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Kinetics and Adsorption Equilibrium Study of Free Fatty Acid (FFA) from Crude Palm Oil (CPO) on Anionic Resin

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Abstract. Crude Palm Oil (CPO) is obtained from palm fruit extraction. Free Fatty Acid (FFA) level is one of the most important parameters to determine the CPO quality. The standard FFA level in the industry is less than 5%. In the palm oil processing industry, FFA levels in CPO have been minimized through vacuum distillation processes. However, due to the emulsified water in oil and long departure waiting time in port, FFA levels in CPO raise to above 5% resulting in lower quality and selling price. This study has developed a novel approach to mitigate this problem by using anionic resin as an adsorbent to decrease the FFA level. We investigated the kinetics and equilibrium behavior of FFA adsorption in CPO on the anionic resin. The adsorption was conducted in several resin dose (17.5%; 25%; 33.33%; 43%). The kinetic study shows that the FFA adsorption kinetics on anionic resin follows the Pseudo-second-order rate model with the value of k_2 vary between 2.1034×10^{-4} – 1.7375×10^{-3} and the q_e value is in the range of $103.627 - 163.880$ (mg/g). The equilibrium study shows that the Freundlich isotherm model is the fittest. The K_f values are obtained between 4.16– 15.02, and the n values are in the range of 1.62 – 2.05. The thermodynamic observation was also involved in this study. The value of ΔH^o and ΔS^o are 28.59 kJ/mol and 91.25 J/mol/K respectively. The results show that the reaction is endothermic, spontaneous, and feasible.

Keywords: Adsorption, Kinetics, Crude Palm Oil, Free Fatty Acid, Anionic Resin

INTRODUCTION

Indonesia is the biggest producer of crude palm oil (CPO) in the world, about 45% of global CPO production (BPS, 2019). CPO is one of the derivative products of palm fruits. It is processed from the mesocarp of the palm fruit. The major component of CPO is 95% triglycerides and minor components of fatty acids, carotenoids, tocopherol, aliphatic alcohols, sterols, and others. The fatty acids in CPO consist of palmitic acid (39-45%) and oleic acid (37-44%). CPO is also rich in triglycerides, it makes CPO have several impurities such as phospholipids, free fatty acid (FFA), and other crude oil and decreases

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its quality (Chung et al., 2018). In the food industry, the favorable level of FFA is less than 5% (Japir et al., 2016). In order to meet its quality, the requirement of the FFA level is below 5%.

Most industries use chemical refining, liquid-liquid extraction, and vacuum distillation to decrease the FFA level of CPO (Jamal & Boulanger, 2010). However, after this process, the CPO still contains emulsified water which can further react with the triglyceride and form FFA. Due to the long storage time in the port or shipping, the raise of the FFA level is unfavorable. Therefore, an effective approach is needed to decrease the level of FFA level.

The promising approach to reducing the FFA level is using an anionic resin adsorbent (Ilagen, 2014, Cren & Meirelles, 2012, Jamal & Boulanger, 2010). Anionic resin has a structure of solid polystyrene with an amine functional group. Since it has a diameter of 0.5 to 1.0 mm, microscopic pores, and alkalinity, it can be used as a porous adsorbent of acid due to the interaction between the functional group (Dardel, 2015). In addition, the anionic resin can bind a molecule that has a specific charge within different bond strengths. This principle underlies this study.

The kinetics and equilibrium study is needed as a prior basis to scale up the deacidification method using the anionic resin of crude palm oil at the industrial level. Moreover, the kinetics and equilibrium approach will give insight (mechanisms, sorption capacity, thermodynamics) into the adsorption phenomena of FFA from CPO on the anionic resin. In this study, adsorption kinetics were approached with pseudo-first-order, pseudo-second-order, chemisorption, and intraparticle diffusion rate model. Meanwhile, the single-site Langmuir and Freundlich isotherm models are used as the equilibrium model. Further calculations on thermodynamic parameters are applied.

