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Isothermal Adsorption of Used Cooking Oil Purification Using Avocado Seed Adsorbent

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Abstract

High consumption of cooking oil has an impact on the availability of used cooking oil. Used cooking oil can cause pollution if the processing is not sound. So we need an alternative as a solution for handling cooking oil waste. Adsorption using avocado seed adsorbent is the choice because the morphological structure and other characteristics meet the specifications for the adsorption of used cooking oil. This study aimed to determine the acid number, viscosity, density and isothermal adsorption from avocado seeds as an adsorbent in used cooking oil. The method used was by varying the adsorbent doses of 100, 200 and 300 mg L^{-1} with contact times of 30, 60, 90, 120 and 150 minutes. Adsorption was carried out at a temperature of 70ºC and a stirring speed of 200 rpm. The results obtained for the acid numbers at various adsorbent doses at 150 minutes reached 6.22, 4.98 and 3.12 mg KOH g^{-1}. Viscosity at different adsorbents reached 54.2, 46.23 and 45.44 $mm^2\ s^{-1}$, while the density reached 898.92, 897.17 and 896.55 kg m^{-3}. Langmuir isothermal adsorption obtained R^2 value in the equation reached 0.9365 and Freundlich reached 0.9496, so the Freundlich equation model is more recommended for use in the adsorption process because the regression value is close to 1.

INTRODUCTION

The need for cooking oil for the Indonesian people will reach 5.7 million litres for all allocation categories in 2022 and is projected to increase yearly. The demand for households is estimated at 3.9 million litres consisting of 1.2 million litres of premium packaging, 231 litres of simple packaging and 2.4 million litres of bulk (Irmanelly et al., 2022). This figure shows the availability of used cooking oil which is very large. Used cooking oil is a waste from the use of cooking oil is used repeatedly, causing the quality of the cooking oil to decrease and changes in the physicochemical properties of the oil (Bangar et al., 2022). These changes resulted in the colour of cooking oil becoming dark, thick, smelly and foaming, as increased water content, peroxide value and free fatty acids caused by repeated heating. Repeated heating at 160-180ºC accompanied by water and air contact causes degradation, oxidation, polymerization, hydrolysis and reactions with metals (Cárdenas et al., 2021). Excessive use of used cooking oil can cause cancer, deposition of fat in blood vessels and reduce brain intelligence. Apart from impacting human health, the used cooking oil produced can damage and

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cause environmental pollution (García-Vargas et al., 2020). This background encourages an alternative solution using the adsorption method to improve the quality of used cooking oil with the direct contact technique using an adsorbent. Used cooking oil that has gone through an adsorb process has a higher economic value and is one of the ingredients for biodiesel (Rodriguez et al., 2022). The key to the success of the adsorption process lies in selecting the proper adsorbent. In this study, an adsorbent from avocado seed powder was used because it has a specific surface area, pore volume, absorption ability, and high separation efficiency (Cheikhyoussef & Cheikhyoussef, 2022). They choice of avocado seeds as adsorbents because they have a water content of 12.67%, ash content of 2.78%, minerals of 0.54%, the starch content of 23%, so avocado seeds are effectively used as adsorbents in used cooking oil (Tefera et al., 2020). FTIR Spectroscopy analysis on avocado powder has five main functional groups, namely carbonyl groups (C=O), hydroxyl groups (O-H), amide groups (N-H), alkene groups (C=C) and nitro groups (NO_2). Functional groups containing amino acids cause charged surfaces to bond to each other through peptide bonds between the carboxylic and amine groups (Solangi et al., 2021).

