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Batch Adsorption of Tannins from Stevia Leaf Extract using Activated Carbon: An Investigation into Adsorption Isotherms and Adsorption Energy

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Abstract

Stevia leaf extract (*Stevia rebaudiana Bertoni*) could have been utilized as an alternative natural sweetener because it possessed a sweetness level 300 times that of sucrose sugar. However, stevia leaf extract still contained a bitter taste attributed to the presence of tannins. The method that can be used to reduce tannin content is batch adsorption using activated carbon. This study aimed to investigate the batch adsorption process for the tannin content of stevia leaf extract using activated carbon with variable adsorption times ranging from 5 to 180 minutes, which included the appropriate adsorption isotherm model and adsorption energy. Stevia leaves were extracted through maceration with 70% ethanol. The results of the stevia leaf extract were adsorbed in batches using activated carbon treated with 1M NaOH. The analysis was carried out by testing the tannin content (mg/g TAE) using a UV-Vis spectrophotometer at a wavelength of 735 nm and calculating the adsorption isotherm and adsorption energy. The results showed that the tannin content before adsorption was 0.910 mg/g TAE, and the lowest tannin content was 0.040 mg/g TAE at 100 minutes. The tannin content decreased between 5–90 minutes, remained constant, reached equilibrium at 95–120 minutes, and increased again at 125–180 minutes. The suitable adsorption isotherm model was the Freundlich isotherm with a value of R^2 = 0.9998; K_F = 25.293 [(mg/g)(L/mg)$^{1/nf}$], and adsorption energy = -8.03 kJ/mol. The adsorption that occurred was classified as physical adsorption.

Keywords: Adsorption batch, adsorption energy, isotherm adsorption, stevia leaf extract, tannin content

1. Introduction

The need for staple foods for the community continues to increase every year, one of which is the need for sweeteners. Sweeteners are food ingredients that are added to food and beverages to add sweetness, improve the physical and chemical properties of food ingredients, and become a source of calories for the body. Sweetener is an important ingredient that is widely used by the food and beverage industry. Generally, there are two types of sweeteners used, namely synthetic sweeteners such as cyclamate and natural sweeteners in the form of white granulated sugar made from sucrose (Arshad et al., 2022). Long-term use of both kinds of sweeteners can harm one's health by increasing the risk of obesity, diabetes, cancer, and renal failure (Ghusn et al., 2023).

Stevia (*Stevia rebaudiana bertoni*) is a plant from the Compositae family and contains several chemical compounds, including phenolics, diterpenes, triterpenes, stigmasterol, diterpene glycosides, and tannins. Stevia rebaudiana is one of the stevia plant species that can produce a sweet taste (Lemus-Mondaca et al., 2012). The sweet taste is due to the low-calorie content of steviol glycosides in the extract. Stevia is also hypoglycemic, meaning it can lower blood sugar levels, making it safer for health, and can be consumed by diabetes sufferers (Martono & Dewi, 2013). Stevia leaves can be consumed in the form of extracts obtained through an extraction process using polar solvents under certain conditions.

Several previous studies stated that stevia leaf extract still produces a bitter taste, so the level of sweetness is reduced (Shukla et al., 2012). The cause of the bitter taste is due to the tannin component in it (Padhi et al., 2022). Thus, it is necessary to undergo a tannin component separation process first to reduce bitterness and enhance the sweetness of stevia leaf extract (Joshi et al., 2022). Tannins are complex polyphenolic compounds consisting of the elements C, H, and O and have a molecular weight of 1701.19 g/mol, easily soluble in water and

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organic (polar) solvents (Falcão & Araújo, 2018; Fraga-Corral et al., 2020). Figure 1 shows the chemical structure of tannin.

