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BLEACHING PROPERTIES OF ALUMINA-PILLARED ACID-ACTIVATED MONTMORILLONITE

POLYCARPOS FALARAS,[1] FANI LEZOU,[1,2] GEORGIOS SEIRAGAKIS,[3] AND DIMITRIOS PETRAKIS[4]

[1] Institute of Physical Chemistry, NCSR "Demokritos", 153 10 Aghia Paraskevi Attikis, Greece
[2] National Technical University of Athens, Chemical Engineering Department, Iroon Politechniou 9, 157 80, Zografou, Athens, Greece
[3] MINERVA S.A., Edible Oils Enterprises, 31 Valaoritou St., 14452 Metamorphosis, Attica, Greece
[4] Department of Chemistry, University of Ioannina, 45332, Ioannina, Greece

Abstract—The bleaching of cottonseed oil by alumina-pillared (Al-pillared) acid-activated clays was investigated. Acid activation of a Ca-rich montmorillonite (CMS STx-1) following treatment with 1, 4, and 8 eq/L sulfuric-acid solutions, as well as subsequent pillaring with alumina, produces new materials. These materials have bleaching properties dependent upon the extent of activation of the clay prior to pillaring. The pillared acid-activated montmorillonites possessed higher bleaching efficiency compared to pillared products of the untreated clay. Mild activation of the montmorillonite matrix, pillaring with the Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, and calcination temperatures to 500°C produced materials with the best fractional degree of bleaching. Direct comparison to the performance of a commercial bleaching earth (Tonsil Optimum 214, Sud-Chemie AG, Moosburg, Germany) shows that the efficiency of the Al-pillared acid-activated montmorillonite may be improved. The optimization of the bleaching process is achieved via a judicious utilization of intermediate surface area, relatively high acidity, and enhanced pore volume.

Key Words—Acid Activation, Alumina-Pillared Montmorillonite, Bleaching, Clay, Cottonseed Oil.

INTRODUCTION

Crude cottonseed oil is a vegetable oil of dark reddish color containing free fatty acids, triglycerides, pigments, and numerous minor components such as gossypol, phospholipids, tocopherols, and hydrocarbons (Padley *et al.*, 1996). The oil is commonly subjected to a refining process, usually following four successive operations: degumming, neutralizing, bleaching, and deodorizing (Gumuskesen and Cakaloz, 1992). During the bleaching, coloring matter, peroxides, and other impurities are removed from the raw oil and a sufficiently light-colored product of enhanced appearance and improved stability is produced (Pritchard, 1994). Bleaching earths, usually natural clays or clays chemically activated with mineral acids and thereby possessing enhanced surface area and acidity, are commercially used as powdered adsorbents (Breen, 1991; Morgan *et al.*, 1985; Griffiths, 1990; Boki *et al.*, 1992; Hymore, 1996).

Although the use of acid-activated clays as catalysts and adsorbents is well established, the application to cottonseed oil bleaching is restricted by the lack of thermal stability (Pinnavaia, 1983; Bovey and Jones, 1995). Improved stability and enhanced chemical activity of the clay is easily achieved via pillaring processes (Bukka *et al.*, 1992). Intercalation of organic, inorganic, or organo-metallic species into the interlayer of a clay via ion-exchange processes and subsequent treatment at elevated temperatures produces thermally stable pillared clays (Brindley and Sempels, 1977; Occelli and Tindwa, 1983). In the most common type of pillaring, polymeric cationic hydroxy metal complexes are easily converted to robust oxide pillars between the layers. This is the case of the Keggin ion: $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, the polycation agent used for the preparation of alumina-pillared clays (Pinnavaia *et al.*, 1984; Jones, 1988).

The properties of alumina-pillared (Al-pillared) clays have been extensively investigated, and many studies involve the synthesis of Al-pillared acid-activated clays and their applications (Mokaya and Jones, 1993, 1994, 1995a, 1995b; Mokaya *et al.*, 1993a, 1993b, 1994). Acid activation of montmorillonite prior to pillaring with alumina strongly influences the characteristics and activity of the material, generally resulting in a new material with physicochemical properties intermediate between those of conventional pillared clays and acid-activated clays (Mokaya and Jones, 1995a, 1995b).

