The Mechanism of Chlorophyll Adsorption on Acid-Activated Clays

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Acid-activated montmorillonite clays are widely used to remove chlorophyll from edible oils. The exact properties of the clay responsible for the adsorption are still little understood as is the manner in which the chlorophyll is adsorbed. We report here various techniques applied to probe the nature of the interaction between the adsorbed chlorophyll molecule and the clay surface by following the adsorption properties of montmorillonite clays acid activated to varying degrees. Ion exchange of these acid-activated materials enables further control of their acidity; the influence of the exchangeable cation on the adsorption process is shown to decrease with increasing levels of acid activation, suggesting a possible existence of acid sites not associated with the cation. The nature of the acidity of the adsorbent (clay) is shown to change following chlorophyll adsorption; the chlorophyll molecule is believed to adsorb as a protonated species. We discuss the effect upon the chlorophyll adsorption process of the level of acid activation, the cation exchange capacity, and residual negative charge of the clay. © 1994 Academic Press, Inc.

1. INTRODUCTION

The treatment of montmorillonite clay minerals with hot mineral acid enhances their intrinsic properties and results in improved adsorbent and catalytic characteristics (1). The activation process proceeds via the removal of octahedral ions and any isomorphously substituted tetrahedral ions from the matrix of the clay. As a result, the layer charge and the cation exchange capacity (CEC) of the clay are reduced. The adsorptive properties of such activated clays depend on the chemical nature of the clay surface, and the sorption process is influenced by the electrostatic interaction between the adsorbate molecules and the adsorption sites on the clay surface, the nature of the exchangeable cation occupying the interlayer region of the clay, and the extent to which the cation is hydrated.

The removal of chlorophyll and its various derivatives from vegetable oils is essential because they impart an objectionable color and also act as photo prooxidants

which reduce the oxidative stability of the oil. In commercial processes acid-activated clays are the most widely used materials for chlorophyll removal (2, 3). Numerous studies have been reported concerning the mechanism of chlorophyll adsorption on clays and several attempts to relate physical/chemical properties of the clay to the observed adsorption efficiency have been made (4–9). The adsorption capacity of an acid-activated clay may peak either before (7) or after (5) the achievement of maximum surface area, depending on the exact origin of the clay. Morgan et al. (7) reported that pores of diameter 20–50 Å are suitable for adsorption and attributed a reduction in adsorption capacity at high levels of acid activation to the formation of a material with pores of diameters above 60 Å. Taylor et al. (8), however, more recently reported that pores of diameter 50–200 Å are the most suitable and also demonstrated a relationship between surface acidity (as determined by Hammett indicator measurements) and adsorption capacity. The exact identity of the specific acid sites involved and the changes in the chlorophyll molecule following adsorption have not, however, been reported.

We have demonstrated elsewhere that pore volume (in the mesopore range) and the presence of strong acid sites are key factors in the adsorption process (10). Here we report on the nature of the acid sites which are involved, and in particular, we explore the effect of the level of acid activation on the ability of the clay to irreversibly adsorb the chlorophyll molecules. The nature of the adsorbate is also discussed in view of the fact that chlorophyll in oil exists in various forms. We use the term chlorophyll as a general term to include all the chlorophyll derivatives present in oil. For simplicity it is assumed that the chlorophyll exists in two forms: chlorophyll a and b and the corresponding pheophytin derivatives (i.e., pheophytin a and b).

