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Optimisation using Central Composite Design for Adsorption of Virgin Coconut Oil

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Abstract

Development of coconut-based industries in Indonesia has excellent prospects, especially Virgin Coconut Oil (VCO) as a nutritional supplement for health. In order to produce high quality of VCO, this research developed activated carbon betung bamboo (Dendrocalamus asper) as bio-adsorbent in adsorption process. The composition of bio-adsorbent in chromatographic column has been optimized using central composite design (CCD). Bio-adsorbent were characterised by using Scanning electron microscopy (SEM) and fourier transform infrared spectroscopy (FTIR), the average poresize of 1.59 μm was calculated using equation. Adsorption isotherm data have been described by Freundlich and Langmuir models and resulted the adsorption equilibrium constant of kf of 80.68 mg $g^{-1}$and k_L of 0.056 L mg^{-1}. Pseudo-second-order kinetic model resulted adsorption rate constant, k of 0.004 g mg-1 min-1 with a good fitting R^2 of 0.997. This optimum process condition was achieved on adsorption time of 33 hours, 150 gr of bio-adsorbent and 411.75gr of adsorbed (neat VCO), that produced odorless and colorless VCO, density of 0.91630gr/mL and FFA concentration of 0,0602 %, which. were fulfil the standard of SNI-3741-2013 and APCC.

Keywords: *CCD, adsorption; fixed bed column; bio-adsorbent; Dendrocalamus asper*

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INTRODUCTION

Indonesia is the largest coconut producer in the world. Its production reaches 18 million tons per year but this commodity is still not much developed (Prahara, 2018). Research from the Ministry of Industry states that there are still many old coconut trees (not productive), but replantation is running slowly, even many coconut plantations are changing functions. In addition, the next challenge for government is developing an integrated coconut processing industry in Indonesia. These products are produced for primary products and have not been processed further. This situation decreases the economic value of coconuts. One of the solution that can increase the economic value of coconut is producing the high quality of Virgin Coconut Oil (VCO). VCO has been acknowledged as the healthiest crop oil and can be extensively used in various fields such as food, beverage, medicinal, pharmaceutical, nutraceutical, and cosmetics (Vijayasanthi, *et al.*, 2020). VCO is clear and tasteless, odorless oil that is processed from coconut meat. The incrediable health benefit of VCO is due to the unique type of saturated fats presents in the oil. Therefore it is considered the healthties of all dietary oils. VCO contains high, medium and short chain saturated fatty acids, which is around 92% as shown in Table 1 (National Standarization Agent, 2013). VCO has benefits such as, increasing human body's resistance to disease and accelerating the healing process (Benzhi, *et al*., 2005).

Table 1. Fatty acid profile of Virgin Coconut Oil

Fatty acids (g/100 g oil)	Standard, SNI
Caproic acid	0.10 – 0.95
Caprylic acid	4 – 10
Capric acid	4 – 8
Lauric acid	45 – 56
Myristic acid	16 – 21
Palmitic acid	7.5 – 10.2
Stearic acid	2 – 4
Cis-9-Octadecanoic acid (C 18:1 n-9)	4.5 – 10
Cis-9,12-Octadecadienoic acid (C-18:2 n-6)	0.7 – 2.5
Arachidic acid (C20:0)	-

High quality VCO is odorless, colorless, and free of sediments. The odorless VCO can be produced by adsorption by using activated carbon or often also referred as charcoal as adsorbent, which has porous solid consisting mostly of free carbon elements and each covalently bonded and has a very large surface area. This activated carbon was produced from materials that contains much carbon by heating at high temperatures (Biswas, *et al*. 2018). The effect of heating process is to avoid air leakage in the heating chamber so that the material containing carbon is only carbonized and not oxidized (Branca *et al*. 2016). Activated carbon is used in the process of purifying air, gas, solution or liquid. Absorption is determined by the surface area of the particles and this ability can be higher if the carbon is activated with chemicals or by heating at high temperatures. Meanwhile, adsorption is the process by which a substance such as charcoal or activated carbon binds other substances onto its surfaces. A carbon-impregnated pad is used for adsorption of liquid and gas impurities.

The adsorption uses fixed bed chromatography column, which need a lot of activated carbon. Activated carbon consists of 87-97% carbon and the rest in the form of hydrogen, oxygen, sulfur and nitrogen and other compounds formed from the manufacturing process (Chang, 2014). Activated carbon is useful in gas purification, catalysts, as a filter and deodorizer in the drug and food industry, water filtration, deodorizing in the water treatment industry, as a reusable solvent, and energy storage (Giri *et al*., 2011, Benzhi *et al*., 2005). At present biomass is widely used as activated carbon, such as coconut shell, oil palm shell, wood, and bamboo (Xiuli *et al*. 2012).
Bamboo plant is one of the many types of tropical plants found in Indonesia and one species of bamboo plants in Indonesia is the betung bamboo (*Dendrocalamus asper*), as shown in Figure 1a-b. Betung bamboo is a species of bamboo that is still very minimal utilization, this is because not many people know the benefits of the betung bamboo. Betung bamboo plants have chemical properties including levels of cellulose, lignin, pentosan, ash and silica. Cellulose levels ranged of 42.4- 53.7%, lignin levels amounted to between 19.8--26.6%, levels of pentosan amounted around 1.24-3.77%, ash 1.20-3,76%, and silica levels ranged from 0.10-1.78% (Liese and Kohl, 2015). The carbon-rich lignocellulose is an indispensable composition as the basis for active carbon (Yu and Gao, 2017).

