

Acid-Treated Soy Hull Carbon Structure and Adsorption Performance

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ABSTRACT: The objective of this study was to evaluate the effect of 14 N phosphoric acid and 12 N hydrochloric acid treatments on soy hull carbon structure and adsorption performance. Scanning electron micrographs showed that acid treatments disrupted the carbon structure whereas X-ray diffraction data indicated that hydrochloric acid had a greater effect than phosphoric acid in creating a more amorphous carbon structure. Both acids significantly reduced carbon pH from 9.8, but hydrochloric acid reduced the pH to a much greater degree (pH 2.77) than phosphoric acid (pH 5.95). Both acids increased the carbon titratable surface charge. The greatest increase was in surface lactone and phenol groups, but increases were also seen in noncarboxylic carbonyls and the generation of carboxyls. Acidified carbon was most effective as a phospholipid adsorbent, and its lower affinity for other oil components may be due to competitive adsorption. Nonacidified carbon and hydrochloric acid-treated carbon adsorbed most free fatty acids, whereas the nonacidified control and commercial carbon control were most effective at adsorbing peroxides. However, vacuum adsorption conditions alone increased the contents of saturated carbonyls that were probably formed by peroxide cleavage.

Paper no. J9371 in *JAOCS* 77, 785–790 (July 2000).

KEY WORDS: Acidified soy hull carbon, adsorption, carbonyls, free fatty acids, peroxides, phospholipids, scanning electron microscopy, titratable surface groups.

Soy hulls are a low-value oilseed by-product used mainly as fuel, animal feed, and human dietary iron or fiber supplement (1). They have been investigated as a novel alternative source of inexpensive carbon to make high-value commercial adsorbent carbons (2–5). The physicochemical properties of ground soy hull, boiled soy hull, and soy hull carbon prepared by pyrolysis were compared. X-ray diffraction (XRD) studies showed that pyrolysis increased the amorphous structure and surface polarity relative to the crystalline cellulose structure of ground and boiled soy hull (2). Furthermore, pyrolysis heating time and temperature had significant effects on the microstructure and chemical properties of soy hull carbon (3–5). Higher pyrolysis temperatures resulted in expansion

and disruption of cellular structure, producing a predominantly amorphous structure. Surface alkalinity increased with increasing pyrolysis temperature and longer heating times. Studies using XRD showed that higher temperatures decreased the random carbon structure, creating a more ordered pattern.

Soy hull carbons were evaluated as an alternative adsorbent in the adsorption of minor oil components from crude soy oil (3–5). Although crude soy oil is not commercially processed by adsorption, it was used to evaluate competitive adsorption between minor oil components, as it is difficult to observe adsorption using degummed-alkali refined oil, because of minimal levels of minor oil components. Increasing carbonization times produced carbons that enhanced the adsorption of free fatty acids (FFA) from the oil, which related to increased alkalinity of the adsorbent. Increasing carbonization temperatures produced carbons with a greater ability to reduce oil peroxide value (PV). Carbons obtained by heating hulls at 400°C for 5 min gave the best overall adsorption performance, but pigments were not adsorbed at any time.

Acidification is known to open carbon adsorbent pores and modify the surface chemistry to enhance adsorption (6). The objective of this study was to observe the effect of soy hull carbon acidification on soy carbon's physical structure, surface chemistry, and adsorption performance.

MATERIALS AND METHODS

Soy hull carbon preparation. Soy hulls (Riceland Foods, Stuttgart, AR) were cleaned by removing pebbles, twigs, and other material, and then ground to a particle size of <100 mesh. The ground soy hulls were then carbonized in an air atmosphere in a Isotemp Programmable Forced-Draft muffle furnace (Fisher Scientific Company, Fairlawn, NJ) by heating to 400°C and holding at 400°C for 5 min. The carbon was immediately covered with aluminum foil to limit further oxidation, cooled to room temperature in a desiccator, and stored in air-tight amber glass bottles (4,5). Ten grams of each soy hull carbon was stirred with 250 mL of 14 N orthophosphoric acid or 12 N hydrochloric acid for 2 h in a rotary evaporator (Rotavapor BÜCHI, Labortechnik AG, Flawil, Switzerland) at room temperature. The acidified carbon was then filtered using #1 filter paper, washed in an excess of deionized water

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to a constant pH, dried in an oven at 70°C for 3 hr and then stored in an air-tight container. Carbon samples were stored in air-tight amber glass bottles.

