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SUNFLOWER OIL BLEACHING BY ACID-ACTIVATED BENTONITE

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Abstract

Two bentonite clays with different mineralogical compositions from Mendoza, Argentine, were activated with H_2SO_4 solutions of 4 and 8 N at 90°C for 3.5 hours. This treatment affected clay structural properties as was shown by thermogravimetry, infrared spectrometry and chemical analysis. Bleaching efficiency for sunflower oil was strongly dependent on acid concentration used for clay activation. The samples have bleaching capacity comparable to the standard. The mineralogical composition of natural clays has influenced the properties of activated clays.

Keywords: Acid-treated clays, bentonite, oil bleaching

I. INTRODUCTION

Acid activated bentonites have been used as solid acid catalysts and catalyst supports for a number of organic applications that requires an extreme degree of reaction control of considerable industrial interest.[1-4] It has also been used in the foodstuffs industry, sulphur production, forest and water conservation, in chemical industry, environmental protection, the paper industry[5, 6] as well as for bleaching of vegetable oils.[7-9] The bleaching of edible vegetable oils involves the removal of a variety of impurities wich include phosphatides, fatty acids, gums, trace metals, etc. followed by decolorization. The bleaching capacity of bentonites is greatly increased by activation treatment. While some of these clays are naturally bleaching, some have to be treated with mineral acids.[10-13] Bentonite consists predominately of smectite a 2:1 clay mineral containing an octahedral sheet between two tetrahedral sheets. Smectite crystals are negatively charged due to the substitution of the trivalent aluminium ions by bivalent ions like Mg^{2+} and Fe+ and substitution of tetrahedral Si^{4+} by Al^{3+}.[14] Activation proceeds with partial dissolution of smectite and includes an initial replacement of the interlayer cations by H^+, followed by dissolution of the octahedral and tetrahedral sheets with subsequent release of structural cations. This attack alters the structure, chemical composition and physical properties of the clay while increasing the adsorption capacity.[15] Christidis *et al.*[8] examined the bleaching capacity and acid activation of bentonites from Aegean, Greece, observing in a five-fold increase of the surface area of raw materials. The activated samples have been rendered suitable for bleaching of rapeseed oil. It was determined that the optimum bleaching capacity in not associated with maximum surface area and the optimum conditions for activation are obtained using a variety of combinations of acid stregth and residence time. Despite numerous studies, no definite relationship exists between the performance of the acid-activated clay and the composition or properties of the original clay. Hence, each clay has to be specifically activated and tested for its performance.[16] The preparation of acid-activated bentonite must be controlled in order to obtain maximum bleaching capacity.[14]

The present study deals with the acid activation of Argentine bentonites and testing of their bleaching capacity for sunflower oil, in comparison with the bleaching capacity of a standard commercial bleaching clay.

II. EXPERIMENTAL

Two natural bentonites (named as K and W) from two different deposits of the Mendoza province, Argentine, were used as the starting

materials. A commercial product, Tonsil, was used for the evaluation of the bleaching capacity of the experiments. Alkali-refined sunflower oil was gently donated by Bunge Alimentos S.A (Gaspar-SC, Brazil).

The bentonite sample (40g) was treated with 400mL of 4 N or 8 N sulphuric acid (analytical grade) at 90°C for 3.5h in an instantaneously stirred at a glass reaction vessel with reflux. After the acid treatment, the sample was filtered and washed with distilled water until it would be free of SO_4^{2-}. The samples were dried at 60°C for 12h and ground to pass through a 0.074mm sieve. Activated samples were designated as K4, K8, W4 and W8, where the numerical value indicates the concentration of acid solution used for the treatment. Bleaching experiments were conducted in a procedure analogous to that of the American oil Chemical Society (AOCS) Official Method Cc 8a-52. The bleaching process was carried out under a vacuum of 450 mmHg at the constant temperature of 100°C with a contact time of 30min. Stirring and heating were carried out by means of on electric heating band wrapped and a mechanic stirrer. The ratio of the mass of clay to the volume of acid solution was 1:10 (w/v). During the bleaching, a stream of N_2 was maintained above the oil surface. The hot oil and clay mixture was filtered under vacuum and the color of the bleached oil was measured spectrophotometrically (WFJ525-W UV-visible spectrophotometer). The bleaching capacity percentage (BC) of the clays was determined from the equation[17]:

$$[(A_0 - A)/A_0] \times 100$$

where "A_0" and "A" are the absorbance of neutral oil and bleached oil, respectively, at the maximum absorbance of the neutral oil (at wavelength 420nm). The structural changes of the Argentinean acid bentonites were examined by means of thermogravimetric (TGA) and infrared spectrometric (IR) analyses and chemical analysis (XRF). TGA was performed with a Netzsch STA 409 thermal analyzer at a heating rate of 10°C.min^{-1} under a flow of atmospheric air of 35mL min^{-1}, in the temperature range 25-1000°C. IR spectra were recorded in the region 4000-350cm^{-1} with a Perkin-Elmer 16 PC spectrophotometer, using the KBr pellet technique. Chemical compositions of the samples were determined by X-ray fluorescence technique with a Philips PW 2400 spectrometer.

