Soy Hull Carbon as Adsorbents of Crude Soy Oil Components: Effect of Carbonization Time

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ABSTRACT: Studies were conducted to evaluate the performance of soy hull carbon adsorbents as affected by carbonization time. Carbonization was done by heating soy hulls to 400°C for up to 30 min. Increased carbonization time resulted in elevated surface pH and titratable alkalinity. The effectiveness of adsorbents in binding minor soy oil components was studied. Free fatty acids content was decreased 70% with adsorbents carbonized for 30 min. Peroxides were adsorbed, but increasing carbonization time did not alter absorption by carbons. A similar trend was observed with the adsorption of total phospholipids. The residual lutein content of crude soy oil was not affected by the adsorbents. X-ray diffraction studies showed that carbonization at 400°C converted the polysaccharide-based structure of soy hull to an amorphous, highly disorganized, random structure. Increase in carbonization time resulted in broadening of the diffraction pattern between 5 and 25° 2θ. Infrared spectra of soy carbon samples revealed presence of asymmetric C-H stretch, symmetric C-H bends, and C=O groups. The intensities of these spectra decreased with time of carbonization.

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Adsorbents such as bleaching clays are widely used by vegetable oil processors to remove minor oil components such as free fatty acids (FFA), peroxides, carotenoids, and phospholipids. Adsorption bleaching processes involve treatment of crude oil with adsorbents at 100°C under reduced pressure. Several adsorbents are commercially available for use in the oil processing industry. Carbon in several forms is used as an adsorbent in clarification of beverages (1), water treatment (2), and removal of dyes (3) and herbicide and pesticide residues (4,5). Carbon is not used frequently in commercial oil processing; however, it is effective when used with bleaching clay (6). Studies also report the use of carbon in processing of sesame oil micella (7) and squash seed oil (8).

Soy hulls are a low-value co-product of the soybean industry that are used as fuel and in animal feeds (9). Studies on alternative uses of agricultural by-products including soy hulls have been reported (10,11). Soy hulls have been classified as single-use metal adsorbents (10). Studies have also been reported on preparation of granulated activated carbons as adsorbents of organic compounds and in wastewater treatment (11). In our previous investigation, soy hull carbon was produced and used as an adsorbent of minor crude soy oil components (12,13). Structural changes brought about by pyrolysis and the polar nature of the carbon surface were suggested as reasons for the adsorption properties of soy hull carbon. Carbon possesses transient surface properties which may be affected by pyrolysis conditions including time and temperature. The objective of this investigation was to evaluate the adsorbent performance and structure of soy hull carbon adsorbents as affected by carbonization time. Adsorption studies were conducted to evaluate the soy hull carbon as adsorbents of crude soy oil components, and the structure of adsorbents were elucidated by X-ray diffraction (XRD) patterns and diffuse reflectance Fourier transform infrared (FTIR) spectroscopy.

MATERIALS AND METHODS

Crude soy oil and soybeans. Crude soy oil and soybeans were donated by Riceland Foods (Stuttgart, AR). Soybeans were dehulled in a blender, and soy hull carbon was prepared by incinerating soy hulls to 400°C for <1, 10, 20, and 30 min in a muffle furnace (Thermolyne, Type 1500 Furnace; Sybron Corp., Dubuque, IA) and cooled to room temperature in a desiccator. Soy hull carbon samples incinerated for <1, 10, 20, and 30 min were designated as Scarb <1, Scarb10, Scarb20, and Scarb30, respectively. They were stored in screw-capped sample bottles in a desiccator until further evaluation.

pH and titratable acidity. Soy carbon samples (500 mg) were dispersed in 15 mL of neutralized distilled deionized water and stirred for 15 min. The samples were filtered, pH readings were obtained before adding two drops of phenolphthalein indicator, and samples were titrated with 0.1 N HCl to a colorless endpoint.

XRD and FTIR spectroscopy. XRD patterns of soy hull carbon adsorbents were analyzed using a Phillips X-ray diffractometer (X'pert; Phillips Electrical Co., Almelo, The Netherlands) at a generator voltage of 45 kV, and diffraction

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angle of 4 to 45° 2θ. The FTIR spectrum of the soy carbon samples was investigated using a Nicolet Model 410 FTIR instrument (Nicolet Analytical Instruments, Madison, WI). Spectra were obtained by co-adding 100 interferograms at a resolution of 4 cm^{-1}.

Bleaching. Crude soy oil (100 g) was stirred and heated in a rotary evaporator in a hot water bath (Rotavapor R-114; Büchi, Switzerland) at 100°C under 2 mm Hg pressure for 20 min with 2 g of soy carbon adsorbents. The oil after treatment was filtered twice to remove the adsorbent residue. Lutein content (14), peroxide value (PV) (15), residual FFA (16), and total phospholipid content (17) of the oil samples were evaluated.

