Chlorophyll Adsorption by Alumina-Pillared Acid-Activated Clays

Robert Mokaya[a], **William Jones**[a,*], **Mary E. Davies**[b] and **Mavis E. Whittle**[b]

[a]Chemistry Department, University of Cambridge, Cambridge CB2 1EW and [b]Laporte Research and Development, Widnes, WA8 0FE, United Kingdom

Clays, acid-activated to an optimum level, have been pillared with alumina to give semi-crystalline expanded materials with surface acidities, pore volumes and average pore diameters generally higher than those of the corresponding pillared materials derived from a clay matrix not previously acid-activated. The chlorophyll adsorption capacity of the pillared acid-activated materials is significantly greater than that of pillared, nonactivated clays.

The procedures used in the preparation of these pillared acid-activated clays (*i.e.*, temperature of pillaring, method of drying and calcination temperature) have a significant influence on chlorophyll adsorption capacity because they influence both the physical and the chemical properties of the final pillared material. This variation provides a useful means of relating the various properties of the pillared materials to the chlorophyll adsorption capacity. As a result, a correlation has been demonstrated between adsorption capacity and a combination of pore volume and number of strong acid sites (of strength $pK_a < -1.5$) present in the pillared material. Optimal adsorbents were obtained from freeze-dried samples prepared by exchange at 20°C and calcination in air at 500°C.

KEY WORDS: Acid-activation, adsorption, alumina-pillared clays, clays, chlorophyll, freeze-drying, Hammett indicators, montmorillonite, porosity, surface acidity, surface area.

Bleaching earths (clays) have been used for many years as adsorbents of pigments present in biological systems, and they have proven to be indispensable in the bleaching process that removes chlorophyll from vegetable oils (1). Properties associated with the clay that have been identified as being important in chlorophyll adsorption include surface area, pore volume, pore size distribution, particle size and surface acidity (2–4).

Montmorillonites, the clays of frequent choice for acid-activation, possess a three-layer phyllosilicate structure. Their structural formula (showing idealized isomorphous octahedral substitution) is indicated by:

$$M_x(Si_8)\,[Al_{4-x}\,Mg_x]\,O_{20}\,(OH)_4\,.\,nH_2O$$

where x ∿ 0.7.

When montmorillonites are acid-activated as a result of treatment with hot mineral acid, H^+ ions attack the aluminosilicate layers *via* the interlayer region (2). This attack alters the structure, chemical composition and physical properties of the clay while increasing the chlorophyll adsorption capacity. It has been demonstrated that surface acidity and pore volume are particularly important for chlorophyll adsorption (4). Therefore, our aim has been to prepare a range of clay-based materials and to correlate microstructure and surface acidity to observed chlorophyll adsorption capacities (Mokaya, R., W. Jones, M. E. Whittle and M. E. Davies, unpublished data). In doing so, we hope to determine the possible mechanism of the adsorption process, as well as to design more efficient adsorbents.

As part of this investigation we commenced a study of the potential application of pillared clays as bleaching materials. In addition, pillaring provided a powerful means of varying the properties of acid-activated clays, thereby allowing a correlation to be made between the efficiency of chlorophyll adsorption and certain physicochemical properties of the pillared acid-activated clays and clays in general. Pillared clays result from the introduction into the parent clay, through ion-exchange, of large polymeric inorganic cations. These cations are located between the clay sheets and result in an expanded clay structure. Following calcination, the cations are converted to oxides, thereby generating cross-linked porous materials with the oxide pillars bridging the clay sheets (5). To our knowledge, no systematic study of pillared clays has been made for chlorophyll adsorption, and in particular, the concept of pillaring acid-activated clays does not appear to have been explored.

In this paper we concentrate on the characteristics of pillared acid-activated clays (in both the precursor and calcined forms), although useful comparative information for pillared nonactivated clays has been included. Previous studies of chlorophyll adsorption on pillared nonactivated clays have been restricted to a brief comparison of their chlorophyll adsorption characteristics with those of conventional clays and other layered materials (4).

