RECOVERY OF PHYSIOLOGICALLY ACTIVE COMPONENT CONTAINED IN PALM FATTY ACID DISTILLATE USING ADSORPTION WITH ACTIVATED CARBON

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1. Introduction

Oil palm has been subjected to considerable research as the utilization of palm oil-based products in many industries such as pharmaceuticals, food, biofuels, and animal feedstocks are rapidly increased.

Indonesia is currently the largest producer and exporter of Crude Palm Oil (CPO) worldwide with an estimated production amount of 31 million tons CPO per-year in 2017[1]. With a large amount of CPO being produced and refined, palm oil industry also generates large wastes mainly empty fruit bunches, palm oil mill effluent, palm fatty acid distillates (PFAD), and plantation residue.

PFAD is a deodorizer distillate which generated during the deodorization process of CPO refining[2]. The quantity of PFAD is about 4% from CPO[3]. Commonly PFAD is used as fatty acids source for non-food industries mainly oleochemical industries and usually used for soap, feed and oleochemicals[4]. It contains fatty acids and glycerides of 96.1% and other physiologically compounds such as tocopherols and tocotrienols (0.48%), phytosterols (0.37%), squalene (0.76%) and other hydrocarbons (0.71%)[5], Unfortunately, PFAD has not been explored yet as its physiologically active source.

Vitamin E which consists of tocopherols and tocotrienols is an essential vitamin for the human body which has antioxidant, anti-cancer and anti-aging activity.

As an essential vitamin, Vitamin E (VE) cannot be self-produced by the human body and needs to be obtained from the food supplement. Palm fruit is one of the best sources for the tocopherols and tocotrienols besides the rice grain and annatto seed[6].

The main objective of this study is to recover the physiologically active components (PACs), in this case vitamin E from palm fatty acid distillates by adsorption experiment using activated carbon. Areas of the study are including characterization of real palm fatty acid distillates, adsorption of vitamin E in model of PFAD by activated carbon, and desorption of vitamin E from activated carbon by alkanes.

2. Experimental

Fig. 1 shows the operation to recover PACs from PFAD by adsorption-desorption. In stage one, the PACs will be recovered from PFAD by adsorption. In stage two, the desorbing solvent introduced to recover adsorbed PACs in loaded AC.

In adsorption experiment, model of PFAD prepared as feed, and commercial AC was chosen as adsorbent. Also, the adsorption experiment of PAC, in this case vitamin E in alkanes are carried out in order to find proper desorbing solvent recover vitamin E in activated carbon. The desorption experiment to recover vitamin E from loaded sample of activated carbon from adsorption experiment are undergo by using hexane as desorbing solvent.
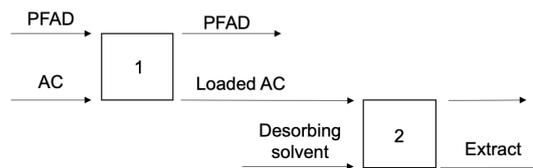
Fig 1. Operation to recover PACs from PFAD

2.1 Palm Fatty Acid Distillates (PFAD) Sample Characterization

PFAD sample was obtained from Indonesian Palm Oil Research Institute (IOPRI) from CPO refinery industry in Medan, Indonesia. The moisture content in PFAD was determined by the Association of the Official Analytical Chemists [AOAC, 1990] method. Free fatty acids (FFAs) amount in the PFAD was determined by standard titration method Ca 5a-40 [AOCS, 1998]. The iodine value was determined by Standard method of oil and fats 993.20 [AOAC, 1997]. The saponification value was determined by AOCS standard method Cd 325. The determination of free fatty acid value was carried out by measurement of Fatty acid methyl esters (FAMEs) for all the samples of PFAD were prepared and the fatty acid composition was determined by IUPAC standard method 2.301 [IUPAC, 1976].

2.2 Adsorption Experiment of Vitamin E in Model of Palm Fatty Acid Distillates

A model of PFAD was brought into contact with AC (granular type, CAS RN®: 7440-44-0 purchased from Wako Chemical Japan) in a $100 \times 10^{-6} \, m^3$ Erlenmeyer flask with a screw cap. The granular activated carbon-shaped crushed into small sized particles and sieved (425×10^{-6} m

aperture, Tokyo Screen Co., Ltd.). The mixture was shaken on hot plate using magnetic stirring and allowed to reach equilibrium. The mixture then was filtered and the filtrate was sent for analysis by UV-vis spectrophotometer with wavelength 292nm. The batch adsorption condition detailed on Table 1.

