# Soy Hull as an Adsorbent Source in Processing Soy Oil

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**ABSTRACT**: Soy hull, a co-product of the soybean industry, was evaluated as an adsorbent source for processing soy oil. Ground soy hull (<100 mesh), boiled soy hull, and soy hull carbon were each added to crude soy oil at various levels in the laboratory under commercial bleaching conditions. The free fatty acid (FFA), peroxide value (PV), pigments, and total phospholipid contents (PL) of treated samples were measured. The microstructure (scanning electron microscopy, SEM), X-ray diffraction patterns (XRD), and Fourier transform infrared (FTIR) spectra of the soy hull adsorbents were also examined. The soy hull carbon was more efficient as an adsorbent relative to the ground or boiled soy hulls. The differences between ground and boiled soy hulls in the reduction of FFA were not significant. The effectiveness of adsorbents to reduce PV was: soy hull carbon > boiled soy hull = untreated soy hull; and for PL adsorption: soy hull carbon = ground soy hull > boiled soy hull. Boiling resulted in an open, porous structure, as evident from the SEM data, but carbonization did not affect the particle size. The XRD patterns of ground and boiled soy hulls were similar to those of powdered amorphous cellulose, but the carbon was more amorphous and had a random structure, as well as a more polar surface, as revealed by the FTIR spectra.
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**KEY WORDS:** Adsorbents, carbon, FT–IR, oil processing, SEM, soy hull, X-ray diffraction.

Food oil processing industries use bleaching clays as adsorbents to remove residual free fatty acids (FFA), carotenoids, and phospholipids (PL) from crude oils to help to produce light-colored, bland and stable oils acceptable to consumers. Commercial bleaching processes involve the treatment of crude oil with bleaching clays at 100°C under reduced pressure, and several different types of bleaching materials are commercially available for this purpose (1). Alternative sources of inexpensive adsorbents from low-value agricultural co-products, such as rice hull silica (2) and soy hull carbon (3), have been reported. In addition, inexpensive indigenous clays from Nigeria (4) and Zambia (5) have been studied as adsorbent sources.

Soy hulls are important co-products of the soybean industry and are used both as fuel and in animal feeds (6). In a previous study, soy hull carbon was produced and used as an adsorbent of minor crude soy oil components. Soy hull carbon's affinity for crude soy oil components was in the order phospholipid > peroxides > free fatty acid > lutein (3). This suggests that there is a polar adsorbent surface on the carbon. Because pyrolysis would oxidize and remove these groups, boiling might expand the product by breaking the internal hydrogen bonds of the cell wall polymers, exposing polar OH groups. The objective of this study was to evaluate the performance of milled soy hull, boiled soy hull, and soy hull carbon as adsorbents of crude oil components. Studies of the adsorbent microstructure were done by scanning electron microscopy (SEM), X-ray diffraction (XRD), and diffuse reflectance Fourier transform infrared (FTIR) spectroscopy.

## MATERIALS AND METHODS

*Crude oil and soybeans*. The crude soy oil and soybeans were donated by Riceland Foods (Stuttgart, AR).

*Soy hull adsorbents*. Soybeans were dehulled in a blender and milled once in a Udy Cyclone Sample Mill (Udy Corporation, Fort Collins, CO) to obtain a particle size of 100 mesh or less. The milled soy hull was boiled in water for 2 h and centrifuged at 1500 × *g* for 15 min, and the residue was dried in an oven at 70°C for about 8 h. The dried residue was stored in airtight plastic bags. The soy hull carbon was prepared by heating milled soy hull to 400°C and cooling it to room temperature in a desiccator. The untreated ground soy hull, boiled treated soy hull, and soy hull carbon were placed in airtight plastic bags in a desiccator until used.

*Bleaching*. Crude soy oil (100 g) was stirred and heated in a rotary evaporator in a hot-water bath (Rotavapor R-114; BÜCHI Labortechnik AG, Flawil, Switzerland) at 100°C under 2 mm Hg pressure for 30 min with 2, 4, or 6 g of soy hull adsorbents. The oil after treatment was filtered twice to remove the adsorbent residue. The lutein content (7), peroxide value (PV) (8), residual FFA (9), and total PL content (10) of the oil samples were evaluated.

*Statistical analyses*. Three replications of the experiment were performed in a randomized complete block design. Data were analyzed by the least square means procedure (11), and the differences reported are significant at ($P < 0.05$) unless specified otherwise.

