Rice Hull Ash Adsorbent Performance Under Commercial Soy Oil Bleaching Conditions

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ABSTRACT: Rice hull silica and a rice hull carbon ash were evaluated as adsorbents for the soy oil bleaching process under commercial temperature and pressure conditions. Their performance in adsorbing pigment, phospholipid, free fatty acids, and peroxides was compared with that of a commercial bleaching clay and silica hydrogel. With the exception of phospholipid binding, rice hull-derived adsorbents were ineffective. Rice hull silica showed potential as a phospholipid adsorbent but was not as effective as the synthetic silica hydrogel on an adsorbent weight basis. However, it was a superior adsorbent when the data were expressed as adsorbate bound per unit surface area. The low surface area of the rice hull silica limits its commercial viability. It may have value in areas of the world where rice hulls are plentiful and an inexpensive phospholipid adsorbent is required for oil processing. Research is in progress to increase the surface area of rice hull silica for commercial oil processing.

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KEY WORDS: Adsorbents, bleaching, rice hull ash, rice hull silica, surface area.

The commercial bleaching of soy oil is important in producing a light-colored oil that is acceptable to consumers and in removing residues of previous refining steps. Bleaching is achieved by adsorption of oil pigments onto bleaching clay at 100°C under reduced pressure (1). The major pigment removed from the oil is the xanthophyll lutein. Residual free fatty acids (FFA), phospholipids (PL), and peroxide oxidation products remaining after alkali-refining and the degumming process are also adsorbed. Bleaching clay is a montmorillonite and effectively binds lutein and PL. Synthetic silica hydrogel adsorbents are often added to the clay, to selectively bind PL and thus reduce competition between pigment and PL for clay adsorption sites. Thus, addition of silica hydrogels enhances binding of both lutein pigment and PL from the oil.

There is interest in examining alternatives to conventional bleaching adsorbents. In Nigeria, the bleaching effectiveness of local Nsu and Okija clays were examined because montmorillonite clays were unavailable (2). Rice hull silica (RHS) has also been examined as an alternative adsorbent in vegetable oil processing. Rice hulls have little value and constitute a significant waste disposal problem. Nevertheless, they may be readily utilized as a mineral resource.

X-ray diffraction studies show that rice hull ash is an amorphous silica in the form of Opal CT (3). However, excessive combustion produces a more crystalline Opal C form, which is a poor adsorbent. Incomplete burning yields a high-carbon ash. Combustion conditions are therefore important determinants of adsorbent quality.

Amorphous RHS was shown to adsorb lutein (4), FFA (5), and PL (6) from a soy oil/hexane miscella at room temperature, while a high-carbon ash was not effective. Subsequent Fourier transform infrared spectroscopy studies showed the nature of the adsorption of FFA and PL from hexane onto synthetic amorphous silica and the probable adsorption mechanisms (7,8). Furthermore, the infrared spectrum of RHS is similar to that of synthetic amorphous silicic acid (9).

The objective of this study was to examine the soy oil adsorption bleaching performance of RHS and a carbon-rich rice hull ash under simulated commercial temperature and pressure conditions, as used in industrial bleaching. A commercial bleaching clay and silica hydrogel were also used as a basis for comparison.

MATERIALS AND METHODS

Oil and adsorbents. Alkali-refined oil (Riceland Foods, Stuttgart, AR), a 50% carbon rice hull ash (Producers Rice Mill, Stuttgart, AR), an RHS (Comet Rice, Maxwell, CA), a bleaching clay, Filtrol 160 (Engelhard, Cleveland, OH), and a silica hydrogel, Trisyl (W.R. Grace, Baltimore, MD) were used.

Bleaching. One-hundred grams of oil were stirred with a magnetic stir bar and heated at 100°C under 2 mm Hg pressure for 30 min with variable amounts of each adsorbent. Each determination was made in duplicate. Lutein (10), peroxide value (11), PL phosphorus (12), and FFA (13) were measured before and after adsorption. Adsorbent dose was then plotted against the residual concentrations after bleaching.

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Surface area measurements. The surface areas of the RHS, silica hydrogel, and bleaching clay were measured. Samples were degassed at 133°C for 20 h prior to analysis. The surface area was measured by the BET isotherm method with a model 2100E Accusorb surface area analyzer (Micrometrics, Norcross, GA) and nitrogen as the adsorbate (14).

The bleaching experiment was repeated with the RHS, silica hydrogel, and bleaching clay at an adsorbent dose equivalent to a surface area of 300 m^2/g.

Statistical analysis of the bleaching data was by analysis of variance with least significant difference values based on a 95% confidence level ($P < 0.05$).