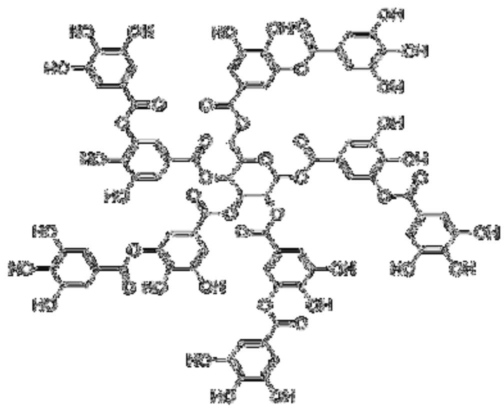

Figure 1. Chemical structure of tannin

The initial tannin content of stevia leaf extract is 850 ppm (Saraswati et al., 2021). Several previous research results have proven that the tannin content of stevia leaf extract can be reduced through adsorption using activated carbon adsorbents, as has been done by Kusumaningsih et al, (2015), who managed to reduce tannin levels by up to 39.74%. The activated carbon used was activated with NaOH, in accordance with previous research conducted by Saraswati et al, (2021). Additionally, NaOH is environmentally friendly and can introduce more hydroxyl groups (O-H) to activated carbon, making it more optimal for adsorbing organic components such as tannins, which also feature numerous hydroxyl groups (O-H) (Heidarinejad et al., 2020).

Adsorption is one of the process techniques for separating a component (adsorbate) from liquid or gaseous fluids due to mass transfer and attractive forces between the adsorbate molecules and the surface-active site of the adsorbent (Artioli, 2008). The tannin adsorption process of stevia leaf extract is greatly influenced by several factors, one of which is the adsorption time. Adsorption time is an important parameter because it can influence the amount of tannin adsorbed on activated carbon and can be the basis for determining the best adsorption operating conditions to produce the most optimal reduction in tannin content. So, the purpose of this study was to examine the batch adsorption process for the tannin content of stevia leaf extract using activated carbon with variable adsorption times (5–180 minutes), which included the appropriate adsorption isotherm model and adsorption energy.

2. Methodology

2.1. Materials

The materials used are commercial stevia leaves from Bogor City, 98% standard tannic acid, 70% ethanol, methylene blue, NaOH, activated carbon, distilled water, demineralized water, 35% Na_2CO_3, and Folin-Ciocaltieu reagent. All reagents were of analytical grade. The equipment used is a maceration extraction reactor (IKA/LR-2.ST Package 2), vacuum oven (Memmert V029, Germany), rotary vacuum evaporator (Buchi/R-215), moisture balance (Kern/MLS50-3HA), orbital shaker (IKA/KS 130 basic), digital pH meter (OHAUS ST 350), UV-Vis spectrophotometer (Mecasys/Optizen POP), and Fourier-Transform Infrared Spectroscopy (FTIR).

2.2. Preparation of Stevia Leaf

Stevia leaves are first separated from the stems. Next, the leaf size was reduced to 80 mesh, and the initial water content was measured using a moisture balance. Furthermore, drying was carried out using a vacuum oven at 55oC and pressure 155–157 mBar for 3 hours, checking the water content every 1 hour until it was below 10%. Dried stevia leaves are stored in tightly closed plastic.

2.3. Preparation of Stevia Leaf Extract

Stevia leaf extraction is carried out by maceration in a maceration extraction reactor. The extraction of stevia leaves is carried out at a temperature of 55°C for 1 hour with a stirring speed of 100 rpm. The solid–solvent ratio is 1:10 (Chandra, 2015), or 100 grams of stevia leaves and 1000 mL of 70% ethanol as solvent. Furthermore, stevia leaf extract was separated from the solvent using a rotary vacuum evaporator at a temperature of 57^{o}C and a pressure of 149–150 mBar. The result of this extraction is called stevia leaf extract.

2.4. Activation of Activated Carbon

This process begins with reducing the size of activated carbon to 100 mesh. Then make a 1M NaOH activator solution by dissolving 10 grams of NaOH in 250 mL of distilled water. Next, activation was carried out by immersing 50 grams of activated carbon in 250 mL of 1M NaOH solution for 24 hours. Furthermore, vacuum filtration was carried out to separate the activated carbon from the 1M NaOH solution. The filtered activated carbon is washed repeatedly using distilled water until it approaches a neutral pH (~7).

2.5. Adsorption of Stevia Leaf Extract

The adsorption process was carried out by adding 0.2 grams of 1M NaOH-activated carbon to 10 mL of stevia leaf extract. The characteristics of the activated carbon used in tannin adsorption include a surface area of 532.90 m²/g and a pore diameter of 5.33 mm. Adsorption was carried out in batches at a rotation speed of 150 rpm at room temperature (25±5ºC), for 5–180 minutes. Adsorption samples were taken every 5 minutes and filtered using the Whatman 41 filter paper. Then the adsorption extract samples were stored in 10 mL glass bottles to continue testing for tannin content.