Scanning electron microscopy (SEM). The microstructure of soy hull adsorbents was observed using SEM (model S-2300, Hitachi, Tokyo, Japan). The samples were sputter-coated with gold in a Hummer JR sputter coater (Technics EMS, Inc., Springfield, VA) before examination.

XRD. XRD patterns of the samples were obtained by using a dual goniometer X'pert XRD system (Philips Electronic Instruments, Almelo, The Netherlands) at a generator voltage of 45 kV and diffraction angle of 4–60° 2 θ angle (4,5).

pH. Soy hull carbon samples (2 g) were dispersed in 20 mL of distilled deionized water, stirred for 15 min, and filtered. The pH of the filtrate was measured. The mean of triplicate determinations was obtained for each sample (5).

Titrateable surface functional groups. Surface functional groups were measured according to the method of Toles *et al.* (6) using a commercial Calgon carbon (Calgon Carbon, Pittsburgh, PA) for comparison. Carbon samples (0.5 g) were suspended in 20 mL of a 0.1 N solution of either sodium ethoxide (in 100% ethanol) (total functional groups titration), sodium hydroxide (phenol, lactone, and carboxyl titration), or sodium bicarbonate (carboxyl titration) and stirred in a closed container for approximately 24 h. Then, an aliquot of the slurry was filtered and 10 mL was added to 15 mL of 0.1 N hydrochloric acid. The hydrochloric acid neutralized the unreacted base and prevented the adsorption of atmospheric carbon dioxide by base. The solution was then back-titrated with 0.1 N sodium hydroxide using a PC-Titrate autotitrator (Radiometer America Inc., Cleveland, OH). Triplicate determinations were made. The volume of excess OH⁻ was converted to titrateable functional groups. The results are expressed as mmol H⁺ eq/g carbon (6).

Bleaching. One hundred grams of crude soy oil was stirred with 2 g of each carbon adsorbent in the rotary evaporator and heated at 100°C in a hot water bath under 2 mm Hg pressure for 30 min. The commercial Calgon carbon was used as a control sample. The oil was then filtered to remove carbon residue and stored in air-tight, amber bottles at 4°C. The residual FFA (7), phospholipids (PL) (8), PV (9), and total polar compounds (10) of the oil samples were evaluated in triplicate. Three replications of the experiment were performed in a randomized complete block design. Data were analyzed using fit *y* by *x* analysis (11) and differences reported are significant at *P* < 0.05 unless specified otherwise.

RESULTS AND DISCUSSION

SEM. The electron micrographs of nonacidified soy hull carbon, 14 N phosphoric acid, and 12 N hydrochloric acid-treated soy hull carbons are shown in Figure 1. Soy hull pyrolysis produced a complete char with an uneven surface, as previously observed (7). The hourglass cell residue is clearly shown (Fig. 1A). During carbonization below 400°C, less dense materials may be easily pyrolyzed creating internal

