

Reducing Free Fatty Acid in Used Cooking Oil Using Bagasse Adsorbent

Wannahari, R* , Nordin, M.F.N. Marinah, M

Faculty of Agro Industry & Natural Resources, Universiti Malaysia Kelantan, Locked bag 36, Pengkalan

Chepa 16100 Kota Bharu, Kelantan, Malaysia

b10d007f@siswa.umk.edu.my*

+60-148454103

Abstract

The used of bagasse as adsorbent is not common or apparent. This is odd especially for several reasons; (1) the structural component of bagasse which is made up of carbon material is suitable as adsorbent, (2) bagasse is in abundance, easily available and not used led to waste issue and (3) adsorbent bagasse further reduce solid waste disposal, and hence reducing one source of environmental pollution. This study was undertaken to explore the possibility of using bagasse as adsorbent. Specifically, bagasse is being experimented to reduce the harmful content such as FFA (Free Fatty Acid) in used cooking oil. The variation of adsorbent weight and contact time are used in this research as parameters to determine the effective time and the amount of adsorbent that should be used in the oil refining process. From the experiment conducted, it can be established that bagasse when use as an adsorbent can reduce FFA to 82.14% which is lower the harmful limit. This result is obtained when 7.5 gram of bagasse for 60 minutes contact time was used. For isotherm adsorption, isotherm Freundlich has a higher level of linearity than Langmuir. Isotherm Freundlich is about 99.61 % and Langmuir is 98.9% for FFA in contact time variation. For weight variation, the level of linearity Langmuir is 19.67 %; which is higher than Freundlich which only reached by 16.78%. This result advocates that the Freundlich isotherm mechanism is more suitable for FFA absorbance levels in contact time variation, while the Langmuir suitable for weight variation.

Key Words: Bagasse, Adsorbent, Recovery, Used Palm Cooking Oil, Free Fatty Acid, Isotherm.

1. INTRODUCTION

The use of palm cooking oil that has been used more than once is common in our society today. There are several reasons for this habit. The perception of some people that the food will be more delicious fried using used oil, and also for economic reasons. During the frying process, oil will experience degradation reactions caused by heat, air, and water, resulting in oxidation, hydrolysis and polymerization. Degradation reaction products contained in this oil will reduce the quality of the oil and cause adverse effects for humans (Bhattacharya, et al. 2008⁽²⁾).

The indicators of poor oil quality include elevated Free Fatty Acids (FFA), change of color, low smoke point, low iodine value, total polar material, high foaming properties and increased viscosity (Loh Soh Kheang, et al. 2006⁽⁷⁾). From the results of previous research of purification used cooking oil, silica gel is known to have the ability to reduce the value of FFA which amounted to 33.3%. While activated carbon (magnesium oxide) could reduce the FFA value of 6.5%, aluminum oxide reduces the FFA value by 30.2%, activated clay (Acid-activated spent bleaching earth) led to FFA reduction of 11.8%.

This research attempt to explore the use of natural adsorbent made up of bagasse from sugarcane waste

to recover the used cooking oil. Structural component of bagasse made up from carbon material makes bagasse suitable as adsorbent.

The parameters used in measuring the quality of used cooking oil in this research are Free Fatty Acid (FFA), amount of hydrolysis. Adsorbent weight variation and contact time will be used in this research to find the effective time and level of adsorbent that should be used to reduce FFA value.

Recycling of disposed oils and waste products from sugarcane juice into purified frying oil and bagasse to be used as adsorbent are expected to reduce waste disposal problems that are consistent with the current discussion today and decrease the prospect of endangering the ecosystem.

2. METHODOLOGY

In this study SAS (Statistical Analysis Software) is used to determine initial design and analysis of data. This study appreciates that there are several factors that affect the refining process of cooking oil. However for the purpose of this study, only two factors, weight and contact time were experimented. For weight, the maximum weight

used was 10 g and the minimum weight is 5 g. While for the contact time, the longest time is 60 minutes and the fastest is 10 minutes. By entering the weight factor and time, as a variable, SAS will provide the experimental design after 13 run.

