Value-Added Utilization of Banana Peel (*Musa acuminata*): Adsorption Fatty Acid and Extending the Life of Activated Carbon

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Abstract. Cooking oil saturation due to frequent use for frying will result in a higher fatty acid content. Activated carbon made from the banana peel (*Musa acuminata*) with micro-mesoporous specifications can absorb free fatty acids. Banana peels are pyrolyzed into charcoal then activated alkaline at a temperature of 650°C. Then the activated carbon is washed and mashed to obtain activated carbon powder as an adsorbent by batch. FTIR carried out adsorption analysis on cooking oil to reduce carboxylic acid in used cooking oil. The regeneration process is carried out using surfactants to save on the use of necessary materials so that they need to be recycled. The experimental results based on isothermic equilibrium show that the Freundlich model can describe the adsorption process well at 28°C with a maximum adsorption capacity of 10 mg/g. The lifespan of activated carbon can only be extended once regeneration, reaching an adsorption capacity of 65% of fresh activated carbon's ability.

Introduction

Repeated use of cooking oil at high temperatures reduces the quality of cooking oil. Low-quality cooking oil has a rancid odor, darker color, increased viscosity, moisture content, free fatty acids, and a peroxide number [1]. Low-quality cooking oil will undergo a digestion process if used for frying food and increases the low-density lipoprotein (LDL) content. The higher LDL content in the blood can lead to hypertension, cancer, cardiovascular, and coronary heart disease. Cooking oil waste cannot be disposed of directly into the environment, so it needs to be refined [2] or reprocessed into biodiesel [3]. Cooking oil can be purified using supercritical extraction [4] and adsorption [2]. However, supercritical pads require a somewhat complicated process due to high pressure operating conditions, precise operation controls, and high investment. In contrast, adsorption can be done with natural materials, both inorganic and organic materials. Another advantage is that biomaterials are easily modified from the size, pore shape, and recycled materials used for other products.

Several studies on adsorption explain that activated carbon and adsorbate have not been well optimized. Because the type of biomaterial is less modified and the operating conditions are less efficient [5], and they have not utilized recycled materials. Biomaterials derived from waste or waste in the form of biomass are more promising when used as adsorbents. Biomass which has lignin and cellulose more than 20% dry weight, is selectively selected to obtain a sufficient amount of fixed carbon [2]. The development of activated carbon can be done by increasing its adsorption capacity, namely surface area, uniform pore size, and pore pores. Activated carbon can be produced from biowastes such as banana peel [5,6], watermelon skin [7], and coffee husk ash [2]. On the other hand, in tropical Indonesia, banana cultivation can proliferate and bear fruit. Banana products are widely preferred for various kinds of snacks so that banana peels can be used because they contain 59.6% hemicellulose, 14.2% cellulose, 12.8% lignin, and ash 13.4% [8].

The pyrolysis and activation processes are the stages in activated carbon production to increase the adsorption capacity by increasing the surface area. KOH [9], NaOH [10], H_3PO_4 [11], K_2CO_3 [9], H_2SO_4 [12], and $ZnCl_2$ [8,11] are activators of inorganic compounds at a specific temperature. This study uses inorganic KOH as an activator because the pore results obtained have a narrow pore size range. The types of pores obtained are micropores and mesoporous, so that the prediction to absorb free fatty acids is quite good. The carbon potential functional group is hydroxyl which can bind carboxylates so that the free fatty acids in cooking oil are reduced.

The used activated carbon can be saved by regenerating it [13] by washing it to dissolve adhered fatty acids. Surfactant solutions can have hydrophobic properties to attract carboxylic acids with water [14] so that some free fatty acids are released. Furthermore, the activated carbon is dried and activated by heating at high temperatures. To further release the remaining water and dissolve the hydrophilic groups, a desorption process can be recycled. This study aims to obtain the optimal adsorption temperature following the adsorption isotherm equilibrium model, characterization of banana peel activated carbon and influential functional groups, and the effectiveness of regeneration of activated carbon using surfactants. The adsorption process's operating conditions can be studied for equilibrium at a suitable temperature, and the adsorption capacity of regenerated carbon can be obtained.

Materials and Methods

Materials. Technical grade ethanol (C_2H_5OH) 96%, used cooking oil, aqua dest, Technical grade Potassium Hydroxide (KOH) 90%, Oxalic Acid ($H_2C_2O_4$) p.a Merck. Hydrochloric Acid (HCl) 32% Merck, Surfactant 15% (sodium alkylbenzene sulfonate and sodium lauryl ether sulfate) were prepared in 120 mL distilled water, Activated carbon 650°C.