MATERIALS AND METHODS

A natural montmorillonite clay (from Surrey, South England), designated M, was used as the starting material. The clay contained Ca^{2+} as the predominant exchangeable cation and had a cation exchange capacity of ∿90 meq/100 g. Clay M was acid-activated in concentrated sulfuric acid for 16 h to yield an optimum acid-activated clay suitable for pillaring, designated AM. Aluminum chlorhydrate solution, kindly supplied by Albright and Wilson (Warley, West Midlands, United Kingdom) was used as the source of the pillaring species. The solution contained 50% w/w aluminum chlorhydrate calculated as the dihydrate $[Al_2(OH)_5Cl.2H_2O]$ and was about 6.4 M in aluminum.

The precursor-pillared clays were prepared by adding, with stirring, known amounts of M or AM to the pillaring solution at either 20 or 80°C. A constant solution/clay ratio of 50 mL/g was maintained throughout all the preparations, and the exchange was carried out for 1 h with constant stirring. The resulting slurry was repeatedly washed, centrifuged in fresh deionized water and reslurried until free of Cl^- ions (as tested by $AgNO_3$). The resulting material was then redispersed in a minimum amount of deionized water and either air-dried or freeze-dried to obtain the precursor-pillared clays. The precursor-pillared materials were designated as follows: M exchanged at 20°C, PM20; M exchanged at 80°C, PM80; AM exchanged at 20°C, PAM20; and AM exchanged at

---

[*] To whom correspondence should be addressed at Chemistry Department, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom.

80°C, PAM80. These precursor materials were then calcined in air at either 300 or 500°C to obtain the calcined samples (5). (Those calcined at 500°C are designated CPM20, CPM80, CPAM20 and CPAM80, respectively.)

Al^{3+}-exchanged materials were prepared from 1.0 N solutions of $AlCl_3.6H_2O$. Contact time was 24 h with some stirring. The exchanged clay was then washed free of Cl^- ions and either air- or freeze-dried.

Surface areas, pore volumes and pore size distributions were obtained with a Micromeritics ASAP 2000 analyzer (Houndhills, Hampshire, United Kingdom) at liquid nitrogen temperatures. Hammett indicators were used to determine the surface acidity in the pK_a range −3–6.8. Elemental compositions were determined by X-ray fluorescence techniques with a Philips PW 1400 X-ray fluorescence spectrometer (Eindhoven, The Netherlands).

For the bleaching test, a known amount of clay was added to a super degummed (SDG) rapeseed oil (which contains *ca.* 8000 ppb chlorophyll) at 100°C and stirred for 35 min. The adsorbent was removed by filtration, and the amount of chlorophyll remaining in the oil was measured by standard analytical techniques (3). Values shown are the mean two independent measurements with reproducibility of 1%.

RESULTS

Surface area, average pore diameter and pore volume measurements for the precursor and calcined materials are shown in Table 1. Elemental analyses of M, AM and their pillared derivatives are given in Table 2. Surface acidity measurements are shown in Table 3.

Chlorophyll adsorption capacity measurements for the precursor- and calcined-pillared acid-activated clays are shown in Figure 1 for air-dried materials and in Figure 2 for freeze-dried materials. Chlorophyll adsorption capacities for the equivalent materials derived from the nonactivated clays are shown for comparison in Figures 3 and 4. The results demonstrate that the pillared acid-activated materials are better adsorbents of chlorophyll than their nonactivated analogues. In addition, freeze-dried materials adsorb more chlorophyll than the air-dried analogues.

DISCUSSION

Physical properties. The physical properties of the pillared products clearly depend upon several factors (Table 1). A higher exchange temperature promotes more efficient incorporation of aluminum polycations into the interlayer region for both M and AM. The original exchangeable cations (mainly Ca^{2+}) are replaced during this exchange (Table 2). High alumina incorporation has been reported to result in a more ordered material, with a higher number of uniformly distributed pillars in the interlamellar region (6).