RESULTS AND DISCUSSION

Adsorption of lutein from soy oil by different adsorbents is shown in Figure 1. The bleaching clay was the only adsorbent to substantially reduce the lutein content. The silica and hydrogel slightly reduced the lutein concentration in the oil. The high-carbon rice hull ash was ineffective in reducing lutein levels. The absence of adsorption by RHS is in contrast to lutein binding from soy oil/hexane miscellas and may be due to the much larger concentrations of triglyceride (TG). TG competes with lutein for polar adsorption sites and inhibits adsorption (10). The bleaching clay effectiveness is due to its protonation and adsorption of lutein (15).

Small amounts of bleaching clay are more efficient at adsorbing lutein than larger amounts. This has also been observed in the adsorption of soy lutein from hexane miscellas on silicic acid (10).

Figure 2 shows the change in peroxide concentrations after adsorption treatment. Bleaching clay was the only adsorbent to greatly reduce peroxide concentrations, with 0.75% rice hull carbon ash producing a slight but significant reduction.

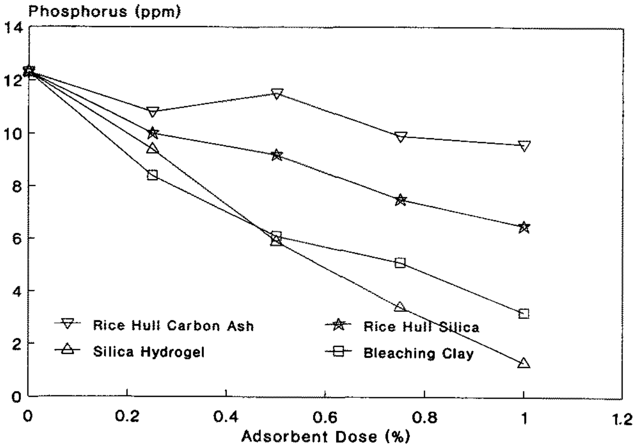

FIG. 2. The peroxide value of soy oil bleached with various amounts of rice hull carbon ash, rice hull silica, silica hydrogel, and bleaching clay by mixing at 100°C for 30 min under reduced pressure. Determinations were made in duplicate. $LSD_{0.05}$ is 0.54.

The reduction in PL phosphorus levels is shown in Figure 3. The RHS significantly reduced oil phosphorus levels, but the rice hull carbon ash was only slightly effective. The commercial adsorbents were much more effective, with the silica hydrogel adsorbing most at doses above 0.5%. The performance of RHS may be due to the ionic interaction between PL and amorphous silica, which would be stronger than the weaker polar forces involved in binding FFA and lutein (8).

Small amounts of bleaching clay are not more efficient than large amounts in binding PL, as was observed in lutein adsorption (Fig. 1).

Figure 4 indicates that there was no reduction in FFA levels with any of the adsorbents used. However, there was a slight increase in FFA in the presence of the silica hydrogel.

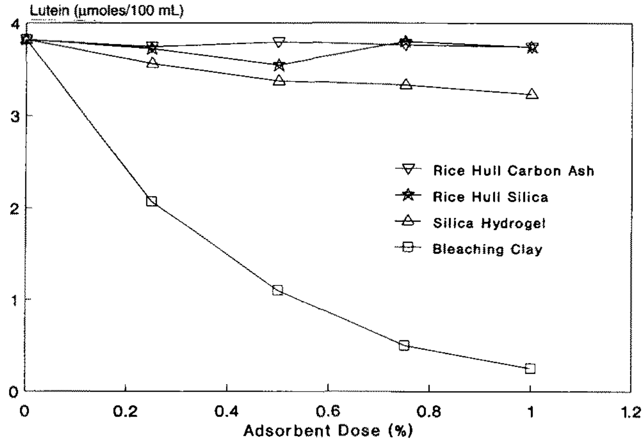

FIG. 1. The lutein pigment content of soy oil bleached with various amounts of rice hull carbon ash, rice hull silica, silica hydrogel, and bleaching clay by mixing at 100°C for 30 min under reduced pressure. Determinations were made in duplicate. $LSD_{0.05}$ is 0.12.