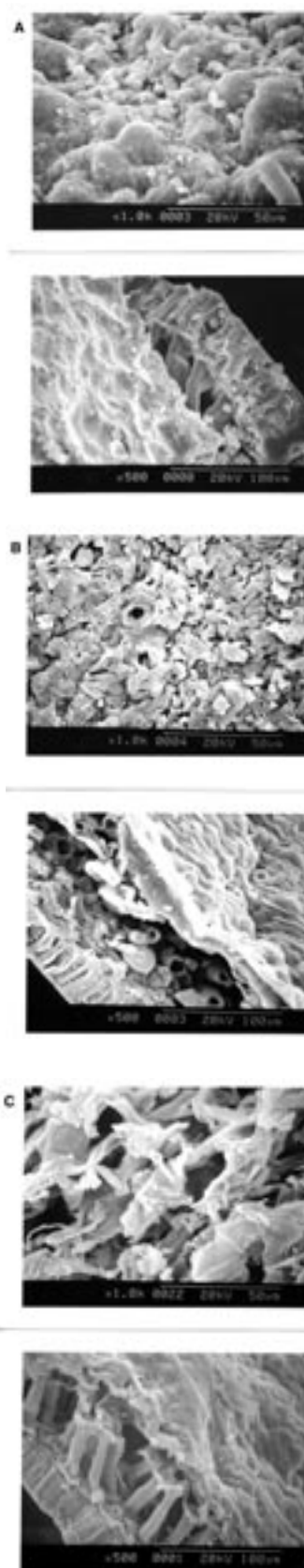


FIG. 1. Scanning electron micrographs of (A) nonactivated soy hull carbon, (B) 14 N phosphoric acid-activated soy hull carbon, and (C) 12 N hydrochloric acid-activated soy hull carbon.

pressure that disrupts the cuticle and hourglass cell; however, the basic structure of soy hull is retained. The micrograph of soy hull carbon acidified by 14 N phosphoric acid (Fig. 1B) showed that acid treatment fractured the cuticle resulting in flaws, cracks, crevices, and small pores in the small particles. The hourglass cell residue was dislodged and broken, increasing the space in this layer. The micrograph of 12 N hydrochloric acid-treated soy hull carbon (Fig. 1C) showed that the cuticle morphology was broken and flaked by the acid, resulting in a porous cuticle structure. The hourglass cell layer was collapsed, and some hourglass cells were detached. The effects of 14 N phosphoric acid and 12 N hydrochloric acid on soy hull carbon were different. Phosphoric acid displaced carbonized hourglass cells, whereas hydrochloric acid treatment produced pore structure on the carbon surface with only partial disruption of hourglass cell structure.

XRD. The XRD pattern of nonacidified soy hull carbon is shown in Figure 2A. The broad smooth hump between 15 and 35° 2 θ diffraction is a characteristic feature of amorphous carbon (4), indicating that pyrolysis converted the crystalline cellulose structure (2) to an amorphous, random, and disorganized carbon. A small peak at a *d*-spacing of 3.4 Å (26° 2 θ) indicates a graphite structure (7). The other peaks of 2.9 Å (31° 2 θ) and 2.6 Å (34° 2 θ) correspond to intermolecular and interatomic distances (7). The strong pattern around 20° 2 θ indicates a range of intermolecular and interatomic distances of approximately 4 Å. The XRD pattern of 14 N phosphoric acid-activated soy hull carbon is shown in Figure 2B. There is little difference between the XRD patterns of nonacid-treated and phosphoric acid-treated carbon. Figure 2C shows the XRD pattern of soy hull carbon activated by 12 N hydrochloric acid. The peak of *d*-spacing of 3.4 Å (26° 2 θ) was retained, presumably because the acid treatment removed the other small intermolecular and interatomic distances. The amorphous XRD pattern from 5 to 30° 2 θ was different from that of nonactivated and phosphoric activated soy hull carbon. This indicates specific increases in larger intermolecular and interatomic distances corresponding to 5–10 Å.

pH. The pH and standard deviation of nonactivated soy hull carbon was 9.8 ± 0.00 , which confirms a previous report (7). Oxides and hydroxides of potassium, sodium, magnesium, and calcium (7) probably caused this high pH. The 14 N phosphoric acid-activated soy hull carbon had a pH of 5.95 ± 0.05 , whereas 12 N hydrochloric acid activation produced a carbon pH of 2.77 ± 0.06 . The decrease in pH is probably due to leaching of alkaline salts resulting in increased acidity. This greater effect of hydrochloric acid may be due to differences in pK_a between the acids. Hydrochloric acid was completely ionized ($pK_a \sim -10$), whereas phosphoric acid was partially ionized in the analyzed system ($pK_1 \sim 2.5$, $pK_2 \sim 7.2$, and $pK_3 \sim 12.35$). Hydrochloric acid therefore contributed more H^+ than phosphoric acid at the pH of carbon and oil, which produced the greater reduction in carbon pH. The differences in the carbon XRD patterns produced by acids may also be explained by differences in the H^+ concentration (Fig. 2).

