Recovery of Useful Bioactive Substances in Palm Fatty Acid Distillates by Adsorption Using Palm Kernel Shell Activated Carbon

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1. Introduction

Palm oil industry is a major agroindustry in Southeast Asian countries. Palm oil produced from oil palm accounts for about 36 percent of the world's total vegetable oil and fat production [1]. Palm oil is widely used as a raw material for margarine, edible oil, detergents, paints, inks, and cosmetics. It has attracted attention in recent years as a feedstock for biomass fuels (biodiesel) and is therefore the most widely consumed vegetable oil and fat in the world today. Although this industry has been developed to contribute to economic activities in respective countries, there still are issues on the waste treatment, byproduct utilization and so on in the production process to be solved for the further development.

Palm kernel shell, PKS, is one of the solid byproducts generated in the oil production. According to statistics, about 120 grams of PKS is produced for every kilogram of palm oil produced[1]. Then, PKS was thermally treated to prepare activated carbon, and the wastewater from the oil production was treated using PKS activated carbon, PKSAC, to remove harmful organic compounds, such as phenolic compounds, and colored compounds of lignin [2].

Palm fatty acid distillate, PFAD, is also a byproduct obtained from refinery of crude palm oil. Major compounds of PFAD are free fatty acids of palmitic and oleic acids used in soap, animal feed, and oleochemical industries. As minor compounds, bioactive substances were contained in PFAD, such as Vitamin E (VE: 60-200 ppm), Phytosterols (St: 400-7500 ppm), Squalene (Sq: 400-2800 ppm) [3], and so on. These substances have the property of acting on specific physiological regulatory functions of the organism. VE prevents oxidation of lipids in the body [4]; lower the percentage of (LDL) cholesterol in the blood and Sq is expected to activate metabolism, purify the blood, and beautify the skin. Although these compounds in PFAD is expected to bring further profit to the palm oil industry, the recovery technique has not been fully studied. In our previous study, VE in the model PFAD could be recovered by adsorption using commercial activated carbon [5].

The objective of this study was to recover useful bioactive substances in PFAD by adsorption using PKSAC. PKSAC was prepared by physical activation using steam as activating agent, and the PKSAC were characterized in terms of the yield and specific surface area. Then, the equilibrium adsorption of bioactive substances in PFAD using PKSAC was studied.

2. Experimental method

2.1. Production of PKSAC

Fig. 1. shows a representation of the production process of PKSAC.

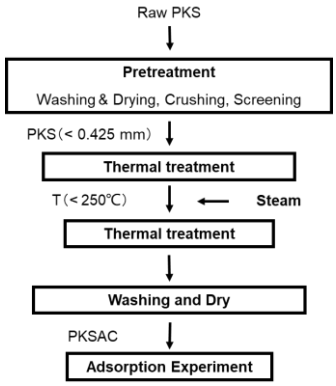

Fig. 1 production process of PKSAC

In this experiment, palm kernel shells (PKS) obtained from a private company in Krabi province are washed with ion-exchanged water and dried in a dryer as a pretreatment. The dried palm kernel shells are then crushed in a crusher, and the powder with a diameter smaller than 0.425 mm is collected by sieving and used for the production of activated carbon.

The palm PKS was measured with an electronic balance, placed evenly on the sample tray of the heat treatment device, the tray was placed in the device, and then the device was sealed. Atmospheric gas was run for 10 minutes to expel the air inside the appliance before heating. After 10 minutes, heating was started. When the temperature inside the furnace reached 523K, steam supply was started. After the holding time, the nitrogen gas was turned off, the power was turned off, and the water vapor supply was turned off after 30 minutes. After the temperature inside the furnace drops to 473K, open the device and let the sample tray cool naturally. When the temperature reaches a level that can be touched by hand, take out the sample tray, weigh the weight of the solid remaining in the tray and the weight of the liquid obtained in the condenser with an electronic balance, and determine

the yield of the solid from the mass balance relationship. Condition of the experiment shown on Table 1.

