The Adsorption of β-Carotene I. by Bleaching Earths

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ABSTRACT

Activities of various bleaching earths for removal of β-carotene from acetone solution were found to be in the decreasing order tonsil, fuller's earth, silica, and kaolin. Experimental evidence indicated that except for silica, in addition to physical adsorption, processes involving chemisorption and subsequent chemical reaction proceeded on the surface of the clay minerals. An Arrhenius activation energy of the order of 10 kcal mol^{-1} was found for the adsorption of β-carotene from a solution in acetone on tonsil. Metallic ions, such as Fe^{3+}, are suggested to be the active sites for chemisorption and reaction. Oxygen was not essential for activity.

INTRODUCTION

The increasing production of palm oil in recent years and its high content of carotenoid compounds (1,2) prompted us to study the possibility of using this oil as a source of β-carotene.

The industrial bleaching of palm oil often leads to unrecoverable carotenoids (3). It has been suggested that, in the bleaching of palm oil, color fading may be due at least partially to oxidation of the carotenoids with the clay acting as catalyst (4). Earlier studies proposed that the bleaching of palm oil by clay is a purely physical adsorptive process with all the carotene recoverable from the filter cake (5,6). A later study using carbon as the bleaching agent showed that carotenes could only be recovered if an antioxidant, like hydroquinone, was added to the carbon (7). In view of these conflicting results, we undertook to study the interactions of β-carotene with bleaching earths that were readily available to us.

EXPERIMENTAL

The β-carotene used was obtained from Merck Co. Germany and was recrystallized from an acetone/benzene mixture. The recrystallized substance was dried and stored in a darkened vacuum desiccator. All solvents used were Analar grade and were dried with activated molecular sieve 5A before use. Tonsil, which is a bentonite type material, was a gift from Lever Borther's palm oil refinery, Kuala Lumpur, Malaysia; Fuller's earth was purchased from Hopkin & Williams Ltd., England; kaolin from Riedel Co., Germany, and silica from Merck Co. Germany. All the adsorbents were commercial samples, pretreated at $\sim$500 C and used without further purification.

Heat treatment of the adsorbents was carried out in a muffle furnace set at the appropriate temperature in porcelain crucibles in the presence of air for 4 hr. Adsorption experiments were carried out in stoppered flasks with continuous swirling. To determine the concentration of the supernatant solution after the adsorption, the contents of the flask were allowed to settle, a few milliliters of the clear solution were pipetted out and diluted to the appropriate concentration before the absorption spectrum was obtained using a Perkin-Elmer 402 uv-vis spectrophotometer. The concentration was then determined from an absorbance-concentration calibration curve. In the experiments to obtain the adsorption isotherms, a series of carotene in acetone solutions with known concentrations were prepared, and to 10 ml of each of these solutions, a known weight (1 g) of the adsorbent was added. The carotene concentration of the supernatant solution was determined after 45 min.

RESULTS AND DISCUSSION

Adsorption Isotherms

Purified β-carotene in acetone solution, which is orange in color, absorbs in the uv-vis region at 453 nm with two shoulders at 478 nm and 430 nm (FIG. 1, curve a). When this solution was allowed to come into contact with clay minerals; tonsil, fuller's earth, or kaolin, the supernatant solution turned greenish over a period of time. The intensity of the absorption of this supernatant solution in the region of 453 nm decreased while two new peaks at 330 nm and 360 nm appeared and increased in intensity with time, (FIG. 1, curve b), clearly indicating that the adsorption cannot be purely physical.

When the adsorbent was tonsil or Fuller's earth, the absorption at 478, 453 and 430 nm completely disappeared after continuous stirring for 24 hr. These absorptions were replaced by peaks at 360 and 330 nm (FIG. 1, curve c). The supernatant solution turned green, while the adsorbent which was originally white assumed a greenish grey color. In contrast, when silica was used as the adsorbent, the peak at 453 nm decreased in intensity without any accompanying increase in absorption at 330 nm and 360 nm after 24 hr.