The bleaching of clays is generally thought to involve molecular-sieving properties, electrostatic-field strength interactions, catalytic action, and equilibrium adsorption (Taylor *et al.*, 1984; Henderson, 1993). Adsorption phenomenon mainly involves carotene or chlorophyll attraction and adhesion to the acid sites in the bleaching earth. Working on cottonseed oil, Falaras *et al.* (1999) attempted for the first time to correlate the physicochemical properties of acid-activated montmorillonite with its bleaching efficiency. They observed a linear dependence of the bleaching efficiency on the clay-surface area and acidity. They proved that medium activation of the clay was most effective in

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bleaching cottonseed oil, resulting in the best color index and the lowest peroxide value. However, the results showed that the acid-activated clays thus prepared generally do not present very high adsorbing ability, and this ability is much lower than that of the commercial bleaching earth (Tonsil).

In the present contribution, investigation of the activity of the clay for cottonseed oil bleaching is extended to include Al-pillared acid-activated montmorillonites derived from a variety of acid-activated substrates. By using a natural and untreated montmorillonite, and three acid-activated montmorillonites (corresponding to mild, medium, and strong-acid activation) as starting materials, the properties and bleaching abilities of acid-activated and Al-pillared acid-activated clays can be compared. The objective of the work was to investigate the physical and chemical properties of the pillared materials to determine how these properties might affect the capacity for adsorbing colored species from edible oils, and more specifically, to explain the bleaching efficiency in the processing of Greek cottonseed oil. Thus, the extent to which the bleaching efficiency of the final pillared product depends on the level of the acid activation can be determined.

EXPERIMENTAL

The clay (CMS STx-1), a Ca-rich montmorillonite (cation-exchange capacity of 80 meq/100 g) from Gonzales County, Texas, USA, was obtained from the Clay Minerals Society Source Clay Repository. The clay was purified using sedimentation and the size fraction of <2 μm was separated. Three different acid-activated clays, M_1, M_4, and M_8, were prepared by treating the Ca-rich montmorillonite (M) with sulfuric acid of concentration 1, 4, and 8 eq/L, respectively (Falaras and Lezou, 1998; Falaras *et al.*, 1999). Fifty grams of the montmorillonite were ground and magnetically stirred with 250 mL of H_2SO_4 (analytical grade Riedel-de Haën AG, Seelze, Hannover, Germany) at 80°C for 2 h in a round-bottom flask. The slurry was cooled in air, centrifuged, and washed twice with distilled water. The samples were then dialyzed against deionized water until the pH was neutral and the conductivity was stable.

The pillaring hydroxy-aluminum solutions were prepared by adding, dropwise and under vigorous stirring, adequate volumes of 0.25 M NaOH to 0.5 M $AlCl_3$ to achieve the desired OH^-/Al^{3+} molar ratio of 2.5. The Al concentration in the final solution was 0.2 mol/L. Aqueous suspensions (1 wt. %) of the clay (untreated or acid activated) at the same pH value with the pillaring solution, were added slowly at room temperature to the polyoxoaluminium solution under vigorous stirring. The aluminum was present in large excess, typically 15 mmol Al (meq clay)$^{-1}$, to ensure complete saturation of exchange sites. The mixture was allowed to age 2 h at room temperature under stirring and, after standing for 24 h, the slurry was centrifuged and suspended in fresh deionized water three times. The filtrate was placed on a dialysis membrane and flushed with distilled water until free of Cl^- ions (as tested by $AgNO_3$). The final product was air-dried and then calcined from 100 to 500°C (Pinnavaia *et al.*, 1984).

