

Adsorption of Carotene from Palm Oil by Acid-Treated Rice Hull Ash

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Rice hull ash obtained by heat treatment and acid activated followed by washing was not effective as an adsorbent for carotene in palm oil in contrast to that reported for adsorption of soy oil lutein. However, unwashed acid-activated ash had activity much higher than carbon and silica but slightly less than a commercial bleaching clay. Heat treatment of raw rice hulls at temperatures below 300°C resulted in the most active adsorbent after acid activation. Drying the unwashed acid-activated ash at temperatures higher than 200°C reduced the activity. The activity of the acid ash was attributed to adsorbed acid. The results also suggested that the removal of carotene in palm oil was caused by chemical interactions involving the adsorbed acid and the carotene. The small amount of Fe³⁺ in the ash was not responsible for the activity.

KEY WORDS: Acid treatment, carotene adsorption, palm oil, rice hull ash.

The annual world production of palm oil in 1990–1991 was 11.2 million tons, challenging the position of soy oil as the leading edible oil (1). Palm oil refining has thus become an important sector in major palm oil-producing countries such as Malaysia and Indonesia.

Crude palm oil has an intense orange color because of its high carotenoid content, which can amount to as much as 600 ppm (2). Thus, a major consideration in the refining of the oil is the removal of the carotenoid components along with the other impurities. Two refining processes are in use, chemical refining and physical refining. In chemical refining, adsorptive bleaching with clay removes almost all of the colored compounds, whereas in physical refining a large portion of the carotenoid pigments are removed by the bleaching clay with the remainder being removed during deodorization. Commercial bleaching clays are generally acid-activated montmorillonite clays. The acid activation dissolves some of the aluminum ions from the lattice and leaches mineral salts constituents, which causes the surface and pore structures to be modified. The process also replaces exchangeable cations with H⁺ ions (3). It has been demonstrated that the adsorption of carotene by bleaching clays is a chemical process (4), and that the acid sites and metallic ions, such as Fe³⁺, are active sites for adsorption (5).

A number of investigations have been carried out recently to examine other materials, such as zeolites (6), carbon (7), okija clay of Nigeria (8), clay from Turkey (9) and silicic acid (10), as alternatives to conventional bleaching clays. It has also been reported that rice hull ash can be converted into an effective adsorbent for lutein in soy oil, and that acid activation promotes adsorption (11). Acid-treated rice hull ash, obtained by heating raw ash at 500°C and above, followed by acid treatment and washing until nearly neutral, has been reported to

have activity comparable to bleaching clay for the adsorption of soy oil lutein (10).

The present investigation is a study of the effect of acid treatment of rice hull ash on the adsorptive activity for carotene in palm oil.

EXPERIMENTAL PROCEDURES

Crude palm oil obtained from Palmex Industries Sdn. Bhd. (Penang, Malaysia), with an iodine value of 55, a peroxide value of 2 meq/kg, a free fatty acid content of 2.2% and a moisture content of 0.1% was used without further treatment. The activated carbon used in this work was bought from BDH Chemicals Ltd. (Poole, England), silica from Merck Co. (Darmstadt, Germany) and acid-activated bleaching clay Filtrol 105 was donated by Palmex Palm Oil Refineries (Penang, Malaysia).

Raw rice hulls were obtained from a local rice miller. These hulls were washed with deionized water to remove any adhering dirt particles and dried overnight at 120°C. They were then heated at temperatures between 200 to 800°C in a muffle furnace for 10 h with circulation of air. The resulting materials were then ground and sieved to produce a particle size of less than 180 μm. This material was designated untreated ash. The pH values of these materials were between 8 and 9.

The ash was stirred with 20% H₂SO₄ for 5 h at room temperature, filtered under suction, then further dried at 120°C overnight and stored in stoppered glass bottles. These materials were designated unwashed acid ash. Washed acid ash was obtained by washing the acid-treated ash with deionized water until the ash attained a pH between 4 and 5, drying in an oven at 120°C overnight and storing in stoppered glass bottles.

