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Original research article

Removal of Free Fatty Acid from Used Palm Oil by Coffee Husk Ash

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ABSTRACT

Reduction of free fatty acid (FFA) in used palm oil was determined after treatment of waste cooking oil with an adsorbent derived from coffee bean husk ash. Coffee husks were burned at 600 °C for 12 hrs to obtain the adsorbent ash. Free fatty acid removal efficiency was optimized with respect to ash dosage, contact time and temperature. It was found that shaking ash (1 g) with waste palm oil (50 g) at 250 rpm and 30°C for 330 min gave the highest reduction in free fatty acids (FFA) (1966 mg/g). The adsorption isotherm was followed by Temkin ($R^2 = 0.9283$) and Freundlich models ($R^2 = 0.9146$). The adsorption of FFA at all adsorbent doses followed pseudo-second order kinetics ($R^2 = 0.9817$-0.9999). A thermodynamic study revealed that the changes in enthalpy, entropy and Gibbs free energy were 89.07 kJ/mol, -0.25 kJ/mol.K and -5.15 to -12.17 kJ/mol, respectively. The coffee husk ash (5 g ash / 50 g waste palm oil) was found to reduce FFA by 100% at 30°C.

Keywords: Coffee husk; Used palm oil; Free fatty acid; Adsorption; Ash

1. Introduction

Frying is widely used as a convenient method of cooking around the world. However, the frying process requires high temperatures ranging from 150 to 200°C which result in chemical deterioration of the oil. In order to avoid health risks from by-products of this deterioration, cooking oil must not be repeatedly re-used. Used oil should either be re-purposed (e.g. as a biofuel) or sacrificed with financial loss. The physical and chemical changes which occur in cooking oil after repeated frying are evident in its increased viscosity, odor, darkening, foaming and a lower smoke point [1]. Various chemical reactions, including oxidation, hydrolysis, cyclization, polymerization and degradation occur during the frying process, to give volatile compounds, free fatty acids, lipid peroxides, hydrocarbons and polymers [2-3]. These compounds are toxic and pose a significant risk to human health. Ingestion of repeatedly heated oil increases the risk of high blood pressure, cardiovascular disease and atherosclerosis [4-5]. Although waste

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oils can be used as a biodiesel feed stock, FFAs must first be removed to avoid engine corrosion and side reactions during combustion [6-7].

Many methods have been investigated either to prolong the useful life of cooking oil or purify it for re-use. These include addition of antioxidants, and esterification to prevent deterioration, or the use of filter aids and membrane technology for purification. Adsorption is also a promising method to refine contaminated oil. Both natural and modified materials have been used as adsorbents, including silica gel, magnesium silicate, zeolite, clay, alumina, charcoal, chitosan and activated carbon [8-10]. Agricultural waste provides an economical and readily available source of adsorbents. The effectiveness of adsorbents from plant waste has been demonstrated using sugarcane bagasse, olive waste, rice hulls and *Salacca zalacca* [11-14].

In Southern Thailand, the total production of Robusta coffee is about 17,028 tons per year [15], resulting in a huge residue of coffee husks after dehulling the coffee cherries. Coffee husks have been used to produce animal feed or as a substrate to grow mushrooms. Alternatively, they can be converted into biofuel or bioactive compounds. However, these processes still require considerable technical development before they could be considered economically viable. Coffee husks have also been reported as potential adsorbents for heavy metals and synthetic dyes [16-18].

This work aims to reduce free fatty acid (FFA) in used palm oil by adsorption onto coffee husk ash. The optimum conditions of adsorbent dose, contact time and temperature for FFA treatment are reported as well as adsorption isotherms, kinetics and thermodynamics.

2. Methodology

2.1 Preparation of used cooking oil

New cooking palm oil (Bag No. 303) was bought from a local shop in Pattani province, Thailand. About 5 kg of oil was used to fry 400 g potatoes for 1 hr then the fried potatoes were removed. Another 400 g potatoes was immersed in the used oil and cooked in the same way. After 5 cooking cycles over a total of 5 hrs the used cooking oil had acquired a brownish colour and the final batch of potatoes was removed.

