Recovery of used vegetable frying oil by two-step adsorbents

Jenjira Wonglamom[1] and Nuansri Rakariyatham[2,3,]*

[1] Biotechnology, Faculty of Graduate School, Chiang Mai University, Chiang Mai 50200, Thailand
[2]Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[3]Faculty of Health Science, Nation University, Lampang 52000, Thailand
* e-mail: nuansri1@yahoo.com

Abstract

The frying process is one of the most commonly used cooking methods in the food industry. Vegetable frying oil that is normally used continuously at high temperatures over long periods of times can result in oil degradation and a reduction in food quality. Although food quality can be retained through, the use of new oil, the production costs also increase. Therefore, this study aims to extend the life of vegetable frying oil by treatment with activated charcoal (AC) and bentonite (BE). Three treatments (15% w/v) including single adsorbent (AC or BE), adsorbent combinations (BE:AC ratio 2:1, 1:1 and 1:2) and two-step adsorbents (AC and then BE, BE and then AC) were investigated for the purposes of improving the physico-chemical parameters (free fatty acids, FFA; acid value, AV; peroxide value, PV; total polar materials, TPM; conjugated dienes, CD and color) of used vegetable frying oil. Each treatment was mixed in with used vegetable frying oil at 150°C, stirred for 30 min and vacuum filtered through Whatman's no. 1 filter paper. The results showed that the two-step treatment (AC and then BE) exhibited the highest ability to improve the physico-chemical parameters of the vegetable oil when compared with the single adsorbent (AC or BE), three adsorbent combinations (BE:AC ratio 2:1, 1:1 and 1:2) and the two-step application of BE and then AC. Of these treatments, the %FFA, %TPM, %CD, AV and PV could improve the state of the vegetable frying oil to nearly fresh quality.

Keywords: activated charcoal, bentonite, used oil, fatty acid, adsorbent

Introduction

Oil degradation takes place during the frying process under high temperatures in the presence of air and moisture, and is influenced by the composition of the food. This condition is subjected to thermal oxidation, hydrolysis and polymerization. A variety of reactions affect the chemical and physical properties of the oil (Yilmaz and Bulu 2012). The products of thermal oxidation and polymerization are nonvolatile compounds, hydro peroxides and cyclic peroxides. The latter two products could then decompose into volatile compounds (Khan et al. 2007). The hydrolysis reaction and heat treatment result in an increase the free fatty acids. In addition, the degradation of the frying oil can reduce the quality of the fried food products and cause adverse effects to humans (Yilmaz and Bulu 2012). However, an attempt to improve the quality of the frying oil in order to reduce costs is preferable by industry.

There are many adsorbent materials, which have been studied for the purposes of improving frying oil. Khan et al. (2007) showed that activated charcoal and magnesium oxide could improve fried *silybum marianum* oil. The report by Okiel et al. (2011) found that bentonite had the effect of adsorbing organic pollutants. Moreover, the combination of Hubersorb 600, Magnesol and Britesorb could reduce the amount of free fatty acids, total polar material and improve the color of the frying oil when compared with the used frying oil (Lin et al. 1999). In addition, Yilmaz and Bulu (2012) reported that the mixed adsorbents of natural zelolite, lime and diatomaceous earth has been effective in improving viscosity, turbidity, free fatty acid, peroxide value, conjugated dienes and the total polar materials of used oil. However, the use of two-step adsorbents for improving the quality of the oil is limited. Therefore, this study aims to extend the life of the frying oil resulting in cost benefits through the two-step treatment (AC and then BE, BE and then AC) compared with the single treatment (AC or BE) and three combination treatments (BE:AC ratio 2:1, 1:1 and 1:2).

Methodology

Used vegetable frying oil

The used vegetable frying oil was taken during May 2014 from Ton Payom Market, Chiang Mai, Thailand.

Adsorbent treatment

Thirty gram of activated charcoal and bentonite (15% w/v) was individually mixed with 200 ml of used vegetable frying oil at 150°C and stirred for 30 min (Yilmaz and Bulu, 2012; Lin et al., 1999). After that, the mixture of the adsorbent and the used vegetable frying oil was filtered through Whatman's no. 1 filter paper under the vacuum. The treated oil samples were kept in brown glass bottles until being used.