Four alumina-pillared (Al-pillared) montmorillonites were made by intercalating the Keggin ion $[(Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ into the framework of one natural montmorillonite (M) and three acid-activated montmorillonite samples (M_1, M_4, and M_8). These montmorillonites are: Al-pillared Ca-rich montmorillonite (PM), Al-pillared mild acid-activated montmorillonite (PM_1), Al-pillared medium acid-activated montmorillonite (PM_4), and Al-pillared strong acid-activated montmorillonite (PM_8). X-ray diffraction (XRD) patterns were obtained using a Siemens D-500 X-ray diffractometer, using CuKα (λ = 1.54050 Å), with a secondary graphite monochromator. Elemental analysis was performed using a Perkin Elmer (Optima 3000) ICP spectrometer. Acidity of the clays was determined by NaOH titration (Kumar *et al.*, 1995) and the temperature-programmed desorption (TPD) of ammonia was used to evaluate the total (Lewis + Brönsted) surface acidity of the materials (Breen *et al.*, 1987; Ladavos *et al.*, 1996).

The surface areas and the pore volumes of the samples were determined by a Sorptomatic 1900 volumetric adsorption-desorption apparatus, using nitrogen as adsorbent at 77 K. Prior to the determination of the adsorption-desorption isotherms, the samples were degassed at 200°C in vaccum at 5×10^{-2} mbar for 20 h. The specific surface area of the samples was calculated by applying the Brunauer-Emmett-Teller (BET) equation (Braunauer *et al.*, 1938) using the linear part ($0.05 < P/P_o < 0.15$, where P/P_o is relative pressure) of the adsorption isotherm and assuming a closely packed BET monolayer, with the molecular area of the adsorbate $a_m(N_2) = 0.162$ nm^2 at 77 K (Gregg and Sing, 1982).

To discriminate between the external and mesoporous surface area *vs.* the micropore volume, we made use of the a_s-plot method (Ladavos *et al.*, 1996; Gregg and Sing, 1982). The a_s plots, defined as $a_s = (n/n_s)_{ref}$, (where n_s and n are the amount of N_2 adsorbed by the reference solid at $P/P_0 \neq s$ and $P/P_0 = s$, respectively) are proposed as a very valuable tool to investigate the porosity of solids. According to Gregg and Sing (1982), it is convenient to set $a_s = 1$ at $P/P_o = 0.4$, because monolayer coverage and microporous filling occurs at $P/P_o < 0.4$, whereas capillary condensation occurs at $P/P_o > 0.4$. The nitrogen volume, V, adsorbed at a relative pressure, P/P_o, is plotted as a function of the a_s value from the reference material at the corresponding P/P_o value. This plot provides information about the porous structure of the adsorbent. In

Table 1. Cottonseed oil bleaching efficiencies for pigments and peroxides for Al-pillared and Al-pillared acid-activated montmorillonites.

[1]Sample	FDB (%)[2]	Peroxide value (meq/kg)[3]	Lovibond Oil Color Index (in red-yellow units)
Unbleached oil	—	3.4	9.0R–80Y
Oil bleached with M	34	3.2	7.5R–80Y
Oil bleached with PM	88	3.2	6.4R–80Y
Oil bleached with PM_1	94	2.8	5.5R–70Y
Oil bleached with PM_4	91	2.6	5.6R–60Y
Oil bleached with PM_8	85	2.4	5.0R–59Y
Oil bleached with Tonsil	100	1.9	2.3R–35Y

[1] M = Ca-rich montmorillonite, PM = Al-pillared montmorillonite, PM_1 = Al-pillared mild acid-activated montmorillonite, PM_4 = Al-pillared medium acid-activated montmorillonite, PM_8 = Al-pillared strong acid-activated montmorillonite.

[2] Fractional degree of bleaching FDB(%) = $(A_{unbleached} - A_{bleached})/A_{unbleached} \times 100$, where $A_{unbleached}$ and $A_{bleached}$ are the absorbencies of unbleached oil and bleached oil, respectively, at the absorbance maximum of the untreated cottonseed oil (412 nm). The corresponding values of the industrial bleaching earth (Tonsil optimum 214 FF) were taken as reference (100%).

