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Optimization of Nanobentonite-CuO Adsorption for Reducing 3-MCPDE, Free Fatty Acids, and Peroxide Values in Bulk Cooking Oil: A Study of Adsorption Efficacy and Isotherm Modeling

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***Abstract*— Indonesia is the largest palm oil producing country in the world. A factor that affects the quality of cooking oil is the presence of diglycerides and free fatty acids. Diglycerides in palm oil serve as precursors for the carcinogenic chemical 3-Monochloropropane-1,2-diol ester (3-MCPDE), whilst elevated concentrations of free fatty acids (ALB) might compromise oil stability. Numerous investigations indicate that the cooking oil present in the population includes the 3-MCPDE molecule at levels ranging from 8,150 to 58,140 µg/kg. The maximum permissible amount is 2 µg of 3-MCPDE per kilogram of body weight per day. The pillarization process involves the amalgamation of $Cu(NO_3)_2$ and NaOH inside an activated bentonite solution. The adsorption analysis of 3-MCPDE employing nanobentonite-CuO was performed using Gas Chromatography Mass Spectrometry (GC-MS) in accordance with the AOCE Cd 29a-2013 method, while free fatty acid and peroxide values were evaluated by a titration method that accounted for temporal variations. The peak efficacy of Nanobentonite-CuO in adsorbing the 3-MCPDE molecule was seen at 15 minutes, with an adsorption efficiency of 52.4%. Peroxide numbers achieved ideal performance at 45, 60, and 75 minutes, with an adsorption efficiency of 80%, whilst free fatty acids reached top performance at 75 minutes with an adsorption efficiency of 76.69%. The adsorption of 3-MCPDE compounds, free fatty acids, and peroxide content by Nanobentonite-CuO, as indicated by Adsorption Isotherm modeling, conforms to the Freundlich Isotherm, implying a physical adsorption mechanism.**

***Keywords*— 3-MCPDE, Free Fatty Acids (FFA), Peroxide Number, Nanobentonite-CuO**

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I. INTRODUCTION

Oil palm is one of the leading plantation commodities in Indonesia, playing a strategic role in the country's economic development. The 2019 United States Department of Agriculture report indicates that Indonesia is the preeminent global producer of palm oil, with a production capacity of 42.50 million metric tons of Crude Palm Oil (CPO), accounting for 58% of worldwide palm oil output. Diglycerides (DAG) and free fatty acids (FFA) are constituents that influence the quality of cooking oil. Diglycerides in palm oil serve as precursors for the synthesis of the carcinogenic chemical 3-Monochloropropane-1,2-diol ester (3-MCPDE), whilst elevated concentrations of free fatty acids may compromise the oil's stability[1]. [2] indicate that diglycerides (DAG) have a strong propensity to react with other precursors, resulting in the creation of 3-Monochloropropane-1,2-diol ester (3-MCPDE) compounds in palm oil cooking oil.

According to the research by [3] , all palm oil cooking oil available on the market includes the chemical 3-Monochloropropane-1,2-diol ester (3-MCPDE), with concentration levels varying from 8,150 to 58,140 µg/kg. Moreover, according to the study by [2], commercially available cooking oil includes the chemical 3-Monochloropropane-1,2-diol ester (3-MCPDE) at concentration ranges between 13,940 and 33,920 µg/kg. The Food and Agriculture Organization (FAO) and World Health Organization (2019) established that the maximum permissible limit for 3-Monochloropropane-1.2-diol ester (3-MCPDE) in food, referred to as Tolerable Daily Intake (TDI), is 2 µg of 3-MCPDE per kg of body weight per day [4]. This signifies that exposure to 3-Monochloropropane-1,2-diol ester (3-MCPDE) has beyond the defined maximum levels or Tolerable Daily Intake (TDI). Due to the elevated levels of 3-Monochloropropane-1,2-diol ester (3-MCPDE) in cooking oil, a decrease in its concentration is imperative.

The chemical 3-Monochloropropane-1,2-diol ester (3-MCPDE) may be hazardous to humans due to the release of 3-Monochloropropane-1,2-diol and glycidol from its parent ester upon intake. The unbound form of 3-Monochloropropane-1,2-diol ester (3-MCPDE) has the potential to develop malignancies in rats in animal experiments. Consequently, 3-Monochloropropane-1,2-diol ester (3-MCPDE) is classified as a carcinogen and is assessed as non-genotoxic [5]. The International Agency for Research on Cancer (IARC) classifies 3-Monochloropropane-1,2-diol ester (3-MCPDE) as a probable human carcinogen, whereas glycidol is designated as genotoxic and carcinogenic.