Bentonite and activated charcoal were mixed at various ratios of 2:1 (combination A), 1:1 (combination B) and 1:2 (combination C). Thirty gram of each combination (15% w/v) was mixed with 200 ml of used vegetable frying oil at 150°C, stirred for 30 min and then filtered through Whatman's no. 1filter paper under the vacuum conditions. Treated oil samples were kept in brown glass bottles until being used.

The two-step treatment of AC and then BE was conducted by mixing 30 g of activated charcoal (15% w/v) with 200 ml of used vegetable frying oil at 150°C and stirring the mixture for 30 min. The slurry was vacuum filtered through Whatman's no. 1 filter paper. The filtered oil was then mixed with bentonite (15% w/v). The treated oil samples were kept in brown glass bottles until being used. The two-step treatment of BE and then AC was also prepared in the same manner in which BE was mixed with the used vegetable oil first and then followed by AC.

Percentage of free fatty acids (%FFA)

The percentage of free fatty acids was determined the using AOCS method (Debnath et al. 2012), with slight modifications. Five gram of the oil sample were dissolved in 20 ml of 95% ethanol, and titrated against 0.1 N sodium hydroxide solutions using phenolphthalein as an indicator. The percentage of free fatty acids was expressed as % oleic acid.

Peroxide value (PV)

The peroxide value was assayed by a method presented from Debnath et al. (2012). The mixture of acetic/chloroform (3:2 v/v) was used to dissolve 5 g of the oil sample, then 0.5 ml of saturated potassium iodide (KI) were added and the oil sample was allowed to stand at ambient temperatures for 1 minute. 30 ml of distilled water were used to stop the reaction, and the mixture was titrated against 0.1 N sodium thiosulfate solutions using starch as an indicator. The peroxide value was expressed as milliequivalent of oxygen/kilogram of oil.

Acid value (AV)

The acid value was assayed by titration (Chen et al. 2013). The oil sample (0.5 g) was dissolved in 20 ml of diethyl/ethanol (1:1 v/v), and titrated against 0.1 N potassium hydroxide solutions using phenolphthalein as an indicator. The acid value was expressed as milligram of potassium hydroxide/gram of oil.

Percentage conjugated dienes (%CD) (Bhattacharya et al. 2008)

0.5 g sample was added to purified iso-octane (10 ml) in a 125 ml flask, and then adjusted to a final concentration of 0.05 g/l. The absorbance was then measured at 233 nm. The percentage of conjugated dienes was calculated as follows:

$$\%\ CD = 0.84(As/bc - K_o)$$

where K_o = absorptivity by acid or ester groups (0.07 for esters, 0.03 for acids)
As = observed absorbance at 233 nm
b = cuvette length in cm,
c = concentration of sample, g/l of the final dilution

Percentage of total polar materials (%TPM)

The total polar materials were determined through the use of a cooking oil tester (testo 270) (Yilmaz and Bulu 2012) by immersing the probe of the instrument into warm oil samples (temp > 40 ^{o}C, 50 ml).

Percentage of quality of oil improvement

The percentage improvement of each treatment compare with untreated oil was calculated as follows:

$$\%\ \text{improvement} = \frac{(\text{value of untreated oil} - \text{value of treated oil})}{\text{value of untreated oil}} \times 100$$

Color determination

The color of the oil samples was determined by colorimeter (color quest XE). The color values were showed as L*, a*, b* values. L* represents the lightness or brightness of the oil, ranging from 0 (black) to 100 (white). The letters a* and b* range from (-) 60 to (+) 60. The letter a* represents redness to greenness, a negative value indicates greenness and a positive indicates redness. The letter b* represents yellowness to blueness, a negative value indicates blueness and a positive value indicates yellowness.

Statistical analysis

Each experiment was done in triplicate and the readings are presented in terms of mean ± SD. The data was analyzed using the SPSS statistics 17.0 and were considered significantly different at $p < 0.05$.