Table 1 The principal conditions for batch equilibrium adsorption

Feed	Model of PFAD (mixture of Oleic acid and α-tocopherols)
Volume of feed solution, V_0 [m³]	
Concentration of vitamin E, C_0 [kmol m⁻³]	0.025
	0.01-0.1
Adsorbent	Commercial AC
Mass ratio of adsorbent to volume of feed solution, S_0/V_0 [-]	0.05
Time [h]	120
Temperature [K]	313

2.3 Desorption Experiment of Vitamin E in Alkanes Solvents

Solvent has important role in eluent, deciding the separation capacity. In the case of adsorption, there will be further step needed to recover vitamin E in which we choose to do desorption experiment. Some alkanes were chosen in this experiment due to their non-polarity and since vitamin E is a non-polar molecules, non-polar solvent will work better to dissolve vitamin E. In this experiment, hexane and n-octane are used to investigate the adsorption kinetics of vitamin E in activated carbon. The sample and AC preparation were same as for the adsorption experiment. The mixture was shaken (Thomastat T-N22S, Thomas Kagaku Co., Ltd.) with set temperature at 300K for 5 days to reach equilibrium. After that, the mixture was filtered and the filtrate was sent for analysis by UV-Vis spectrophotometer in wavelength 292nm. Condition of the experiment shown on Table 2.

Table 2 Condition of Batch Adsorption Vitamin E and Alkanes Mixture in Activated Carbon

Liquid phase	Mixture of α-tocopherols and Alkanes (Hexane, n-Octane)
Volume of feed solution, V_0 [m³]	
Concentration of vitamin E, C_0 [kmol m⁻³]	0.025
	0.01-0.1
Adsorbent	Commercial AC
Mass ratio of adsorbent to volume of feed solution, S_0/V_0 [-]	0.05
Time [h]	120
Temperature [K]	300

The desorption experiment started with the filtration of used activated carbon from adsorption experiment and filtered using filter paper [Advantec, 5C 125mm] then the mass of filtered AC weighed in order to estimate the value vitamin E adsorbed in AC and the rest of mother liquid which could not be filtered and still contains some vitamin E and oleic acid. In 0.00025 m³ conical flask, the AC

added for desorption experiment, 2.5 x10⁻⁵ m³ of alkane solution was taken into the conical flask and shaken in controlled water bath shaker for 5days at 300K, and analyzed in UV-Vis Spectrophotometer to calculate the desorbed amount of vitamin E. The condition showed in Table 3.

Table 3 Desorption of Vitamin E using Hexane as Desorbing Solvent

Feed	Loaded AC, Mixture of Oleic acid and Vitamin E
Mass of feed solution, L_0 [kg]	0.003-0.005
Concentration of vitamin E, C_0 [kmol m⁻³]	0.05-0.1
Desorbing solvent	Hexane
Mass ratio of solvent to volume of feed solution, S_0/L_0 [-]	0.5
Time [hr]	120
Temperature [K]	300

3. Result and Discussion
3.1 Characterization of Palm Fatty Acid Distillates (PFAD)

The PFAD characterization analysis included physical and chemical analysis of the PFAD. The results shown in Table 4.

Table 4 Result of PFAD Characterization

Parameters	Value	Unit
Moisture content	0.07	-
Iodine Value	48.7	kg I₂ kg⁻¹
Saponification value	0.197575	kg KOH kg⁻¹
Free Fatty Acid Value	0.9424	-
*Palmitic acid (C16:O)	0.46	-
*Oleic acid (C18:1)	0.39	-
*Lauric acid (C12:0)	0.001	-
*Myristic acid (C14:0)	0.008	-
*Palmitoleic acid (C16:1)	0.001	-
*Linoleic acid (C18:2)	0.094	-
*Stearic acid (C18:0)	0.040	-
*Linolenic acid (C18:3)	0.002	-
*Arachidic acid (C20:0)	0.002	-
Vitamin E (α-tocopherols)	0.298	kg m⁻³
Squalene	2.13043	kg m⁻³
Sterols	3.841294	kg m⁻³

*FFA quantification was done by Indonesian Palm Oil Research Institute

The fatty acid value is 94.24% in this experiment, some references mentioned in some palm oil distillates, the FFA content usually in the range of 80-95% (Moh et al., 1999). This indicated that there was no problem in the deodorization process, and that the quality of the recovered refined palm oil has been maintained.

