

Purification of FAME by Rice Hull Ash Adsorption

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ABSTRACT: Rice hull ash (RHA) and silica gel were used for purification of FAME by adsorption of FFA at atmospheric conditions. Studies demonstrated that silica gel is a better adsorbent than RHA in purifying FAME. However, both adsorbents were effective in reducing FFA levels from FAME extracts. The FFA adsorption efficiency increased with high FAME concentration and high adsorbent dosage. But FAME adsorption also increased with larger doses of adsorbent. The adsorption isotherms of FFA were determined with both adsorbents. FFA adsorption displayed Freundlich-type isotherms.

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KEY WORDS: Adsorption, adsorption isotherms, competitive adsorption, fatty acid methyl ester, rice hull ash.

FAME derived from vegetable oils and animal fats (biodiesel) have attracted considerable attention during recent years as an alternative to petroleum-based diesel fuel. Biodiesel has environmental advantages, relative to conventional diesel, as a renewable, biodegradable, and nontoxic fuel that does not require engine modification. FAME are produced by methanolysis of fats and oils with alcohols in the presence of an alkaline catalyst. Methyl esters are purified by distillation under vacuum and at high temperatures. The purity level of the diesel has a significant effect on its properties. Contaminating glycerides and FFA can cause serious combustion problems. Therefore, European Union biodiesel standards demand 99% purity (1).

Seventy-eight percent of FAME production cost comes from refining the raw material (2). Cheaper raw materials and processing costs would affect profitability positively. If energy costs could be reduced by alternative technology, the importance of FAME would increase. For this reason we reported an *in situ* esterification method of rice bran oil that was more cost effective than the alternative methods (3–5).

Rice hull ash (RHA), obtained by commercial combustion of rice hulls, has been used as a silica-based adsorbent to remove minor lipid components from vegetable oils (6–9). RHA was used to remove lutein, FFA, and phospholipids from soybean oil–hexane miscella (6–9). Proctor *et al.* (9) also showed that the adsorption of oleic acid onto RHA occurred by surface hydrogen bonding of the carboxylic acid and by the process of FFA adsorption, which followed Freundlich isotherms. Saleh and Adam (10) reported that lauric, myristic, and stearic acids adsorbed on RHA according to

a Langmuir isotherm (10). Ooi and Lean found that rice ash could selectively adsorb MG in the presence of DG (11).

The objectives of this study were (i) to demonstrate the removal of FFA from FAME by adsorption on RHA at room temperature, (ii) to determine the isotherm behavior of FFA adsorption onto RHA from FAME, and (iii) to compare RHA adsorption with that of commercial silica gel.

MATERIALS AND METHODS

Preparation of crude methyl esters. Crude methyl esters were prepared by *in situ* esterification according to the method of Özgül and Türkay (3,5). Rice bran containing approximately 70% FFA was refluxed for 1 h with methanol and 5 mL of concentrated sulfuric acid as a catalyst. The mixture was vacuum-filtered, and the filtrate was washed with 100 mL methanol. After adding water (100 mL) to the methanol phase, the solution was extracted with hexane (3 × 50 mL), and the combined extracts were washed with water. Hexane extracts were dried over anhydrous sodium sulfate and evaporated to obtain crude methyl ester.

Analysis of methyl esters. The FFA content of FAME was determined by titration with standard 0.01 N NaOH solution (12). FAME, TG, and polar substances (MG, DG, and sterols) were separated by polarity gradient column chromatography (13) and subsequently quantified. The chromatography column consisted of 25 g of silica gel, 0.5–1.0 mm particle diameter (Macherey-Nagel Co., Düren, Germany) that was transferred in hexane to an 18-mm diameter column. One gram of crude methyl ester was dissolved in hexane and applied to the column. Initially, a mobile phase of hexane/diethyl ether (99:1 vol/vol) was added to elute methyl esters. Fifty-milliliter fractions were collected throughout the separation and analyzed for methyl esters, TG, FA, and polar substances by TLC (12). The hexane/diethyl ether (99:1) eluent was applied until no more methyl ester was eluted. A mobile phase of hexane/diethyl ether (96:4 vol/vol) was then used to elute TG until TLC analysis showed no further TG was being eluted. FA were then eluted with hexane/diethyl ether (90:10 vol/vol) by TLC. Subsequent elution with hexane/diethyl ether (80:20 vol/vol) and (70:30 vol/vol) and finally ethyl ether eluted a mixture of MG, DG, and sterols, which were not resolved by column chromatography and constituted “polar substances.” Methyl esters, TG, FA, and polar substances were quantified by combining the appropriate fractions and recording the weights after evaporating the solvent. The FFA gravimetric analysis was in agreement with the FFA titration data.

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Preparation of adsorbents. RHA with a surface area of 5.9 m²/g was obtained from a rice mill (Trace, Turkey). The ash was heated at 500°C for 2 h in a muffle furnace (6) to remove residual carbon from the dark gray ash, after which 5.86% weight loss was detected. No weight loss was found on prolonged heating at this temperature and at 600, 700, and 800°C. The ash and commercial silica gel (surface area 2319 m²/g) were both sieved to obtain particles within the size range of 106–212 µm diameter.

