Isotherm adsorption of free fatty acid

by Wara Dyah Pita Rengga

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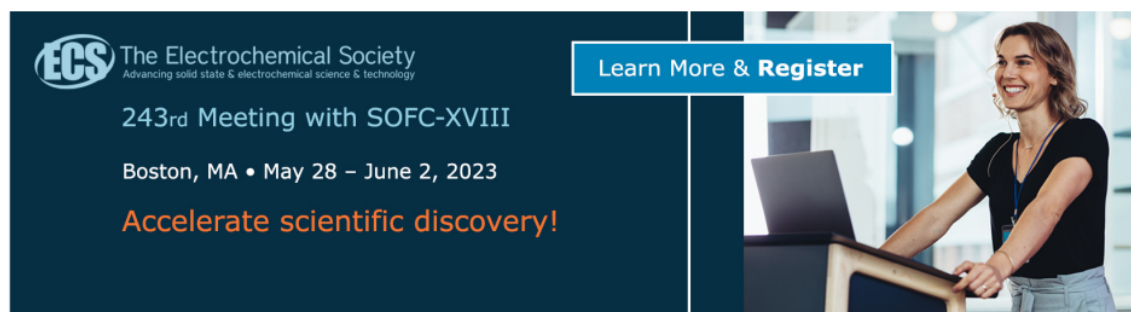# Isotherm adsorption of free fatty acid in waste cooking oil used activated carbon of banana peel as bio-adsorbent

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Isotherm adsorption of free fatty acid in waste cooking oil used activated carbon of banana peel as bio-adsorbent

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Abstract. The reduction of free fatty acids from the remaining cooking oil was successfully adsorbed by activated carbon from the banana peel biomass. The difference in activation temperature in making activated carbon causes it to adsorb free fatty acids, different from frying frozen fries in palm oil. The method used is adsorption with a batch system. The adsorbent used was biocarbon from banana peels, activated at 600, 650, and 700°C for 1 hour. Powdered activated carbon products were used in the adsorption process with a pass size of 200 mesh. Isotherm modeling with 1% activated carbon content in used cooking oil was carried out to determine the equilibrium constant in the Temkin, Langmuir, Freundlich, and Dubinin Radushkevich models. The suitability for adsorption of free fatty acids, which tends to approximate the Freundlich model. Adsorption of free fatty acids with activated carbon at 700°C effectively follows the Freundlich Isotherm Adsorption Model ($R^2 = 0.97$) with physical adsorption energy, and the maximum capacity is 27.404 mg/g as seen from other isotherm models.

1. Introduction

The importance of cooking oil as a food ingredient is widely used to process food ingredients as a savory taste. The main content of cooking oil is triglycerides formed from glycerol and various fatty acids [1]. This cooking oil also contains small amounts of sterols and free fatty acids (FFA), pigments, and hydrocarbons [2]. The availability of cooking oil on the market is quite different, namely packaged cooking oil and bulk cooking oil. This bulk cooking oil has low quality because it is only filtered one time, and the condition is not protected in the package so that it was exposed to the environment. Comfortable to react with air and fluctuating temperatures resulting in cooking oil containing FFA higher than packaged cooking oil [3,4]. The limit of FFA levels is difficult to be stable to follow SNI 01-3741-2013, namely 0.6. The acid number expresses the indicator for the free fatty acid content in oil. FFA can react further into aldehydes and ketones [2,5], which indicate rancidity in cooking oil. Besides, high-fried foods' consumption can worsen blood quality because it turns out that high free fatty acid content can increase cholesterol levels, especially Low-Density Lipoproteins [6].

The problem of dirty cooking oil has been done a lot. Some choose to dispose of used cooking oil [7,8], process it into biodiesel [9,10], and improve cooking oil performance [11,12]. The choice of cooking oil to be reprocessed was due to no small amount of cooking oil being used so that the discourse to keep using it was facilitated by processing it in a small capacity in small industries using cooking oil or in households. The results are auspicious because they use banana peel biomass converted into activated carbon to adsorb FFA under SNI.

Some of the most frequently used equations to describe adsorption isotherms are the Langmuir and Freundlich models. Also, Temkin and Dubinin-Radushkevich isotherms were used [13]. Besides, the adsorption isotherm's shape provides information about the FFA molecule's adsorption affinity on activated carbon with surface area and pore size characteristics [14]. Moreover, the adsorption energy was represented by the model. In this study, the adsorption isotherm technique was used to verify the affinity between activated carbon and FFA of used cooking oil. Four isotherm models are used, and error analysis is carried out to test the adequacy and accuracy and several parameters, and the adsorption capability can be explored further.