2.6. Determination of Tannin Content

This process begins by preparing a folin-ciocaltieu reagent and a 35% Na_2CO_3 solution. Next, prepare a standard solution of tannic acid at 20, 40, 60, 80, and 100 ppm for making a tannic acid standard curve and determining the maximum wave. Samples of stevia leaf extract before and after adsorption for 5–180 minutes were taken in 1 mL each and then diluted with demineralized water to 50 ml. Next, another 1 mL was taken, then mixed with 0.5 mL of folin-ciocaltieu reagent and 1 ml of 35% Na_2CO_3 solution and added with 7.5 mL of demineralized water until the color of the sample changed to purplish-blue and covered with aluminum foil for 90 minutes (Rammika, 2016). Then the sample's absorbance was measured using a UV-Vis spectrophotometer at a maximum wavelength of 735 nm. Tannin levels are expressed in units (mg/g TAE) or Tannic Acid Equivalent using Equation 1 (Shewakena et al., 2017).

$$\text{Tannin content}\left(\frac{\text{mg}}{\text{g}}\text{TAE}\right) = \frac{\text{C x V x Fp}}{\text{w}} \qquad (1)$$

C is the tannin content (mg/L), V is the stevia leaf extract volume after dilution (L), Fp is the dilution factor (in this case we use 50), w is the mass of stevia leaf extract (g).

2.7. Functional Group Analysis

The functional group test was carried out using IRSpirit/ATR-S Serial No. A224158/Shimadzu FTIR spectrometer in the scanning ranges of 360-4700 cm^{-1} at room temperature on activated carbon samples before and after activation by 1M NaOH as well as stevia leaf extract samples before and after adsorption. The activated carbon and stevia leaf extract were ground and mixed with potassium bromide.

3. Results and Discussion

3.1. Effect of Adsorption Time on Tannin Levels of Stevia Leaf Extract

Adsorption of tannins from stevia leaf extract was carried out using batch adsorption with varying adsorption times of 5–180 minutes, and samples were taken every 5 minutes. This treatment aims to determine a more accurate tannin content profile (Bonilla-Petriciolet et al., 2017). The tannin content before adsorption was 0.910 mg/g TAE (Tannin Acid Equivalent). Tannin content (x) was calculated by substituting the absorbance value (y) in the following tannic acid standard curve (Figure 2).

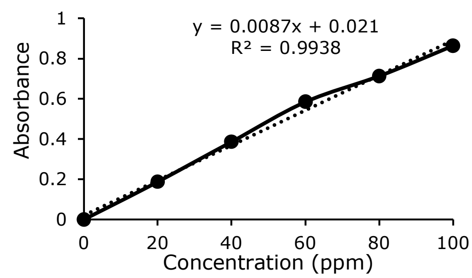

Figure 2. Tannic acid standard curve

Changes in tannin content over time can be seen in Figure 3. At the beginning of adsorption, the tannin content graph appears to decrease more quickly until the adsorption time is 5 minutes. This condition generally occurs because at the beginning of adsorption, the surface of the activated carbon adsorbent still has many empty pores and the active site (site) has not been filled with adsorbate. Because the tannin adsorbate is derived from stevia leaf extract, it is easier to occupy empty pores and active sites, which causes the process of attracting tannin adsorbates to the surface of the adsorbent to be faster (Gaweł-Bęben et al., 2015; Hidayati et al., 2016).

Furthermore, the tannin levels were seen to continue to decrease significantly until the adsorption time was 90 minutes, and the remaining tannin levels still contained at that time were 0.041 mg/g TAE. This is because the longer the adsorption time, the more hydrogen bonds are formed between the tannin hydroxyl groups and activated carbon, and the more tannin adsorbates occupy the empty pores and active side of the activated carbon, so that the remaining tannin content in the stevia leaf extract decreases.

