

Investigation of Adsorption Isotherms of Myristic, Palmitic and Stearic Acids on Rice Hull Ash

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The adsorption of myristic, palmitic and stearic acids on rice hull ash from isooctane as solvent was studied and conformed to a Langmuir isotherm. Monolayer coverage was determined to be **40.08, 38.43** and **37.27 mg/g**, respectively. The free energy of adsorption, ΔG_{ads}° , for the adsorption was determined to be **-6.25, -6.32 and -6.39 kcal mol⁻¹** for the adsorbates, respectively. The equilibrium parameter indicated that rice hull ash is a good adsorbent for myristic, palmitic and stearic acids examined.

Key words: Adsorption, free energy of adsorption, Langmuir isotherm, myristic, palmitic, stearic acids, rice hull ash.

Introduction

Free fatty acids in vegetable oil result from breaking triglyceride ester bonds, free fatty acids are normally removed during the refining process in industry, but the use of acid-activated clay for bleaching of vegetable oils can increase free fatty acids considerably¹. Free fatty acid adsorption is determined by factors such as oil moisture and soap content, and the temperature and duration of contact with the activated clay².

Rice hulls are disposed of in many countries by burning, which has caused much environmental pollution. Since rice hull ash is a cheap source of silica^{3,4}, Proctor and Palaniappan⁵ showed that rice hull ash can adsorb free fatty acid from soy oil. Ooi and Leong⁶ showed that rice hull ash could selectively adsorb monoglycerides.

Liew et al.⁷ studied the adsorption of carotene in the crude palm oil on acid-activated rice hull ash. Armstead et al.^{8,9} showed that only the monomeric forms (at low concentration) of the fatty acid are surfaceactive and are adsorbed onto a silica surface. Nawar and Han¹⁰ reported that the adsorption of octanoic acid onto silica gel followed the Langmuir isotherm, while the adsorption of free fatty acids onto rice hull ash from soy oil miscella follows a Freundlich isotherm.

Adam et al.³ produced and characterized the rice hull ash. It was reported that eluting a solution of crude palm oil in isooctane through a column of this ash successfully removed all free fatty acids^{4,11}.

The adsorption of characteristics of a solute onto the adsorbent can be studied through the Langmuir isotherm¹²:

$$\frac{q}{qm} = \frac{K_A X_e}{1 + K_A X_e} \quad (1)$$

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 the 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:

$$\frac{X_e}{q} = \frac{X_e}{q_m} + \frac{1}{K_A q_m} \quad (2)$$

According to equation 2, a plot of X_e/q versus X_e gives a straight line with slope equal to $1/q_m$, and intercept is $1/(K_A q_m)$. K_A can be related to the adsorption free energy, ΔG_{ads}° , by the following equation^{13,15}:

$$\Delta G_{ads}^\circ = -RT \ln K_A \quad (3)$$

where **R** is the gas universal constant (**1.987 cal mol⁻¹ K⁻¹**) and **T** is the absolute temperature (**Kelvin**). The Langmuir constant can be used to determine the suitability of the adsorbent to the adsorbate by using the factor **R**¹²,

$$R = \frac{1}{1 + K_A X_0} \quad (4)$$

where X_0 is the initial amount of adsorbate. 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”¹⁶.

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; **q** < **R** < **1.0**, suitable and **R** = **0**, irreversible¹⁶.

In this study, we aimed to study the adsorption of myristic, palmitic and stearic acids onto rice hull ash by means of Langmuir isotherms and calculate constants for each acid bound.

Experimental

Materials

Preparation of rice hull ash: The rice hulls supplied from Sun Inc. Co., in Edirne (Uzunköprü) were thoroughly washed to remove dirt and grime. The rice hulls were rinsed a few times with distilled water and then air-dried. The washed rice hulls were burned in a muffle furnace (Model 1913, Kermanlar, İstanbul, Turkey) at 500°C for 5 h.

The ash obtained was lightly ground in a mortar and sieved through 200 (75 μm) and 400 (38 μm) mesh by means of a test sieve shaker (Octagon 200, Endecotts Ltd., London, U. K.) respectively. The ash fraction retained on the 400 mesh was collected and labelled rice hull ash, and this ash was used as the adsorbent in our study.

Hulls burned at 500°C gave ash that had the specific pore surface area of **150 m² g⁻¹**. The specific pore surface area was determined by a gas-adsorption apparatus¹⁷. This apparatus consists of a mercury manometer, a mercury-filled gas burette, six stopcocks, a ground-glass joint; a vacuum pump, a tank containing inert gas (nitrogen gas is used in our experiments) and the adsorbent matter (rice hull ash).

Preparation of NaOH solution: A solution of 0.005 M NaOH was prepared and standardized with potassium hydrogen phthalate and phenolphthalein as an indicator.