(a) (b)

Figure 1. (a) Raw material, (b) activated carbon of betung bamboo

Activated carbon from betung bamboo is used to purify VCO, where the composition of activated carbon is referred to as bio-adsorbent activated carbon. Bamboo is used as an adsorbent after going through various processes. Cellulose from betung bamboo is a homogeneous fiber and its lignin can form a matrix pore structure, which has a high calorific value that is equal to 10924 cal/g after going through a process of carbonation at 500^{o}C.

In this research, betung bamboo (*Dendrocalamus asper*) is used as activated carbon to eliminate the distinctive odor, color and free fatty acid content of VCO. VCO has been purified using betung bamboo as bio-adsorbent in order to optimize the composition of adsorbent in the chromatographic column. Bio-adsorbent of betung bamboo was characterised by using scanning electron microscopy (SEM) in order to study the morphology. Few researchers have studied applicability of activated carbon from suitable biomaterials, which can effectively removed odor from aqueous solution. Kindi *et al*. (2018) was found the ability of palm empty fruit bunch to adsorp fenol from grey water. Fenol removal of 96.9–98.5% were achieved using chromatography colomn for 1 hour at temperature of 600^{o}C. Bikash *et al.* (2016) was studied the adsorption of dye using bioadsorbent and reached the removal of methylen blue (MB) of 99.78%. Similar experiment was found by Garg *et al.* (2014) that was achieved the dye adsorption of 95% by using indian rosewood sawdust.

Adsorption is process of agglomerating dissolved substances (soluble) that exist in solution, by surface of substance or absorbent object, in which a physical chemical bond occurs between the substance and its absorber. Adsorption can be divided into two types, namely physical adsorption (caused by Van Der Waals force (the cause of gas condensation to form liquid) that is on the surface of the adsorbent) and chemical adsorption (there is a reaction between substances absorbed by the adsorbent, the amount of the substance that is adsorbed depends on the characteristic of the solid which is a function of pressure and temperature). The adsorption rate can be also defined as the number of substances adsorbed per unit time, that could be influenced by several things, namely, (a) types of adsorbents; (b) type of adsorbed; (c) surface area of adsorbent; (d) concentration of adsorbed; (e) process temperature; (f) centrifugal rotational rate Freundlich and Langmuir model were used to describe the adsorption rate (Bikash *et al*. 2016). Moreover, Pseudo-first-order and second order kinetic model were used also to determine the kinetics study (Bikash *et al*. 2016).

The statistical design of the experimental approach by Response Surface Methodology (RSM) with Design Expert Version 11 software was used to obtain optimum results. In statistical design, a Central Composite Design (CCD) is an experimental design useful in response surface methodology (RSM) to build a second order (quadratic) model for the response variable (Behken 1960). After designed experiment is performed, linear regression is used, sometimes iteratively, to obtain results. Coded variables are often used when constructing this design. Many researchers have studied the application of CCD in adsorption and filtration process, however the adsorption capasities of such materials are not up to the mark (Dutta *et al*., 2011, Chattoraj *et al*. 2013, Herdiansyah *et al*., 2017, Ezekannagha *et al*., 2017). Therefore, the tremendous demand to explore a suitable biomaterial that can effectively adsorb or filtrate the oilywater was higly needed to reach high quality of product (Liou, 2010, Madrakian *et al*., 2011, Loh, 2017, Kusworo *et al*, 2020). RSM consists of a collection of mathematical and statistical techniques that aim to explain the interactions between various types of response variables by sorting experiments that are designed to get the optimum response. This method was firstly introduced in 1951 by PMP (Behnken, 1960). This model uses a level 2 polynomial approach. The strengths of this approach are that it can explain an interaction of various variables, even though we do not know the characteristics of a process for example a two-order process, as follows,

$$Y = f\,(x1, x2, xn, \ldots\ldots xn + 1) + e \qquad (1)$$

where x1 and x2 are independent variables that influence and y is the response of functions that depend on x1 and x2. While the value of e is an error from the response. This helps to find the optimum condition of Y value where interaction between variables can produce a maximum model. In this study a class of three level complete factorial designs (Central Composite Design-CCD) was used to determine the optimization values of the operating variables. A statistical approach was executed using a factorial design of three variables namely time, adsorbed (VCO) and bio-adsorbent of betung bamboo.