Palm oil in hexane miscellas was prepared by stirring heated crude palm oil into spectrargrade hexane that had been dried before with activated 4A molecular sieve in volumetric flasks. Most experiments were performed by adding the ash, usually 3 g, into 50 mL of palm oil hexane miscellas in black stoppered plastic bottles, which in turn were placed in a shaker at 30°C. Samples of the solution were withdrawn with a pipette fitted with a sintered glass filter. All experimental data are means of duplicates.

Carotene contents were measured by using a digital ultraviolet spectrometer at 446 nm after the withdrawn oil samples were diluted appropriately with spectrargrade hexane. Pure β-carotene (>99%) obtained from Sigma Chemical Co. (St. Louis, MO) was used to prepare the calibration curve.

The pH of the ash was determined on the supernatant after stirring 1 g of the sample in 50 mL of distilled water.

RESULTS AND DISCUSSION

Preliminary experiments indicated that untreated ash obtained by heating alone had little activity for the adsorption of carotene from palm oil. The ash after treatment with acid and washing improved the adsorptive activity but still did not significantly decolorize the palm oil. However, when the unwashed acid ash was shaken

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with a 20% wt/vol crude palm oil, containing 520 ppm of carotene, in hexane, the residual carotene content in solution decreased rapidly during the first 15 min, then gradually during the next hour (Fig. 1). Thereafter, the residual carotene content in solution decreased slowly. Thus, for subsequent experiments, carotene contents were measured after a contact time of 1.0 h for comparison of adsorptive activities.

The relative adsorptive activities, as measured by the residual carotene contents at various amounts of untreated and unwashed acid ash, were compared with some common adsorbents (Fig. 2). The untreated ash had less activity than silica and carbon, which in turn have much lower adsorptive activities for carotene than the unwashed acid ash and a commercial bleaching clay (Filtrol). PreadSORption of acid on carbon increased its adsorptive activity (Fig. 2). However, the activities of such acid-treated materials were still appreciably lower than those of unwashed ash and Filtrol.

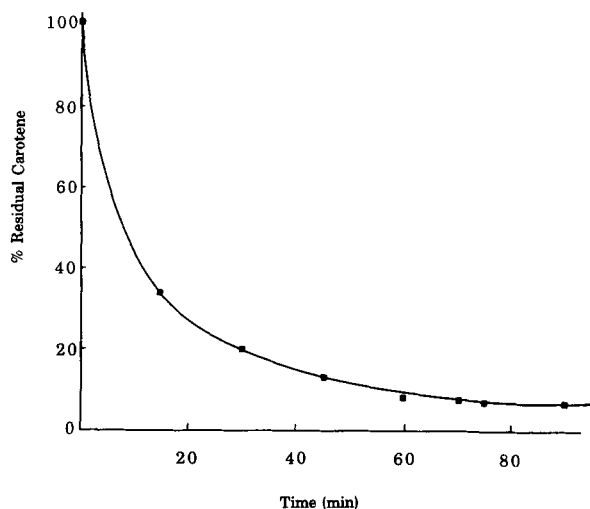


FIG. 1. Effect of contact time with 3 g of unwashed acid ash on residual carotene.

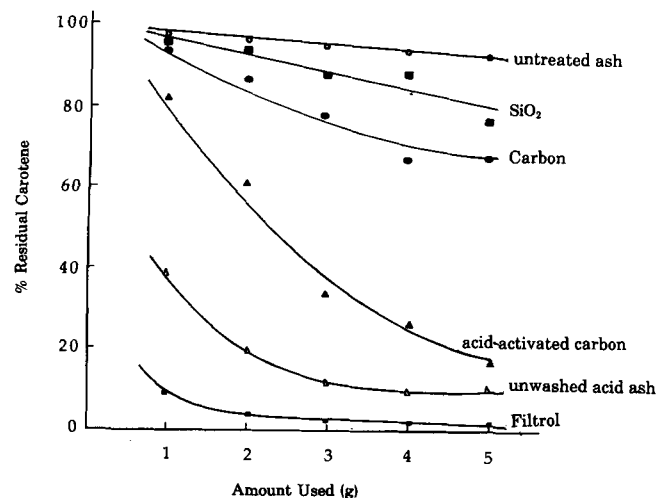


FIG. 2. Effect of the amount of untreated rice hull ash, SiO_2 , carbon, acid-treated carbon, unwashed acid ash and Filtrol on residual carotene.

