

Reduction of Peroxide Value in Used Palm Cooking Oil Using Bagasse Adsorbent

Wannahari. R*

Nordin. M.F.N.

Faculty of Agro Industry & Natural Resources
Universiti Malaysia Kelantan, Locked bag 36, Pengkalan
Chepa 16100 Kota Bharu
Kelantan, Malaysia

Abstract

Bagasse is a waste from utilization of sugarcane. Constituent structures of bagasse derive from carbon materials that make bagasse suitable to be an adsorbent. However the Used of bagasse as an adsorbent is not common today. The uses of bagasse as adsorbent by activate it with a solution of NaOH for 200 minutes. In this study, bagasse will be used to reduce peroxide value in used cooking oil. Peroxide value is measure of oxidation or rancidity which can reduce the qualities of food. In the used cooking oil, peroxide value will increase as a result of cooking oil heating process. 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 experiments conducted, it can be established that bagasse adsorbent able to reduce the peroxide value of used cooking so that value still in the range of standard. The highest reduction of peroxide value from this experiment is 21%. This result is obtained when using 7.5 gram of bagasse for 10 minutes contact time. Equilibrium of peroxide value studied using the freundlich isotherm and isotherm langmuir. Results indicate the used of different contact time variation has a higher linearity both freundlich and langmuir isotherm.

Key Words: Bagasse, adsorbent, used cooking oil, peroxide value, reduction, isotherm.

1. INTRODUCTION

Palm oil is a common cooking ingredients and originate in western Africa, it has spread to most part of the tropical and subtropical zones of the, but particularly to Malaysia and Indonesia (Richard D. O'Brien, 2009).

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). Recycling used cooking oil using adsorbents, such as silica gel, magnesium oxide, aluminium hydroxide gel and activated clay, has been studied (Lin and Reynolds, 1998; Miyagi & Nakajima. 2003) for improving the quality parameter of used cooking oil. The indicators of poor oil quality include elevated Free Fatty Acids (FFA), change of color, low smoke point, low iodine value, total polar material, peroxide value, high foaming properties and increased viscosity (Loh Soh Kheang, et al. 2006).

The parameter used in measuring the quality of used cooking oil in this research is peroxide value. Peroxide value is measure of oxidation or rancidity and the color darker is also effect from oxidation. 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 in the oil refining process. From the results of previously research of purification used cooking oil, silica gel is known to have the ability to reduce the value of PV, high compared to most other adsorbent which amounted to 65.1%. While activated carbon (magnesium oxide) could reduce the PV of 7.8%, aluminum oxide reduce 20.8%, activated clay (Acid-activated spent bleaching earth) 46.9 %.(Pandey, G. N, Careney. G. C. 2008). 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 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. There are 2 factors used in this study that is weight and time.

Both these factors affect to the used cooking oil refining process. For weight, the maximum weight used was 10 g and the minimum weight is 5 g. While for the time, the longest time is 60 minutes and the fastest is 10 minutes. By entering the weight factor and time a variable, SAS will provide the experimental design with 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 Peroxide Value (PV) 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:

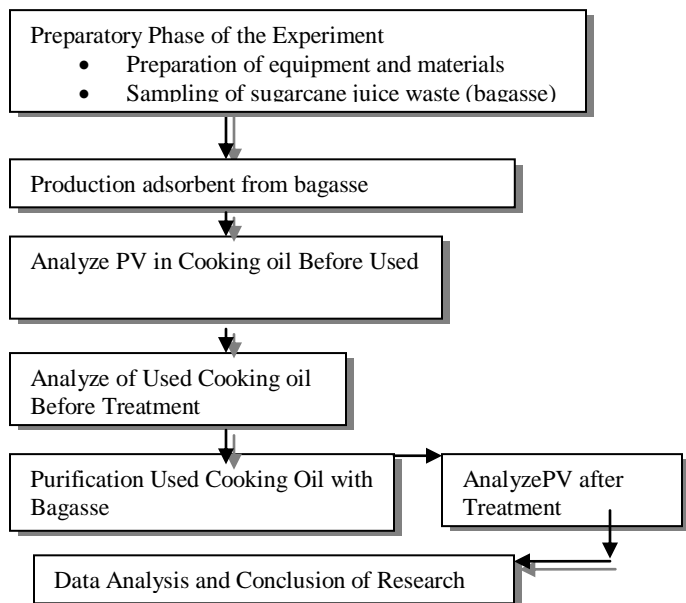


Figure 1: Flow Chart of Experiment

2.2 Materials and equipment

The materials used are derived from waste from sugarcane juice (bagasse) usually obtain from stall selling sugarcane juice. The used cooking oil on the other hand is based on cooking oil that has been condition by the researcher. Activation of bagasse will be 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

Source of bagasse will be obtained from stalls of sugarcane juice, which is usually located at the edge of the road, Kota bharu, Kelantan. There are several steps must be done before the activation of bagasse, like:

- Sorted to obtain the bagasse fiber, coir further cut for ease of drying and milling.
- Bagasse fibers wash with water to remove sand, soil or other regulators.
- Bagasse fibers that have been dry milled with a grinder into powder and sifted to obtain a diameter of $\pm < 600 \mu\text{m}$.
- Before use, bagasse powder is washed with aquadesh, and then dried at room temperature.

To activate bagasse, heat the bagasse at 200°C for 120 minutes in oven. Activated the heated bagasse with NaOH solution and then heated again for another 1.5 hours. Filter the mixture and then to heat them 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). In this research, the used cooking oil which will be purified has been used in 3 times 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 the smell terrible. The most extreme cooking oil changes occurred after the cooking oil used to fry the fish dry.

2.5 Purification Used cooking oil.

There are 2 factors that affect the oil refining process in this research, the weight and contact time. Weight is, how much we used bagasse adsorbent for the purification, and the contact time is, how long it taken to mixing adsorbent with used cooking oil. Method of oil purification with adsorbent according to Yustinah, 2009 research is described in the flowchart below.

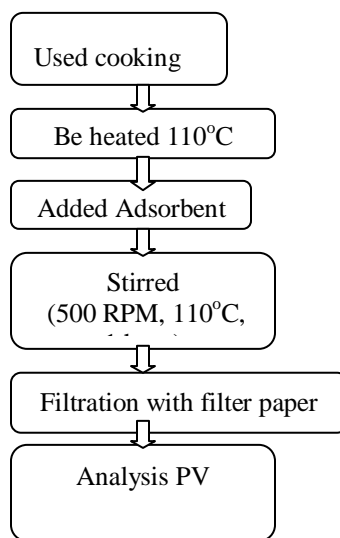


Figure 2: Flow Chart of Used Oil Purification Process

2.6 Determination of Peroxide Value.

About 5 ± 0.05 g sample in 250 ml close Erlenmeyer and add 30 ml acetate acid. Shake the mixture so it blends thoroughly. Add 0.5 ml KI. Rest for 1 minute and shake once a while and then add 30 ml aquadesh (distil water). Titrate with 0.1 N Na₂S₂O₃ until the yellow color disappears. Add 0.5 ml amilum liquid; continue titration until the blue colors begin to disappear. Peroxide value is recorded in ml-equivalent from peroxide in every 1000 g. (AOCS,2009)

$$\text{Peroxida value} = (\text{ml Na}_2\text{S}_2\text{O}_3 \times \text{Normality Na}_2\text{S}_2\text{O}_3 \times 1000) / \text{weight samples} \dots\dots\dots (1)$$

2.7 Isotherm for Adsorption

Type of isotherm adsorption can be used to determine the mechanism of adsorption of substances Peroxide Value (PV) by bagasse. Adsorption isotherm with liquid phase usually adheres to Freundlick 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 (Reynolds. 1996). At Isotherm Freundlich considering the level of heterogeneity (differences in strength) of surface and factor of trapped ions in the pore adsorbent so that the process happens by multilayer adsorption. At this research shows Freundlick and Langmuir isotherm of peroxide value with variation of variable weight and time.