Preparation of fatty acid solutions: Myristic acid (Merck), palmitic acid (Merck) and stearic acid (Merck) were used without further purification. All fatty acids were dissolved and made up to 200 mL with isooctane (Merck). These stock solutions had a concentration of ca. 2.00×10^{-3} M.

Methods

Samples of rice hull ash (predried at 110°C and cooled in a vacuum desiccator) 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 mL conical flasks with glass stoppers. 20 mL 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 (type 3047, Köttermann Labortechnik, Uetze-Hanigsen, Germany).

The samples were equilibrated in a thermostated waterbath (type ZD, Grant Instruments Ltd., Cambridge, U. K.) and maintained at 25°C for another 30 min. At the end of 1 h, 5 mL of the supernatant was pipetted into 20 mL neutralized isopropyl alcohol and titrated with the standard NaOH and phenolphthalein as an indicator. A blank titration on 5 mL of the untreated stock fatty acid solution was also carried out.

Results and Discussion

Figure 1 shows the adsorption isotherms of myristic, palmitic and stearic acids from isooctane solution. As can be seen in Figure 1, the data coverage to a horizontal plateau. This plateau corresponds to the formation of a monolayer of adsorbent on the rice hull ash.

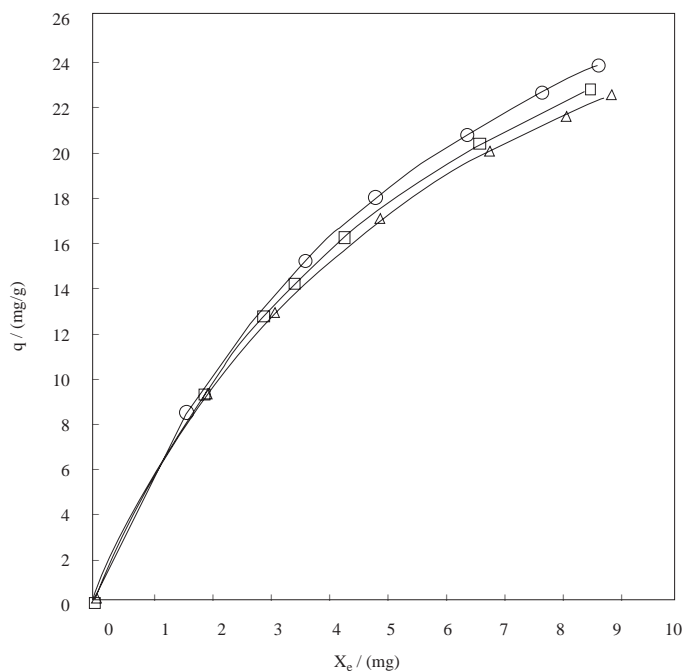


Figure 1. The adsorption isotherm plot of $q(\text{mg/g})$ vs $X_e(\text{mg})$: \circ : myristic acid, \square : palmitic acid and Δ : stearic acid.

Figure 2 is the linear plot of the adsorption data related to Figure 1. The Langmuir constants and other derived parameters from this plot are shown in Table 1. The decrease in the amount of adsorbate

adsorbed to form a monolayer coverage with increasing number of carbon atoms in the fatty acid chain may be due to the higher molecular weight and decreasing mobility of the fatty acid chain. Because it becomes difficult for the fatty acids with the long chain to penetrate into the pores of the rice hull ash.