Statistical analyses. Three replications of the experiment were performed in a randomized complete block design. Data was analyzed using least square means procedure (18) and the differences reported were significant at $P < 0.05$.

RESULTS AND DISCUSSION

Pyrolysis for longer duration increased the pH and titratable alkalinity of soy hull carbon (Fig. 1). The increase was linear as observed by an increase in the millimoles of hydrochloric acid required to neutralize the alkalinity. The carbon surfaces possess several heteroatoms (non-carbon atoms) with an electronegativity different from that of carbon atoms. These differences in electronegativity impart surface heterogeneity to carbon that affects the number and type of surface functional groups (19). These differences include both Brønsted acid and base groups, the content and balance of which greatly influence the adsorbent properties of carbon. Functional groups on carbon surfaces such as carboxyls, lactones, phenols, carbonyls, ethers, pyrones, and chromenes include oxygen and hydrogen atoms. Heating of carbon surfaces results in the loss of hydrogen and oxygen, two major non-carbon atoms found on carbon surfaces, thus causing a loss of acidic functionalities primarily as CO_2. This phenomenon could result in a net increase in the number of groups with Brønsted base characteristics, such as pyrones, pyrilium ions, and carbanion ions contributing to the alkalinity of carbon surfaces.

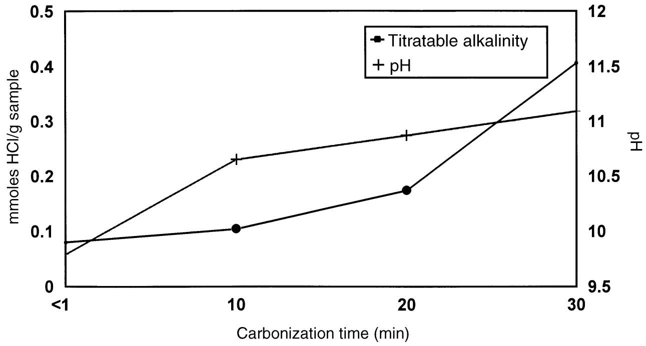

FIG. 1. The pH of soy hull carbon in an aqueous suspension, and the amount of hydrochloric acid required to obtain a phenolphthalein endpoint (titratable alkalinity). Soy hull carbon was carbonized by heating to 400°C and held for <1, 10, 20, and 30 min, respectively.

The XRD patterns of soy carbon samples are presented in Figure 2. Carbonization at 400°C destroyed the polysaccharide-based structure of soy hull, resulting in an amorphous and highly disorganized random structure. An increase in carbonization time resulted in broadening of the pattern between 5 and 25° 2θ, indicating an increase in larger interatomic distances corresponding to 3.5–12.0 Å.

Infrared spectra of Scarb <1 revealed a broad hump between 3600 and 3200 cm^{-1}, a shoulder at 3100 cm^{-1}, distinguishable peaks at 2950, 2925, 2870, 1700, 1600, and 1450 cm^{-1} (Fig. 3, trace I). In addition, weak bands were observed at 870, 800, and 750 cm^{-1}. The broad hump at 3600 to 3200 cm^{-1} corresponds to surface-bonded water, and its intensity decreased with increasing heating time (Fig. 3, traces II–IV). Absorbance at 3100 cm^{-1} corresponds to aromatic-H stretching, the intensity of which increased with increasing heating time. Peaks at 2950 and 2925 cm^{-1} correspond to asymmetric C-H stretches since stretching vibrations between atoms of unequal mass such as C-H give highest energy peaks. The peak at 2870 cm^{-1} corresponds with symmetric C-H bends. The peaks at 1700 and 1600 cm^{-1} are due to C=O stretching, the latter possibly from a conjugated quinone-like carbonyl group. The presence of such a carbonyl group at 1605 cm^{-1} was reported for cellulose carbon heated at 400°C (20). The peak at 1450 cm^{-1} corresponds to CH_2 bending. As the heating time increased, the peak at 1700 cm^{-1} was not observed and the intensity of peak at 1600 cm^{-1} relative to 1450 cm^{-1} decreased, suggesting a relative decrease in surface acid groups. This is consistent with the increase in titratable alkalinity with increased heating time. Bands of lower intensities at 870, 800, 750 cm^{-1} correspond to aromatic CH bends. The increased intensities of these groups with heating time indicate an aromatic surface structure due to heating. As the carbonization time was increased, the peaks corresponding to C-H bonds decreased, indicating a disruption of the surface and "widening" of the pore diameter. This is con-

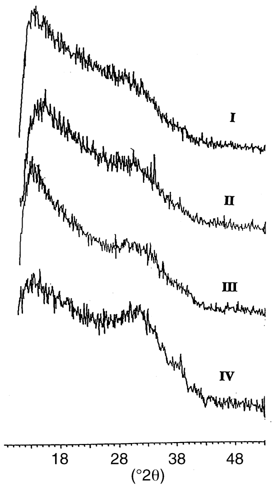

FIG. 2. X-ray diffraction patterns of soy hull carbon adsorbents (*y* axis not on a common scale); traces I, II, III, and IV are soy hull carbon carbonized by heating to 400°C and holding for <1, 10, 20, and 30 min, respectively.