[3] The peroxide value corresponds to all substances in the bleached oil capable of oxidizing potassium iodide (K1) and was determined in terms of milliequivalents of peroxide per 1000 g of sample, according to the AOCS Official Method Cd 8-53.

the present study, the treatment was performed using Na-rich montmorillonite heated at 800°C for 3 h, with a specific surface area of 5 m^2g^{-1} as the reference material. The slope of the first linear part of the V-a_s plot gives the mesopore + external surface area $S_{m,e}$ ($S_{m,e} = 2.87 \times V_{ads}/a_s$) whereas the positive intercept gives the microporous volume, $V_{\mu p}$, after conversion of the gas volume adsorbed at 77 K [$V_{\mu p} = V_{ads}(STP) \times 0.001547$], where STP is "standard temperature and pressure".

Typical samples of "overflowed" neutral (neutralized with soda) cottonseed oils were obtained from Manos S.A. Oil Industry (Piraeus, Greece). This oil was difficult to bleach, probably because the cottonseeds were exposed to elevated temperatures. Bleaching experiments were conducted in open vessels containing a stirred dispersion of clay (2%) in cottonseed oil heated to 120°C for 5 min in a procedure analogous to that of the American Oil Chemical Society (AOCS, 1996) Official Method Cc 8a-52. The color of the oil was determined according to the AOCS Official Method Cc 13e-92 on a Lovinbond Automatic Tintometer (Type D) equipped with 2.54-cm cells. This method determines color by comparison with glasses of known color characteristics, and it is applicable to all normal fats and oils, provided that no turbidity is present in the sample. Absorption spectra (350–1100 nm) were obtained using a U-2000 Hitachi double-beam spectrophotometer. The peroxide content was determined in terms of milliequivalents of peroxide per 1000 g of sample, according to the AOCS Official Method Cd 8-53. To practically estimate the bleaching efficiency of the materials, a commercial bleaching earth (Tonsil Optimum 214 FF, Sud-Chemie AG, Moosburg, Germany) was used for comparison.

RESULTS

Before bleaching, the crude cottonseed oil was neutralized with soda, and therefore, the acid value was not affected by the bleaching procedure. The clay efficiency for pigment adsorption was measured spectrophotometrically at 412 nm, where the unbleached oil shows the main absorption peak. The performance of each clay is reported in Table 1 in the form of the fractional degree of bleaching, FDB (%). Note that acid activation and pillaring favor the bleaching process. The FDB results show that the bleaching efficiencies of the pillared montmorillonites can be ranked in the order: PM_8 (85%) < PM (88%) < PM_4 (91%) < PM_1 (94%).

The pillared materials showed high bleaching efficiencies, comparable to that obtained with a commercial industrial bleaching earth (Tonsil) and more than twice that of the untreated clay (Falaras *et al.*, 1999). Mild activation of the montmorillonite before pillaring is the most convenient treatment for increasing the efficiency of the cottonseed oil bleaching procedure.

In addition to high bleaching-efficiency values, the results also show that the Al-pillared acid-activated montmorillonites retained large amounts of peroxides and these clays show a significantly reduced cottonseed oil color index (Table 1). In the latter case, the pillared material derived from strong acid-activated montmorillonite gives the best results (*i.e.*, lowest peroxide value and Lovinbond color index).

The most important properties of clay materials affecting the adsorptive bleaching of vegetable oils include: surface acidity, surface area and porosity, degree of acid activation, particle size, and moisture content (Taylor *et al.*, 1989). To understand the bleaching activity of the clay, characterization of physicochemical properties must be made. The elemental analysis determined on an ignited (0% H_2O) basis (Table 2) shows changes in the clay composition following acid treatment and consequent pillaring. Major differences between the pillared materials are related to an increase in silica content and the concomitant decrease of alumina. Pillaring of an acid-activated matrix generally resulted in a product with a fewer number of alumina pillars than the corresponding pillared material obtained from the parent framework. Thus, there was a decrease of the cation-exchange capacity (CEC) of the activated substrate (depletion of the octahedral alumina sheet) (Breen *et al.*, 1995), thereby reducing the number of $[Al_{13}]^{7+}$ species by limiting ion-exchange between the silicate layers.