MATERIALS AND METHODS

Materials

Palm oil was obtained from PT. Surya Dumai Pekanbaru, Riau. Anion Resin (Amberlite IRA402Cl), NaOH Pellets, oleic acid, oxalic acid, and phenolphthalein indicators were obtained from PT. Brataco Yogyakarta. Ethanol (96% v/v) was obtained from Food and Bioprocess Lab, Chemical Engineering Department, Universitas Gadjah Mada.

Adsorption Experiment

Prior to use, the anionic resin was pretreated by submerging respectively into 1M NaOH solution with a 150 g/L ratio for 30 minutes to activate the base groups of resin. After that, the resin is filtered and neutralized, then dissolved in 1:2 (v/v) 96% ethanol for 100 minutes to increase the resin's swelling ability in the CPO. The resin is separated by filter paper in a vacuum and followed by the drying process until the mass is constant (Meirelles & Antonio, 2015, Restana, 2017, Nugraha, 2017).

Several doses of resin (17.5%, 25%, 33.33%, 43% w/w) were submerged in 20 grams of CPO and put in the shaker. The CPO sample was collected and analyzed at a certain interval time. The FFA level (%FFA, gr/gr) in the CPO sample was measured with the titration method. One gram of CPO was added to 15 mL of ethanol (96% v/v) as a solvent and phenolphthalein as an indicator. The mixture was heated over an electric stove for 15 minutes and titrated using NaOH until the color changed from light orange to dark orange (Ohimain et al, 2010). The Volume (V_{NaOH}, L) and concentration (M_{NaOH}, mol/L)

of NaOH were used to calculate the FFA contents ($\%FFA$) using Eq. (1), where the MW_{FFA} and W_{CPO} were the molecular weight of free fatty acid (g/mol) and weight of CPO (g), respectively.

$$\%FFA = \frac{V_{NaOH}\, M_{NaOH} MW_{FFA}}{W_{CPO}}\, x\, 100 \quad (1)$$

Kinetic Study

The kinetic study was conducted by observing the %FFA in the CPO over time. The observation is conducted for several adsorbent doses. The adsorbed amount of FFA in the resin (q_t, mg/gr) was calculated using Eq. (2). While the kinetics parameters were obtained by minimization of the sum of absolute deviation (SAD) as described in Eq. (3).

$$q_t = \frac{10(\%FFA_0 - \%FFA_t) W_{CPO}}{W_{Resin}} \quad (2)$$

$$SSE = \sum \left(\left(q_{t,data} - q_{t,calc} \right)^2 \right) \quad (3)$$

Equilibrium Adsorption Isotherm

To describe the equilibrium behavior of FFA adsorption on the resin in CPO, the equilibrium study was conducted by varying resin dose and treatment temperature (30, 45, and 60 °C). The procedure of the equilibrium study is similar to the kinetics study aside from the prolonged treatment time that was conducted for 5 hours. The equilibrium parameter was obtained using a linear regression method of Freundlich and Langmuir's models (Jamal & Boulanger, 2010).

RESULTS AND DISCUSSION

FFA Adsorption Kinetics Study

From the trend of the FFA level that is presented in Figure 1(a), it can be known that the level of FFA decreases significantly with the increasing of resin dose. It happens because the higher the resin dose, the more unoccupied amine functional groups in anionic resin are ready to interact with FFA, therefore the FFA level will decrease significantly (Mirelles & Antonio, 2015). Furthermore, the adsorption kinetics is verified using four models namely pseudo-first-order, pseudo-second-order, chemisorption, and intra-particle diffusion model (Aljeboree et al., 2017).

Lagergreen's First Order Model

This model is also called pseudo-first-order rate model that expressed on Eq. (4). Where q_t is the amount of FFA adsorbed at a given time ($mg\ FFA/g\ resin$), q_e is the amount of FFA adsorbed at equilibrium ($mg \frac{FFA}{g} resin$), k_1 is the first-order-adsorption kinetics constant (min^{-1}), and t is the contact time.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (4)$$

Pseudo Second-Order Model

The equation of pseudo-second-order is expressed in Eq. (5). Where k_2 is the second-order-adsorption kinetics constant (min^{-1}).

