Chlorophyll Adsorption on Acid-Activated Clay

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An acid-activated clay (Çanakkale montmorillonite from Turkey) was used to adsorb chlorophyll from hexane solutions. The phenomenon seems to be mainly driven by the interaction of chlorophyll with acid sites. The adsorption of chlorophyll on Brönsted acid sites was indicated by a characteristic infrared band for the -OH group at 3671 cm^{-1}. The variations in the structure of clay mineral and chlorophyll during adsorption have been examined by differential thermal analysis, thermogravimetry and infrared spectroscopy of the activated clay before and after adsorption of chlorophyll. Oxidation of adsorbed chlorophyll was completed at quite a high temperature.

KEY WORDS: Activated clay, adsorption, Brönsted acid sites, chlorophyll, decolorization, differential thermal analysis, infrared, Lewis acid sites, montmorillonite, thermogravity.

Pigments found in fats and oils are still not entirely characterized, and their fate during bleaching is not well understood. One of the best-known classes of pigments is the carotenoids (1,2), which are largely responsible for the yellow and red colors of most fats.

Olive oil and soybean oil derived from green beans, as well as some inedible tallows have a greenish color due to the presence of chlorophyll and related compounds. With the exception of olive oil, a green tinge is generally undesirable. A green color presents a problem chiefly in the processing of soybean oil to produce edible products. Hydrogenated soybean oil frequently has a greener color than the crude oil because the red and yellow pigments in the oil mask the green. Hydrogenation reveals that the chlorophyll remains during the bleaching process (3). To elucidate the effect of bleaching on the acid-activated clays, the chlorophyll adsorption onto acid-activated montmorillonite from hexane solution was investigated.

It is well-known that bentonites in their natural state have a limited capacity for bleaching of vegetable fats and oils (4,5). To improve the bleaching property, commercial clays are usually acid-activated (6). A considerable number of studies have been carried out on the decolorization of fats and oils, on the adsorption of β-carotene on acid-activated clay and on bleaching earths, but little has been done on the adsorption of chlorophyll in the same materials (7–9).

EXPERIMENTAL PROCEDURES

The chlorophyll adsorbed (mixture of chlorophyll a and chlorophyll b) on acid-activated clay was isolated from dried spinach leaves (10). Acid-activated clay was used as adsorbent. The activated clay was prepared from montmorillonite mineral obtained as raw material from the Çanakkale reserve (Northwest, Turkey) (11,12). The chlorophyll solutions were prepared with anhydrous hexane. The amount of chlorophyll adsorbed from the hexane solution was measured with a spectrocolorimeter (Jena-colorimeter, Jena, Germany) as described previously (11).

The thermal analyses were performed in a Netzcsh differential thermal analysis-thermogravity (DTA-TG) instrument (Selb, Germany) at a heating rate of 10 K min^{-1}, with kaoline heated to 1200°C as inert material. In this process the temperature was changed from room temperature to 1000°C in a static argon atmosphere.

For infrared (IR) experiments, the sample was mixed with spectroscopic KBr (Merck, Darmstadt, Germany) at a ratio 0.02 and ground in an agate mortar. About 1 g of the mixture was placed in a 15-mm dye chamber which was evacuated, and then a transparent pellet was obtained under a simultaneously applied pressure of 10 ton•inch^{-2}. IR spectra of the pellets were taken on a Perkin-Elmer model 577 spectrophotometer (Norwalk, CT).

RESULTS AND DISCUSSION

The absorption spectrum of chlorophyll in hexane solution, which has a green color in the visible region, gives absorption bands at 660, 642, 613, 575 and 530 nm (Fig. 1). After adsorption on clay, the solutions with an initial concentration of more than 50 ppm turned light green. The absorption peaks did not shift, but decreased in intensity. When the initial solution had a concentration of less than 50 ppm, no distinct absorption spectrum was obtained, because most of the chlorophyll was adsorbed from solution by the activated clay.

Apparent adsorption curves were obtained by plotting the number of moles adsorbate/g of adsorbent, ($n_o\ \Delta x_1/m$) *vs.* the mole fraction (x_1) of chlorophyll in the supernatant fluid, where n_o is the amount of initial solution, Δx_1 is the difference between the mole fraction of chlorophyll in solution before and after adsorption, and m is the amount of adsorbent (13). The apparent adsorption isotherm of chylorophyll by acid-activated clay at 30°C is given in Figure 2. According to the isotherm (Fig. 2), the first stage of adsorption was completed at the solution concentration of about 2000 ppm, which is greater than the amount of chlorophyll in vegetable oil (14).