The activities of the various adsorbents, which were untreated but previously activated during manufacture, to remove β-carotene from solution in acetone were investigated. The amount adsorbed per gram of adsorbent ex-

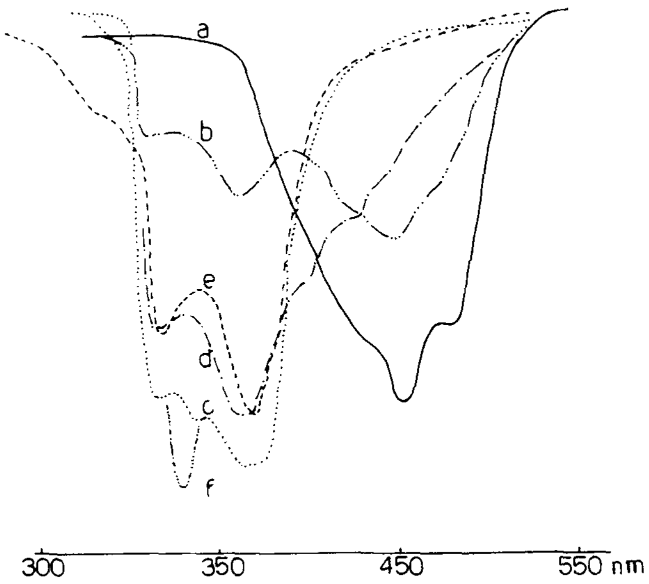

FIG. 1. Absorption spectrum: (a) β-carotene in solution before addition of adsorbent, (b) supernatant solution of β-carotene + tonsil, ½ hr after addition of tonsil, (c) supernatant solution of β-carotene + tonsil, 24 hr after addition of tonsil, (d) supernatant solution of β-carotene + tonsil, 24 hr after addition of tonsil in the absence of oxygen, (e) β-carotene + $FeCl_3$, 24 hr after addition of $FeCl_3$ and (f) β-carotene + $FeCl_3$ + hydroquinone, 24 hr after addition of $FeCl_3$ + hydroquinone.

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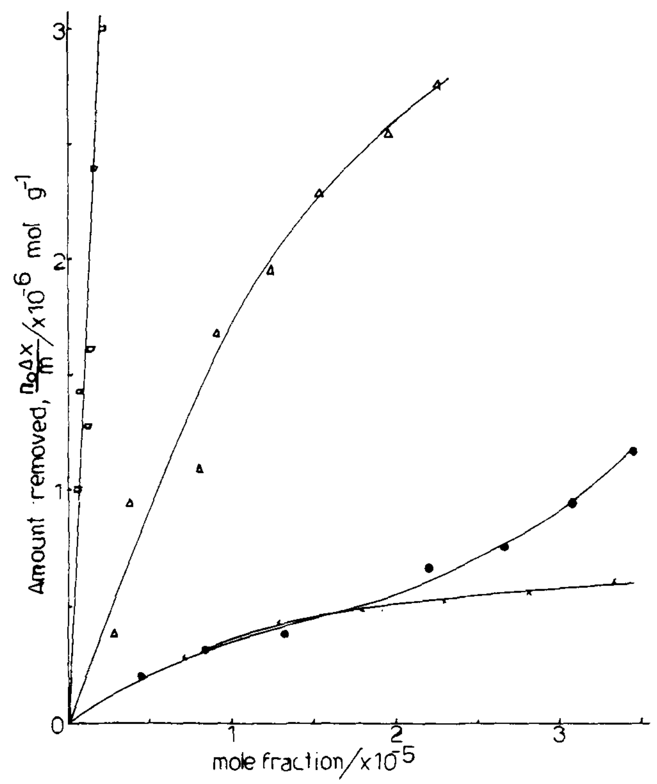

FIG. 2. Apparent adsorption isotherm of β-carotene by tonsil (□), Fuller's earth (Δ), kaoline (x) and silica (●) plotted as amount removed in mol g^{-1} vs. concentration of supernatant solution in mol fraction.