2.2 Preparation of ash from coffee husks

Robusta coffee husks were collected from a Coffee factory in Chumphon Province, Thailand. They were burnt in a furnace at 600°C for 12 hrs to obtain coffee husk ash which was kept in a plastic bag and stored in a desiccator.

2.3 Batch adsorption

A typical experiment was performed in a 100 mL Erlenmeyer flask, shaking the flask at 250 rpm throughout the study. Coffee husk ash (1-5 g) was added to the 50 mL oil sample and the suspension was shaken at 30°C for a desired period of time (30-330 min). The oil was allowed to settle for 20 min. The supernatant was then used to analyse the FFA left in the treated oil. All experiments were analysed in triplicate and only average values are reported, as the maximum error did not exceed 5%.

2.4 Determination of Free fatty acid (FFA)

The FFA content of oil was determined by the titration method according to AOAC method [19]. 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 and persisted at least for 1 min. FFAs content was calculated from Eq. (1) and expressed as milligrams palmitic acid per gram of oil.

$$FFA(mg/g) = \frac{C_{NaOH}\times V_{NaOH}\times 25.6\times 1000}{W_{oil}\times 100} \qquad (1)$$

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

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

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

Where C_i and C_t (mg/L) are the initial and final FFA concentrations, 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 Characterization of coffee husk ashes by Energy dispersive spectroscopy (EDS)

EDS analysis revealed that coffee husk ashes contained a variety of elements in differing proportions (Table 1). Potassium, present as potassium oxide (K_2O) was found to be a major constituent of coffee husk ash. The ash contained relatively little SiO_2 or P_2O_5 which are also known as good adsorbents.

Table 1. EDS of coffee husk ash.

Elements	Weight (%)
O	44.27
K	27.87
C	10.10
Ca	9.13
Si	1.87
Mg	2.13
S	1.37
P	1.10
Al	0.63
Fe	0.57
Cl	0.53
Na	0.25

3.2 Effect of contact time and adsorbent dosage on FFA

The fried cooking oil sample contained initial FFA content about 4.7% which was used for further removal by coffee ashes. The effect of time and adsorbent dose on FFA removal was examined using 5 different dosages of coffee ashes (1, 2, 3, 4, 5 g) in 50 mL of fried oil. As shown in Fig. 1, the percentage of FFA in treated oil with coffee husk ash was subsequently reduced. Using coffee husk ash 3-5 g, the FFA adsorption efficiency occurred rapidly over the first 30 min and then gradually slowed until equilibrium was attained at 210 min. It is proposed that high availability of active sites on adsorbents and FFA at the beginning stage. Then, active sites and %FFA decreased resulting in lower adsorption rate. Most adsorption have revealed the similar observation. However, the equilibrium times for adsorption is variable depending on many parameters including of structure and chemical properties of adsorbent, adsorbent dose, temperature, concentration of adsorbate [20-22]. On the other hand, FFA was adsorbed slowly onto the ash dosing 1-2 g due to much lower amount of adsorbent active sites.

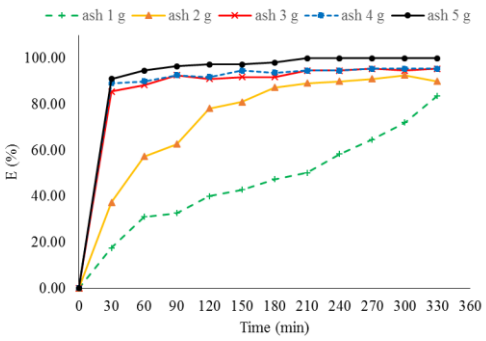

Fig. 1. Effect of contact time (30-330 min) and dosage of adsorbent (1-5 g) on adsorption of FFA from 50 g of oil.

The FFA adsorption depended on the adsorbent dose. As observed in Fig. 2, the increasing of coffee husk ash dose from 1 to 5 g improved the percentage of FFA reduction (73.7-100.0%). It was indicated that the more adsorbent mass provided the more active sites and surface to remove FFA. Conversely, as the adsorbent dose was increased, the adsorption capacity decreased indicating a less efficient manipulation of active sites in the adsorbent. This result has also been reported by other researchers [23, 24]. The binding sites in 1 g of coffee husk ash are enough for maximum FFA adsorption capacity (962.79 mg/g) from 50 g of fried oils.