Titrateable surface functional group. Figure 3 shows the

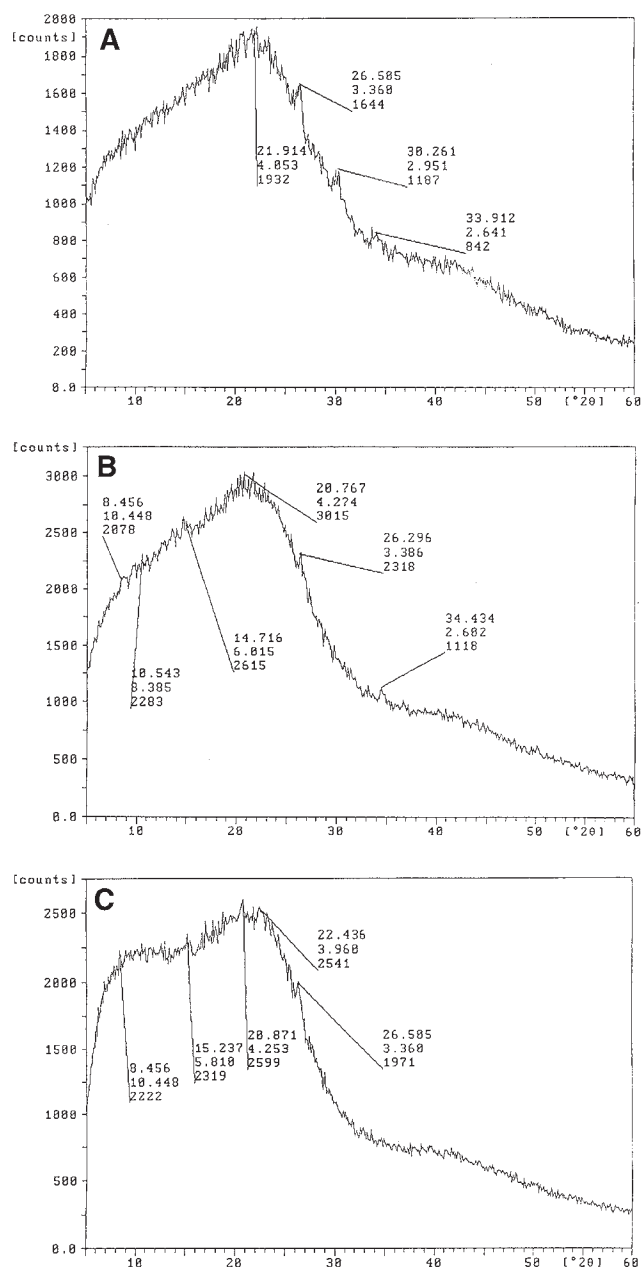


FIG. 2. X-ray diffraction pattern of (A) nonactivated soy hull carbon, (B) 14 N phosphoric acid-activated soy hull carbon, and (C) hydrochloric acid-activated soy hull carbon obtained at a generator voltage of 45 kV and diffraction angle of 4–60° 2 θ .

distribution of carbon surface functional groups. The Calgon carbon contains the least total functional groups, in which noncarboxylic carbonyl groups had the same amount as lactone and phenol groups, while the carboxyl group content was relatively low. There were no carboxyl groups, only carbonyl, lactone, and phenol groups in nonactivated soy hull carbon with most groups being lactone and phenol. The total of functional groups was slightly higher in nonacidified soy hull carbon than Calgon control carbon. Phosphoric acid treatment produced variable total functional groups and noncarboxylic