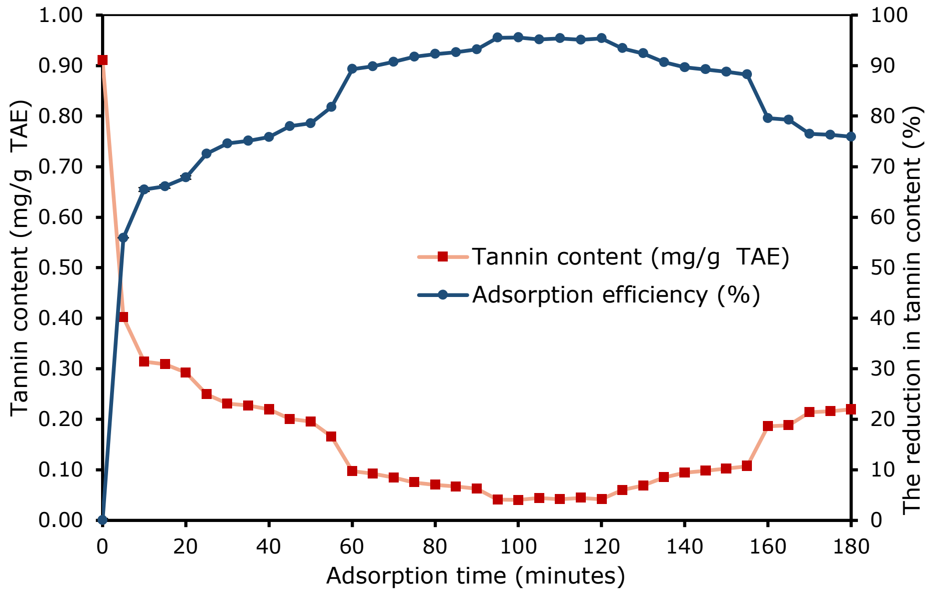

Figure 3. The tannin content at each adsorption time

The second condition profile shows that tannin levels tend to be constant at an adsorption time of 95–120 minutes, which indicates that there is a very small change in tannin levels and tannin levels tend to be constant. The remaining tannin levels that are still contained in this time period are 0.040–0.044 mg/g TAE. This condition is because the surface of the activated carbon is thought to be saturated, which indicates that the number of empty pores and active sites (sites) is starting to decrease and has reached maximum capacity. So that activated carbon is no longer able to extract tannins from stevia leaf extract optimally, and tannins can no longer occupy empty pores and active sites on the surface of activated carbon (Shamima et al., 2023). Furthermore, the tannin content at the adsorption time of 95–120 minutes has also reached equilibrium.

This is proven by calculating the coefficient of variation to show the accuracy of the tannin content values over that time period, whether they tend to be constant or not(Bonilla-Petriciolet et al., 2017). The coefficient of variation was calculated with Equation 2. The coefficient of variation was obtained at 4.17% and this value was below 5%, so it was proven that the tannin content data in that time range was accurate, tended to be constant, and reached equilibrium time (de Hoyos-Martínez et al., 2019).

The third condition profile shows that the tannin content slowly increases again at an adsorption time of 125–180 minutes. Tannin levels in this time period were 0.060–0.220 mg/g TAE. This condition is referred to as a desorption event, which is thought to be because the tannin adsorbate is released from the surface of the activated carbon and enters the solution(Ganjoo et al., 2023).

$$\text{Coefficient of variant} = \frac{\sigma}{\mu} \quad (2)$$

σ is the standard deviation of tannin content (mg/g TAE) at a constant time, and μ is the average tannin content (mg/g TAE) at a constant time.

This is because the longer the active carbon is in contact with the stevia leaf extract until the equilibrium time has passed, it can cause the functional group bond interactions and forces between the tannin adsorbate and the active side of the activated carbon adsorbent to become weaker and cause collisions between tannin adsorbate and adsorbent particles quickly and continuously, so that the tannins can be released and increase the tannin levels in the stevia leaf extract again (Li et al., 2022; Mariana et al., 2021; Tangarfa et al., 2019).

3.2. Functional Group of Activated Carbon and Stevia Leaf Extract

Figures 4 and 5 show the IR spectra of activated carbon before and after activation by 1M NaOH solution and stevia leaf extract before and after adsorption. The types of functional groups in activated carbon and tannin can cause the adsorption process to occur. These functional groups can attract tannin adsorbates due to the van der Waals attraction, differences in charges between atoms, and the similar properties of polar functional groups. The attraction force between tannins and activated carbon tends to be greater than the attraction force between tannins in solution, so that tannins can be attracted to and stick to empty pores and active sites on the surface of activated carbon (A. Ma et al., 2021; Tangarfa et al., 2019).