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

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

while the linier form for Freundlich adsorption equation

$$q_e = K_F C_e^{b_F} \dots\dots\dots (3)$$

- Ce equilibrium concentration of adsorbate in the solution (mg mL⁻¹);
 qe amount of adsorbate adsorbed on the adsorbent at equilibrium (mg g⁻¹);
 qm 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 peroxide concentration, usually expressed as peroxide value, is measured by oxidation or rancidity in its early stages and should be not more than 10 (milliequivalents peroxide/1000g sample) in cooking oil (Richard D. O'Brien, 2009). Percentages reduce Peroxide Value (PV) after purification process can be seen in Table 1 while the relationship between two variables: weight and time with the PV can be seen in Figure 3.

Table 1 Peroxide Value and Percentages of Reduce

No	Time (mnt)	Weight (gr)	ml Na ₂ S ₂ O ₃	PV (meq)	% reduce
1	New Cooking oil		0.5	10	control
2	Used Cooking oil		1.5	30	.-
3	10	5	1.5	30	0.00
4	10	10	1.5	30	0.00
5	60	5	1.4	28	6.67
6	60	10	1.1	22	26.67
7	10	7.5	1.45	29	3.33
8	60	7.5	1.1	22	26.67
9	35	5	1.4	28	6.67
10	35	10	1.3	26	13.33
11	35	7.5	1.2	24	20.00
12	35	7.5	1.3	26	13.33
13	35	7.5	1.4	28	6.67
14	35	7.5	1.4	28	6.67
15	35	7.5	1.2	24	20.00

From Table 1 can be seen that any variations in treatment that has been done, there is a reduction in PV that differ according the ability of adsorbent to purified based on the weight and time which given in treatment. The highest percentage reduction of PV is obtained at 60-minute contact time while weight adsorbent used was 7.5 grams and 10 grams. Both of treatments have the same reduction that is 26.67 %. The maximum standards for PV in the cooking oil released by Codex Stan 210-1999 (Refined, Bleached, Deodorization) Palm Oil is 10-15 milliequivalents of active oxygen/kg oil. Base on this standard, treated used cooking oil can't reduce the PV to maximum standard value, but have improvement by reduce the PV.

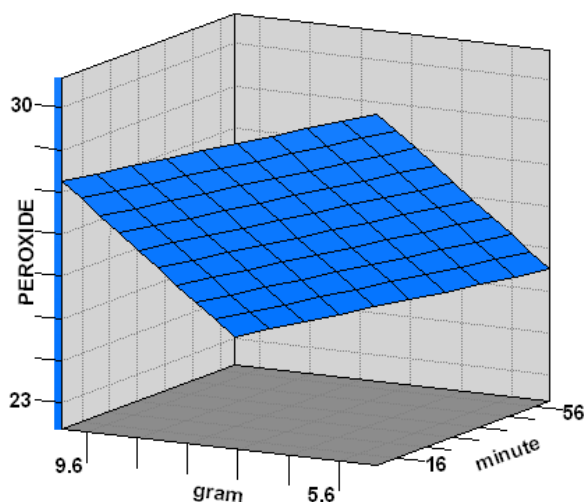


Figure 3: The Relationship between weight, time and PV

Through the chart above, can be seen 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 is used, and then the PV obtained tends to be smaller. This shows that the length of time factor, affecting the level of impairment of PV. In this study, the longest contact time is 60 minutes, which showed the highest PV impairment compared with other times.

On the other hand at the same time variation, with the use of different adsorbent weight, found a curve almost horizontal. In general, the curve shows the use of more adsorbent bagasse not necessarily able to reduce the value of PV. This is because there are number 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 which contained in Table 2, where the value Pr> F which can be significantly affecting the reading of PV is the variation of time where the value Pr> F is 0.0038, which means the value was less than 0.05. While the value Pr> F of weight variation is 0.1087, that's indicates that the variable heavy weight is not so affect the value of peroxide.