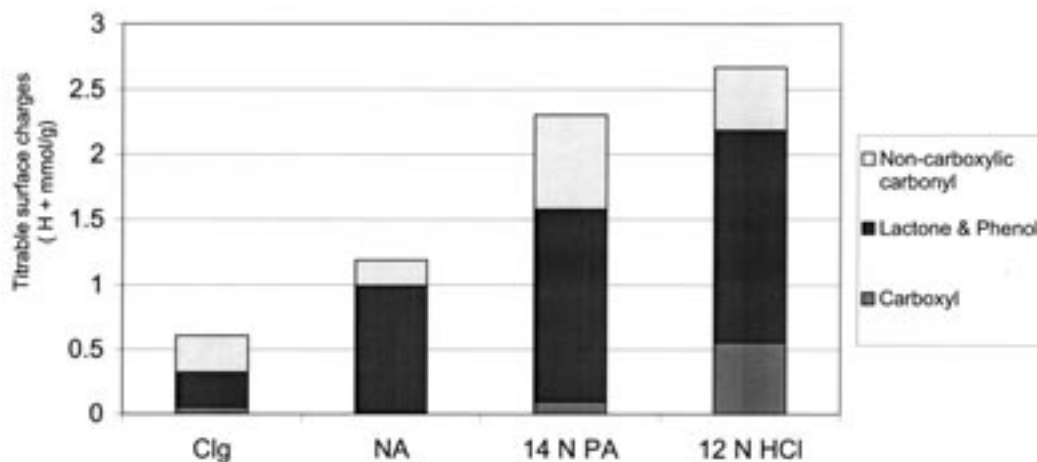


FIG. 3. Titratable surface functional groups of soy hull carbons. Soy hull carbon (NA) was activated by phosphoric acid (PA) or hydrochloric acid (HCl). The control is a commercial Calgon carbon.

carbonyl groups. Hydrochloric acid treatment increased the quantity of carbonyl, lactone, phenol, and carboxyl groups. In particular, carboxyl groups were greatly increased. As a result, the total number of functional groups was significantly elevated. Gergova *et al.* (12) found that physical activation dictated the types of functional groups formed. Relatively mild oxidation treatments give rise to acidic surface groups (13). Acidic functional groups can also be obtained by exposing the carbon to oxygen at temperatures between 200 and 700°C, with the highest degree of acidity occurring with exposure at around 400°C (14). Toles *et al.* (15) found that air activation and quench methods resulted in increased carbonyl content and also that these carbons had significantly higher titratable surface charges than any of the other activation methods studied including activation only, standard, and continuous methods (6). However, the carbons usually contain more oxygen than can be explained by the functional groups detected (16–18).

Adsorption bleaching. Figure 4A shows the PL content of crude soy oil with 2% level nonacid-treated soy hull carbon, 14 N phosphoric acid- and 12 N hydrochloric acid-activated soy hull carbon, and commercial Calgon carbon by processing under commercial bleaching conditions. All carbons significantly reduced total PL levels relative to the crude oil content ($P < 0.05$). Particularly, 14 N phosphoric acid-activated and 12 N hydrochloric acid-activated soy hull carbon showed the greatest PL adsorption. Thus, the better performance of acid-activated soy hull carbon may be due to increased surface functional groups relative to nonacid-treated carbon.

The FFA reduction in crude oil samples is presented in Figure 4B. Soy hull carbons and Calgon carbon caused a statistically significant, but small, FFA reduction. Nonactivated soy hull carbon produced the greatest reduction in FFA. Previous studies showed that a high dose (6%) of nonacid-activated soy hull carbon considerably reduced the FFA content (2), and an increase in carbonization temperature and time increased FFA adsorption (4,5). Acid treatment reduced surface

carbon pH and produced carboxylic acid groups on the carbon surface. Consequently, acid-treated soy hull carbon reduced the FFA adsorption relative to nonactivated soy hull carbon. However, the increased polar groups due to acid activation may provide potential hydrogen-bonding capacity for FFA. In addition, FFA molecules may easily access the adsorption sites in a structure with large pores, resulting from acid treatment. Treatment with 14 N phosphoric acid resulted in the least adsorption of FFA, probably because of the large amount of carboxylic acid group formed on the carbon surface (19), which produced strong acidity that repelled the adsorption of FFA. Adsorption of FFA was not as great as PL, probably owing to PL being better able to compete for adsorption sites.