Acid sites on bleaching clay and other adsorbents are effective adsorption centers for carotene (4). The above results demonstrated that sulfuric acid adsorbed on various adsorbents can function similarly. Further, the activities of the washed and unwashed acid ash were studied and the results compared in Figure 3. The washed acid ash obtained by heating at temperatures from 200 to 800°C, followed by acid treatment and washed to pH 4–5, had low activities for adsorption of carotene in palm oil. The washed acid ash obtained after heat treatment at 200°C was most active. The amount of carotene removed from solution was about 0.43 mg per g of adsorbent. Although the amount of carotene removed was similar to the adsorption of lutein from soy oil [≈ 0.3 mg per gram of adsorbent (10)], the washed acid ash was not effective in removing carotene from palm oil.

The unwashed acid ash had much higher activity than the washed acid ash. Generally, the washed acid ash removed less than 20% of the carotene. About 90% of the carotene in the palm oil hexane miscella was removed by the 200 and 300°C unwashed acid ash. The activity of unwashed acid ash decreased when ashing temperature increased. The higher activity of the lower-temperature ash may be explained by the difference in compositions of the materials. At ashing temperatures lower than 500°C, the raw hull was incompletely combusted, and the resulting materials were composite mixtures of silica and carbonaceous materials (12). The acid retained on these materials may be much higher, leading to higher activity. The decreasing activities of the ash, obtained by heat treatment at temperatures higher than 500°C, which are nearly pure silica, may be caused by a collapse of the surface area, which in turn caused less acid to be retained.

The role of acid in the adsorptive activity of the ash was further demonstrated. The 300°C unwashed acid ash was dried at various temperatures. The resulting materials were used as adsorbents. As the drying temperature of the unwashed acid ash was increased from 120 to 500°C, the pH of the resulting ash increased from 0.7 to 6.4. At the same time the activity decreased markedly as the temperature of drying increased above 200°C (Fig. 4). As the pH of the ash reached 6.4 at the drying temperature of 500°C,

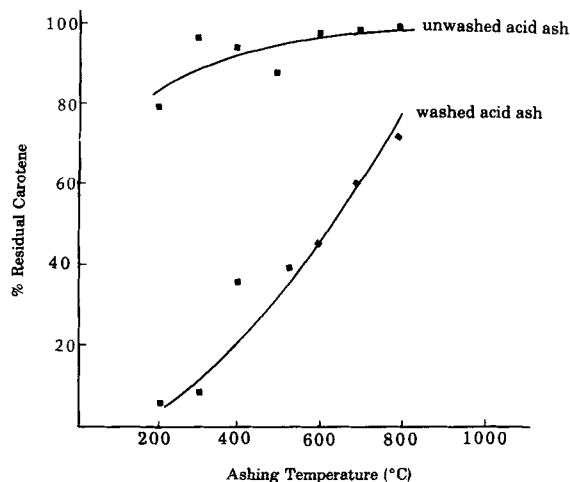


FIG. 3. Effect of activation temperature on the residual carotene after adsorption by rice hull ash samples.

