CLARIFICATION OF COTTONSEED OIL: HOW STRUCTURAL PROPERTIES OF TREATED BENTONITES BY ACID AFFECT BLEACHING EFFICIENCY

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Abstract − **Natural occurring bentonites may show very little activity for bleaching oils and fats. For that reason, acid-activation of bentonites with inorganic acids is usually carried out to promote earths' adsorptive capacity during clarification of vegetable and animal oils and fats, as well as mineral oils. In this work we used two acid-activated natural bentonites from Mendoza, Argentina, with different mineral compositions and submitted them to acid treatment with hydrochloric acid to further clarify cottonseed oil. Both clays were treated with HCl at 4 and 8N for two hours in order to evaluate important structural properties modifications that may affect oil bleaching. X-ray diffraction, thermal and chemical composition analyses were performed. Cottonseed oil clarification experiments were run in previously established appropriated laboratory conditions. It was shown that clarification efficiency is strongly dependent on the acid concentration and natural clay mineral compositions used to activate the bentonites for the clarification process.**

Keywords − **Oil clarification, acid-activated clay, bleaching of vegetable oil.**

I. INTRODUCTION

Bleaching is an important step in the refining of fats and vegetable/animal oils for industrial applications. In edible oil processing, bleaching is responsible for a clarified oil that is more stable and also more attractive to the consumer. Clarification is usually performed by an adsorption process which preferentially uses acid-treated clays to remove undesirable oil components. 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. Such light-colored oil influences consumers' preferences but are also beneficial for quality and stability (Proctor and Palaniappan, 1989).

Adsorbent earths used for clarification are bentonite clays with high montmorillonite content. In their natural state they show very low decolorizing effect; however,

when treated with strong inorganic acids, particularly with hydrochloric and sulfuric, they develop a high clarification power. Hydrogen ions from the acid attack the aluminosilicate layers via the interlayer region (Taylor and Jenkins, 1987). It is believed that the increased clay adsorption capacity results from this process that alters the structure, chemical composition, and physical properties of the clay (Mokaya *et al.*, 1993).

Several acid treatment experiments under different operating conditions have been reported in the literature, in particular the choice of inorganic acid used, treatment time, and temperature (Hassan and A.-Khalek, 1998, Foletto *et al.*, 2003, González-Pradas *et al.*, 2005, Nguetnkam *et al.*, 2005, Tyagi *et al.*, 2005). Earth original mineral composition has, of course, a decisive effect on clay bleaching properties, but it with worth noticing that impurity levels are also critical in establishing the quality of the material produced by the acid-activation treatment with respect to its clarification capacity.

In this work, we report structural properties modification of two natural bentonites promoted by HCl treatment and how they affect structural parameters and consequently bleaching clay efficiency for the clarification of cottonseed oil.

II. MATERIALS AND METHODS

Two natural clays from the Mendoza Province, Argentina (identified here as K and W samples) were taken as starting materials. Samples of K and W earths have been characterized as described elsewhere (Foletto *et al.*, 2000). Table 1 reports mineralogical composition of the studied clays. Major phases detected include smectite, quartz and feldspat in sample K, and smectite, quartz, feldspat, caulinite and gypsum in sample W, in that order of occurrence. According to these results, bentonite W is richer in clay components (smectite + caulinite) (49.5%) than bentonite K (35%). It also contains less impurities, 50.5% (quartz, feldspat, gypsum and others) when compared to sample K (65% of quartz, feldspat and others).

Dried earth samples were crushed to 200 mesh; 40 g of each sample were added to 400 mL of hydrochloric acid 4 and 8 N under mechanical stirring. Acid treat-

Table 1. Composition of the natural bentonites K and W used in this work, given in weight percent (% wt.) (Foletto *et al.*, 2000).