*Scanning electron microscope study*. The microstructure of each soy hull adsorbent was investigated with a scanning elec-

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tron microscope (Hitachi Model S-2300; Hitachi, Tokyo, Japan) at an accelerated voltage of 25 kv and a beam angle of 90°.

*XRD.* The X-ray diffraction patterns of soy hull adsorbents were obtained with a Philips X-ray diffractometer (X'pert; Phillips Electrical Co., The Netherlands) at a generator voltage of 45 kV and 2θ diffraction angle of 4–60°.

*FTIR.* The FTIR spectra of the soy hull samples were investigated with a Nicolet Model 410 FTIR instrument (Nicolet Analytical Instruments, Madison, WI). The spectra of the samples were obtained by co-adding 100 scans at a resolution of 4 $cm^{-1}$.

## RESULTS AND DISCUSSION

The lutein content of the samples was not reduced by the addition of any of the soy hull adsorbents, indicating little affinity for pigments (data not presented).

All soy hull adsorbents significantly reduced the FFA content of the crude soy oil ($P < 0.05$) (Fig. 1). An FFA reduction of 30–50% was observed with 2 g of each adsorbent, but the addition of untreated and boiled soy hull at levels greater than 2 g did not produce any further reduction. However, soy hull carbon was more efficient when added at the 6% level, with about 75% reduction in the FFA content. Thus, the efficiency of the soy hull adsorbents in reducing the FFA content was in the order: soy hull carbon > untreated soy hull = boiled soy hull. There were no significant differences in ability to reduce FFA between the untreated and boiled soy hulls. The reduced adsorption of ground and boiled soy hull, compared to soy carbon, is probably due to fewer adsorption sites, smaller pore size, and lower relative surface polarity of ground and boiled soy hulls.

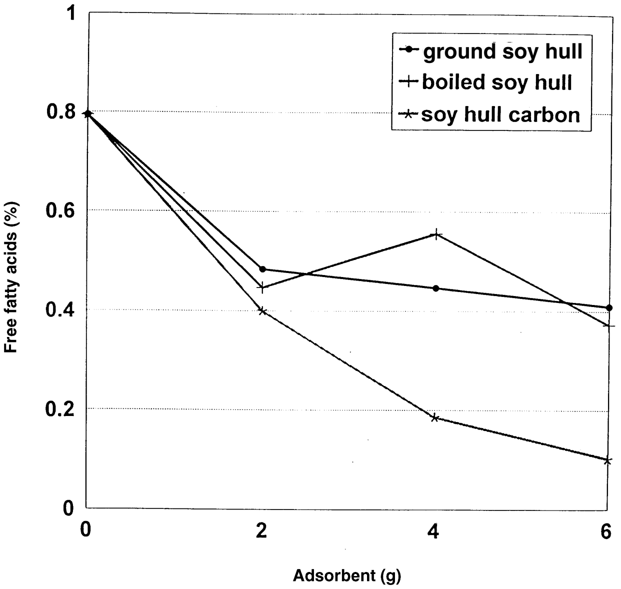


**FIG. 1.** Residual free fatty acid in crude soy oil after mixing with various amounts of soy hull adsorbents at 100°C under reduced pressure for 30 min ($n = 9$, coefficient of variation = 21.71).

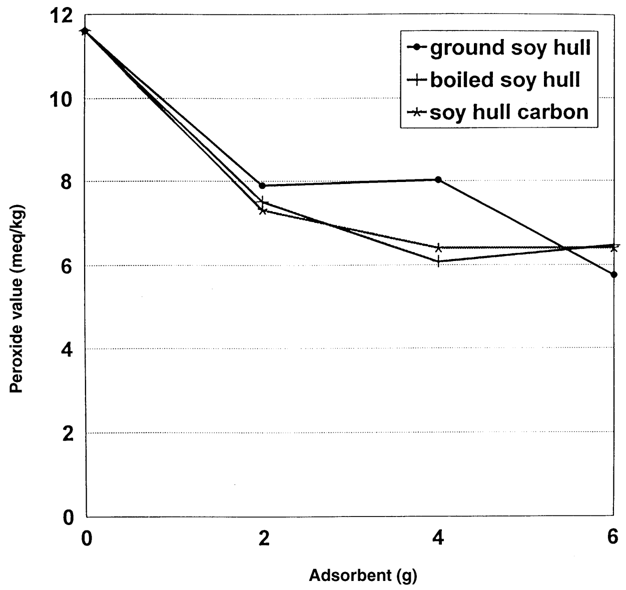


**FIG. 2.** Residual peroxide value of crude soy oil after mixing with various amounts of soy hull adsorbents at 100°C under reduced pressure for 30 min ($n = 9$, coefficient of variation = 7.04).