2. EXPERIMENTAL

Two montmorillonites clays, one from Surrey, England (M), and the other from Los Trancos, Spain (L),

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TABLE 1
Properties of English (M) and Spanish (L) Acid-Activated Montmorillonite Clays

Activated clay	BET S.A. (m²/g)	Acidity[a] (meq H⁺/g)	%SiO₂	%Al₂O₃	%Fe₂O₃	%MgO
AM1(0.35)[b]	243	1.36(58)[c]	58.1	10.8	6.0	2.5
AM2(0.60)	343	0.44(38)	70.5	8.8	4.4	1.8
AL1(0.25)	224	0.24	64.0	19.3	3.3	3.7
AL2(0.60)	350	0.98	69.1	10.8	2.4	2.5
AL3(1.25)	251	0.21	82.5	2.0	0.3	0.4

[a] Protonic acidity, determined according to Ref. (12).
[b] Acid/clay ratios of the activation media.
[c] CEC in meq/100 g.

were used as the starting materials. M had a surface area of 81 m²/g and a wt% composition of SiO_2 and Al_2O_3 of 55.6 and 14.1%, respectively. The corresponding values for L were 60 m²/g and 61.2 SiO_2 and 23.6% Al_2O_3. M and L were acid activated under carefully controlled conditions with 98% sulphuric acid to yield clays activated to various levels (10). The designation and properties of the variously acid-activated clays (AM1 and AM2 from M and AL1–AL3 from L) are given in Table 1. Elemental analysis of the clays was obtained using a Philips PW 1400 X-ray fluorescence spectrometer. Cation exchange capacities were determined using a method described by Diddams (11). Ion exchanged samples with Al^{3+}, Na^+, Li^+, and Ti^{4+} were prepared using 1.0 N solutions of the corresponding chloride salt. A contact time of 24 hr was used. The clays were washed free of Cl^- ions (as tested by $AgNO_3$) and air-dried. The protonic acidity of the acid-activated clays was determined using the method described by Holm et al. (12). The surface acidity of the acid-activated clays was monitored using infrared spectroscopy of adsorbed pyridine.

TABLE 2
Chlorophyll Adsorption Capacity of Acid-Activated Spanish Montmorillonite (AL) Clays, Activated to Varying Degrees

	% chlorophyll adsorbed		
% adsorbent dosage	AL1 (0.25)[a]	AL2 (0.60)	AL3 (1.25)
0.25	30.0 (A)	80.1	13.0 (E)
0.50	65.6 (B)	97.7	40.9 (F)
0.75	82.6 (C)	100.0	75.6
1.00	91.9 (D)	100.0	96.8 (G)
1.25	98.7	100.0	99.4 (H)

Note. Letters A–H signify oils from the bleaching process which are used in later studies.
[a] Acid/clay ratios at which the clays were prepared.

TABLE 3
Change in Amount of Chlorophyll Bound when Cakes of AL1 and AL3 Were Reused

		% Change in amount of chlorophyll	
% Original dosage	% Cake dosage	AL1	AL3
0.25	0.25	−0.6	+1.6 (J)
0.50	0.25	−0.9	+5.7 (K)
	0.50	−0.6	+9.0
0.75	0.25	−3.6	+8.5 (L)
	0.50	−12.1	+11.8
1.00	0.25	−5.0	+6.8 (M)
	0.50	−14.1	+9.5

Note. Positive and negative signs show percent desorbed or adsorbed, respectively. Letters J–M signify oils from the bleaching process and which are used in later studies.

Chlorophyll adsorption capacities for the clays were obtained using standard bleaching tests; a known amount of clay (see Tables 2, 3, and 4) was added to a sample of super degummed (SDG) rapeseed oil containing about 8000 ppb of chlorophyll and <1 ppm phosphorus. Various clay dosages from 0.25 to 1.25 g of clay to 100 g of oil (ca. 0.25 to 1.25 wt%) were investigated. The mixture of the oil and the clay was stirred at 100°C for 35 min. The adsorbent was then removed by filtration and the amount of chlorophyll remaining in the oil measured using a CL500 Lovibond Colourscan. This method determines

TABLE 4
Amount of Chlorophyll Removed from Prebleached SDG Rapeseed Oil by Fresh 0.25% AL1 or AL3