Results

Figure 1 shows the effects of each treatment on free fatty acids. The results indicated that the activated charcoal, bentonite, their combinations (BE:AC ratio 2:1, 1:1 and 1:2) and the two-step treatment (AC and then BE, BE and then AC) can significantly reduce the amount of free fatty acids. The single treatment of activated charcoal (0.24%) significantly reduced the amount of free fatty acids better than bentonite (0.37%). Whereas, the combination treatments (BE:AC ratio 2:1, 1:1 and 1:2) could reduce free fatty acid amounts nearly as well as the activated charcoal treatment but better than the bentonite treatment. Moreover, the two-step treatment (AC and then BE, BE and then AC) could reduce free fatty acids amounts nearly as well as a single treatment of activated charcoal. On the other hand, the results of acid value improvement (Figure 2) of each treatment also showed a corresponding reduction in free fatty acid levels.

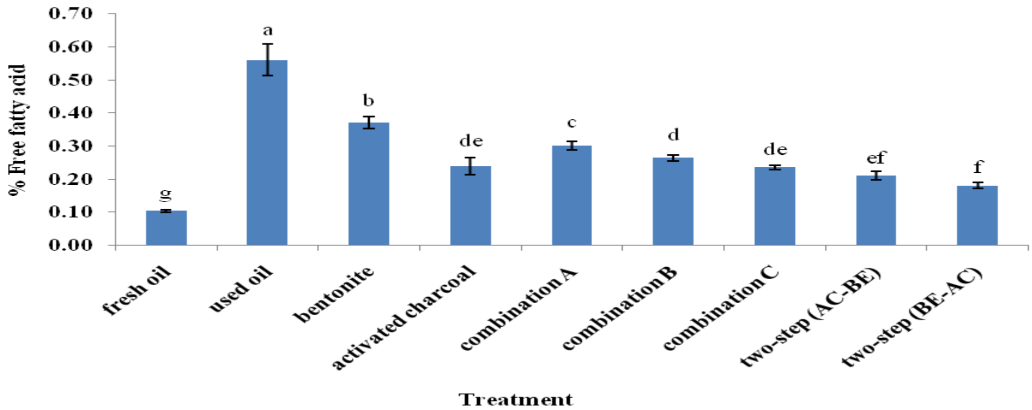

Figure 1 Effect of adsorbent treatment on free fatty acid (%), combination A (BE:AC, 2:1), combination B (BE:AC, 1:1), combination C (BE:AC, 1:2), two-step AC-BE (AC and then BE), two-step BE-AC (BE and then AC)

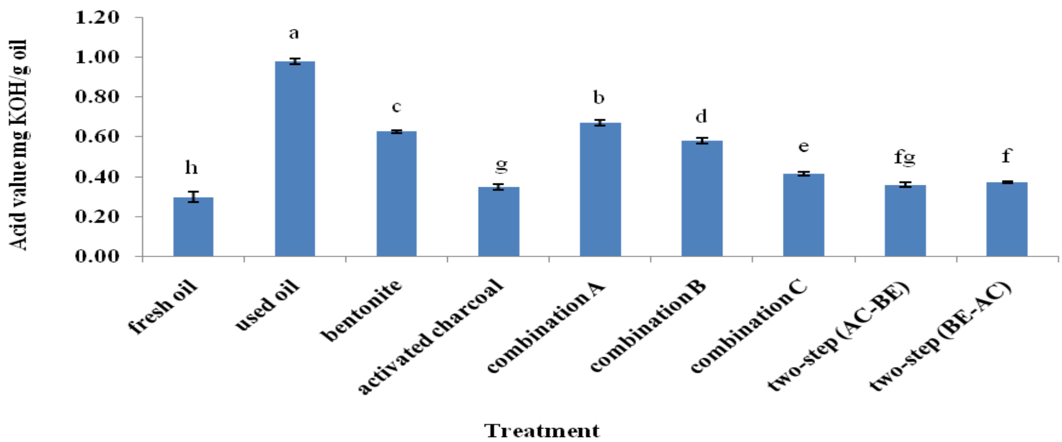

Figure 2 Effect of adsorbent treatment on acid value, combination A (BE:AC, 2:1), combination B (BE:AC, 1:1), combination C (BE:AC, 1:2), two-step AC-BE (AC and then BE), two-step BE-AC (BE and then AC)