2.1 Design of Experiment

This experiment involves two main stages, adsorbent bagasse making process and used cooking oil refining using bagasse adsorbent. The success of bagasse as an adsorbent can be seen by comparing the value of FFA of the new cooking oil, used cooking oil and cooking oil after treatment with the bagasse adsorbent.

The Flowchart below illustrates the stages of research:

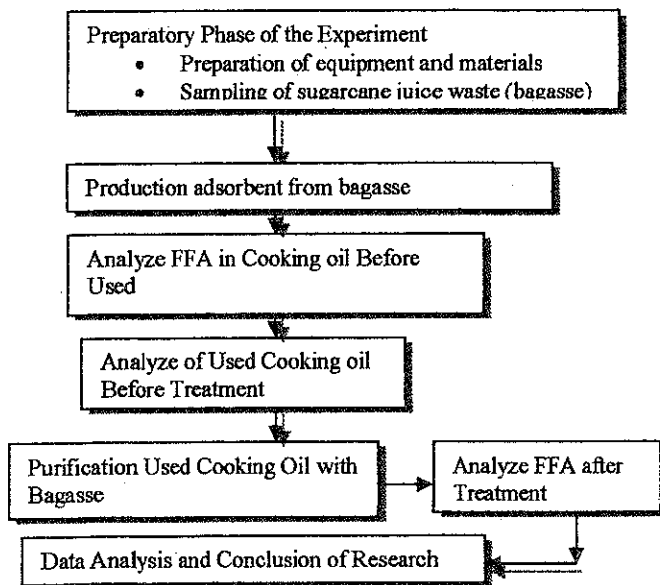


Figure 1: Flow Chart of Experiment

2.2 Materials and equipment

The materials used are derived from waste from sugarcane juice (bagasse) usually obtain from stall selling sugarcane juice rather easily. The used cooking oil on the other hand is based on cooking oil that has been condition by the researcher. Accordingly, the bagasse will be activated using NaOH solution. The instrument used is a Whatman filter paper # 41, Thermometer, Rotavapor R-210 BUCHI Switzerland, Chemical laboratory support equipment Such as mixers, electric stove, Erlenmeyer, pipettes drops, balance sheet measures, and weights.

2.3 Preparation of bagasse adsorbent

Bagasse will be obtained from stalls selling sugarcane juice, which is conveniently and usually located by the roadside around Kota Bharu, Kelantan, Malaysia. The following steps must first be undertaken before activating the bagasse:

- Sorted to obtain the bagasse fiber, coir further cut for ease of drying and milling.
- Bagasse fibers are thoroughly washed with water to remove sand, soil or other regulators.

- Bagasse fibers that have been dry milled will be grinder into powder and sifted to obtain a diameter of $\pm < 600 \mu\text{m}$.
- Before the use, bagasse powder is washed with aquades, and then dried at room temperature.

To activate bagasse, the bagasse is heated at 200°C for 120 minutes in oven. These heated bagasses are then mix with NaOH solution and then heated again for another 1.5 hours. Finally, the mixture is filtered and heat again at 200°C for 90 minutes

2.4 Preparation of used cooking oil

Cooking oil that has been used for frying will experience color change, turbidity, and odor, which means reduce of quality (Richard D. O'Brien, 2009⁽¹⁰⁾). In this research, the used cooking oil which will be purified has been used in 3 cycles of frying, to fry potatoes, chicken and dried fish. Cooking oil that has been used for cooking three different foods have become very murky, dark colored and has terrible smell. The most extreme cooking oil changes occurred after the cooking oil used to fry the dried fish.

2.5 Purification Used cooking oil

The two factors that affect the oil refining process investigated in this research; the weight and contact time. Weight is a measure for how much bagasse adsorbent was used for the purification, and the contact times represent the length of processes in mixing adsorbent with the used cooking oil. Method of used cooking oil purification with adsorbent according to Yustinah, (2009⁽¹¹⁾) and described in the flowchart below.

