USE OF SEQUENT ADSORPTION WITH ACTIVATED NATURAL ZEOLITE AND ACTIVATED CHARCOAL AS ADSORBENT TO IMPROVE THE QUALITY OF WASTE COOKING OIL

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Abstract

Cooking oil which is exposed to high temperatures of up to 200 °C during the cooking process, leads to the formation of hazardous substances that are potentially dangerous to human health. However, people sometimes use the same cooking oil repeatedly without considering the negative effects that it causes. In this work, we investigated the use of two different types of adsorbent namely activated charcoal and activated zeolite sequentially to improve the quality of waste cooking oil (WCO) using the adsorption method. It was found that for 30 mL of WCO, the optimum dose of adsorbent was 7.5 g and the optimum contact time was 20 minutes. When these two types of adsorbent were applied sequentially for the purification of WCO at the optimum conditions, the result obtained indicated the lower value of the acid number, peroxide number, viscosity, and water content, compared to the WCO that treated only with a single type of adsorbent.

Keywords: waste cooking oil, sequent adsorption, charcoal, zeolite

Introduction

It is regarded as a commonplace that the Indonesian people and probably in the other developing countries, the same cooking oil is used again and again to prepare the food to save cost, and frequently carrying out in roadside food stall, hotels and restaurant to save the expenditure and make the profit without knowing the adverse effect of reusing of repeatedly cooking oil[1]. Waste cooking oil (WCO) which is exposed to high temperatures of up to 200 °C during the cooking process, leads to the formation of hazardous substances that are potentially dangerous to human health. WCO can also have a detrimental effect on the environment if discarded to the environment without proper treatment[2]. Therefore, it is urgent to select a suitable way to handle the WCO before it is used again or wasted in the environment. The quality of cooking oil is usually decreases due to the exixtence of impurities derived from hydrolysis of triglycerides, oxidation, and dimerization or polymerization during frying[3]. The existence of the impurites can be determined using several parameters such as acid number, peroxide number, viscosity, water content and so on. Therefore its quality can be improved again by removing the impurities contained in the

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WCO, reflected by the value decreasing of each parameter. The treated WCO can also be used as raw materials for the production of biodiesel[4].

Several techniques can be employed to remove the impurities from the WCO such as extraction[5], adsorption[6], and membrane technology[7]. Because of the benefits such as low cost, high efficiency, simplicity, and environmentally friendly, adsorption is the more preferred method compared to the others. In addition, in the adsorption technique, many types of adsorbent can be used such as zeolite, bentonite, calcium silicate, SiO_2, $Al(OH)_3$, aluminum silicate, alumina, silica and citric acid, porous rhyolite, activated carbon, and so on. These adsorbents are easily found in our neighborhood.

The use of a single adsorbent in the adsorption process has been widely used and gives good results as well. However, the disadvantage of using a single adsorbent is that adsorbents with a certain degree of polarity and pore size are only able to adsorb adsorbents with a suitable degree of polarity and size. Even though, the impurities contained in the WCO are probably in the wider ranges of polarity and pore size. Therefore, by combining two or more adsorbents that have differences in polarity and pore size, the range of adsorbable impurities contained in the WCO is also wider. In this work, natural zeolite and coconut shell charcoal activated with NaCl was used as a consecutive adsorbent to improve the quality of WCO, based on the parameters of ACID number, peroxide number, viscosity, and water content.

Zeolite is a natural porous mineral in which the partial substitution of Si^{4+} by Al^{3+} results in an excess of negative charge which is compensated by alkali and alkaline earth cations (Na^+, K^+, Ca^{2+}, or Mg^{2+})[8]. Besides the negative charges, zeolite also has a pore size between 0.2-1.0 nm, therefore zeolite has the character both as an ion exchanger and as molecular sieve[9]. On the other hand, charcoal is a material with high porosity, consisting of a hydrophobic graphene layer as well as hydrophilic surface functional groups, making them beneficial for sorption[10]. However, both natural zeolite and charcoal have a relatively low adsorption capacity as their cavity is usually filled with impurities. Therefore, it is important to wash these adsorbents with a certain solvent in order to remove the impurities from the cavity. In our previous work[11], we found that the surface area of the natural zeolite activated with NaCl 0.3 M (26.721 m2/g) was almost indifferent to that which was activated with HCl 0.5, 1.0, and 3.0 M (26.902, 26.850, and 26.384 m^2/g). In this work, we choose NaCl 3.0 as an activator agent as it is a non-toxic agent compared to the HCl.