Peroxide value. Figure 4C shows the PV reduction of crude soy oil samples. Commercial Calgon carbon had the greatest effect on PV reduction. Soy hull carbons had little effect on PV reduction relative to Calgon carbon. The low adsorption may be due to competition from other minor oil compounds. However, bleaching temperature alone could cause peroxide cleavage, as shown in Table 1. Bleaching conditions, in the absence of adsorbent, affected PV and the content of saturated carbonyls content of crude soy oil (Table 1). The PV was slightly, but statistically significantly, reduced, and unsaturated carbonyls levels did not change. However, saturated carbonyls significantly increased under bleaching processing conditions without adsorbents relative to crude oil ($P < 0.05$). The cleavage of peroxide may result in the formation of carbonyl compounds. Thermolytic products can be detected in triacylglycerols after heating an hour in a vacuum at 180°C, but the products of thermal decomposition of lipids in aerobic and anaerobic conditions are different (20). Under anaerobic conditions, unsaturated lipids usually produce acyclic and cyclic dimers, whereas saturated ones result in acids, hydrocarbons, propenediol esters, acrolein, and ketones. Since adsorption processing was performed under vacuum, and thermal decomposition was at minimal oxygen

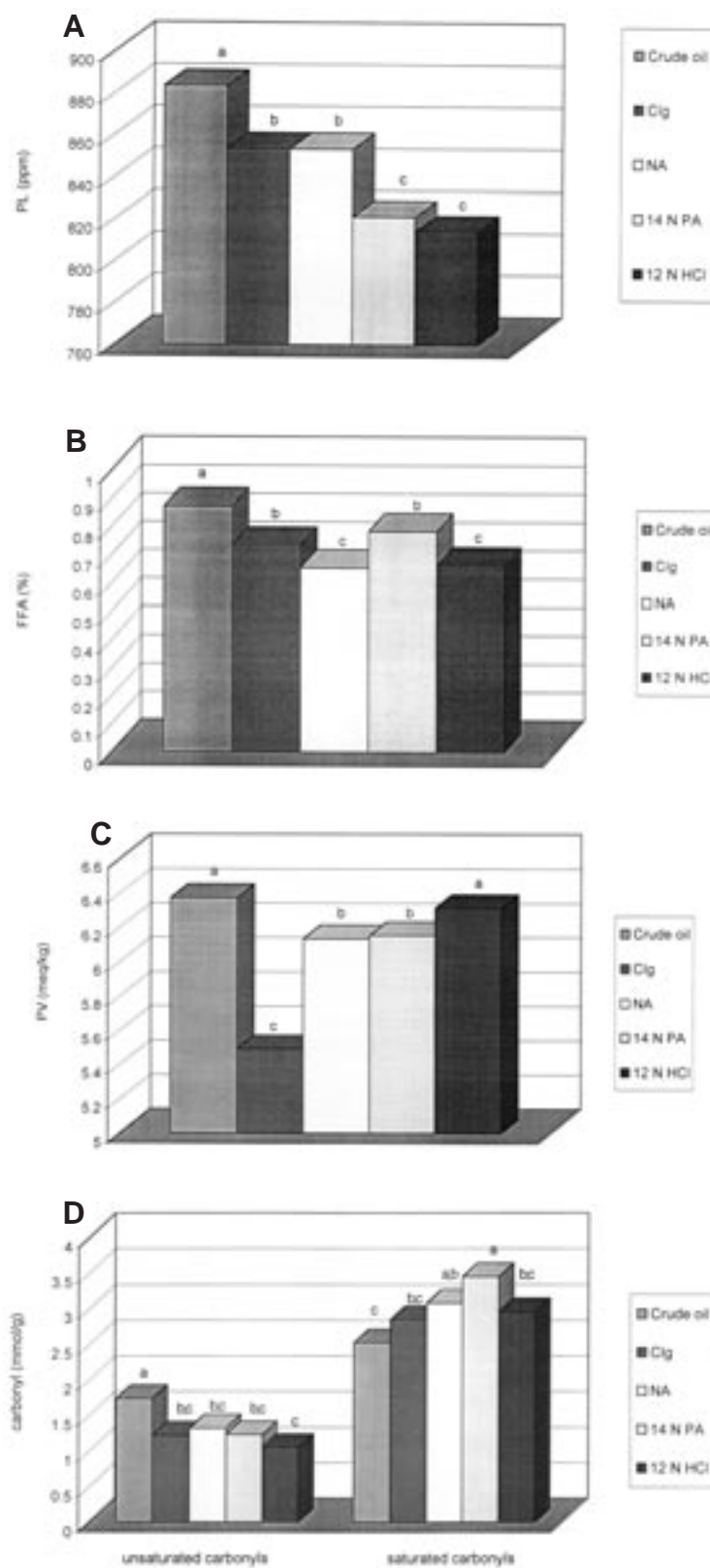


FIG. 4. Content of minor oil compounds in 100 g crude soy oil heated to 100°C for 30 min at 2 mm Hg with 2 g of either non acid-activated soy hull carbon (NA), 14 N phosphoric acid-treated soy carbon (14 N PA), or 12 N hydrochloric acid-treated soy carbon (12 N HCl). The controls were unprocessed crude oil and oil processed with a commercial Calgon carbon (Clg). (A) Total phospholipids (PL), (B) free fatty acids (FFA) (C) peroxide value (PV), and (D) polar (Carbonyl) compounds. Data are means of triplicate determinations. Those with different superscripts (a–c) indicate significant differences between samples ($P < 0.05$).

TABLE 1
Peroxide Value (PV) and Carbonyl Content of Oil Under Bleaching Conditions (at 100°C and 2 mm Hg) in Absence of the Adsorbent

	Crude soy oil	Crude oil after bleaching, processing ^a
PV value (meq/kg)	6.58 ^b	6.43 ^c