Adsorption system and adsorption isotherms. Miscellas were prepared by making solutions of 2, 5, and 10% (vol/vol) crude methyl esters in hexane. Zero, 1-, 2-, 3-, and 4-g doses of ash and silica gel were added to each 50-mL methyl ester/hexane miscella. Miscellas were stirred in a thermostatically controlled water bath at 25°C for 30 min, beyond which no further net adsorption was found to occur. The adsorbent was then allowed to settle for 2 min. Miscellas were filtered through filter paper (Filtrak 17N, Niederschlag, Germany) to remove any residual adsorbent. Ten-milliliter samples were then titrated with standardized NaOH solution to determine FFA contents (12). Another 10 mL was evaporated, and the methyl ester contents of samples were determined by means of column chromatography (13). Freundlich isotherms were plotted as mg of FFA, expressed as oleic acid, adsorbed per g of ash vs. residual concentration of FFA for each amount of ash used. A log/log plot was also prepared to observe the Freundlich constants, *K* and *n*.

RESULTS AND DISCUSSION

The crude methyl ester extract obtained from rice bran contained 82.9% FAME, 3.28% TG, 2.92% FFA, and 10.9% polar substances.

Table 1 shows the ester and FFA contents of various crude esters after adsorption using 1 and 4 g of either RHA or silica gel. Both silica gel and RHA reduced FFA in the oil, and larger RHA and silica gel doses were more effective in reducing FFA levels than small ones. Methyl ester contents increased with increasing silica gel doses. In contrast, there was no increase in methyl ester content with increasing RHA above 5% miscella concentration. When 1 g of ash was used, methyl ester purity increased 7%, but there was a 2% increase in purity with 4 g of ash in 10% solution. It is difficult to explain the why the smallest residual FFA levels were produced with 10% miscella and 4-g doses of adsorbent. This may be related to multilayer binding and competitive adsorption. Methyl ester purity did not change significantly, but nearly half the FFA in crude methyl ester was adsorbed by 4 g of ash. This can be explained by the greater ease with which FFA is adsorbed compared to other species. Lipids can be separated by adsorption chromatography based on functional group polarity. Both the nature and number of functional groups are important factors. Adsorption affinities increase with functional groups as follows: -CH₃ < O-alkyl < C=O < -NH₂ < -OH < COOH (15). Minyu and Proctor (16) reported that methyl esters had the lowest adsorption affinity of organic

TABLE 1
Adsorption of 2, 5, and 10% (vol/vol) Crude Methyl Ester^a in Hexane on Rice Hull Ash and Silica Gel at 25°C

Adsorbent	Miscella concentration	Adsorbent quantity (g)	Ester content after adsorption (%)	FFA content after adsorption (%)
Rice hull ash	2	1	81.2	2.71
		4	86.6	2.02
	5	1	75.9	2.56
		4	76.6	2.35
	10	1	89.1	2.06
		4	84.6	1.67
Silica gel	2	1	92.7	2.73
		4	97.4	2.47
	5	1	85.5	2.25
		4	92.9	1.36
	10	1	89.7	1.96
		4	91.8	1.19

^aInitial methyl ester content of the crude ester was 82.9%, and initial crude ester FFA content was 2.92%.

functional groups studied, much less than that of acid groups (ester < aldehyde < ketone < acid < alcohol). Therefore, FA are much more likely to be adsorbed by a polar surface than methyl esters. Table 1 shows that silica gel is a better adsorbent to purify FAME than RHA, with less loss of FAME than with a similar level of FFA.

The Freundlich isotherms (Fig. 1) show the difference in the adsorption performance of silica gel and RHA. The curves are linear because the FFA concentration is too low to exhibit the typical Freundlich curve or because adsorption is reduced owing to competition (16,17). RHA particle shape and size are very irregular. Fixed masses of ash may have widely differing surface areas, which could explain the reduced *R* value relative to silica gel. Silica gel has better adsorption performance than RHA, probably because it has a much greater surface and moisture content than RHA (7,17). These characteristics will significantly enhance the adsorption of polar solutes (17).

Figure 2 shows the log/log plot for both adsorbents. The Freundlich constants are *K* and *n*, which are found by determining the intercept and slope, respectively. The constant *K* gives an overall indication of the adsorption value of the adsorbent, and *n* represents the adsorption exponent, which indicates the efficiency of the adsorption at varying solute concentrations. The greater *K* value for the silica gel indicates it is a better adsorbent overall than RHA. The greater *n* value for RHA shows that it has the ability to adsorb more FFA with increasing residual concentration. This may be due to the ionic adsorption mechanism (9).