2. Methods

The survey and the availability of ingredients from the original kapok banana peel were collected from various regions in Semarang, Indonesia. After collection, the samples were washed with deionized water before being treated. The adsorbent is initially dried in cut conditions with a maximum size of 1 cm^2 and dried in the sun for three days to remove all moisture. The dry sorbent was ground, and the particle size was 60 mesh (0.250 mm) and separated by a 60 mesh sieve and called dried banana peel powder and stored for further analysis.

Practical work and analysis of the laboratory were carried out in the Chemical Engineering Laboratory of Universitas Negeri Semarang and Kasetsart University. Activated carbon was made in Indonesia. The cooking oil used is cooking oil for manufactured products in Thailand. Frying was worn on French fries. Used cooking oil was served in cooking oil, which is then used for frying potatoes several times until the initial concentration of carboxylic acid in cooking oil is higher than 0.3 of the cooking oil requirements.

All chemicals, reagents, and solvents were used in this work. Analytical reagents are purchased from Merck (Germany) or Sigma-Aldrich (Germany). A standard solution was prepared for titration, and successive dilutions are made with distilled water to make a working solution.

Banana peels were made into carbon, which begins with the Carbonization process. Carbon from banana peels is heated at 300°C for 1 hour and becomes carbon, called banana peel charcoal, by showing black powder. Charcoal was mixed with a technical KOH solution in 600 mL aquadest with a ratio of carbon and KOH 1:6 (w/w). The mixture was then heated at 100°C until a slurry was formed. The slurry formed is then put into the furnace at temperature variations of 600, 650, and 700°C for 1 hour until it becomes activated carbon. Activated carbon was washed using a 0.1 M HCl solution until a neutral pH was obtained and rinsed using distilled water. After obtaining neutral activated carbon, it was then dried using an oven at 105°C until a constant weight was obtained. The activated carbon is crushed and sieved to obtain a grain size of 200 mesh.

The activated carbon was then used as an adsorbent. Adsorbents were used to treat used cooking oil specifically to reduce FFA levels. 10 mL of cooking oil sample, put into Erlenmeyer and added 50 mL of ethanol. On the hot plate, the test solution was stirred until a homogeneous solution was formed. Three drops of phenolphthalein indicator were dropped while continued titration with 0.1 N NaOH solution until a pink change occurred and did not disappear within 30 seconds. The free fatty acid test was repeated two times on the same samples.

2.1. Preparation of Adsorbent

They were cooking oil adsorption process using activated carbon with a ratio of 100: 1 cooking oil to activated carbon at 50 mL cooking oil. Stirring for 1 minute, and the adsorption process was carried out for 24 hours. The adsorption study was carried out by batch adsorption method by varying different parameters, namely the activation temperature of the adsorbent preparation, namely 600 650 and 700°C, and the effect of initial concentration, which affects the adsorption phenomenon. For this purpose, the initial concentration of cooking oil with free fatty acids was varied in the range of more than 0.3, keeping all other parameters constant. To study the adsorption between activated carbon and banana peels. The equilibrium relationship required the correct adsorption isotherm sign to predict the correct absorbent parameters and behavior against different adsorption systems.

2.2. Free Fatty Acid Content

Free fatty acid tests were carried out on cooking oil before and after adsorption samples. 10 g of cooking oil samples were added 50 mL ethanol. Sample heated using an electric stove to 70ºC until homogeneous. Samples were added three drops of Phenolphthalein indicator and titrated using KOH solution until the endpoint. The free fatty acid test was repeated two times on the same samples.

2.3. Equilibrium Isotherms.

The adsorption equilibrium was fundamental to optimize the adsorption system design to remove FFA from used cooking oil. It is essential to find the most suitable correlation for the equilibrium curve. The adsorption system can be designed with the adsorption isotherm as an equilibrium isotherm, representing the amount of solute adsorbed per unit weight of the sorbent [15]. This isotherm uses an equilibrium concentration of the sorbent at a constant temperature. The research proposes many isotherms in this respect based on an adsorption system, including Langmuir, Freundlich, Temkin, and Dubinin Radushkevich [16]. Adsorption was carried out using a non-linear adsorption model.