Result and Discussion

Preparation of adsorbent

Both natural zeolite and charcoal used were those that pass the 250 mesh sieve. This small particle size allows the increase of the contact area both with the activating agent and with the adsorbate. This process produced the activated adsorbent (activated zeolite and activated charcoal).

Determination of adsorbent's surface area

One of the important parameters affecting the ability of an adsorbent to adsorb an adsorbate is surface area. In this experiment, the surface area was determined using methylene blue (MB) that can be conducted in three steps.

Determination of maximum wave length of MB

The maximum wavelength of a compound is the wavelength where the absorbance is maximum. At this point, the sensitivity of absorbance measurement is the highest. Therefore, the measurement of absorbance in the next step will be done at this wavelength. The result of he determination of the maximum wavelength is shown in Figure 1.

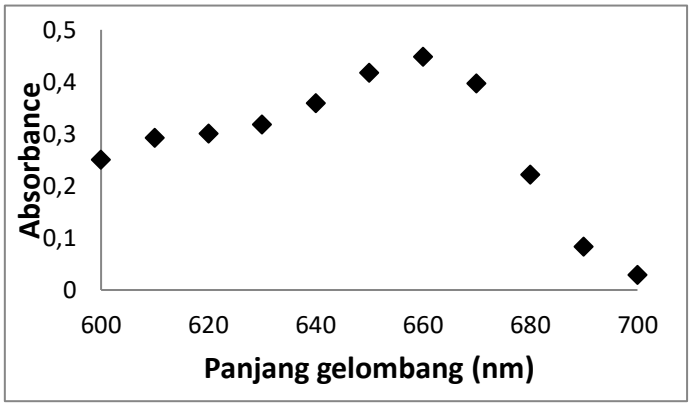

Figure 1. Determination of maximum wavelength of MB

Based on Figure 1, it is known that the maximum wavelength of MB is 660 nm. This wavelength will be applied in the preparation of the calibration curve and measurement of the MB solution after contacted with the adsorbent.

Preparation of calibration curve

The calibration curve of MB was prepared by measure the absorbance of MB solution at various concentrations at 660 nm of wavelength. The result of the measurement is presented in Figure 2.

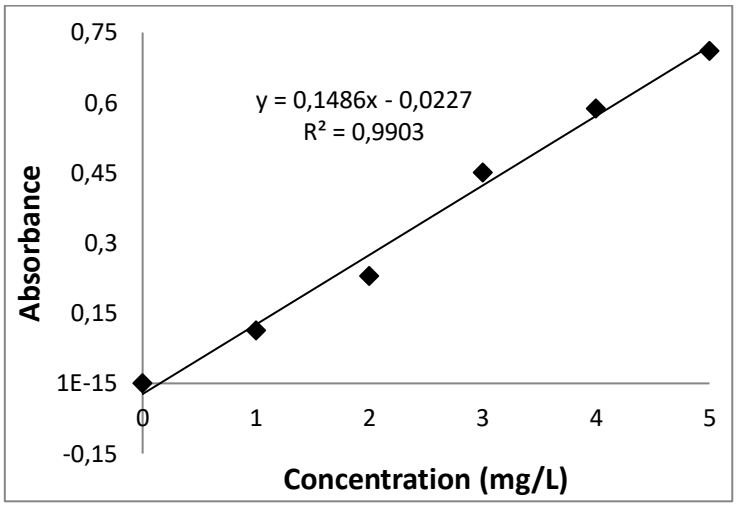

Figure 2. Calibration curve of MB

Based on the curve presented in Figure 2, the linear regression equation (y=0.1486x -0.227) can be derived and this equation will be employed to calculate the concentration of unadsorbed MB in the filtrate after contact with the adsorbent.

