Adsorption Isotherms of Fatty Acids on Rice Hull Ash in a Model System

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The adsorption of lauric, myristic and stearic acids on rice hull ash (RHA) from isooctane as solvent was studied and conformed to a Langmuir isotherm. Monolayer coverage was determined to be 35.7 ± 2.5, 43.5 ± 2.2 and 36 ± 5 mg/g, respectively. The free energy of adsorption, ΔG^o, for the adsorption was determined to be −6.64, −6.23 and −6.49 kcal mol^{-1} for the adsorbates, respectively. The equilibrium parameter indicated that RHA is a good adsorbent for the three fatty acids examined.

KEY WORDS: Adsorption, crude palm oil, free energy of adsorption, free fatty acid, Langmuir isotherm, rice hull ash.

Free fatty acids (FFA) in vegetable oil result from breaking triglyceride ester bonds. FFA are normally removed during the refining process, but the use of acid-activated clay for deodorization and bleaching of palm oil can increase FFA considerably (1). FFA adsorption is determined by factors such as oil moisture and soap content, and the temperature and duration of contact with the activated clay (2). Refined palm oil quality will be reduced if FFA increase during refining.

Rice hulls (RHs) are disposed of in many countries by burning, which has caused much environmental pollution. Because rice hull ash (RHA) is a cheap source of silica, this study is an attempt to test its adsorptive capabilities and to test it as a potential material for the removal of FFA from palm oil.

Proctor and Palaniappan (3) showed that RHA can adsorb FFA from soy oil. Ooi and Leong (4) showed that RHA could selectively adsorb monoglycerides. They reported that monoglyceride adsorption was better than that of diglycerides from a 20% miscella mixture of hexane and palm oil at 80°C. Most recently, Liew *et al.* (5) studied the adsorption of carotene on acid-activated RHA. They reported a rapid decrease in the residual carotene in the crude palm oil (CPO) on adding unwashed acid-activated RHA. However, these studies were conducted on uncharacterized RHA.

Armistead *et al.* (6,7) showed that only the monomeric form (at low concentration) of the fatty acid are surface-active and are adsorbed onto a silica surface. Nawar and Hau (8) reported that the adsorption of octanoic acid onto silica gel followed the Langmuir isotherm, while the work of Proctor and Palaniappan (3) showed that the adsorption of FFA onto RHA from soy oil miscella follows a Freundlich isotherm. Adam *et al.* (9) produced and characterized the RHA. It was reported that eluting a solution of CPO in isooctane through a column of this ash successfully removed all FFA (10,11). Eluting the column with acetone desorbed the FFA, which were then identified by gas chromatography/mass spectrometry (GC/MS). This success prompted us to investigate the adsorption properties of RHA toward FFA in a model system.

The adsorption characteristics of a solute onto the adsorbent can be studied through the Langmuir isotherm:

$$\frac{q}{q_m} = \frac{K_A X_e}{1 + K_A X_e} \qquad [1]$$

where X_e (mg) is the amount of adsorbate in solution at equilibrium, q (mg/g) is the amount of adsorbate adsorbed per gram of adsorbent, q_m (mg/g) is the amount of adsorbate adsorbed to form a monolayer coverage and K_A is the Langmuir adsorption equilibrium constant.

Adsorption data can be fitted to the Langmuir isotherm in its linear form as:

$$\frac{X_e}{q} = \frac{X_e}{q_m} + \frac{1}{K_A q_m} \qquad [2]$$

K_a can be related to the adsorption free energy (ΔG^o_{ads}) (12–14) by the following equation:

$$\Delta G^o_{ads} = -\,RT\,ln\,K_A \qquad [3]$$

where R = gas universal constant; and T = temperature (Kelvin). The Langmuir constant can be used to determine the suitability of the adsorbent to the adsorbate by using the factor R below, where X_o is the initial amount of adsorbate:

$$R = \frac{1}{1 + K_A X_o} \qquad [4]$$

This factor R is a direct function of K_A which is related to the slope $1/q_m$ of the linearized Langmuir expression. R is known as the "constant separation factor" or "equilibrium parameter" (15).

