Structure and Performance of Soy Hull Carbon Adsorbents as Affected by Pyrolysis Temperature

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ABSTRACT: Soy hulls were evaluated as a source of adsorbent carbon for vegetable oil processing. Soy hull carbon was prepared by burning ground soy hulls (<100 mesh) at 300, 400, 500, or 700°C in a muffle furnace. The structure of the soy hull carbon was studied by scanning electron microscope (SEM), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR). Crude soy oil was processed with the soy hull carbon products at 2% (w/w) in the laboratory under commercial bleaching conditions. Free fatty acids (FFA), peroxide value, phospholipid phosphorus (PLP), and lutein content of the treated samples were determined. SEM of the samples revealed particle size ranging from 1 to 2 mm. Increasing the pyrolysis temperature resulted in expansion and disruption of cellular structure. FTIR spectra of the carbon samples showed major differences in peak intensities at 3600 to 3200, 1600, and 1450 cm^{-1} due to pyrolysis temperature. XRD revealed a predominantly amorphous structure with increasing pyrolysis temperature, which also resulted in an increased alkaline surface. Soy hull carbon decreased the FFA content of oil samples compared to that of crude oil, with the exception of carbon that was prepared at 300°C ($P < 0.05$). A similar trend was observed in the adsorption of peroxides; however, no trends were observed in the adsorption of PLP or lutein. Higher pyrolysis temperature decreased randomness of the carbon and imparted a certain degree of structural order. This may be beneficial in providing physical access of the adsorbate molecule to the adsorbent surface.

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KEY WORDS: Adsorbent, carbon, FTIR, SEM, soy hull, X-ray diffraction.

Crude soybean oil is refined to remove pigments, such as lutein and chlorophyll, free fatty acids (FFA), phospholipids (PL), and oxidation products. The refining process includes degumming, neutralization, bleaching, and deodorization to produce bland, light-colored oil ready to use. The commercial bleaching process is performed by subjecting degummed oil to adsorbents, such as bleaching clays, at 100°C under reduced pressure (1). There is interest in identifying alternatives to conventional adsorbents, such as rice hull silica (2) and soy hull carbon (3). The oil processing industry uses carbon adsorbents in addition to clays during bleaching to bind PL, thus increasing adsorption of the oil pigments onto the bleaching clay (2).

Currently, soy hull is a co-product of soybean processing and is disposed for $100 a ton (Riceland Foods Inc. Sales Division, personal communication, 1997). Methods to improve soy hull utilization will add value to this underutilized commodity. In a previous study, soy hulls have been found useful as single-use metal adsorbents (4). Studies have also been reported on preparation of granulated activated carbons from soy hull as adsorbents of organic compounds and in wastewater treatment (5). Previous studies conducted on soy hull adsorbents include preparation and evaluation of ground and boiled soy hull as adsorbents (6) and the effect of pyrolysis time on the performance of soy hull carbon adsorbents in oil processing (7). Soy hull carbon was a more efficient adsorbent than ground or boiled soy hulls. Their abilities to reduce peroxide value (PV) were in the order: soy hull carbon > boiled soy hull = untreated soy hull; and for PL, soy hull carbon = ground soy hull > boiled soy hull (6). FFA content of crude soy oil decreased with increasing in soy hull carbonization time, with a 70% FFA reduction by adsorbents that were carbonized for 30 min. Competition for adsorption sites on the carbon surface resulted in varying levels of adsorption of PL and peroxides (7).

The objective of this study was to evaluate the effect of pyrolysis temperature on the structure and performance of soy hull carbon adsorbents. Soy hull carbon was prepared at 300, 400, 500, and 700°C and evaluated for effectiveness in removing undesirable crude oil components, including FFA, peroxides, PL, and lutein. Studies on the structure and surface properties of the adsorbents included microstructure by scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, diffuse reflectance Fourier-transform infrared (FTIR) spectroscopy, and atomic absorption spectrophotometry.

MATERIALS AND METHODS

Crude soybean oil and soy hulls. Crude soybean oil and soy hulls were obtained from Riceland Foods (Stuttgart, AR).