EXPERIMENTAL

Preparation of VCO

The fresh coconut milk was used as raw material that brought from local market. Coconut milk has to be unfrezzing before conducting experiment and unused coconut milk is stored in refrigerator at 4 ºC. The tools used to produce VCO are glass scales (Kiramas), beaker glass (pyrex 500 mL), erlenmeyer (duran 250 mL), measuring cup (pyrex 500 mL), glass spatula, filter paper (whatmann 40), analytical balance sheet (Fujitsu), waterbath (Thermo Scientific), drafting funnel (Pyrex 1000 mL) magnetic stirrer hotplate (Scilogex). The chemicals used are water soluble demulsifier (Tergitol TM NP-4 Surfactant). These chemicals are belonging to noninonic surfactant that destabilized the dispersed phase of emulsion. The stability of emulsion study included the physical properties such as viscosity, interfacial and surface tension, viscosity and oil droplets size.

Preparation of adsorbent

Adsorbent preparation was already made by betung bamboo (*Dendrocalamus asper*), which prepared in few steps. The used tools to produce bio-adsorbents are cutters, digital thermometers (Thermo Scientific), iron furnaces, aluminum containers, spray bottles, spatulas, mortals and mortars, 70-100 mesh canting / sieve (Astro Mesh), ovens (Memmert Oven), furnace (Neytech Vulcan Muffle), Column Chromatography, stopwatch / hour, glass bottles, porcelain cups (duran), desiccator (normax) instrument, Scanning Electron Microscopy (SEM TESCAN VEGA 3), picnometer (pyrex 50 mL) , dropper pipettes, petri dishes (duran), titration devices, measuring flasks (pyrex 100 mL), volume pipettes (pyrex 10 mL), rubber bulp, aluminum foil.

Firstly, tools and materials were prepared completely, then bamboo cutted to size of 6-12 mesh and sieved. The bamboo will be carbonized at varied temperature 400, 500 and 600 ºC for 20, 40, and 60 minutes, respectively. The charcoal of betung bamboo was blended until crystal formed to size of 70-100 mesh. Bio-adsorbent betung bamboo is ready to be activated with NaCl solution until the surface of the adsorbent becomes wet and damp. Finally, the charcoal was put into the furnace and burn at temperature of 180 ° C for 2 hours. As the activated carbon has cooled, it is sieved again by measuring 70-100 mesh and the activated carbon is ready for use (Liese and Kohl, 2015, Chang, 2014). Charcoal of Betung bamboo subsequently activated in physics by using water vapor at 900 ºC for 20, 40 and 60 minutes. Carbon was characterised of yields carbonization includes levels of shrinkage mass and proximate analysis like analysis of water content and ash content, whereas on activated carbon from yield activation is done by testing the numbers iodine and analysis of the yield value.

Characteristic of Bio-adsorbent

The morphology of bio-adsorbent was analyzed using a scanning electron microscope (SEM, S-800M, Hitachi High Technology Co.Ltd., Tokyo, Japan). In order to observe the surface bio-adsorbent. Samples were first frozen in liquid nitrogen and then submitted to fracture. All samples were sputter-coated with a thin gold film prior to SEM observation at magnification of 8k.

Adsorption isotherm process of VCO

Virgin Coconut Oil (VCO) as an adsorbed and activated carbon of betung bamboo (*Dendrocalamus asper*) as bio-adsorbent are weighed in varied ratio. After weighing, it put into the chromatography column to process of adsorption for 24, 30, 33 and 42 hours. Droplets are carried out from the chromatography column to analyze odor, color, density and free fatty acids (FFA).

Study of adsorption isotherm was analysed using Freundlich equation (Eq. 2) and Langmuir isotherm equation (Eq.3) as follows,

$$\text{Log } Q_e = \log k_f + (1/n) \log C_e \quad (2)$$

$$(C_e/Q_e) = (C_e/Q_m) + (1/k_L.\ Q_m) \quad (3)$$

where Q_e (mg.g^{-1}) and C_e (mg.L^{-1}) are solid phase concentration and liquid phase concentration of adsorbed at equilibrium, respectively. Q_m (mg.g^{-1}) is the maximum adsorption capacity and k_L (L.mg^{-1}) is the energy of adsorption. Freundlich isotherm contants k_f and (1/n) can be evaluated by plotting og log (Q_e) versus log (C_e), k_f (mg g^{-1}) (L/mg)$^{1/n}$) and n indicates adsorption capacity and adsorption intensity or the heterogeneity factor, respectively. The Langmuir constant Q_m and k_L can be estimated by plotting (C_c/Q_e) versus C_e (Ansari *et al.*, 2010).

Kinetic study was determined using two most accepted models, such as Lagergren's Pseudo-first-order kinetic (Eq. 4) and Pseudo-second-order kineics models (Eq. 5). These equations are as belows,

$$\text{Log } (Q_e – Q_f) = \log Q_e – (k_1/2.303)t \quad (4)$$

$$t/Q_t = (1/k_2.\ Q_e^2) + (1/Q_e)t \quad (5)$$

where Q_t and Q_e are amount of VCO (adsorbed) (mg g^{-1}) at time ,t and equilibriu and k_1 (min^{-1}) is the Lagergren rate constant of first order adsorption and k_2 (gm g^{-1} min^{-1}) is the second order adsorption rate constant, respectively (Bikash *et al.*, 2016).