SHORT COMMUNICATION

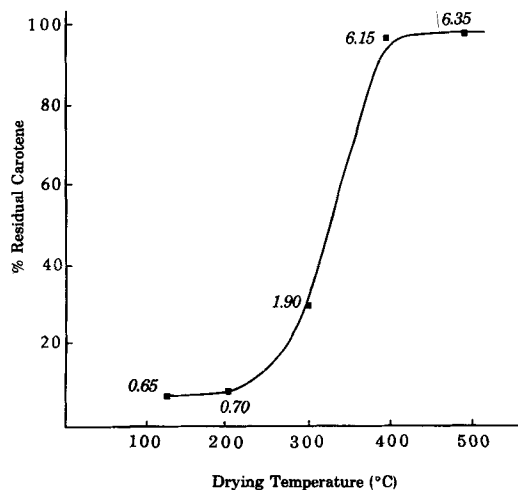


FIG. 4. Effect of drying temperature on the relative adsorptive activity of rice hull ash activated at 300°C and treated with 20% H₂SO₄. The figures adjacent to the points show the pH of the adsorbents.

the residual carotene amounted to more than 90%. It is unlikely that the surface area of the material appreciably decreased at this temperature. The change in activity was probably caused by the change in acidities of the materials.

Rice hull ash contains small amounts of ferric and other cations. The concentration of ferric ions in the ash obtained by heating at 500°C was about 0.1% (12). Fe³⁺ ions in bleaching clays are highly active on the removal of β-carotene from solution (5). The activity increases linearly with the amount of exchanged Fe³⁺ ions in the clay. In this work, precipitation of less than 1% ferric ions on the surface of the ash had little effect on the carotene adsorption. Thus, the small amount of Fe³⁺ ion originally present on the ash was not responsible for the high activities of the acid-treated sample.

The ash obtained by heating at 300°C was treated with different concentrations of sulfuric acid, ranging from 5 to 30%, followed by drying at 120°C. The activities of the resulting materials were studied for adsorption of carotene in palm oil. Initially, the activity was observed to increase with increases of sulfuric acid concentrations. At 10% concentration, maximum activity was observed while the use of higher acid concentrations only resulted in similar activity levels (Fig. 5.).

The results may be summarized as follows. Untreated rice hull ash has little activity for adsorption of carotene from palm oil. PreadSORPTION of sulfuric acid on the ash greatly increased the carotene removal activity to a level approaching that of a commercial bleaching clay. PreadSORPTION of acid similarly increased the activity of carbon. Washing and drying at high temperature of the acid-treated ash removed the acidity and led to greatly decreased activity. Ferric ions, which were presented in small concentration in the ash, were not responsible for the high

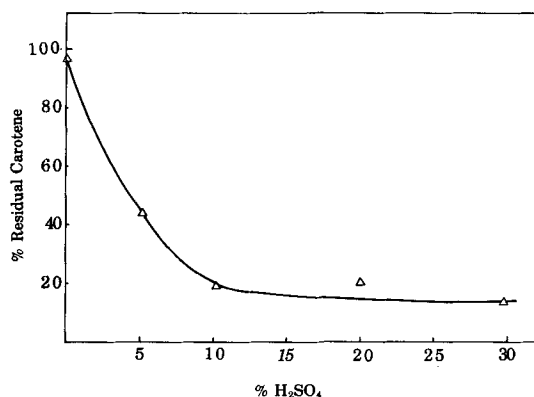


FIG. 5. Effect of H₂SO₄ concentration used for activating rice hull ash on the adsorptive activity of the ash.

carotene removal activity of the unwashed acid ash. The activity of the acid ash was thus demonstrated to be associated with the preadsorbed acid.

For silica (4) and carbon (13), the carotene removal from solution was found to be caused through physical adsorption, whereas the removal of carotene by H⁺-exchanged clays from solution was likely caused by a chemisorption process, followed by a reaction involving the acid sites and the adsorbate (4). On the unwashed acid ash prepared for the present work, the formation of a green-colored compound, which disappeared over a period of time, was clearly observed, especially with the more acidic ash. It is thus likely that carotene removal from crude palm oil in hexane miscellas by the highly acidic rice hull ash was a result of the surface reaction involving the adsorbed acid.

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