Soy hull carbon adsorbents. Soy hulls were ground to a particle size of <100 mesh, placed in a crucible, and carbonized in air in a muffle furnace (Thermolyne Corporation, Des Moines, IA) at 300, 400, 500, and 700°C. Samples were

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placed in glass screw-cap test tubes and stored at room temperature until evaluation.

SEM study. The microstructure of soy hull adsorbents was investigated with a SEM (Hitachi Model S-2300, Tokyo, Japan) at an accelerated voltage of 25 kV, at a beam angle of 90°. Micrographs of soy hull carbons, at magnifications ranging from 100 to 6000× and at the various pyrolysis temperatures, were used to explain the effects of pyrolysis on the microstructure of adsorbants.

Elemental analyses. The composition of soy hull carbon samples was determined by the atomic absorption spectrophotometric method (8).

pH. Carbon samples (5 g) were dispersed in 15 mL of distilled deionized water, stirred for 15 min, and filtered through Whatman No. 1 filter paper (Whatman International Ltd., Maidstone, England), and the pH of the filtrate was measured with a pH meter (Orion Model 410A; ATI Orion Laboratory products Group, Boston, MA).

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

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

Adsorption processing of crude oil. Adsorption bleaching of crude soy oil was performed in duplicate on 100 g crude soybean oil with carbon adsorbents at the 2% level. The samples were placed in a rotovap (Rotavapor R-114; BÜCHI Labortechnik AG, Flawil, Switzerland) for 30 min under a vacuum at 2 mm Hg in a boiling waterbath (Waterbath B-480; BÜCHI Labortechnik AG) and then immediately vacuum-filtered. All bleached oil samples were collected in a 125-mL Erlenmeyer flask, stoppered and stored at 4°C. FFA (9), peroxide value (10), lutein content (11), and PL phosphorus content (12) of the oil samples were determined.

Statistical analysis. Three replications of the experiment were performed in a randomized complete block design. Data were analyzed by the least square means procedure (13), and the differences reported were significant at ($P < 0.05$) unless specified otherwise.

RESULTS AND DISCUSSION

Structure and surface functional groups. Figures 1 to 4 represent the microstructure of soy hull carbon samples. Carbon samples showed a particle size range of 1–2 mm. Micrographs with magnifications from 100 to 6000× were used to explain the changes in microstructure. Carbonizing at 300°C did not produce a complete char, and the soy hull retained its biological structure, as shown by the cross-section (Fig. 1, 100×). Greater magnification (6000×) of this sample revealed the heterogeneous nature of the adsorbent surface. Pyrolysis at 400°C produced a complete char (Fig. 2, 500×) and an undulating surface (Fig. 2, 6000×). Increasing the temperature to 500°C resulted in expansion of the soy hull, as evident from the "blister like" surface (Fig. 3, 100×). This expansion appeared to continue until collapse, which resulted in an irregular and relatively porous surface (Fig. 3, 1500×). Carbons pro-

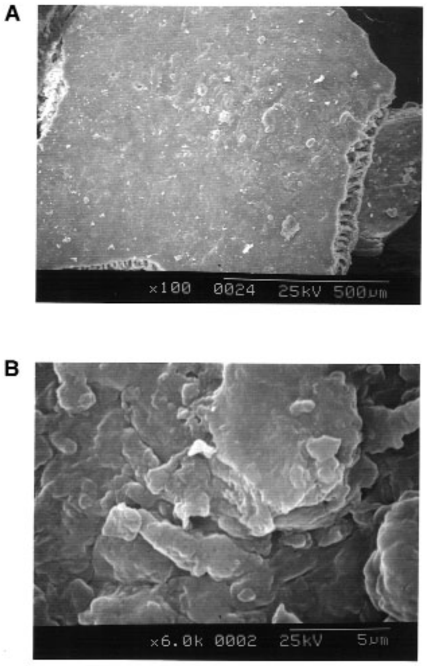

FIG. 1. Scanning electron microscopy of soy hull carbon produced at 300°C; (a) magnified × 100 and (b) × 6,000.