Bentonite is a smectite clay mostly composed of montmorillonite. Montmorillonite possesses a stratified structure and expands upon immersion in water, rendering it highly effective as an adsorbent. Bentonite possesses exceptional adsorption characteristics owing to its diminutive colloidal particle size and elevated surface ion capacity. Numerous research have investigated the use of bentonite for the adsorption of inorganic elements, including Cd^{2+}, Pb^{2+}, Mn^{2+}, NO_3, Ni, and Fe ions, as well as for the adsorption of various organic molecules [6]. Pillaring is a modification of bentonite that improves its adsorption capability. This occurs due to cation intercalation from the pillaring agent into the interlayer of bentonite [7]. Pillaring can be accomplished by incorporating different substances, including metallic compounds. Bentonite pillaring employs metal ions including Al^{3+}, CO^{2+}, Cu^{2+}, Fe^{3+}, and Cr^{3+}. Pillaring enhances the functionality of bentonite, hence increasing its efficiency. This alteration results in enlarged pores inside the bentonite. The superior characteristics of pillared bentonite render it possibly more efficacious as an adsorbent [8].

II. MATERIAL AND METHODS

A. Synthesis of Cu Nanobentonite Using $Cu(NO_3)_2$

The formulation of the pillaring solution adheres to the technique specified by [9] with alterations. Initially, 3.6 grams of NaOH were dissolved in 100 mL of distilled water and stirred with a glass stirrer. Subsequently, 9.6 grams of $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in 100 mL of distilled water. The NaOH solution was slowly added into a beaker holding the $Cu(NO_3)_2 \cdot 3H_2O$ solution via the side of the tube. Stirring was sustained for 30 minutes following the amalgamation of the liquids.A suspension was formulated with a 1:25 ratio of active bentonite to distilled water and agitated for 30 minutes.

The pillaring agent was included into the bentonite suspension and agitated for 12 hours at ambient temperature. The mixture was subsequently filtered and rinsed with distilled water. The filtrate was subsequently dried in an oven at 110°C and calcined at 500°C for a duration of 4 hours. Subsequently, the bentonite was subjected to ball milling for 5 hours at a velocity of 350 rpm.*Adsorption Process of Bulk Cooking Oil with Nanobentonite-CuO*

The adsorption process was initiated by introducing 100 grams of bulk cooking oil with 2 grams of Nanobentonite-CuO. Subsequently, the mixture was stirred for 15, 30, 45, 60, and 75 minutes at a temperature of 35˚C. The samples were then centrifuged at a speed of 600 rpm for 15 minutes at room temperature.

B. Characterization of Bulk Cooking Oil After Adsorption with Gas Chromatography-Mass Spectroscopy (GC-MS) Analysis

The analysis of the 3-Monochloropropane-1.2-diol ester (3-MCPDE) compound content in bulk cooking oil was conducted using GC-MS instrumentation, employing the AOCS Cd 29a:2013 method.

C. Determination of Free Fatty Acid Content

5 grams of bulk cooking oil, both before and after adsorption, were placed into an Erlenmeyer flask. Subsequently, 15 mL of n-hexane and 30 mL of 96% alcohol were added, followed by the addition of 3-5 drops of Phenolphthalein indicator. The bulk cooking oil was then titrated using 0,1 N KOH until a pink color appeared. This procedure was repeated three times [10]. To determine the free fatty acid content, it can be calculated using the formula:

$$\%\ \text{FFA} = \frac{(\text{V titration x Normality KOHx MW Palmitic Acid})}{(\text{Sample Weight (g)x 1000})} \times 100\%$$

D. Determination of Peroxide Value

Five grams of bulk cooking oil, before to and subsequent to adsorption, were dissolved in a 20 mL combination of glacial acetic acid and chloroform in a ratio of 3:2. Subsequently, 5 drops of potassium iodide solution were added, and the mixture was agitated for 1 minute until a rich yellow hue developed. Subsequently, 20 mL of distilled water was incorporated. The solution was titrated with 0.1N sodium thiosulfate solution,

added dropwise (2 drops) until the yellow hue diminished. Subsequently, 5 drops of starch indicator were introduced until a dark hue developed, and titration proceeded with 0.1N sodium thiosulfate until the dark hue vanished. The operation was conducted thrice .

$$\text{Peroxide Number} = \frac{(\text{V titration x Normality Na2S2O3 x 1000})}{(\text{Sample Weight (g)})}$$

E. Determination of Adsorption Isotherm Methods

The adsorption capacity of Nanobentonite-CuO for 3-MCPDE compounds, free fatty acids, and peroxide values was evaluated using Langmuir and Freundlich isotherm models. The Langmuir isotherm was analyzed using the following equation:

$$\frac{1}{Qe} = \frac{1}{Qm} + \frac{1}{KI.Qm}\frac{1}{Ce} \quad (1)$$

Plotting 1/Qe against 1/Ce yields a linear equation, where 1/Qm serves as the intercept and 1/(K1.Qm) represents the slope, so facilitating the determination of Qm and the constant for KL [11]. The Freundlich equation test is conducted utilising the subsequent equation: $\frac{x}{m} = Qe = K_f C_e^{1/n}$ (2)

$$\text{Log } Qe = \text{Log } Kf + \frac{1}{n}\log C_e \quad (3)$$

Plotting log Qe against log Ce will yield a linear equation with log KF as the y-intercept and 1/n as the slope. A linear equation with Log KF as the intercept and 1/n as the slope, allowing for the determination of the values of n and KF.