Figure 3 shows the amount of FFA bound per gram of adsorbent. FFA adsorbed per gram of adsorbent changed with adsorbent dose and miscella concentration. A similar observation was reported for adsorption of FFA and lutein on RHA and silicic acid (6,7,17). By increasing FAME concentration in the miscella, much greater FFA adsorption on RHA and silica gel was obtained. For all concentrations, silica gel was the

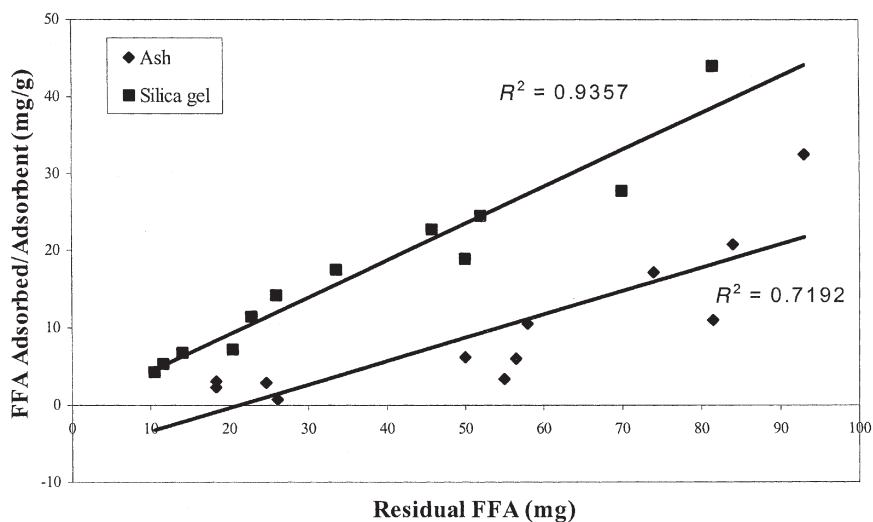


FIG. 1. FFA in crude methyl ester adsorption isotherms at 25°C.

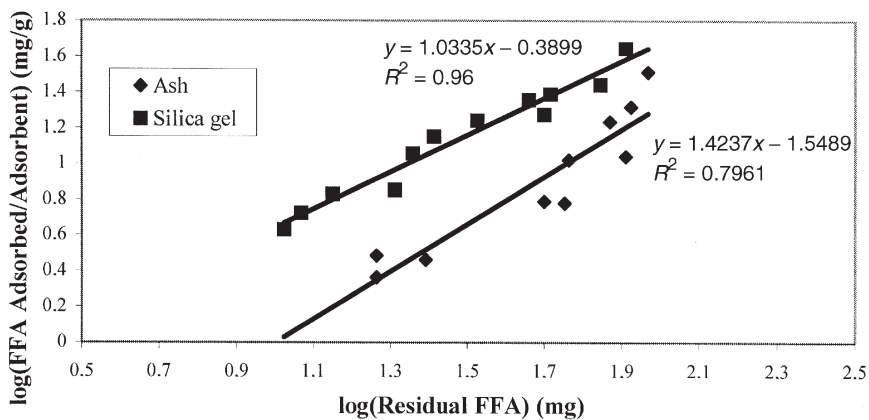


FIG. 2. FFA in crude methyl ester after adsorption, expressed as Freundlich isotherms at 25°C.

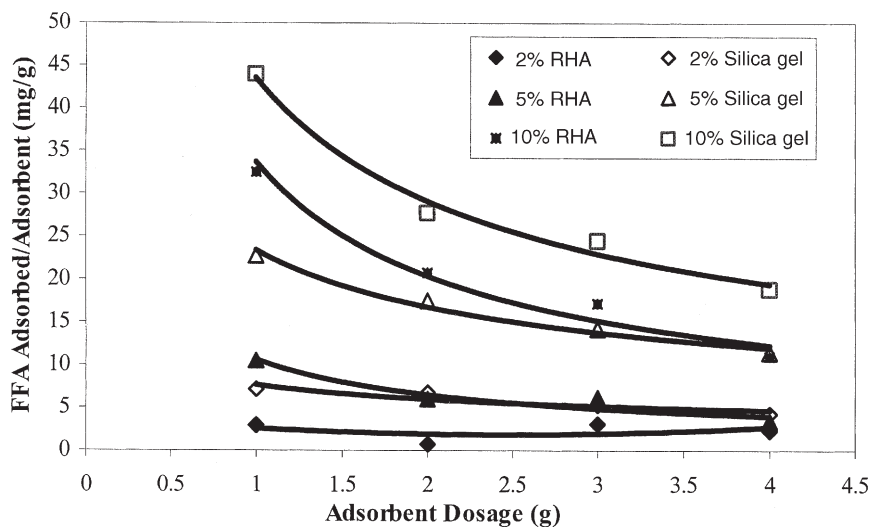


FIG. 3. Quantity of FFA adsorbed per gram of adsorbent at 25°C.

more effective adsorbent, and the efficiency of FFA adsorption declined with dosage.

FAME extracts were purified by FFA adsorption using RHA and silica gel. RHA selectively adsorbed FFA and other impurities relative to the methyl esters. As a result of this, an increase in methyl ester content was determined. However, the results showed that RHA is not as effective as silica gel in adsorbing FFA from methyl esters.

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