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Research Article

Adsorption of Free Fatty Acid from Waste Palm Oil on Pineapple Peel Ash

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Abstract: Free fatty acid removal in used palm oil by ash of pine apple peels as low cost adsorbent was investigated. The adsorption was optimized with respect to contact time (30-330 min), the amount of adsorbent (0.5-2.0 g) and the temperature (30-60°C). It was found that 2 g of ash in 50 g used palm oil at 250 rpm, 30°C provided the highest adsorption in 81.39%. Additionally, the data was better fitted to Langmuir isotherm (R^2 =0.9954) than Freundlich isotherm. The adsorption kinetic was consistent with pseudo-second-order (R^2 = 0.9980). Furthermore, the adsorption thermodynamics study was revealed that the change in enthalpy, entropy and Gibbs free energy were -48.614 kJ/mol, -0.124 kJ/mol.K and -11.042 to -7.322 kJ/mol respectively.

Keywords: Pineapple peel; Used palm oil; Free fatty acid; Adsorption, Ash

1. Introduction

Frying is a principal food preparation method which is widely used among consumers and food industries. Typically, frying involves immersing of foods in heated oil (150–190°C) resulting in deterioration of the oil. Under heat treatment, various reactions occur including hydrolysis, isomerization, polymerization, decomposition and oxidation to give volatile compounds, free fatty acids (FFA), lipid peroxides, hydrocarbons and polymers (Bordin *et al*., 2013; Gao *et al*., 2016). Nevertheless, repeating of frying causes the physical and chemical changes in oil comprising an increased viscosity, odor, darkening, foaming and a lower smoke point.

Waste frying oil is a potential and promising starting material for biodiesel production (Rahadianti and Martha, 2018). It can be converted into biodiesel by the transesterification reaction using alkali, acidic or enzymatic catalyst (Kawentar and Budiman, 2013; Kolhe *et al*., 2017). However, the waste oil with FFA in excess of 5% can give rise to the saponification reaction which consumes the catalyst and reduces its effectiveness resulting in a low ester conversion. Besides, the soap formation inhibits the separation between the biodiesel and glycerol leading to the reduction of biodiesel yield (Banani *et al*., 2015; Hoa *et al*., 2014). Therefore, the removal of FFA from waste oil is crucial prior conversion to fatty acid methyl ester and finally on the biodiesel yield.

Various methods have been used to purify cooking oil including the use of filter aids and membrane technology (Kumar and Bhowmick, 1996). Adsorption is also a favorable method to refine contaminated oil. Both natural and modified materials have been used as adsorbents, comprising silica gel, magnesium silicate, zeolite, clay, alumina, charcoal, chitosan and activated carbon (Miyagia and Nakajimab, 2003; Dülger and Yilmaz, 2013; Putranti *et al*., 2017; Clowutimon *et al*., 2011). Agricultural waste provides an economical and readily available source of adsorbents. The effectiveness of adsorbents from plant waste has been demonstrated using coffee husk ash, sugarcane bagasse, olive waste, rice hulls and *Salacca zalacca*. (Chairgulprasert, 2018; Wannahari and Nordin, 2012; Basuny, 2014; Ermi *et al*., 2015).

Pineapple is one of the popular fruit which contains high vitamin C, manganese, enzymes and antioxidant (Cassellis *et al.,* 2014). Everyday, pineapples are consumed freshly throughout the world and also imported to industries for fruit cans providing massive of peel wastes. However, their residues are utilized in various ways namely as bromelain, ethanol, antioxidant, organic acid, acids, anti-dyeing agent, fiber, animal feed, energy and carbon and adsorbents for removal of dyes, heavy metals and toxic substances (Yamuna and Kamaraj, 2016; Selvanathan and Subki, 2015; Fu *et al*., 2016).

Thus, this work applied pineapple peel ash as adsorbent to reduce free fatty acid in used palm oil. The optimum conditions of adsorbent dose, contact time and temperature for FFA treatment are examined as well as adsorption isotherms, kinetics and thermodynamics.