Table 2. Elemental composition[1] (wt. %) for Al-pillared montmorillonites. Corresponding *d* value and pillar height are given.

Sample	SiO_2	Al_2O_3	MgO	Fe_2O_3	CaO	*d*(001) (Å)	[2]Pillars height (Å)
M	78.99	16.63	3.87	0.77	1.87	12.21	—
PM	65.11	30.31	2.09	0.87	0.05	17.29	7.69
PM_1	69.46	27.23	1.86	0.84	0.05	18.02	8.42
PM_4	70.32	26.71	1.84	0.73	0.06	17.54	7.94
PM_8	70.93	26.42	1.80	0.67	0.03	17.86	8.26

[1] The sum of K_2O, TiO_2, MnO_2, and P_2O_5 does not exceed 1%.

[2] Calculated by subtracting the thickness of the silicate layer (9.6 Å) from the *d* value of the corresponding Al-pillared acid-activated clay.

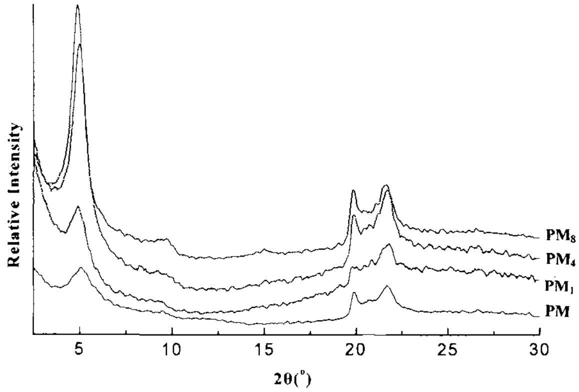

Figure 1. X-ray diffraction patterns for oriented films of Al-pillared (PM) and Al-pillared acid-activated montmorillonites (PM_1, PM_4, and PM_8).

XRD patterns show the influence of the clay substrate (untreated or acid activated) on the structure of the pillared clay sample (Figure 1). There is no evidence of crystalline impurities and each tracing shows a well-defined and intense first-order peak near 2θ of ~5°. The (001) reflection corresponds to the basal spacing of the clays and the results (Table 2) are in good agreement with reported values (Pinnavaia *et al.*, 1984). For the pillared materials, a basal spacing of ~18 Å was observed, suggesting that the pillaring species are similar. However, PM_1, PM_4, and PM_8 show small shifts of the (001) reflection indicating that the network of the pillars is influenced slightly by the degradation of the layer periodicity, probably from the acid-activation process before pillaring (Komadel *et al.*, 1990; Falaras *et al.*, 2000). These small shifts of the *d*(001) peak are consistent with pillars of slightly different height (Table 2). The sharpening of the XRD patterns for PM_1, PM_4, and PM_8 materials suggests that pillaring increases the face-to-face orientation of the clay platelets. The *d* value obtained from the full width at half maximum (FWHM) of the (001) peak may be used to determine the average number of aggregated clay platelets (MacEwan and Wilson, 1980). The analysis of XRD patterns gives the higher value (27 aggregated clay platelets) for the PM_1 material (Falaras *et al.*, 2000). The presence of the (003) reflection at 2θ = 21.53° (4.13 Å) indicates that the structure of the clay was partially preserved, even under strong activation. The broad hump at 2θ = 15–30° is attributed to amorphous silica (Komadel *et al.*, 1990). However the non basal *hk* two-dimensional band arising from diffraction from the random stacking of layers is stronger in acid-activated substrates. The diffraction peak at 2θ = 19.6° (*d* = 4.53 Å) is the summation of *hk* indices of (02) and (11) (Chen *et al.*, 1995).