In this work, various adsorption isotherm models are attached to the experimental equilibrium data to verify which model presents the best adjustment. The Temkin isotherm model assumes that all the molecules' adsorption heat decreases as the molecules on the adsorbent surface increase. On the other hand, the binding energy distribution provides uniformity so that, up to the maximum adsorption energy. The Temkin isotherm could be explained by Equation (1). Langmuir's theory assumes that adsorption occurs at a specific homogeneous site within activated carbon and, once an FFA molecule occupies a site, no additional adsorption can occur. The Langmuir isotherm model could be described as in Equation (2). Freundlich's isotherm model is used to describe multilayer adsorption with interactions between adsorbed molecules and heterogeneous surface energy systems. Freundlich's isotherm can be shown in Equation (3). The Dubinin-Radushkevich isotherm model assumes that activated carbon is proportional to the micropore size. The adsorption equilibrium is related to the adsorption potential, expressed in terms of temperature, as stated in Equation (4)

2.4. Error Analysis

Analysis of the approach was used by minimizing the distance between the experimental data points and the theoretical model's prediction. Through the Microsoft Excel solver, add-in function for all models tested [17].

$$q_e = B_T \ln(K_T) + B_T \ln(C_e) \qquad\qquad [1]$$

$$q_e = \frac{q_m . K_L . C_e}{1 + K_L . C_e} \qquad\qquad [2]$$

$$q_e = K_F . C_e^{\frac{1}{n}} \qquad\qquad [3]$$

$$q_e = q_m . \exp\left(-K_{ad}\left(RT . \ln\left(1 + \frac{1}{C_e}\right)^2\right)\right) \qquad\qquad [4]$$

3. Result dan Discussions

The equilibrium isotherm in the adsorption system between activated carbon and used cooking oil was designed to determine each ingredient's properties. Isotherm equilibrium represents the amount of solute in the cooking oil, which was then transferred by the adsorbed per amount of sorbent weight [15]. This isotherm uses an equilibrium concentration of the sorbent at constant room temperature with activated carbon adsorbent, which had a difference in the activation temperature. Used cooking oil uses the concentration of free fatty acids and is expressed in the acid number. The study proposes several isotherms in this regard, which were based on the adsorption system, including Temkin, Langmuir, Freundlich, Dubinin Radushkevich. Adsorption was carried out using a non-linear adsorption model [18] by varying the initial low concentration [2]. Because the activated carbon, which was superior, can adsorb cooking oil that had not been too damaged with a value of less than 10 mg/L. The non-linear

form for all adsorption isotherm models was presented with a constant value as given in the curve shape in Figure 1. The data was brought closer to the model equation so that a model could be selected that can explain the constants in equilibrium conditions in Table 1. The best use of activated carbon was on activation 700°C [19] with regression R^2 reached 0.97, and the highest adsorption capacity was 27.404 mg/g. It is almost the same as the optimal performance of activated carbon, which is average at 700°C but uses 2 hours, which is more saved in this study.

The discussion was carried out from each model that had a function of the constants obtained and predicts the actors' adsorption ability. Temkin adsorption isotherm discusses that the absorption of heat in the adsorption process will not remain constant. This adsorption heat decreased due to the interaction between activated carbon and used cooking oil like the previously described phenomenon. The non-linear form used in the Temkin model indicates that the equilibrium constant Kad was related to the binding energy (E) and showed that the adsorption heat increases when using activated carbon with an activation temperature of 700°C. The model shows the exothermic nature of the adsorption reaction as a constant B_T value greater than 0, which indicated heat loss during the process.

Langmuir adsorption isotherm was based on the monolayer's adsorption on activated carbon by free fatty acids present in used cooking oil. The energy in the adsorption system was considered constant. The dimensionless constant RL was calculated using the Langmuir constant (K_L), and the initial concentration (Co) showed the suitability of the Langmuir model identified with a homogeneous system. If the R_L value is between 0 and 1, then the system was deemed suitable for adsorption purposes that explain the adsorption process's favorability was calculated using Equation (5). The calculated R_L value was less than 1 (0.748-0.773); hence the adsorption process was favorable.

$$R_L = \frac{1}{(1+K_L C_o)} \qquad\qquad [5]$$

Furthermore, the experimental data and the predicted results obtained for this work were closely correlated with the highest R^2 and the Freundlich Model making this model applicable. The Freundlich adsorption isotherm was developed for heterogeneous systems and provides the concept of multilayer adsorption on the sorbent surface. Freundlich's adsorption capacity (K_F) is an indicator of a system for adsorption that was considered promising if the K_F value is found in the range 1-20, and the results obtained in this study, KF are 1.0-1.5. Likewise, the adsorption intensity shown by the constant n indicates the suitability of the model for adsorption purposes if the value of n is above 1 (1.2-1.3). The R^2 value obtained from the graph is 97% significant, representing the suitability of this model for the adsorption of free fatty acids into the activated carbon of banana peels. We tried to compare between activated carbon and zeolite adsorbents, that in the Freundlich isotherm model, the ability of activated carbon and zeolite to FFA in used cooking oil shows almost the same n value, n>1. The K_F value for activated carbon is almost higher. 2 times, which means that the affinity for heterogeneous sites is higher than that of zeolites [2].