Effect of contact time on the adsorption of MB

MB with a concentration of 50 mg/L was used to evaluate the effect of contact time on adsorption. Due to the interaction with the adsorbent, MB was partially adsorbed by the adsorbent. The unadsorbed MB was measured and the adsorbed MB can be calculated from its difference with the initial concentration such as shown in Figure 3.

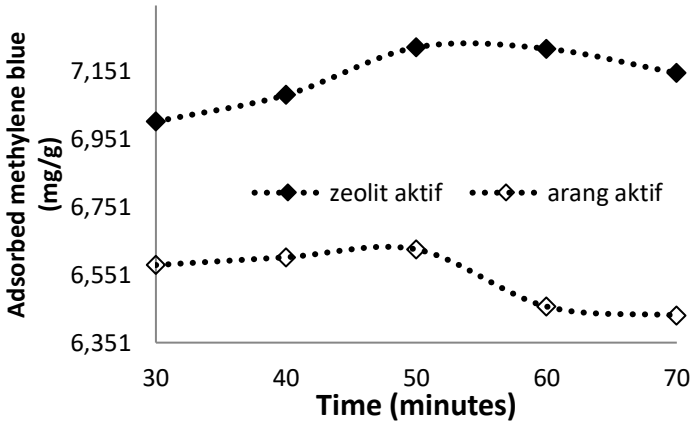

Figure 3. Effect of the contact time on the adsorption of MB

It can be seen from Figure 3 that, optimum contact time for both adsorbents was achieved at 50 minutes with the adsorbed MB was 6.974 (activated charcoal) and 7.219

mg/g (activated zeolite) respectively. At the contact time of higher than 50 minutes, the amount of adsorbed MB decreased. It is because the MB already bound to the adsorbent is released into the solution again due to the stirring process.

Determination of the adsorbent's surface area

Based on the adsorbed MB presented in Figure 3, the surface area of each adsorbent can be evaluated using equation 1.

$$S = \frac{X/m \; x \; N \; x \; a}{Mr \; x \; 1000 \; mg/g} \qquad (1)$$

where S: the surface area (m^2/g), X/m: adsorbed MB (mg MB/g adsorbent), N: Avogadro'snumber (6.02×10^{23} $mole^{-1}$), a: the surface area of adsorbent that can be covered by one molecule of MB (197×10-20 m^2) and a: molecular weight of MB (320.5 g/mole). The surface area of adsorbent at each contact time is presented in Table 1. As a comparison, the surface area of the adsorbent without activation[12] is also presented in this Table.

Table 1. The surface area of adsorbent at each contact time

Time (minutes)	Surface area (m^2/g)			
	Activated charcoal	**Unactivated charcoal**	**Activated zeolite**	**Unactivated zeolite**
30	25.248	25.496	26.421	25.581
40	25.255	25.558	26.450	**26.338**
50	**25.810**	**25.586**	**26.977**	25.775
60	25.784	25.295	26.980	25.775
70	25.792	25.537	26.957	25.896

Data in Table 1 shows that the washing of adsorbent with NaCl 3.0 M, increases the surface area of the adsorbent. It is because of the dissolution of impurities from the cavity and the surface of the adsorbent. This adsorbent was then applied in the purification of WCO.

Determination of optimum condition for adsorption

The adsorption process is influenced by several factors. However, in the case of the practical application for improving the quality of WCO, there are two most important parameters affecting the process, namely adsorbent dose and contact time. In this experiment, the optimum condition was decided by visual observation of the color of WCO after contact with the adsorbent.

Dose of adsorbent

The optimum dose of adsorbent is the dose of adsorbent resulting in the highest level of clarity. In our previous work[13], it is found that the optimum dose of activated zeolite for purification of WCO was 7.5 g. The result of interaction between activated charcoal and WCO is shown in Figure 4.