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (5)$$

Chemisorption

Chemisorption generally is described using the Elovich equation as given in Eq. (6). This equation is applicable for some chemisorption processes. This model assumes that the rate of adsorption of solute is decreasing exponentially as the amount of adsorbed solute increases. The parameters involved in this model are α and β which correspond to the initial adsorption rate

$(mg/g/min)$ and desorption constant respectively.

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (6)$$

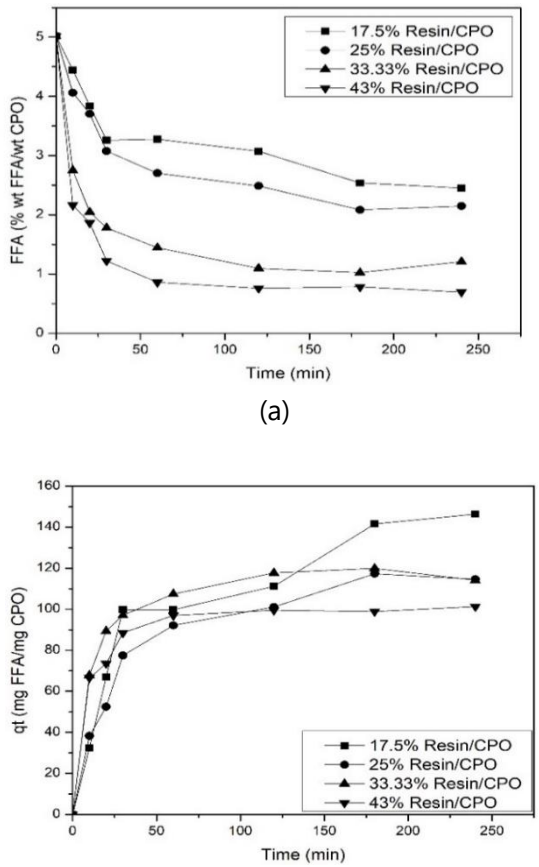


Fig. 1: Free Fatty Acid Content in the CPO (a) and Resin (b) Over Time

Intra-particle Diffusion

This model is usually used to determine the mechanism that controls the process. This model is evaluated by plotting $\sqrt{t}$ vs q_t. The slope obtained from linear regression corresponds to the rate constant ($mg/g/\sqrt{min}$), while the C is the boundary layer thickness. The equation is described in Eq. (7).

$$q_t = k_p\sqrt{t} + C \quad (7)$$

Inferring Figure 2 and Table 2, it can be seen that the adsorption kinetics of FFA in CPO using anionic resin are more represented by a pseudo-second-order rate model. This is consistent with the literature and theoretical basis that the pseudo-second-order rate model represents the adsorption kinetics of FFA in several vegetable oils than other models (Mirelles & Antonio, 2015, Zhang, 2012).

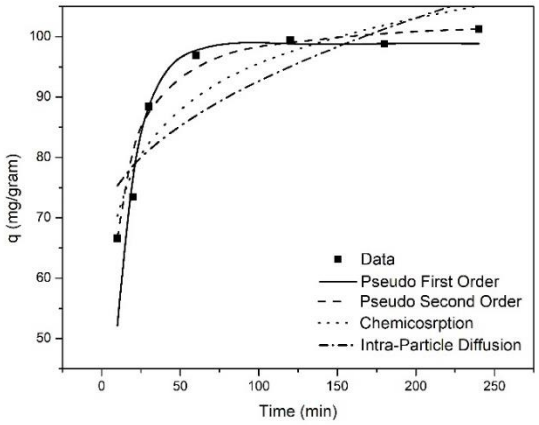


Fig. 2: Evaluation of Adsorption Kinetics Model of FFA into Resin

This phenomenon occurs because the pseudo-second-order time variable is directly involved in the regression equation, so the accuracy of this approach is better than the pseudo-first-order rate model which only involves q_t in the regression equation. In addition, the pseudo-first-order rate model primarily models the physical adsorption phenomenon, while the pseudo-second-order model primarily models the chemical adsorption phenomenon and FFA adsorption on CPO is chemical adsorption due to the formation of bonds between the amine groups on the resin and -COOH on the FFA (Mirelles & Antonio, 2015). Even though several researchers predict the adsorption mechanism using kinetic study, further evaluation needs to be tested.