The adsorption process of tannins in stevia leaf extract can occur due to the presence of similar functional groups in both activated carbon adsorbents and tannins. Specific functional groups on activated carbon can alter its surface properties to become either more polar or non-polar, attracting adsorbates with similar functional groups from the bulk solution (Pego et al., 2019). These functional groups can attract specific adsorbates due to unbalanced attractive forces, differences in charges between atoms, and the similarity in the properties of polar or non-polar functional groups. The attractive forces between the adsorbate and the adsorbent are generally stronger than the forces between adsorbates in the solution, causing the adsorbate to be drawn and adhered to the empty pores and active sites on the adsorbent surface (Kuang et al., 2020; Worch, 2021).

a. Hydroxyl (O-H)

Hydroxyl groups (O-H) (stretching) appear in activated carbon before and after NaOH is activated. Hydroxyl groups (stretching) also appear in all stevia leaf extract samples in the wave range 3850–3100 cm^{-1} (Silverstein et al., 2005). The hydroxyl group on activated carbon is thought to be formed from the oxidation process, the breaking of the water molecule structure at a temperature of 150°C–240°C during carbonization, and the reaction between water vapor and free compounds on the activated carbon surface (Hafizuddin et al., 2021; Togibasa et al., 2021). In stevia leaf extract samples, the hydroxyl group (O-H) (stretching) is thought to come from the phenolic component, namely tannin (Gaweł-Bęben et al., 2015; Shukla et al., 2012). The hydroxyl groups in the stevia leaf extract sample before adsorption appear in the wave ranges 3850–3100 cm^{-1} and 1450–1330 cm^{-1}, both of which appear to have lower peaks and transmittance values than the stevia leaf extract sample after adsorption. This condition shows that the hydroxyl functional group, which is thought to come from tannin after adsorption, has decreased because it has been adsorbed by activated carbon, which indicates that the tannin component in stevia leaf extract is reduced (Tangarfa et al., 2019). The hydroxyl group is polar and plays a role in the formation of hydrogen bonds between the hydroxyl groups of activated carbon and tannins.

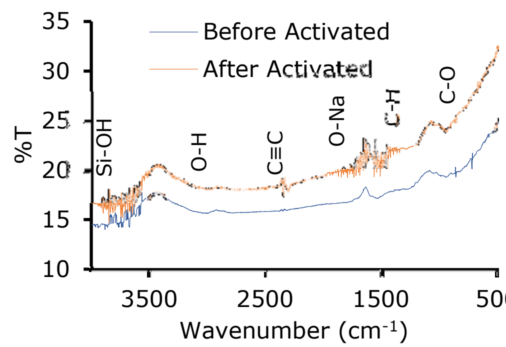

Figure 4. Spectrum-IR of activated carbon before and after activation by 1M NaOH solution

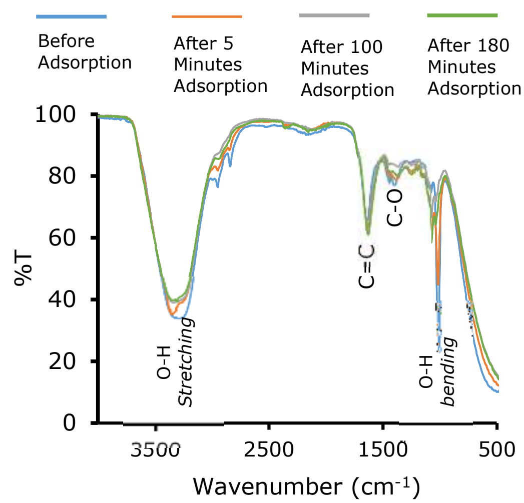

Figure 5. Spectrum-IR of stevia leaf extract before and after adsorption

b. Alkena (C=C) & Alkuna (C≡C) aromatic

In activated carbon and stevia leaf extract, aromatic alkene groups (C=C) were found in the wave range 1675–1500 cm^{-1} and are non-polar (Silverstein et al., 2005). In the activated carbon adsorbent, this group appeared allegedly due to the increase in temperature during the carbonization process and the time during activation, which caused the H atoms to evaporate so that the C atoms would join and form carbon double bonds (H. T. Ma et al., 2017). This group indicates that the activated carbon has increased levels of high-purity carbon. In the stevia leaf extract sample, the aromatic alkene group is thought to have come from a sweetening component, namely stevioside (Arumugam et al., 2020; Zaini et al., 2022). In the activated carbon adsorbent, there is also an alkyne functional group (C≡C) that is non-polar in the wave range 2400–2100 cm^{-1}.