III. RESULTS AND DISCUSSION

The mineralogical compositions of two clay samples were determined by Foletto *et al.*[18] Smectite is the main clay mineral in both samples (35% in K and 47% in W). The K bentonite contains quartz and feldspar as impurities, whereas W bentonite contains also gypsum and kaolinite. Table N° 1 shows the chemical analysis of the bentonites after treatments with sulfuric acid. The interlayer cations of the bentonites were removed. The residual Ca^{2+}, Na^+ and K^+ are due to the

presence of impurities such as micas and feldspars, which are insoluble in acid medium.[19] Part of the Mg^{2+}, $Fe^{2+/3+}$ and Al^{3+} was removed from the octahedral sheet. Ti^{4+} cations remain were insoluble. The increase of Si^{4+} and the reduction of the octahedral cations, which were originated by an increase of the acid concentration resulted in an increase of the Si/(Al+ Mg +Fe) ratio. The loss of weight by dehydroxylation (%) of the samples was obtained from TGA curves in the range 450-750°C (Figure N° 1); the TGA curves were used for the evaluation of the attack of the octahedral sheets after acid treatment (Table N° 2). The octahedral sheet destruction was calculated as a relative reduction percentage of the weight loss, with respect to the original sample. The activated K samples showed 14 to 19% of destruction of the octahedral sheet, while the activated W samples showed 12 to 15% of destruction. These results showed that even at high acid concentration (i.e., concentration of 8 N), the structures of smectites were not totally destroyed.

Figure N° 2 shows the infrared spectra of the original and the acid treated bentonites. No important changes were observed, although the bands Si-O-Al (525 cm^{-1}) and Si-O-Si (465cm^{-1}) were modified. The intensity ratios of both bands are shown in Table N° 3. Table N° 3 presents the results of the characterizations of the natural and activated samples and bleaching of the sunflower oil. Figures N° 3, 4 and 5 show the relation between the structural changes and bleaching capacity of the bentonites. The results of the analyses indicate that an increase of the acid concentration causes a greater attack on the bentonite structure, and consequently improves the bleaching capacity. The level of clay attack was bigger for the K that the W sample.

Table N° 1. Results of XRF analysis, expressed as oxides (%).

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	*r
K	69.53	15.58	3.49	1.56	0.65	2.70	1.23	0.55	0.09	3.00
K4	77.45	12.55	2.03	1.02	0.35	0.85	1.10	0.55	0.01	4.35
K8	78.51	10.32	1.59	0.85	0.32	0.88	1.04	0.54	0.01	5.37
W	65.18	17.51	4.53	1.18	1.57	2.24	0.86	0.42	0.08	2.56
W4	73.08	14.70	3.43	0.64	0.18	0.57	0.71	0.42	0.01	3.50
W8	75.87	13.06	2.86	0.59	0.18	0.59	0.71	0.42	0.01	4.12

*r: Si^{4+} / (Al^{3+}+ Mg^{2+}+$Fe^{2+/3+}$) ratio.

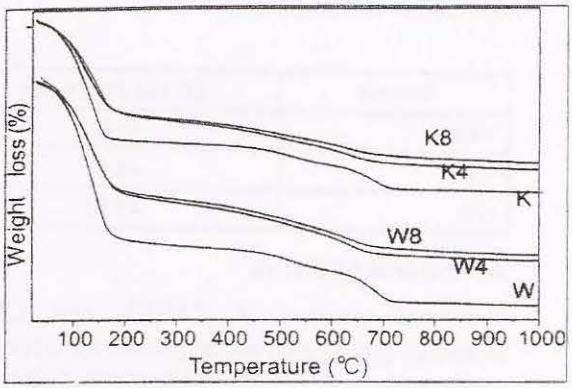

Figure N° 1. TGA curves of the natural and activated samples.

Table N° 2. Results obtained of TGA curves.