2. Materials and Methods

2.1 Preparation of materials

Used cooking palm oil was collected from the same local market in Rusamelae district, Pattani province which contained initial FAA about 4.11%. Pineapple peels were also collected from a local market in Pattani province,. They were chopped and sun dried for 24 hrs. Then they were burnt at 600°C for 6 hrs. The obtained pineapple ash was kept in a plastic bag and stored in desiccator until used.

2.2 Adsorption study

Adsorption study was performed using the batch adsorption method by varying different parameters including contact time, adsorbent dose and temperature to find the best conditions for the removal of FFA from used palm oil. A typical experiment is performed in a 100 mL Erlenmeyer flask by adding pineapple ash (0.5-2.0 g) in to the 50 g of used palm oil and the suspension was shaken at 250 rpm. After a desired period of time (30-300 min), it was allowed to settle for 20 min. The supernatant was then used to analyse the FFA left in the treated oil. All experiment were analysed in triplicate.

2.3 Determination of Free fatty acid

The amount of FFA was determined by titration method following to AOAC method (AOAC, 2015). The 30 mL diethyl ether: ethanol 1:1 (v/v) was added to dissolve 2.0 g of oil sample. The solution was then added with 1% phenolphthalein and titrated with 0.1 M potassium hydroxide until a permanent faint pink appeared. The amount of FFA was calculated from equation (1) and express as milligrams palmitic acid per gram of oil.

$$\mathrm{FFA\,(mg/g)} = \frac{C_{NaOH} \times V_{NaOH} \times 25.6 \times 100}{W_{oil} \times 100} \quad (1)$$

Where C_{NaOH} (mol/L) is the concentration of sodium hydroxide used for titration , V_{NaOH} (mL) is the volume of sodium hydroxide used by oil sample, W_{oil} (g) is weight of test oil. The FFA adsorption capacity (q_t, mg/g) and the adsorption efficiency (E, %) were calculated from equations (2) and (3).

$$q_t = \frac{(C_i - C_t) \times V_{oil}}{W_{ads}} \quad (2)$$

$$E\,(\%) = \frac{(C_i - C_t) \times 100}{C_i} \quad (3)$$

Where C_i and C_t (mg/L) are the initial and final FFA, respectively. V_{oil} (mL) is the volume of the oil and W_{ads} (g) is the weight of the adsorbent.

3. Results and Discussion

3.1 Effect of contact time

The effect of contact time on removal of FFA was studied using four different dosages of pineapple ash (0.5, 1.0, 1.5 and 2.0 g) in 50 g of used oil at 30°C for 30-330 min and the results were displayed in Figure 1. At the beginning stage, the rate of adsorption occurred rapidly and gradually decreased until equilibrium was obtained. It was reported that the adsorption equilibrium depends on various parameters involving structure and mass of adsorbent, temperature and concentration of adsorbate (Kalapathy and Proctor, 2000; Sathivel and Prinyawiwatkul, 2004; Baptiste *et al.*, 2013). This might be ascribed to the high accessibility of active sites on adsorbents and high concentration of FFA at initial stage promoting adsorption. Later, the absence of readiness active sites and FFA concentration led to a poorer adsorption (Liang *et al.*, 2010; Pathania *et al.*, 2017).

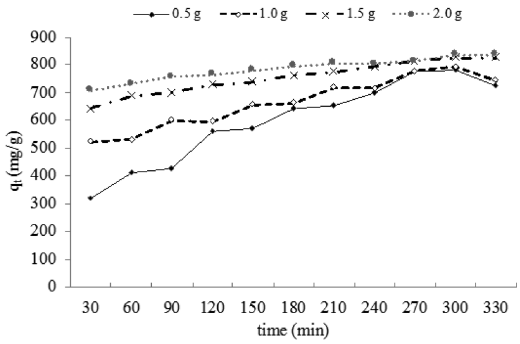

Figure 1. Effect of contact time (30-330 min) and dosage of adsorbent (0.5-2.0 g) on adsorption of FFA from 50 g of oil at 250 rpm, 30°C

