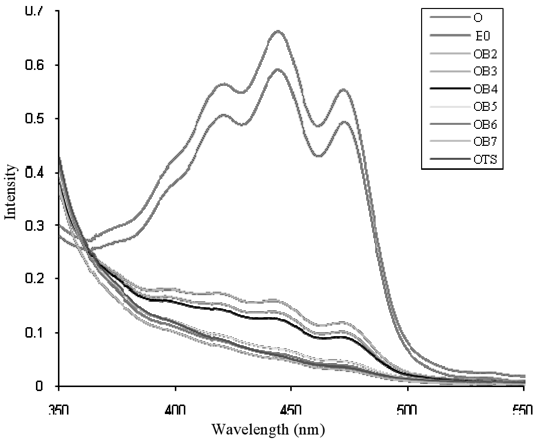

Fig. 4. Complete absorption spectra of the colza–soybean oil and the same oil treated with clay samples (O = unbleached oil; OB0–OB7 = oils bleached with the specified clay samples; OTS = oil bleached with the standard).

intensities of these bands show considerable decrease after bleaching the oil with activated samples and almost disappear after bleaching with samples activated by high acid concentrations. According to the results given in Table 1 and 2, bleaching efficiency increases proportionally to the removal of octahedral cations from bentonite structure. In their experiments to evaluate the bleaching efficiency of two bentonites with different smectite content, Foletto et al. (2006) found that the more the removal of octahedral cations from the bentonite original structure, the larger or better the decolorizing power of the acid activated bentonite, even if the activated sample was originated from a bentonite containing less clay minerals. The maximum bleaching efficiency of the sample is obtained for the sample activated with 7N acid concentration; a performance which is above that of the standard commercial product. Table 1 and 2 suggest that the maximum bleaching efficiency does not necessarily corresponds to the maximum for specific surface area. That is due to the fact that bleaching process is not merely a physical adsorption process and other properties such as cation exchange capacity, as well as acidic and catalytic properties must be taken into account [20].

Table 2. Bleaching efficiency results for the natural and acid activated bentonite samples

Sample	Bleaching efficiency (%)
B0	6.35
B2	73.3
B3	78.3
B4	81.5
B5	96.4
B6	99.6
B7	102.6

4. CONCLUSIONS

Leaching of a bentonite clay containing sodium montmorillonite as the major clay mineral, caused important structural modifications. Dissolution of octahedral cations (Mg^{2+}, Fe^{2+}, Al^{3}) increased continuously with increasing H_2SO_4 concentration; among them Mg^{2+} cations were more prone to dissolve than Fe^{2+} and Al^{3}. XRD results indicated partial destruction of the smectite and removal of gypsum and calcite. Partial destruction of montmorillonite increased the specific surface area by a factor of 7 (from 23 to 171 m^2 g^{-1}). Leaching of the bentonite with 7N sulfuric acid yielded a sample which was more efficient in bleaching than the commercial bleaching clay. The overall results led to the conclusion that the Iranian bentonite clay can be converted into potent adsorbent for bleaching vegetable oils which permits a wider application area for the bentonite.

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