The PV reduction of crude oil samples is presented in Figure 2. All hull adsorbents were effective in reducing the crude oil PV, and the reduction was significant at 2-g levels ($P < 0.05$). Increasing the amount of adsorbent above 2 g did not result in a significant reduction in PV, because most of the peroxides were already bound. This was similar to the findings for soy hull carbon reported by Proctor and Harris (3). The soy hull carbon and boiled soy hull were more effective in reducing PV than the ground soy hull, as indicated by their overall mean values. The differences between soy hull carbon and boiled soy hull were not significant. The ability of the adsorbents to reduce PV of samples were in the order: soy hull carbon = boiled soyhull > ground soy hull.

Soy hull adsorbents (2 g) caused a significant reduction in the total PL content of the crude oil ($P < 0.10$) (Fig. 3). Soy hull carbon and untreated soy hulls were more effective than boiled soy hull at PL adsorption. Increasing the level of adsorbent to more than 2 g did not result in a significant reduction of total PL for any adsorbent. The affinity of total PL in crude oil for the adsorbents was in the order: soy hull carbon = ground soy hull > boiled soy hull.

Soy hull carbon showed superior adsorbent performance throughout. The carbon surface contains both a wide range of functional groups, including carboxyl, phenol, and carbonyl groups, and ring-bound species, such as pyrans and pyrones, which are known to possess surface functionality (12). Carbon surfaces are capable of forming chemical and physical bonds with a wider spectrum of substances than any other material (12). The forces responsible for adsorption might include hydrogen bonds and Van der Waal forces. The ground hulls performed similarly or better than the boiled hulls in ad-

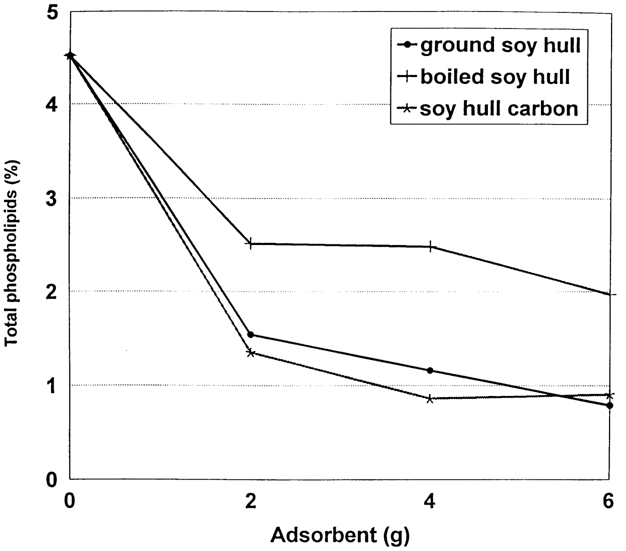


**FIG. 3.** Total phospholipid content in crude soy oil after mixing with various amounts of soy hull adsorbents at 100°C under reduced pressure for 30 min ($n = 9$, coefficient of variation = 70.38).

sorbing PL, although there was little difference in the final peroxide levels. Boiling did not appreciably improve soy hull adsorption. We thought that boiling the hulls would break the hydrogen bonds between the cell wall polysaccharides cellulose and pectins, which would create a larger adsorbent surface. However, the carbon's adsorption performance was equal to or better than that of the processed hulls. Therefore, furnace heating may not cause a major reduction in the number of adsorption sites. To investigate the structural differences between the soy hull preparations, the morphology and particle sizes were examined with a scanning electron microscope, and the crystalline organization was studied by XRD. The functional groups on the carbon surface were examined by FTIR.