Isothermal adsorption analysis is important in the process of improving the quality of used cooking oil using avocado seed adsorbents. Isothermal adsorption shows the ability of adsorbate molecules to interact with the adsorbent surface under equilibrium conditions (Majd et al., 2021). The Langmuir adsorption isotherm is most widely used to describe the adsorption equilibrium of the liquid phase. Langmuir is often used because of its simple form (Das et al., 2020). Langmuir was the first to propose the theory of coherent adsorption onto flat surfaces based on kinetics (Işık & Uğraşkan, 2021). The assumptions used by Langmuir to develop the isothermal adsorption equation include a homogeneous solid surface with constant adsorption energy at all active sites, adsorption on the surface is localized and the active adsorption sites can only accommodate one molecule. In addition to Langmuir, the Freundlich isothermal adsorption equation is used for adsorption in the liquid phase (Muluh et al., 2017). The weakness of Freudnlich can not be used in a concentration range that is too wide. From this background, this study aimed to determine the effectiveness of avocado seed adsorbents and to analyze isothermal adsorption in refining used cooking oil

MATERIALS AND METHOD

Tools and Materials

The equipment used in this study included a Miyako blender, analytical balance (Ohaus), bench furnace (BF-01), magnetic stirrer, filler, clamp, centrifuge tube (Merck), centrifuge (Kaida), 100 mesh sieve, stative and clamps, hot plate, desiccator (pyrex), measuring cup (Pyrex), beaker (pyrex), Erlenmeyer (pyrex), funnel (pyrex), separating funnel (pyrex), porcelain mortar (pyrex), Ostwald Viscometer, IR Prestige Fourier Transform Infrared Shimadzu Spectrophotometer, Scanning Electron Microscopy (SEM) ASTM E1508. The materials used include avocado seed, cooking oil, methanol Merck 1.06009.2500, chloroform Merck 1.02445.2500, potassium hydroxide Merck 1.05033.0500, phenolphthalein indicator Merck 1.07233.0100, hydrochloric acid Merck 1.00317.2500, one lab water one, Whatman filter paper No. 42, distilled water.

Methods

The research procedure consisted of preparing used cooking oil, preparing avocado seeds, and adsorption of used cooking oil using avocado seed adsorbents.

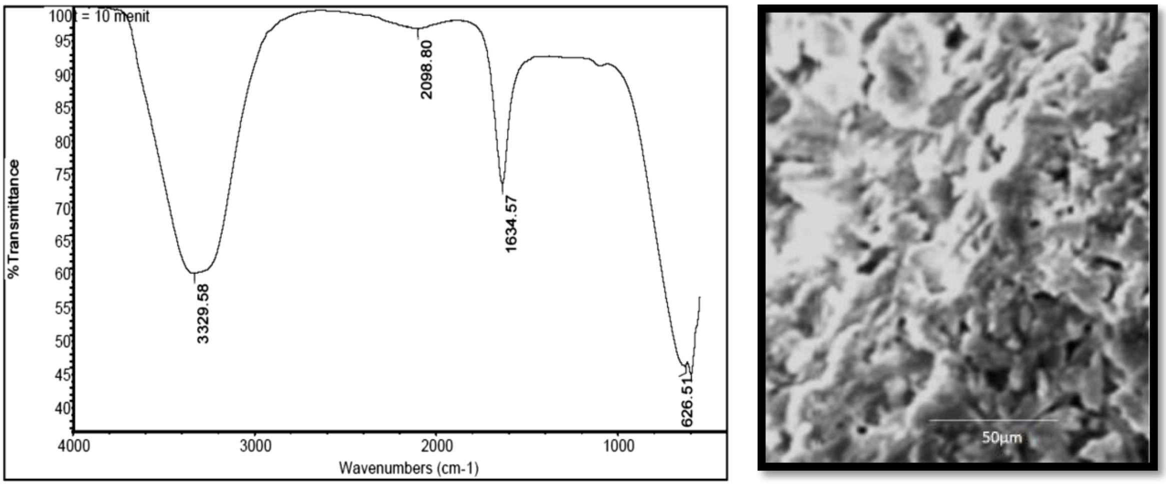
Cooking Oil and Avocado Seeds Preparation

Used cooking oil from three times frying was filtered to remove solid impurities. The filtered oil was deposited for 24 hours to precipitate the impurities that were also filtered. The top of the oil was separated as feed in the adsorption process and acid number test.