The slope of the linearized Langmuir isotherm can be used to interpret the type of adsorption by using the values of R as follows: $R > 1.0$, not suitable; $R = 1.0$, linear; $0 < R > 1.0$, suitable and $R = O$, irreversible (15).

The objective of this work was to study RHA adsorption of three FFA in a model system by means of Langmuir isotherms and obtain constants for each FFA bound.

EXPERIMENTAL PROCEDURES

Preparation of RHA. The RH obtained from a rice mill in Penang, Malaysia were thoroughly washed to remove dirt and grime (9,10). The RH were rinsed a few times with distilled water and then air-dried. The washed RH were burned in a muffle furnace at 480°C for 5 h. The ash obtained was lightly ground in a mortar and sieved through B.S. 200 (75 μm), 400 (38 μm) and 400 (38 μm) mesh, respectively. The ash fraction retained on the 400 mesh was collected and labeled RHA, and this ash was used as the adsorbent in this study. In our previous work (9,10), we had shown that hulls burned at this temperature gave ash that had the highest specific pore surface area of 152 m^{2}g^{-1}. The specific pore surface area was determined by porosimetry measurements in an Autoscan-60 mercury porosimeter with an X-Y recorder model PCR-2 from Quantachrome Corporation (Syosset, NY). Chemical analysis of this ash showed that it contained *ca.* 94% SiO_2 (9,10).

NaOH solution. A solution of 0.005 M NaOH was prepared and standardized with potassium hydrogen phthalate and phenolphthalien as indicator.

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Fatty acid solutions. Lauric acid (0.08 g, 99% from BDH Chemicals, Dorset, United Kingdom), myristic acid (0.09 g, 99–100% from Sigma, St. Louis, MO) and stearic acid (0.11 g, 98% a gift from Palmex Industries Sdn. Bhd., Penang, Malaysia) was used without further purification. All fatty acids were dissolved and made up to 200.0 mL with AR-grade isooctane. These stock solutions had a concentration of *ca.* 2.00 × 10^{-3} M.

Methods. Samples of RHA (predried at 110°C and cooled) of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 g were weighed (to the nearest 0.1 mg) into separate 50.0-mL conical flasks with glass stoppers. Twenty milliliters of the stock fatty acid solution (2.00 × 10^{-3} M) were pipetted into each conical flask. The samples were shaken for 30 min by a mechanical shaker. The samples were equilibrated in a waterbath (type FK 2; Haake, Berlin-Lichterfelde, West Germany), fitted with a Line Heater (type F 4391; Haake) and maintained at 30.0 ± 0.5°C for another 30 min. At the end of 1 h, 5.0 mL of the supernatant was pipetted into 20.0 mL neutralized isopropyl alcohol and titrated with the standard NaOH and phenolphthalein as indicator (16,17). A blank titration on 5.0 mL of the untreated stock fatty acid solution was also carried out.