Table 1. Condition of the production of PKSAC

Feed	Palm kernel shell (< 4.25×10^{-6} m)
Mass of Feed, F_0 [kg]	0.01
Atmosphere Gas	N_2, H_2O
Flow rate [m^3 h^{-1}]	0.003 (N_2)
	0.003 (N_2), 0.003 (H_2O)
Temperature, T [K]	1073, 873, 873
Time [h]	1, 1, 2

The obtained PKSAC was washed using 1L of ion exchange water at 373K. The washed sample was dried in a dryer for 24 hours before storage in a container.
The produced PKSAC is measured for specific surface area using a specific surface area analyzer and then used in equilibrium adsorption experiments.

2.2. Batch adsorption of useful bioactive substances in model PFAD

In this experiment a mixture of oleic acid with a useful bioactive substance (VE, Sq, St) was used for the model PFAD. The Commercial AC (CAS RN®: 7440-44-0) and the three PKSACs prepared in Experiment 2.1. as adsorbents.

A model of palm fatty acid distillate was brought into contact with activated carbon in a 100 × 10-6 m3 conical flask with a screw cap. The Commercial AC was in granular form and before use it was crushed into small particles and sieved to a diameter of less than 425 x 10-6 m. The mixture was shaken on a hot plate using magnetic stirring to bring it to equilibrium. After that, the mixture was filtered and the filtrate was analyzed.

In this experiment a UV-Vis spectrophotometer (UV-1280, Shimadzu Manufacturing Co., Ltd.) was used to analyze the VE, Sq and St were analyzed by gas chromatography (GC-2010, Shimadzu Manufacturing Co., Ltd.). The batch adsorption conditions are detailed in Table 2. The condition for the analysis of VE is organized in Table 3. and for the Sq and St are shown in Table 4.

Table 2. Conditions for Batch Equilibrium Adsorption

Feed solution	Oleic acid with bioactive substances (VE, St, Sq)
Mass of Feed [kg]	2.5×10^{-2}
Adsorbent	Commercial AC, PKSACs
Mass of Adsorbet [kg]	5×10^{-2}, 1×10^{-4}
Concentration of adsorbate in feed solution, $C_{i,0}$ [kmol m-3]	0.02 - 0.065 (VE) 0.002 - 0.65 (Sq) 0.002 - 0.035 (St)
Contacting time, t [h]	48
Contacting temperature, T [K]	300

Table 3. Conditions for the analysis of VE

Feed solution	Oleic acid with VE
Diluent	Heptane
Mass ratio of Diluent Feed [-]	29
Wavelength [m]	2.7×10^{-7} - 3.15×10^{-7}
Absorbance range [-]	-4 - 4
Contacting temperature, T [K]	300

Table 4. Conditions for the analysis of Sq and St

Feed solution	Oleic acid with Sq Oleic acid with St
Diluent	m-Xylene
Internal standard solution	1-Propanol
Carrier gas	N_2
Temperature of Injection Port [K]	573
Temperature of Column [K]	423 (5min) – 553 (20min)
Rise Rate [K / min]	2
Temperature of Detector [K]	573

3. Results and discussion

3.1. Characterization of activated carbon

PKSAC produced in Experiment 2.1. is shown in Fig.2.

Raw PKS Crushed PKS PKSAC

Fig. 2 PKSAC

The yield and specific surface area, a, of the palm kernel shell activated carbon produced are summarized in Table 5 and compared with data for commercial activated carbon.

Yield is the ratio of the amount of substance actually obtained to the maximum amount of that substance that can theoretically be obtained (theoretical yield) in a chemical process to obtain a certain substance. In the case of this experiment, the yield of activated carbon, Y [-], can be expressed by the following equation Here F1 is the mass of PKSAC obtained in the heat treatment [kg]

$$Y = \frac{F_1}{F_0} \quad (1)$$

Table 5. Characterization of Activated Carbon

AC	T [K]	T [h]	Y [-]	a [m^2 kg^{-1}]
600-1	873	1	0. 33	1.35
600-2	873	2	0. 32	85.5
800-1	1073	1	0. 24	401
Commercial AC	-	-	-	940

The yield of PKSAC (600-2) held at 873 K for 2 hours

was lower than that of PKSAC (600-1) held at 873 K for 1 hour, but not by much. On the other hand, the yield of PKSAC (800-1) held at 1073 K for 1 hour was clearly lower than that of 600-1 and 600-2. From the above, it can be said that the yield of palm kernel shell activated carbon is less related to retention time and more related to temperature.