Selected avocado seeds that were old washed crushed using a blender until smooth, and then sifted using a 100 mesh sieve. Avocado seed powder was put into a beaker and activated using 1 M hydrochloric acid. The ratio of adsorbents was; hydrochloric acid (w/v) of 1:2 and heated for 2 hours. After heating, the solution was washed using distilled water to remove residue and neutralize the pH. Avocado seed adsorbents were dried in an oven at 60°C for 24 hours and then cooled in a desiccator.

Used Cooking Oil Adsorption

Fifty grams of used cooking oil was heated to a temperature of 70°C, added avocado seed



(a) (b)

Figure 1.(a) FTIR of functional group and (b) SEM of avocado seed adsorbent

adsorbent was at a dose of 100 mg L^{-1}, 200 mg L^{-1} and 300 mg L^{-1}, then stirred for 30, 60, 90, 120 and 150 minutes with stirring speed 200rpm. The adsorption results were filtered and analyzed for acid number, viscosity, density, and isothermal adsorption.

Acid Number Analysis

Oil weighing 0.5 grams was added to chloroform and ethanol (ratio 1:1), three drops of phenolphthalein indicator and then titrated using 0.1 M potassium hydroxide. The equation of the acid number was affected by the molecular weight of KOH, the volume of KOH (V) and the normality of KOH (N) according to Eq. (1) (Rodriguez et al., 2022).

$$\text{Acid Number} = \frac{\text{BM KOH x V KOH x N mg KOH}}{\text{Sample Volume}} \quad (1)$$

Viscosity and Density Analysis

The Ostwald viscometer was used at a temperature of 40ºC with a value of 0.09841mm^2 s^{-2}, and then the flow time was recorded. Density measurement using a 5 ml pycnometer.

Langmuir Adsorption Isothermal Analysis

Langmuir adsorption isothermal defines the maximum adsorbent capacity due to a single adsorbate layer on the adsorbent's surface according to Eq. (2) (Majd et al., 2021).

$$\frac{C_c}{q_c} = \frac{1}{K_L\, q_m} + \frac{C_c}{q_m} \quad (2)$$

Cc is equilibrium concentration (mg L^{-1}), q_c is adsorbed adsorbate at equilibrium (mg g^{-1}), KL is Langmuir constant (L mg-1), and qm is adsorbed capacity (mg g^{-1}). On the Langmuir adsorption isothermal graph with $1/q_c$ as the y-axis and $1/C_c$ as the x-axis will form the line equation y = bx + a, which determines the value of q_m and K_L, where q_m is 1/a and K_L is the value of b.

Freundlich Adsorption Isothermal Analysis

The Freundlich adsorption isothermal shows heterogeneous adsorption sites according to Eq. (3).

$$\log q_c = \log K_F + \frac{1}{n}\log C_c \quad (2)$$

C_c is the equilibrium concentration (mg L^{-1}), K_F and n is the Freundlich constant. From the data, log q_c as the y-axis and log C_c as the x-axis. The graph is a linear line with a slope of 1/n and an intercept log K_F.

RESULTS AND DISCUSSION

Functional groups and morphology of avocado seed adsorbents

Determination of the functional groups contained in the avocado seed adsorbent was analyzed using the Fourier Transform Infrared (FTIR) at a wavelength of 500 – 4000 cm^{-1}. Figure 1 (a) shows the O-H spectra at a wavelength of 3329.58 cm^{-1}, an absorption peak area of 2098.80 cm^{-1} produces C-H chain vibrations, an absorption area of 1634.57 cm^{-1} produces C=C vibrations and an absorption area of 625.51 cm^{-1} produces a peak C-O vibration. Determination of the functional groups produced in the spectra indicates that there is a polymer structure of tannins present in avocado seeds. Tannins are secondary metabolites of the polyphenol group, in which the functional groups O-H and C=O interact with positively and negatively charged particles found in used cooking oil. Other research states that the presence of O-H, C-H and C-O functional groups comes from 22% of the fat found in avocado seeds, where the structure in the fat is in the form of ethanol and carboxylic acids, while the C=C group comes from lignin (García-Vargas et al., 2020).