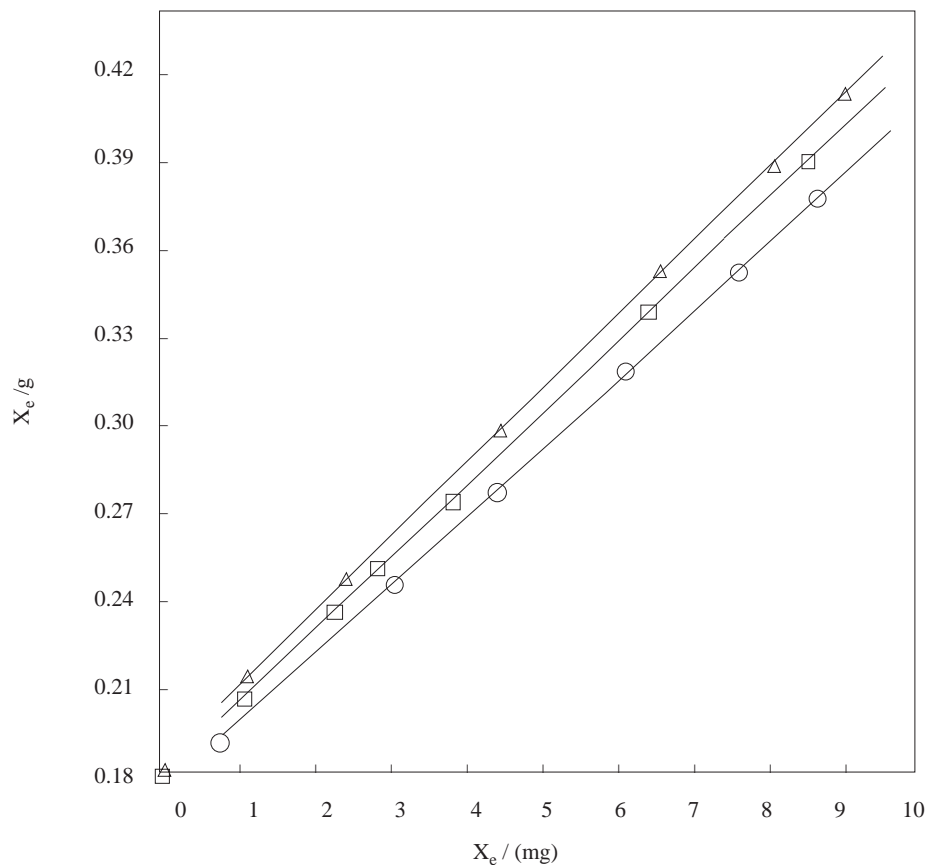


Figure 2. The Langmuir plot of X_e/q vs X_e (mg): \circ : myristic acid, \square : palmitic acid and Δ : stearic acid.

Table 1. Langmuir constants and other derived parameters obtained for adsorbing myristic, palmitic and stearic acids.

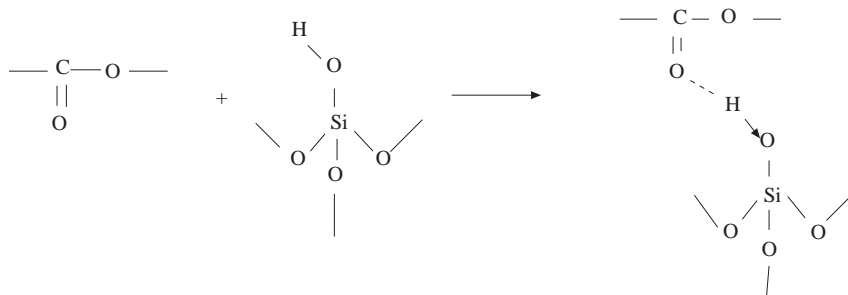
Fatty acid	q_m (mg/g)	K_A (mg^{-1})	ΔqG°_{ads} (kcal mol^{-1})	R ($X_0=10$ mg)
Myristic acid, $C_{14:0}$	40.08	0.1657	-6.25	0.3764
Palmitic acid, $C_{16:0}$	38.43	0.1668	-6.32	0.3748
Stearic acid, $C_{16:0}$	37.27	0.1680	-6.39	0.3731

Stearic acid adsorption on metal powders were shown to follow the Langmuir isotherm, but the data did not fit the Freundlich isotherm¹⁵. Similar isotherms were produced when a range of fatty acids were used with silica as the adsorbent¹⁵. Nawar and Han¹⁰ also concluded that the Langmuir isotherm is followed by octanoic acid adsorption on silica. Our study corroborates these earlier findings that free acid adsorption follows a Langmuir isotherm rather the Freundlich isotherm as observed by Procter and Palaniappan⁵.

Ottewil and Tiffany¹³ calculated ΔG°_{ads} for stearic acid adsorption onto a rutile (TiO_2) 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 (Al_2O_3) from benzene solution¹⁵. Our value of -6.39 to -6.25 kcal

mol^{-1} is comparable to and in agreement with that in the literature (-7 to -6 kcal mol^{-1} is comparable to and in agreement with that in the literature (-7 to -6 kcal mol^{-1}).

The value of ΔG_{ads}° indicates that the process of adsorption is one of physisorption via hydrogen bonding of the carbonyl oxygen of the free fatty acid onto the silanol hydrogen at the rice hull ash silica/solvent interface. The carbonyl oxygen of the free fatty acid reacts with the silanol hydrogen, and the free fatty acid molecule may be adsorbed on the surface by forming a hydrogen bond with the silanol hydrogen (Scheme 1)^{8-10,11,18}.



Scheme 1. The adsorption of the carbonyl oxygen of the free fatty acid onto the silanol hydrogen.

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 rice hull ash for myristic, palmitic and stearic acids is, on the average, 38.59 mg of fatty acid per gram of adsorbent.

Table 1 shows that the values of **R** for rice hull ash lies between 0.373 and 0.377, i.e., $0 < \mathbf{R} < 1.0$. These values indicate that rice hull ash is a good adsorbent for myristic, palmitic and stearic acids used in our study.

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