Saturated Fatty Acid Adsorption by Acidified Rice Hull Ash

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ABSTRACT: Rice hull ash (RHA) was treated with 1.0 M HNO_3 (RHA-A1) and another batch was treated with 14.0 M HNO_3 (RHA-A14). RHA-A1 and RHA-A14 had a pH of 6.58 and 6.13, respectively. Adsorption of saturated fatty acids (C_8, C_{10}, C_{12}, C_{14}, C_{16}, and C_{18}) was carried out on RHA-A1 and RHA-A14 at 32 ± 1°C. The adsorption data conformed to the Langmuir isotherm. The specific surface area of RHA-A1 was 183.84 $m^2\ g^{-1}$ while that of RHA-A14 was 174.67 $m^2\ g^{-1}$. The specific pore volume of RHA-A1 was 0.216 $cm^3\ g^{-1}$ while that of RHA-A14 was 0.234 $cm^3\ g^{-1}$. The acid-treated ash, RHA-A14 (q_m = 0.43 ± 0.03 mmol g^{-1} where q_m is the amount of adsorbate adsorbed to form a monolayer coverage on the ash particles) showed a twofold increase in the adsorption of fatty acid per gram ash compared to RHA-A1 (q_m = 0.25 ± 0.03 mmol g^{-1}). The free energy of adsorption, $\Delta G°_{ads}$, was determined to be –7.06 ± 0.10 and –6.75 ± 0.11 kcal mol^{-1} for RHA-A1 and RHA-A14, respectively. The reduced $\Delta G°_{ads}$ values observed for RHA-A14 were attributed to the electrostatic repulsion of the hydrophobic chain of the fatty acid adsorbed on adjacent sites and brought into close proximity of each other. The $\Delta G°_{ads}$ values showed that the process of adsorption took place through physisorption on both RHA.

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KEY WORDS: Adsorption, fatty acids, free energy of adsorption, Langmuir isotherm, rice hull ash.

Use of acid-activated clay for deodorization and bleaching of palm oil is an important step in the refining process. The use of acid-activated clay caused the breaking of the triglyceride ester bonds (1), which contributes to an increase of free fatty acids (FFA) in the refined oil.

In our previous studies, we examined the use of untreated alkaline rice hull ash (RHA) as an adsorbent for the removal of FFA. The alkaline ash (2,3) was used to study the adsorption characteristic toward FFA in a model system (4). The result indicated a high affinity toward FFA adsorption from isooctane solvent. When palm oil in isooctane was eluted through a column of the alkaline ash, all the FFA were removed (5). Proctor *et al.* (6) suggested the alkaline metal ions, especially K^+, present in the alkaline ash will react with the fatty acid-forming carboxylate ions. This mechanism was suggested to contribute to the adsorptive capacity of the RHA. Liew *et al.* (7) found that treating the ash with sulfuric acid increased the acid adsorption sites (i.e., Si-OH groups). Similar acid treatment was shown to remove potassium ions (8).

Proctor *et al*. (6) also showed that the adsorption mode of oleic acid onto RHA partially occurred by surface hydrogen bonding of the carboxylic acid. Hau and Nawar (9) reported that the adsorption of octanoic acid onto silica gel followed the Langmuir isotherm. The review by Proctor and Toro-Vazquez (10) showed that the adsorption of vegetable oil onto commercial bleaching clay followed the Freundlich isotherm. However, it is known that the Freundlich isotherm is a special case (i.e., the lower concentration limit) of the Langmuir isotherm (11).

The adsorption data can be fitted to the Langmuir isotherm (4) in its linear form as:

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

where X_e (mg) is the amount of adsorbate in solution at equilibrium and q (mg/g) is the amount of adsorbate adsorbed onto the adsorbent and q_m (mg/g) is the amount of adsorbate adsorbed to form a monolayer coverage on the ash particles. K_A is the Langmuir adsorption equilibrium constant. K_A can be related to the adsorption free energy ($\Delta G°_{ads}$) (12–14) by Equation 2:

$$\Delta G°_{ads} = -RT \ln K_A \qquad [2]$$

where R = gas universal constant and T = temperature (Kelvin).