To evaluate the effective dose, 50 g of used palm oil was shaken with ash of 0.5 g to 2.0 g at 30°C for 330 min. As demonstrated in Figure 2, both capacity and efficiency of FFA removals increased with increasing the mass of ash. It is proposed that the more adsorbent dose provided the more active sites and surface to adsorb FFA. The less active sites of 0.5 g ash could not effectively contact with FFA. As the mass of ash increased, the sorption sites are more available leading to the more efficiency of FFA removal. The optimum dose of ash is 2 g at which the maximum FFA adsorption (81.39% and 835.62 mg/g) was achieved.

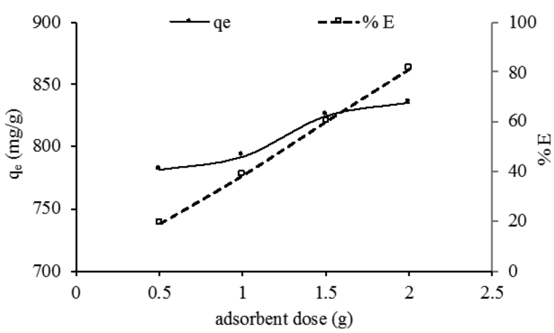

Figure 2. Effect of adsorbent dose (0.5-2.0 g) on adsorption of FFA [oil sample 50 g, contact time 330 min at 250 rpm , 30°C].

3.2 Adsorption kinetics

The two common models for pseudo-first-order (Lagergren, 1898) and pseudo-second-order kinetics (Ho and Mckay, 1998) were employed to examine the adsorption kinetics for FFA removal. The pseudo-first-order model is given as equation (4) and its integration with partial condition (q_t = 0, t = 0) results in the equation (5).

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (4)$$

$$\log(q_e - q_t) = \log q_e - K_1 t/2.30 \quad (5)$$

Where q_t and q_e are the FFA adsorption capacities at time t (min) and at equilibrium respectively. K_1 is the first-order rate constant. The plot between $\log(q_e-q_t)$ and t gave the regression coefficient (R^2) of 0.8970.

The pseudo-second-order and its linearized model were illustrated in equations (6) and (7). Apparently, the plot between and t in Figure 3 exhibited higher regression coefficient (R^2 = 0.9710-0.9980) (Table 1) than those of pseudo-first-order model. It is indicated that the FFA sorption onto pineapple ash can be approximated more appropriately by pseudo-second order kinetic model than the first-order kinetic model.

$$\frac{dq_t}{dt} = K_1(q_e - q_t)^2 \tag{6}$$

$$t/q_t = 1/K_2 q_e^2 + t/q_e \tag{7}$$

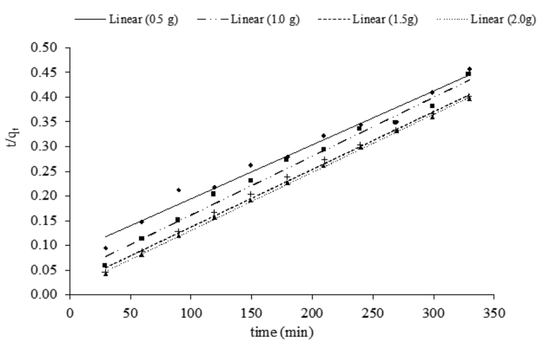

Figure 3. Pseudo-second-order plot on FFA removal by pineapple ashes.

Table 1 Pseudo-second-order parameters of FFA adsorption onto pineapple ash.