Natural Bentonite	Smectite	Caulinite	Quartz	Feldspat	Gypsum	Others
K	35	–	37	20	–	8
W	47	2.5	27	13	4	6.5

ment was carried out at 90°C for two hours, under reflux; clays were separated by filtration and washed several times with purified water to remove remaining chloride ions. The washed material was dried at 55°C, and again crushed to 200 mesh. The resulting acid-activated clays were denominated K4, K8, W4 and W8, according to their corresponding 4 *N* and 8 *N* HCl treatments

Unbleached cottonseed oil was gently supplied by Vicentín S.A.I.C. (Argentina). Clarification experiments used 1% clay dosage (1 g dried clay·99 g^{-1} oil). The bleaching stirred vessel was kept at 100°C for 30 min, when color removal was considered completed or adsorption virtually reached equilibrium. The system operated under vacuum (310 mmHg) and constant nitrogen flow, to avoid air oxidation. For comparison, experiments were performed also with untreated natural clay samples. Cottonseed oil clarification capacity was determined by absorbance readings at 405 nm using a digital WFJ525-W(724) UV-Visible spectrophotometer, and reported as percentage bleaching efficiency (% *BE*), according to the following equation:

$$\%BE = \left(1 - \frac{A}{A_0}\right)\cdot 100 \equiv 100\left(1 - \psi\right) \qquad (1)$$

where A/A_o is the relative absorbance, considering as reference an equilibrium clarified oil, and ψ, a dimensionless pigment concentration (i.e., $\psi \equiv c/c_o$, pigment relative molar concentration in the oil), is assumed to be proportional to the relative absorbance.

Clay samples were characterized by X-ray diffraction (XRD), differential thermal analysis (DTA), thermogravimetry (TG) and Chemical Analysis (CA). XRD patterns were obtained from a Philips 3020 analyzer equipped with a PW 3710 controller, using Cu-Kα (λ = 1.5405 Å) radiation and Ni filter at 40 kV and 20 mA; angular velocity was 1°(2θ)·min^{-1} and scanning intervals from 3 to 40°(2θ); DTA/TG profiles were produced by a Netzsch STA 409 thermal analyzer with a temperature ramp of 10°C·min^{-1}, operating under dry air (35 mL·min^{-1}) in the temperature range 25–1000°C; chemical analyses were performed by X-ray fluorescence using a Philips PW-2400 equipment.

III. RESULTS AND DISCUSSION

Treatment with hydrochloric acid of samples K and W produced important structural changes, as can be seen from XRD patterns shown in Fig. 1. The most pronounced modification occurred in the smectite peak d(001), shifted and reduced after acid attack; on the other hand, since the smectite peak is still present after the acid treatment, we may assume that the structure has

been only partially destroyed. That balance between acid attack and structural preservation may hold the key for the establishment of optimal bleaching parameters.
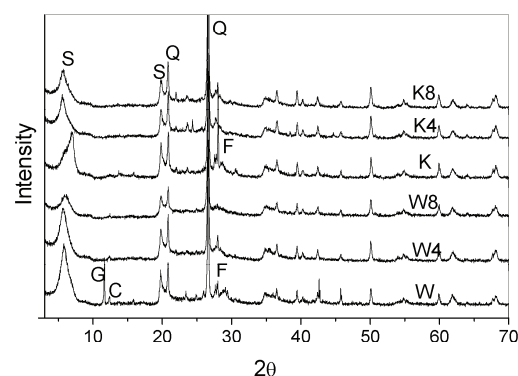

Fig. 1. X-ray diffraction patterns of bentonites K and W for natural and acid-activated samples (S = smectite; Q = quartz; G = gypsum; C = caulinite; F = feldspat).

Table 2 reports chemical composition of bentonites as determined by X-ray fluorescence. Silica, iron, aluminum, magnesium, calcium, sodium, potassium, titanium and manganese oxides were quantified; weigth loss under fire at 1000°C has been also computed. Magnesium octahedral content (MgO$_{oct}$) presents in natural earths was evaluated based on the difference between its total amount in the original clay (MgO$_{total}$ = 1.56% in the K sample and 1.18% in the W sample) and the content of interlamelar MgO (0.05% in K and 0.23% in W). Interlamelar MgO was determined by the ammonium acetate method. In acid-activated samples, interlamelar MgO was extracted during acid treatment and the results were obtained by chemical analysis using X-ray fluorescence corresponding to MgO$_{oct}$. The amount of Ca^{+2}, Na$^+$ and K$^+$ removed by acid treatment corresponds to the exchangeable cations that are present in original samples. However, a considerable amount of those elements is still found in the activated clays due to the presence of impurities, mainly feldspat that has calcium, sodium and potassium and is insoluble in acid solutions (Barrios *et al.*, 1995). Silica was enriched by the acid-treatment and one can also observe a significant removal of oxides in the octahedral position (Al$_2$O$_3$ + Fe$_2$O$_3$ + MgO$_{oct}$). The increase in the amount of silica is attributed to loss of smectite structural cations. For stronger acid treatment (8 *N* solution) both bentonites showed greater structural damage, as can be seen from a decrease in the amount of octahedral oxides (Table 2).