This work is an extension of our previous adsorption studies (2,4,6) on RHA in our effort to utilize the agricultural waste resulting from rice-milling activity. In this work, the raw ash was treated with nitric acid to remove all the metal cations. We were interested to know the adsorptive capacity of RHA after removing the alkaline metals, especially the K^+ ions that were present in the untreated ash. The oxidizing nature of the acid may be useful in removing most of the residual metal ions and changing the adsorbent surface. Since one of the main objectives of our work is to extend the use of RHA as an adsorbent in the processing of palm oil, we have used all the major fatty acids found in palm oil in this study. The major fatty acids found in palm oil are caprylic (C_8), capric (C_{10}), lauric (C_{12}), myristic (C_{14}), palmitic (C_{16}), and stearic (C_{18}) acids. The objectives of this paper were (i) to study the effect of different concentrations of nitric acid on the specific surface area and

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pore volume of the rice hull ash; (ii) to determine its adsorptive capability toward the fatty acids in a model system; and (iii) to determine the physical parameters from the adsorption isotherm, i.e., q_m and $\Delta G°_{ads}$.

EXPERIMENTAL PROCEDURES

Preparation of RHA-A1 (treated with 1.0 M HNO_3) and RHA-A14 (treated with 14.0 M HNO_3). The rice hull was obtained from a rice mill in Permatang Tok Jaya (Penang, Malaysia). The RHA was prepared by a method previously described (2–4). The RHA was stirred in 1.0 M HNO_3 for 24 h. The resulting ash was thoroughly washed with water and then rinsed with distilled water until the filtered water gave a constant pH. The ash was dried in an oven at 110°C for 24 h. The dried ash was labeled RHA-A1 and was kept in a desiccator for further use. A similar portion of RHA was stirred in 14 M HNO_3 for 24 h and then washed and dried as previously described. The dried ash was labeled RHA-A14 and also stored in a desiccator. The specific surface area and specific pore volume of RHA, RHA-A1, and RHA-A14 were determined at 77 K using Micrometrics ASAP 2000 (accelerated surface area and porosimetry system) nitrogen adsorption porosimeter from Micrometrics Instrument Corp. (Norcross, Germany).

Fatty acid solutions. C_8 (0.07 g, 99%), C_{10} (0.09 g, 99%), C_{12} (0.10 g, 98%), C_{14} (0.12 g, 98%), C_{16} (0.13 g, 98%), and C_{18} acids (0.15 g, 98%) (all the fatty acids were donated by Acidchem International, Seberang Prai, Malaysia) were dissolved and diluted separately in AR-grade isooctane to 250.0 mL. These stock solutions had a concentration of *ca.* 2.00×10^{-3} M.

Method. Samples of RHA-A1 (or RHA-A14, predried at 110°C) of 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 g (to the nearest mg) were weighed into separate 50.0-mL conical flasks with screw cap stoppers. Twenty milliliters of the stock solution (*ca.* 2.00×10^{-3} M) was pipetted into each conical flask. The samples were shaken for 30.0 min at 32 ± 1°C with an orbital shaker (model Hotech 729; Hotech Instruments Corp., Taipei, Taiwan) at 320 rpm. The shaking was stopped and the solution was allowed to settle for 30 min. Supernatant (5.0 mL) was pipetted into 20.0 mL of neutralized 1-propanol and titrated with the standardized 2.5 mM NaOH and phenolphthalein as indicator (15). A blank titration on 5.0 mL of the untreated stock fatty acid solution also was carried out. The Microsoft Office 2000 Excel program was used to draw the graphs using the data obtained from these experiments.

RESULTS AND DISCUSSION

Characterization of RHA. The treatment of RHA with nitric acid showed an increase in the acidity of the ash. Table 1 shows the pH values of a 2% suspension of the prepared ash. The acidity of the ash increased with the concentration of the acid used to treat it. This can be explained by the leaching away of the metal ions that were incorporated during the formation of the husk. The metal ions found in the ash had been determined to be Fe, Ca, Mg, Na, K, and Mn in the form of their respective oxides (2,16). When mineral acids leach metal ions out of the metals, pores of various sizes could be generated, leading to changes in the pore volume and the pore surface area of the ash.

The nitrogen adsorption study revealed the surface area of the treated ash increased markedly from the untreated ash as shown in Table 1. Table 1 also shows the specific pore volume of the ash studied. An increase of 27% in the specific surface area was observed when the ash was treated with 1.0 M HNO_3. The specific surface area was expected to increase further on treating the ash with 14.0 M HNO_3. However an increase of only 20% was observed. A second determination of the specific surface area for RHA-A14 (from a different batch of RHA) produced similar results. The average pore diameter of RHA-A14 is much larger than that of RHA-A1. The larger pore diameter in RHA-A14 (as a result of the stronger leaching effect of the 14 M HNO_3) will result in a reduction in the surface area for a given mass of adsorbent. The observed variation in the specific surface area of all three RHA is consistent with the variation of the pore diameter. The pore volume increased by 3% when treated with 1.0 M HNO_3, but on treating the ash with 14.0 M HNO_3 an increase of 12% was observed. This is consistent with the stronger leaching power of the more concentrated acid. A similar observation was made by Ng *et al.* (17) when activated clay was treated with mineral acid. The opening up of new pores and the enlargement of existing pores due to the greater leaching effect of the stronger acid increased the total number of adsorption sites on the surface. The silanol groups have been shown to be the adsorption sites for the fatty acids (6,18) on bleaching clays and silica gels.

