TO EVALUATE AN ACID ACTIVATED BENTONITE FROM KHORASAN (IRAN) FOR USE AS BLEACHING CLAY

M. M. Kashani Motlagh, Z. Amiri Rigi & A. A. Yuzbashi

Abstract: The present investigation involves the preparation, characterization and bleaching property evaluation of a set of adsorbents, prepared by the acid activation of a bentonite clay collected from khorasan region, Iran. The acid activation experiments were carried out by hydrochloric acid solutions of various concentrations in the range of 2–7 N at 80±2 °C for 2 hours. Surface area measurements, chemical composition and mineralogical analysis of the prepared samples were performed. Activated samples were 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 results showed that the activated bentonite at ~ 5 N acid concentration, would attain desirable adsorption properties suitable for bleaching of edible oils.

Keywords: Acid activation, Bentonite, Bleaching clay

1. Introduction

Due to its adsorptive and catalytic properties, bentonite is widely used in a variety of applications [1–12]. These properties arise from lamellar structure of its clay minerals which composed of stacked alumina silicate layers. Major clay minerals in bentonite are smectites [2]. Bentonite may also contain other clay minerals and non clay minerals [13]. Each smectite is a 2:1 layer clay mineral which shares the common feature that two tetrahedral sheets sandwich a sheet of octahedrally coordinated metal ion, [14]. Partial substitution of a divalent metal ion for octahedral Al and a trivalent metal ion for tetrahedral Si results in a net negative charge and subsequent interaction with positive ions such as Na+ and Ca2+ (exchangeable cations) to form an interlayer hydrated phase. Bentonites are found in nature abundantly. However, most of them should undergo appropriate physical or chemical treatments such as acid activation, ion exchange and heating in order to promote their surface properties.

Acid activation of bentonites is one of the most important processes that have been performed to achieve desirable structural condition in edible oil bleaching applications [15–18]. Compared to natural bentonites, acid activated bentonite clays (which usually known as bleaching clays) show a much more higher bleaching capacity. During acid treatment of the clay, initially interlayer cations are replaced with H+ ions followed by partial destruction of aluminum octahedral and silicon tetrahedral sheets with subsequent dissolution of structural cations. It is believed that this process results in the de–lamination of the structure, which consequently increases clay specific surface area and pore volume which improves the adsorption capacity of color producing substances from the oil.

The mechanism of retention of the pigments, including carotene and carotenoids, at the surface of an activated clay is not clear. There are small quantities of chlorophylls found in nearly every type of edible oil which also contributes to the coloration. The chlorophyll molecule is believed to be adsorbed as a protonated species, pointing out the importance of the acid properties of the bleaching clay [19]. The surface acidity and the porous structure of bentonite can be changed to the desired extent by acid activation [20–22]. The desired changes in the physicochemical properties of a bentonite occurring as a result of acid activation depend considerably on the condition of acid activation such as the acid concentration and the duration and temperature of the activation process [21–28]. To explain these changes acid reactions of various bentonites have been intensively investigated [29–35]. The present study was therefore carried out in order to evaluate the adsorption capacity of a bentonite from khorasan region after acid activation with HCl, for decolorization of edible oils.

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2. Experimental
A bentonite clay obtained from Khorasan region, Iran, was used as primary material. Studies were performed on the air-dried and sieved (<149 µm) samples. 5 g of the sample was mixed with HCl solutions (100 ml) of various concentrations (2–7 N) and the resulting suspension was heated at 80±2 ºC for 2 hours under continuous stirring. The slurry was cooled, filtered and washed thoroughly with distilled water to remove remaining chloride ions (tested by AgNO₃ solution). It was dried initially at room temperature followed at 70 ºC 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 H2 to H7 which the numbers indicate the concentration of HCl used during the activation process. The untreated clay is designated as BN. The cation exchange capacity of the natural bentonite was obtained by Kjeldahl method [36]. The decrease in mass of the sample, which was heated for 2 hours at 900 ºC, was reported as the loss on ignition (L.O.I.). The chemical analysis of the natural sample, as well as the amount of the dissolved cations during acid activation was performed with ICP–AES by ICPS–7000 ver. 2. The crystalline phases in the samples were determined by XRD (Philips PW3710). The specific surface area was measured at 77 ºK by BET method with a Micromeritics Gemini 2360 instrument using N₂ gas.