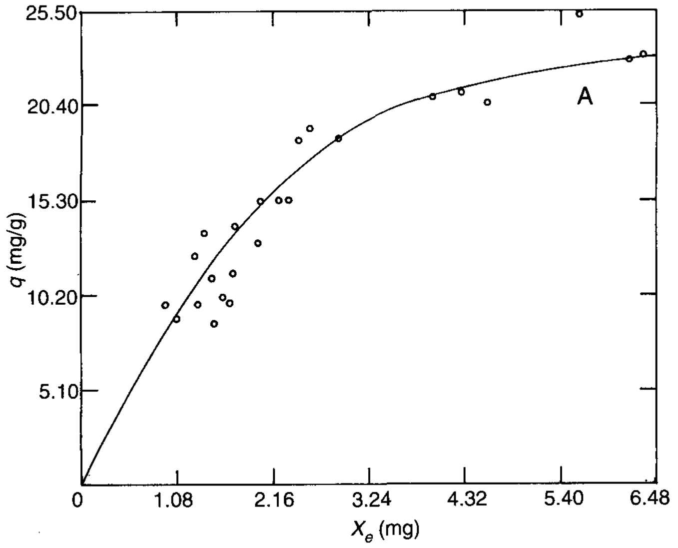
RESULTS AND DISCUSSION

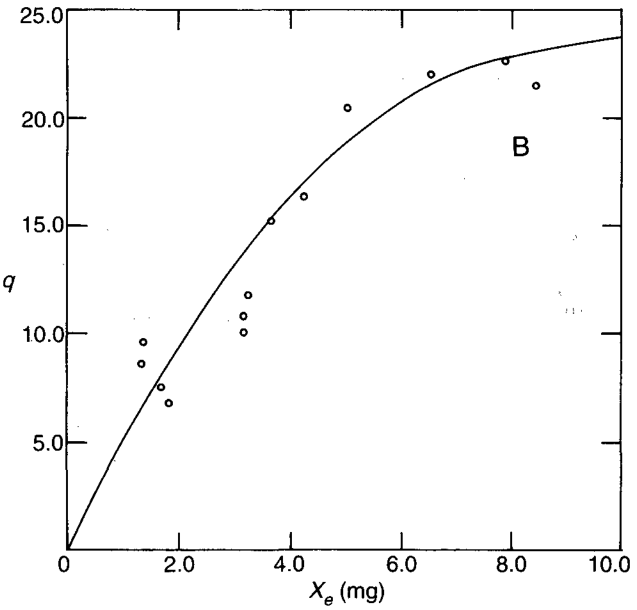
Figure 1 shows the adsorption isotherm of lauric, myristic and stearic acids from isooctane solution. Although there is scatter, the data converge to a horizontal plateau. The plateau corresponds to the formation of a monolayer of adsorbent on the RHA.

Figure 2 is the linear plot of the adsorption data related to Figure 1. Accepting the scatter of the data, we can obtain straight line plots by using statistical methods. The straight lines are drawn by the linear least-square method, and the Langmuir constants and other derived parameters are as shown in Table 1.

The percent probability, $P_n(|r|\geqslant)$, shows excellent confirmation of straight lines for all plots. This confirms that the adsorption does follow a Langmuir isotherm.

Stearic acid adsorption on metal powders were shown to follow the Langmuir isotherm, but the data did not fit the Freundlich isotherm (14). Similar isotherms were produced when a range of fatty acids were used with silica as the adsorbent (14). Nawar and Hau (8) also concluded that the Langmuir isotherm is followed by octanoic acid adsorption on silica. Our study with a model system corroborates these earlier findings that FFA adsorption follows a Langmuir isotherm rather than the Freundlich isotherm as observed by Proctor and Palaniappan (3). The shapes of the isotherms in both studies are similar. This