*SEM.* The microstructures of the adsorbents are presented in Figures 4–6. Figure 4 shows a wide variety of particles between 10 and 100 μm in size, and some are larger with a compact rigid structure. Figure 5 shows the boiled soy hulls structure to be more porous than nonboiled hulls, with openings between sheets of cell wall materials. Thus, boiling produced a porous swollen structure, but this did not result in enhanced adsorption. Heating the soy hull to carbon (400°C) did not change the SEM morphology (Fig. 6) relative to untreated soy hulls (Fig. 4), despite the severe carbon oxidation. Thus, chemical rather than SEM morphological changes are probably responsible for its performance.

*XRD.* The XRD pattern of ground soy hull is shown in Figure 7A. It is almost identical to that of amorphous cellulose (13), with peaks around 20° and 15° $2\theta$, indicating an interatomic distance between polymers of about 4.0 and 5.8Å. The broad nature of the peaks indicates a range of interatomic distances that are typical of amorphous structures. Figure 7B shows that the effect of boiling the soy hulls is to increase the number of 5.8Å distances relative to the 4.0Å distances. This is reflected in the more open SEM structure observed in Figure 5. Heating the hulls to 400°C destroys the cellulose by combustion and increases the amorphous structure. This is shown by the loss of the cellulose pattern and the broad "hump," which indicates disorganization and a random struc-

**FIG. 4.** Scanning electron micrograph of ground soy hull, magnification × 300.

**FIG. 5.** Scanning electron micrograph of boiled soy hull, magnification × 300.

ture. The strong pattern between 5–10° 2θ values indicates larger interatomic distances than in hull cellulose, suggesting potentially better access by lipid molecules.

*FTIR spectroscopy*. The FTIR spectra of the soy hull adsorbents present three distinct features (Fig. 8A–C). The infrared spectra of the ground soy hull revealed a broad band from about 3600 to 3000 $cm^{-1}$, a maximum at 3350 $cm^{-1}$, and sharper peaks at 2930 and 1730 $cm^{-1}$ (Fig. 8A). The broad band from 3600 to 3000 $cm^{-1}$ is probably due to adsorbed water. The presence of aromatic groups, including -CH=O, -$CO_2H$, and -CH=CH$CO_2H$, attached to $C_6H_5$ units is generally indicated by an infrared absorption maximum from 3100 to 3000 $cm^{-1}$ (14) as seen in the soy hull carbon samples (Fig. 8C). However, this band was not observed in the ground and

