X-Ray Diffraction and Scanning Electron Microscope Studies of Processed Rice Hull Silica

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The structure and composition of processed rice hull ash were studied to better understand its adsorption of the soy oil components, lutein and free fatty acids. The silica-rich ash was composed largely of low order cristobalite and tridymite in the form of opal CT, with variable particle size. On heating of the ash there was conversion to a more ordered form of opal C, fusing of particles, and loss of potassium. Acid washing, following heating, also removed potassium and slightly reduced particle size further. Crystal form, particle size, particle fusion and potassium content may be important factors influencing ash adsorption of soy oil components.

KEY WORDS: Cristobalite, opal C, opal CT, rice hull ash, silica, tridymite.

Rice hulls contain a very high concentration of silica and were investigated in the early 1950's by ceramic engineers as a source of raw material (1,2). More recently, rice hull ash has been evaluated as an adsorbent of vegetable oil components (3,4), and in the future may have value in the commercial bleaching of vegetable oils. Currently, montmorillonite clays are used to adsorb carotenoids and chlorophyll to decolorize soy oil. In addition, residual phospholipids, soaps and free fatty acids (FFA) remaining after previous refining steps are bound.

An inorganic ash prepared from rice hulls can adsorb the carotenoid lutein (3) and FFA (4) from a crude soy oil/hexane miscella. The inorganic ash is derived from commercially combusted rice hulls which contain approximately 45% carbon. The inorganic ash consists almost exclusively of silica, in the form of cristobalite and tridymite (5).

The ash is prepared by heating partially burned rice hulls at 500°C. Temperatures greater than 500°C decrease the adsorption properties of the ash (3,4). Acid treatment decreases the pH of the ash and promotes adsorption of lutein (3), but decreases adsorption of FFA (4). Adsorption follows a Freundlich isotherm, and is similar to the adsorption of lutein by silicic acid (6).

The objective of the following investigation was to obtain a better understanding of processed rice hull ashs by studying ash structure and composition. The effects of thermal and acid treatment on structure and composition were examined using X-ray diffraction, electron microscopy and energy dispersive analytical X-ray spectrometry (EDAX).

MATERIALS AND METHODS

Sample preparation. Rice hull ash was prepared according to the method of Proctor and Palaniappan (3,4). Partially combusted rice hull ash, or "raw ash", donated by Riviana Foods (Houston, TX), was heated at 500°C for 10 hr in a muffle furnace. Additional samples were heated in a similar manner at 800°C and 1000°C. These samples will be referred to as alkaline ash.

Samples of ash heated at 500°C were acid activated by mixing with 20% sulfuric acid followed by repeated rinsing with distilled water, as described by Proctor and Palaniappan (3,4), and designated acid ash.

Sample analysis: X-ray diffraction. Alkaline ash or acid ash were ground with a pestle in a mortar to a fine powder for analysis. Copper Kα radiation was generated by a Philips 3500 X-ray diffractometer (Philips, Cincinnati, OH), utilizing an acceleration voltage of 35 kv and a current of 15 mamp. A diffraction angle of 4-40°C 2θ was scanned at a rate of 1 deg/min and 500 cps full scale.

Scanning electron microscopy (SEM). The appearance of the ashes was observed with a ISI scanning electron microscope (Los Angeles, CA). A 30 kv accelerating voltage was utilized, with an electron beam directed at an angle of 45° to the samples. Inorganic composition of various ash types was found with a EDAX 9900 instrument.

RESULTS AND DISCUSSION

The X-ray diffraction data from raw ash, alkaline ash (obtained by 10 hr at 500°C), and acid ash (obtained by sulfuric acid treatment of alkaline ash) are in Figure 1. There is a well defined peak at approximately 22° 2θ in all three samples. This corresponds to a d spacing of 4.0-4-1 Å, which is characteristic of α-cristobalite. α-Cristobalite exists in opal minerals. Opals are classified on the basis of the degree of order. Listed in decreasing level of organization, there are: opal C, opal CT and opal A, and can be distinguished by X-ray diffraction patterns (7,8). The traces in Figure 1 are typical of opal CT (7). Such an organization indicates a disordered, relatively open structure (7,8), potentially capable of adsorption. Although the raw ash consists of opal CT, it was not capable of adsorption of soy lutein components at room temperature (3), probably because of carbon residue on the ash surface.