The main feature of an effective adsorbent is a well-developed pore structure. The pore structure and characterization can be analyzed using SEM to show an overview of the adsorbent surface topography. Based on the results of the SEM test, in Figure 1(b) it is shown that the avocado seed adsorbent has gaps and cavities between the particles. In the adsorption process, used cooking oil fills the surface of the adsorbent and fills the empty holes so that there is an interaction between the adsorbent and the cells. The adsorbent powder of avocado seeds has an oval shape with tight bonds and the same size and is homogeneous. The granules are smooth and not broken (Cheikhyoussef & Cheikhyoussef, 2022).

Effect of variations in adsorbent dosage and adsorption time on the acid number, viscosity and density

At the time of preparation, 50 grams of used cooking oil was heated to a temperature of 50°C, added avocado seed adsorbent at a dose of 100 mg L^{-1}, 200 mg L^{-1} and 300 mg L^{-1} then 0.5 gram sample was taken for analysis of acid number, viscosity, density and isothermal adsorption.

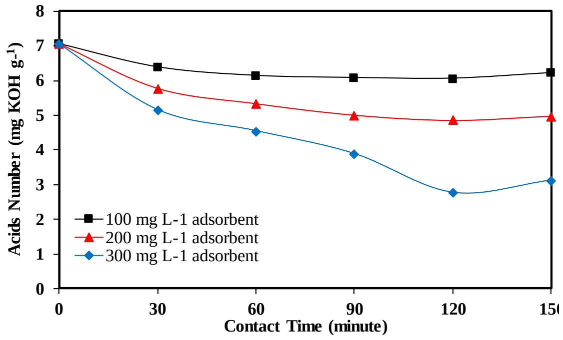


Figure 2. Acid number at different adsorbent doses and contact time.

Figure 2 shows the effect of the avocado seed adsorbent dose and the contact time of the adsorption process on the acid number. The acid value of used cooking oil before adsorption was 7.06 mg KOH g^{-1}. At various doses of adsorbent 100 mg L^{-1}, 200 mg L^{-1}, 300 mg L^{-1}, the lowest adsorption rate was obtained at a dose of 300 mg L^{-1} with an acid value of 2.77 mg KOH g^{-1} at 120 minutes contact time. The highest acid number at the adsorbent dose of 100 mg L^{-1} was 6.39 mg KOH g^{-1}. The acid number decreased from 30 to 120 minutes from the three doses of adsorbent. Based on the results of the study, the mass of the adsorbent and contact time affected the acid number in the adsorption of used cooking oil. The greater the mass of the adsorbent, the smaller the acid number after adsorption. The decreased levels of acid number occur because avocado seed powder can absorb free fatty acid molecules due to the presence of cellulose. Cellulose contains many hydroxyl groups (-OH) which are electronegative (basic) and polar. These properties can interact with the carboxylic acid group (COOH) of free fatty acids which are electropositive (acidic) and polar (Waluyo, et al., 2020). Increasing the mass of the adsorbent causes more collisions between the adsorbate and the active surface of the adsorbent. The longer the adsorption time, the longer the contact between the adsorbate and the adsorbent occurs so that the absorption of the acid number increases (Mohamed et al., 2022). However, at the adsorption contact time of 150 minutes, there was an increase in the acid number from the acid number at 120 minutes. This was distributed because when the used cooking oil adsorption time lasted 150 minutes, the adsorbent was saturated to release free fatty acids. So that the effective time in this study for the adsorption of used cooking oil using an adsorbent is 120 minutes. The optimal operating time is different for the type of adsorbent, it also depends on the duration of the adsorbent activation. Another study explained that the use of bagasse adsorbent takes 48 hours to reduce its acid number to 15% for the same temperature (50°C). Under the same operating conditions, activated carbon has the same optimal operating time as the avocado seed adsorbent (120 minutes).This proves that the avocado seed adsorbent is more effective than bagasse adsorbents and same effective with activated carbon (Waluyo et al., 2020).