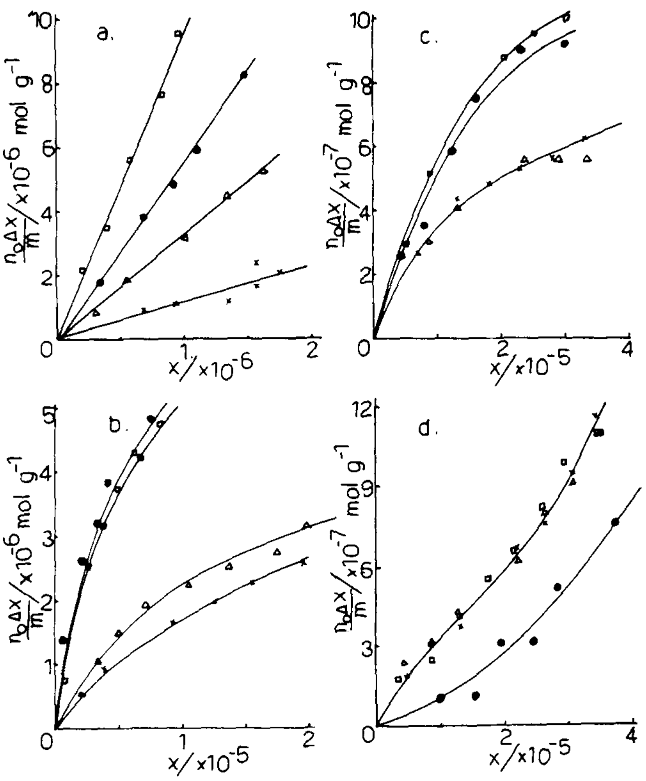

FIG. 3. Apparent adsorption isotherms of β-carotene by the adsorbents studied, at different temperature of pretreatment (a) tonsil, (b) Fuller's earth, (c) kaolin and (d) silica; at 600 C (●), 400 C (□), 150 C (Δ) and no heat treatment (x).

pressed in terms of $\frac{n_o \Delta x}{m}$, where n_o is the number of moles of substances (solute and solvent) originally present, Δx is the change in mole fraction of β-carotene and m is the number of grams of adsorbent, was plotted against the mole fraction of β-carotene in the supernatant solution. As seen in Figure 2, the activities of the various adsorbents for removal of β-carotene at 30 C decreased in this order: tonsil, Fuller's earth, silica, and kaolin. The isotherm for tonsil is a straight line and possibly corresponds to the low concentration portion of the Langmuir adsorption isotherm. For Fuller's earth and kaolin, isotherms of the Langmuir type were obtained. For silica, an s-shaped curve was obtained.

It is difficult to obtain an exact comparison of the activities of the various adsorbents. A rough estimate from the apparent adsorption isotherms indicates that silica and kaolin are comparable in activity while Fuller's earth has activity of the order of about 10 times more. Tonsil is very much more active than Fuller's earth.

Effect of Heat Treatment of the Adsorbents

Heat treatment of solid adsorbents greatly affects their physical properties as well as their catalytic activities because of either changes in surface area or development of surface active sites or both (8). The activity for removal of β-carotene from solution for the adsorbents under study increased after heat treatment for 4 hr in air at 150, 400 and 600 C (FIG. 3).

For tonsil, the activity increased rapidly with increase in heat treatment up to 400 C but leveled off and then decreased when the temperature was increased from 400 to 600 C. The activities for the untreated, 150, 400 and 600 C heat-treated samples are in the ratio of 1:3:9:5 (FIG. 3, a). The activity of Fuller's earth remained unchanged when heat-treated at 150 C, but increased rapidly after heat treatment at 400 C, and no further significant change in activity was observed when the sample was heated to 600 C. The samples heated at 400 C were ca. 7 times more active than the untreated sample (FIG. 3, b). For kaolin, the activity of the 150 C treated samples were comparable to the untreated sample. The samples heated at 400 C were about twice as active, and the activity of the samples at 600 C were slightly lower than the samples treated at 400 C (FIG. 3, c). For silica, the adsorptive activity remained relatively unaffected when heated in air up to 400 C. Heat treatment at higher temperatures decreased the activity appreciably. Samples heat-treated at 600 C were about half as active as the untreated sample (FIG. 3, d).