The DTA and TG curves of the activated clay before and after adsorption are shown in Table 1. The curves of the sample with adsorbed chlorophyll show that the magnitude of the first endothermic peak did not increase much and the weight loss corresponding to this peak rose from 5.8% to 6.0%. Considering the fact that the green color of the adsorbed sample did not change at this temperature, the increase in magnitude of the first endothermic peak may be due to the desorption of hexane, which was adsorbed in the pores of the clay during heating. When the sample was heated, the exothermic peak of the adsorbed chlorophyll appeared at 320°C, which resulted from the oxidation of adsorbed chlorophyll. The position and magnitude of the dehydroxylation peak of the acid-activated clay did not change after adsorption of chlorophyll, but the weight loss corresponding to this range increased from 1.6% to 3.0%. This effect indicates that oxidation of adsorbed chlorophyll was completed at a higher temperature than the upper limit of the exothermic peak. During the exothermic reaction, the oxidation of hydrogen to water and of carbon to petroleum coke occurred, and the color of the sample turned from green to black.

The IR spectrum of acid-activated clay has been given

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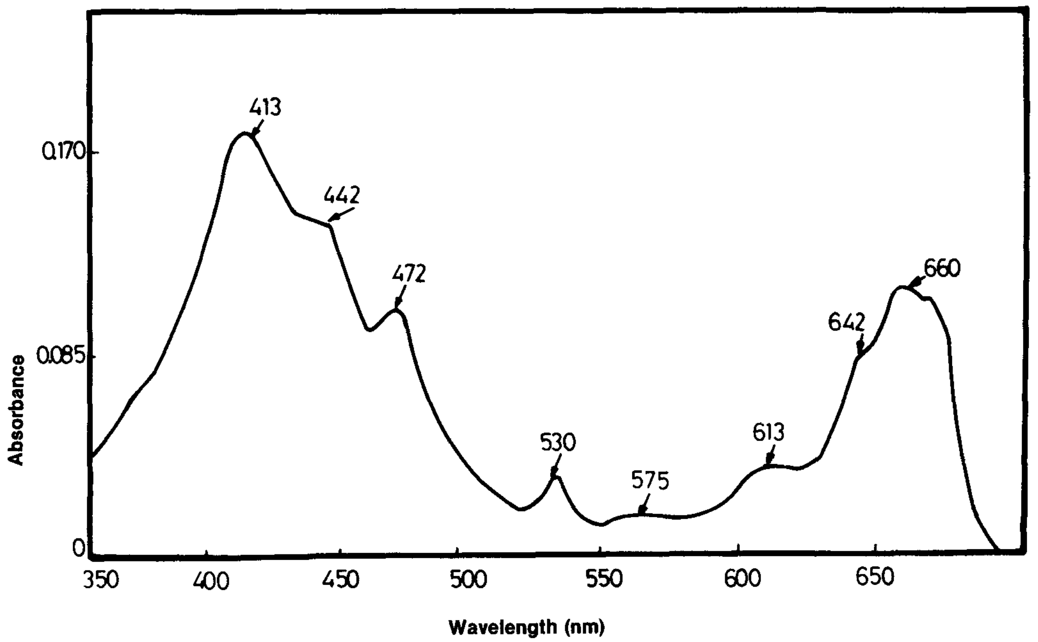

FIG. 1. Absorption spectra of chlorophyll in hexane.