		Chlorophyll adsorbed		
	Available chlorophyll	Percentage		
Prebleached oil[a]	(ppb)	AL1	AL3	μmole/g
A (AL1)[b]	5705	47.9		1.230
B (AL1)	2805	48.7		0.613
C (AL1)	1415	54.1		0.244
D (AL1)	660	56.1		0.168
E (AL3)	7120		28.3	0.903
F (AL3)	4840		45.5	0.989
G (AL3)	260		72.7	0.072
H (AL3)	60		50.0	0.008
J (AL3 cake)	8320		15.9	0.593
K (AL3 cake)	8660		15.9	0.620
L (AL3 cake)	8890		16.6	0.665
M (AL3 cake)	8750		16.8	0.661

[a] See Tables 2 and 3 for identification of oil.
[b] Initial adsorbent.

the total amount of chlorophyll present in the oil but does not distinguish between chlorophyll a/b and pheophytin a/b.

3. RESULTS AND DISCUSSION

3.1. Identification of Acid Sites

The acidity of clays M, AM1, and AM2 (see Table 1) was modified by ion exchange with various cations of different polarizing powers—thus resulting in varying abilities to generate Brønsted acidity in the interlamellar region of the clays (13). The chlorophyll adsorption data of the cation exchanged clays are summarized in Fig. 1. It emerges that acidic cations (e.g., Al^{3+}) improve chlorophyll adsorption capacity, whereas nonacidic cations (Na^+ and Li^+) have the opposite effect. Previous work has shown that the nature of the Brønsted acid sites on M and AM1 differ (13). In the case of M the acidity is primarily associated with protons resulting from polarization of the interlayer water by the interlayer cations and, therefore, strongly depends on the nature of the interlayer cation. The acid sites for AM1, on the other hand, originate both from acidic interlayer water (i.e., from water polarized by the interlayer cation) and from protons on the matrix of the clay (i.e., protons that replace the leached octahedral cations on the clay matrix (14).

The Brønsted acidity of M (with the highest cation exchange capacity) is therefore expected to be significantly affected by changes in the nature of the exchangeable cation. Al^{3+} and Ti^{4+} would increase the Brønsted acidity while Na^+ would have the opposite effect. The fact that a similar trend is observed for the chlorophyll adsorption capacity (see Fig. 1) suggests that Brønsted acid sites are helpful for the adsorption process. Indeed, Na^+-exchanged M, which has only trace amounts of Brønsted acidity (13), has almost no chlorophyll adsorption capacity. The Brønsted acidity of AM1—with a significant contribution from nonexchangeable lattice acidity—is found to be less dependent upon the nature of the cation, with the changes in chlorophyll adsorption capacity being less drastic than those observed for M.