c. Carbonyl (C-O)
Ketone carbonyl (C-O) has a stretching-bending vibrational type in the wave range 1.230–1.100 cm^{-1} and is polar. In samples of stevia leaf extract, phenol carbonyl groups (C-O) were found with stretching vibration types in the wave range of 1260–1000 cm^{-1} (Silverstein et al., 2005). The phenol carbonyl group is thought to originate from the phenolic tannin component in stevia leaf extract.

d. Siloxane (Si-O) & Silanol (Si-OH)
Siloxane (Si-O) is found in activated carbon adsorbents and is detected in the wave range 1110–830 cm^{-1}, while silanol (Si-OH) is detected in the wave range 3800–3200 cm^{-1} both of which are polar (Silverstein et al., 2005). Si (silicon) is one of the metal impurities commonly found in activated carbon.

e. Alkane (C-H)
In activated carbon, aromatic alkane stretching (C-H) and alkane bending (C-H) groups appear in the wave ranges 1000–600 cm^{-1} and 1475–1300 cm^{-1}, respectively (Silverstein et al., 2005). Both appear on the activated carbon adsorbent before and after being activated by 1M NaOH, but tend to experience a decrease in wave number. Both groups are non-polar (Wade & Simek, 2016).

f. O-Na
O-Na appears in the wave range 1600–1400 cm^{-1} and appears more in the carbon adsorbent after activation (Alshuiael & Al-Ghouti, 2020; Togibasa et al., 2021). This is due to the addition of the Na element from the NaOH activator solution, and binds to the O atom on the adsorbent during the activation process. When Na components are trapped in the pores, it can increase the pore size of the activated carbon adsorbent.

The adsorption process of tannins with activated carbon is also caused by van der Waals forces, which involve permanent polarity. Permanent polarity occurs due to the presence of tannins and active carbon, which have polar functional groups (Fraga-Corral et al., 2020; Wade & Simek, 2016). Van der Waals forces can occur in other polar functional groups found in tannins. In polar functional groups, there are differences in charge, which tend to be weaker. The difference in charge is thought to come from the surface of the activated carbon, which tends to have a positive charge and several polar groups from the tannins of stevia leaf extract, which have a negative charge. The surface of NaOH-activated carbon can be positively charged due to reduction and oxidation reactions (Raymundo-Piñero et al., 2005). NaOH acts as an oxidizer and causes the C atom in active carbon to lose electrons and become positively charged (Puspitasari et al., 2021; Tseng, 2007). Meanwhile, the negative charge is thought to come from the O atom of the polar group of tannin, which has a partially negative charge (δ-).

Based on the reduction and oxidation reactions, it shows that the element Na has been reduced to an oxidation number of 0, which indicates that NaOH acts as an oxidizing agent (oxidator). The presence of van der Waals forces causes the tannin adsorbate to be retained on the surface of the activated carbon adsorbent. An illustration of the role of functional groups and van der Waals forces in the tannin adsorption process using activated carbon is shown in Figure 6.

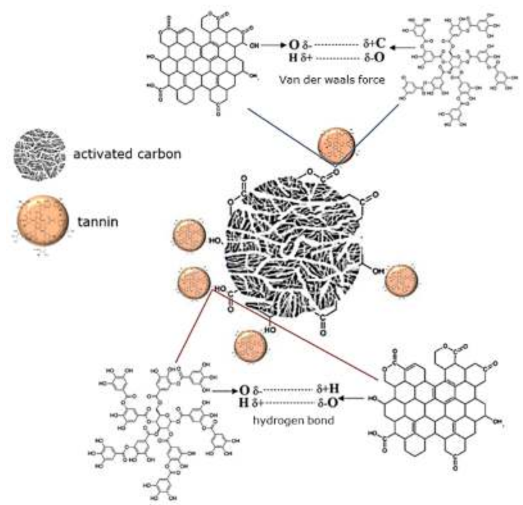

Figure 6. Illustration of hydrogen bonds and Van der Waals forces between tannin and activated carbon