III. RESULT AND DISCUSSION

A. Analysis of 3-MCPDE Content in Bulk Cooking Oil

The concentration of the 3-MCPDE compound in cooking oil is determined as its initial level prior to the adsorption process. The analysis is performed using Gas Chromatography-Mass Spectrometry (GC-MS) following the AOCS Cd 29a-13 method.

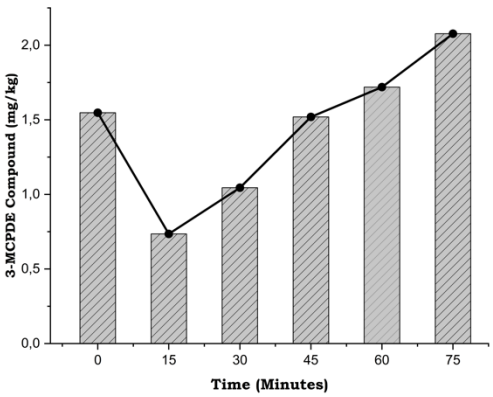


Fig 1. Bar diagram of 3-MCPDE compound content in bulk cooking oil before and after adsorption

The initial concentration of the 3-MCPDE in bulk cooking oil samples was 1.547 mg/kg. According to Fig 1, the concentration of the 3-MCPDE in the cooking oil diminished following adsorption with Nanobentonite-CuO. Nonetheless, at specific intervals, there was an elevation in the concentration of the 3-MCPDE molecule in bulk cooking oil. This phenomena can be linked to the adsorption process, wherein temperature, time, and agitation influence the increase of 3-MCPDE chemical levels. The 3-MCPDE molecule has significant temperature sensitivity. This corresponds with the findings of [12], indicating that temperature and heating duration are determinants that elevate 3-MCPDE and glycidyl ester (GE) concentrations, achieving their maximum levels. The levels of 3-MCPDE and GE are affected by the overall frying duration, including intermittent frying methods, establishing a positive association between the concentration of 3-MCPDE and the frying length. Research by [13] demonstrates that extended frying or heating of oil inside food matrices accelerates the breakdown of 3-MCPDE compounds.

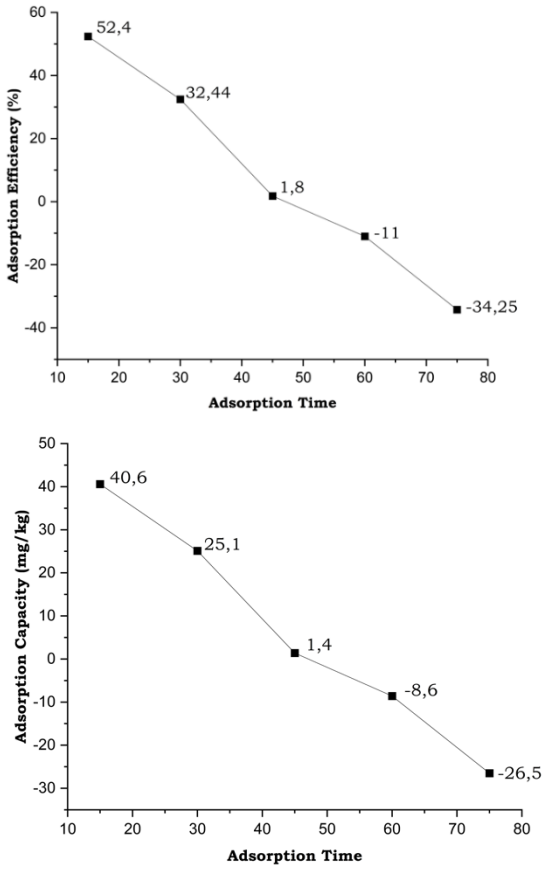


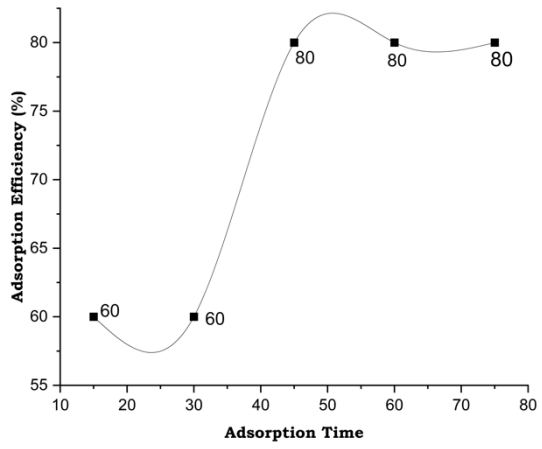
Fig 2. Graph of Adsorption Efficiency (%) and Adsorption Capacity (mg/kg) of Nanobentonite-CuO in Adsorbing 3-MCPDE Compound