These observations can be explained in terms of the known effect of heat treatment on solid adsorbents. Since these adsorbents have been calcined at ca. 500 C during their preparation, heat treatment at below 500 C should not change their physical structure appreciably. However, heat treatment at higher temperatures, depending upon the stability of the adsorbent concerned, may lead to a collapse in structure, thus decreasing the surface area. To test this, the surface area of tonsil after heat treatment at various temperatures were measured by the BET method with nitrogen adsorption. The untreated sample had a surface area of 171 m^2 g^{-1}, while the 400 and 600 C heat-treated samples had surface areas of 189 m^2 g^{-1} and 105 m^2 g^{-1} respectively. Thus, the physical structure of tonsil collapsed when heat-treated at 600 C as indicated by the decrease in surface area. The decrease in activity for tonsil, and similarly for kaolin and silica, when heat-treated at 600 C may thus be explained by a decrease in available sites for adsorption/reaction.

Although the surface area of the adsorbents did not increase with heat treatment below 400 C, such treatment drove off excess water or other gases and burnt off any organic matter present. This process exposed the active sites that may be responsible for chemisorption and subse-

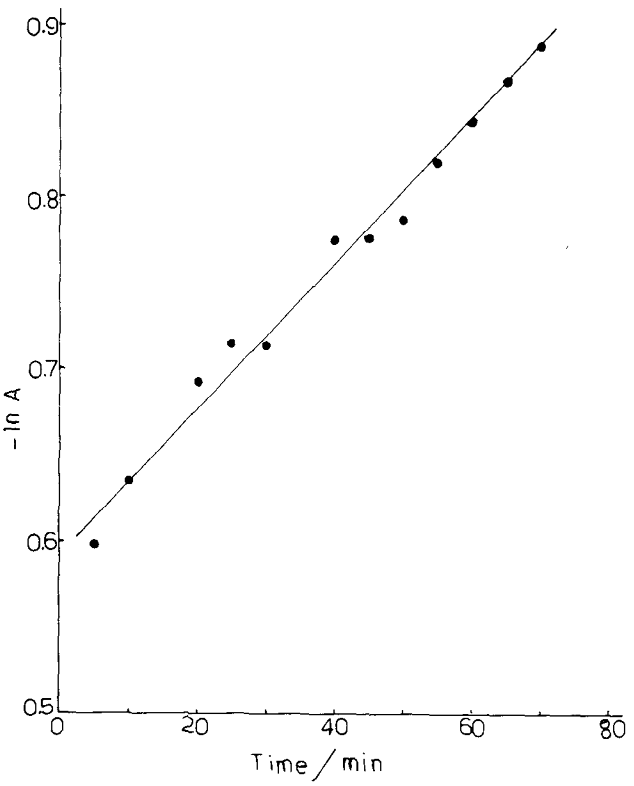

FIG. 4. First order rate plot for the removal of β-carotene by tonsil at 27 C, plotted as a negative logarithm of the absorbance of the supernatant solution vs. time.

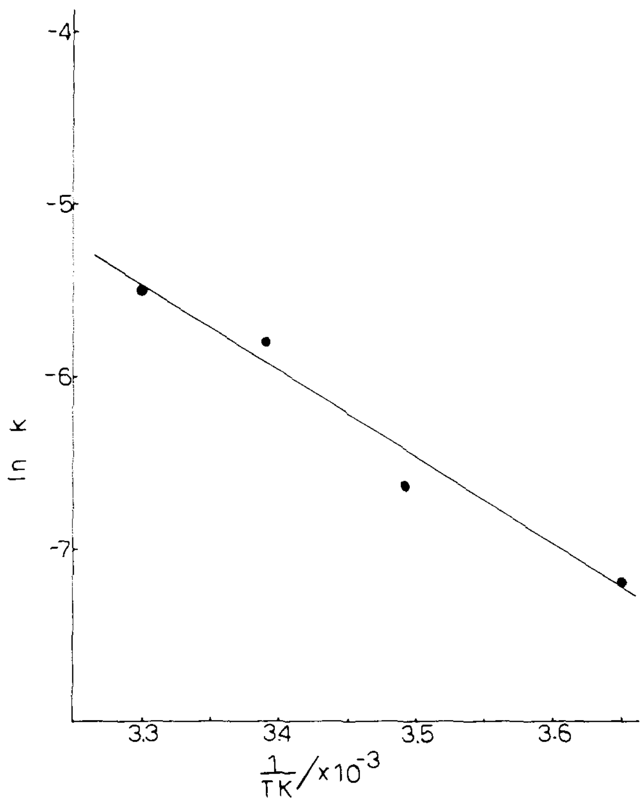

FIG. 5. Arrhenius plot for removal of β-carotene by tonsil.