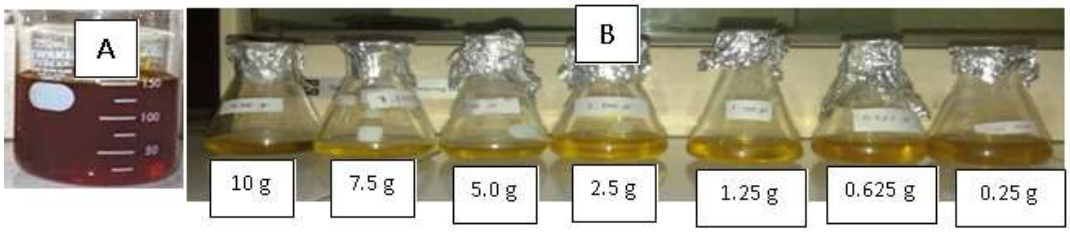

Figure 4. The purity level of WCO (A) before treatment, (B) after treatment at a various dose of activated charcoal

Figure 4 indicated that a dose of 7.5 g of activated charcoal contacted with 30 mL of WCO for 30 minutes resulted in the product with the highest clarity.

Contact time

The optimum contact time means the time needed by WCO to interact with adsorbent resulting in the WCO with the highest clarity. It is determined by interacting with a 7.5 g of adsorbent with 30 mL of WCO at various times. In our previous work (13), we found that by use of activated zeolite as adsorbent it was needed 20 minutes to reach the highest purity. Therefore, in this work, we only investigated the effect of contact time using activated charcoal as an adsorbent. The result of experiment is presented in Figure 5.

Figure 5. Effect of contact time on the purity of WCO

From the results shown in Figure 5, it can be seen that the highest WCO purity is obtained even from the 20th minute. The addition of contact time relatively did not change the purity of WCO.

Application of the sequent adsorption for purifying the WCO

The optimum conditions found in the previous experiment were then applied to purify the WCO using both types of adsorbents sequentially. The optimum conditions found were 7.5 g of activated zeolite and activated charcoal respectively, with 20 minutes of stirring. At first, 7.5 g of activated charcoal interacted with 30 mL of WCO for 10 minutes. The mixture was filtered and the filtrate was contacted once again with activated zeolite for 10 minutes. The filtrate of the second treatment was analyzed for several parameters of oil quality determinants such as ACID number, peroxide number, viscosity, and water content. As a

comparison, the experiment was also conducted using the same adsorbent at the first and second treatment. The result of experiment is shown in Table 2.

Table 2. Quality of WCO after interacted with several types of adsorbent

Parameters	Unused oil	WCO	Type of adsorbent		
			AC - AZ	AC – AC	AZ - AZ
Acid number (mg KOH/g)	0.223	2.618	0.244	0.336	0.498
Peroxide number (meq/kg)	1.061	11.800	1.866	4.000	3.200
Viscosity (mm^2/s)	30.960	71.853	31.997	36.630	36.30
Water content (% b/b)	0.407	1.128	1.000	1.093	1.058

AC: activated charcoal, AZ: activated zeolite

The result showed in Table 2 indicate that the WCO treated with two different types of adsorbent (AC-AZ) sequentially, produced a lower value of interested parameters, compared to the WCO that was interacted with the two same types of adsorbent (AC-AC, AZ-AZ) sequentially. We also measured the interesting parameters of oil that have not been used for cooking (unused oil). The result shows that the value of each parameter is too close to the value of the treated WCO.

Conclusion

It was experimented with the use of activated charcoal and activated zeolite, sequentially in order to improve the quality of WCO. We found that for 30 mL of WCO, the optimum dose of adsorbent was 7.5 g and the optimum contact time was 20 minutes. When these two types of adsorbent were applied for the purification of WCO at the optimum conditions, the result obtained indicated the lower value of the acid number, peroxide number, viscosity, and water content, compared to the WCO that treated only with a single type of adsorbent.