In the case of specific surface area a, 600-2 is 80 times greater than 600-1, and 800-1 is 400 times greater than 600-1, indicating that the specific surface area of PKSAC is strongly related to retention time and experimental temperature.

3.2. Batch adsorption of useful bioactive substances in model PFAD

The main objective of the batch equilibrium adsorption study was to determine the adsorption performance of activated carbon on a mixture of useful bioactive substances and oleic acid. Here I chose to compare the concentrations of useful bioactive substances in oleic acid before and after the adsorption experiments to check whether the adsorption of various substances by AC was carried out successfully. I also chose to observe the yield of AC, R_i on various substances, R_i [-], and to compare the amount of substances adsorbed per g of AC, q_i [kmol g-AC^{-1}], to evaluate the adsorption performance of AC on VE, Sq and St.

Then for the yield of useful bioactive material from activated carbon, it is defined as follow

$$R_i = \frac{(C_0 - C_i)}{C_0} \quad (2)$$

The material balance relationship of useful bioactive substance i can be written as

$$C_{i,0}V_0 + q_{i,0}M_0 = C_{i,e}V + q_iM \quad (3)$$

From the material balance equation, q_i can be defined as follow, where the volume of the mixture before and after the adsorption experiment and the mass of the activated carbon are approximately equal.

$$q_i = \frac{(C_0 - C_i)V}{M} \quad (4)$$

Adsorption of VE

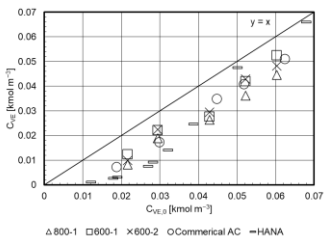

Fig. 3 Concentration differences of VE in the liquid phase before and after adsorption

* HANA [4]: data from previous studies.

From the results of VE concentration before and after adsorption in Fig. 3., it can be seen that both commercial AC and prepared PKSAC can adsorb VE.

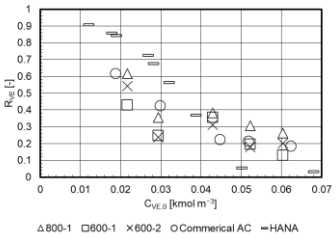

Fig. 4 Yield of AC on VE

From the yield of activated carbon for VE (Fig. 4.), there was a significant trend of lower yield of VE in AC as the initial concentration of VE increased. This is due to the better adsorption capacity of AC for lower concentrations of VE.

*Due to the different amounts of AC used, a longitudinal comparison between Commercial AC and PKSACs is not possible from the Fig. 4.

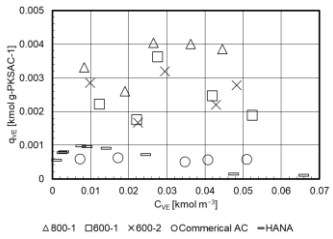

Fig. 5 Adsorption Isotherm of VE in Oleic Acid

In terms of the amount of VE adsorbed by AC, in general, there was a relatively large variation. This may be due to the fact that the UV spectrophotometer used in the analysis of VE has high requirements for environmental and other conditions, resulting in some errors during the experiment. However, according to the overall results in Fig. 5., the prepared PKSAC has a slightly better adsorption capacity for VE compared to the commercial AC.

But, no significant differences were seen in the three different PKSACs prepared.

Adsorption of Sq

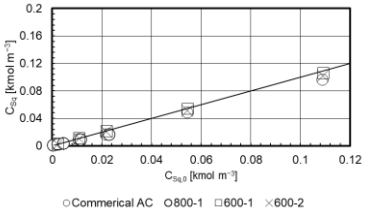

Fig. 6 Concentration differences of Sq in the liquid phase before and after adsorption

As with VE, it can be seen from Fig. 6. that AC can successfully adsorb Sq.