The Dubinin-Radushkevich isotherm was successfully applied for the adsorption of heterogeneous systems, including solid and liquid. The Dubinin-Radushkevich isotherm has found up-and-coming applications for determining absorption properties, whether physical or chemical. The Kad constant obtained is used in equation 6 to calculate the E value for research whose value is less than 8 kJ/mol, i.e., 5.6-6.5 kJ/mol, and shows physical adsorption properties. Because the E value is 8–16 kJ/mol, it reflects chemical adsorption. Activated carbon, which has an active functional group site on its surface, tends to have physical adsorption rather than chemistry, especially if what is absorbed is an organic compound type adsorbate through hydrogen bonding [20].

$$E = \frac{1}{((2)K_{ad})^{1/2}} \qquad\qquad [6]$$

Langmuir, Freundlich, Temkin, and Debinin Radushkevich adsorption isotherm data showed the Freundlich model curve equation's highest regression value. This model showed the interaction of used cooking oil on the surface through a multilayer mechanism with the interaction between FFA molecules

on the activated carbon surface. Free fatty acids that were identical to free fatty acids interact with the activated carbon surface with a phenol functional group with a carboxylic group through hydrogen bonding, physical adsorption [21]. Adsorption can be preferred on adsorbents with low surface polarity, so the option to increase the adsorption capacity is to modify the surface chemistry by reducing chemical groups present on the activated carbon.
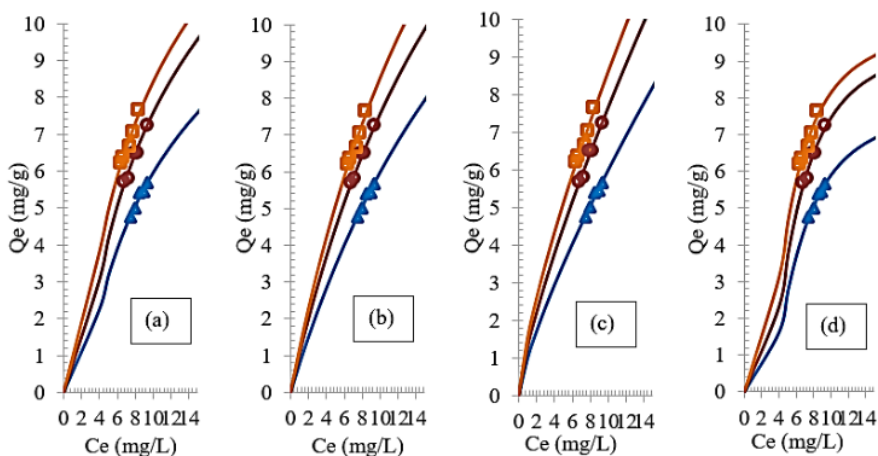

Figure 1. Non-linear plotting of the Temkin (a), Langmuir (b), Freundlich (c) and Dubinin (d) equations for variation of activation 600°C △ , 650°C ⊙ , 700°C □

Table 1. Non-Linear Parameters of isothermal models for Sorption of FFA on an activated carbon

Model	Carbon activation temperature		
	600°C	650°C	700°C
Temkin			
B_T (J/mol)	4.047	4.942	5.030
K_T (L/g)	0.436	0.463	0.532
R_T^2	0.97	0.97	0.96
Langmuir			
q_m (mg/g)	23.183	25.22	27.404
K_L (L/mg)	0.035	0.043	0.045
R_L	0.773	0.748	0.752
R^2	0.97	0.97	0.96
Freundlich			
K_F (mg/g) (L/mg)n	1.004	1.295	1.538
N	1.2884	1.2958	1.3365
R^2	0.97	0.97	0.97
Dubinin-Radushkevich			
q_s (mg/g)	7.871	9.686	10.103
K_{ad}	0.016	0.014	0.012
E (kJ/mol)	5.610	5.902	6.518
R^2	0.98	0.96	0.94

4. Conclusion

Four adsorption isotherm models were tested in this research work; equilibrium sorption investigations fitted into the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherms. Freundlich isotherm best describes FFA's adsorption onto activated carbon from the banana peel, suggesting that adsorption was onto a non-uniform site using activated carbon, activated at 700°C. However, initial rapid adsorption was onto a uniform site; thus, the maximum monolayer adsorption capacity was 27,404 mg/g. The energy adsorption suggests that the uptake FFA was physical adsorption.

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