Phospholipid Adsorption onto Rice Hull Ash from Soy Oil Miscellas

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Phospholipid was adsorbed from soy oil miscellas by rice hull ash, with small doses of adsorbent binding most efficiently. Adsorption increased with residual phosphorus, suggesting that less accessible adsorption sites were being used as residual values increased, probably due to the heterogeneous nature of the ash. Binding of phospholipid was enhanced by isopropanol, as has been found for adsorption on silicic acid.

KEY WORDS: Cristobalite, isotherms, phospholipid, rice hull silica, soy oil miscella.

A variety of nontriglyceride materials is present in crude soy oil and has to be removed by processing to produce a stable oil of acceptable quality (1). Conventional refining practices include separation of phospholipids by hydration, with 1–3% water. The phospholipids are then precipitated (1). Free fatty acids are separated as soaps by alkali-refining (2). Oil pigments, residual phospholipids and residual free fatty acids are subsequently adsorbed by montmorillonite clay during a high-temperature, low-pressure bleaching process (1).

Brown and Snyder (3,4) reported that phospholipids can be adsorbed from a soy oil hexane miscella onto a synthetic silicic acid at room temperature and pressure. Phospholipid adsorption followed a Freundlich isotherm and was enhanced by the presence of 1% isopropanol (IPA). The reduced energy needs of ambient-temperature adsorptive separation, relative to current processing methods, could be used to economic advantage (3). However, such adsorption processing would create a greater demand for silica adsorbents.

An inexpensive source of amorphous silica derived from rice hull ash has been reported (5,6). Amorphous cristobalite is obtained by burning hulls to produce an inorganic residue. The rice hull ash has an alkaline pH but an ash with lower pH can be produced by acid washing to remove trace minerals. Rice hull ash cristobalite can adsorb the soy oil carotenoid lutein (5) and free fatty acids (7) from a soy oil miscella under ambient conditions.

There is interest in examining alternatives to conventional bleaching clays in areas in the world where conventional adsorbents are unavailable (8). Rice hull ash could be invaluable in third-world economies where energy and mineral resources are limited, and it could also be a useful supplement to montmorillonite clays in the developed world.

The objective of this study was to examine the adsorption of phospholipid on rice hull cristobalite from a soy oil/hexane miscella by means of isotherm studies. The results have been compared with previous findings with rice hull cristobalite and synthetic silica adsorption studies.

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.

Rice cristobalite production. Adsorbent was produced according to the method of Proctor and Palaniappan (5). Partially combusted rice hull ash was supplied by Riviana Foods (Houston, TX). Because the ash contained appreciable amounts of carbon, further combustion was necessary to obtain almost exclusively inorganic material. Samples were heated to 500°C for 10 h in a muffle furnace. This material was designated "alkaline ash" (pH 8.7). Forty grams of alkaline ash was mixed with 1 L of 20% (vol/vol) sulfuric acid for 5 h at 20°C before being washed with an excess of deionized water, filtered and dried in an oven at 100°C for 4 h. This material was designated acid ash (pH 6.6).

Phospholipid analysis. The phosphorus content of the soy oil miscellas was measured by the phosphomolybdate colorimetric reaction after wet ashing (9) as used by Brown and Snyder (3,4).

Isotherm studies. The method was adapted from Brown and Snyder (3,4). Isotherms were obtained by preparing 100-mL vol of 10, 20, 30 and 50% (vol/vol) soy oil/hexane miscellas. The phosphorus content of each miscella was determined. The miscellas were then agitated with a magnetic stirrer for 15 min in a closed vessel with 0.5 g alkaline ash at 20°C. The residual phosphorus in the miscella was then measured after adsorption. The residual phosphorus remaining after adsorption was plotted against the amount of phosphorus adsorbed per gram of adsorbent.

The experiment was repeated with 1.0 g of alkaline ash and 0.5 g of acid ash. Isotherms were also obtained with 0.5-g doses of alkaline ash and acid ash with 1% IPA.

RESULTS AND DISCUSSION

The pattern of phospholipid phosphorus adsorption from soy oil miscella onto alkaline rich hull ash is shown in Figure 1. Adsorption is such that the smaller dose of ash is more efficient than the larger one. A similar result was obtained by Brown and Snyder with silicic acid (3). Adsorption increases as residual phosphorus increases throughout. In contrast, Brown and Snyder (3,4) found no additional binding of phosphorus to 1.0 g of silicic acid at residual values greater than 8 mg/100 ml, with a maximum adsorption of about 7.0 mg/g of adsorbent. The continuing availability of adsorption sites in rice hull ash is probably related to the fact that rice hull ash is more heterogeneous and porous than synthetic silicic acid (6). Adsorption sites on the ash are probably of various accessibility, and less inaccessible sites are more likely to be found as phospholipid concentration increased (10). Hence, ash may have a larger surface area per gram than silicic acid but many of the adsorption sites may be difficult for adsorbing species to find.