**FIG. 6.** Scanning electron micrograph of soy hull carbon, magnification × 300.

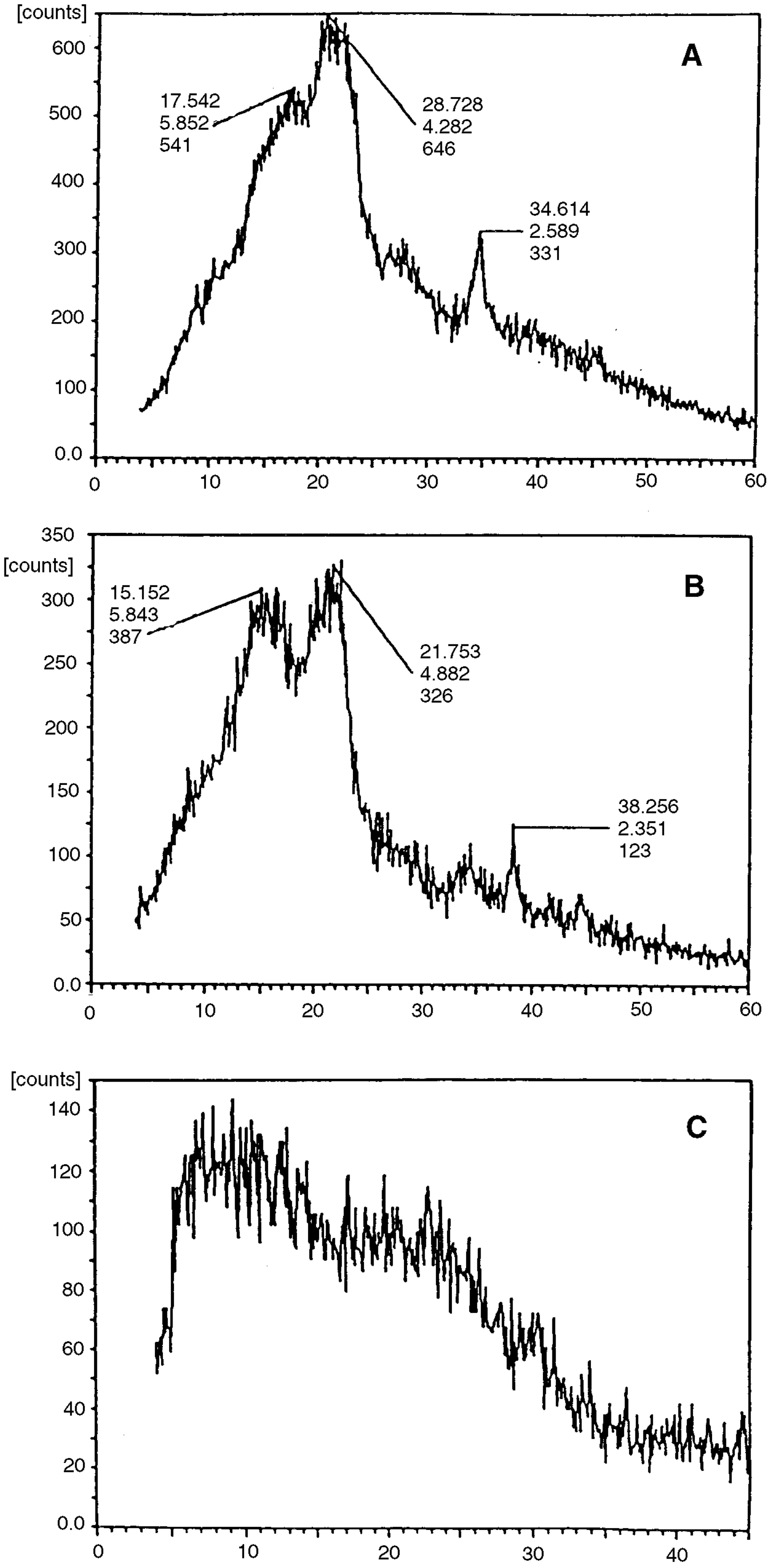
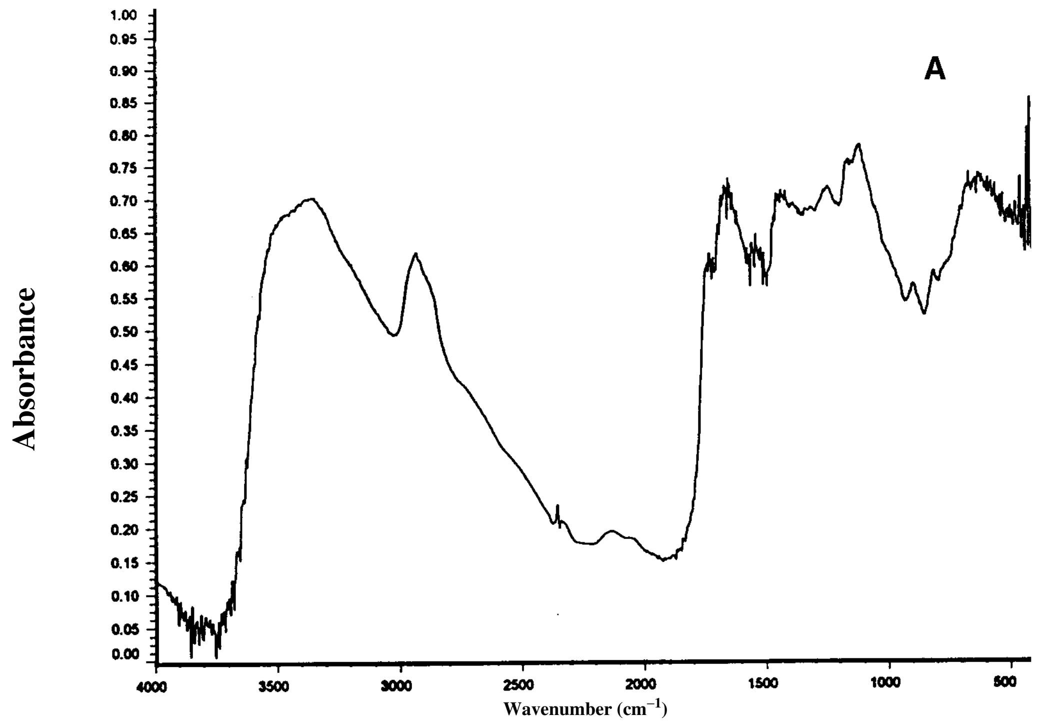


**FIG. 7.** X-ray diffraction patterns of soy hull adsorbents: (A) ground soy hull, (B) boiled soy hull, (C) soy hull carbon. Horizontal axis is (°2θ).