Table 3 gives the specific surface area, porosity, and acidity of each clay. By using the N_2 adsorption-desorption data, the BET surface area, meso-external surface area $S_{m.e}$ ($S_{m.e}$ is the real surface area which excludes the surface area of the micropores), total pore volume (TPV), and microporous volume $V_{\mu p}$ (Ladavos *et al.*, 1996) were determined. The BET surface area (Table 3) of the untreated clay (61 m^2/g) increases with pillaring (255 m^2/g) and this change in surface area depends on the acid-activation process before pillaring. The BET surface area of the Al-pillared acid-treated clays (PM_1, PM_4, and PM_8) is lower than that of the pillared Ca-rich montmorillonite (PM), but increases with increasing level of acid treatment of the pillaring substrate (Table 3). The commercial bleaching earth (Tonsil), shows an intermediate surface area (176 m^2/g). Note that pillaring on the acid-activated matrix generally increases the meso-external surface area and the total pore volume. Among the pillared samples, the PM_1 sample maintains the smaller fraction of micro-

Table 3. BET surface area (S_{BET}), mesopore-external surface area ($S_{m.e}$), total pore volume (TPV), micropore volume ($V_{\mu p}$), acid-site density and acidity, and corresponding ratios for Al-pillared and Al-pillared acid-activated montmorillonites.

Sample	S_{BET} (m^2/g)	$S_{m.e}$ (m^2/g)	$S_{m.e}/S_{BET}$	$V_{\mu p}$ (cm^3/g)	TPV (cm^3/g)	Acid site density (sites/$Å^2$)	Acidity (meq/100 g)	Percentage of strong acid sites
M	61	47	0.77	0.009	0.126		4	0
PM	255	66	0.26	0.081	0.183	0.008	36	33.9
PM_1	174	60	0.35	0.050	0.147	0.025	72	41.7
PM_4	204	57	0.28	0.065	0.175	0.028	95	56.1
PM_8	226	53	0.23	0.074	0.185	0.021	79	40.2
Tonsil	176				0.387		90	

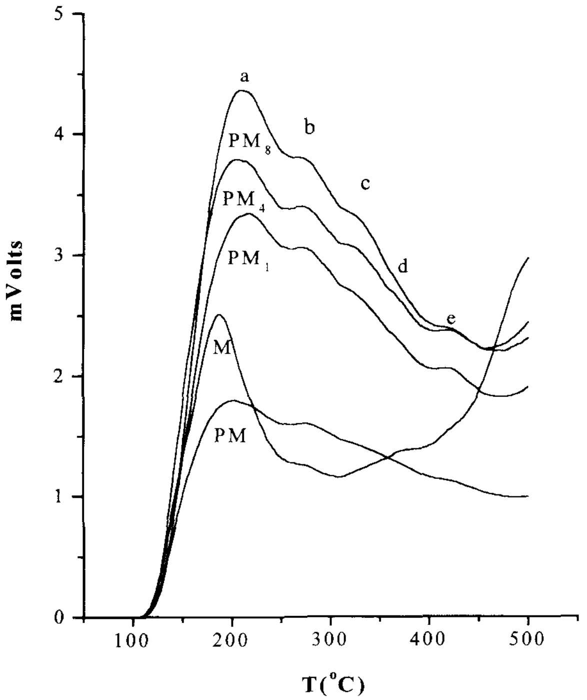

Figure 2. Ammonia TPD profiles of Ca-rich montmorillonite (M), Al-pillared (PM), and Al-pillared acid-activated montmorillonites (PM_1, PM_4, and PM_8).

pores ($V_{\mu p}$/TPV) but the higher fraction of meso-external surface area to BET surface area ($S_{m,e}/S_{BET}$). However, total pore volume of Tonsil was found to be twice the corresponding value of the pillared acid-activated materials.