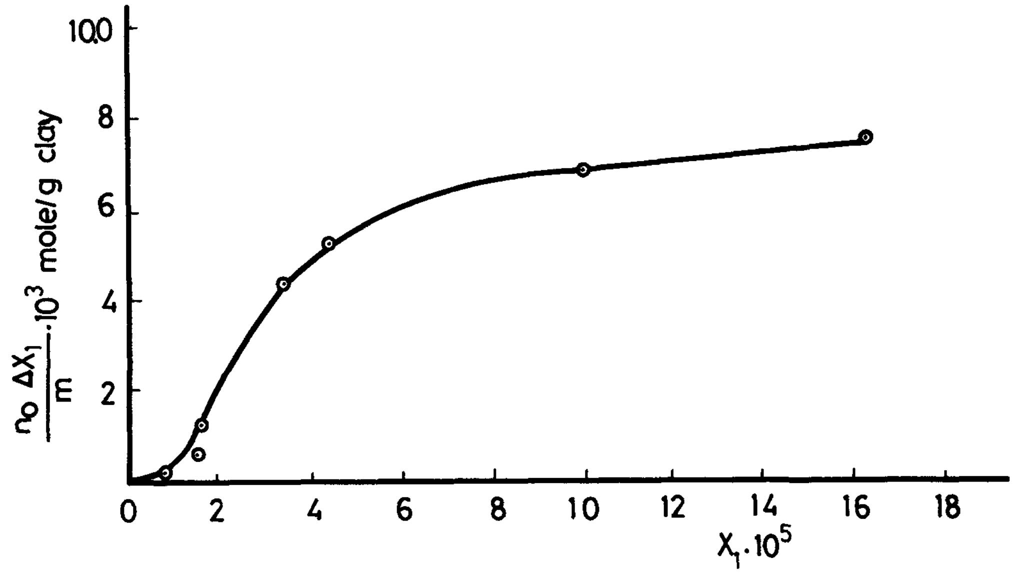

FIG. 2. Apparent adsorption isotherm of chlorophyll on activated clay at 30°C.

TABLE 1

DTA and TG Results of Activated Clay Before and After Chlorophyll Adsorption

Sample	Peak range (°C)	Peak temperature (°C)	Reaction	Weight loss (%)
Acid-activated clay	30–185	105	Endothermic	5.8
	185–450	225	Exothermic	1.6
	450–1000	—	Endothermic	1.6
Chlorophyll-adsorbed clay	30–185	100	Endothermic	6.0
	185–450	330	Exothermic	3.0
	450–1000	—	Endothermic	3.0

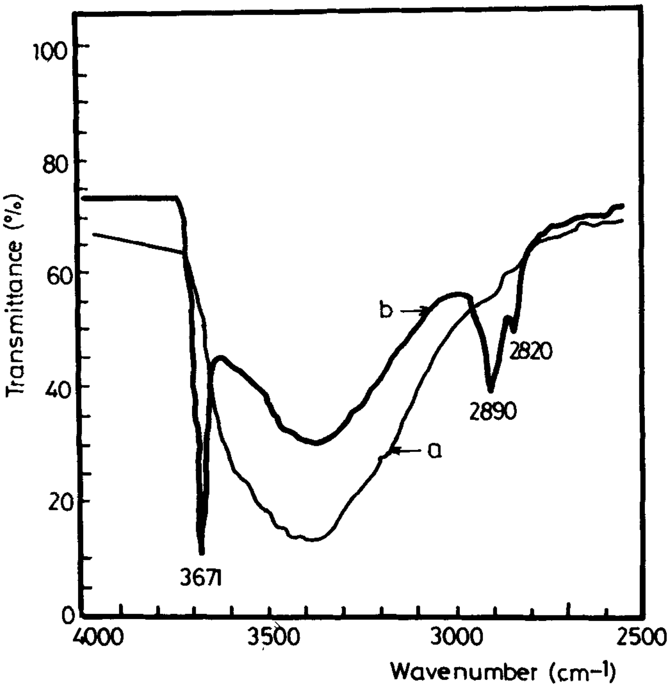

FIG. 3. IR spectra of activated clay a, before adsorption; and b, after adsorption in the 4,000 cm^{-1}–2500 cm^{-1} range.

in a previous paper (12). IR spectra of the activated clay show the characteristic absorption bands in the range of 1,400 cm^{-1}-400 cm^{-1} corresponding to the Si-O and Si-O-R vibrations, where R represents the octahedric cations. At the end of the chlorophyll adsorption, the half-widths and intensities of all those bands have decreased. Therefore, the mineral lattice has gained a more ordered situation as a result of chlorophyll adsorption.

In the IR spectrum of acid-activated clay, the band at 3,610 cm^{-1} rises from the stretching vibrations of the free hydroxyl groups in the octahedral layer, and the band at 3,400 cm^{-1} is due to the stretching vibrations of the hydroxyl which take place in the H-bridged Si-OH groups and interlayer water (12,15). After the adsorption of chlorophyll, the adsorption bands in the range 3700–2500 cm^{-1} have become narrower and their intensities have decreased; and three new bands have appeared at 3671 cm^{-1}, 2890 cm^{-1} and 2820 cm^{-1} (Fig. 3). The last two bands rise from the C-H stretching after chlorophyll adsorption. The sharp band at 3671 cm^{-1} of -OH N-H groups is due to the chlorophyll (phaeophytin) adsorbed on the acid-activated clay. As a consequence of the removal of magnesium from the chlorophyll structure, phaeophytin was formed in acidic media (10). Phaeophytins are weak bases (9). The acid-activated clays have strong Lewis and Brönsted acid sites (9,11,12,16–18).

As a result of an acid-base reaction (9), the adsorption of chlorophyll (phaeophytin) on acid-activated clay occurs. As a consequence, it seems that the adsorption of chlorophyll on acid-activated clay is mainly a chemical process stemming from the interaction of chlorophyll with the Lewis and Brönsted acid sites of clay.

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