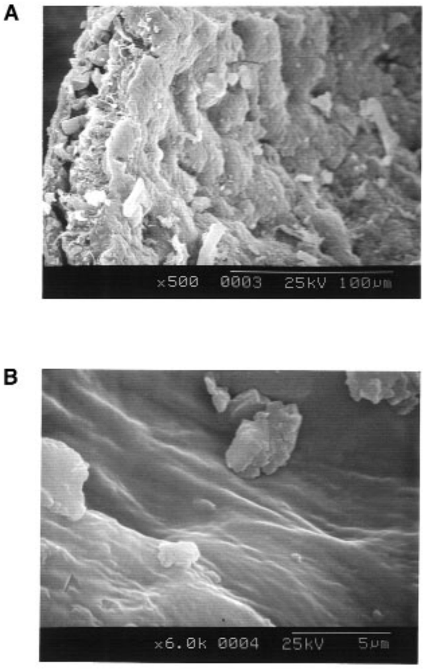

FIG. 2. Scanning electron microscopy of soy hull carbon produced at 400°C ; (a) × 500 and (b) × 6,000.

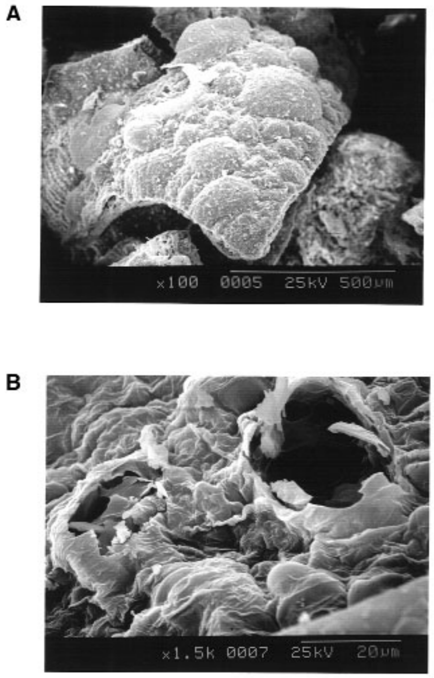

FIG. 3. Scanning electron microscopy of soy hull carbon produced at 500°C; (a) × 100 and (b) × 1,500.

duced at 700°C revealed the presence of ash as white fluffy material on the carbon particles (Fig. 4, 100×). Carbons produced at 700°C also showed the presence of a somewhat ordered structure due to burning off of less dense material, resulting in uniform carbonization of the soy hull remnants (Fig. 4, 400×).

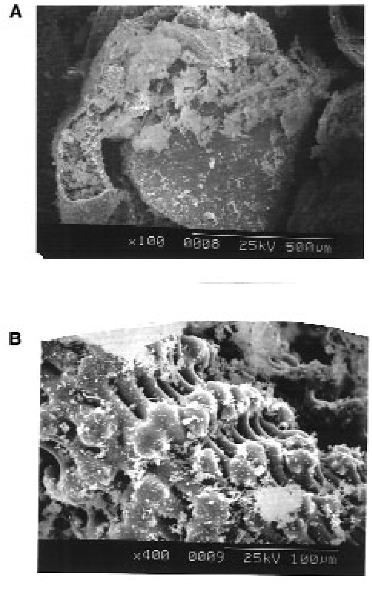

FIG. 4. Scanning electron microscopy of soy hull carbon produced at 700°C; (a) × 100 and (b) × 400.