It is expected that increasing incorporation of the pillaring species will increase, to a maximum value, both the pore volume and average pore diameter. Beyond this maximum, further incorporation will result in more interlayer space being occupied by the pillaring species than is generated by the increased expansion resulting from pillaring. As a result, average pore diameters and pore volumes will then decrease. The optimum incorporation of alumina for samples derived from AM seems to be between 10.4% (wt%) for PAM20 and 15.2% for PAM80. Because PAM80 and CPAM80 have lower chlorophyll adsorption capacities than PAM20 and CPAM20 (Figs. 1 and 2), it appears that a reduction in pore volume and average pore diameter has a negative effect on the chlorophyll adsorption capacity for these types of pillared materials.

TABLE 1

Surface Areas, Pore Volumes and Average Pore Diameters for the Various Materials Studied

Clay type[a]	BET S.A. (m^2/g)		Pore volume (cc/g)		Average pore diameter (Å)	
	FD[b]	AD[c]	FD	AD	FD	AD
PAM20	223	191	0.31	0.27	40.3	38.9
PAM80	121	87	0.20	0.16	45.7	42.0
CPAM20	284	322	0.38	0.37	38.6	34.2
CPAM80	259	257	0.30	0.29	33.8	32.5
PM20	103	188	0.11	0.15	29.8	24.5
PM80	204	188	0.15	0.14	22.2	21.0
CPM20	200	172	0.18	0.17	27.0	28.9
CPM80	293	270	0.21	0.19	21.0	20.3

[a] Clays: M, natural montmorillonite; AM, acid-activated suitable for pillaring; PM20, M exchanged at 20°C; PM80, M exchanged at 80°C; PAM20, AM exchanged at 20°C; PAM80, AM exchanged at 80°C; Cs preceding the abbreviations indicate that the precursor materials were calcined in air.

[b] Freeze-dried.

[c] Air-dried.

TABLE 2

Elemental Analysis Results for M, AM and Their Derivatives[a]

Clay type	%Al_2O_3	%SiO_2	%CaO	SiO_2/Al_2O_3
M	14.1	55.6	4.7	6.7
AM	10.8	58.1	4.3	9.1
PM20	23.0	48.6	0.7	3.6
PM80	28.0	45.0	0.1	2.9
PAM20	19.6	53.6	<0.1	4.7
PAM80	23.2	51.8	<0.1	3.8

[a] Clays as described in Table 1.

Despite the fact that all the materials reported in Table 1 have average pore diameters considerably larger than the cross-sectional dimensions of the chlorophyll molecule (12 × 15 Å), the amount of adsorbed chlorophyll continues to increase with increasing average pore size. This observation supports the suggestion that chlorophyll may interact with the clay surface in agglomerates (7) and, as a result, pores of diameter less than the size of the chlorophyll agglomerates present in the oil are unfavorable for adsorption. This point is, furthermore, supported by the observation (Table 1) that freeze-dried samples generally adsorb more chlorophyll than air-dried counterparts (Figs. 1–4); freeze-drying is known to promote face-to-edge or edge-to-edge layer aggregation of the clay, thereby generating both macroporosity and microporosity, as well as larger average pore diameters and pore volumes (8). By comparison, air-dried samples essentially follow a face-to-face layer aggregation, which favors formation of a more closely packed and ordered material with pores primarily in the micropore range. However, it is worth noting that