Acid treatment and pillaring modify the acidic properties of the clays. The acidity (surface acidity and acid-site density) increases by pillaring the acid-activated matrix and acidity is at a maximum for the pillared sample with a substrate of medium acid activation (95 meq/100 g), which is higher than that observed on Tonsil (90 meq/100 g). In temperature-programmed desorption (TPD) profiles, (Figure 2), the maximum desorption rate occurs at ~200°C. In addition to this main peak (Figure 2a), four local maxima or shoulders appear at higher temperatures (Figure 2b–2e). This result suggests that the surface-acid sites are distributed in five acid-strength categories. The higher temperature of ammonia desorption suggests stronger acid sites (the strong-acid sites correspond to the desorbed amount of ammonia at temperatures >300°C). The percentage desorption of each event can be estimated by approximating the TPD profile with five Gauss-type components by using a simulation. For the untreated clay, which was dried at 120°C, the increase in the signal in the higher temperature region (T > 300°C) is attributed to dehydroxylation and the fitting process used only two Gauss components. The results of the fitting procedure, which produced a center and a percentage for each component (Table 3), show that the strong-acid sites per gram of pillared clay increase in the order PM < PM_1 ≈ PM_8 < PM_4 and vary between 33.9–56.1% of the total acidity. In contrast with the pillared clays, we did not observe the presence of strong-acid sites in the untreated clay.

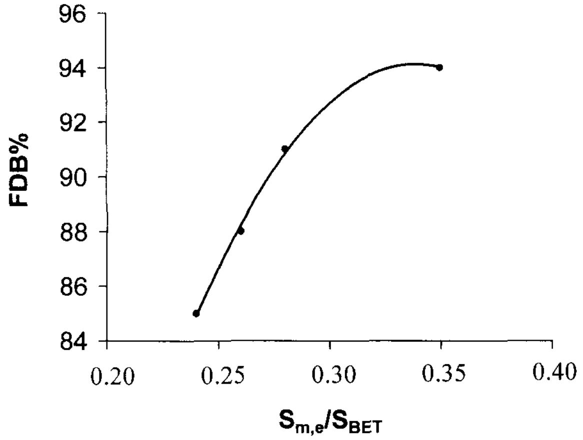

Figure 3. Dependence of bleaching efficiency (FDB% values) on $S_{m,e}/S_{BET}$ ratio.

DISCUSSION

The external surface area, the porosity, and the acidity of the pillared clays play important roles in their bleaching activity. Acid activation causes dramatic changes at the edges of clay platelets, thereby increasing the surface area of the materials. Furthermore, the acid treatment reduces the CEC and affects both the octahedral and tetrahedral sheets (Breen *et al.*, 1995) as well as the amount of the incorporated alumina by pillaring. The alumina props the adjacent silicate layers apart, increasing the interlayer spacing and enhancing microporosity. Small numbers of micropores and a high ratio of meso-external surface area to BET surface area produce an enhanced bleaching efficiency of the clay. In fact, for the pillared clays, the bleaching efficiency increases in an inverse manner with the enhancement of the volume of the micropores. Thus, among the pillared montmorillonites, the PM_1 material possesses the smaller number of micropores and the higher fraction of meso-external surface area, and it shows the greatest bleaching efficiency. The bleaching efficiency does not correlate with the acidity of the material, acid-site density, BET surface area, surface area of micropores ($S_{BET} - S_{m,e}$), total pore volume, or the volume of micropores. Plotting the FDB(%) values as a function of the ratio $S_{m,e}/S_{BET}$ and using a polynomial fit, a second-order curve was obtained with a correction coefficient of $R^2 = 0.998$ (Figure 3). Thus, both moderate surface area and a high $S_{m,e}/S_{BET}$ ratio may partially explain the relatively high FDB(%) values of the PM_1 pillared material.

The PM_8 sample contains the higher surface area and the higher pore volume among the Al-pillared acid-activated clays. Most of this surface area and pore volume are probably generated from internal cavities of meso-pore and macro-pore sizes, which could facilitate the bleaching process. In fact, the bleaching process with acid-activated clays is generally a combination of catalytic action (peroxide destruction) and equilibrium adsorption (pigment removal from the oil) (Henderson, 1993). Impurities in the oil, such as carotenes and chlorophyll, can rapidly diffuse through the sample and adhere to most of the active acid sites on the clay surface.