Activated Carbon Production. Banana peel sun-dried as an Activated Carbon Production raw material. The dried banana peel was milled and sieved with 60 *mesh*. The solution-making process of 1000 mL aqua dest was added with 112 g KOH and 33.8 g banana peel powder. The solution was heated to 100°C using an electric stove until 200 mL slurry was formed; the solution was stirred until homogeneous during the heating process. The solution was activated using a furnace with a 10°C/minute heat rate until it reached 650°C and 700°C. After the furnaced chunk of activated carbon was washed with aqua dest and HCl until neutral or pH 7. Activated carbon was dried using an oven with a temperature of 100 °C. Activated carbon was milled using a mortar and sieved with 200 mesh size.

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. Samples heated using an electric stove to 70°C 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.

Cooking Oil Characterization. Characterization of functional groups that changed in the formation of oxidation products in cooking oil samples was carried out using FTIR (Perkin Elmer Model Frontier FT-IR 96681).

Adsorption Isotherm. Cooking oil adsorption process using activated carbon with a ratio of 100:1 cooking oil to activated carbon. 30 g cooking oil with the concentration specified in mg KOH/ g samples. Cooking oil and activated carbon samples conditioned using an incubator to adsorption temperature for 28, 30, 35, 40, and 45°C. Cooking oil samples were added 0.3 g of activated carbon, stirred for 1 min, and the adsorption process for 24 hours.

Adsorption isotherm describes the relationship between liquid phase equilibrium and concentration in the adsorbent. Some adsorption models are available to describe adsorption equilibrium data. This research using Langmuir and Freundlich model. The model can be represented by Eq. 1 and 2.

$$Qe = \frac{(Qm \cdot b \cdot Ce)}{(1 + b \cdot Ce)} \qquad (1)$$

$$Qe = K_f \cdot Ce^{1/n} \tag{2}$$

Qe is the amount of adsorbate adsorbed in the adsorbent (mg/g). Qm is the maximum adsorption capacity (mg/g), b is the Langmuir constant (L/g). Ce is the Acid number concentration of cooking oil samples after adsorption. K_f is Freundlich constant, n is adsorption intensity. Data analyzed using Sum of Squared Total (SST) and Sum of Squared Error (SSE) to obtain R^2, Qm, b, K_f, n are trial variables shown in Eq. 3, 4, and 5. The solver method is used to obtain the best R^2 value.

$$SST = \sum_{i=1}^{n}(qe \text{ experiment} - \overline{qe} \text{ experiment})^2 \tag{3}$$

$$SSE = \sum_{i=1}^{n}(qe \text{ experiment} - qe \text{ count})^2 \tag{4}$$

$$R^2 = 1 - \frac{SSE}{SST} \tag{5}$$

Regenerated Activated Carbon. The used cooking oil that has been absorbed is released from activated carbon—starting with activated carbon washed by 4% surfactant in distilled water. Furthermore, the sample was stirred for about 1 minute, and the soaking process was carried out for 24 hours. The activated carbon was separated from the washing solution through a filtration process. Then the activated carbon is rinsed with 240 mL of distilled water, repeated twice. The process is continued by drying the activated carbon for 1 hour at a temperature of 100°C until the weight is constant. This carbon is then activated by heating at 700°C for 1 hour so that later it can be reused for the adsorption process called the 1st, 2nd recycled activated carbon (regeneration).