Unsaponifiable matter (UM) content is made up mostly of minor components such as higher aliphatic alcohols, sterols, squalene, pigments and hydrocarbons. These

components are partially distilled off and accumulate in the distillate during de-odorization of the palm oil.

Saponification value is a measurement of the free and esterified acids present. The number of saponification value in this sample is 0.197575kg KOH kg^{-1} which is quite lower compared to other experiment reported by Moh et al. (1999) which shows some kinds of PFAD have saponification value at range 0.2003–0.2154 kgKOH kg^{-1}. Variety of saponification value could be as effect of palm oil processing mills which in every industry has their own preferred purification of crude palm oil. The quantification of unsaponifiable matters or specifically on determination of physiologically active component as mentioned was determined by High Performances Liquid Chromatography given that sterols has 64% composition over all minor components, squalene 33%, and vitamin E specifically α-tocopherols only accounted as 3% of total identified physiologically active components in PFAD.

3.2 Adsorption of Vitamin E in Model of Palm Fatty Acid Distillates

The Langmuir model was employed to predict the adsorption performance of commercial activated carbon. Maximum adsorption occurs when the surface is covered by a monolayer of adsorbate. For the adsorption of a solute (adsorbate) from solution the Langmuir isotherm can be written as follows:

$$q = \frac{q^* K_L C}{1 + K_L C} \qquad (1)$$

Where q^* is saturated adsorbed amount of vitamin E [kmol kg-AC^{-1}], K_L is Langmuir constant [m^3 kmol^{-1}], C_0 and C is concentration of the vitamin E at initial and at equilibrium [kmol m^{-3}].

The material balance relationship of vitamin E adsorption can be written as,

$$V_0 C + S_0 q = V C + S q \qquad (2)$$

And the fractional removal of vitamin E, Y [–], could be defined by:

$$Y = \frac{V_0 C_0 - V C}{V_0 C_0} \qquad (3)$$

Where V_0 and V is the volume of liquid at initial and at equilibrium [m^3], S_0 and S is the mass of adsorbent at initial and at equilibrium [kg], and q is the adsorbed amount of vitamin E at equilibrium [kmol kg-AC^{-1}].

The fractional removal of vitamin E in oleic acid showed in Fig. 2, the increase of feed concentration made lower concentration of vitamin E could be adsorbed in activated carbon. This is due to the better adsorption capacity of activated carbon in small amount of vitamin E.
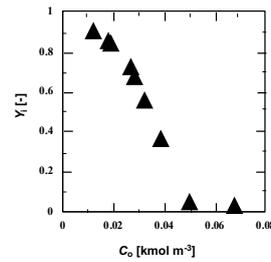
Fig. 2 The Fractional Removal of Vitamin E in Oleic Acid

3.3 Desorption of Vitamin E in Alkanes Solvent

The result of adsorption isotherm of vitamin E in model PFAD and in alkanes solvent is shown at Fig. 3.

The fractional recovery of vitamin E by desorption, Y [–], could be defined by:

$$Y = \frac{1}{q_0} \frac{V (C - C_0)}{m} \qquad (4)$$

Where V is the volume of solution [m^3], C_0 and C is the concentration of vitamin E at initial and equilibrium [kmol m^{-3}], and q_0 is the initial solid phase of vitamin E concentration [kmol kgAC^{-1}].