Figure 2 illustrates that an extended adsorption duration correlates with a diminished capacity of the adsorbent to mitigate MCPD chemicals. The ideal adsorption of the 3-MCPDE molecule transpires at 15 minutes, achieving a reduction of 52.4% with an adsorbed quantity of 0.812 mg/kg. With an increase in adsorption time, the fraction of the 3-

MCPDE molecule rises correspondingly. The efficacy of nano bentonite in adsorbing the 3-MCPDE molecule is noted for a duration of 45 minutes, achieving an adsorption efficiency of 1.8%. This phenomenon arises due to the saturation of the adsorbent, rendering it incapable of accommodating 3-MCPD compounds in used cooking oil, which consequently leads to an increase in the amounts of 3-MCPDE compounds. Adsorbent saturation is the threshold at which an adsorbent has attained its maximal capacity and can no longer absorb further material [14]. Factors contributing to adsorbent saturation include starting adsorbate concentration, pH levels, adsorbent dosage, particle size, temperature, and contact time [15] [16]. Factors influencing the elevation of 3-MCPDE chemicals include temperature and contact duration. 3-MCPD compounds may escalate in accordance with temperature fluctuations, which can amplify their presence. Extended contact time and temperature conditions result in a rise of the 3-MCPDE compound, rendering the adsorbent incapable of absorbing the 3-MCPDE present in the oil. The formation of the 3-MCPDE chemical correlates with the increasing contact time and temperature during the adsorption process. Temperature influences the adsorption process by increasing the transfer rate of materials into the adsorbent's pores. Nonetheless, too elevated temperatures may result in desorption[17].

B. Analysis of Peroxide Value Adsorption in Bulk Cooking Oil

The peroxide number estimates the milliequivalents of peroxide present in 1000 grammes of fat or oil, serving as an essential measure of the degree of deterioration in a certain fat or oil. Unsaturated fatty acids can react with oxygen to produce peroxides (16). The Peroxide number serves as a crucial metric for oxidative rancidity, indicating the extent of lipid oxidation by measuring the concentration of primary oxidation products [18].



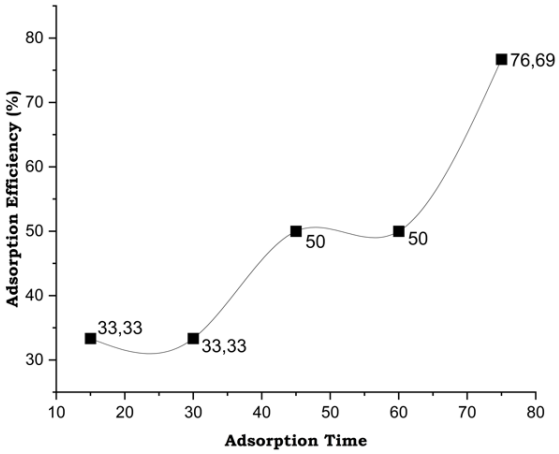


Fig 3. Graph of Adsorption Efficiency (%) and Adsorption Capacity (mg/kg) of Nanobentonite-CuO in Adsorbing Peroxide Value.

The analysis of peroxide value adsorption in bulk cooking oil utilising Nanobentonite-CuO indicates that an extended adsorption duration correlates with an increased proportion of peroxide value absorbed by Nanobentonite-CuO. The adsorption effectiveness of Nanobentonite-CuO for peroxide compounds is 60% at 15 and 30 minutes, peaking at 80% for adsorption durations of 45, 60, and 75 minutes at a temperature of 35°C. As stated in [19], prolonged adsorption duration correlates with an increased content of adsorbed peroxide value. A longer contact time between bentonite and used cooking oil results in the entrapment of a greater number of contaminants. Nevertheless, the results indicate that the adsorption contact time at a designated duration does not escalate, as evidenced by the 15 and 30-minute intervals, during which merely 60% of the peroxide value is adsorbed, yielding a peroxide value of 3.88 meq O_2/kg. At 45, 60, and 75 minutes, the adsorption efficiency ascends to 80%, with a peroxide value of 1.94 meq O_2/kg, indicating that the adsorbent has attained its maximal adsorption capacity. Oils exhibiting peroxide values more than 10 meq O_2/kg are deemed unstable and susceptible to rancidity, while those with lower peroxide values (below 10 meq O2/kg) indicate favourable stability against oxidation[20]. Peroxide is the principal major oxidation product. An elevated concentration of peroxide results in diminished oxidative stability [21].

