Adsorption of Soy Oil Free Fatty Acids by Rice Hull Ash

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Studies demonstrated that free fatty acids can be adsorbed from a soybean oil/hexane miscella by inorganic rice hull ash. A 1% dose was effective in diminishing free fatty acid concentrations but acid activation reduced the adsorption. Binding of free fatty acids followed a Freundlich isotherm with smaller doses of ash adsorbing more efficiently. Addition of isopropanol to the miscella promoted the adsorption, while water deactivation of the ash had no effect, possibly because water occupied sites not accessible to free fatty acids. Impaired adsorption behavior of ash heated above 700°C could have been due to disruption of the crystal form. The adsorption behavior of rice hull ash may be more fully understood with a better knowledge of adsorbent structure.

A variety of nontriglyceride material is present in crude soybean oil and must be removed to produce an oil of acceptable quality. Conventional refining practices include the separation of phospholipids by hydration (1–3% water) followed by centrifugation (1). Free fatty acids (FFA) are precipitated as soaps, prior to separation by centrifugation (2). Carotenoid and chlorophyll pigments are adsorbed from the oil by bleaching clays at low pressure and high temperature (3). Residual soaps and phospholipids are also adsorbed.

A method for removal of phospholipids from soybean oil in hexane by room temperature adsorption on silica has been described (4). Binding was promoted by 1% isopropanol (IPA) in hexane. Adsorption of FFA onto silica has been reported from a synthetic system of fatty acids (5) and from vegetable oil on zeolites and bleaching clay (6).

In this study, the adsorption of FFA from soybean oil onto a novel adsorbent, rice hull ash was investigated. The ash is a silicate material composed of cristobalite and tridymite (7). Proctor and Palaniappan (8) demonstrated that this material is effective in binding the soy oil pigment, lutein, at 20°C. Acid activation enhanced lutein binding but heat treatment above 600°C reduced it. The pH of a 4% slurry of the nonacid activated ash is 8.7 while that of the acid activated adsorbent is 6.6.

The purposes of this investigation was to study the adsorption of soy oil FFA onto inorganic rice hull ash and to compare the results with recent findings on adsorption of soy oil lutein. The effect of acid activation, heat, dosage and mode of adsorption is discussed.

MATERIALS AND METHODS

Oil and solvents. Crude soy oil was obtained by commercial extraction and stored at 4°C. Soy oil miscellas were prepared by diluting soy oil with hexane. Miscella polarity was modified by addition of IPA.

Ash production. Unless stated otherwise, the adsorbent was prepared as follows. Partially combusted rice hulls were supplied by Riviana Foods (Houston, TX). Since the ash contained appreciable amounts of carbon, further combustion was necessary to obtain an exclusively inorganic material. Samples were heated at 500°C for 10 hr in a muffle furnace. This material was designated as "alkaline ash" (pH 8.7). Forty grams of alkaline ash was mixed with 1 L of 20% (v/v) sulfuric acid for 5 hr at 20°C before being washed with an excess of deionized water, filtered and dried in an oven at 100°C for 4 hr. This material was designated as "acid ash" (pH 6.6).

Free fatty acid analysis. The FFA content was determined by titration according to the AOAC official method (9).

Ash dosage and free fatty acid adsorption. Zero, 1, 2, 3, 4, and 5 g doses of acid and alkaline ash were each added to 100 ml of 20% (v/v) soy oil/hexane miscella of known FFA content. The miscellas were agitated with a magnetic stirrer for 15 min in a closed vessel at 20°C. The residual FFA content was then measured and expressed as a percentage of the miscella, with five replicate readings taken for both adsorbents at each dosage.

Isotherm studies. Free fatty acid isotherms were determined by preparing 100 ml volumes of 10, 20, 30 and 40% (v/v) soybean oil/hexane miscellas. The FFA content of each miscella was determined before a known weight of alkaline ash was added. The miscellas were agitated with a magnetic stirrer for 15 min in a closed vessel with 2, 1 or 0.5 g of alkaline ash. Isotherms were plotted as moles of FFA, expressed as oleic acid, adsorbed per g of ash vs residual concentration of FFA, for each amount of ash used.

Miscella polarity. The isotherm experiment was repeated with 1% v/v IPA in the miscella. The results were compared with those obtained without IPA.

Water deactivation. Alkaline ash was deactivated by adding 5, 10, and 15% w/w water to a flask that was immediately sealed and rotated several times to evenly distribute the moisture. After overnight incubation, an isotherm was obtained with 2 g quantities of hydrated ash, as described above.

Ashing temperature. The effect of ashing temperature on the adsorption of FFA was measured by heating the ash for 10 hr at 500°C, 600°C, 700°C, 800°C, 900°C and 1000°C. The residual FFA content of 100 ml of a 40% soy oil/hexane miscella was measured, and expressed as a percentage of the miscella, after incubation with 2 g of alkaline ash.