The XRD patterns of carbon samples produced at 300, 400, and 500°C are presented in Figure 5. XRD patterns of ground soy hull are identical to that of cellulose (6). Carbonization at temperatures of 300°C and above destroyed the polysaccharide-based structure and resulted in an amorphous and highly disorganized random structure. Increased carbonization time resulted in broadening of the pattern between 5 and 20° 2θ, indicating an increase in larger interatomic distances, corresponding to 4 to 20 Å. Absence of a sharp peak in this region denotes that these samples were predominantly amorphous. However, when the temperature was increased to 700°C, the material appeared to lose some of the amorphous structure, as evident from increased diffraction intensities (peaks) (Fig. 6). These peaks correspond to intermolecular and interatomic distances within and between the carbon sheets, indicating a definite, recurrent spacing between graphene sheets of the carbons produced. Typically, in a crystalline carbonaceous structure, such as graphite, the interatomic distance between two carbon atoms of adjacent car-

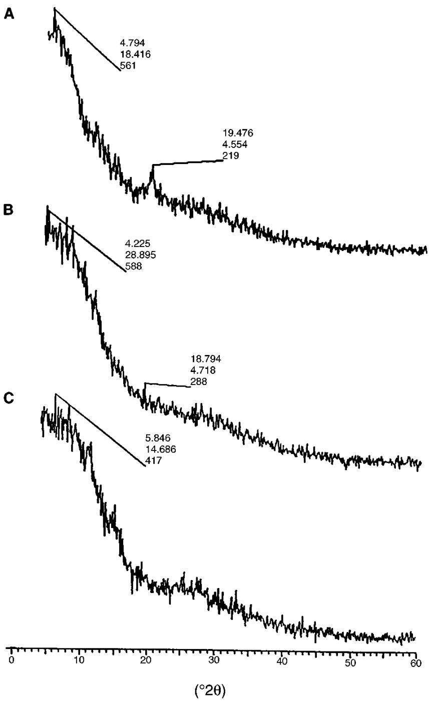

FIG. 5. X-ray diffraction patterns of soy hull carbons; (A) 300°C, (B) 400°C, and (C) 500°C.

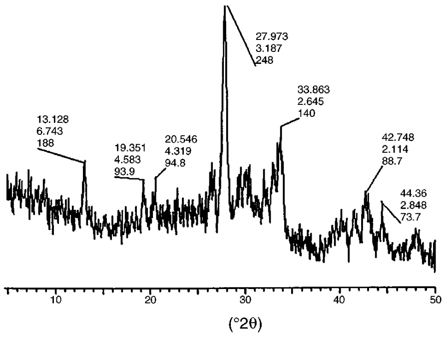

FIG. 6. X-ray diffraction patterns of soy hull carbon produced at 700°C.

bon sheets is about 3.4 Å. In this study, a sharp peak was observed at a d-spacing of 3.2 Å for carbons produced at 700°C. Other peaks observed for this carbon might be due to the inorganic salts present in the ash component of the carbon. Based on these observations, we propose that increased pyrolysis temperature burns off the less dense components of soy hull, resulting in a relatively less amorphous structure, which might be facilitated by a thermodynamically favored molecular arrangement.

Increased pyrolysis temperature resulted in an increase in pH (increased alkalinity) of the adsorbents. The pH values were 9.0, 10.6, 11.2, and 11.7 for soy hull carbons produced at 300, 400, 500, and 700°C, respectively. In a previous study, we observed that carbonizing for longer durations resulted in an alkaline surface (7). Higher temperatures caused a change in the elemental composition of the carbons produced. Copper, manganese, calcium, magnesium, and potassium contents of carbon samples increased significantly due to the destruction of organic matter as the pyrolysis temperature was increased from 300 to 700°C (Table 1). Oxides and hydroxides of these elements behave as strong bases. This explains the increase in the surface alkalinity of carbon. In addition, heating of a carbon surface results in a loss of acidic functionalities, primarily as CO_2. This phenomenon could result in a net increase in the number of groups with Brϕnsted base characteristics, such as pyrones, pyrilium ions and carbanion ions, which contribute to the alkalinity of a carbon surface (14).

Infrared spectra (FTIR) of carbons produced at 300°C revealed a broad hump between 3600 and 3200 cm^{-1}, a shoulder at 3100 cm^{-1}, and distinguishable peaks at 2950, 2925, 2850, 1700, 1600, and 1450 cm^{-1} (Fig. 7). The broad hump at 3600 to 3200 cm^{-1} corresponds to surface-bonded water, and its intensity decreased with increasing heating temperature. The peaks at 2950 and 2850 cm^{-1} correspond to symmetric C-H bends. The peak at 1700 cm^{-1} is due to C=O stretching from a carbonyl group. Presence of such a carbonyl group at 1605 cm^{-1} was reported for a cellulose carbon heated at 400°C (14).