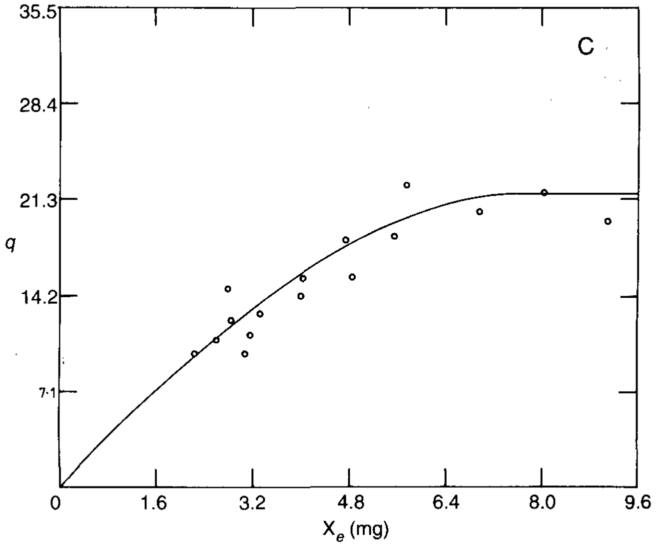
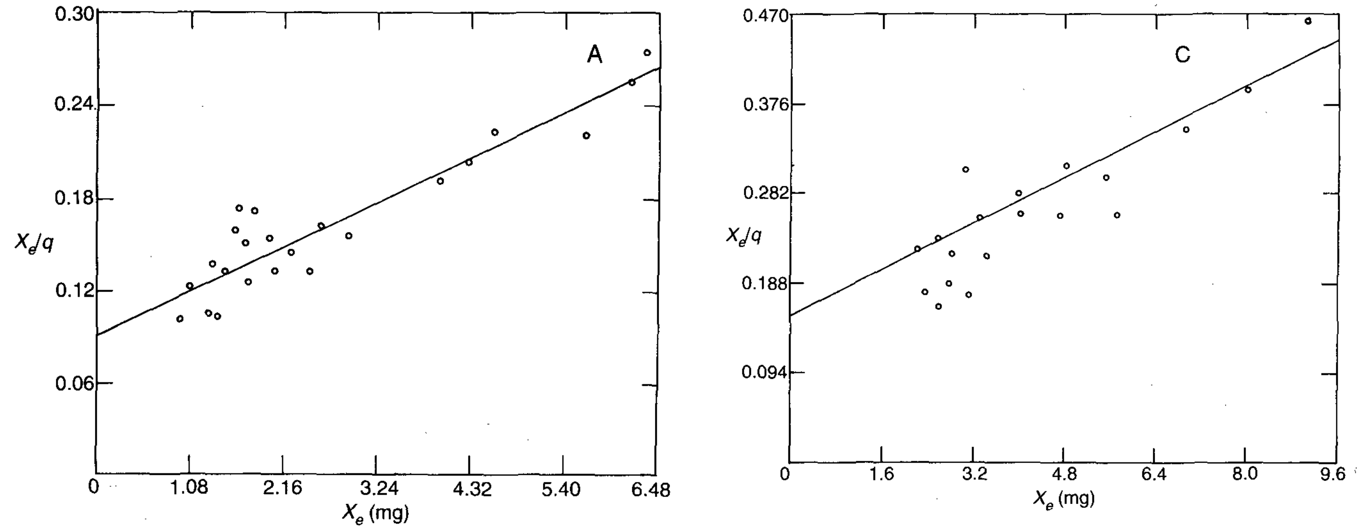


FIG. 1. (A) The adsorption isotherm obtained when 8 mg of lauric acid is dissolved in 20 mL isooctane and incubated at 30°C with variable amounts of rice hull ash (RHA) for 60 min; q (mg/g) is the amount of adsorbate adsorbed per gram of adsorbent, and X_e (mg) is the amount of adsorbate in solution at equilibrium. (B) The adsorption isotherm obtained when 10 mg of myristic acid is dissolved in 20 mL isooctane and incubated at 30°C with variable amounts of RHA for 60 min. The terms on the axis are as described in Figure 1A. (C) The adsorption isotherm obtained when 11 mg of stearic acid is dissolved in 20 mL isooctane and incubated at 30°C with variable amounts of RHA for 60 min. The terms on the axis are as described in Figure 1A.