Characteristics and Quality of VCO

Odor and color determination

The measurement of odor and color parameters was carried out organoleptically and the test based on compare with SNI, 5 both samples VCO, were tested using a color route tool for organoleptic test and density test using weighing glass tools and analytic balance. Measurement and data collecting was done 3 times (triple) to avoid data errors and get consistent results.

The color of VCO is determined by the presence of pigments that remain after the bleaching process. It is because the fatty acids and glycerides are colorless. Orange or yellow due to the presence of carotene pigments which are soluble in oil.

The smell and flavor in oil are naturally available also due to the presence of short chain fatty acids that effect of oil damage. While the typical smell of palm oil is due to the beta-ionone compound. The melting point of VCO is in the temperature range because palm oil contains several kinds of fatty acids which have different melting points

Measurement of relative density

Relative density of VCO samples was measured according to the AOAC method (AOAC,2000) by temperature at 30^{0}C.

Measurement of fatty acid

Fatty acid profile of VCO samples was measurement as fatty acid methyl esters (FAMEs), which were prepared according to the AOCS method (AOCS, 2000). Prepared FAMEs were injected to the gas chromatography (Shimadzu, Kyoto, Japan) equipped with the flame ionisation detector (FID) at a split ration of 1:20. A fused silica capillary column (0.25 mm), coated with bonded polyglycol liquid phase, was used in order to analyse the fatty acids. The analytical condition were injection port temperature of 250 ^{o}C and detector tempetarature of 270 ^{o}C. Oven was set up from 170-225 ^{o}C at a rate of 1 ^{o}C/min (no initial or final hold). Retention time of FAME standards were used to identify chromatographic peaks of the samples. Fatty acid content was calculated based on the peak ration and expressed as g fatty acid/100 g oil.

Measurement of Acid value and Free Fatty Acid (FFA)

Acid value of all VCO samples was measurement by the AOCS method (AOCS, 2009) and FFA was analysed by following equation using the conversion factor of 2.81 for lauric acid.

$$\text{Acid value} = \%\ \text{FFA} \times 2.81 \quad (6)$$

Optimization of bio-adsorbent composition with CCD

The obtained data from the chromatography column is analysed by Response Surface Methodology to find the optimum composition of bio-asorbent and adsorbat to face the high quality of VCO. As determine before that the high quality VCO is odorles, colorless, low viscosity, and low FFA. This research used central composite design (CCD) to find the optimum composition. CCD has been widely used statistical method based on the multivariate non linear model for optimization of composition variables of adsorption. The used of regression model equations and composition conditions will be determined by the appropriate experiments. CCD was used for fitting a secind-order model whuch requires only a minimum number of experiments for modelling (Behnken, 1060). The CCD consists of 2n factorial runs (coded to the usual ± notation) with 2n axial runs (±α,0,0,...0), (0, ±α ,0,0,...0), (0,0,..., ±α) and accentor runs (six replicates, 0,0,0,...,0). The number of factors n increases the number of runs for a complete replicate of the design, that is given in equation (7).

$$N= 2^n + 2n + n_c \qquad (7)$$

Basically the optimization process involves three major steps, namely, (1) performing the statistically designed of experiment (DoE); (2) estimating the coefficients in a mathematical model, and (3) predicting the response and validating the adequacy of the model. DoE is generated using Design Expert Version 11 by inputting factor data, responses with minimum and maximum levels have been determined. Figure 2 shows the design factors chosen to determine the number of factors and responses. An empirical model was developed to correlate the responses to the adsorption process. Based on second order quadratic model as given by Equation (1) in order to analyze the effect of factors interactions.

Figure 2 showed the reguler two-level factorial design that was used in response surface methodology that design for 2 to 9 factors where each factor is set to 2 levels. Fractional factorials can be used for screening many factors to find the significant few.The color coding represent the design resolution Green (characterisation in resolution III or higher), Yellow (screening in resoluiton IV), Red (Ruggeness treating in resolution III).

This study uses 3-factor variables (black color), then according to the rule of thumb RSM with central composite design (CCD) by determining the maximum and minimum values of each factor specified, as in Table 2. The results of the input maximum and minimum values get a Design of Experiment (DoE) adsorption pattern of 12 times the measurements as tabulated in the following Table 3.