There are minor differences in the traces. Peaks of the acid and alkaline ash are more intense than those of raw ash, probably because the cristobalite in raw ash is diluted with carbon. In the trace from alkaline ash there is a peak at 26.2° 2θ, which would indicate a small quantity of quartz.

Data describing the changes in form of rice hull cristobalite when heated to temperatures of 500°C, 800°C and 1000°C are shown in Figure 2. When the temperature is raised from 500°C to 800°C there is evidence of opal C formation as shown by greater peak intensity at 22° 2θ and an additional peak at 36° 2θ (7,8). In addition, there is tridymite stacking, as marked on the trace. This represents a change in structure from a disordered random stacking of cristobalite and

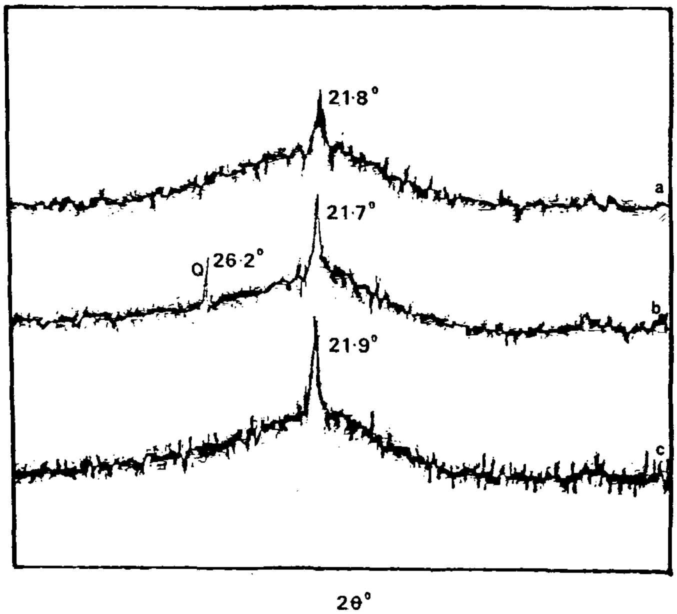

FIG. 1. Powder X-ray diffraction patterns of (a) raw rice hull ash; (b) alkaline ash heated at 500°C; and (c) acid-activated ash previously heated at 500°C. The x axis is 2 × the Bragg diffraction angle (2θ). Q = quartz, other peaks are cristobalite.

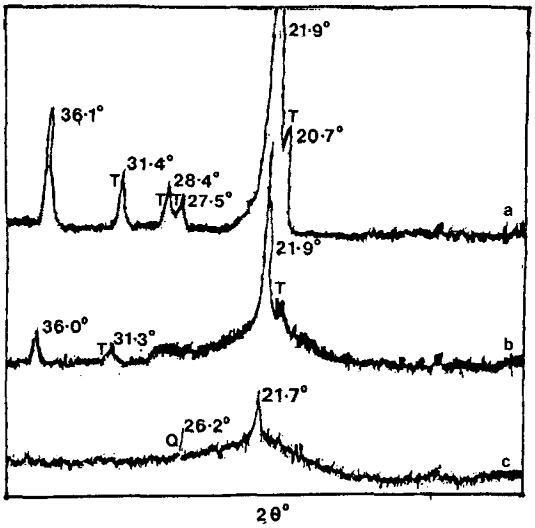

FIG. 2. Powder X-ray diffraction patterns of (a) alkaline ash heated at 1000°C; (b) 800°C; and (c) at 500°C. The x axis is 2 × the Bragg diffraction angle (2θ). Q = quartz, T = tridymite, other peaks are cristobalite. (Traces are not exactly superimposable on the same x axis scale.)

tridymite, typical of opal CT, to highly ordered cristobalite and tridymite as found in opal C (8). Cristobalite, in this form, is a cubic closed packed silica, stacked in an ABCABC pattern, and tridymite is a hexagonal closed packed silicon oxide with ABABAB packing (8). This increase in crystal organization would effectively reduce the available surface area and restrict adsorption capacity, as has been observed (3,4). Heating to 1000°C increases the intensity of the cristobalite peaks at 22° 2θ and 36° 2θ and tridymite stacking become increasingly evident. Additional peaks, not shown on the trace, were observed at 42.6° 2θ, 44.7° 2θ, 46.9° 2θ and 48.5° 2θ. These are typical of opal C (7).