C. Analysis of Free Fatty Acid Adsorption in Bulk Cooking Oil

Free Fatty Acid (FFA) refers to a fatty acid that exists in an unbound state, not associated with triglycerides. Free Fatty Acid (FFA) is produced via hydrolysis and oxidation reactions [22]. The composition of free fatty acids in oil is mostly determined by its free fatty acid components. The principal fatty acids in palm oil are palmitic acid and oleic acid [23].

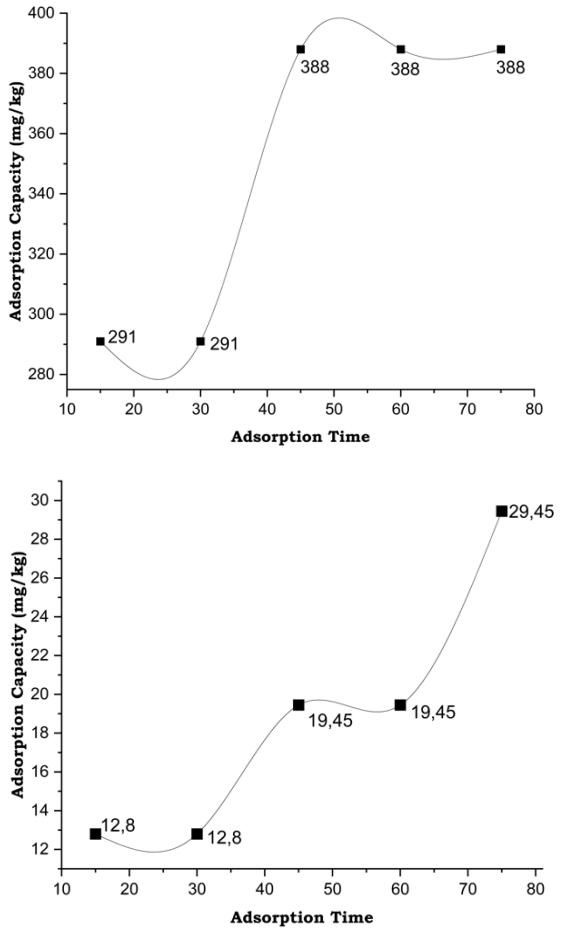


Fig 4. Graph of Adsorption Efficiency (%), Adsorption Capacity (mg/kg) of Nanobentonite-CuO in Adsorbing Free Fatty Acids

FFA is a critical metric in assessing oil quality. The elevated free fatty acid level in oil might lead to its degradation, resulting in a reduced shelf life. The fatty free acid content in oil is a consequence of triglyceride hydrolysis. The hydrolysis step yields free fatty acids and glycerol molecules [24]. Free Fatty Acid serves as a precursor compound for the synthesis of 3-MCPDE in palm oil, in conjunction with TAG, MAG, and DAG. Consequently, the adsorption of Free Fatty Acid is essential to mitigate the production of 3-MCPDE molecules in cooking oil.

The rate of free fatty acid reduction by Nanobentonite-CuO escalates with extended contact duration. The adsorption of nano bentonite on free fatty acids is efficient due to the availability of its pore surface. As contact time increases, a greater quantity of free fatty acids is absorbed into the pores of Nanobentonite-CuO. The graph demonstrates that the efficacy of decreasing free fatty acids improves with prolonged contact time. The adsorption data indicate a substantial decrease in free fatty acids relative to contact time. The reduction in free fatty acid concentration is directly related to contact time; more contact time results in a greater quantity of adsorbed free fatty acids.

Figure 4 indicates that the reduction in free fatty acids exhibits the most significant percentage decrease, achieving 80% from 0.7% to 0.1%, with an adsorption capacity of 29.45 mg/kg during a contact duration of 75 minutes. The minimum percentage reduction in free fatty acids is 33.33%, declining from 0.7% to 0.5%, with an adsorption capacity of 12.8 mg/kg during contact durations of 15 and 30 minutes. The SNI 3741-2013 standard stipulates that the maximum permissible concentration of free fatty acids is 0.6%. Consequently, the cooking oil absorbed with Nanobentonite-CuO has achieved the maximum criterion for free fatty acid content in cooking oil. Contact time significantly affects the efficacy of decreasing free fatty acids in Crude Palm Oil; an extended duration correlates with enhanced efficiency [25]. Research by [26] indicates that the use of natural bentonite is ineffective in diminishing free fatty acids, as indicated by a negligible reduction of only 2.38%, with levels recorded at 3.44% prior to adsorption and 3.36% subsequent to adsorption. Adsorbed with bentonite for 60 minutes at a concentration of 3%.