RESULTS AND DISCUSSION

Figure 1 shows the change in residual free fatty acid of a 20% soybean oil miscella upon incubation with acid or alkaline ash. Alkaline ash was much more effective than acid ash in reducing FFA content. The difference in the adsorptive capacity of the ashes was particularly marked at dosages greater than 2 g. The re-

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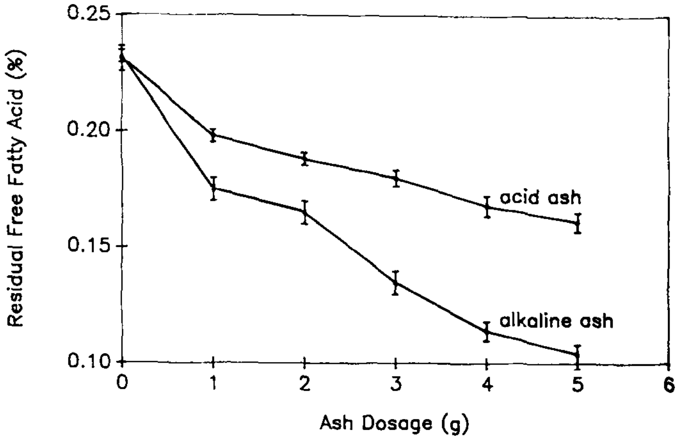

FIG. 1. residual free fatty acid concentrations of the miscellas were determined by incubating 100 ml of 20% miscella (v/v) crude soy oil/hexane for 15 min at 20°C with variable amounts of alkaline rice hull ash and acid rice hull ash. Free fatty acid were measured by titration with 0.1N sodium hydroxide. Bars indicate the standard error of the mean of five replicates.

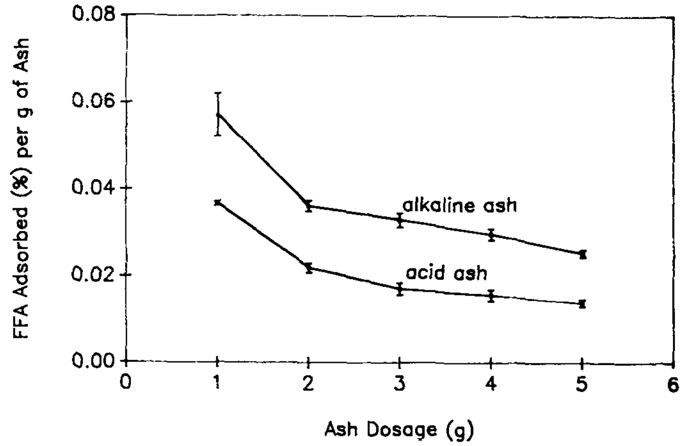

FIG. 2. Free fatty acids (FFA) adsorbed per g of adsorbent was determined by incubating 100 ml of 20% miscella (v/v) crude soy oil/hexane for 15 min at 20°C with variable amounts of alkaline ash and acid ash. Free fatty acid concentrations were measured by titration with 0.1N sodium hydroxide. Bars indicate the standard error of the mean of five replicates.

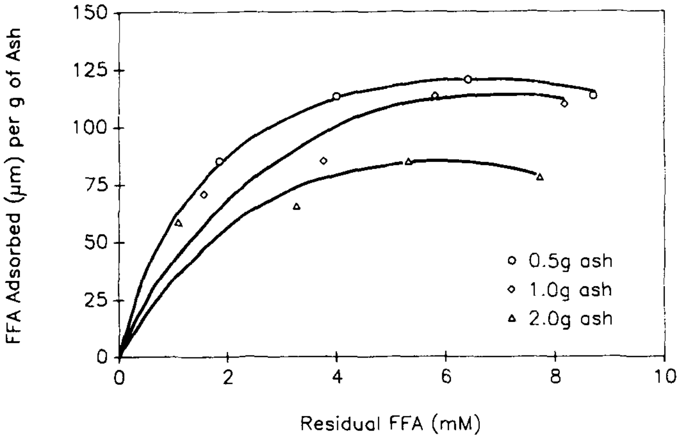

FIG. 3. Free fatty acid (FFA) isotherms were determined by incubating 100 ml of 40%, 30%, 20%, 10% v/v crude soy oil/hexane miscella for 15 min at 20°C with variable amounts of alkaline rice hull ash. Free fatty acid was obtained by titration with 0.1N sodium hydroxide.

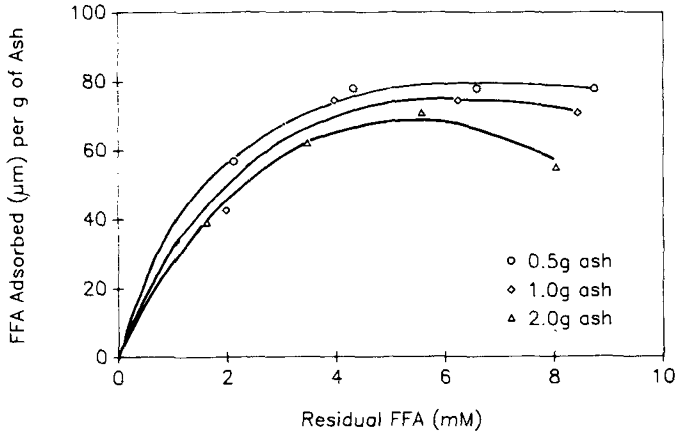

FIG. 4. Free fatty acid (FFA) isotherms were determined by incubating 100 ml of 40%, 30%, 20%, 10% v/v crude soy oil/hexane containing 1% IPA for 15 min at 20°C with variable amounts of alkaline rice hull ash. Free fatty acid was obtained by titration with 0.1N sodium hydroxide.

duction in residual FFA content using 5 g of acid ash (0.23%-0.17%) was accomplished with only 2 g of alkaline ash.