Figure 2 shows DTA/TG profiles for natural and acid-activated clays. Temperature of the first endothermic peak (*i.e.*, first valley) in Fig. 2a corresponds to the loss of interlamelar water, and is slightly increased after

Table 2. Chemical composition of bentonites (% wt.).

Sample	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO$_t$	MgO$_{oct}$	CaO	Na$_2$O	K$_2$O	TiO$_2$	MnO	$WL^\dagger$
K	69.53	15.58	3.49	1.56	1.51	0.65	2.70	1.23	0.55	0.09	4.60
K4	75.12	13.49	2.09	1.15	1.15	0.35	0.93	1.11	0.54	0.01	5.20
K8	75.54	13.00	1.90	1.11	1.11	0.35	0.86	1.11	0.52	0.01	5.60
W	65.18	17.51	4.53	1.18	0.95	1.57	2.24	0.86	0.42	0.08	6.24
W4	71.46	15.88	3.78	0.79	0.79	0.24	0.62	0.77	0.41	0.01	6.05
W8	72.91	15.31	3.48	0.71	0.71	0.18	0.58	0.66	0.40	0.01	5.76

† WL: Weigth loss under fire at 1000°C.

acid treatment for both clays. The two natural bentonites showed two endothermic peaks in the region 450–720°C implying a loss of hydroxyl groups: one at 540–550°C corresponds to the presence of beidellite (a smectite), and the peak at 690°C is indicative of the presence of montmorillonite (Grim and Kulbicki, 1961). Acid treatment modified those peaks, shifting their positions to lower temperatures; the beidellite peak disappeared almost completely. From Fig. 2b we were able to compute the destruction of octahedral sheets caused by acid attack, and express it as percent destruction in the last column of Table 3. That estimate was based on the difference of weight loss between the activated and natural samples in the temperature range corresponding to the desidroxylation (450 to 750°C).

When HCl concentration was doubled, from 4 to 8 N, an increase in the structural destruction was observed. Destruction was more pronounced for the K clay (43.27%) than for the W sample (25.65%) when considering the increase in acid concentration. Acid activation increased the bentonite clarification capacity by 2.5 to 7 times, depending on the bentonite and acid concentration considered. K4 and K8 samples showed a slightly superior adsorption capacity when compared to W4 and

W8 samples, respectively. That was attributed to the fact that K samples were more attacked by the acid during the activation process, as shown in Table 3 and referred as % destruction of octahedral sheet. That is in agreement with what was found for cottonseed oil clarification efficiency, as shown in Fig. 3. The K clay was more efficient for the clarification of cottonseed oil when compared to the W clay, for all samples studied.

Table 4 shows a summary of the most important results taken from this work (values for destruction of the octahedral sheet and bleaching efficiency are also grouped by convenience). In Table 4, $I_{smectite}/I_{quartz}$ (second column) represents the relative intensity between the smectite peak d(001) and the quartz peak (2θ = 26.6) as reported in Fig. 1; the ratio SiO$_2$/(Al$_2$O$_3$ + MgO$_{oct}$ + Fe$_2$O$_3$) (third column) was taken from Table 2; % destruction and %BE were taken from Table 3 (fourth column) and Fig. 3, respectively.