D. Adsorption Isotherms

The study of adsorption isotherms denotes an equilibrium relationship between the quantity of adsorbate retained by the adsorbent as a function of concentration and temperature, or the balance between the concentration of the adsorbate in the fluid and on the adsorbent's surface at a constant temperature. Freundlich and Langmuir isotherms are prevalent types of adsorption isotherms utilised in solid-liquid adsorption. In the Langmuir isotherm, a plot of Q_e/C_e vs C_e is generated, whereas for the Freundlich isotherm, a plot of log Qe against log Ce is established [27]. The establishment of the equilibrium model relies on a high coefficient of determination (R_2). Adsorption equilibrium is a mathematical representation of a particular isothermal state for each adsorbent. Consequently, each adsorbent and adsorbate have its own adsorption equilibrium [28]. Thus, adsorption isotherms are crucial in providing information about the optimal use of adsorbents.

a) Freundlich Isotherm

The Freundlich Isotherm equation is based on the formation of a monolayer of adsorbate molecules on the surface of the adsorbent. However, in Freundlich adsorption, the active sites on the surface of the adsorbent are heterogeneous. The Freundlich adsorption isotherm assumes that adsorption occurs physically, allowing more adsorption to take place on the adsorbent surface. In physical adsorption, the adsorbate is not strongly bound to the adsorbent surface, allowing it to move from one part of the surface to another, and the surface left behind can be replaced by another adsorbate. Physical adsorption can occur due to the presence of Van der Waals forces, and weak attractive forces between the adsorbate and the adsorbent surface [28].

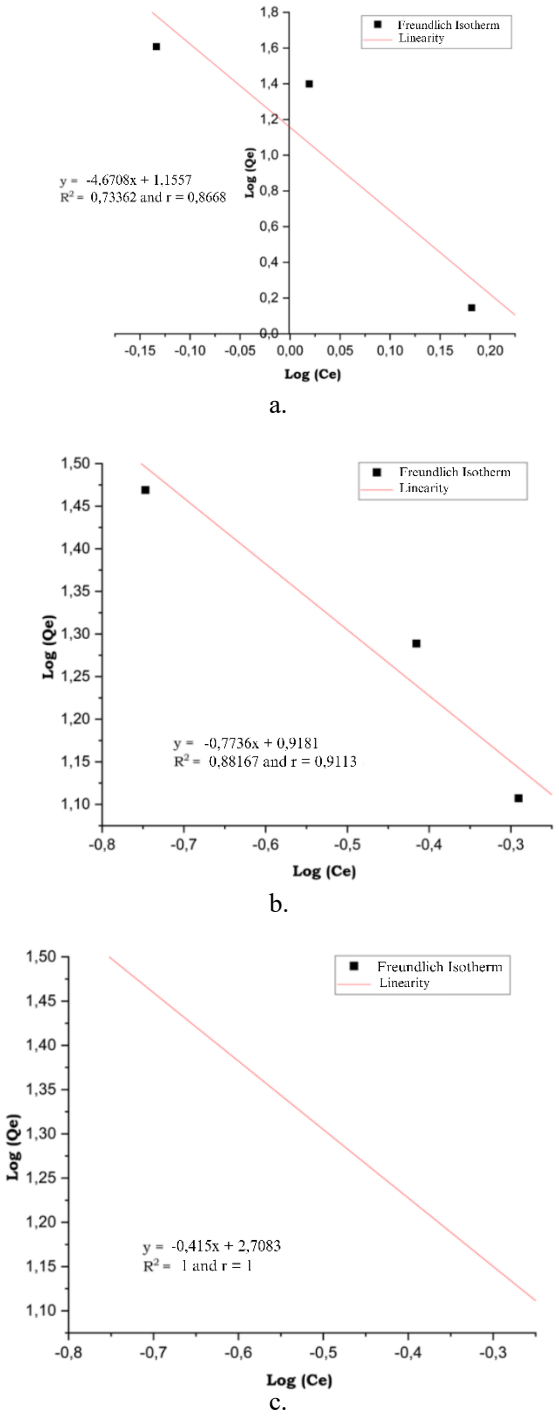


Fig 5. Freundlich Isotherm a) Adsorption of 3-MCPDE Compound, b) Adsorption of Free Fatty Acids, c) Adsorption of Peroxide Value

Based on the curves in **Fig 5**, by plotting the data of log Qe against log Ce in Freundlich modeling, linear regression values were obtained as follows: For the adsorption of the MCPD compound, the linear regression equation is y = -4.6708x + 1.1557 with an R-Square (R^2) value of 0.73362. The correlation coefficient (r) value is approximately 0.8668. For Free Fatty Acids adsorption, the linear regression equation is y = -0.7736x + 0.9181 with an R-Square (R^2) value of 0.88167. The correlation coefficient (r) value is approximately 0.9113. For Peroxide Value adsorption, the linear regression equation is y = -0.415x + 2.7083 with an R-Square (R^2) value of 1. The correlation coefficient (r) value is approximately 1. It can be concluded that the variables x (log Ce) and y (log Qe) have a strong linear relationship. If the R2 value approaches 1 in the linear data plot, the experimental data follows the equilibrium model [29].