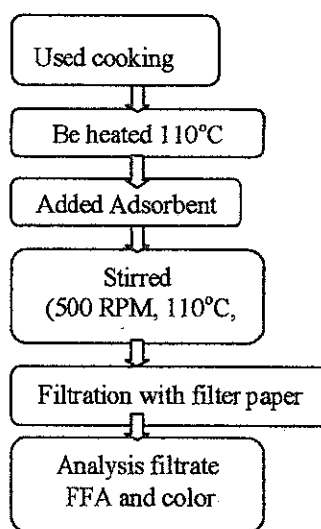


Figure 2: Flow Chart of Used Oil Purification Process

2.6 Determination of FFA.

About 28.2 g of well mixed oil added with 50 ml ethyl alcohol and 1 % phenolphthalein. The mixture is then titrated with 0.1 N NaOH with

vigorous shaking until a permanent faint pink appeared and persisted at least for 1 minute (AOCS, 2009⁽¹⁾). The FFA content is calculated as percentage of oleic acid by using Equation 1.

$$\% \text{ FFA} = (V \times N \times 28.2) / m \dots\dots (1)$$

Where, m is the mass of the test portion, in grams, N the normality of NaOH, and V the volume of NaOH consumed, in milliliters.

2.7 Isotherm for Adsorption

Type of isotherm adsorption can be used to determine the mechanism of adsorption of Free Fatty Acid (FFA) substance by bagasse. Adsorption isotherm with liquid phase usually adheres to Freundlich and Langmuir type. At the Langmuir isotherm adsorbent having a homogeneous surface and can only adsorb one molecule substances and only formed a single layer at the maximum adsorption. Isotherm Freundlich shows the level of heterogeneity (differences in strength) in surface and factor of trapped ions in the pore adsorbent. As such, the process advocates a multilayer adsorption. The result from this research shows that Freundlich and Langmuir isotherm of FFA base on the variable weight and time.

The linear form of the Langmuir adsorption equation can be represented as equation number 2

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_A q_m} \dots\dots\dots (2)$$

while the linear form for Freundlich adsorption equation as:

$$q_e = K_F C_e^{1/n} \dots\dots\dots (3)$$

Where,

- C_e equilibrium concentration of adsorbate in the solution (mg mL⁻¹);
- q_e amount of adsorbate adsorbed on the adsorbent at equilibrium (mg g⁻¹);
- q_m monolayer adsorption capacity (mg g⁻¹);
- K_A Langmuir adsorption equilibrium constant (mL mg⁻¹), which is related to the energy of adsorption.
- K_F Freundlich adsorption equilibrium constant (mL mg⁻¹)

3. RESULTS AND DISCUSSION

The reaction of water and fats at frying temperature produces Free Fatty Acid (FFA). FFA analyses are the quality indicators that determine the amount of hydrolysis (Richard D. O'Brien, 2009⁽¹⁰⁾).

Percentages reduce of FFA value after purification process can be seen in Table 1 while the relationship between two variables: weight and time with the value of FFA can be seen in Figure 3.

Table 1. FFA Value and Percentages of Reduce

No	Time (minute)	Weight (gram)	ml NaOH	FFA (%)	% reduce
1	New Cooking oil		0.2	0.018	control
2	Used Cooking oil		1.4	0.127	-
3	10	5	0.6	0.055	57.1
4	10	10	0.6	0.055	57.1
5	60	5	0.35	0.033	75.0
6	60	10	0.3	0.027	78.6
7	10	7.5	0.5	0.045	64.3
8	60	7.5	0.25	0.023	82.1
9	35	5	0.5	0.045	64.3
10	35	10	0.5	0.045	64.3
11	35	7.5	0.4	0.036	71.4
12	35	7.5	0.45	0.041	67.9
13	35	7.5	0.4	0.036	71.4
14	35	7.5	0.45	0.041	67.8
15	35	7.5	0.4	0.036	71.4

From Table 1, it can be seen that any variations in treatment, there is a reduction in FFA values that

differ according the ability of adsorbent to purified based on the weight and time allocated in the treatment. The highest percentage reduction of FFA is obtained at 60-minute contact time and 7.5 grams adsorbent used, producing a reduction to 82.144 %. The maximum standards for FFA value in the cooking oil released by PORAM (Palm Oil Refiners Association of Malaysia) for RBD (Refined, Bleached, Deodorization) Palm Oil is 0.1%. Base on this standard, treated used cooking oil at various condition resulted in the allowable limits.