Unsaturated carbonyls (mmol/g)	1.53 ^b	1.47 ^b
Saturated carbonyls (mmol/g)	2.05 ^b	2.90 ^c

^aWithout adsorbents.

^{b,c}Significant differences in rows between samples ($P < 0.05$) by triplicate determination.

pressure, ketones could be produced from saturated triacylglycerols, which contributed to the saturated carbonyl content. In contrast, thermolytic products of unsaturated lipids did not increase carbonyl compounds. This is consistent with the results that showed unsaturated carbonyl content affected and saturated carbonyl content increased due to the bleaching processing conditions.

Polar compounds. Figure 4D shows the change in unsaturated and saturated carbonyl content of crude soy oil. Unsaturated carbonyl content was significantly reduced by all adsorbents. The saturated carbonyl content increased after processing due to thermolytic products of saturated lipids, probably caused by cleavage of peroxide. However, 12 N hydrochloric acid-treated soy hull carbon and Calgon carbon produced the only reduction of saturated carbonyl which made the total level of saturated carbonyls insignificantly different from the original level, although they were slightly increased. This could be related to larger intermolecular and interatomic distances between the two carbons. In addition, the polar adsorption sites possibly enhanced adsorption of saturated carbonyls.

Soy hull carbon has a highly disorganized amorphous structure with potential adsorption sites capable of binding to these minor crude oil components. Acid treatment changed the physical and chemical surface properties of carbon and increased surface functional groups, making the carbon surface more polar. These changes modified the adsorption properties of the carbon. Acidified carbons were most effective as a phospholipid adsorbent and their lower affinity for other adsorbents may be due to competitive adsorption.

ACKNOWLEDGMENTS

The authors wish to thank the Arkansas Soybean Research and Promotion Board for supporting this work and Riceland Foods for donating soy hulls. Published with the approval of the Director, Arkansas Experimental Station, manuscript #99084.

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[Received September 1, 1999; accepted April 21, 2000]