3.3. Surface Area and Pore Diameter of Activated Carbon

The surface area and pore diameter of activated carbon are also factors that influence the adsorption process and determine the maximum adsorption capacity (qm). The following are the results of calculating data on the surface area of activated carbon before and after being activated by 1M NaOH. Table 1 shows an increase in the surface area and pore diameter values of activated carbon after activation with 1M NaOH. The resulting surface area meets the requirements, which range from 300–

3500 m^2/g (Kwiatkowski, 2011). The increase in surface area is also directly proportional to the increase in pore diameter, and it can be seen that the activated carbon produced is classified as mesoporous (2–50 nm). The increase in surface area and pore diameter was due to the activation process using a 1M NaOH solution for 24 hours. The activator entered between the hexagonal layers of the carbon adsorbent and opened the closed pore surface, resulting in a reduction in water content, ash, and levels of volatile substances, which are impurity components, as well as increased levels of carbon (Sriatun et al., 2020).

Table 1. Surface area and pore diameter of carbon active before and after activation

Sample	Surface Area (m^2/gr)	Pore Diameter (nm)
SbA	520.66	5.21
StA	532.90	5.33

SbA: Before activated by NaOH 1M
StA: After activated by NaOH 1M

Table 1 proves that the activated carbon adsorbent has a larger pore diameter (5.33 nm) than the diameter of the tannin molecule (1.1–1.6 nm), so that the tannin adsorbate can be adsorbed on the surface pores of the carbon adsorbent. active. In addition, the activation process can also cause a reduction in ash content. This is due to the reaction of NaOH with SiO_2 according to Equation 3 (Zhang et al., 2019).

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \quad (3)$$

SiO_2 is one of the impurity ashes found in activated carbon (Hieu et al., 2015). After the reaction with NaOH, SiO_2 will dissolve in the activator solution and will be wasted when the activated carbon is washed using distilled water (Fertani-Gmati et al., 2014). Dissolving SiO_2 causes the ash content to decrease, so that the surface pores of activated carbon open larger and increase the surface area and pore diameter. The reduction in the ash content of the adsorbent after activation was also proven through the results of the FTIR test, the peaks in the wave range 1110–830 cm^{-1} decreased, indicating a reduced ash content.

3.4. Isotherm Adsorption

Based on Figure 3, the tannin content within the time range of 95–120 minutes had reached equilibrium conditions and was subsequently used for the calculation of adsorption isotherms using the Freundlich and Langmuir adsorption isotherm equations. The two models were chosen because they were considered better for determining the adsorption capacity, type of adsorption, and the layer formed on the activated carbon adsorbent (Worch, 2021). The selection of the appropriate adsorption isotherm model is based on the R^2 value closest to 1 (Ho, 2004). The parameters of the Langmuir and Freundlich adsorption isotherm models are shown in Table 2.

Table 2. The parameters of the adsorption isotherm model.

The adsorption isotherm models	The value of parameters		Units
Freundlich	R^2	0.9998	-
	K_F	25.293	[(mg/g)(L/mg)$^{1/nf}$]
Langmuir	R^2	0.9832	-
	q^m	22.883	mg/g
	θ	0.954	-
	K_L	-1.063	L/mg

Based on the R^2 value in Table 2, it is proven that the Freundlich isotherm adsorption model is more suitable for the tannin adsorption process of stevia leaf extract using an activated carbon adsorbent and shows that the surface of the adsorbent used is heterogeneous. The heterogeneous adsorbent surface shows that the adsorption that occurs is classified as physical adsorption, and the adsorbate forms a multilayer layer (Alaqarbeh et al., 2021). This is also consistent with the research by Istiana & Prasetya (2020), which demonstrated that tannin adsorption using activated carbon follows the Freundlich model (Istiana & Prasetya, 2020). Physical adsorption can occur because, during the adsorption of phenolic compounds such as tannin, hydrogen bonds and van der Waals forces are formed between the tannin adsorbate molecules and the surface of the activated carbon adsorbent (Cao et al., 2020). The calculations for the Freundlich isotherm are in accordance with Equations 4 and 5.

$$q_e \quad = K_F Ce^{1/nf} \quad (4)$$

$$log\ log\ q_e \ = \frac{1}{nf}\ C_e + log\ log\ K_F \quad (5)$$

C_e is the tannin content in stevia leaf extract at equilibrium after adsorption (mg/L), q_e is the tannin adsorbed capacity per gram of activated carbon at equilibrium (mg/g), K_F is the Freundlich adsorption constant [(mg/g)(L/mg)$^{1/nf}$], and 1/nf is the

Freundlich heterogeneity factor or intensity parameter.
Furthermore, the K_F value (Freundlich constant) was also calculated, and it was found to be 25.293 [(mg/g)(L/mg)$^{1/nf}$]. The K_F value (Freundlich constant) indicates the maximum capacity (q_m) of the tannin adsorbate that can be attached to the activated carbon surface.