Referring to the linear equation of the Freundlich isotherm, where Kf is the Freundlich constant, which is a relative indicator of adsorption capacity. The relative ability of an adsorbent to adsorb an adsorbate can be observed from the value of Kf; the larger the Kf value, the greater the adsorption capacity of an adsorbent. Similarly, the strength of the interaction between the adsorbent and adsorbate can be observed from the value of 1/n; the smaller the value of 1/n, the stronger the interaction between the adsorbent and adsorbate [28].

TABLE I
Freundlich Isotherm Model Parameters for Nanobentonite-CuO Adsorbents

Test Data	r	R^2	Kf (L/g)	n
3-MCPDE Compound	0,8668	0,73362	14,3119	-0,21409
Free Fatty Acids	0,9113	0,88167	8,2813	-1,2926
Peroxide Value	1	1	510	-2,4096

Based on the **Table 1**, it is evident that the Kf values for the adsorption of the 3-MCPDE compound, Free Fatty Acids, and Peroxide Value are 14.3119 L/g, 8.2813 L/g, and 510 L/g, respectively. Additionally, the values of n are -0.21409 for 3-MCPDE compound, -1.2926 for Free Fatty Acids, and -2.4096 for Peroxide Value, with the heterogeneity intensity (1/n) values sequentially being -4.6709, -0.771, and -0.4151. According to [29], if the value of 1/n = 1, the adsorption occurs entirely on a homogeneous surface, and if the value is between 0 and 1, the adsorption process takes place on a semi-heterogeneous surface. However, if the value for 1/n > 1, the adsorption process occurs on a heterogeneous surface. Furthermore, the value of 1/n < 1 indicates that adsorption proceeds normally, but if 1/n > 1, adsorption occurs weakly [30]. Based on this, it can be concluded that the Freundlich adsorption parameters for the 3-MCPDE compound, Free Fatty Acids, and Peroxide Value by Nanobentonit-CuO occur semi-heterogeneously.

b) Langmuir Isotherm

The Langmuir isotherm theory assumes that the adsorbent surface is uniform, all adsorbed molecules do not interact with

each other, all adsorbed molecules follow the same mechanism, and a monolayer is formed at the point of maximum adsorption. There are four basic assumptions of the Langmuir isotherm model: a) Molecules are adsorbed at specific sites on the adsorbent surface, b) Each site accommodates only one molecule (monolayer), c) The quantity of each site is determined by the surface geometry, d) The adsorption energy is the same at each site [30].

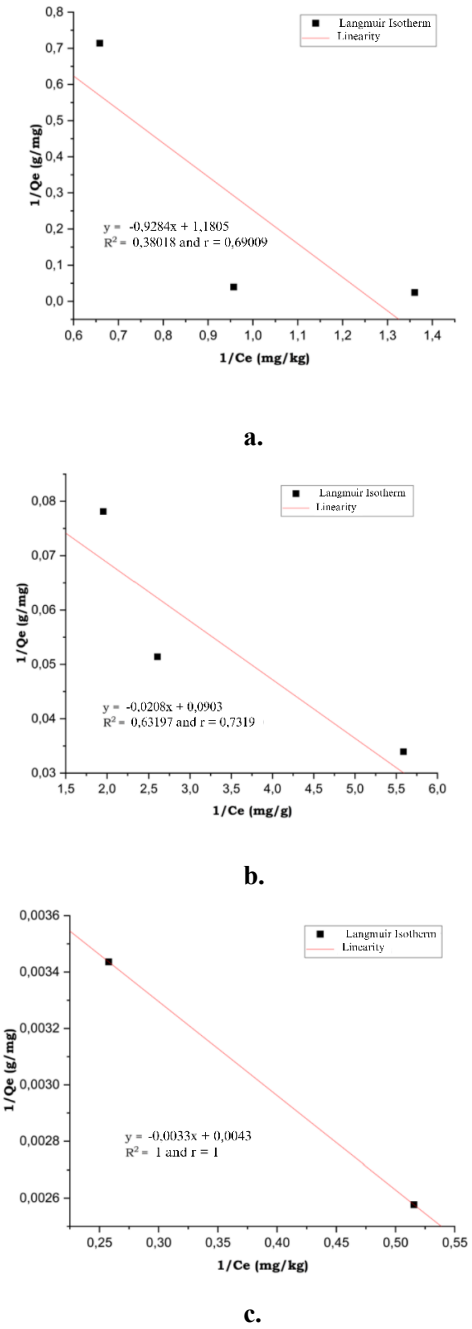


Fig 6. Langmuir Isotherm a) Adsorption of 3-MCPDE, b) Adsorption of Free Fatty Acids, c) Adsorption of Peroxide Number