Loss of the disordered structure upon heating may significantly contribute to the loss of ash adsorption capacity. However, when rice hulls are commercially converted to raw ash they are heated at temperatures equal or greater than 1000°C. Their relatively amorphous state may be due to the thermal insulation properties of the ash itself (1).

The SEM photographs in Figures 3a and 3b show the appearance of raw ash when magnified × 20 and × 100, respectively. It appears as a heterogenous mass of coiled and fragmented sheets. The dome-shaped outline, of the epidermal cells is responsible for the 'corn cob' appearance (1).

The SEM structure of alkaline ash heated at 500°C is shown in Figures 4a and 4b. Particle size is considerably reduced on heating and is in a variety of shapes and sizes. Although there is much fracturing, the "corn cob" appearance is still evident. At higher magnification the internal silica "cell walls" are exposed, giving a "ribbed" appearance (Fig. 4c). Particle sizes range from approximately 10–1000 microns. The SEM structure is very dissimilar from that of a commercial adsorbent. Observations with official acid-activated bleaching clay (American Oil Chemists' Society, Champaign, IL) showed uniform spherical particle no larger than 30 microns in diameter (data not shown).

Upon acid activation there is slight decrease in particle size, probably due to additional handling and processing, but otherwise there is little difference relative to alkaline ash (Figs. 5a and 5b).

Heating to 800°C results in a somewhat "glassy" appearance of the ash at 100 × magnification (Figs. 6a and 6b). This coincides with the conversion of opal CT to opal C and loss in adsorptive capacity (3,4). At 1000°C (Figs. 7a and 7b) the "glassy" appearance becomes more obvious. There are very few small particles, and some ash fragments appear to be fused together.

Inorganic chemical analyses of the SEM samples were done by EDAX as shown in Table 1. Silicon and potassium were the only elements detected, with silicon by far the most abundant. Silicon oxide is 96% of the raw ash with the remaining 4% being potassium oxide. Jones (2) reported 94.5% silicon oxide and 1.1% potassium oxide in the raw ash. Smaller amounts of the oxides of Ca, Mg, Na and P also were present. However, Jones did not report the ashing temperature.

There was little difference in silica content of the inorganic material of raw ash and 500°C heated alkaline ash, except that the potassium oxide content was reduced and 1% aluminum oxide was detected (not