A similar pattern of rice hull adsorption was shown in the binding of the yellow pigment lutein from soybean oil, except that acid ash had the greater adsorptive capacity (8). Acid activation apparently did not increase adsorption of FFA, as is reported for soy oil pigment to montmorillonite earths (10) and rice hull ash (8). Studies of the physical nature of the ash and the structural changes caused by acid activation may help to explain the adsorption behavior of both FFA and pigments.

The percentage of FFA bound per g of adsorbent was expressed as a function of dosage (Fig. 2). The results complimented the data in Figure 1. Alkaline ash was the more effective adsorbent, and the efficiency of adsorption declined with dosage.

The difference in the fatty acid adsorption abilities of acid and alkali adsorbents may be related to their effect on the dissociation of fatty acids. Dissociated fatty acids would be polar compounds more likely to be adsorbed. Since the pK for fatty acids is approximately pH 8, a change in the dissociation of fatty acids could explain the decreased adsorption by the acid ash.

Isotherm studies shown in Figure 3 demonstrated that adsorption is according to a Freundlich isotherm, as reported for soy lutein binding to acid ash (8) or silicic acid (11) and phospholipid to silicic acid (4). More FFA was adsorbed per g of ash with smaller adsorbent doses. The addition of IPA to the miscellas (Fig. 4) enhanced the adsorption of FFA but the differential dose response was maintained. A similar effect of IPA was observed on the adsorption of phospho-

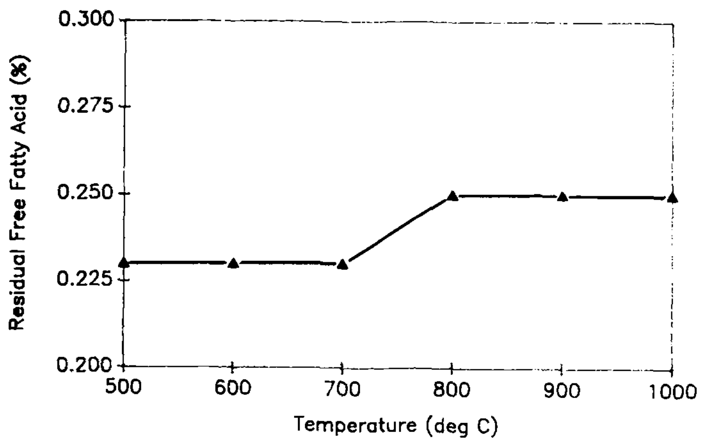

FIG. 5. Residual free fatty acids were determined by incubating 100 ml of 40% crude soy oil/hexane miscella with 2 g of alkaline ash, prepared by heating partially combusted ash at various temperatures. Each point was the mean of five replicates. The standard error of the mean was zero for each point.

lipids onto silica (4). Hydrogen bonding of IPA to weak acidic sites (4,5) may promote FFA binding by hydrophobic interaction. Alternatively, there may be a partitioning of FFA between the polar miscella and preadsorbed lipid material on the ash. In contrast to these findings, IPA inhibited the adsorption of soy oil lutein on silica, probably due to competition for adsorption sites (11). Triglyceride competition occurs in the adsorption of phospholipids (12) and lutein (11) from soy oil on silica, and may be a factor in the adsorption of soy oil components onto rice hull ash. This will be investigated in future studies.

Water deactivation did not have an effect on adsorption of FFA (data not shown). This would seem unusual since the polar IPA promoted adsorption to the ash. It may be that water occupied sites not accesible to FFA. This emphasizes the need for structural data on the adsorbent material.

Figure 5 shows that ashing temperatures above 700°C increases the residual FFA, presumably due to impaired adsorption. Residual values increased from 0.23% to 0.25% when the ash was heated between 700° to 800°C. A similar finding was reported on the adsorption of lutein from a soy oil miscella (8). Impaired adsorption of lutein was observed when ash was heated above 600°C (8). The evidence suggests that at about 700°C the ash undergoes a structural change.

This investigation indicates that FFA is adsorbed with lutein pigment (8) from soy oil on rice hull ash. However, acid activation inhibits FFA binding, indicating the mode of adsorption differs from that of lutein. Heating the ash above 600°C reduces adsorption. To obtain a better understanding of the adsorption process, we plan to collect data on the structural chemistry of rice hull ash and the changes caused by acid activation.

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