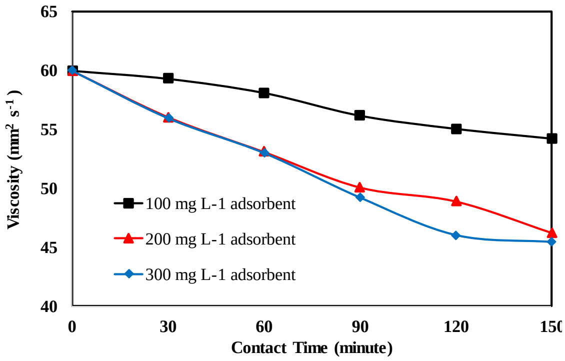


Figure 3. Viscosity at different adsorbent doses and contact time.

Figure 3 shows the relationship between contact time and viscosity at various adsorbent doses. Used cooking oil has a shelf life of approximately 1 month without further use. The viscosity of used cooking oil before being adsorbed was 60.02 mm^2 s^{-1} and decreased after being adsorbed to 45.44 mm^2 g^{-1} at an adsorbent dose of 300 mg L^{-1}. This decrease was due to the storage period affecting the viscosity in the presence of an oxidation reaction resulting in the degradation of the compound. Oxidation reactions occur with the formation of fatty acid radicals and then the formation of long chains in alkanes resulting in an increase in viscosity (Rodriguez et al., 2022). The viscosity of used cooking oil is greater than that of fresh oil. This happens because the density is lower and has undergone heating so that the friction in the inner layers of the oil is significant so that the viscosity increases. As a result of heating, there is an accumulation of more and more water and oil degradation so that the viscosity increases due to the formation of polymers (Muluh et al., 2017). The presence of impurities also causes the increase in the viscosity of used cooking oil and hydrolysis reactions occur as a result of which the molecular weight of the oil increases and the spindle friction becomes heavier. The viscosity of used cooking oil increases with the presence of O-H group bonds in triglycerides. The more adsorbent doses cause the number of particles that are affected by Van der Waals forces between the surface of the adsorbent and adsorbate adsorbed on used cooking oil. The existence of micro-adsorbent pores causes capillary phenomena and potential energy differences between the avocado seed adsorbent, contact time and used cooking oil (Işık & Uğraşkan, 2021).

Figure 4 shows the relationship between adsorbent dose and contact time on the density of used cooking oil. The density of used cooking oil before being adsorbed reached 912.12 kg m^{-3}. Density decreased with the length of contact time and adsorbent dose. The density reached 896.55 kg m^{-3} at an adsorbent dose of 300 mg L^{-1}. Avocado seed adsorbent compared to activated carbon adsorbent, under the same conditions a decrease in density also occurred from 912.12 kg m^{-3} to 902.22 kg m^{-3}. The density of the oil has decreased because the adsorbent can adsorb used cooking oil well so that the impurities contained in used cooking oil decrease quite a lot, the molecular bonds in the oil can be reduced a lot, and are able to remove the smell and color of the oil. In addition, the longer the adsorption time, the higher the absorption of impurities in used cooking oil. The absorption of these impurities is affected by the stirring temperature, where the adsorption process using high temperatures can cause an increase in density. The water content contained in used cooking oil after the heating process can increase the molecular weight of used cooking oil which also increases the density of used cooking oil. If there is an increase in the density of the oil, it is due to the incomplete removal of the initial oil impurities so that it can increase the density of the oil (Miskah et al., 2018).