A decrease in the cation exchange capacity of acid-activated montmorillonites (due to increasing acid treatment) results in a decrease in the contribution of the exchangeable cation to the total Brønsted acidity of the clay. Indeed, as shown in Fig. 1, the chlorophyll adsorption capacity of AM2 is less affected by a change of interlayer cation as compared to AM1. Na^+ exchange reduces the adsorption capacity of AM2 by only 5.5%, compared to a reduction of 18% for AM1. The magnitude of the reductions, therefore, confirms that the acidity of AM2 is less dependent on the exchangeable cation. As the level of acid treatment increases there is a change from interlayer Brønsted acid sites to matrix (lattice) proton sites. This change is likely to be beneficial to the chlorophyll adsorption process because it results in the introduction of stronger acid sites which are readily accessible to the
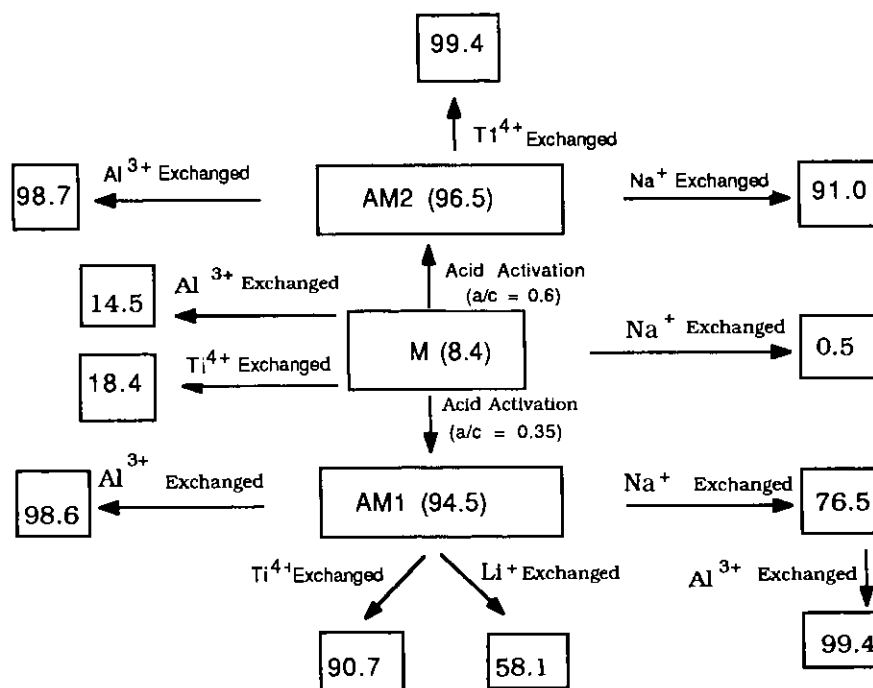

FIG. 1. Chlorophyll adsorption data for air-dried cation exchanged clays (the values are given as percentage chlorophyll adsorbed).

chlorophyll molecule. Furthermore, lattice acid sites are stronger because they are not associated with interlayer water which tends to reduce the strength of acid sites with $pK_a < -1.7$ (15). The data in Fig. 1 also show a greater reduction of the chlorophyll adsorption capacity of AM1 due to lithium exchange compared to sodium exchange, possibly due to the migration of the small Li^+ ion into the matrix of the activated clay where it disrupts the matrix protons. Li^+ is known to occupy octahedral sites on the clay structure which are associated with the lattice protons (16).

3.2. Effect of Chlorophyll Adsorption on the Nature of Acidity of the Clay Surface

An infrared study of pyridine adsorbed on AM1 before and after contact with SDG rapeseed oil was undertaken to determine the effect of the adsorbed chlorophyll molecule on the acidity of the clay surface. Pyridine adsorbed on a Brønsted acid site shows a characteristic band at $1540\ cm^{-1}$, whereas pyridine on a Lewis acid site absorbs at ca. 1450 and $1620\ cm^{-1}$. A band at $1490\ cm^{-1}$ is associated with pyridine on both Brønsted and Lewis acid sites (17). The spectra obtained are shown in Fig. 2.

The acidity of AM1 is mainly of the Brønsted type. The number of Brønsted acid sites which were able to interact with pyridine are reduced when AM1 is contacted with
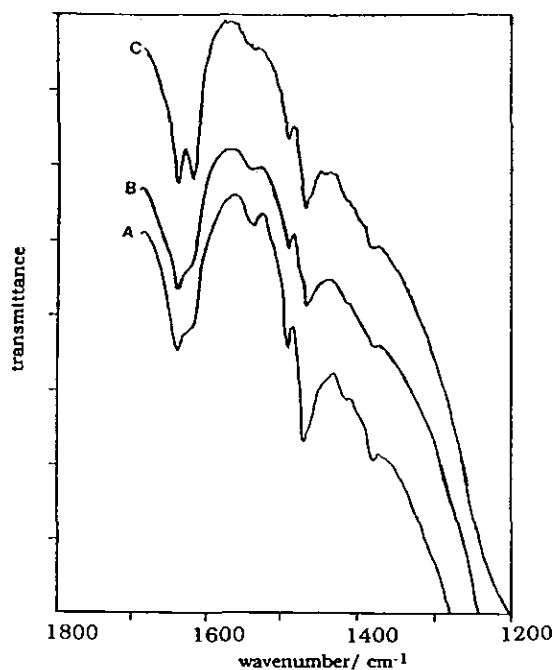
FIG. 2. Infrared spectra of pyridine adsorbed on an acid-activated montmorillonite (AM1) treated as follows: (A) acid-activated clay + refined rapeseed oil; (B) acid-activated clay + super degummed rapeseed oil + benzaldehyde; (C) acid-activated clay + super degummed rapeseed oil.