Table 2. ANOVA for PV

No	Source	Pr>F
1	Time	0.0038
2	Weight	0.1087

The Optimization Result of PV 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 PV is:

$$\text{Peroxide} = 34.50513 - 0.113333 \alpha - 0.533333 \beta \text{ (meq/kg oil) } \dots\dots\dots (4)$$

3.1. Isotherm for Peroxide Value

At the Figure 4 Isotherm Freundlich on Peroxide value (PV) for weight variation indicates that the curve is different each time variations. The curve linier in $t = 10$ minute and 60 minute where R^2 value are 1 and 0.98. While in $t = 35$ minute, R^2 value is 0.4.

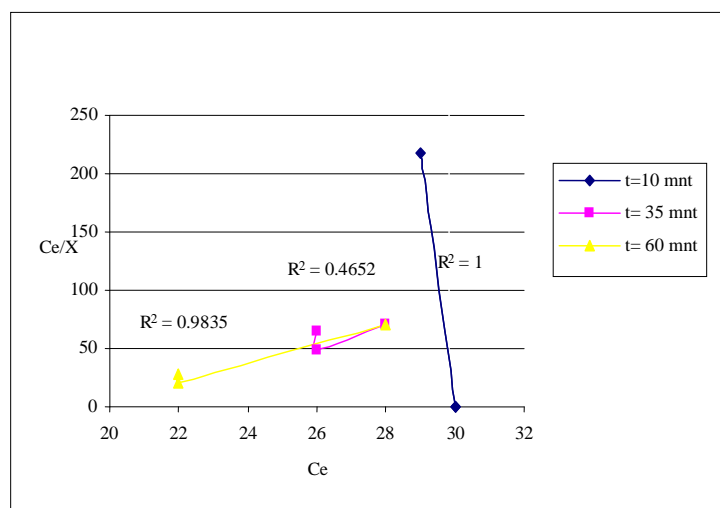


Figure 4: Isotherm Freundlich for PV with Weight Variation

Isotherm Freundlich for PV with time variation in Figure 5 indicates that the curves for the time variation at 5 g and 7.5 g adsorbent that have been used have a good linearity. This shows the time variation of each variable weight going for the type of isotherm Freundlich with the highest R^2 value is 1. But when weigh was added until 10 g, R^2 value has decrease to 0.17. That shown there is a limit of used bagasse as adsorbent. The more of adsorbent we gave, didn't mean it can't reduce more of value of peroxide.