Sample	Weight loss range 450 - 750 °C	Octahedral sheet destruction (%)
K	2.69	0.00
K4	2.08	22.67
K8	1.80	33.08
W	3.28	0.00
W4	2.59	21.04
W8	2.44	25.61

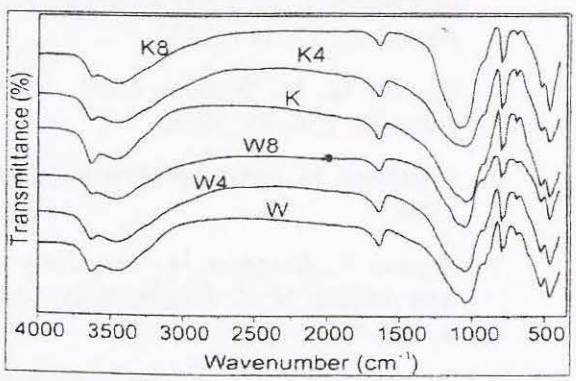

Figure N° 2. Infrared spectra of natural and activated samples.

Table N° 3. Structural changes and oil bleaching capacity of natural and activated samples.

Sample	IR(1)	CA(2)	TG(3)	BC (%) Sunflower(4)
K	0.44	3.00	0.00	11.83
K4	0.26	4.35	22.67	39.74
K8	0.13	5.37	33.08	48.68
W	0.44	2.56	0.00	11.00
W4	0.34	3.50	21.04	35.20
W8	0.22	4.12	25.61	45.60

(1) Si-O-Al/Si-O-Si ratio (obtained from IR spectra, Figure N° 2).

(2) Si/(Al+Mg+Fe) ratio (obtained from chemical analysis, Table N° 1).

(3) Octahedral sheet destruction (%) (obtained from TGA curves, Table N° 2).

(4) Bleaching capacity (BC) in sunflower oil.

The acid activated K bentonites showed a slightly superior bleaching capacity than the acid W bentonites and this behavior could be attributed to the higher acid attack of the K smectite structure when compared to the W smectite. Comparing the mineralogical compositions, the sample K presents more MgO content than sample W. It has been observed that smectites with greater MgO contents in their structure are more activated by mineral acids than those smectites with minor MgO content.[20] An optimization in the experimental conditions of acid treatment of the W bentonite probably would cause a higher attack in its structure and consequently would lead to a better adsorptive capacity, because this sample has higher clay content than K bentonite.[18]

The best bleaching capacity results of the activated bentonites obtained in this paper were compared with a commercial sample, as shown in Table N° 4. The retention of color impurities from sunflower oil by Tonsil (commercial sample) were similar to the bentonites treated with 8N sulphuric acid.

IV. CONCLUSION

Attack on the bentonite structure as a result of the sulfuric acid treatment is strongly dependent on the acid concentration. These treatments effects under clay structural properties were tested by thermogravimetric, infrared spectrometric analysis and chemical analysis. The activated samples were tested in order to verify their bleaching capacity in sunflower oil and were compared to a standard commercial bleaching clay. Bleaching efficiency was strongly dependent on acid concentration used for clay activation. The treated samples have shown a bleaching capacity compared to the standard. The mineralogical composition of natural clays have influenced the properties of treated clays and these properties increased its bleaching power.

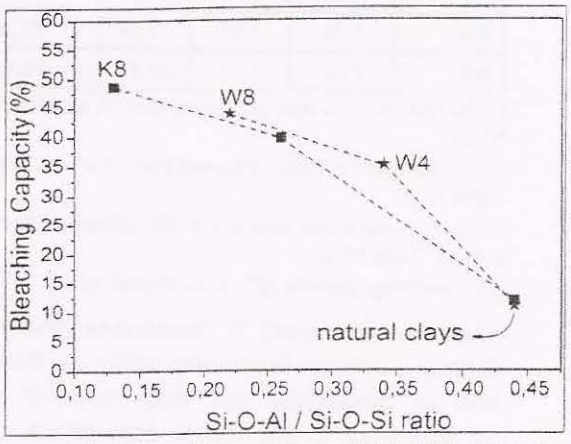

Figure N° 3. Bleaching capacity *vs.* Si-O-Al / Si-O-Si ratio.

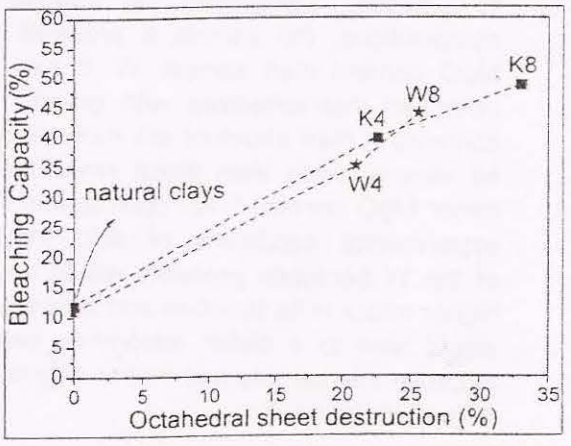

Figure N° 4. Bleaching capacity *vs.* octahedral sheet destruction.