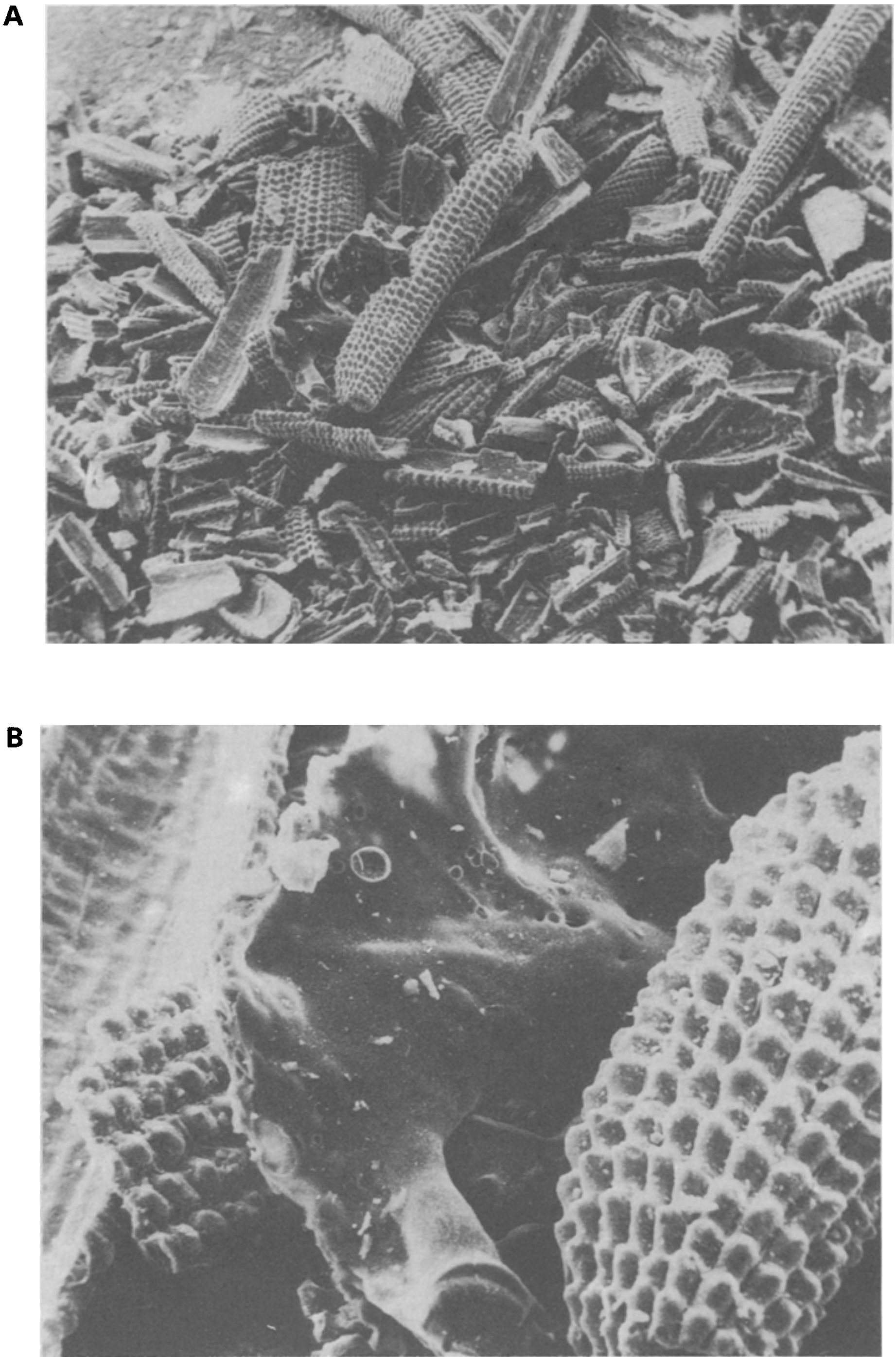

FIG. 3. SEM micrographs of raw ash, magnification (a) × 20, and (b) × 100.