	Number of factors								
Runs		2	3	4	5	6	7	8	9
	4	2^2	2_{III}^{3-1}						
	8		2^3	2_{IV}^{4-1}	2_{III}^{5-}	2_{III}^{6-3}	2_{III}^{7-4}		
	16			2^4	2_{V}^{5-}	2_{IV}^{6-2}	2_{IV}^{7-3}	2_{IV}^{8-}	2_{III}^{9-}
	32				2^5	2_{VI}^{6-1}	2_{IV}^{7-2}	2_{IV}^{8-}	2_{IV}^{9-}
	64					2^6	2_{VI}^{7-1}	2_{V}^{8-}	2_{IV}^{9-}

Figure 2. Reguler Two-Level Factorial Design from RSM

Table 2. Level of maximum and minimum factor

Factors	Unit	Code	Level	
			Minimum	Maximum
Adsorption time	hour	x_1	24	42
Bio-adsorbent	gram	x_2	100	200
Adsorbed (VCO)	mL	x_3	400	500

Tabel 3 DoE of VCO Adsorption

Std	Run	Factor		
		Time,hour	Bio-adsorbent	Adsorbed, g
5	1	24	100	457.5
6	2	42	100	457.5
8	3	42	200	457.5
1	4	24	100	366
7	5	24	200	457.5
11	6	33	150	411.75
12	7	33	150	411.75
10	8	33	150	411.75
9	9	33	150	411.75
3	10	24	200	366
4	11	42	200	366
2	12	42	100	366

In this study, the used design was Central Composite Design (CCD) matrix. Table 3 showed the DoE (Design of Experiment) stage in VCO adsorbeds and betung bamboo bio-adsorbents (*Dendrocalamus asper*) with Design Expert Version 11. The DoE were created by determining the number of factors and responses as parameters and measuring variables, respectively.

RESULTS AND DISCUSSION

Characterization of bio-asorbent

The charactristics of bio-adsorbent was identified four response, namely odor, color, relative density and free fatty acid content. Tabel 4 illustrated the composition of VCO after adsorption.

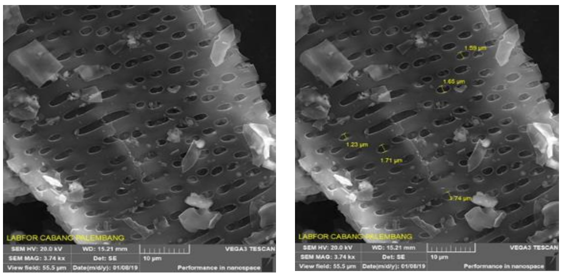
Table 4 Composition of produced Virgin Coconut oil

Component	Unit	Total	Standard, SNI
Odor	None	1	1-2
Color	None	1	1-2
Relative Density	gr/mL	0.917	0.915-0.917
Free Fatty Acid	%	0.057	0.03-0.09

Effect of Surface Morphology on Adsorption

The results of the surface morphology analysis of the bio-adsorbent were obtained using scanning electron microscope- (SEM) as in Figure 3. Figure 3 a and b showed surface morphology of bio-adsorbent obtained using an electron microscope scanning the field emission with magnification 374 times for each sample a and b. In Figure 2a and 2b illustrated of bio-adsorbent used by SEM with magnification of of 8740 and 8750. The bio-adsorbent pores are spread evenly on the surface area.

The pore diameter can also be measured using the same tool, which is an average of 1.59 µm, as shown in Figures 4. In the adsorption process the absorption process occurs where the absorbed molecule will be inside the absorbing molecule, so that in this study it can be proven that the absorbed VCO meets the bio-adsorbent pores. The average pore diameter of the bio-adsorbent can be carried out through SEM and the bio-adsorbent density is analyzed by a pycnometer with an average density of 0.915 gr / mL-0.916 gr / mL, free fatty acids (ALB) 0.03% -0 09%.



(a) (b)

Figure 3(a-b). Surface morphology of bio-adsorbent using SEM

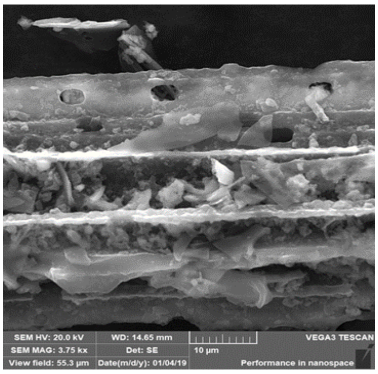


Figure 4. Porosity and average pore diameter of bio-adsorbent

The effects of the different pore structures (and related adsorption kinetics) of the carbons on the dynamic removal of selected toxicants or impurities. As can been seen, the bio-adsorbent, which displays the higher total porosity and average pore size tends also to higher adsorption rate constants removes significantly more of impurities. These higher rates do of course apply to significantly higher volumes of pore filling for the bio-adsorbent material.

Design of Experiment of VCO adsorption

The process in the fixed bed chromatography column, as shown in Figure 5, is carried out using Design of Experiment (DoE) obtained from Response Surface Methodology (RSM) with Design Expert 11.0 software.

The Expert Design 11.0 program with Response Surface Methodology (RSM) Box Behnken Design is used to examine and select process conditions from a combination of factor levels that produce an optimal response. The main idea of this method is to know the effect of independent variables on responses, get a model of the relationship between independent variables and the response and get the process conditions that produce the best response. In addition, the advantages of the RSM method include that it does not require large amounts of experimental data and does not require a long time (Yuliwati *et al.*, 2017).

Figure 5. Fixed Bed Chromatography Column

In this study, DoE was used to obtain an experimental design so that the optimum composition of bio-adsorbent (Betung bamboo) and adsorbed (VCO) was obtained. The design resulting from the RSM method is as shown in Table 6.