Fatty acid adsorption on RHA-A1 and RHA-A14. Figure 1

TABLE 1
The Nitrogen Adsorption Parameters for RHA, RHA-A1, and RHA-A14[a]

Sample	pH	Specific surface area (m^2 g^{-1})	Specific pore volume (cm^3 g^{-1})	Average pore diameter (Å)
RHA	8.83	145.15[b]	0.209	57.55
RHA-A1	6.58	183.84	0.216	47.08
RHA-A14	6.13	174.67	0.234	53.28

[a] The pH values were obtained from a 2% suspension of RHA, RHA-A1, and RHA-A14 at 32 ± 1°C. RHA, rice hull ash; A-1 and A-14 indicate the molarities of HNO_3 used in acidification treatments.
[b] The value obtained for this sample using a mercury porosimeter (Refs. 2,4) was *ca.* 150 m^2 g^{-1}.

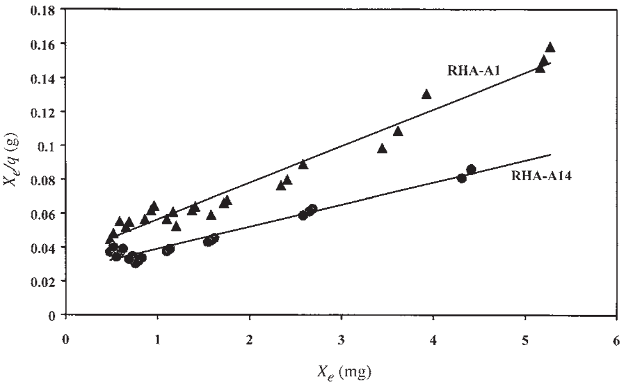

FIG. 1. The linear isotherm of the Langmuir plot (equation 1) for capric (C_{10}) acid adsorption when 7.2 mg of the acid was dissolved in 20 mL of isooctane and incubated at 32 ± 1°C with variable amounts of the ash for 60 min: ▲ onto RHA-A1; ● onto RHA-A14. RHA, rice hull ash; A1 and A14 indicate the molarities of HNO_3 used in acidification treatments; X_e, amount of absorbate in solution at equilibrium; q amount of adsorbate adsorbed onto the absorbent.

shows the representative linear form of the Langmuir plot for C_{10} acid on RHA-A1 and RHA-A14. All of the fatty acids were found to conform to the Langmuir adsorption isotherm with a Pearson's correlation coefficient of $r_o \geq 0.93$. Table 2 shows the Langmuir parameters for all the fatty acids for adsorption onto RHA-A1 and RHA-A14, respectively. The *Pn* values [the percent probability of *n* number of points on the graph not having a linear correlation (19)] indicate that the adsorption of fatty acids by RHA-A1 and RHA-A14 conform to the Langmuir isotherm, within the concentration range used in this study.

The monolayer coverage (assuming the linearity shown by r_o indicates the adsorption follows the Langmuir isotherm), as shown by the q_m values for RHA-A14, increased compared to RHA-A1 because of the increase in specific pore volume. From Table 2, it can be seen that for the same RHA, q_m increases with the molecular weight of the fatty acids. However, if the number of adsorption sites is constant for each RHA (i.e., per gram), then the number of moles of fatty acid adsorbed to form the monolayer should be the same for all the acids, irrespective of the chain length. This was observed if the units of q_m were converted to mmols g^{-1}. Table 3 shows the values of q_m in mmols g^{-1} for RHA-A1 and RHA-A14 to be 0.25 ± 0.03 and 0.43 ± 0.03, respectively. The q_m values for RHA-A14 increased twofold compared to that for RHA-A1. This is in accordance with the increase in the specific pore volume. In contrast, the q_m values found for lauric, myristic, and stearic acids on the untreated RHA were *ca*. 0.17 mmol g^{-1} (2,4). The smaller value for the untreated RHA is expected because of its lower specific surface area.