Results and Discussion

Adsorption Equilibrium Model. The adsorption ability of free fatty acids from cooking oil was brought closer to the Langmuir and Freundlich model. Both models give $R^2 > 0.9$. The Freundlich isotherm model tends to be dominant because the R^2 obtained is higher than the Langmuir adsorption isotherm model [15]. The Freundlich model can be seen in Fig. 1, indicates that the adsorption of free fatty acids on chemically activated carbon KOH occurs by physical adsorption, namely the hydrogen bond between the carbon's surface and the carboxylic acid from cooking oil which is more detailed in the FTIR analysis. At constant pressure, physical adsorption decreases with an increase in temperature. At low concentrations at the adsorption equilibrium, it indicates that the adsorption temperature of 28°C provides a higher adsorption capacity than higher temperatures. However, there are certain conditions where at a high concentration, the adsorption ability at low temperatures is lower than at 30 and 35°C can be seen in Table 1, this is the effect that the higher the concentration becomes concentrated, and at low temperatures, it will inhibit adsorption [16]. The used cooking oil flow rate constrained the saturation concentration of the function of temperature. The effect of high temperature can also cause the carboxylic acid that has been adsorbed on the activated carbon surface to be released. The presence of heat energy so that a desorption process will occur and carboxylic acid dissolves back in cooking oil and is released from the adsorbent surface [17].
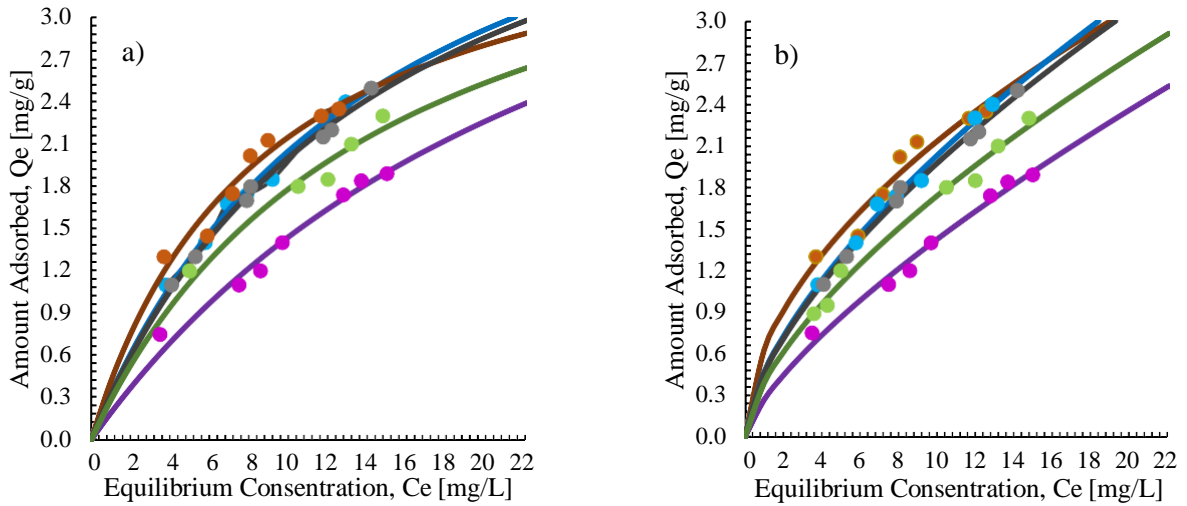
Figure 1. Equilibrium Adsorption for a) Langmuir Model, b) Freundlich Model.
(●28ºC, ●30ºC, ●35ºC, ●40ºC, and ●45ºC).

Table 1. Equilibrium Adsorption Free Fatty Acid by Banana Peel's Activated Carbon.

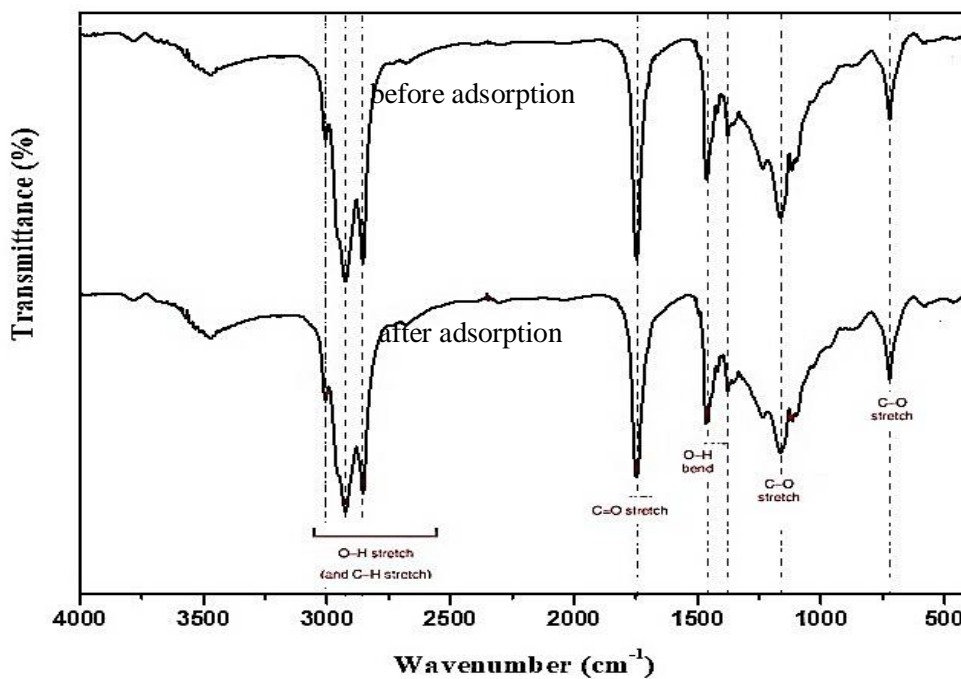| Isotherm Model		Adsorption Temperature ºC				
		28	30	35	40	45
Langmuir	Qm (mg/g)	4.033	5.037	4.994	4.400	5.280
	K_L (L/g)	0.114	0.069	0.067	0.068	0.038
	R^2	0.940	0.970	0.980	0.98	0.97
Freundlich	n	1.884	1.563	1.568	1.537	1.380
	K_f	0.628	0.465	0.455	0.389	0.269
	R^2	0.930	0.960	0.990	0.980	0.970