Table 5 described that adsorption of VCO was carried out 12 times in the chromatographic column with the composition of bio-adsorbent (betung bamboo) 100 gr, 150 gr, 200 gr and adsorbed (VCO) 366 gr, 411.75 gr, 457.5 gr in the time span of adsorption in the chromatographic column for 24 hours, 33 hours and 42 hours. The results obtained are in accordance with the VCO standard quality standards for odors and colors in the range of values 1-2 (odorless and slightly characteristic coconut odor), an average density of 0.915 gr/mL-0.917 gr/mL, free fatty acids (FFA) 0.03 -0.09 %. This proves that the deodorization process using betung bamboo (Dendrocalamus asper) bio-adsorbent works very well. Betung bamboo has a very good deodorization ability because it can eliminate odors and clear the color of VCO better than bio-adsorbent from coconut shell in research.

The Effect of Time on Odor, Color and Free Fatty Acid composition

The effects of time, bio-adsorbent and adsorbed on odor are analyzed in this section, where the results of the study show that the odor produced has a value of 1 which means it is very odorless. The value of this analysis proves that the influence of time, bio-adsorbent and adsorbed significantly influences odor, color, density and FFA (free fatty acid) indicators.

Based on Table 6, the ANOVA value for odor obtained predicted R^2 of 0.9200, which means that the chosen model is cubic polynomial as a model with high polymial deviation. The resulting intercept is 1.63 with a standard error of 0.0871, which is also evidenced through the discussion in Figure 6 that shows in the cubic model the effect of the three time factors, bio-adsorbent and adsorbed on the odor response, which was produced odor of 1.6. This value also becomes the center point at 4 cube points. These four points minimize the value of errors that might occur for all three factors at once with a value of 1.625 being the maximum value (Chowdury and Das, 2010).

Table 5. Adsorption of VCO using DoE

Std	Run	Factor			Response			
		Time, hour	Bio-adsorbent	Adsorbed, g	Odor	Color	Density, g/mL	FFA, %
5	1	24	100	457.5	2	2	0.9163	0.0857
6	2	42	100	457.5	2	2	0.918	0.0908
8	3	42	200	457.5	2	1	0.9155	0.0417
1	4	24	100	366	1	1	0.9153	0.0387
7	5	24	200	457.5	1	1	0.9151	0.0439
11	6	33	150	411.75	1	1	0.9161	0.0437
12	7	33	150	411.75	1	1	0.9161	0.0437
10	8	33	150	411.75	1	1	0.9161	0.0437
9	9	33	150	411.75	1	1	0.9161	0.0437
3	10	24	200	366	2	2	0.9150	0.0323
4	11	42	200	366	2	2	0.9151	0.0457
2	12	42	100	366	1	1	0.9156	0.0806

Table 6. Anova analysis of odor

Factor	Coeff	SS	Df	MS	F-value	P-value
Model	14.10		4			
X_1	-0.63	2.10	1	2.45	62.34	0.0021
X_2	1.35	1.04	1	2.04	56.89	0.0002
X_3	-3.42	1.70	1	1.75	50.31	0.0004
$X_1 X_2$	-0.64	0.36	1	0.34	7.89	0.0003
$X_1 X_3$	-2.61	0.09	1	0.31	9.54	0.0031
$X_2 X_3$	12.4	0.08	1	0.07	6.01	0.0345
$X_1^2X_3$	-0.85	1.08	1	0.09	3.78	0.0184
X_2^2	0.94	1.03	1	0.04	4.87	0.0032
X_3^2	-3.17	1.09	1	0.04	3.96	0.004
Residu	1.30	0.14	3	0.03		
Total Odor	1.6	8.71	8	3.78	62.34	0.0005
	Std dev				0.9330	
	R^2				0.9200	
	Adj R^2				0.9002	

Regression equation model after the insignificant variable omitted as below.

$$Y_1 = 14.10 – 0.63 X_1 + 1.35 X_2 – 3.42 X_3 – 0.64 X_1X_2 – 2.61 X_1X_3 + 12.4 X_2X_3 – 0.85 X_1^2X_2 + 0.94 X_2^2 - 3.17 X_3^2 \quad (3)$$

where the measured Y_1 is defined as the odor rejection in the permeate solution and X_1, X_2, and X_3 represent time of adsorption, amount of bio-adsorbent and amount of adsorbed.

Based on Table 7, the ANOVA value for color, obtained predicted R^2 of 0.9301, which means that the chosen model is cubic polynomial as a model with high polymial deviation. The resulting standard deviation of 0.9472 with a standard error of 0.0857.

$$Y_2 = 12.08 + 0.46 X_1 + 0.79 X_2 – 8.52 X_3 + 0.28 X_1X_2 – 2.61 X_1X_3 – 0.57 X_2X_3 – 0.29 X_1^2X_2 + 0.46 X_2^2 - 2.40 X_3^2 \quad (4)$$

where the measured Y_2 is defined as the odor rejection in the permeate solution and X_1, X_2, and X_3 represent time of adsorption, amount of bio-adsorbent and amount of adsorbed.