Figure 3 demonstrates the effect of the adsorbent treatments on peroxide value. It was found that peroxide value was decreased by the adsorbent treatments. The single adsorbent (AC or BE) can significantly reduce peroxide values compared with used oil (% quality of oil improvement 50.61 and 35.89, respectively), when compared with used vegetable frying oil. The combination treatments (BE:AC ratio 2:1, 1:1 and 1:2) reduced peroxide value (% quality of oil improvement 37.45-38.63%), when compared with the used vegetable frying oil. The two-step treatment (AC and then BE, BE and then AC) could reduce peroxide value nearly as effectively as the single adsorbent (AC or BE). In consideration of the total polar materials and the conjugated dienes (Figure 4 and Figure 5), the results showed a small reduction of these parameters compared with the used oil.

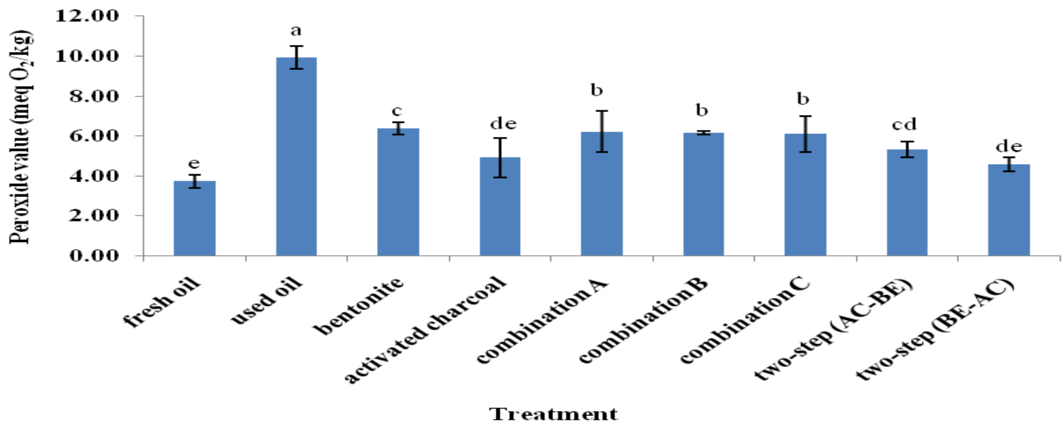

Figure 3 Effect of adsorbent treatment on peroxide value (%), combination A (BE:AC, 2:1), combination B (BE:AC, 1:1), combination C (BE:AC, 1:2), two-step AC-BE (AC and then BE), two-step BE-AC (BE and then AC)

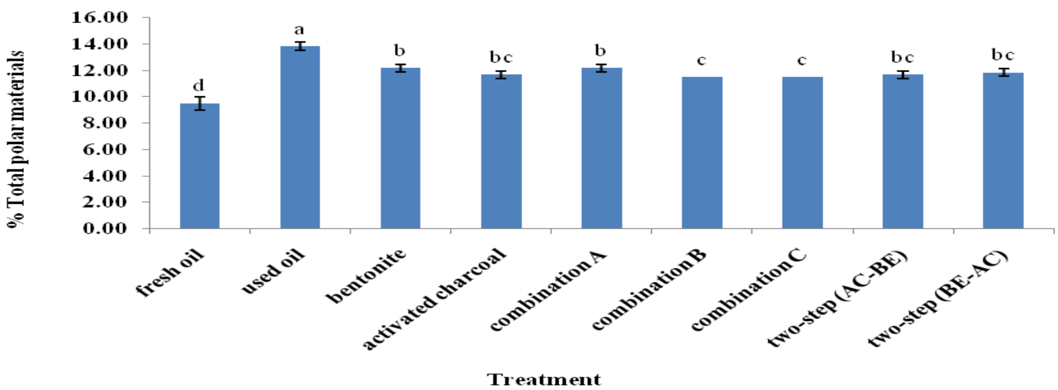

Figure 4 Effect of adsorbent treatment on total polar material (%), combination A (BE:AC, 2:1), combination B (BE:AC, 1:1), combination C (BE:AC, 1:2), two-step AC-BE (AC and then BE), two-step BE-AC (BE and then AC)

The colors of the used vegetable frying oil and the treated oil were evaluated and compared with the new oil (Table 1). The results showed that the lightness value (L*) of the treated oil increased when compared with the used vegetable frying oil (12.70). The lightness values (L*) of bentonite and the two-step treatment (AC and then BE) were found to be better than the other treatments. In addition, these treatments could reduce the redness value (a*) (1.81 and 1.12, respectively) and the yellowness value (b*) (5.67 and 6.4, respectively) nearly as much as the new oil. Although, the single adsorbent treatment (AC or BE) showed a higher oil recovery level than the two-step treatment, but could not improve both the chemical and physical properties of the oil.