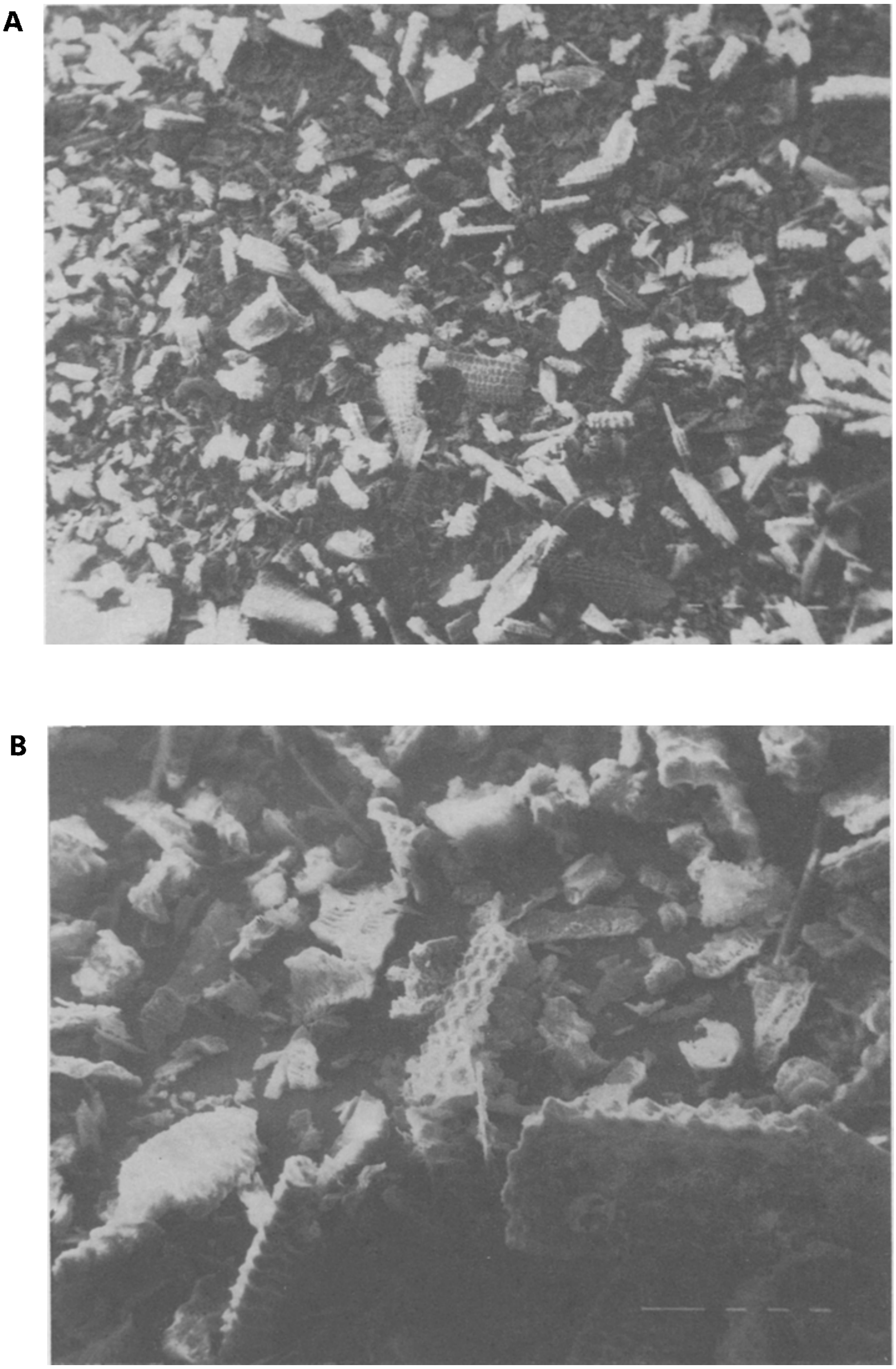

FIG. 4. SEM micrographs of alkaline ash (500°C), magnification (a) × 19; (b) × 100 (long bar is 100 μ); and (c) × 1000 (long bar is 10 μ).

FIG. 4c

FIG. 5. SEM micrograph of acid activated ash, magnification (a) × 20, and (b) × 100 (long bar is 100 μ).