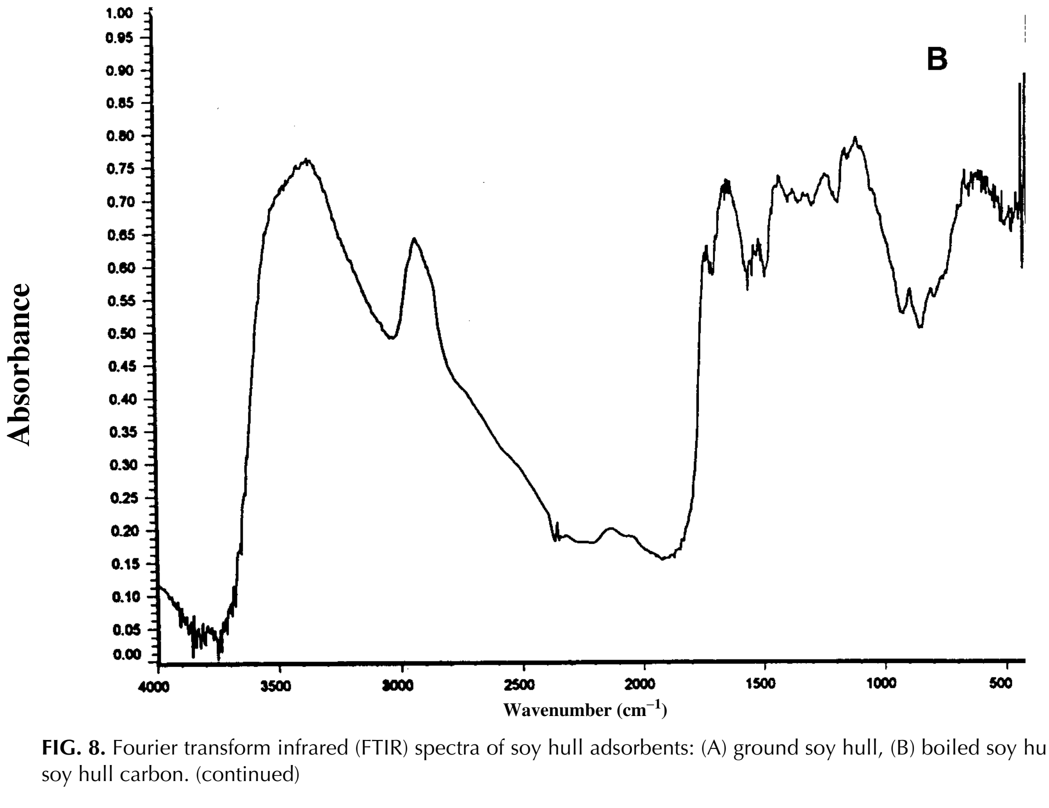
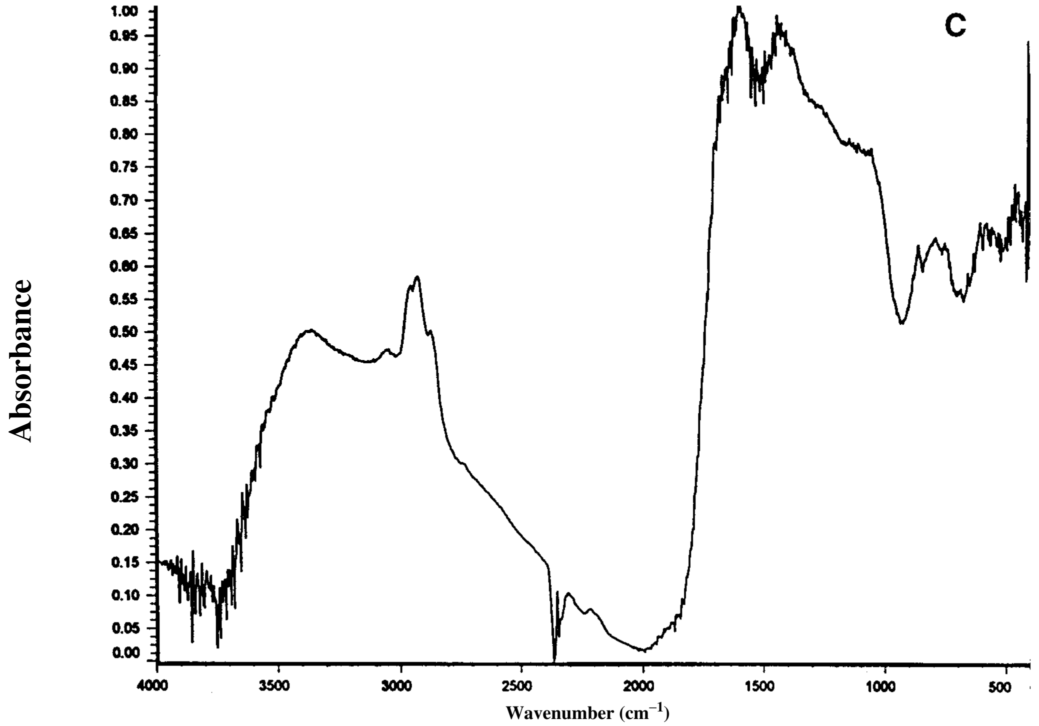