Validity of the selected model used for optimizing the process parameters has to be tested using Anova analysis. All these coefficient variables are analyzed by multiple regression analysis and response contour plot is generated using the software Design-Expert.

Based on Table 8, the ANOVA analysis for density, obtained predicted R^2 of 0.9554, which means that the chosen model is cubic polynomial as a model with high polymial deviation. The density of 0.917 cP with a standard error of 0.0913 showed with the cubic model that influenced the three factors, namely time, amount of bio-adsorbent and amount of adsorbed. These values become the center point at 4 cube points that minimize the occured value of errors at once.

$$Y_3 = 9.86 – 2.19 X_1 + 1.98 X_3 – 3.42 X_4 + 2.96 X_1X_2 – 0.11 X_1X_3 – 0.15 X_2X_4 + 0.07 X_1^2X_2 – 1.77 X_2^2 + 3.40 X_3^2 \quad (5)$$

Table 7. Anova analysis of color

Factor	**Coeff**	**SS**	**Df**	**MS**	**F-value**	**P-value**
Model	12.08		3			
X_1	0.46	1.04	1	1.75	72.80	0.0004
X_2	0.79	1.65	1	1.80	55.21	0.0003
X_3	-8.52	1.40	1	2.04	49.10	0.0006
$X_1 X_2$	0.28	1.05	1	2.50	9.20	0.0062
$X_1 X_3$	-2.61	1.09	1	3.79	4.27	0.0345
$X_2 X_3$	-0.57	0.70	1	0.21	4.67	0.0397
$X_1^2X_2$	-0.29	1.04	1	0.40	3.54	0.0025
X_2^2	0.46	0.05	1	0.09	3.21	0.0041
X_3^2	-2.40	0.45	1	0.05	4.01	0.007
Residu	1.30	0.1	3	0.07		
Total Color	1.5	8.57	4	5.28	72.80	0.0005
	Std dev				0.9472	
	R^2				0.9301	
	Adj R^2				0.6786	

Table 8. Anova analysis of density

Factor	**Coeff**	**SS**	**Df**	**MS**	**F-value**	**P-value**
Model	9.86		4			
X_1	-2.19	1.07	1	1.95	54.81	0.0004
X_3	1.98	1.65	1	2.31	56.09	0.0039
X_4	-3.42	0.94	1	1.19	46.23	0.0004
$X_1 X_2$	2.96	1.15	1	0.25	6.49	0.0002
$X_1 X_3$	-0.11	0.09	1	0.23	7.52	0.0003
$X_2 X_4$	-0.15	1.07	1	0.09	6.61	0.0032
$X_1^2X_2$	0.07	0.78	1	0.27	4.01	0.0002
X_2^2	-1.17	1.10	1	0.31	3.59	0.0039
X_3^2	3.40	1.15	1	0.01	3.04	0.0004
Residu	1.90	0.13	3	0.06		
Total density	0.917	9.13	5	4.18	54.82	0.0005
	Std dev				0.9025	
	R^2				0.9554	
	Adj R^2				0.9181	

where the measured Y_3 is defined as the density rejection in the permeate solution and X_1, X_2, X_3 and X_4 represent time of adsorption, amount of bio-adsorbent and amount of adsorbed.

Based on Table 9, the ANOVA value for free fatty acid (FFA), obtained predicted R^2 of 0.9306, which means that the chosen model is cubic polynomial as a model with high polymial deviation. The resulting standard deviation of 0.9330 with standard error of 0.0959, and the value of bio-adsorbent and adsorbed on the FFA response of 0.0602 %. This value also becomes the center point at 4 cube points. These four points minimize the value of errors that might occur for all three factors at once.

$$Y_4 = 14.10 – 0.63\ X_1 + 1.35\ X_2 – 3.42\ X_4 – 0.64\ X_2X_3 – 2.61\ X_2X_4 + 12,4\ X_3X_4 – 0.85\ X_1^2X_2 + 0.94\ X_2^2 - 3.17\ X_3^2 \quad (6)$$

where the measured Y_4 is defined as the FFA rejection in the permeate solution and X_1, X_2, X_3 and X_4 represent time of adsorption, amount of bio-adsorbent and amount of adsorbed.

Table 9. Anova analysis for FFA

Factor	Coeff	SS	Df	MS	F-value	P-value
Model	14.10		4			
X_1	-0.63	0.09	1	2.01	63.78	0.0004
X_2	1.35	1.09	1	1.96	52.67	0.0029
X_4	-3.42	1.10	1	1.18	26.81	0.0004
$X_2 X_3$	-0.64	1.01	1	0.36	6.66	0.0003
$X_2 X_4$	-2.61	1.20	1	0.05	8.98	0.0003
$X_3 X_4$	12.4	1.06	1	1.08	5.92	0.0028
$X_1^2X_2$	-0.85	0.78	1	1.00	4.00	0.0004
X_2^2	0.94	0.99	1	2.01	2.92	0.0002
X_3^2	-3.17	0.97	1	1.49	3.21	0.0039
Residu	1.30	1.30	4	0.07		
Total FFA	0.0602	9.59	5	3.28	63.78	0.0005
	Std dev				0.9330	
	R^2				0.9306	
	Adj R^2				0.9002	

Validation of Predictive and Actual Values for Optimum Conditions

Validation of predictive values is also tabulated on Table 10. The odor and color response had residues of 1.6 and 1.5 respectively.