SDG rapeseed oil. No reduction was observed when AM1 was contacted with a similar refined oil containing only trace amounts of chlorophyll. The reduction in the number of Brønsted acid sites able to interact with the pyridine is a result of the presence of chlorophyll and not the oil. This reduction in Brønsted acidity is accompanied by an apparent increase in Lewis acidity—either the Brønsted acid sites are converted to Lewis acid sites or existing Lewis acid sites are now available to interact with pyridine due to the removal of Brønsted acid sites. That the band at ca. $1617\ cm^{-1}$ is due to pyridine adsorbed on Lewis acid sites is confirmed by the reduction in the intensity of the band after contact with benzaldehyde. Benzaldehyde, unlike pyridine, reacts selectively with the Lewis acid sites (18) and has no effect on Brønsted sites. The pyridinium band at ca. $1540\ cm^{-1}$ therefore, remains essentially unchanged.

The dependence of adsorption capacity on Brønsted acidity is a strong indication that protons are necessary in the adsorption of chlorophyll on clay. We propose, therefore, that the adsorption proceeds via either one or both of the following mechanisms: (1) the transfer of a proton (or protons) from the clay surface to the chlorophyll molecule in the oil phase, and the resulting protonated species is then adsorbed onto the clay and held electrostatically. The higher the number of protons available the higher the number of chlorophyll molecules that can be protonated prior to adsorption. (2) Adsorption of nonprotonated chlorophyll molecules onto Brønsted acid sites, i.e., without removal of the protons from the clay prior to adsorption. In this mode of adsorption the nonprotonated chlorophyll molecules have to gain access to the proton sites; therefore, materials with higher pore volumes and larger pore sizes (properties which accompany acid activation) are the most suitable.

3.3. Reversibility of Chlorophyll Adsorption

Three types of acid-activated clays derived from the Los Trancos montmorillonite (see Table 1) were investigated. The chlorophyll adsorption data for the three acid-activated clays is given in Table 2 and Figs. 3A and 3B. As the level of acid activation increases the adsorption capacity goes through a maximum Figure 3A shows that the percentage of chlorophyll adsorbed by AL2 as a function of clay dosage increases rapidly to reach a maximum value at ca. 0.5% clay dosage while that of AL3 increases linearly up to 1.0% clay dosage. AL1 exhibits behavior intermediate between that of AL2 and AL3.