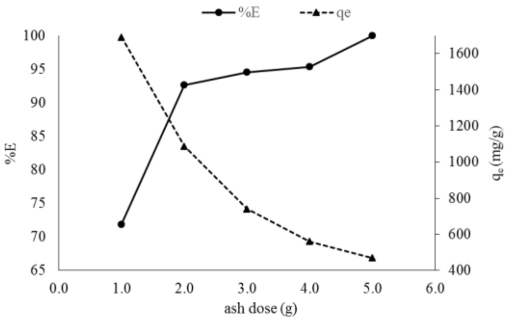

Fig.2. Effect of adsorbent dose (1.0-5.0 g) on removal of FFA by coffee husk ash [fried oil 50 g, contact time 300 min].

3.3 Adsorption kinetics

The kinetics of FFA adsorption by coffee husk ash was investigated using the two models of pseudo-first-order [25] and pseudo-second-order [26] as shown in Eq. (4) and (5).

$$\log(q_e - q_t) = \log q_e - K_1 t/2.30 \qquad (4)$$

$$t/q_t = 1/K_2 q_e^2 + t/q_e \qquad (5)$$

Where q_t and q_e (mg/g) correspond to the quantities of FFA adsorbed onto the coffee husk ash at time t (min) and at equilibrium time, respectively. K_1 and K_2 are the first and second order rate constants.

The plot between log (q_e-q_t) and t for FFA adsorption exhibited low regression coefficient (R^2) indicating that the data could not be acceptably fitted this model. In contrary, FFA adsorption data at all adsorbent doses could be modelled by pseudo-second-order plot which exhibited the straight curves with high regression coefficients (R^2) as shown in Fig. 3 and Table 2. The K_2 constants increase with the absorbent dose and the calculated q_e values are close to the experimental q_e values.

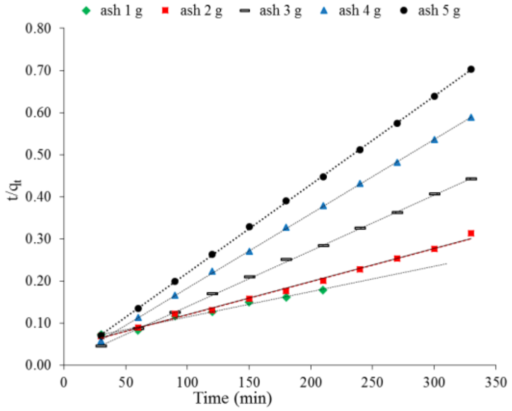

Fig.3. Pseudo-second-order plot on FFA removal by coffee husk ashes.

Table 2. Pseudo-second-order parameters of FFA adsorption by coffee husk ash.

Ash Dosage (g)	Pseudo-second-order parameters:			
	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	K_2 ($\times10^{-3}$)	R^2
1	1690	1667	0.068	0.9817
2	1088	1250	0.014	0.9939
3	740	769	0.211	0.9996
4	560	561	0.428	0.9999
5	470	476	0.451	0.9999

3.4 Adsorption Isotherm

The sorption data were evaluated using Langmuir, Freundlich and Temkin isotherms. The Langmuir isotherm is based on a monolayer adsorption process onto a homogeneous surface identical active sites. The energy of adsorption is constant and no transmigration of adsorbate occurs over the surface [27]. The linear equation for tis isotherm is shown in Eq. (6).

$$C_e/q_e = 1/q_m K_L + C_e/q_m \tag{6}$$

Where q_e (mg/g) is the mass of FFA adsorbed per unit mass of coffee husk 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 equilibrium constant. The plot between specific sorption of FFA (C_e/q_e) and equilibrium concentration (C_e) gave the linear Langmuir curve in Fig 4.