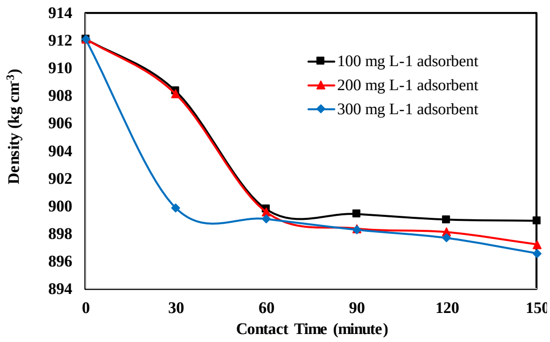


Figure 4. Density at different adsorbent doses and contact time

Langmuir and Freundlich adsorption isotherms

The change in the concentration of used cooking oil by the adsorption process was carried out by determining the Langmuir and Freundlich isotherms as a straight-line equilibrium curve. The various factors that influence the adsorption of used cooking oil using avocado seed adsorbents cause different isothermal adsorption patterns, so it is necessary to evaluate the type of adsorption and the phenomena that occur (Majd et al., 2021). Experimental data will be used to characterize the adsorption equilibrium.

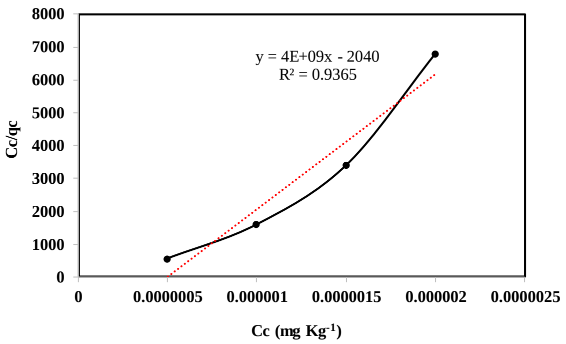


Figure 5. Langmuir Isothermal Curves

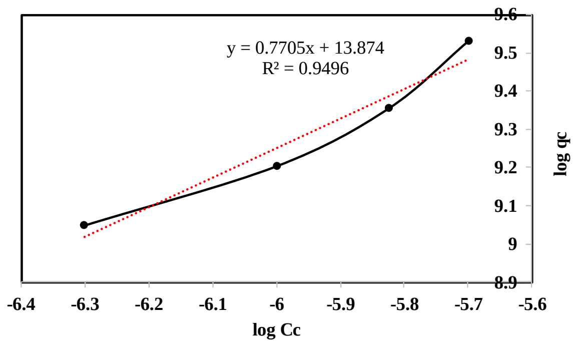


Figure 6. Freundlich Isothermal Curves

Figures 5 and 6 show that in the adsorption process of used cooking oil using 300 mg L^{-1} avocado seed adsorbent, the amount of used cooking oil adsorbed by the adsorbent increases linearly with increasing equilibrium concentration of C_c, and this phenomenon corresponds to the dynamic thermodynamic boundary conditions. The amount of adsorbate that is adsorbed reaches the saturation capacity. Using the Langmuir and Freundlich isotherm equations, q_c is the amount of adsorbate per mass, and C_c is the equilibrium concentration of the adsorbate. For the Langmuir equation, the value of $R^2 = 0.9365$ is obtained, and for the Freundlich equation, the value of $R^2 = 0.9496$. Based on the linear value, it was shown that the adsorption process of used cooking oil used avocado seed adsorbent in this study used the Freundlich equation. This is evidenced by the value of the coefficient of determination R, which is closest to the number 1 (Majd et al., 2021).

CONCLUSION

Adsorbents with high capacity are urgently needed to deal with used cooking oil waste. Avocado seed powder is effectively used as an alternative adsorbent in the adsorption process of used cooking oil because of its high adsorption capacity. The effective absorbent dose reached 300 mg L^{-1} with a contact time of 150 minutes. The results of the SEM analysis showed that the morphology of the avocado seeds according to the pores and cavities met the characteristic specifications of the adsorbent for used cooking oil. The acid number, viscosity and density reached 3.12 mg KOH g^{-1}, 45.44 mm s^{-2} and 896.55 kg m^{-3} also showed the effectiveness of the performance of the avocado seed adsorbent.

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