The tenacity with which the adsorbed chlorophyll molecules are held by AL1 and AL3 was investigated by studying the behavior in fresh oil of used clays (so-called cakes). AL2 cakes were not investigated because, except 'for the cake arising from the 0.25% dosage, they would
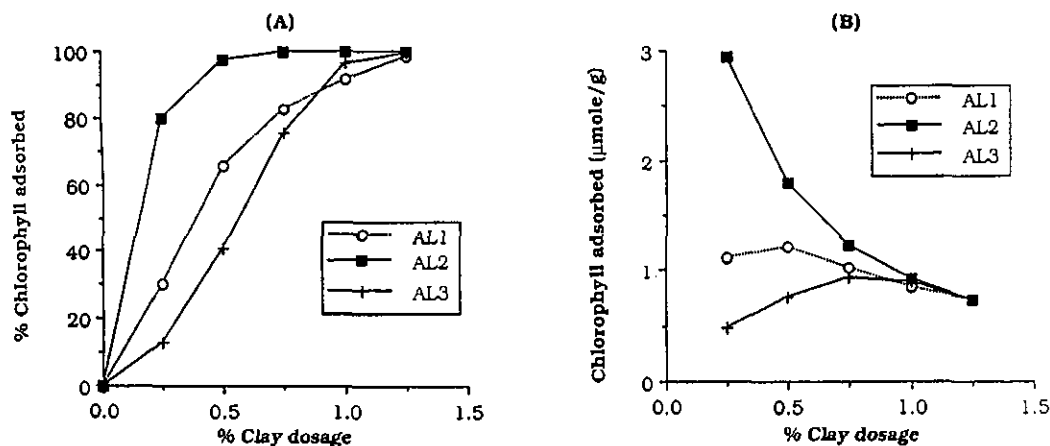
FIG. 3. Percentage chlorophyll adsorbed with various doses of acid-activated Spanish montmorillonite. The montmorillonite was activated at an acid/clay ratio of 0.25 (AL1), 0.60 (AL2), and 1.25 (AL3).

adsorb more chlorophyll due to the presence of unused adsorption sites (Fig. 3). The AL1 and AL3 cakes were washed in hexane (3 × 25 ml) under gentle vacuum, prior to contact with fresh oil. The resulting changes in chlorophyll amounts are shown in Table 3.

It is well established that the surface area and surface acidity of montmorillonites reach an optimum level with increasing acid treatment (5). For the three samples AL1, AL2, and AL3 the optimum level is considered as having been attained in AL2. Clays AL1 and AL3 possessed fairly similar levels of surface acidity and surface area, thereby representing either side of the maxima (Table 1). The one parameter which reduces with increasing levels of acid activation is the cation exchange capacity—AL3 has a lower CEC compared to AL1. This lower CEC is a reflection of a lower residual negative charge. The observation that the AL3 cake desorbed chlorophyll while the AL1 cake did not (and indeed adsorbed more) suggests that residual layer charge is a key factor in the adsorption and that the adsorbed chlorophyll molecules may be held electrostatically to the clay as positively charged (protonated) species; the higher the negative charge on the clay, the stronger the interaction and vice versa. This is consistent with observations made earlier that there is a transfer of protons (protonation) from the clay to the chlorophyll molecule upon or before adsorption.

3.4. Effect of Desorbed Species upon Subsequent Chlorophyll Removal

To investigate the effect of the desorbed species (in oils J, K, L, and M; see Table 3) on the adsorption properties of AL1 and AL3, prebleached oils (i.e., oils already contacted with clays AL1 and AL3 or their cakes) were further bleached with fresh samples of AL1 or AL3. The oils marked A to D in Table 2 which had been prebleached with AL1 were further bleached with fresh AL1, and those marked E to H in Table 2 (which were already

bleached with AL3) and J to M in Table 3 (which had been contacted with AL3 cake and contained desorbed species) were further bleached with fresh AL3. The chlorophyll adsorption achieved from these oils is given in Table 4. Oils with desorbed species (J–M) had much lower amounts of chlorophyll removed compared with the other oils (A to H).

The presence of the desorbed species in oils J–M clearly hampers the adsorption process. For oils without desorbed species (A–H), however, an increase in adsorption per gram of adsorbent is observed (compare Tables 2 and 3). It appears that some of the adsorption sites on the fresh adsorbents were blocked when contacted with oils J–M, resulting in a decrease in adsorption. This site-blocking phenomenon may rest in the fact that some of the chlorophyll in oils J–M (with desorbed species) is taken up by the fresh adsorbents in such a way as to inhibit further adsorption. We suggest that this decrease in the efficiency of clays in bleaching oils J–M results from a variation in the chlorophyll composition within these oils; i.e., the relative amounts of chlorophyll a/b and pheophytin a/b in A–H differ from those in J–M.