The peak at 1600 cm^{-1} corresponds to -COO^- groups, and the peak at 1450 cm^{-1} corresponds to carboxylate groups (-COOH). As the pyrolytic temperature increased from 300 to 400°C, intensity of the peak at 1600 cm^{-1} increased and suggested surface oxidation (Fig. 7). In samples pyrolyzed at 500°C, the peak at 1700 cm^{-1} was not present (Fig. 8). However, the intensity of the peak at 1600 cm^{-1} increased as a result of further surface oxidation. Soy hull carbons produced at 700°C showed a significantly distinguishable broad peak at 1450 cm^{-1} (Fig. 8) with a relative decrease in peak intensity at either 1600 or 1700 cm^{-1}. Other peaks between 1550 and 1700 cm^{-1} are due to skeletal vibrations. This strongly suggests the increased concentration of carboxylate groups as a function of higher temperature. Absence of the broad hump between 3600 and 3200 cm^{-1} in these samples indicates a total decomposition of the cellulose-based soy hull structure and the loss of surface-bonded moisture (Fig. 8). These samples also revealed peaks at 600, 875, 1050, and 1100 cm^{-1}, possibly resulting from the concentration of alkaline earth elements.

Performance of soy hull carbons as adsorbents. An increase in carbonization temperature increased the ability to adsorb FFA of the samples (Fig. 9), which is probably related to the increased adsorbent alkalinity. Proctor and Palaniappan (16) found that alkaline rice hull ash was effective in binding FFA from crude oil/hexane micella. The increase in the surface alkaline groups due to pyrolysis supports the theory that strong electrostatic interactions between surface alkaline groups and the amphiphilic FFA are responsible for their strong adsorption to the adsorbent surface. Formation of carboxylate groups due to increased pyrolysis temperature, as revealed by FTIR spectra, suggests that these carboxylates react with oxides of alkaline metals to produce corresponding hydroxides that participate in the adsorption of FFA:

$$XO + RCOOH \rightarrow XOH + RCOO^{-}X^{+}$$

where X represents the appropriate alkaline earth element. In

TABLE 1
pH and Elemental Composition of Soy Hull Carbons Affected by Pyrolysis Temperature[a]

Sample[b]	pH	Cu (ppm)	Mn (ppm)	Ca (%)	Mg (%)	K (%)
300°C	9.0	29.96	195.9	1.12	0.46	2.15
400°C	10.6	38.05	264.34	1.59	0.65	3.01
500°C	11.2	49.36	334.39	1.98	0.81	3.83
700°C	11.7	82.64	946.49	4.81	2.09	6.01

[a] Mean of triplicate measurements.

[b] 300, 400, 500, and 700°C refer to soy hull carbons prepared at those temperatures.