**FIG. 8.** Fourier transform infrared (FTIR) spectra of soy hull adsorbents: (A) ground soy hull, (B) boiled soy hull, (C) soy hull carbon. (continued)

boiled soy hull samples, probably due to interference by adsorbed surface water. Lignin present in soy hulls (15) might also contribute to the aromatic groups found on the surface. In addition, the seed coat of soybeans contains several phenolic acids and flavonoids that might contribute to aromatic groups. The infrared band at 2930 cm$^{-1}$ corresponds to an asymmetric -CH stretch and symmetric -CH, and the band at 1730 cm$^{-1}$ denotes the presence of -C=O stretch. The band at



2354 cm$^{-1}$ is due to atmospheric carbon dioxide and is ignored as background. Boiling the soy hull did not result in any apparent changes in the surface functional groups (Fig. 8B). However, carbonization seems to have produced such changes (Fig. 8C). In these samples, the intensity of the peak at 2930 cm$^{-1}$ has increased relative to the broad peak at 3350 cm$^{-1}$, a finding that is the opposite of the infrared spectra of ground and boiled soy hulls. Pyrolysis resulted in the reduction of adsorbed surface water and aromatic groups, probably due to the combustion of lignin and the decomposition of phenolic and flavonoid compounds. An infrared band around 1730 cm$^{-1}$ shows the presence of -C=O stretch, and the intensity of this band is greater in the soy carbon samples. Oxidation during pyrolysis may be responsible for an increase in surface carbonyl groups, which would render the surface more polar. This would explain the better adsorption properties of soy carbon.

The amorphous nature of soy hull cellulose may be responsible for its adsorption capacity. However, the reduction in PL adsorption after boiling the hulls suggests that water-soluble polysaccharides, such as pectin, may also have lipid adsorption properties despite swelling of the hull. Pyrolysis of the hull produces the most amorphous and random crystal structure, with a more polar surface that improves adsorption.

In summary, boiling soy hulls created a more porous material with a larger proportion of cellulose fibers with greater interatomic distances. Expansion of the cellulose may improve accessibility of adsorbate to cellulose hydroxyl adsorption sites, but this did not result in greatly enhanced adsorption performance, with the possible exception of PL binding. In contrast, no SEM differences in carbon morphology, relative to the untreated soy hulls, were observed. However, carbon interatomic distances and the presence of carbonyl adsorption sites were greater in the soy hull preparations. Thus, the superior adsorption by the carbon could be due not only to better lipid accessibility but also to a greater concentration of surface carbonyl groups, which are more polar than hydroxyls. Therefore, combustion did not result in a net loss of adsorption sites but created new more effective ones.

The general trend in competitive adsorption of the oil species agrees with that reported by Proctor and Harris (3), i.e., PL > FFA > PV, and the relative polarity of the adsorbing functional groups, i.e., phosphate > carbonyl > peroxide. PL adsorption to a polar surface occurs mainly through the phosphate group and has been shown to be stronger to polar surfaces than that of fatty acids or triglycerides (16). The ability of soy hull carbon to bind more FFA than the other adsorbents may be due to an excess of adsorption sites after the PL adsorption equilibrium has been reached, which does not occur with the other adsorbents.

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