3.4.1. Competition between Chlorophyll a/b and Pheophytin a/b

Chlorophyll a/b contain a central Mg atom and, therefore, have a tendency to exist in aggregates or oligomers; the central Mg with 4-coordination is coordinatively unsaturated and, therefore, one or both of the Mg axial positions must be occupied by a molecule possessing a lone pair of electrons capable of acting as an electron donor so as to alleviate the coordination unsaturation. Chlorophyll a/b have a keto C=O and two ester C=O functions that can act as electron donors. Thus, chlorophyll a/b have an intrinsic combination of lone pair donor and acceptor properties and are able to aggregate, and as a result exist in oligomers much larger than the size of

one chlorophyll molecule (i.e., 12 × 15 Å) (3). Pheophytin a/b molecules (in which Mg^{2+} has been replaced by $2H^+$) are less likely to aggregate and therefore exist as monomers.

An additional factor which must be considered is the nature of interaction between the clay surface and the various chlorophyll derivatives. It has previously been reported (19–23) that free base porphyrins in which two nitrogen atoms are in the pyrolic form and the remaining two are in the aza form—for example, meso-tetraphenyl porphyrin ($TPPH_2$)—can react with protons on the surface of clays to produce the protonated porphyrin dication ($TPPH_4^{2+}$). The pheophytin a/b molecules may undergo such a reaction to yield protonated dications that can be held on the clay electrostatically. The chlorophyll a/b oligomers, on the other hand, first have to be dispersed as monomers and demetallated before they can be protonated. It is thus possible that these molecules are unable to undergo significant protonation and are adsorbed on the clay surface in a different manner. On this basis the pheophytin a/b monomers are likely to be adsorbed as dications and the chlorophyll a/b molecules as oligomers. The oligomers, due to their size, are not able to enter the pores of the clay and, therefore, block the openings (entrance) of some pores. This mode of adsorption will render part of the pore volume unavailable and prevent access to acid sites within the pores. The total effect is that there will be fewer adsorption sites available for the pheophytin a/b monomers. The results in Table 4 suggest that some adsorption sites are unavailable when fresh adsorbent is contacted with oils J to M (a phenomenon not observed for oils A to H), suggesting that the amount of chlorophyll a/b is increased in these oils due to the desorption of chlorophyll from AL3 cake (see Table 3).

The principal difference between AL1 and AL3 is the level of residual layer charge. When cakes of AL1 and AL3 are contacted with fresh oil, a new equilibrium is established between the chlorophyll in the oil and the chlorophyll on the clay. The AL1 cake, due to its high layer charge, is able to strongly hold the adsorbed pheophytin dications, and, therefore, no desorption occurs, i.e., the equilibrium is shifted to the clay. The AL3 cake, due to its low layer charge, is not able to hold the adsorbed pheophytin molecules with as much tenacity and thus the equilibrium is shifted to the oil. During the subsequent establishment of the new equilibrium some chlorophyll a/b is desorbed along with the pheophytin into oils J to M; the net effect is that the amount of chlorophyll a/b oligomers in these oils is increased, leading to the (adsorption) site-blocking phenomenon observed when the oils are contacted with fresh adsorbent.

The chlorophyll adsorption data in Table 4 (in μmole/g) are shown against the available chlorophyll (C_T) in Fig. 4. A linear relationship is obtained up to 6000 ppb C_T
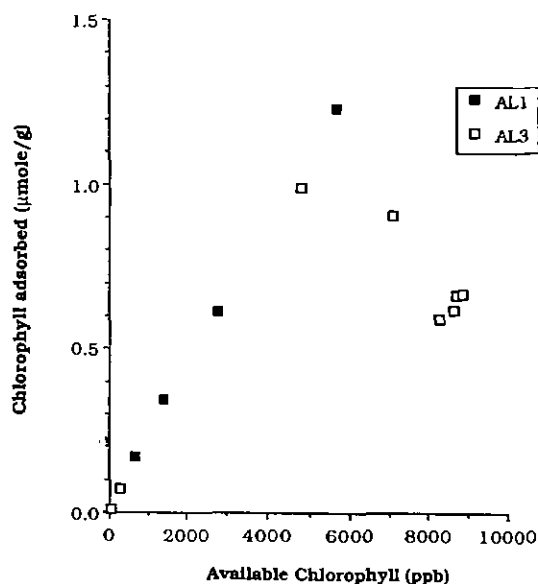

FIG. 4. Chlorophyll adsorbed from prebleached super degummed rapeseed oil as a function of initial chlorophyll content.