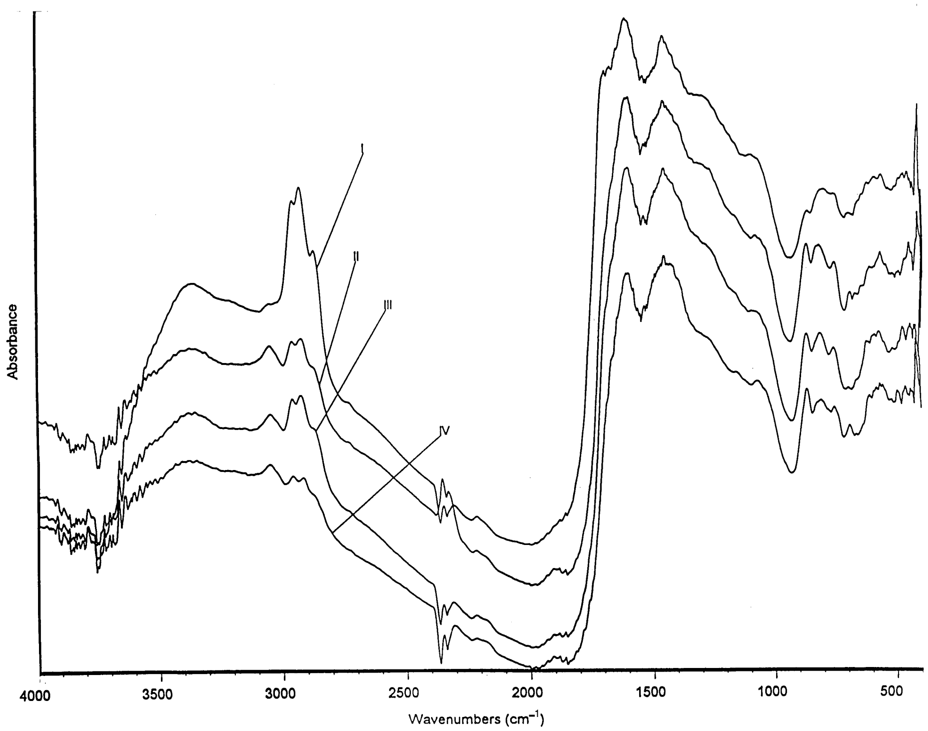

FIG. 3. Fourier transform infrared spectra of soy hull carbon samples (*y* axis not on a common scale); I, II, III, and IV are soy hull carbon carbonized by heating to 400°C and holding for <1, 10, 20, and 30 min, respectively.

sistent with the XRD pattern of Scarb30, which revealed a broadening between 5 and 25° 2θ.

The residual lutein content of crude soy oil was not affected by the adsorbents. This supports earlier findings that carbon is not an efficient adsorbent of carotenoid pigments (20) possibly because it cannot compete for adsorption sites (14). An increase in carbonization increased the ability to adsorb FFA of the samples (Fig. 4). The FFA content of the oil decreased with carbon prepared at increasing carbonization times. This corresponds with the increase in adsorbent alkalinity. Scarb30 was the most efficient adsorbent of FFA with about 70% reduction in FFA.

Reduction in PV content of soy oil samples is presented in Figure 5. There was a significant reduction in PV of samples treated with Scarb<1. Increase in carbonization time did not improve the PV-adsorbing capacity of soy carbon samples. A similar trend was observed with total phospholipid adsorption (Fig. 6); however, Scarb<1 and Scarb10 were effective

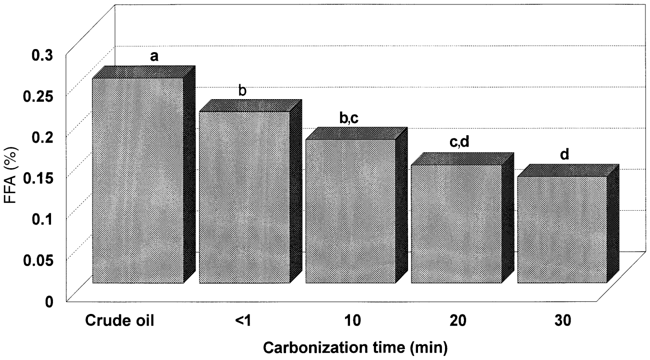

FIG. 4. Free fatty acid (FFA) content of crude soy oil as affected by addition of soy hull carbon adsorbents. Soy hull carbon was carbonized by heating to 400°C and held for <1, 10, 20, and 30 min, respectively. Mean values are reported; mean values with different superscripts (a–d) indicate significant differences between samples (*P* < 0.05).