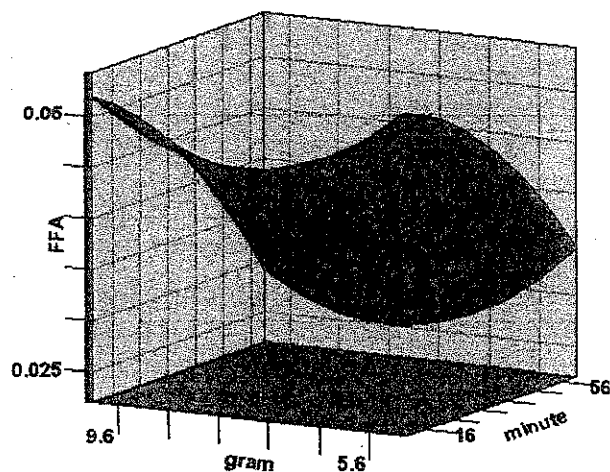


Figure 3: The Relationship between weight, time and FFA

Figure 3 above, shows the relationship of weight adsorbent, with the length of contact time. At the same weight with different time variations, the curve that forms a smooth arch, which progressively decreases. This means that the longer the contact time, the FFA obtained tends to be smaller. This shows that the length of time factor, affects the level of impairment of FFA. In this study, the longest contact time is 60 minutes, which showed the highest FFA impairment compared with other length of times.

On the other hand at the same time variation, with the use of different adsorbent weight, a curve which tends to curve toward the center is established. In general, the curve shows that, using more adsorbent bagasse does not necessarily able to reduce the value of FFA.

Through variation of the existing weight of 5, 7.5, and 10 g, it can be seen from the weight 5-7.5 g, a decline in the value of FFA significantly, while the weight 7.5-10 g value obtained by the more elevated FFA. This shows that there is weight effective for bagasse adsorbent for better recovery of cooking oil. But then again, the result also proves that the used of more and more bagasse will not necessarily lead to a more and more reduction in the FFA. This is because there are several point of saturation use of adsorbent,

where the saturation rate was the turning point limits adsorbent to adsorb completely.

It can also be seen from data analysis by ANOVA as illustrated in Table 2, where the value $Pr > F$ which can be significantly affecting the reading of FFA is the variation of time. Where the value $Pr > F$ is < 0.0001 , which means the value was less than 0.05. While the value $Pr > F$ of weight variation is 0.388, this indicate that's indicates that the weight variable does not affect the value of FFA.

Table 2. ANOVA for FFA

No	Source	Pr>F
1	Time	<0.0001
2	Weight	0.3888
3	Time x Weight	0.2976

The Optimization Result of FFA supported by SAS, states that the titration reading be in units smaller than 0.05 ml. This will produce accurate results and prove the significance of data. However, results obtained in the study are based on units of 0.05, which reduces the accuracy, and this is due to the limited equipment available.

- Predictive Models

From the data obtained. If time is α , β is weight so the value of FFA is:

$$\text{FFA} = 0.1134 + 0.000073\alpha - 0.017886\beta - 6.01 \text{ E-}6\alpha^2 - 0.000018 \alpha \beta + 0.001215 \beta^2 \dots (4)$$

3.1. Isotherm for Free Fatty Acid

Figure 4 depicts the isotherm Freundlich on FFA for weight variation indicates that the curve is not linear at each time variations. Curve is skewed to the right which shown the level of linearity of weight variation increases with less processing time. The highest R^2 value of existing curve amounted to 16.78%.