Figure 2. Used Cooking Oil FTIR Spectrum for adsorption.

Cooking Oil Characterization. There are functional groups that support the adsorption process of free fatty acids, which are oxidation products and polar compounds from used cooking oil. The removal ability of free fatty acids, namely carboxylic acids from used cooking oil, was evaluated using Fourier Transform Infrared (FTIR). FT-IR spectra of cooking oil in the conditions before (a) and after (b) the adsorption process as shown in Fig. 2. There is a significant difference at the

1749 cm^{-1} peak, which shows the C = O stretching carbonyl. This peak was long before and after the adsorption process became reduced. The spectrum at the peak of 1236 cm^{-1} is a stretching C-O bond belonging to the carboxylate acid group. The O-H strain band appears as a band in the 3300-2500cm^{-1} region, centered on about 3000 cm^{-1} which usually exists as hydrogen-bonded dimers. There is a strong wideband for the O – H strain. The carboxylic acids showed that unlike the O-H strain band observed in alcohols, the O-H strain of carboxylic acids appeared as an extensive band in the 3300-2500 cm^{-1} region, centered at about 2928 cm^{-1}. The 3006 cm^{-1} spectrum corresponds to the symmetrical stretching vibration of the CH double bond cis. The O-H curvature of carboxylic acids occurs at the peaks of 1465 and 722 cm^{-1}[3,6]. Reduction of the carboxylic acid or free fatty acid functional groups in used cooking oil in the adsorption process means that the activated carbon is running well. This study supports that used cooking oil contains more carboxylic acids than cooking oil after adsorption[18].
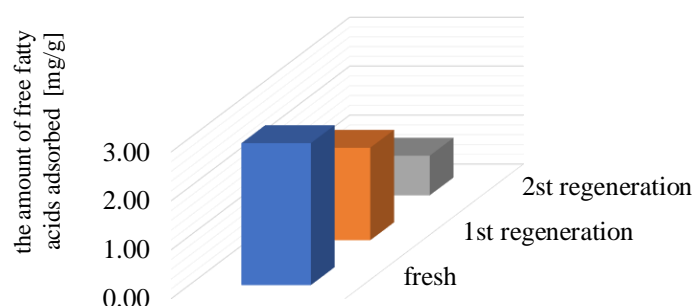

Figure 3. The Ability of Banana Activated Carbon to Use Fresh, First, and Second Regeneration Activated Carbon To Absorb Free Fatty Acids.

It has regenerated activated carbon for reuse. The ability to adsorb was retested using the same procedure as for adsorption and differed only with activated carbon as the adsorbent. The concentration of free fatty acid adsorption, which can be absorbed in the adsorbent using freshly activated carbon, reaches 2.90 mg/g. In contrast, carbon that has been regenerated once has a lower adsorption ability reaching 1.98 mg/g, as shown in Fig. 3. The waste activated carbon was regenerated again to get the second one and have the lowest ability of 0.81 mg/g. The recommendation that can be given to regenerated carbon is that the 1st regenerated carbon has 65% adsorption ability of fresh activated carbon. On the other hand, the ability of the 2nd regeneration activated carbon has decreased its ability, namely 28%, and is not suitable for reuse. There are not many active sites available for hydrogen bonding anymore, so activated carbon can only be utilized until the first regeneration. Regeneration is also carried out on waste-activated carbon at high temperatures and chemically [19].

Acknowledgement

Summary

Activated carbon from banana peel powder has been used to reduce levels of free fatty acids in cooking oil. The bond between free fatty acids and activated carbon occurs because of the hydrogen bonds. The adsorption isotherm conditions at room temperature (28oC) have a higher overall adsorption capability. Physical adsorption is limited by the natural energy of the adsorbate to release some of the adsorbed compounds. The time extension of activated carbon is up to 65% efficient with just one cycle.

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