It is apparent that the acid treatment with HCl caused important structural changes in the bentonites studied. Those evidences come from chemical analysis, X-ray diffraction and thermal analyses. According to the results, %BE, that is, bleaching efficiency or clarification, increases proportionally to the removal of octahe-
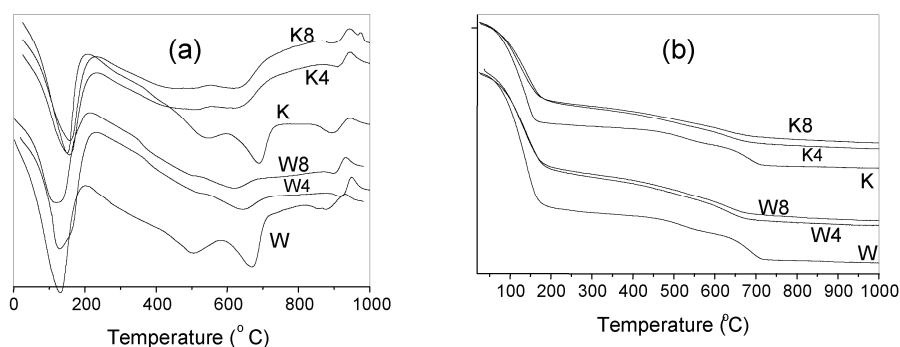

Fig. 2. (a) DTA and (b) TG profiles for natural and acid-activated samples W and K.

Table 3. DTA/TG parameters showing the effect of temperature treatment on studied clay samples.

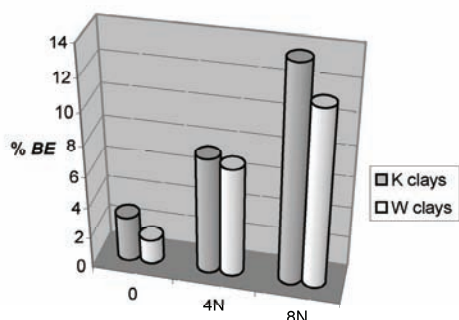| Sample	Temperatures (°C)		Weight loss between 450 and 750°C	% Destruction of the octahedral sheets
	Loss of water (H$_2$O)	Loss of hydroxyl group (OH$^-$)		
K	150	550, 690	2.69	–
K4	155	640	2.32	13.75
K8	157	640	2.16	19.70
W	157	540, 690	3.28	–
W4	162	642	2.89	11.89
W8	155	642	2.79	14.94

Fig. 3. Cottonseed oil clarification efficiency for selected bentonites. Clarification experiments were carried out at 100°C under vacuum, with 1% clay dosage.

dral cations from the bentonite original structural, measured by the ratio between SiO_2 and $(Al_2O_3 + MgO_{oct} + Fe_2O_3)$. Table 4 also shows that cation removal from the octahedral sheets is also observed when weight loss attributed to the second endothermic peak at 450–750°C is evaluated.

The ratio between smectite and quartz peaks is representative of the degree of attack suffered by the clay samples with respect to that of quartz, which is not supposed to be altered by the acid treatment (see Fig. 1). Intensity ratios decreased with the increase in acid concentration used for the activation of natural K and W clays, which is strong evidence of what acid treatment does is to destroy the bentonite structure, therefore activating the clay for adsorption and, consequently, removing pigments and other undesirable compounds found in the unbleached oil.

Although increasing acid concentration does improve clarification efficiency, the effect is not necessarily linear in a wider range of acid concentration.

IV. CONCLUSIONS

Acid-activation with hydrochloric acid (HCl) of natural bentonites from Mendoza, Argentina was developed and tested for the bleaching of cottonseed oil. Clarification of activated samples measured as relative absorbance was increased up to seven times with respect to the natural clay, showing an unequivocal evidence of the power of acid treatment for removal of oil colored bodies.

Hydrochloric acid concentration and original mineralogical composition have shown remarkable influence on the clarification process. From the two clays studied, the K sample showed a better result for bleach-

ing cottonseed oil compared to the W sample. Surprisingly, K acid-activated samples were originated from a less smetitic earth, but clarification activity correlates well with a more pronounced destruction of octahedral sheets. We therefore suggest that although the clay content is certainly an important requirement for acid activation, clarification is in fact more related to the degree of octahedral sheet destruction resulted from the acid treatment.

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Table 4. Relation between bentonite structural properties promoted by acid-treatment and cottonseed oil clarification.

Sample	$I_{smectite} / I_{quartz}$	$\dfrac{SiO_2}{Al_2O_3 + MgO_{oct} + Fe_2O_3}$	% Destruction of octahedral sheets	% BE
K	0.26	3.37	–	2.93
K4	0.23	4.49	13.75	7.48
K8	0.20	4.71	19.70	13.73
W	0.31	2.80	–	1.60
W4	0.30	3.49	11.89	7.02
W8	0.22	3.73	14.94	11.33