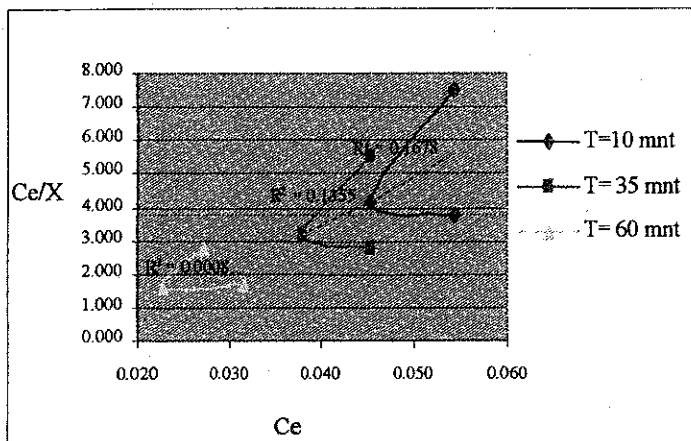


Figure 4: Isotherm Freundlich with weight variation

Isotherm Freundlich for FFA with contact time variation illustrated in Figure 5 indicates that all curves for the time variation of each weight is linear. This shows that the time variation of each weight variation lead to the isotherm Freundlich type with the highest R^2 value of 99.61%.

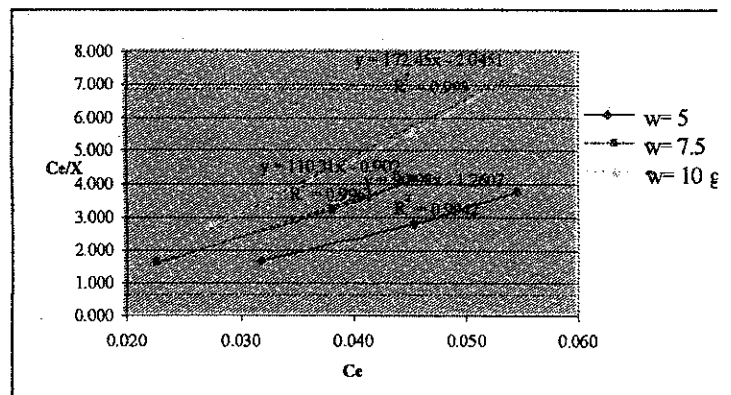


Figure 5: Isotherm Freundlich for Time Variation

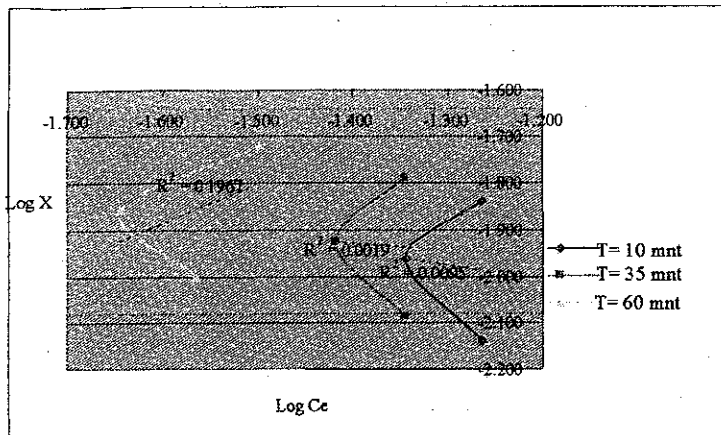


Figure 6: Isotherm Langmuir for Weight Variation

Because of the value of logarithm is very small, the curves in Figure 6 are negative. The curve also shows a line that is not linear and left-leaning, where the longer the time used in purification process, the linearity of the variation in weight will be higher, which the value of R^2 up to 19.67%.