quently reaction, thereby increasing the activity at the surface. This is consistent with the increase in activity of tonsil, Fuller's earth and kaolin if the process is chemical in nature. That chemical reaction proceeded on the surface of these adsorbents was also collaborated by the observation that the absorption spectrum of the product was different from that of β-carotene. With silica as the adsorbent, the absorption spectrum of the supernatant solution remained unchanged after adsorption, indicative of a physical adsorption process. The main factor that influences the activity is thus the extent of the surface area; that the activity of silica remained unchanged when heat treated below ~500 C can thus be explained.

Effect of Temperature of Reaction

When a solution of β-carotene in acetone was swirled a 1 g sample of untreated tonsil at 27 C, the concentration of the β-carotene in the supernatant solution decreased rapidly initially. Therefore the decrease was less rapid. This initial decrease in concentration may be caused by the rapid physical adsorption of β-carotene on the surface. When the natural logarithm of the absorbance at 453 nm was plotted against time after the initial rapid decrease, a straight line was obtained (FIG. 4), indicating a first order decrease in β-carotene concentration with time. The first order rate constant was determined to be 7.0 x 10^{-5} s^{-1} at this temperature. Considering that the apparent adsorption isotherm for β-carotene on tonsil at this concentration range was a straight line, presumably corresponding to the straight line portion of a Langmuir adsorption isotherm, the adsorbed molecule formed less than a monolayer on the surface. The first order dependence of the rate on the supernatant concentration can thus be explained.

The experiment was repeated at 1, 13, 22, and 30 C. The rate increased with increases in the temperature of reaction. The Arrhenius plot is shown in Figure 5. The apparent activation energy was determined to be 10 kcal mol^{-1}. A temperature effect of this magnitude cannot be explained alone by a physical adsorption process of β-carotene on tonsil. However, more work is required to ascertain the nature of the chemical reaction/adsorption that proceeds on this surface.

Effect of Oxygen and Metallic Ion

It has long been known that β-carotene undergoes oxidation with molecular oxygen in homogeneous solution (9,10). The following experiments were carried out with the rigorous exclusion of oxygen from the reaction system. A sample of tonsil was degassed in high vaccum (better than 10^{-5} mm Hg) at 400 C for 3 hr. This sample was then transferred, under an atmosphere of dried nitrogen, into a stoppered flask containing 10 ml of 0.004 g/l β-carotene in acetone solution which had previously been degassed by 3 cycles of freeze-degas-thaw. The resulting mixture was stored under nitrogen for 24 hr. The supernatant solution turned green and the absorption spectrum was measured (FIG. 1, curve d). Very little β-carotene was left in the supernatant solution, being replaced by substance(s) which absorbs at 360 and 330 nm. This absorption spectrum was similar to that of the supernatant solution of the carotene-tonsil system in the presence of air after 24 hr. A similar result was obtained using Fuller's earth instead of tonsil as the adsorbent.

Metallic ions such as Fe^{3+} or Cu^{2+} are known to catalyze the decomposition of β-carotene. (11,12). Experiments were performed to investigate the effect of Fe^{3+} ion which is present in appreciable amount in the samples of tonsil and Fuller's earth used in this investigation. To a 10 ml solution of 0.004 g/l β-carotene in acetone, a few crystals of anhydrous ferric chloride were added. The solution turned green rapidly and after 24 hr, no β-carotene was detected. The resulting substance(s) absorbed at 370 and 330 nm (FIG. 1, curve e).

When a few crystals of ferric chloride and hydroquinone, which is a powerful antioxidant, were added to 10 ml of a 0.004 g/l β-carotene in acetone solution and allowed to stand for 24 hr, the resulting solution absorbed at 340 nm (FIG. 1, curve f).

These results demonstrate that oxygen was not essential for the reaction of β-carotene that occurs on the surface of the clay minerals. It is highly probable that metallic ions, such as Fe^{3+}, which are present on the surface of the clay adsorbent catalyzed the reaction or served as active sites for the chemisorption of β-carotene. It is believed that the reaction is probably an isomerization similar to that reported when alumina was used as an absorbent (13). Studies on the nature of the chemisorption reaction are in progress.

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