References

1. Deshmukh, R.K., 2019, The Effect of Repeatedly Cooking Oils on Health and Wealth of a Country: A Short Communication, *J Food Process Technol*, Vol.10 Iss.8 No:1000807, 1-4. doi: 10.35248/2157-7110.19.10.807.
2. Osseo, L.S., Caputo, G., Gracia, I. & Reverchon, E., 2007, Continuous Fractionation of Used Frying Oil by Supercritical CO_2, *Journal of the American Oil Chemists' Society*, Vol. 81(9), pp. 879-885.
3. Choe, E. & Min, D., 2007, Chemistry of Deep Fat Frying Oils, *Journal of Food Science*, Vol. 72(5), pp. R77-R86.
4. Ullah, Z., Bustam, M.A. & Man, Z., 2015, Biodiesel Production from Waste Cooking Oil by Acidic Ionic Liquid as A Catalyst, *Renewable Energy* Vol. 77, pp. 521-526.
5. Rincón, J., Martínez, F., Rodríguez, L. & Ancillo, V., 2011, Recovery of Triglycerides from Used Frying Oil by Extraction with Liquid and Supercritical Ethane, *The Journal of Supercritical Fluids*, 56(1), pp. 72- 79.

6. Wonglamom, J. & Rakariyatham, N., 2014, Recovery of Used Vegetable Frying Oil by Two Step Adsorbents, *26th Annual Meeting of The Thai Society for Biotechnology and International Conference*, pp. 330-337.
7. Miyagi, A., Nabetani, H. & Subramanian, R., 2011, Purification of Crude Fatty Acids Using A PDMS-Based Composite Membrane, *Separation and Purification Technology*, 77(1), pp. 80-86, 2011.
8. Doula, M.K., 2006, Removal of Mn^{2+} ions from drinking water by using Clinoptilolite and a Clinoptilolite Fe oxide system, *Water Research* 40 (17), 3167–3176.
9. Tsitsishvili, G.V., Andronikashvili, T.G., Kiriov, G.N. dan Filosova, L.D., 1992. *Natural Zeolites*, Ellis Horwood, NewYork 1-14.
10. Patel, H., 2018, Charcoal as an adsorbent for textile wastewater treatment, *Separation Science and Technology*, 53(17), 2797-2812, DOI: 10.1080/01496395.2018.1473880
11. Ola, P.D., Djami, A.G. and Wogo, H. E., 2013, The Use of Activated Natural Zeolite as an Adsorbent on Removing of Rhodamine B from Aqueous Solution, *J Applied Chem. Sci.* Vol. 2 Issue 2; 252-258.
12. Juandi, D., 2015, Peningkatan Kualitas Minyak Jelantah Menggunakan Zeolit Alam dan Arang Tempurung Kelapa Secara Simultan, Skripsi Jurusan Kimia Fakultas Sains dan Teknik, Universitas Nusa Cendana, Kupang.
13. Nesimnasi, A.N., Ola, P. D., 2012, Pemanfaatan Zeolite Alam untuk Meningkatkan Kualitas Minyak Goreng Bekas, *Jurnal MIPA Penelitian dan Pengembangan* Vol. 12 No. 1; 59-68.

Materials and Method

Materials

Natural zeolite from Ende-Flores, Coconut shell charcoal, sample of waste cooking oil (WCO) obtained by using the “bimoli” brand oil for frying three times for 15 minutes, CH_3COOH glacial, Chloroform, NaCl, KI, $Na_2S_2O_3$, KOH, Alcohol and phenolphthalein.

Procedure

Adsorbent preparation

Natural zeolite was cleaned and crushed to be powder. The powder of natural zeolite was sieved with a 250 mesh sieve. The powder that passed the sieve was used as an adsorbent. The coconut shell was cleaned and burned to be charcoal. The charcoal produced was crushed to be a powder which was then sieved with a 250 mesh sieve. The powder that passed the sieve was washed with water until the filtrate of the washing was clear. The washed powder was then dried.