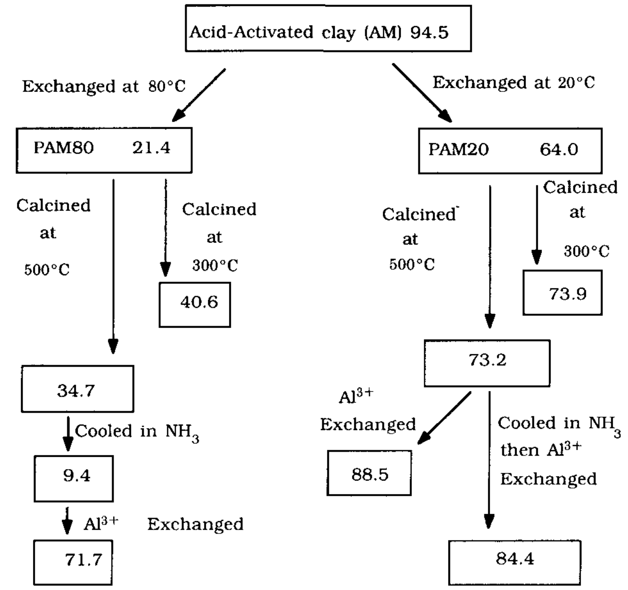

FIG. 1. Chlorophyll adsorption data (as % chlorophyll adsorbed) for air-dried samples of pillared AM. Clays as described in Table 1.

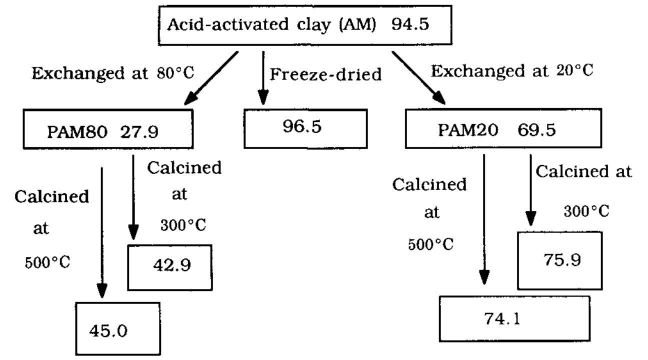

FIG. 2. Chlorophyll adsorption data (as % chlorophyll adsorbed) for freeze-dried samples of pillared AM. Clays as described in Table 1.

due to the pillared nature of the materials in this study, the pore diameters encountered are within a relatively narrow range (from the mid-micropore range to the lower mesopore range) and, thus, most of the pore volume of the materials is associated with pores within this range.

Surface acidity. Table 3 indicates that for both M- and AM-derived materials, the exchange (pillaring) temperature influences the surface acidity of the materials irrespective of whether or not the host matrix has been acid-activated. In all cases, materials prepared at 20°C have higher acidity as compared to materials prepared at 80°C. This is true throughout the range of acid strengths investigated. From a comparison of the chlorophyll adsorption data (Figs. 1–4) and the acidity values (Table 3), it is clear that higher acidity improves chlorophyll adsorption capacity.

Exchange of the polycations into AM has the effect of "propping" open the layers and exposing hitherto inaccessible acid sites. The polycations may, however, block matrix acid sites. Their introduction will also result in the replacement of exchangeable cations, some of which (*e.g.*, Al^{3+}) are very acidic. While the polycations introduce new acid sites (5) *via* hydrolytic reactions, these do not compensate for those sites that have been removed or blocked. A balance is required between opening up the structure and maintenance of acidity. This is better achieved by low-temperature exchange, which does not

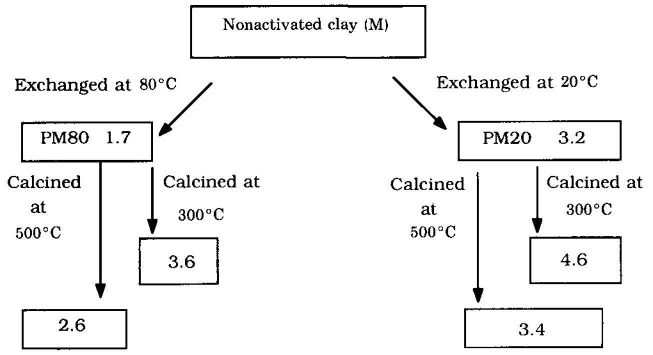

FIG. 3. Chlorophyll adsorption data (as % chlorophyll adsorbed) for air-dried samples of pillared M. Clays as described in Table 1.