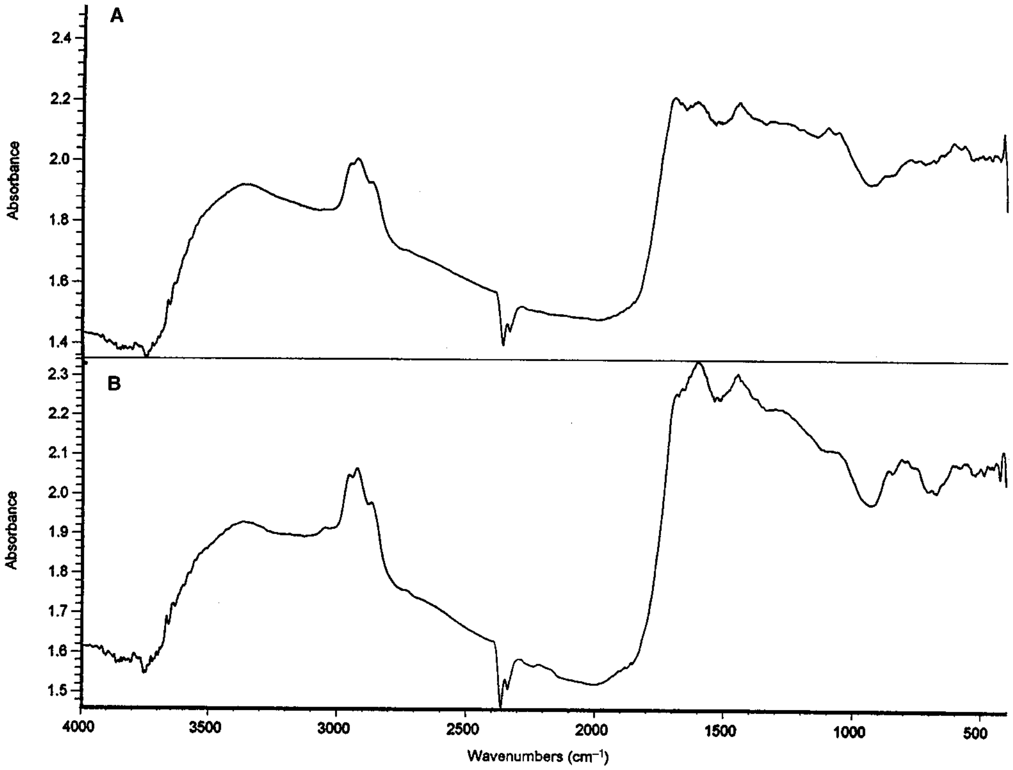

FIG. 7. Fourier-transform infrared (FTIR) spectra of soy hull carbons produced at different temperatures; (A) 300°C and (B) 400°C.

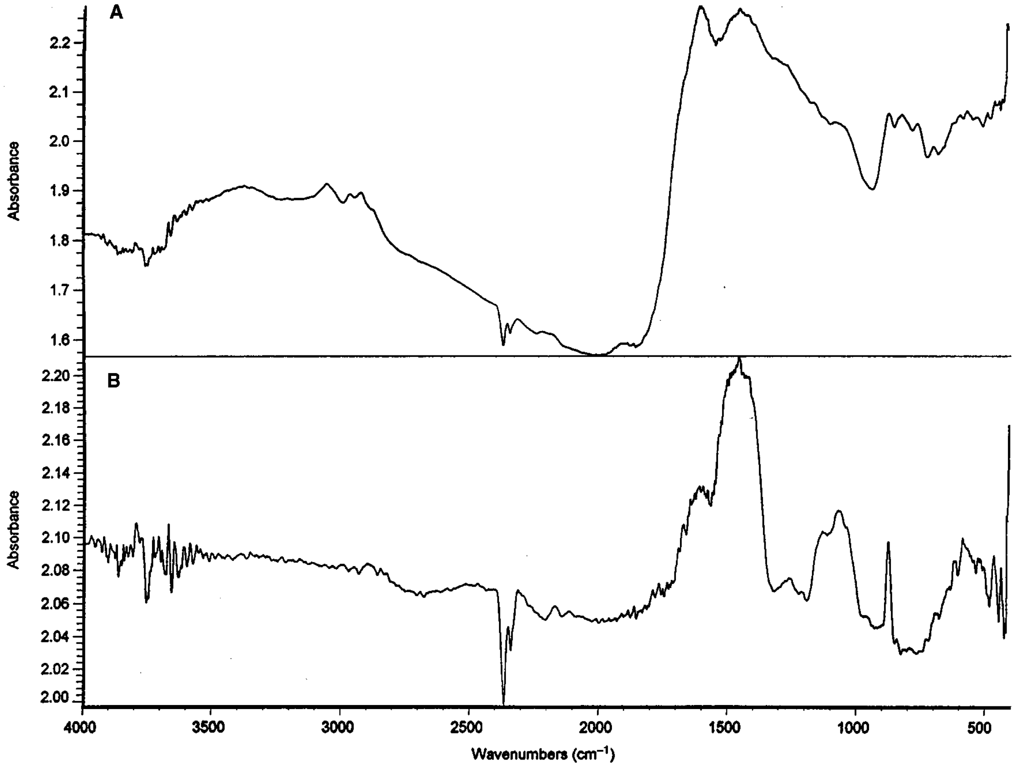

FIG. 8. FTIR spectra of soy hull carbons produced at different temperatures; (A) 500°C and (B) 700°C. See Figure 7 for abbreviation.