The bleaching experiments were carried out in a rotary evaporator instrument (Laborota 4001) under vacuum. The bleaching procedure involved placing of alkalirefined colza–soybean oil into a round-bottom rotary evaporator flask of 250 ml. The flask was evacuated and heated with stirring at 60 rpm 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 the tests. At the end of the experiments, the suspension was filtered using a filter paper. The bleaching efficiency of activated clays was then determined by measuring the color of the bleached oil using a UV–Vis spectrophotometer (Shimadzu UV mini 1240) at 421.0, 444.5 and 472.5 nm. In this study bleaching efficiency (BE %) is defined by the following expression:

\[
BE \% = \left( \frac{T_d - T_0}{T_s - T_0} \right) \times 100
\]  

Where Tₙ, Tₙ and Tₙ are transmittances of the unbleached and bleached oil with the activated and the standard bentonite, respectively, at three wavelengths mentioned above. A commercial bleaching clay was used as standard.

3. Results and Discussion

The bulk chemical analysis (wt. %) of the natural bentonite sample is: SiO₂, 56.6; Al₂O₃, 13.95; Fe₂O₃, 3.59; MgO, 3.59; CaO, 3.70; Na₂O, 5.76; K₂O, 0.30; and loss on ignition (L.O.I.): 12.4. The cation exchange capacity of the natural bentonite was determined as 94 meq/100g. The XRD patterns of the natural and acid activated samples are given in Fig. 1. The natural bentonite contains beidellite and montmorillonite as the major smectite (S) minerals. Other accompanying minerals were found to be quartz (Q), cristobalite (Cr), Calcite (C), gypsum (G) and feldspar (F). The position of (001) reflections of the smectite appears at 1.25 nm for the sample, suggesting that it is in the Na–exchange form [37].

Treatment of the sample with hydrochloric acid produced important structural changes as can be seen from XRD patterns shown in Fig. 1. The most pronounced modification occurred in the smectite mineral can be observed for the peak d(001), which shows gradual reduction in intensity as a result of acid attack. On the other hand, since the smectite 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 [16].

It can be also observed that the characteristic peaks corresponding to gypsum and calcite minerals have disappeared after acid treatment under relatively mild conditions, whereas feldspar is not destroyed, even by activation with high acid concentrations. The chemical analysis of the natural and acid activated bentonite samples is given in Table 1, as the wt. % of metal oxide. Acid treatment modified the bentonite chemistry as is evident from the changes in chemical composition (Table 1). The process resulted in a material with greater silica content and a significant lower abundance of metal oxides.

![Fig. 1. The XRD patterns of the natural and acid activated bentonite samples](www.SID.ir)
cations can be easily distinguished. First group contains; \( \text{Ca}^{2+}, \text{Na}^+ \) and \( \text{K}^+ \) which a considerable amount of them remove after treatment with 2 N acid concentration. Dissolution of these cations remains almost constant by continuing the activation process with higher acid concentrations. The amount of \( \text{Ca}^{2+}, \text{Na}^+ \) and \( \text{K}^+ \) removal by acid treatment corresponds to the exchangeable cations which are located out of the smectite lattice (between layers), so that they dissolve under mild condition.

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 [28] (see Fig. 1). \( \text{Fe}^{2+}, \text{Mg}^{2+} \) and \( \text{Al}^{3+} \) are included in second group which belong to the octahedral sheets. 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 remove from smectite structure.

Octahedral cations removal from the bentonite increases as the acid concentration increases up to 5N after which no appreciable changes in their amount can be observed. 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.

The specific surface area of the natural and acid activated bentonite samples are given in Table 2. An approximately 6-fold increase in the specific surface area of the bentonite, resulted from the acid treatment, producing maximum surface area in sample H5 (Table 2). Increasing of specific surface area arises from the depletion of the cations from the interlayer and octahedral sheets of the smectite mineral, as well as dissolution of soluble impurities such as calcite and gypsum during acid treatment. It is also possible that a part of the specific surface area is associated with the amorphous silica phase formed by the slight destruction of the smectite.