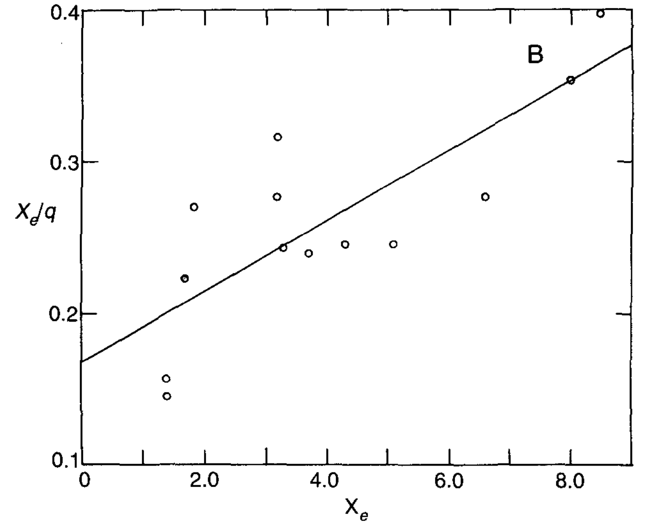


FIG. 2. (A) The linear form of the Langmuir plot for the lauric acid adsorption isotherm. The experimental conditions are as described in Figure 1A. The terms on the axis are as described in Figue 1A. (B) The linear form of the Langmuir plot for the myristic acid adsorption isotherm. The experimental conditions are as described in Figure 1B. The terms on the axis are as described in Figure 1A. (C) The linear form of the Langmuir plot for the stearic acid adsorption isotherm. The experimental conditions are as described in Figure 1C. The terms on the axis are as described in Figure 1A.

is because, at low concentrations, the Langmuir equation reduces to the Freundlich form. Nonetheless, when tested, the adsorption data obtained in this work fit much better to the Langmuir equation as shown by the Pearson's correlation, r_o, in Table 1.

Ottewill and Tiffany (12) calculated ΔG^o_{ads} for stearic acid adsorption onto a rutile surface to be −7 kcal mol^{-1} at 25°C for adsorption *via* the carbonyl oxygen. A value of −6 kcal mol^{-1} has been reported for the adsorption of phenol on alumina from benzene solution (14). The value of −6.64 to −6.23 kcal mol^{-1} is comparable to that in the literature. The free energy of adsorption for palmitic acid in the same system and under the same conditions was −6.61 kcal mol^{-1} (10). The value of ΔG^o_{ads} indicates that the process of adsorption is one of physisorption *via* hydrogen bonding of the carbonyl oxygen of the FFA onto the silanol hydrogen at the RHA silica/solvent interface (6–8,10,11,18). The monolayer coverage (q_m values) for the fatty acids was between 35 to 44 mg/g of adsorbent (Table 1). The monolayer coverage for palmitic acid was 42 mg/g of adsorbent (10). The q_m values show no particular trend for the adsorbent. On the basis of the Langmuir theory of adsorption (i.e., limited to a monolayer of adsorption on the adsorbent), it can be said that the capacity of adsorption of RHA for the fatty acids is, on the average, 39 mg of fatty acid per gram of adsorbent. Table 1 shows that the values of *R* for RHA lies between 0.20 and 0.45. These values indicate that RHA is a good adsorbent for the fatty acids used in this study.

TABLE 1

Langmuir Constants and Other Derived Parameters Obtained for Adsorbing Free Fatty Acids (FFA)[a]

FFA	q_m (mg/g)	K_A (mg^{-1})	n	r_o	P_n (|r|≥)	ΔG^o_{ads} (kcal mol^{-1})	R (X_o = 10 mg)
C_{12}	35.7 ± 2.5	0.31 ± 0.01	24	0.92	<0.05	−6.64	0.244
C_{14}	43.5 ± 2.2	0.137 ± 0.004	13	0.80	<0.1	−6.23	0.422
C_{18}	36 ± 5	0.17 ± 0.01	16	0.87	<0.05	−6.49	0.370

[a] (C_{12}, lauric acid; C_{14}, myristic acid and C_{18}, stearic acid, respectively) rice hull ash; n is the possible number of points that can give a linear correlation; r_o is Pearsons correlation; P_n points will not have a linear correlation (Ref. 19).

In summary, the adsorption of FFA onto RHA follows the Langmuir isotherm. The Langmuir parameters indicate that the adsorption process is physisorption, and that RHA is a good adsorbent for the fatty acids studied. In conjunction with our previous studies (10,11), it can be concluded that the model system used can be adopted for routine removal of FFA from refined palm oil or processed cooking oil. The use of RHA in processing of CPO seems promising, although more work has to be done to determine the quality of the oil after such RHA treatment if RHA is to be used on a commercial scale.

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