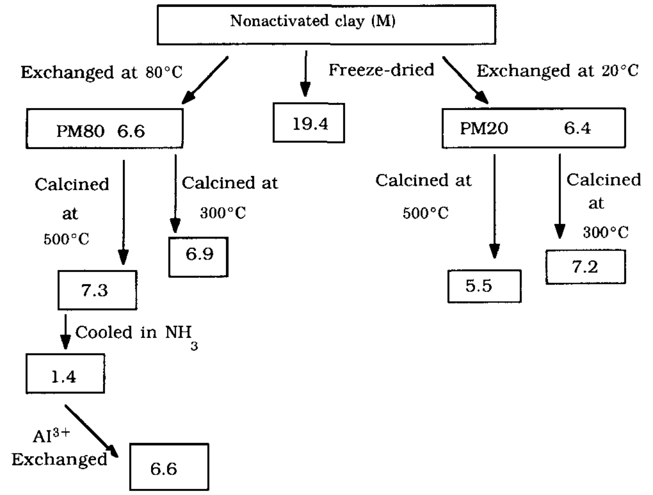

FIG. 4. Chlorophyll adsorption data (as % chlorophyll adsorbed) for freeze-dried samples of pillared M. Clays as described in Table 1.

TABLE 3

Surface Acidity[a] of the Air-Dried Samples Measured with Hammett Indicators

	PK_a value					
Clay type[b]	6.8	4.7	2.8	1.5	−1.5	−3.0
PM20	0.45	0.36	0.25	0.16	0.09	0.05
PM80	0.38	0.25	0.15	0.08	0.05	0.01
CPM20	0.42	0.32	0.20	0.13	0.10	0.05
CPM80	0.35	0.24	0.13	0.10	0.06	0.03
PAM20	0.91	0.72	0.55	0.43	0.32	0.08
PAM80	0.90	0.70	0.50	0.30	0.18	0.07
CPAM20	0.82	0.72	0.60	0.43	0.30	0.13
CPAM80	0.75	0.72	0.45	0.32	0.19	0.09

[a] In meq *n*-butylamine/g clay.
[b] Clays as described in Table 1.

introduce sufficient polycations to completely block the interlayer region but results in the incorporation of fewer, yet sufficient, polycations to prop apart the layers. As a result, hitherto inaccessible acid sites are exposed and most of the initial matrix acidity is maintained.

Influence of calcination. In general, calcination improves the chlorophyll adsorption capacity. Calcination has the effect of dehydroxylating the precursor pillar in the following (idealized) way (9):

$$2[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+} \rightarrow 13Al_2O_3 + 14H^+ + 41H_2O$$

The removal of water from the expanded interlayer region of the clay has the dual effect of generating pore volume (10) and, because low interlayer water contents are known to favor higher acidity (11), creating a more acidic environment. Water removal also results in the creation of a less hydrophilic environment for the (hydrophobic) chlorophyll molecules. These are factors that will, in each case, enhance chlorophyll adsorption. The temperature of calcination (300 or 500°C, Figs. 1–3) does not significantly affect the chlorophyll adsorption capacities of the materials. Both temperatures are lower than the temperature at which Bronsted acid sites are known to significantly convert to Lewis sites, and thus the nature of acidity in the materials calcined at the two temperatures is essentially of the same type.

In all cases, precursor-pillared materials have a higher number of sites with low acid strengths (*e.g.*, pK_a 4.7) compared to the calcined materials. The opposite is the case at strong acid strengths (*e.g.*, pK_a −3.0) (Table 3). This variation in acid site distribution is due to the water present in the precursor-pillared material interacting with acid sites of $pK_a < -1.7$ (*i.e.*, the pK_a value of water) weakening them and thus shifting the acidity to lower strengths. The better adsorption capacity of calcined materials provides further evidence that strong acid sites are responsible for the adsorption process.