Ash dosage (g)	$q_{e\,(exp)}$ (mg/g)	$q_{e\,(cal)}$ (mg/g)	$K_2 \times 10^5$	R^2
0.5	781.71	1000	1.149	0.971
1.0	792.12	1000	2.380	0.987
1.5	824.89	1000	4.761	0.997
2.0	835.65	1000	7.692	0.998

3.3 Adsorption isotherm

To define the equilibrium nature of FFA adsorption, two important isotherm models have been expended. Firstly, the Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent, and it has been used successfully for many adsorption processes of monolayer adsorption (Langmuir, 1918). The linearized Langmuir model is exemplified in the equation (8).

$$C_e/q_e = 1/q_m K_L + C_e/q_m \tag{8}$$

Where q_e (mg/g) is the mass of FFA adsorbed per unit mass of pineapple ash, C_e (mg/mL) is the equilibrium concentration of FFA in oil, q_m (mg/g) is the monolayer adsorption capacity and K_L is the Langmuir constant related to the affinity of the binding sites. The values of K_L and q_m were calculated from the intercept and slope of the plots (versus C_e) in Figure 4a.

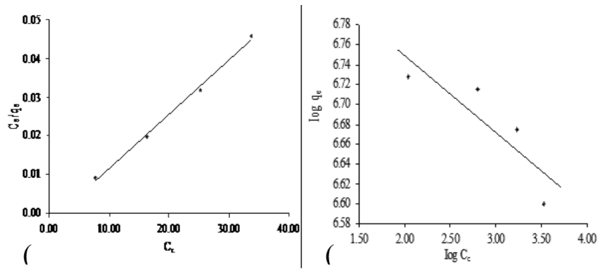

Figure 4. Isotherm plots for FFA adsorption by pineapple ash (4a) Langmuir isotherm (4b) Freundlich isotherm [dose 0.5-2.0 g, and contact time 330 min at 30°C].

The other model, Freundlich isotherm is based on multilayer adsorption onto a heterogeneous surface (Freundlich, 1906). The linearized equation of this model is represented in the equation (9).

$$\log q_e = \log K_F + 1/n \log C_e \tag{9}$$

K_F (L/g) is the Freundlich constant associated with the adsorption capacity and n is an empirical parameter related to the adsorption intensity and surface heterogeneity. The values of n and K_F are calculated from the slopes and intercepts of the linear plots of versus $\log C_e$ in Figure 4b.

According to the regression coefficient in Table 2, the FFA adsorption data were better fitted by Langmuir model ($R^2 = 0.9954$) than Freundlich ($R^2 = 0.7475$) model. The maximum FFA adsorption (q_m) is 1000 mg/g at 30°C . The separation factor, R_L is employed to explain the feasibility and favorability of adsorption process which is defined by the equation (10).

Table 2. Isotherm parameters for the FFA adsorption onto pineapple ash.

Langmuir isotherm		Freundlich isotherm	
Parameters	values	Parameters	values
R^2	0.9954	R^2	0.7475
K_L	0.500	K_F	1.931
q_{max} (mg/g)	1000	1/n	-12.98

$$R_L = \frac{1}{1+K_L C_0} \tag{10}$$

where C_0 is the initial concentration of FFA (mg/g) and K_L is the Langmuir adsorption constant. It was found that the R_L of FFA adsorption onto pineapple ash was 0.046 which is in the range of $0 < R_L < 1$ showing the favorable adsorption process (Dada *et al*., 2012).

3.4 Effect of temperature and thermodynamics

The effect of temperature was investigated at 30-60°C by shaking 2.0 g pineapple ash with 50 g used palm oil at 250 rpm for 300 min. It was found that, the adsorption capacity (q_e) decreased as the temperature increased. To determine whether the process is spontaneous., Gibb's free energy change, ΔG° is the principal criterion parameter. A negative value of ΔG ° supports the spontaneous nature of adsorption at a given temperature.