Pillared clays possess important acidity, both Lewis and Brönsted in character (Benesi and Winquist, 1978; Laszlo, 1987; Malla and Komarneni, 1990; Kumar *et al.,* 1995). Lewis acidity is mainly attributed to the alumina pillars, and Brönsted acidity to the clay matrix. Thus, although the PM clay was not subjected to acid treatment, this clay possesses a significant amount of acidity. Ammonia TPD analysis has shown that a portion of this acidity is related to the presence of weak-acid sites. The acidity of the pillared acid-activated montmorillonites generally increases according the degree of the acid activation of the clay before pillaring (Table 3). This seems to result from a concomitant increase in proportion of the strong-acid sites and is partially attributed to the protonation of the clay framework following acid activation. During the acid-activation process, the surface hydroxyl groups at the broken surfaces of the clay platelets protonate in the same way as the alumina pillars in acidic solutions (Molinard *et al.,* 1994; Petridis *et al.,* 1996). Acidic OH groups of the PM_1, PM_4, and PM_8 clays can directly exchange protons with chlorophyll molecules. In addition, the protonated $AlOH_2^-$ structure can serve as an effective binding site to permit the attachment of pigments and other coloring material contained in cottonseed oil (Falaras *et al.,* 1999). Improved adsorptive properties for the removal of chlorophyll from edible oils were observed by Mokaya and co-workers (Mokaya *et al.,* 1993a, 1994; Mokaya and Jones, 1993). By studying chlorophyll adsorption, they found that the chlorophyll-adsorption capacity of the natural and acid-activated montmorillonites was increased by using the Al^{3+}-exchanged forms. They attributed this result to the increase of Brönsted acidity (Mokaya *et al.,* 1994). Furthermore, pigments such as β-carotene can either be adsorbed directly onto a cation to form a chemisorbed complex or react with the protonic centers present on the clay surface (Morgan *et al.,* 1985). The removal of impurities (transition metals, soaps, and phospholipids) probably occurs by a similar mechanism to that for pigment removal, and the process is dependent on surface acidity. Finally, Taylor *et al.* (1989) found that pigment (carotene and chlorophyll) adsorption from soybean oil is consistent with a high concentration of strong-acid sites.

Besides Brönsted acidity, high hydrophobicity of the clay materials may also be an important reason for the observed enhancement in bleaching efficiency of alumina-pillared acid-activated montmorillonites. Hydrophobicity is a common characteristic of pillared clays (Yariv and Heller-Kalai, 1973). The acid activation of the clay framework is observed to further increase the hydrophobicity of the Al-pillared acid-activated montmorillonite (Schutz *et al.,* 1987). Furthermore, studies on acid-activated organoclays (Breen *et al.,* 1997) attributed their catalytic activity to the hydrophylic and hydrophobic character of the clay surface. The higher hydrophobicity makes the adsorption of an excess of chlorophyll and other pigments on the Al-pillared acid-activated materials easier, thereby concentrating a higher number of colored species on its surface. This result produces greater bleaching efficiency than either untreated montmorillonite or its pillared product. In fact, the protonated clay framework, highly hydrophilic in character, may attract the polar pigments. In contrast, extensive leaching of cations from the octahedral sheet of the acid-activated materials transforms the pillaring substrate to essentially hydrophobic silica, which serves as a better adsorbate for non-polar coloring molecules contained in cottonseed oil.

Among all the materials, the commercial bleaching earth (Tonsil) shows the best bleaching efficiency (higher FDB and lower color-index values). Although the observed FDB values obtained for the Al-pillared acid-activated materials (*e.g.,* absorption curves at 412 nm) approach the performance of Tonsil, the oil color-index values (Table 1) are not satisfactory for a quality bleaching clay. The red color is mainly related to gossypol. Because Tonsil adsorbs gossypol more efficiently than the pillared materials, relatively higher Lovibond red values occur. A detailed study of gossypol adsorption on these materials is necessary to determine the mechanisms of adsorption and to improve the color-index values of the bleached cottonseed oil. The optimization of the bleaching performance of the pillared acid-activated clays may be obtained by a better control of the acid-activation process before pillaring and/or the use of different pillaring substrates. A study to optimize the bleaching properties of an Al-pillared bentonite from the island of Milos, Greece, is in progress.

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E-mail of corresponding author: papi@mail.demokritos.gr

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