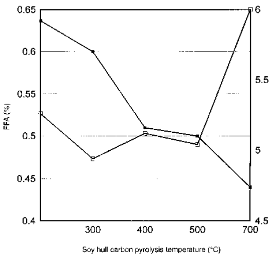

FIG. 9. Free fatty acid (FFA) and lutein contents of crude soy oil samples treated with soy hull carbons (2% wt/vol) prepared at 300, 400, 500, and 700°C. ■, FFA; □, lutein.

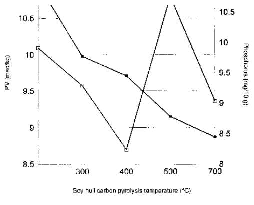

FIG. 10. Peroxide value (PV) and phosphorus contents of crude soy oil samples treated with soy hull carbons (2% wt/vol) prepared at 300, 400, 500, and 700°C. ■, PV; □, phosphorus.

the present study, potassium and magnesium contents of the soy hull carbons increased with pyrolysis temperature (Table 1). These two elements might be the active participants in electrostatic interaction with FFA.

Soy hull carbons did not decrease the lutein content of crude soy oil (Fig. 9). This supports earlier findings that carbon was not an efficient adsorbent of carotenoid pigments (3), possibly because they cannot compete for adsorption sites (3). PV of samples treated with soy hull carbons decreased gradually with an increase in pyrolysis temperature. Samples treated with 400°C carbons showed a 20% reduction. Reductions in PV were significant in samples treated with 400, 500, and 700°C carbons, compared to that of crude oil, while carbons produced at 300°C did not produce a significant reduction (Fig. 10).

An increase in carbonization temperature to 400°C resulted in a significant adsorption of PL phosphorus (Fig. 10). However, carbons produced at 500 and 700°C did not further reduce the adsorption of phosphorus significantly. This indicates that adsorption of PL phosphorus does not show any particular trend with increased pyrolysis temperature. The adsorption pattern of lutein behaved oppositely to that of phosphorus, possibly due to competition between PL and lutein for adsorption sites. This is similar to the competition between chlorophyll and PL reported earlier at higher levels of PL (16). It would increase the dose of adsorbent required for optimal adsorption of PL (16).

The increase in surface alkalinity occurred with increased pyrolysis temperature or pyrolysis time (6); however, other physical and chemical surface changes seem to be quite unique to the method of carbon preparation. These changes might be important in determining the functional value of adsorbent carbons produced from soy hull. Based on the present study, the affinity of minor oil components for soy carbon adsorption sites was: FFA > peroxides > PL > lutein. An increase in carbonization time resulted in increased pH and titratable alkaline groups with potential hydrogen-bonding capacity; however, competition for adsorption sites between FFA and peroxides and PL may have resulted in decreased adsorption of PL relative to FFA. Carbon adsorbents are amorphous and disorganized random structures and adsorb by Van der Waals forces, also termed London dispersion forces. Van der Waals forces are strong but occur over a short distance, indicating the importance of access of the adsorbate molecule to the adsorbent. Additionally, increased alkalinity of carbon surfaces with higher carbonization temperatures will result in acid-base reactions, as evidenced by significant adsorption of FFA. Soy hull carbons prepared at low temperatures have a highly disorganized, amorphous structure with adsorption sites that are capable of binding crude oil components. However, a higher pyrolysis temperature decreases the randomness and imparts a certain degree of structural order. This may be beneficial in providing physical access of the adsorbate molecule to the adsorbent surface. These findings emphasize the variable nature of adsorbent carbon surfaces, depending on the processing conditions, and the possibility of customizing adsorbent carbon for specific applications.

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