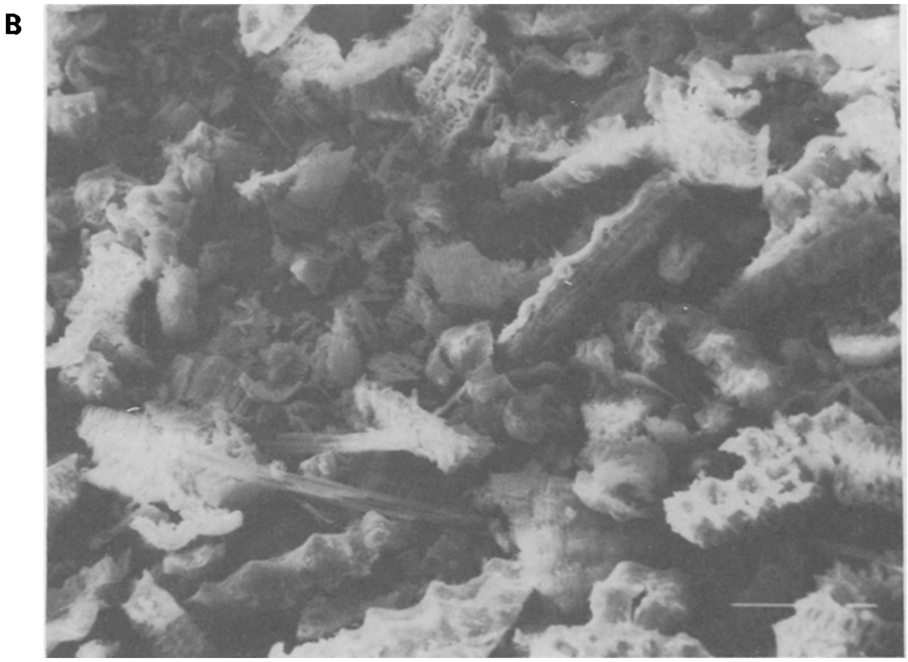

FIG. 5b

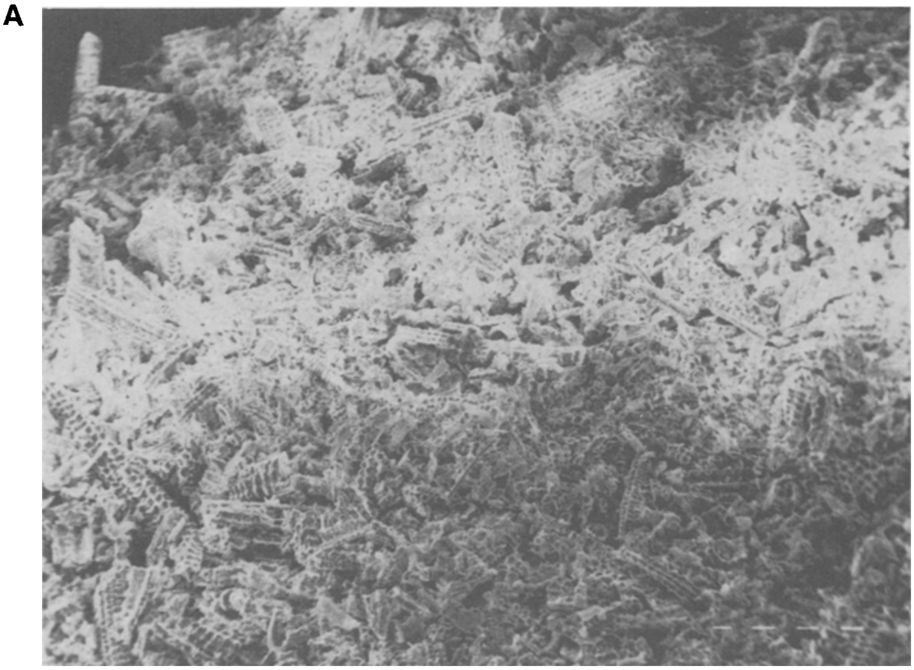

FIG. 6. SEM micrograph of alkaline ash heated to 800°C, magnification (a) × 20, and (b) × 100 (Long bar is 100 μ).

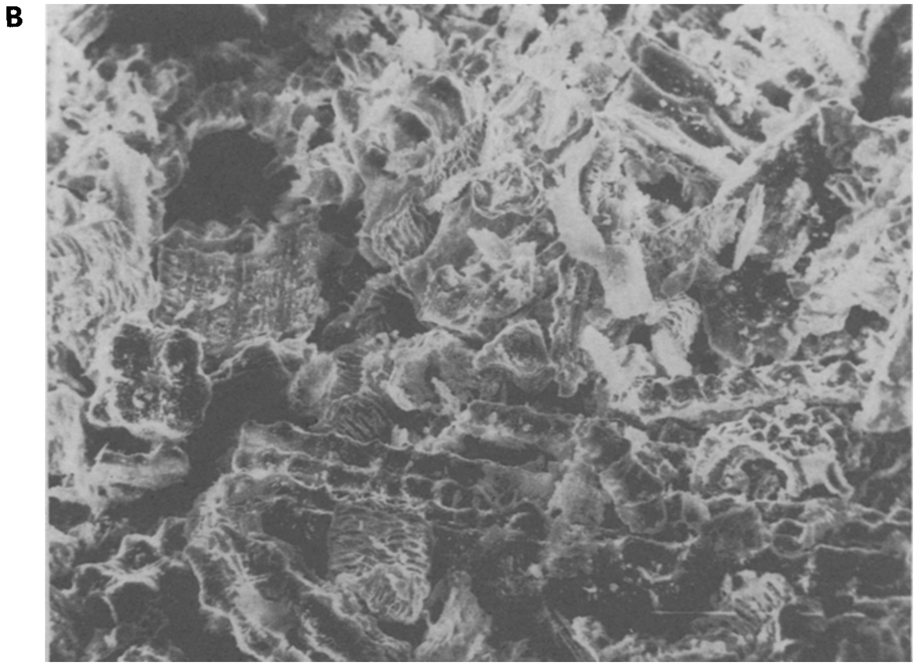

FIG. 6b

FIG. 7. SEM micrograph of ash heated to 1000°C, magnification (a) × 20, and (b) × 100 (long bar is 100 μ).