The bleaching efficiency results for the natural and the activated samples are given quantitatively in Table 2 and illustrated in Fig. 3. The bleached oils are designated as O with the suffix indicating the bentonite sample used for the bleaching process. The adsorption spectrum for the unbleached oil (O) shows three maxima at 421.0, 444.5 and 472.5 nm, the intensities of which reduce slightly after bleaching with the natural sample (Fig. 3). However these bands show considerable decrease after bleaching the oil with activated samples and almost disappear during bleaching with samples activated with high acid concentrations. As seen in Table 2 the bleaching efficiency (BE %) of the activated samples increases with increasing acid concentration to 5N and then remain almost constant, which is in a good agreement with the dissolution behavior of the octahedral cations during acid activation process (see Fig. 2).

**Tab. 1. Chemical analysis (wt. %) of the natural and acid activated bentonite samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO(_2)</th>
<th>AlO(_2)</th>
<th>FeO(_2)</th>
<th>MgO</th>
<th>CaO</th>
<th>NaO</th>
<th>K(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN</td>
<td>56.6</td>
<td>13.95</td>
<td>3.59</td>
<td>3.59</td>
<td>3.70</td>
<td>5.76</td>
<td>0.30</td>
</tr>
<tr>
<td>H2</td>
<td>65.3</td>
<td>12.63</td>
<td>2.69</td>
<td>2.76</td>
<td>1.78</td>
<td>2.85</td>
<td>0.20</td>
</tr>
<tr>
<td>H3</td>
<td>66.1</td>
<td>12.27</td>
<td>2.57</td>
<td>2.72</td>
<td>1.74</td>
<td>2.74</td>
<td>0.20</td>
</tr>
<tr>
<td>H4</td>
<td>67.2</td>
<td>11.78</td>
<td>2.29</td>
<td>2.57</td>
<td>1.67</td>
<td>2.74</td>
<td>0.19</td>
</tr>
<tr>
<td>H5</td>
<td>67.8</td>
<td>11.48</td>
<td>2.18</td>
<td>2.50</td>
<td>1.67</td>
<td>2.76</td>
<td>0.19</td>
</tr>
<tr>
<td>H6</td>
<td>68.7</td>
<td>11.49</td>
<td>2.16</td>
<td>2.51</td>
<td>1.67</td>
<td>2.71</td>
<td>0.19</td>
</tr>
<tr>
<td>H7</td>
<td>68.5</td>
<td>11.49</td>
<td>2.15</td>
<td>2.53</td>
<td>1.74</td>
<td>2.76</td>
<td>0.19</td>
</tr>
</tbody>
</table>

As mentioned before cations removal from bentonite increases its specific surface area, as a result of which bentonite adsorption capacity improves for the bleaching of edible oils. Although there are slight differences in the bleaching efficiencies between the various samples, the material with maximum surface area (H5) doesn't display the highest bleaching efficiency. This may due to the fact that the bleaching
process is not merely a physical adsorption and other properties, such as cation exchange capacity (CEC), as well as acid and catalytic properties must be taken into account [38].

Tab. 2. Bleaching efficiency (BE%) and specific surface area (S\textsubscript{BET}), of the natural and acid activated bentonite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BE %</th>
<th>(S_{BET}) (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN</td>
<td>6.35</td>
<td>23</td>
</tr>
<tr>
<td>H2</td>
<td>77.8</td>
<td>95</td>
</tr>
<tr>
<td>H3</td>
<td>78.7</td>
<td>103</td>
</tr>
<tr>
<td>H4</td>
<td>83.9</td>
<td>112</td>
</tr>
<tr>
<td>H5</td>
<td>88.9</td>
<td>134</td>
</tr>
<tr>
<td>H6</td>
<td>91.2</td>
<td>131</td>
</tr>
<tr>
<td>H7</td>
<td>91.4</td>
<td>121</td>
</tr>
</tbody>
</table>

4. Conclusion

Acid activation of an Iranian bentonite from Khorasan region containing beidellite and montmorillonite as the major clay minerals led to the following conclusions:

i) XRD results indicated partial destruction for the smectite minerals and removal of gypsum and calcite.

ii) Increase of HCl concentration up to ~ 5 N caused increase of octahedral cations dissolution after which it remained almost constant.

iii) Surface area of the activated samples increased with the acid activation, such that acid activation at ~ 5 N gave rise to a surface area ~ 134 m\textsuperscript{2}/g.

iv) Bleaching experiments showed that the sample activated with 5 N acid, results in comparable bleaching efficiency to that of the commercial bentonite.

References