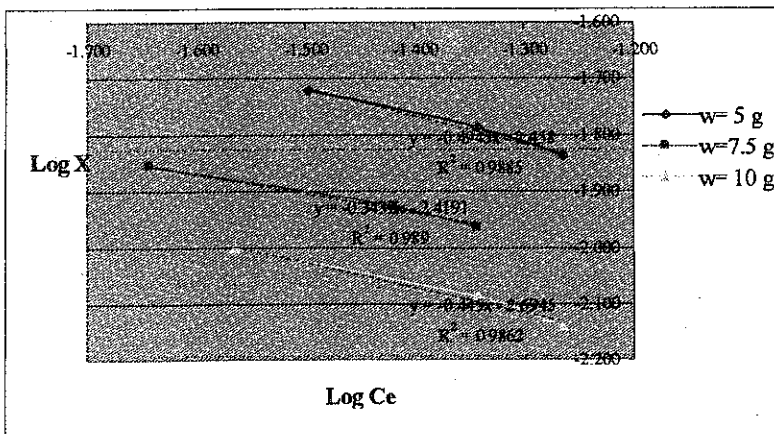


Figure 7: Isotherm Langmuir for Time Variation

Figure 7 describe Langmuir Isotherm for time variation which is of linear curve with a value of R^2

about 98.9%. From these four figures (Figure 4 – 7), the adsorption mechanism is clearly visible for Freundlich and Langmuir isotherm. This is reflected on the time variation curve. When compared to the level of linearity, Isotherm Freundlich has a higher level of linearity that is 99.61% where Langmuir is about 98.9%. But for the weight variation, the high level of linearity is the Langmuir Isotherm which is 19.67% while Freundlich only reached 16.78 %.

4. CONCLUSION

The result of this study established that bagasse adsorbent can decrease FFA by 82.14%. Base on a sample of 150 ml used cooking oil sample, the effective time for treatment to reduce FFA is 60 minutes, while the effective weight of bagasse for the reduction of FFA is 7.5 g. Isotherm adsorption for FFA in time variation shows that isotherm Freundlich has a higher level of linearity than Langmuir, where isotherm Freundlich is 99.61 % and Langmuir is 98.9%. For weight variation, the level of linearity Langmuir is 19.67 %; it's higher than Freundlich which only reached 16.78%. That's means that the mechanism Freundlich isotherm is more suitable for FFA absorbance

levels in time variation while the Langmuir suitable for weight variation.

5. REFERENCE

1. AOCS. 2009. *Official methods and recommended practice of the AOCS*. 6th Edition. USA
2. Bhattacharya, Sajilata, Tiwari & Singhal, 2008. *Regeneration of thermally polymerized frying oils with adsorbents*. Journal of food chemistry, 110, 562-570.
3. Budiono, Agus, 2009. *Pemanfaatan ampas tebu hasil samping pabrik gula menjadi karbon aktif sebagai adsorben Cu⁺²*. Universitas Negeri Malang: Malang
4. Codex Alimentarius Commission 1999, Recommended International Standard for Named Vegetable Oils. Codex Stan 210-1999. FAO and WHO. Rome, Italy
5. Idris, Nor Aini, Abdullah, A & Halim, AH, 1992. *Evaluation of Palm Oil Quality: Correlating Sensory with Chemical Analyses*. PORIM.
6. Lin, S Akoh, C C and Reynolds, A E. 1998. The recovery of used frying oil with various adsorbent. J. Food Lipids, 5:1-16.
7. Loh Soh Kheang, Choo Yuen May, Cheng Sit Foon & Ma Ah Ngan, 2006. *Recovery and conversion of palm olein-derived used frying oil to methyl esters for biodiesel*. Journal of Oil Palm Research. Vol.18. 247-252.
8. Miyagi, A & Nakajima, M. 2003. *Regeneration of used Frying oil using membrane processing*. J Amerr. Oil Chem. Soc, 80: 91-96.
9. Pandey, G. N, Carney. G. C. 2008. *Environmental Engineering*. McGraw-Hill: New Delhi.
10. Richard D. O'Brien, 2009. *Fat and oil*. CRC Press: New York.
11. Yustinah, 2009. *Pengaruh massa Adsorben chitin pada penurunan kadar asam lemak bebas, bilangan peroksida dan warna gelap minyak*. Universitas Muhammadiyah: Jakarta