Table 2. The Kinetics Parameters of All Models at Several Resin Dose

Model	Parameters	Resin dose			
		17.5%	25%	33.33%	43%
Pseudo First Order	$k_1\ (min^{-1})$	0.0318	0.0376	0.0765	0.0750
	$q_e\ (mg/g)$	142.043	114.625	114.0523	98.8492
	SSE	1434.96	340.74	153.25	227.01
Pseudo Second Order	$k_2 \times 10^4\ (g/mg/min)$	2.1034	3.4963	9.6962	17.3754
	$q_e\ (mg/g)$	163.880	125.497	124.098	103.627
	SSE	912.69	132.33	44.21	66.31
Chemisorption	$\alpha\ (g/mg/min)$	12.3822	13.0729	252.634	680.59
	k_1 (g/mg)	0.03083	0.03997	0.06745	0.09147
	SSE	741.03	216.84	229.69	146.98
Intra-particle Diffusion	$k_p\ (g/mg/min^{0.5})$	7.8862	6.0279	3.4147	2.5306
	$C\ (mg/g)$	31.284	32.463	72.265	67.34
	SSE	1377.78	684.67	540.35	307.35

FFA Adsorption Equilibrium

The equilibrium study was carried out by measuring FFA levels in CPO samples after being adsorbed for 300 minutes with temperature variations of 303.15 K, 318.15 K, and 333.15 K and at several resin doses. It is already known that increasing the adsorbent dose leads to an increase in the %removal of FFA. However, the FFA density in the adsorbent is decreased as presented in Figure 3. It happens due to the increased amount of active site and makes it to be unsaturated during the adsorption process. It is readily understood that the FFA residue in the CPO ($mg\ FFA/g\ CPO$) correlates with FFA content on the resin. The correlation is evaluated using Langmuir linear equation (Eq. (8)) and Freundlich linear equation (Eq. (10)) as presented in Figure 4.

Linearization of the Langmuir model as presented in Eq. (8) consists of 2 parameters, adsorption capacity at full monolayer coverage (q_m) and Langmuir constant (K_L) (Ghosal & Gupta, 2017). This model assumes that all active sites are homogenous. Based on the calculation results, the value of K_L and q_m will increase with increasing temperature. The q_m (mg/g) values obtained were 344.82, 370.55, and 377.79, while the K_L (g/mg) values are 2.36×10^{-3}, 3.79×10^{-3} and 5.93×10^{-3} for temperatures of 303.15 K ($R^2 = 0.972$), 318.15 K ($R^2 = 0.965$), and 333.15 K ($R^2 = 0.986$) respectively. The separation factor of the Langmuir model (R_L) is calculated using Eq. (9). The results are 0.274, 0.190, and 0.131 for temperatures of 303.15 K, 318.15 K, and 333.15 K, respectively. It shows that all R_L value is between 0 and 1, which means that this adsorption is favorable (Ayawei et al., 2017, Hydari et al., 2012)

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L}\frac{1}{C_e} \quad (8)$$

$$R_L = \frac{1}{1+K_L C_o} \quad (9)$$

$$\log(q_e) = \log(K_f) + \frac{1}{n}\log(C_e) \quad (10)$$

Based on the analysis results, the n values are 1.62, 1.66, and 2.05, while the K_f value are

4.16, 6.47, and 15.02 for 303.15 K ($R^2 = 0.988$), 318.15 K ($R^2 = 0.969$), and 333.15 K ($R^2 = 0.951$) The n value shows that it is suitable for adsorption operating conditions because the values are $1.0 < n < 10.0$ (Varnier et al, 2018).