Table 10. Conditions for Optimum Adsorption of VCO with Bio-asorbents

Point	Factors		
	Time (hour)	**Bio-adsorbent (gr)**	**Adsorbed (gr)**
Prediction	33	149.89	411.65
Actual	33	150.00	411.75
Residual	-	0.11	0.10

Point	Responses			
	Odor	**Color**	**Density (cP)**	**FFA (%)**
Prediction	1,6	1,5	0,917	0,0602
Actual	1	1	0,916	0,0606
Residual	0,625	0,5	0,001	0,0004

Meanwhile the result of density and FFA were 0.915736 gr/mL and 0,0602%, which had residues of 0.001 and 0.002, then R^2 of 0.9554 and 0.9306 respectively. Based on Table 10 the validation of predictive and actual values proves the used model is cubic polynomial model. The mathematical model is the result of RSM which can be used to obtain optimum composition values for the maximum odor, color, density and FFA products

Adsorption Isotherm of VCO

Freundich and Langmuir isotherm were used to determine the equilibrium characteristics of adsorption of FFA. The linear form of isotherms and their constants are tabulated in Table 11. The data obtained at equilibrium was fitted with Freundlich isotherm. The Freundlich isotherm reveals the multi layer adsorption (Ansari *et al.* 2010). On the other hand, Ansari et al., (2010) also claimed that pH is an important factor, significantly affected the adsorption of FFA.

Table 11. Summary of parameters for isotherm models

Isotherm models	Equations	Constants
Freundlich	Log Qe = log k_f + (1/n) log (mg g^{-1})	n = 1.45 , k_f = 80.68 mg g^{-1} , R^2= 0.9862
Langmuir	$(C_e/Q_e) = (C_e/Q_m) + (1/k_L.\ Q_m)$	k_L = 0.056 L mg^{-1}; R^2 = 0.9306

where Qe (mg g^{-1}) and Ce (mg L^{-1}) are solid phase concentration and liquid phase concentration of adsorbate at equilibrium respectively. Q_m (mg g^{-1}) is maximum adsorption capacity and k_L (L mg^{-1}) and k_f (L mg^{-1}) (L mg^{-1}) are adsorption equilibrium constant, n is the heterogenity factor.

Adsorption Kinetic

The Pseudo-first-order and pseudo-second-order kinetic models were used to investigate the rate of adsorption of FFA. The linear form of adsorption kinetics and their constants are presented in Table 12.

Table 12. Summary of parameters for kinetics models.

Kinetic models	Equations	Constants
Pseudo-first-order	Log (Qe – Qf) = log Qe – (k1/2.303)t	R^2 = 0.971, k_1 = 0.093 min^{-1}
Pseudo-second-order	t/Qt = (1/k2. Qe2) + (1/Qe)t	R^2 = 0.997 , k_2 = 0.004 g mg^{-1} min^{-1}

where Qe and Q_f are amount of FFA (mg g^{-1}) at time t and at equilibrium and k_1(min^{-1}) is the Lagergren rate constant of first order asorption and k_2 (g mg^{-1} min^{-1}) is the second order adsorption rate constant.

CONCLUSION

The effect of various process parameters namely bio-adsorbent dose, adsorption time and VCO volume to produce high quality of VCO. Based on the results of research that has been done can be summarized that bio-adsorbent betung bamboo has been use successfully to adsorp odor, color, FFA from VCO in order to enhance the quality of virgin coconut oil.

The morphology of bio-adsorbent was characterised by scanning electron micrograph (SEM) and average poresize of 1.59 µm was calculated using equation. The regression analysis showed good fit of cubic model with coeficient of determination R^2 of 0,9306 and model F-value of 0.16. Adsorption isotherm data have been described by Freundlich and Langmuir models and resulted the adsorption equilibrium constant, kf of 80.68 mg g-1, R^2 of 0.9862 and kL of 0.056 L mg-1, R^2 of 0.9306. Pseudo-second-order kinetic model resulted second order adsorption rate constant, k of 0.004 g mg-1 min-1 with a good fitting R^2 of 0.997.

Optimum process condition were achieved on adsorption time of 33 hours, 150 gr of bio-adsorbent and 411.75gr of adsorbed (neat VCO), that produced odorless VCO of 1, colorless of 1, density of 0.916 gr/mL and FFA of 0,0606 %, respectively. It was concluded that betung bamboo is a promised bio-adsorbent for enhancing the VCO quality and also were fulfil the standard of SNI-3741-2013 and APCC.

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