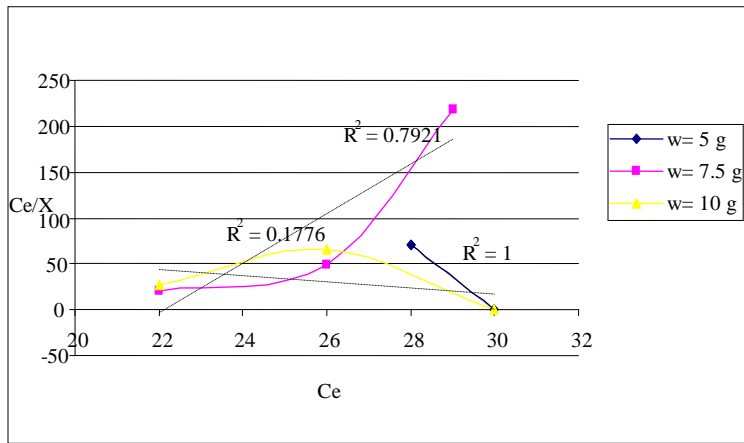


Figure 5: Isoterm Freundlich for PV with Time Variation

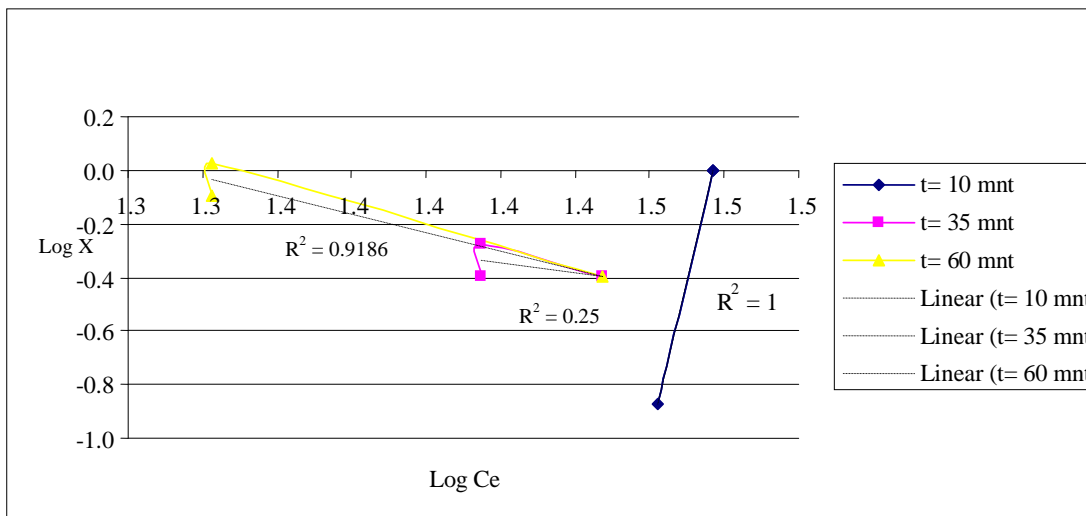


Figure 6: Isothrem Langmuir PV for Weight Variation

Because of the value of logarithm is very small, the curves in Figure 6 are negative curve. Some of the curve also shown the linier curve in $t = 10$ minute and $t = 60$ minute while a line that is not linear and left-leaning in $t = 35$ minute, 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 1.

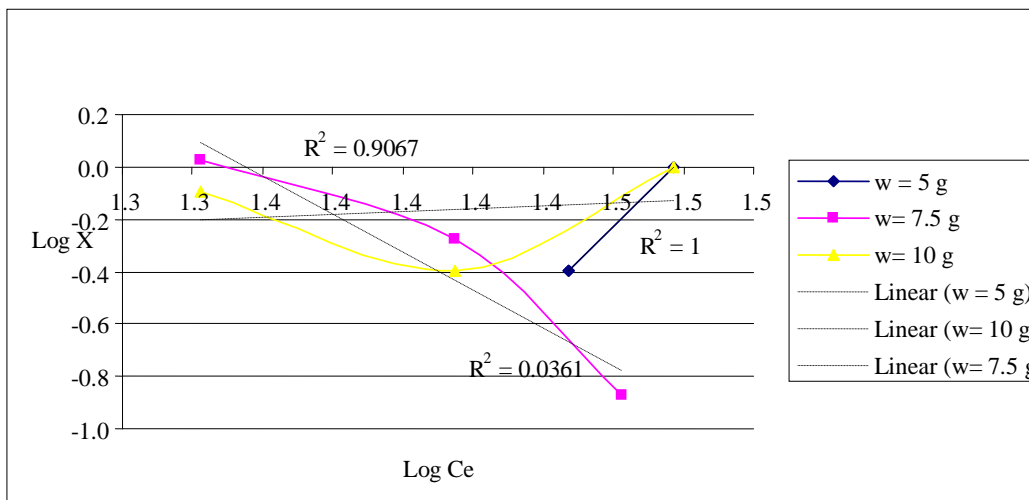


Figure 7: Isothrem Langmuir PV for Time Variation

At the Figure 7. Langmuir Isotherm for time variation indicates a linear curve with a value of R^2 about 1 in weight 5 g. From the four figures (figure 4 – 7), the adsorption mechanism is clearly visible for Freundlich and Langmuir isotherm, which is show in curve for the both of variation.

That's means that the mechanism Freundlich isotherm and Langmuir isotherm are suitable for PV absorbance both of time and weight variation.

4. CONCLUSION

The bagasse adsorbent can decrease Peroxide Value (PV) up to 26.67%. From 150 ml of used cooking oil sample, time effective for treatment to reduce PV is about 60 minutes while the effective weight of bagasse which has been used for the reduction of PV is 7.5 g and 10 g. Isotherm adsorption for PV both of time variation and weight variation was suitable for Freundlich and Langmuir isotherm with R^2 value up to 100 %.

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