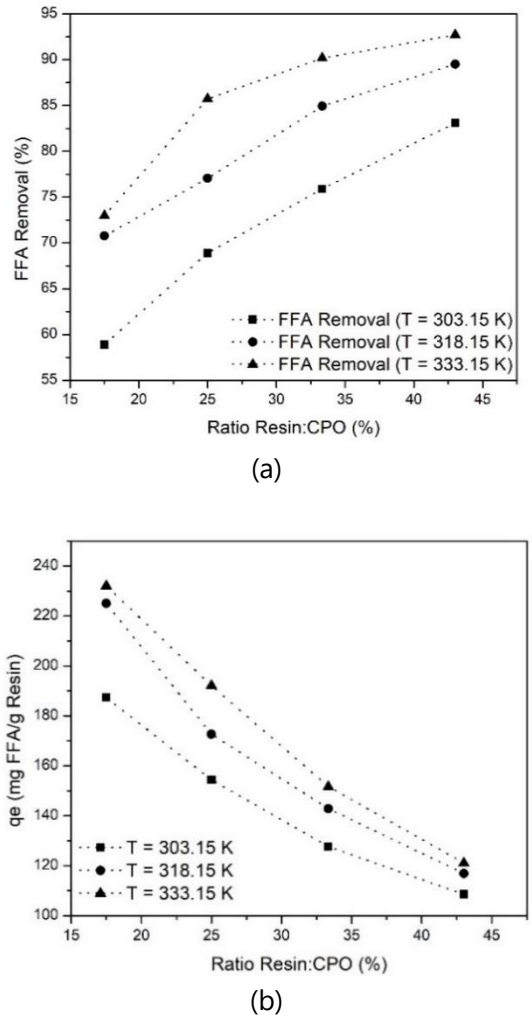


Fig. 3: FFA Removal (a) and FFA Density on Resin (b)

From Figure 4, it can be seen that the adsorption equilibrium is more represented by the Freundlich model. This is consistent with the literature that the Freundlich model is more representative of the FFA adsorption equilibrium in several other types of vegetable oils than the Langmuir model. This happens because the FFA adsorption process on CPO is following the multilayer adsorption (more than 1 layer of the adsorbate film is formed on the surface of the adsorbent). In addition, in the Freundlich model the logarithmic equation is used, where the value of n will be the rank of C_e, so the accuracy of this approach is better than the Langmuir model which only involves the multiplication of constants in its regression equation (Meirelles & Antonio, 2015; Zhang, 2012).

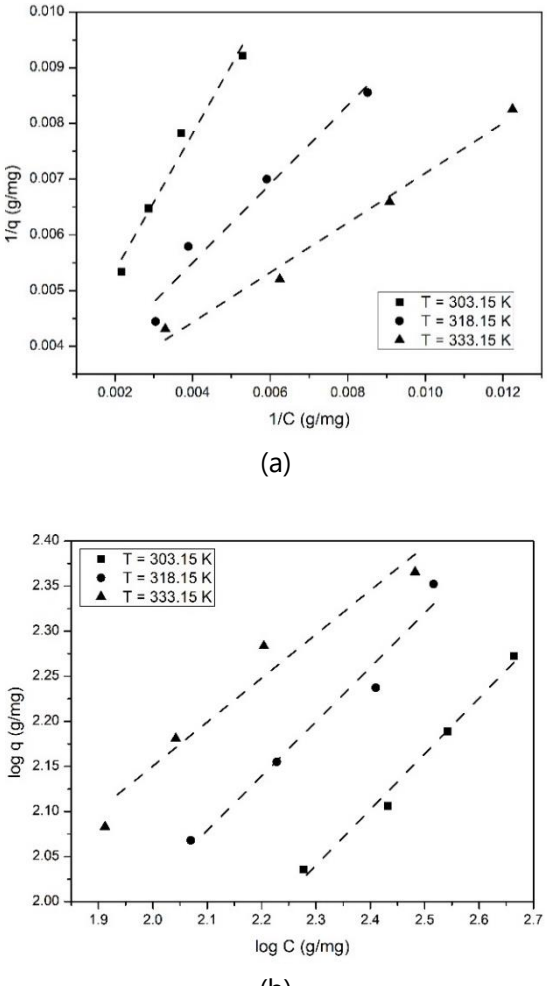


Fig. 4: Adsorption Isotherm Using Langmuir Model (a) and Freundlich Model (b)