A total of 200 g adsorbent powder was immersed in 600 mL NaCl 3 M for 30 minutes while stirring. The results obtained were washed with distilled water until neutral. Then dried in an oven at a temperature of 110 ^oC for 2 hours. This dried powder of zeolite and charcoal hereinafter referred to as activated zeolite and activated charcoal and was used as an adsorbent.

Determination of surface area of adsorbent

Methylene blue solution of 50 mg/L was prepared and diluted it to be 2.0 mg/L. The absorbance of this solution was measured at a wavelength of 500-700 nm with spectrophotometer UV-Vis. This procedure produced the maximum wavelength. In order to construct the calibration curve of methylene blue, the standard solution of methylene blue with concentrations of 1.0, 2.0, 3.0, 4.0, and 5.0 mg/L were prepared. The absorbance of those standard solutions was measured at the maximum wavelength.

A 0.1 g of activated adsorbent was mixed with 15 mL of methylene blue 50 mg/L. The mixture was stirred at various times (30, 40, 50, 60, and 70 minutes). The mixture was filtered and the absorbance of the filtrate was measured at the maximum wavelength. The amount of adsorbed methylene blue can be estimated from the difference between the initial concentration of methylene blue and the unadsorbed methylene blue which was the concentration of methylene blue in the filtrate. The amount of methylene blue adsorbed by adsorbent can be used to calculate the surface area of the adsorbent.

Determination of optimum condition

A 30 mL of WCO was mixed with activated adsorbent at various doses (0.25, 0.625, 1.25, 2.50, 5.00, 7.50, and 10.00 g) and was stirred for 30 minutes. The mixture was filtered and the filtrate produced was visually observed the level of clarity. The optimum dose obtained was used to investigate the optimum contact time with a similar procedure.

Application of the sequent adsorption for purifying the WCO

A 30 mL of WCO was mixed with an optimum dose of activated charcoal. The time needed to stir the mixture was half of the optimum time obtained in the previous experiment. The mixture was filtered and the filtrate was mixed again with an optimum dose of activated zeolite. The mixture was stirred with the mixing time was the same as the mixing with activated charcoal. The mixture was filtered and the filtrate obtained was analyzed its acid number, peroxide number, viscosity, and water content. The same procedure was repeated with the first and second mixing of adsorbent and WCO using the same type of adsorbent.

Analysis of oil quality parameters

Acid number

Weigh 2.5 g of cooking oil in an Erlenmeyer. Add 12.5 mL of alcohol 95 %, heated for 10 minutes in a water heater while stirring. After the solution gets cold, add 2 drops of phenolphthalein indicator and titrate using KOH 0.1 until pink color is observed. The number of acids can be calculated using this equation:

$$Acid\ number\ = \frac{\text{mL KOH} \times \text{M KOH} \times \text{BM fatty acid}}{\text{mass of oil}}$$

Peroxide number

Into a 5 g of oil, add a 30 mL mixture of glacial acetic acid and chloroform in a ratio of 3:2 and close the mixture. The mixture was then shaken until the oil was soluble. Added 0.5 mL of saturated KI into the mixture while being shaken. The solution is let stand for 1 minute, stirred at least 3 times for 1 minute, and immediately add 30 mL of distilled water. Into the mixture added 1-2 drops of 1% starch and then titrated with 0.01 N Na2S2O3 solution dropwise until the solution was colorless. The peroxide number was calculated using this equation:

$$Peroxide\ number\ = \frac{(Vs - Vb) \times N \times 1000}{Sample\ weight}$$

Vb is the volume of $Na_2S_2O_3$ needed for titration of the blank solution, Va is the volume of $Na_2S_2O_3$ needed for titration of the sample solution and N is the normality of $Na_2S_2O_3$.

Water content

Water content was measured using gravimetric method.

Viscosity

Determination of the viscosity of oil using an Ostwald viscometer.