Table 3 also shows the $\Delta G°_{ads}$ values for the adsorption of fatty acids onto RHA-A1 and RHA-A14. The $\Delta G°_{ads}$ values obtained for RHA-A1 and RHA-A14 are relatively constant and are distinctly different from each other. The $\Delta G°_{ads}$ for RHA-A1 is larger than that of RHA-A14. The larger pore volume on RHA-A14 (probably with a larger number of adsorption sites) enables the adsorption of more fatty acid molecules on the surface. However, the presence of a large number of fatty acid molecules adsorbed very close to each other causes electrostatic repulsion of the hydrophobic carbon chain, which remains extended in the solvent. The electrostatic repulsion results in the lowering of $\Delta G°_{ads}$ values for RHA-A14. The $\Delta G°_{ads}$ values of –6.75 and –7.06 kcal mol^{-1} obtained for RHA-A14 and RHA-A1 are consistent with physisorption (12). In our previous study (2,4), the values obtained for lauric, myristic, and stearic acids on the untreated RHA had an average value of –6.49 kcal mol^{-1}. The values of q_m and $\Delta G°_{ads}$ obtained in this study for RHA-A1 and RHA-A14 and those obtained previously for the untreated alkaline RHA are consistent with the changes in the surface area of the three RHA

TABLE 2
Langmuir Constants and Other Derived Parameters for the Adsorption of Fatty Acids onto RHA-A1 and RHA-A14[a]

Fatty acid	Type of RHA	q_m (mg/g)	K_A (mg^{-1})	n	r_o	$Pn = (\lvert r\rvert \geq r_o)$
Caprylic	RHA-A1	39.9 ± 1.3	0.76 ± 0.05	29	0.99	0.00
(C_8)	RHA-A14	68.8 ± 4.7	0.36 ± 0.03	29	0.93	<0.05
Capric	RHA-A1	46.3 ± 1.7	0.62 ± 0.04	27	0.98	0.00
(C_{10})	RHA-A14	76.7 ± 3.5	0.50 ± 0.03	24	0.98	0.00
Lauric	RHA-A1	43.9 ± 2.3	0.54 ± 0.05	22	0.97	0.00
(C_{12})	RHA-A14	81.9 ± 6.0	0.35 ± 0.03	26	0.95	<0.05
Myristic	RHA-A1	49.7 ± 3.7	0.46 ± 0.06	24	0.94	<0.05
(C_{14})	RHA-A14	97.5 ± 7.6	0.27 ± 0.03	27	0.93	<0.05
Palmytic	RHA-A1	61.0 ± 2.2	0.62 ± 0.06	26	0.98	0.00
(C_{16})	RHA-A14	105.5 ± 8.9	0.29 ± 0.03	22	0.93	<0.05
Stearic	RHA-A1	76.0 ± 3.5	0.37 ± 0.03	28	0.97	0.00
(C_{18})	RHA-A14	118.2 ± 8.6	0.27 ± 0.03	24	0.94	<0.05

[a]Samples were incubated at 32 ± 1°C with varying amounts of the ash. q_m = amount of adsorbate adsorbed to form a monolayer coverage (Eq. 1); K_A = Langmuir adsorption constant; n = number of data points used in the linear regression method (Eq. 1); r_o = Pearson's correlation coefficient; Pn = percent probability where the n number of points do not have a linear correlation (Ref. 19); see Table 1 for other abbreviations.

TABLE 3
Values of q_m and $\Delta G°_{ads}$ for RHA-A1 and RHA-A14 at 32 ± 1°C[a]

	q_m (mmol g^{-1})		$\Delta G°_{ads}$ (kcal mol^{-1})	
Fatty acid	RHA-A1	RHA-A14	RHA-A1	RHA-A14
Caprylic (C_8)	0.28	0.48	–7.03	–6.58
Capric (C_{10})	0.27	0.45	–7.02	–6.89
Lauric (C_{12})	0.22	0.41	–7.02	–6.76
Myristic (C_{14})	0.22	0.43	–7.01	–6.68
Palmitic (C_{16})	0.24	0.41	–7.26	–6.80
Stearic (C_{18})	0.27	0.42	–7.01	–6.81
Average[b]	0.25 ± 0.03	0.43 ± 0.03	–7.06 ± 0.10	–6.75 ± 0.11

[a] $\Delta G°_{ads}$, absorption free energy; see Tables 1 and 2 for other abbreviations.
[b] The error shown is the standard deviation (σ_n).

silica. The nitric acid treatment increased the specific surface area significantly. This resulted in the increased capacity for fatty acid adsorption by the acid-treated RHA. While the work of Proctor *et al.* (6) suggested the presence of K^+ increased the FFA adsorption capacity of the ash, our study revealed that removing the alkali metals (by HNO_3 treatment) did not decrease FFA adsorption in the system studied. The increased FFA adsorptions also may be solely due to the increased surface area of the ash on treatment with the acid.

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