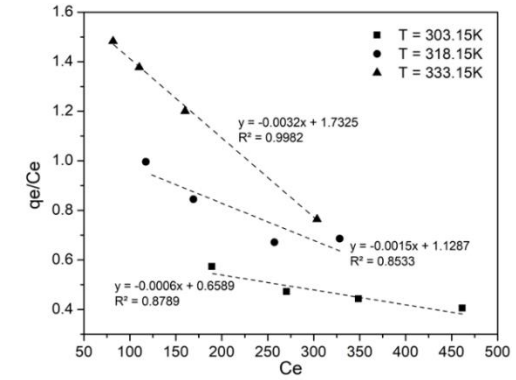
Thermodynamics Study

The thermodynamic behavior of FFA adsorption on the resin is further investigated.

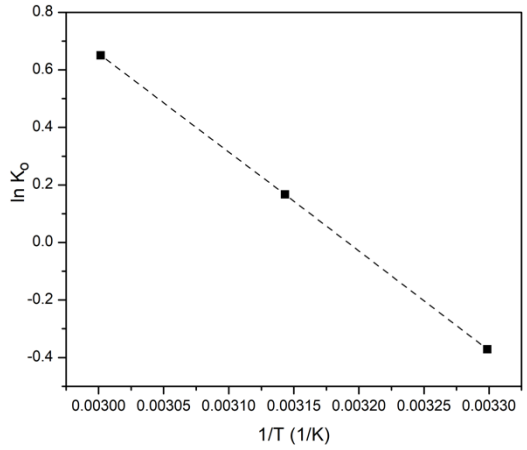
The parameters investigated include Gibbs free energy change (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o). The value of each parameter can be obtained by Van't Hoff equation (Eq. 12), linearization of 1/T vs $\ln K_o$ presented in Figure 5(b).

$$\Delta G^o = -RT \ln K_o \quad (11)$$

$$\ln K_o = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (12)$$



(a)



(b)

Fig. 5: Plot of C_e vs q_e/C_e (a) and 1/T vs $\ln K_o$ (b)

Where K_o the equilibrium constant and can be determined from the intercept of C_e vs q_e/C_e as presented in Figure 5(a). The result of all thermodynamic parameters is presented in Table 3. The value of ΔH^o and ΔS^o are found to be 28.59 kJ/mol and 91.25 J/mol/K respectively. The positive value of enthalpy change means that the process is endothermic and favorable at a relatively high temperature. While the positive value of entropy change explains that randomness at the solid/solution interface is increased (Ayawei et al., 2015). The replacement of adsorbed solvent molecules with adsorbate causes the entropy to increase and further increases the degree of freedom of the adsorbed species. However, it should be noted that the Gibbs free energy (ΔG^o) value at 303.15 K the (ΔS^o is positive, it indicates that the process is not spontaneous. Increasing the temperature leads to a decrease the ΔG^o. In order to maintain the negative value of ΔG^o, it is suggested that the temperature is above 314 K.

Table 3. Thermodynamic Parameters of FFA Adsorption on Resin

T, K	ΔG^o, kJ/mol	ΔH^o, kJ/mol	ΔS^o, $J/mol/K$
303.15	0.9453		
318.15	-0.4425	28.59	91.25
333.15	-1.8015		

CONCLUSIONS

Removal of FFA using adsorption on the anionic resin is successfully conducted. The fittest kinetic model is pseudo-second-order with k_2 (g/mg/min) value is in the range of 2.1034×10^{-4} – 1.7375×10^{-3}. While the Freundlich adsorption isotherm model defines the data well. The K_f values are obtained between 4.16 – 15.02, and the n values are in the range of 1.62 – 2.05. The value of ΔH^o and ΔS^o are 28.59 kJ/mol and 91.25 J/mol/K respectively. The suggested temperature operation condition is above 314 K.

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