Previous investigators have proposed that the protons generated during calcination migrate into the matrix of the clay (9). These protons may, however, be abstracted from the matrix by cooling the calcined material in ammonia solution (a strong base), thus generating NH_4^+ ions in the interlayer region of the material (5,9). NH_4^+, being a nonacidic cation, reduces the chlorophyll adsorption capacity of the pillared material (see Fig. 1). When, however, the NH_4^+ ion is replaced by Al^{3+} (an acidic cation), the adsorption capacity is dramatically enhanced. These observations are in agreement with previous results for nonpillared cation exchanged clays (unpublished data) where acidic cations, such as Al^{3+} or Ti^{4+} (as a result of their high polarizing abilities), create acidic environments conducive for chlorophyll adsorption. Nonacidic cations (*e.g.*, Na^+, Li^+), on the other hand, have the opposite effect (unpublished data).

Relationship between surface properties of the materials and chlorophyll adsorption. The foregoing discussion lays down the basis of an attempt to link the chlorophyll adsorption capacity with surface acidity and pore volume. From the results, it is apparent that in all cases improved surface acidity and pore volume are accompanied by an increase in chlorophyll adsorption capacity. Indeed, a linear relationship between chlorophyll adsorption capacity of the pillared clays and a combination of their pore volume and surface acidity (at pK_a value < -1.5) is observed (Fig. 5). It is clear, therefore, that modification of acid-activated clays may give rise to good adsorbents for chlorophyll, and it is likely that further enhancement of adsorption may occur when other pillaring species are used. Such investigations are currently underway.

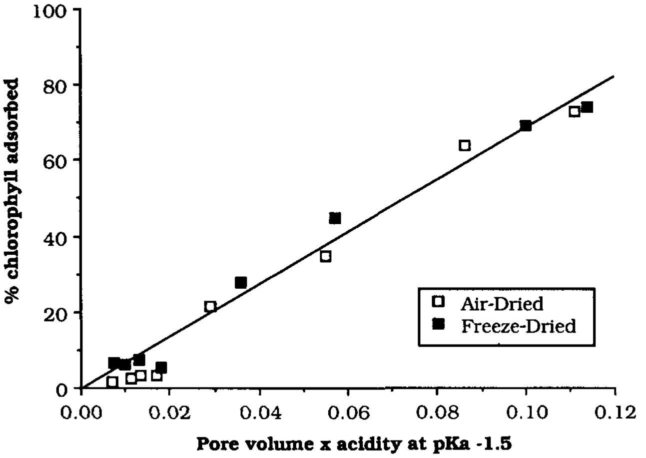

FIG. 5. Relationship between a combination of pore volume and acidity at pK_a −1.5 and chlorophyll adsorption capacity.

ACKNOWLEDGMENTS

We are grateful to Dr. L. Gladden and Paul Grainge for performing the BET analyses. R.M. acknowledges the Cambridge Commonwealth Trust for a studentship.

REFERENCES

1. Rich, A.D., in *Industrial Minerals and Rocks,* 3rd edn., AIME, New York, 1960, p. 93.
2. Taylor, D.R., and D.B. Jenkins, *Soc. Min. Eng. AIME Trans. 282*:1901 (1988).
3. Morgan, D.A., D.B. Shaw, M.J. Sidebottom, T.C. Soon and R.S. Taylor, *J. Am. Oil Chem. Soc. 62*:292 (1985).
4. Taylor, D.R., D.B. Jenkins and C.B. Ungerman, *Ibid. 66*:334 (1989).
5. Figueras, F., *Cat. Rev. Sci. Eng. 30*:457 (1988).
6. Bartley, G.J.J., and R. Burch, *Applied Cat. 19*:175 (1985).
7. Brimberg, U.I., *J. Am. Oil Chem. Soc. 59*:74 (1982).
8. Pinnavaia, T.J., M.S. Tzou, S.D. Landau and R.H. Raythatha, *J. Mol. Cat. 27*:195 (1984).
9. Tennakoon, D.T.B., W. Jones and J.M. Thomas, *J. Chem. Soc., Faraday Trans. 82 (1)*:3081 (1986).
10. Occelli, M.C., and R.M. Tindwa, *Clays and Clay Minerals 31*:22 (1983).
11. Mortland, M.M., and K.V. Raman, *Ibid. 16*:393 (1968).

[Received July 6, 1992; accepted December 31, 1992]