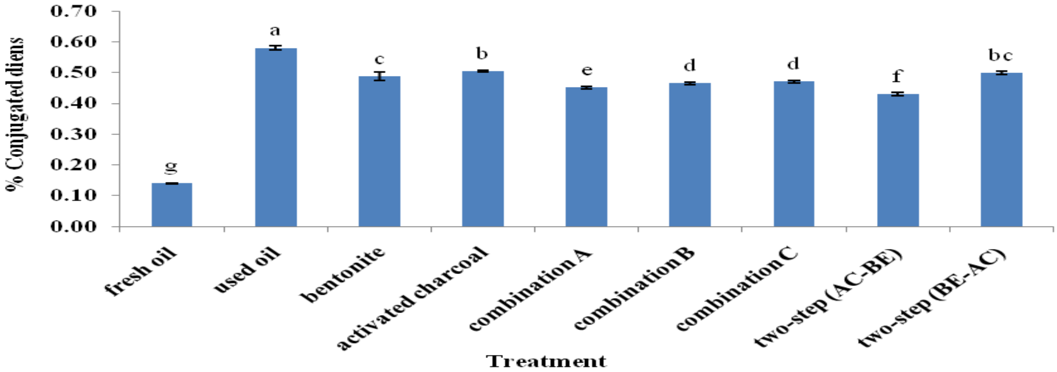

Figure 5 Effect of adsorbent treatment on conjugated dienes (%), combination A (BE:AC, 2:1), combination B (BE:AC, 1:1), combination C (BE:AC, 1:2), two-step AC-BE (AC and then BE), two-step BE-AC (BE and then AC)

Discussion

The effects of the three treatments including single adsorbent (AC or BE), absorbent combinations (BE:AC ratio 2:1, 1:1 and 1:2) and two-step adsorbents (AC and then BE, BE and then AC) were investigated for their capabilities of improving the physico-chemical parameters (free fatty acids (FFA), acid value (AV), peroxide value (PV), total polar materials (TPM), conjugated dienes (CD) and color) of used vegetable frying oil. In the single treatment, activated charcoal exhibited a higher ability of improving the free fatty acids level, acid values and peroxide values than did bentonite. This may be due to the specific adsorption affinity of activated charcoal to small molecular substances, such as free fatty acids and mono-glycerol (Yates and Caldwell 1993). This result corresponded with the reports from Khan et al. (2007), Bhattacharya et al. (2008) and Lin et al. (1999). However, the bentonite treatment alone could improve the color better than the activated charcoal treatment, which resulted from the bleaching properties of bentonite (Foletto et al. 2006). Additionally, the single treatment (AC or BE) could yield slight reduction of % TPM and % CD. This may be due to the low adsorb ability of the non-polar properties of the adsorbent contract non-polar organic compound (McNeill et al. 1986). However, the three combination treatments (BE:AC ratio 2:1, 1:1 and 1:2) could not improve both the chemical and physical properties to the levels of the nearly new oil. This result may be due to the limited amount of adsorbent that was present. Yet, the two-step treatment (AC and then BE, BE and then AC) revealed the ability to improve the chemical parameters. The AC and then BE procedure exhibited higher abilities of improving the color than did BE and then AC.

Conclusion

In this study, it could be concluded that the adsorbent treatment was effective in improving the physico-chemical parameters of used vegetable frying oil. The two-step treatment (AC and then BE, BE and then AC) improved the quality of the used vegetable frying oil more effectively than the single treatment (AC or BE) and the combination treatments (BE:AC ratio 2:1, 1:1 and 1:2).