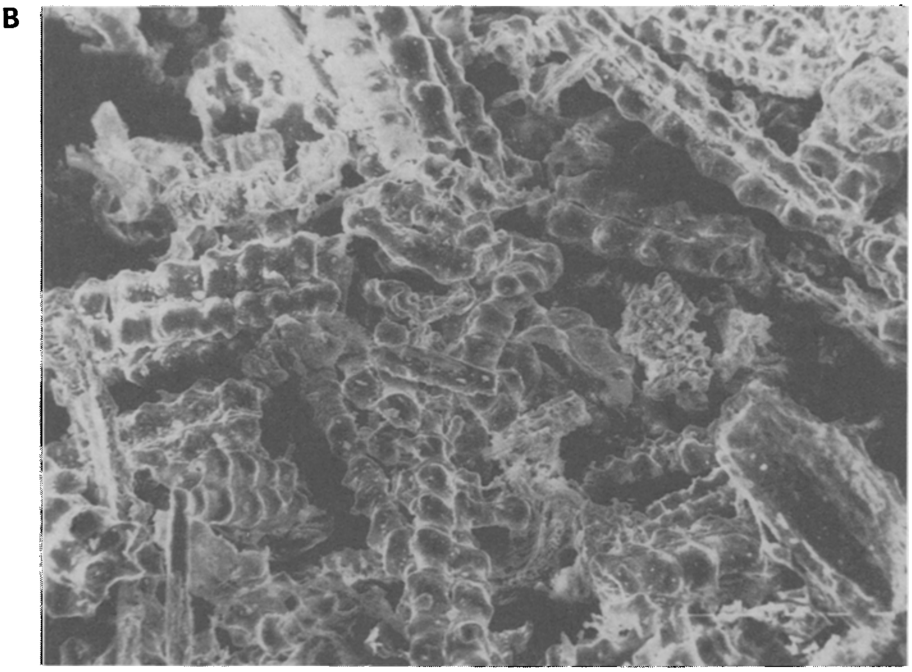

FIG. 7b

TABLE 1

Inorganic Composition of Processed Rice Hull Ash. Data Determined by Using an EDAX 9900

	Silicon oxide (%)	Potassium oxide (%)
Raw ash	96	4
Alkaline ash (500°C)	97	2
Alkaline ash (800°C)	99	1
Alkaline ash (1000°C)	100	—
Acid ash (500°C)	100	—

shown in Table). As the temperature was increased there was a further loss of potassium oxide. At 1000°C the ash was exclusively silica (Table 1).

The effect of acid activation of 500°C treated alkaline ash was the same as with 1000°C treated ash alone, namely the removal of potassium oxide, with a decrease in adsorbent pH. Like the 1000°C treated alkaline ash, the acid ash consisted only of silica, yet it had much greater adsorption properties (3,4).

This investigation has shown that native rice hull silica exists as disordered opal CT. In this form it was capable of adsorbing lutein and FFA from soy oil. On heating, hull silicate is converted from opal CT to a more crystalline opal C structure, resulting in a loss of adsorbent performance and potassium oxide. Enhanced lutein binding by acid activation may be due to the removal of traces of alkali oxide, but the presence of these oxides enhanced binding of FFA. Alkali oxide may possibly compete with lutein for binding sites (3,6) and modify adsorption sites to favor FFA retention (4).

Ash particle size was very variable and heterogenous as compared to conventioal bleaching clays. The original epidermal cell form, preserved in the "corn cob" structure, suggests that there is an internal area in each hollow sphere which is not being used as an adsorbent surface. This is supported by evidence of the insulating properties of the material (1). Insulation properties of the ash could explain the maintainance of the microstructure of the ash after commercial ashing. The data suggest that adsorbent performance might be enhanced by reducing particle size to at least 10 microns, i.e., less than the rice epidermal cell diameter.

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