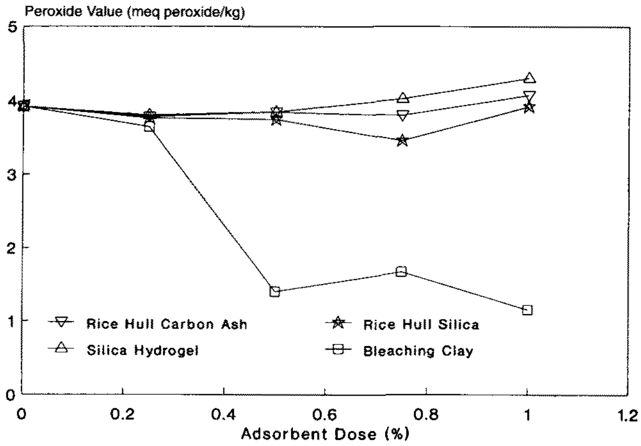

FIG. 3. The phosphorus content of soy oil bleached with various amounts of rice hull carbon ash, rice hull silica, silica hydrogel, and bleaching clay by mixing at 100°C for 30 min under reduced pressure. Determinations were made in duplicate. $LSD_{0.05}$ is 1.47.

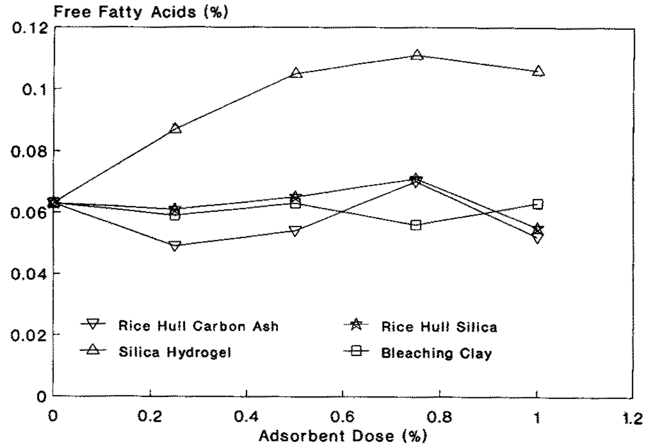

FIG. 4. The free fatty acid content of soy oil bleached with various amounts of rice hull carbon ash, rice hull silica, silica hydrogel, and bleaching clay by mixing at 100°C for 30 min under reduced pressure. Determinations were made in duplicate. $LSD_{0.05}$ is 0.01.

This may be due to moisture loss from the adsorbent and subsequent oil hydrolysis. This observation presumably has no commercial implications as silica hydrogels at the magnitude of the increase would probably not affect oil quality. The lack of FFA adsorption is most likely due to the low FFA levels before adsorption, which is common in alkali-refined oils.

RHS adsorbed PL more effectively than lutein, peroxides or FFA. However, the silica hydrogel was the most effective PL adsorbent. This was due, at least in part, to the much greater surface area of the silica hydrogel.

The rice hull carbon ash was not studied due to its poor performance in the previous study. There was a large variation in surface area, RHS having the smallest (41.22 $m^2\ g^{-1}$), and silica hydrogel the largest (604.04 $m^2\ g^{-1}$). The surface area of the silica hydrogel was approximately twice that of the bleaching clay (303.37 $m^2\ g^{-1}$). The surface area of RHS was less than 15% of that of the clay. Because of the surface area differences, additional adsorption studies were performed on an equal surface area basis.

The data showing oil quality after exposure to 300 m^2 of each adsorbent are given in Table 1. The bleaching clay was the only adsorbent to greatly reduce lutein and peroxide concentrations, other adsorbents produced minor but significant reductions in concentrations. In contrast, FFA levels were not reduced, but silica hydrogel and RHS produced a small increase in concentration. This may be due to residual moisture associated with the adsorbent. RHS was the most efficient phosphorus adsorbent on a surface area basis. However, silica hydrogels are commercially viable phosphorus and fatty acid adsorbents, due to their large surface area and adsorption capacity. RHS may be useful in countries where rice hulls are plentiful and an inexpensive PL adsorbent is needed for oil processing.

Bleaching clay is an effective adsorbent due to its ionic surface and high surface area, capable of binding a wide variety of oil constituents (15). Silica hydrogels are 60% moisture and therefore depend on weaker polar interactions, which limit the species bound. Adsorption capacity of silica hydrogels is enhanced by a high surface area and polar adsorption sites (16). RHS also has a polar surface (3), but adsorption is limited by a relatively small surface area. Further work is being done to enhance RHS surface area and adsorption capacity.

TABLE 1
The Quality of Soy Oil After Bleaching with an Adsorbent Dose Providing 300 m^2 Surface Area (duplicate determinations were made)

	Lutein (μmoles/100 mL)	Peroxide value (meq peroxide/kg)	Phosphorus (ppm)	Free fatty acid (%)
Unbleached control	5.32	10.20	20.00	0.05
Bleaching clay	0.34	3.96	6.72	0.05
Silica hydrogel	4.30	10.14	9.58	0.10
Rice hull silica	4.30	9.16	2.25	0.06
$LSD_{0.05}$	0.04	0.42	1.18	0.01

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