Based on the curves in the **Fig 6**, by plotting the data of 1/Qe against 1/Ce in Langmuir modeling, a linear regression value of y = -9284x + 1.1805 was obtained with an R-Square (R^2) of 0.38018. The correlation coefficient (r) value, which approaches 1, is 0.6900 for the adsorption of the MCPD compound. Then, for Free Fatty Acids with Langmuir modeling, a linear regression value of y = -0.0208x + 0.0903 was obtained with an R-Square (R^2) of 0.63197. The correlation coefficient (r) value, which approaches 1, is 0.724. Meanwhile, for Peroxide Number with Langmuir modeling, a linear regression value of y = -0.0033x + 0.0043 was obtained with an R-Square (R^2) of 1. The correlation coefficient (r) value approaches 1, is 1. Therefore, it can be said that the variables x (1/Ce) and y (1/Qe) have a strong linear relationship. If the R^2 value in the linear curve plot approaches 1, then the experimental data follows the equilibrium model [31].

Referring to the Langmuir Isotherm equation, the intercept value 1/Qm is used to calculate Qm, while the slope value as 1/(kl. Wm) is used to calculate Kl for the adsorption process of MCPD Compound, Free Fatty Acids, and Peroxide Number. The Qm value represents the maximum adsorption capacity of an adsorbent, and Kl is the Langmuir constant, so the higher the Qm value, the higher the adsorbent's capacity to adsorb.

TABLE II
Parameters of the Langmuir Isotherm Model for Nanobentonite-CuO Adsorbents

Test Data	r	R^2	Q_m (mg/g)	K_L (L/g)
3-MCPDE Compound	0,6900	0,38018	0,847	-1,2717
Free Fatty Acid	0,724	0,63197	11,072	-0,230
Peroxide Value	1	1	232,55	-1,3031

Based on the Table 2, it can be seen that the Qm values for the adsorption of MCPD Compound, Free Fatty Acids, and Peroxide Number are 0.847 mg/g, 11.072 mg/g, and 232.55 mg/g, respectively. The Qm value serves as a relative indicator of the maximum adsorption capacity related to the binding energy of an adsorbent, so the higher the Qm value, the higher the adsorption capacity. Additionally, KL values are obtained, which are -1.2717 for MCPD Compound, -0.230 for Free Fatty Acids, and -1.3031 for Peroxide Number. According to [32] , if the KL value approaches 0, the adsorption process is favorable and occurs on a monolayer surface. The Langmuir Isotherm model assumes that the adsorbent surface is homogeneous, and the adsorption energy is the same for all adsorption sites. Chemical adsorption (chemisorption) occurs due to interactions with the active sites of the adsorbent and adsorbate, and these interactions occur only on the monolayer adsorption layer of the adsorbent cell wall surface[33].

Based on the comparison of the R-Square (R^2) values in the Freundlich and Langmuir adsorption isotherm curves, it can be concluded that the adsorption of MCPD Compound, Free Fatty

Acids, and Peroxide Number by Nanobentonit-CuO tends to follow the Freundlich Isotherm model rather than the Langmuir Isotherm model. This is evidenced by the high R-Square (R^2) values in the linear regression equations, where the R^2 values for the Freundlich Isotherm curve are closer to 1 compared to the Langmuir Isotherm model. The R^2 value for the Freundlich Isotherm model is 0.8668, while the Langmuir Isotherm model is 0.6900 for MCPD Compound. Similarly, the R^2 value for the Freundlich Isotherm model is 0.9113, while the Langmuir Isotherm model is 0.724 for Free Fatty Acids. For the Peroxide Number, the R^2 value for the Freundlich Isotherm model is 1, while the Langmuir Isotherm model is also 1.

IV. CONCLUSION

Research indicates that the adsorption duration of nanobentonite-CuO significantly affects the reduction of 3-MCPDE chemicals, free fatty acids, and peroxide values. The adsorption results for the 3-MCPDE chemical indicate that prolonged adsorption period enhances the concentration of the 3-MCPDE component in frying oil. The optimal adsorption duration was 15 minutes, with an adsorption efficiency of 52.4% and an adsorption capacity of 40.6 mg/kg. The elevation of 3-MCPDE compounds is affected by temperature variables. The data indicates that prolonged adsorption duration influences the reduction of free fatty acids, with optimal adsorption effectiveness achieved after 75 minutes, resulting in a decrease of 76.69% and an adsorption capacity of 29.45 mg/kg. The duration of adsorption affects the reduction of peroxide value in bulk cooking oil; a longer adsorption period results in a greater adsorption of peroxide value by Nanobentonite-CuO. Adsorbent saturation has been reached, resulting in no rise at the 45th, 60th, and 75th minutes, with an adsorption efficiency of 80% and a capacity of 388 mg/kg.

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