Meanwhile, in the Langmuir isotherm, it is supported by the calculation of fractional coverage (θ). Fractional coverage (θ), or the closed fraction, is a value indicating the capacity of active sites attached to or covered by the adsorbate on the adsorbent surface. It represents the ratio between the adsorption capacity value that occurs at equilibrium (q_e) and the total or maximum available adsorption capacity (q_m) (Bonilla-Petriciolet et al., 2017). The calculations for the Freundlich isotherm are in accordance with Equations 6, 7, and 8.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{c_e}\left(\frac{1}{K_L\, q_m}\right) \quad (7)$$

$$\theta = \frac{q_e}{q_m} \quad (8)$$

C_e is the tannin content in stevia leaf extract at equilibrium after adsorption (mg/L), q_e is the tannin adsorbed capacity per gram of activated carbon at equilibrium (mg/g), q_m is the maximum capacity of adsorbed tannins per gram of activated carbon (mg/g), K_L is the Langmuir adsorption constant (L/mg), and 1/nf is the Freundlich heterogeneity factor or intensity parameter.

Based on the calculations, the q_m value obtained is 22.283 mg/g, and the fractional coverage (θ) is 0.954. This fractional coverage value aligns with the theory, falling within the range of 0 < θ < 1 (Bashiri, 2013). Based on this value, it can be determined that the fraction of uncovered sites is 0.046, suggesting that there are likely sites not occupied by tannins. This condition could lead to the formation of a multilayer or a stack of adsorbate on top of the initial layer. Subsequently, the calculation of K_L (Langmuir constant) was carried out and obtained a value of -1.0633 L/mg. A negative coefficient indicates that the adsorption of tannins from stevia leaf extract does not conform to the Langmuir isotherm. This negative value also occurred in a study by Kurniasih et al, (2018), where if the constant is negative, the adsorption isotherm model is not suitable for a particular adsorption process (Kurniasih et al., 2018).

3.5. Adsorption Energy

In this study, the adsorption energy at 26°C was calculated using Equation 9 (Tang et al., 2012).

$$\Delta G = -RT \ln K \quad (9)$$

K is the adsorption isotherm equilibrium constant [Freundlich (mg/g)(L/mg)$^{1/nf}$], T is adsorption temperature (Kelvin), R is the universal gas constant (8.314 kJ/mol K).

From the formula above, the energy adsorption is -8.03 kJ/mol. This value is negative and below 20 kJ/mol, which proves that the adsorption of stevia leaf extract tannins occurs physically and spontaneously (Özer & Dursun, 2007).

4. Conclusion

Batch adsorption of tannins from stevia leaf extract using 100 mesh activated carbon adsorbent activated by NaOH 1M showed three different conditions, at 5–90 minutes the tannin level decreased, at 95–120 minutes the tannin level was constant and reached equilibrium, and at 125–180 minutes the tannin level increased again. The tannin adsorption process of stevia leaf extract is caused by 2 factors, namely the presence of functional groups that are dominantly polar, such as hydroxyl groups and the pore diameter of activated carbon is larger than the diameter of the tannin molecule. The appropriate adsorption isotherm model is Freundlich with a value of R^2 = 0.9998; K_F = 25.293 [(mg/g)(L/mg)$^{1/nf}$] with an adsorption energy of -8.03 kJ/mol. The adsorption that occurs is classified as physical adsorption due to the interaction of Van der Waals forces and hydrogen bonds.

Author Contributions

L.K.D: conceptualization, investigation, writing an original draft, reviewing and editing; A.H.S: conceptualization, methodology, supervision; K.P.: research experiment, data analysis, writing an original draft; N.I.M.: research experiment, data analysis. All authors have read and agreed to the published version of the manuscript.

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Data Available Statement

Available on request to the corresponding author.

Conflict of Interest

The author declares that there is no conflict of interest regarding the publication of this manuscript.

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