Thermodynamic parameters of Gibb's free energy change, enthalpy change (ΔH) and entropy change(ΔS) are determined from the following equations (11) and (12). Where R is universal gas constant (8.314 J/mol.K) and T is the absolute temperature in K. The values of (ΔH) and (ΔS) were obtained from the slope and intercept respectively of the plot between
log q_e/C_e versus 1/T in Figure 5.

$$\log q_e/C_e = \Delta S/2.303R - \Delta H/2.303RT \quad (11)$$

$$\Delta G = \Delta H - T\Delta S \quad (12)$$

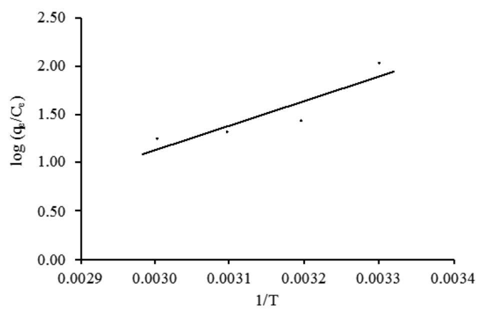

Figure 5. Thermodynamic plot of the FFA adsorption onto pineapple ash [ash dose 2.0 g, contact time 300 min at 30-60°C, 250 rpm]

As seen from Table 3, negative values for Gibb's free energy at all studied temperature confirmed the spontaneous nature as well as feasibility of adsorption reactions (Zawani *et al*.,2009). However, ΔG increases with the increase in temperature meaning that the FFA adsorption is unfavorable at higher temperature. Additionally, the negative value of enthalpy change implied an exothermic force (Liu *et al*., 2003; Djordjevic *et al*., 2011). The small negative value of entropy change corresponding to the reduction of degree of independence of the adsorbed FFA proposing that disordered system is decreased at the interface adsorbate-solution during the adsorption (Özcan *et al*., 2016).

Table 3. Thermodynamic parameters for the FFA adsorption onto pineapple ash.

ΔG (kJ/mol), T (°C)				ΔH (kJ/mol)	ΔS (kJ/mol.K)
30	40	50	60		
-11.042	-9.802	-8.562	-7.322	-48.614	-0.124

3.5 FTIR analysis

FTIR (Fourier Transform Infrared Spectroscopy) was used to investigate the changes in the surface functional groups of pineapple peel ashes before and after loading of FFA. The FTIR spectra were obtained in the wavenumber range of 4000 to 400 cm^{-1} at room temperature (Figure 6).

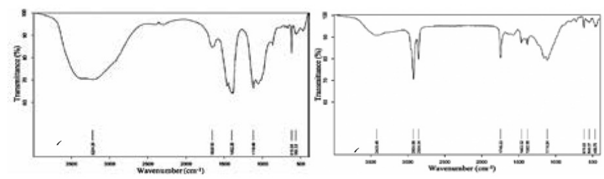

Figure 6. FTIR spectra of (6a) unloaded pineapple ash and (6b) pineapple ashloaded with FFA

As seen in Figure 6a, the FTIR analysis of the unloaded ash showed the sharp peaks of hydroxide, carbonate and phosphate ionsat wavenumbers of 3224, 1658, 1500, 1402and 1119 cm^{-1} respectively.It has been reported that pineapple peel ash contained the high values of calcium, potassium and magnesium. Additionally, sodium, copper, iron, manganese and zinc are also found in small amount (Morais, *et al*; 2017). Therefore, these FTIR bands corresponded to calcium carbonates, calcium hydroxides and magnesium carbonates. After adsorption,the C-H stretching bands of FFA molecule were appeared at 2924, 2854 cm^{-1}(Figure 6b). Furthermore, the bands of hydroxide, carbonate and phosphate ions showed some distinct changed and shifted to 3420, 1745, 1463, 1362 and 1114 cm^{-1} indicating that these groups responds to FFA adsorption.

4. Conclusion

Pineapple peel ash had been performed well as an adsorbent to eliminate FFA from used palm oil. The parameters ofthe mass of ash, the contact time and the temperature have indeed influenced the adsorption process.Increasing contact time improved the adsorption efficiency and capacity then remained constant when the equilibrium is reached. Additionally.the more mass of adsorbent also led to the more adsorption. The experimental data fitted pseudo second order and the Langmiur isotherm.Besides, the negative value of change in Gibb's free energy implied the spontaneous adsorption in nature and the adsorption is favorable at normal temperature with the exothermic type.

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