The Freundlich model is based on multilayer adsorption onto a heterogeneous surface [28]. The linearized equation is shown in Eq. (7).

$$\log q_e = \log K_F + (1/n)\log C_e \tag{7}$$

Where 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 plot of q_e against log C_e gave the straight Freundlich line in Fig. 5.

The Temkin isotherm is based on the assumption that the adsorbent-adsorbate interactions that occur during surface coverage result in a linear decrease in the heat of adsorption [29]. This model is defined by Eq. (8) and (9).

$$q_e = (RT/b)\ln(K_T C_e) \tag{8}$$

$$q_e = B_T \ln K_T + B_T \ln C_e \tag{9}$$

T (K) is the absolute temperature, R (J/mol.K) is the ideal gas constant, K_T (L/mg) is the equilibrium binding constant (at maximum binding energy), b (kJ/mol) is the variation of adsorption energy, and B_T (kJ/mol) is the Temkin constant, corresponding to the heat of adsorption. The plot of q_e and $\ln C_e$ was presented in Fig. (6).

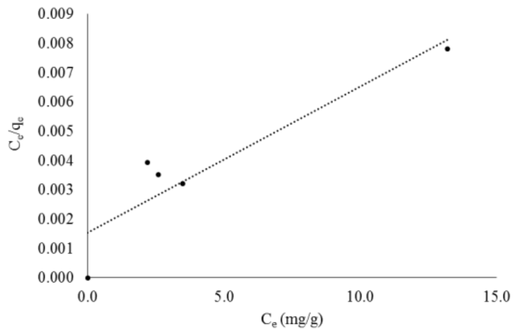

Fig.4. Langmuir isotherm plot for FFA adsorption by coffee husk ash [dose 1-5 g, contact time 300 min at 30°C].

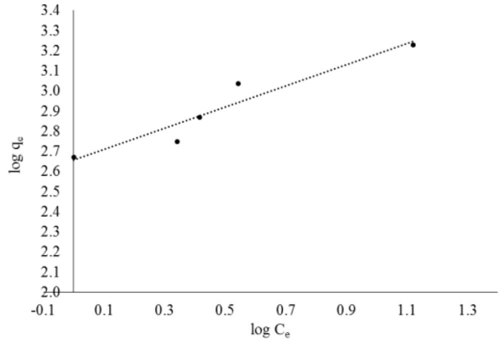

Fig.5. Freundlich isotherm plot for FFA adsorption by coffee husk ash [dose 1-5 g, contact time 300 min at 30°C].

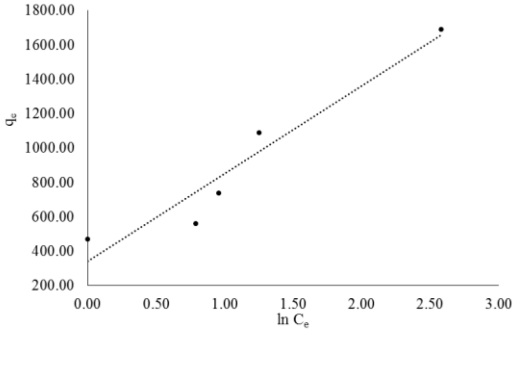

Fig. 6. Temkin isotherm plot for FFA adsorption by coffee husk ash [dose 1-5 g, contact time 210 min at 30°C].

The linear regressions (R^2) and other parameters calculated from all curves displayed in Table 3. It is appeared that the data for FFA adsorption could be fitted to all models. However, according to the regression coefficient, the data were slightly better fitted by Temkin model ($R^2 = 0.9283$) than Freundlich ($R^2 = 0.9146$) and Langmuir model ($R^2 = 0.8510$) respectively. These pointed that coffee ash surfaces are heterogeneous. A 1/n value of < 1 showed that FFA are adsorbed well to the coffee husk ashes which are heterogeneity of active sites. Nevertheless, the heat of adsorption (B_T) from Temkin model are high indicating a strong interaction between FFA and adsorbents.

Table 3. Isotherm parameters for the FFA adsorption onto coffee husk ash.