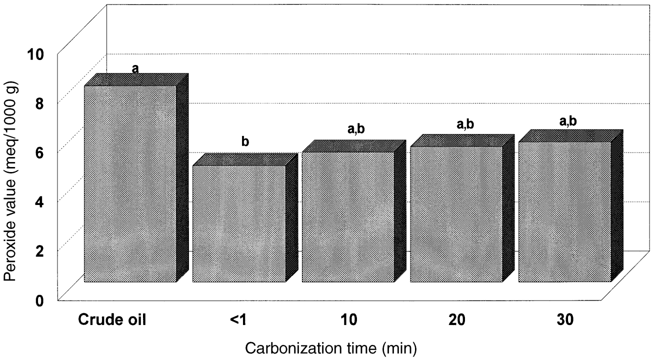

FIG. 5. Peroxide value of crude soy oil as affected by addition of soy hull carbon adsorbents. Soy hull carbon was carbonized by heating to 400°C and held for <1, 10, 20, and 30 min, respectively. Mean values are reported; mean values with different superscripts (a,b) indicate significant differences between samples (*P* < 0.05).

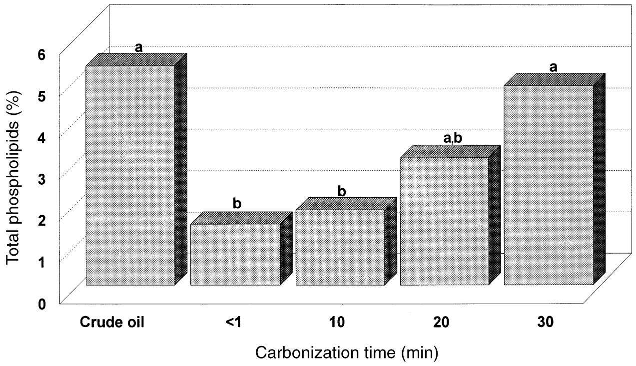

FIG. 6. Total phospholipid content of crude soy oil as affected by addition of soy hull carbon adsorbents. Soy hull carbon was carbonized by heating to 400°C and held for <1, 10, 20, and 30 min, respectively. Mean values are reported: mean values with different superscripts (a,b) indicate significant differences between samples ($P < 0.05$).

in reducing the total phospholipid content of the samples compared to Scarb30 unlike the case of peroxides that did not have a significant adsorption due to increase in carbonization time. Based on these observations, the affinity of minor oil components for soy carbon adsorption sites with increasing heating time was in the order FFA > phospholipids > peroxides > lutein. Although increase in carbonization time resulted in increased pH and titratable alkaline groups with potential hydrogen-bonding capacity, a competition for adsorption sites between FFA, peroxides, and phospholipids may have resulted in decreased adsorption of peroxides and phospholipids over FFA. In addition, steric effects due to differences in molecular sizes may have contributed to the increased affinity of FFA for adsorption sites relative to that of peroxides or phospholipids.

A significant decrease in all the minor components of crude oil except lutein was observed with Scarb<1, a finding consistent with that of Proctor and Harris (12). The affinity of oil components for soy carbon was reported to be phospholipid > peroxides > FFA > lutein (12). However, increase in carbonization time seems to shift the affinity patterns of oil components due to increase in adsorbent pH. An improved FFA adsorption due to increasing heating time could be mainly due to acid-base interaction as a result of increased surface alkalinity, which is aided by an improved access of FFA to the adsorption sites. Carbon adsorbents are amorphous and disorganized random structures which adsorb by Van der Waal forces, termed as London dispersion forces. Van der Waal forces are very strong but they occur over a short distance, indicating the importance of access of the adsorbate molecule to the adsorbent.

Soy hull carbon has a highly disorganized amorphous structure with potential adsorption sites capable of binding to crude oil components. Duration of carbonization process is an important variable that changes the surface properties of carbon thereby changing the dynamics of the adsorption process. Selectivity of carbon adsorbents for minor oil components can be altered by manipulating carbon structure and preparation. Successful development of adsorbent carbon from inexpensive materials such as soy hull improves its value as a potential raw material for production of carbon.

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