The amount of vitamin E adsorbed in AC higher in octane solution compared to hexane solution. It is due to octane is more non-polar compared to hexane, and AC which also non-polar in this case tends to adsorb more vitamin E easily from octane solution than in hexane solution. This indicate the adsorbent more adsorb the adsorbate which has relatively same polarity.
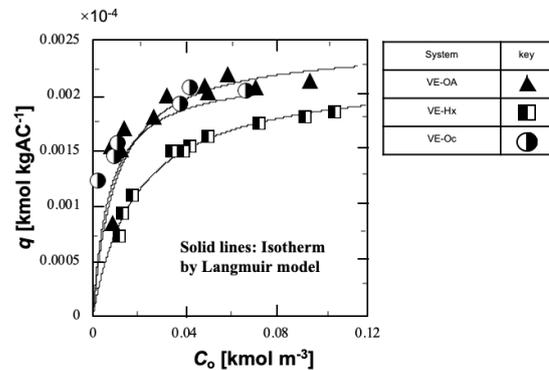
Fig. 3 Vitamin E adsorption isotherm in model PFAD and alkanes solvent

The Langmuir parameter of vitamin E adsorption model PFAD and in alkanes is shown at Table 6.

Table 6 Langmuir parameters for adsorption isotherm of vitamin E in oleic acid, hexane and octane

	$q^* \times 10^{-4}$ [kmol kg-AC^{-1}]	K_L [m^3 kmol^{-1}]
VE-OA	2.4	198
VE-Hx	2.21	52.4
VE-Oc	2.20	139.6

Adsorption isotherm result shows that the adsorption of vitamin E is following the Langmuir-type adsorption isotherm. Also, hexane shows to have lower adsorption ability than octane, in that case we proceed to use hexane as desorbing solvent as it has higher desorption potential than octane. The fractional recovery of vitamin E using hexane as desorbing solvent shown in Fig. 4.

Result shows that in average 0.53 vitamin E recovered from loaded AC using hexane as desorbing solvent.
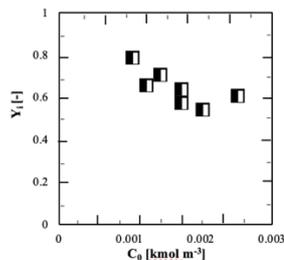
Fig. 4 Fractional recovery of vitamin E using hexane as desorbing solvent

The overall fractional recovery of adsorption-desorption vitamin E from model PFAD using commercial activated is 0.74. Fig. 5 shows the overall fractional removal.
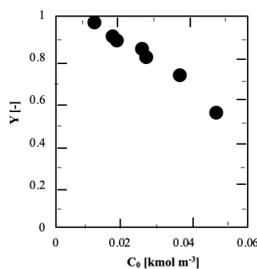
Fig. 5 Overall fractional recovery of vitamin E by adsorption-desorption

4. Conclusion

PFAD sample identified contained of 94.24% FFA content, which mainly are palmitic acid (46%) and oleic acid (39%). Physiologically active components are α - tocopherols (vitamin E) 298 kg m^{-3}, squalene 2.13 kg m^{-3}, and sterols 3,841 kg m^{-3}.

Adsorption of vitamin E in model PFAD by AC give in average 0.56 of initial amount vitamin E adsorbed in AC after equilibrium condition reached. And following Langmuir type isotherm.

Desorption experiment was performed to recover vitamin E from AC, hexane was chosen as desorbing solvent. The desorption resulted in average 0.53 vitamin E recovered from used AC. The desorption isotherm is following Langmuir-type isotherm.

In this experiment, the commercial AC was used as adsorbent and shows significant result in physiologically active component recovery from PFAD. Other types of activated carbon can also be option in future experiment.

6. Nomenclature

q^* : Saturated adsorbed amount of vitamin E [kmol kg-AC^{-1}]

K_L = Langmuir constant [m^3 kmol^{-1}]

C_0 = Concentration of the vitamin E at initial [kmol m^{-3}]

C = Concentration of the vitamin E at equilibrium [kmol m^{-3}]

V_0 = Volume of liquid at initial [m^3]

V = Volume of liquid at equilibrium [m^3]

S_0 = Adsorbent mass at initial [kg],

S = Adsorbent mass at equilibrium [kg],

q = Adsorbed amount of vitamin E [kmol kg-AC^{-1}].

q^* = Saturated adsorbed amount of phenol on PKSAC [kmol kg-AC^{-1}]

Y = Mass ratio of the remained sample relative to the initial one [-]

6. References

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