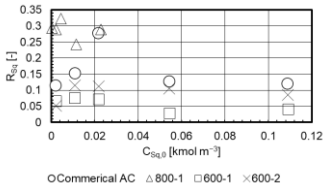

Fig. 7 Yield of AC on Sq

From the yield of AC on Sq (Fig. 7.), it can be observed that the initial concentration of Sq does not have a large effect on the yield. However, a longitudinal comparison of the three prepared PKSACs shows that 800-1 has a stronger adsorption capacity for Sq compared to 600-1 and 600-2. Among them, 600-1 showed a weaker adsorption capacity.

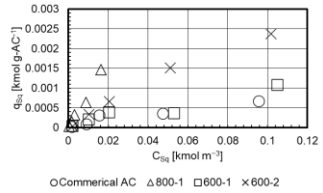

Fig. 8 Adsorption Isotherm of Sq in Oleic Acid

From Figure 8, it can be observed that 800-1 and 600-2 exhibit better adsorption capacity on Sq, with 600-1 being at approximately the same level as Commercial AC.

Meanwhile the adsorption of AC on Sq shows a linear relationship in the concentration range of the experiment.

Considering that the aim of this study was to recover useful bioactive substances from PFAD, the model PFAD was prepared with a content as close as possible to the realistic one. This may lead to a lower concentration of Sq in the model PFAD and a linear relationship in the isothermal adsorption curve.

Adsorption of St

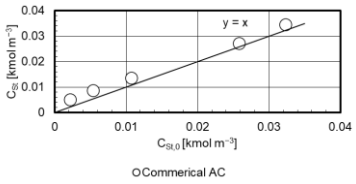

Fig. 9 Concentration differences of St in the liquid phase before and after adsorption

It can be observed in Fig. 9. that after adsorption the concentration of St showed an increase compared to that before adsorption. However, no significant peaks were found in the gas chromatogram for the adsorption of oleic acid by activated carbon. Therefore, the study of St adsorption by AC had to be abandoned in the present study.

4. Conclusion

From the PKSAC production experiments, PKS can be obtained by thermal treatment of PKS under steam activation. The yield of PKSAC decreased with increasing temperature and showed no relationship with retention time. At 873 K, 1 h showed a maximum yield of 0.33. The specific surface area was found to be strongly related to holding time and especially temperature during heat treatment. It is expected that heat treatment at higher temperatures will produce PKSAC with a higher specific surface area.

In the adsorption experiments of AC on useful bioactive substances, it was found that for VE and Sq, the recovery was successful. The maximum yields were about 0.6 and 0.3, respectively. And it was observed that the PKSAC prepared in this study had slightly better adsorption capacity than commercially available AC for these two substances. These results were contrary to the specific surface area of AC, since the analysis of AC in this study was limited to the specific surface area without measuring the pore size and pore area, further analysis of the activated carbon is needed. However, the adsorption capacity of PKSAC observed in the PKSAC adsorption experiments of Sq was consistent with the results of the specific surface area measurements.

The successful recovery of phytol by AC was not observed under the techniques of this study. But, it may be possible to try to improve the adsorption experiments on phytol by changing the analytical methods, etc.

The adsorption experiments in this study were performed for a single substance, and a more realistic multi-component adsorption will be a major topic for the future, as well as the recovery of useful bioactive substances from activated carbon will require further research.

References

[1] United States Department of Agriculture Foreign Agricultural Servicce Oilseeds: World Markets and Trade (2019).

[2] Boontham, W., H. Habaki, and R. Egashira; "Removal of Phenol from Oil Mill Effluent Using Activated Carbon Prepared from Kernel Shell in Thailand's Palm Industry," Journal of Chemical Engineering of Japan, 53, (11), 682~688 (2020)

[3] Teti Estiasih et al,. Bioactive substances of Palm Fatty Acid Distillate (PFAD) from Several, Advance Journal of Food Science and Technology 5(9): 1153-1159, 2013

[4] R. Liu et al,. Study on the antioxidant and lipid-regulating functions of soy phospholipids and VE. China Oils and Fats, 2006

[5] Dae, Hana., H. Habaki, and R. Egashira Recovery of Physiologically Active Component Contained in Palm Fatty Acid Distillate Using Adsorption with Activated Carbon, 2020