Isotherm Parameters		values
Langmuir	q_m (mg/g)	2000.00
	K_L	0.33
	R^2	0.8510
Freundlich	K_F	457.09
	1/n	0.52
	R^2	0.9146
Temkin	K_T (L/mg)	1.95
	B_T (kJ/mol)	508.54
	R^2	0.9283

3.5 Effect of temperature and adsorption thermodynamics

Adsorption capacities for FFA removal onto 1 g of coffee husk ash were carried out at temperature of 30, 40, 50 and 60°C to study the influence of temperature and thermodynamic parameters. The results showed that the amount of FFA adsorbed onto coffee husk ashes decreased with an increase in temperature from 30 to 60°C (Fig. 7).

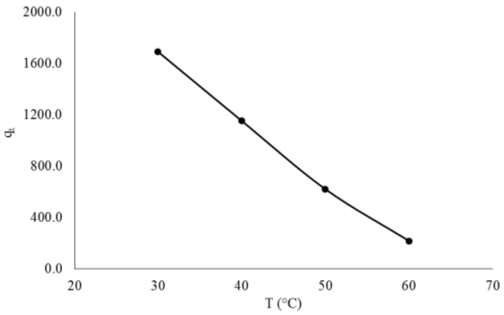

Fig. 7. Effect of temperature on amount of FFA adsorption [fried oil 50g, coffee ash dose 1 g, contact time 300 min].

Thermodynamic parameters of change in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined using the following equations

$$\log(q_e/C_e) = \Delta S/2.303R - \Delta H/2.303RT \quad (9)$$

$$G = \Delta H - T\Delta S \quad (10)$$

Where R is the gas constant (8.314 J/mol.K). The plot between log (q_e/C_e) was illustrated in Figure 8. The values of ΔH and ΔS obtained from the slope and the intercept, and the calculated ΔG were presented in Table 4.

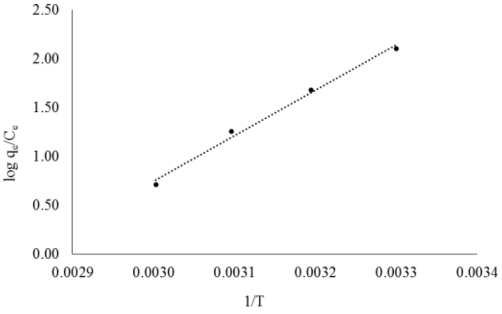

Fig.8. Thermodynamic plot of the FFA adsorption by coffee husk ash [dose 1 g, contact time 300 min].

Table 4. Thermodynamic parameters for the removal of FFA onto coffee husk ash.

Parameters	Values
ΔG (kJ/mol), (°C)	
30	-12.17
40	-10.19
50	-7.67
60	-5.15
ΔH (kJ/mol)	-89.07
ΔS (kJ/mol.K)	-0.25

As shown (Fig. 8.), the FFA adsorption occurred with negative values for ΔG at all temperatures, reflecting that the FFA removal onto coffee husk ash was favourable and spontaneous nature adsorption process. However, the adsorption occurred with less negative values at higher temperature confirming that the adsorption is unfavourable at higher temperature. The negative value of enthalpy change also indicated an exothermic attractive force. The enthalpy change also indicates the type of adsorption. The physical adsorption process gives the heat about 2.1 to 20.9 kJ/mol while the chemical adsorption contributes 80 to 200 kJ/mol [30]. Therefore, the high value of enthalpy change from FFA adsorption referred to the chemisorption process. The change in entropy was also negative value corresponding to the reduction of degrees of independence of the adsorbed FFA proposing that disordered system is decreased at the interface adsorbate-solution during the adsorption.

4. Conclusion

The coffee husk ash has proven to be used for removal of FFA. The adsorption was found to be dependent on contact time, sorbent dose and temperature. Using high dose of adsorbent led to high rate of FFA reduction and high adsorption efficiency but low in adsorption capacity. The experimental data could be well described by pseudo-second-order. Moreover, the data were better fitted to Temkin and Freundlich than Langmuir isotherms. The FFA adsorption was also revealed to be exothermic and a spontaneous process.

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