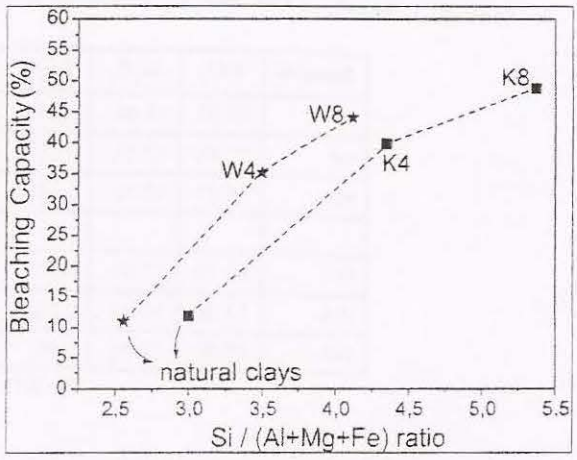

Figure N° 5. Bleaching capacity *vs.* Si / (Al+Mg+Fe) ratio.

Table N° 4. Bleaching capacities of Tonsil and prepared acid bentonites (K8 and W8).

Sample	BC (%) Sunflower
Tonsil	48.57
K8	48.68
W8	45.60

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REFERENCES

1. Mokaya, R. and Jones, W. *Journal of Catalysis*, **153**, 76, 1995.
2. Breen, C.; Zahoor, F.D.; Madejová, J. and Komadel, P. *Journal of Physical Chemistry B*, **27**, 5324, 1997.
3. Volzone, C.; Masini O.; Comelli, N. A.; Grzona, L. M.; Ponzi, E. N. and Ponzi M. I. *Applied Catalysis A: General*, **2**, 213, 2001.
4. Foletto, E. L.; Valentini, A.; Probst, L. F. D. and Porto, L. M. *Latin American Applied Research*, **32**, 141, 2002.
5. Clarke, G. M. Special clays. *Industrial Minerals*, **216**, 25, 1985.
6. O'Driscoll, M. *Industrial Minerals*, **250**, 43, 1988.
7. Srasra, F.; Bergaya, H.; van Damme, H. and Ariguib, N. K. *Applied Clay Science*, **4**, 411, 1989.
8. Christidis, G. E.; Scott, P. W. and Dunham, A. C. *Applied Clay Science*, **12**, 329, 1997.

9. Foletto, E. L.; Volzone, C. and Porto, L. M. *Brazilian Journal of Chemical Engineering*, **20**, 139, 2003.

10. Grim, R. E. *Applied Clay Mineralogy*, McGraw Hill, New York, 442 pp., 1962.

11. Patterson, H. B. W. *Bleaching and Purifying fats and oils: theory and practice*. AOCS Press, Champaign, Ilinois, USA, 242pp., 1992.

12. Norris, F. A. Extraction of fats and oils. In: *Bailey's Industrial Oil and Fat Products*, 2nd ed., New York: Daniel Swern (ed.), John Wiley & Sons, 175-251, 1982.

13. Rossi, M.; Gianazza, M.; Alamprese, C. and Stanga, F. *Food Chemistry*, **82**, 291, 2003.

14. Kirali, E. G. and Laçin, O. *Journal of Food Engineering*, **75**, 137, 2006.

15. Mokaya, R.; Jones, W.; Davies, M.E. and Whittle, M.E. *Journal of the American Oil Chemists' Society*, **70**, 241, 1993.

16. Hymore, F. K. *Applied Clay Science*, **10**, 379, 1996.

17. Falaras P.; Kovais, I.; Lezou, F. and Seiragakis, G. *Clay Minerals*, **34**, 221, 1999.

18. Foletto, E. L.; Volzone, C.; Morgado, A. F. and Porto, L. M. In: VI Jornadas Argentinas de Tratamiento de Minerales, Salta (Argentina), 43, 2000.

19. Barrios, M. S.; Gonzáles, L. V. F.; Rodríguez, M. A. V. and Pozas, J. M. M. *Applied Clay Science*, **10**, 247, 1995.

20. Volzone, C. and Ortiga, J. *Journal of Materials Science*, **35**, 5291, 2000.