Soy oil carotenoid lutein (10) and free fatty acids (7) are also bound in this system. There is therefore simultaneous adsorption of a number of crude oil components. Competition for adsorption sites has been proposed as a means of determining which species bind most effectively (4,10). This competition is affected by the relative affinity for the polar adsorbent surface and the miscella. By modi-

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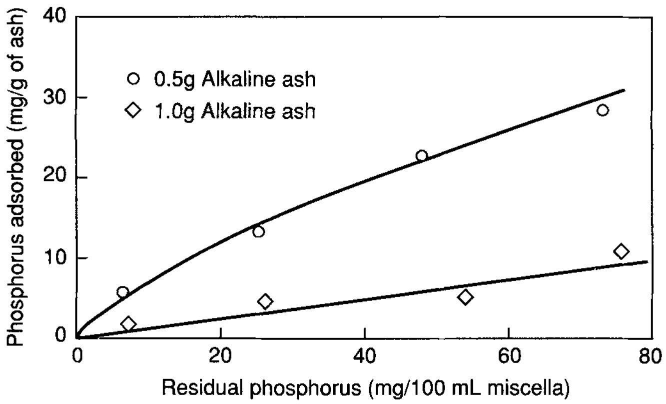

FIG. 1. Phosphorus isotherms were determined with variable amounts of alkaline ash by incubation with 100 mL of 10%, 20%, 30% and 40% (vol/vol) crude soy oil/hexane miscella for 15 min at 22°C.

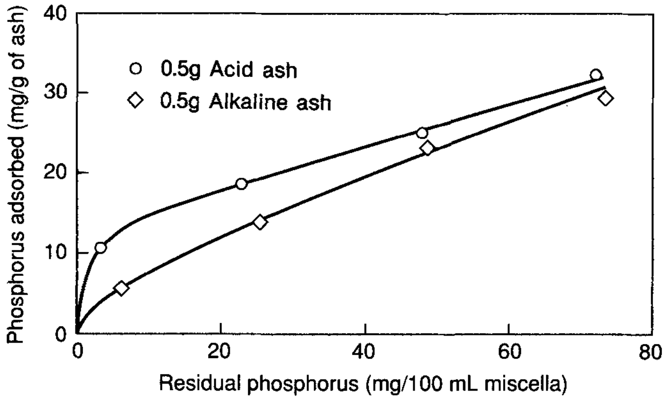

FIG. 2. Phosphorus isotherms were determined with 0.5 g of alkaline and acid ash by incubation with 100 mL of 10%, 20%, 30% and 40% (vol/vol) crude soy oil/hexane miscella for 15 min at 22°C.

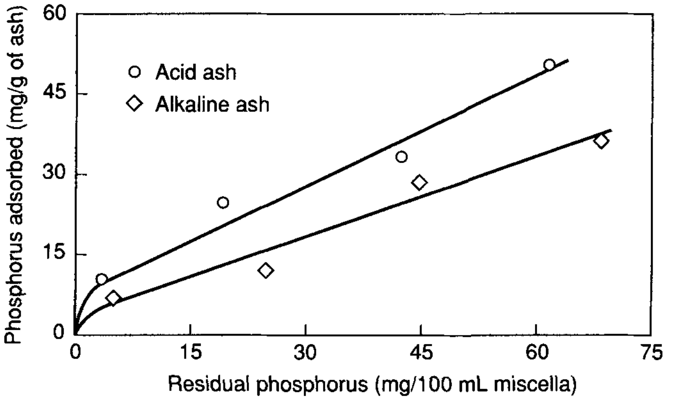

FIG. 3. Phosphorus isotherms were determined with 0.5 g of alkaline and acid ash by incubation with 100 mL of 10%, 20%, 30% and 40% (vol/vol) crude soy oil/hexane miscella with 1% isopropanol for 15 min at 22°C.

fying either the adsorbent or the miscella, it may be possible to control the selective adsorption of oil components.

The adsorption isotherms of acid and alkaline ash are compared in Figure 2. Phospholipid appears to have a slightly greater affinity for acid ash. However, there is little difference in the gradient of the isotherms, and they are close together at higher residual phosphorus levels. The differences are probably due to the removal of residual potassium from the ash, making more silanol groups available on the surface of the ash (6). In addition, the reduced particle size of acid ash resulting from increased handling of the ash may produce a larger surface area (6). In contrast, free fatty acids were much more efficiently adsorbed by alkaline ash (7), while soy lutein had a greater affinity for acid ash (5).

Figure 3 shows the effect of 1% IPA in the miscella on the phospholipid isotherm when 0.5 g of adsorbent was used. Adsorption by both alkaline ash and acid ash was considerably enhanced by the presence of IPA. Thirty milligrams of phosphorus per gram of alkaline ash was bound at a residual phosphorus level of 60 mg/100 mL. This is compared with 25 mg of phosphorus per gram of ash at the same residual level without IPA (Fig. 1). The elevated adsorption is more marked with acid ash. Approximately 50 mg/g of acid ash is bound at 60 mg/100 mL residual level, compared to approximately 25 mg per gram of ash without IPA (Fig. 1). A similar IPA effect was observed in the adsorption of phospholipid by synthetic silicic acid (3).

Under these experimental conditions, IPA promoted the adsorption of soy free fatty acids onto rice hull ash (7) while inhibiting that of lutein (10).

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