(i.e., 75% of total chlorophyll, 25% having been removed in the initial bleach), beyond which adsorption is reduced. The amount adsorbed is therefore proportional to the amount of chlorophyll in the oil, as long as C_T is below 6000 ppb (regardless of whether the adsorbent is AL1 or AL3). The explanation is that oils with $C_T < 6000$ ppb do not contain significant amounts of chlorophyll a/b. Therefore, adsorption site blocking does not occur; the amount of chlorophyll adsorbed is determined by an equilibrium between the oil and the clay which is dependent on the total amount of chlorophyll (C_T) present in the oil. Thus, if the composition of an oil (e.g., oils A–M) in terms of the various chlorophyll derivatives was such that $C\% =$ chlorophyll a/b, then the total amount of chlorophyll adsorbed would start to correlate linearly with clay dosage and with the amount of chlorophyll present in the oil only when all the chlorophyll a/b (i.e., $C\%$ of total chlorophyll) has been adsorbed. This may explain why oils pretreated with some forms of silica are easier to bleach (24). The silica acts to remove some of the chlorophyll a/b oligomers, thus making it easier to remove the remaining pheophytin a/b monomers. Variations of the chlorophyll/pheophytin ratio may also explain the differences observed in the bleachability of different types of oil (25).

Figure 4 suggests that the amount of chlorophyll a/b in the super degummed rapeseed oil is less than 25% of the total chlorophyll. Note that the 25% also includes pheophytin a/b, which was adsorbed along with the chlorophyll a/b in the initial stages of the adsorption; therefore the actual amount of chlorophyll a/b is much less (i.e., ca. 12.5%, assuming that the two species are adsorbed in similar proportion). Although the amounts of

pheophytin a/b and chlorophyll a/b in the oils were not determined, a chlorophyll a/b content of <25% is reasonable and is in general agreement with previous studies on the composition of chlorophyll in rapeseed oil (26).

A second explanation for the observed desorption from clay AL3 may rest in the fact that some montmorillonites when leached at high levels of acid treatment are converted to amorphous silicas which possess high phospholipid adsorption capacity but are poor chlorophyll sorbents. It is thus possible that clay AL3 is a more selective sorbent for phospholipids; when put into a fresh oil containing more phospholipids, the additional phospholipid molecules in the fresh oil displace some pheophytin from the clay, giving higher chlorophyll levels. However, this mechanism is likely to be less important due first to the fact that the degummed rapeseed oil used has a very low phosphorous content (i.e., <1 ppm) and would not have had a significant impact on the adsorption of chlorophyll. Second, clay AL3 (which unlike amorphous silica still contains ca. 10% of the octahedral ions originally present in the raw clay L) has a relatively high chlorophyll adsorption capacity which is uncharacteristic of amorphous silicas derived from clays (24).

4. CONCLUDING REMARKS

We have shown that chlorophyll adsorption on clays is dependent on the Brønsted acidity of the clays. A study of the cakes of acid-activated clays (after chlorophyll adsorption) indicates that Brønsted acid sites are indeed essential for the adsorption process, confirming that the chlorophyll molecules are mainly adsorbed (as protonated species) on these sites and held electrostatically on the clay surface. Due to the electrostatic nature of the interaction, the negative charge on the clay is important. Overactivation reduces the ability of the clay to hold the adsorbate.

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