Table 1: The percentage of oil recovery and the quality of oil improvement**,** when used oil was treated with various adsorbents

Treatment	% Oil recovery	Quality of oil improvement (%)					Color		
		FFA	AV	PV	TPM	CD	L* value	a* value	b* value
new oil	-	-	-	-	-	-	20.90±0.18^{a}	1.64±0.04^{c}	6.25±0.17^{a}
used vegetable oil	-	-	-	-	-	-	12.70±0.03^{g}	2.28±0.14^{a}	3.31±0.08^{c}
bentonite	71.0	33.73	35.95	35.89	12.05	15.88	18.50±0.04^{b}	1.81±0.04^{b}	5.67±0.22^{b}
activated charcoal	54.0	57.31	64.46	50.61	15.66	12.95	13.84±0.13^{f}	-0.92±0.13^{h}	-0.29±0.08^{g}
combination A (BE:AC, 2:1)	47.5	46.13	31.57	37.45	12.05	22.22	15.04±0.02^{c}	0.79±0.04e	2.69±0.14^{d}
combination B (BE:AC, 1:1))	45.0	52.90	40.51	38.01	16.87	19.88	14.60±0.28^{d}	0.62±0.15^{f}	1.95±0.11^{e}
combination C (BE:AC, 1:2)	45.0	57.96	57.60	38.63	16.87	18.91	14.40±0.02^{de}	-0.21±0.08^{g}	1.00±0.21^{f}
two-step (AC and then BE)	43.0	62.535	63.17	46.57	15.64	25.91	18.43±0.06^{b}	1.12±0.06^{d}	6.4±0.05^{a}
Two-step (BE and then AC)	42.0	64.94	60.07	53.69	12.35	14.81	14.37±0.08^{e}	0.50±0.05^{f}	3.38±0.13^{c}

FFA, free fatty acid; AV, acid value; PV, peroxide value; TPM, total polar material; CD, conjugated dienes

Acknowledgements
The authors would like to acknowledge the Faculty of the Graduate School of Chiang Mai University, Department of Chemistry Faculty of Science, Chiang Mai University, Faculty of Health Science, Nation University (Lampang, Thailand) and the Office of the Higher Education Commission Bangkok, Thailand for providing financial support.

References

Bhattacharya A.B., Sajilata M.G., Tiwari S.R. and Singhal R.S. (2008) Regeneration of thermally polymerized frying oils with adsorbents. Food Chem 110:562-570.

Chen W., Chiu C.P., Cheng W., Hsu C. and Kuo M. (2013) Total polar compounds and acid values of repeatedly used frying oils measured by standard and rapid methods. J Food Drug Anal 21:58-65.

Debnath S., Rastogi N.K., Gopala Krishna A.G. and Lokesh B.R. (2012) Effect of frying cycles on physical, chemical and heat transfer quality of rice bran oil during deep-fat frying of poori: An Indian traditional fried food. Food Bioproducts Process 90:249-256.

Foletto E.L., Volzone C. and Porto L.M. (2006) Clarification of cottonseed oil: How structural properties of treated bentonites by acid affect bleaching efficiency. Latin Am Appl Res 36:37-40.

Khan I., Bangash F.K. and Bangash H. (2007) Quality improvement of used fried Silybum marianum oil by treatment with activated charcoal and magnesium oxide. J Chem Soc Pakistan 29:564-568.

Lin S., Akoh C.C. and Estes Reynolds A. (1999) Determination of optimal conditions for selected adsorbent combinations to recover used frying oils. J Am Oil Chem Soc 76:739-744.

McNeill J., Kakuda Y. and Kamel B. (1986) Improving the quality of used frying oils by treatment with activated carbon and silica. J Am Oil Chem Soc 63:1564-1567.

Okiel K., EI-Sayed M. and EI-Kady M.Y. (2011) Treatment of oil-water emuslsion by adsorption onto activated carbon, bentonite and deposited carbon. Egypt J Pet 20:9-15.

Yates R.A. and Caldwell J.D. (1993) Regeneration of oils used for deep frying: A comparison of active filter aids. J Am Oil Chem Soc 70:507-511.

Yilmaz E. and Bulut E. (2012) Frying oil refreshing capacity of a new adsorbent mixture. Acad Food J 10:24-29.