Langmuir and Freundlich isotherm adsorption using activated charcoal from banana peel to reduce total suspended solid (TSS) levels in tofu industry liquid waste

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Abstract. The tofu industry is currently growing very rapidly both on a home industry scale and on a factory scale, in the process of making tofu solid and liquid waste are produced. Solid waste is usually used for animal feed, while liquid waste is not treated. Tofu industrial liquid waste contains very high Total Suspended Solid (TSS), if the liquid waste is disposed of directly into the water it can pollute the aquatic ecosystem. One way to reduce pollution is to use activated charcoal from plantain peels as adsorbent. This study aims to determine the appropriate adsorption isotherm model in the absorption process to reduce the level of Total Suspended Solid (TSS) of tofu industrial wastewater with variations in the mass of activated charcoal (100 grams; 200 grams and 300 grams) and adsorption time (20 minutes; 40 minutes; 60 minutes; 80 minutes and 100 minutes). The equation used in the adsorption process is the Langmuir and Freundlich isotherm adsorption equation. The experimental results show that the largest TSS value adsorbed by activated charcoal is 200 grams with a contact time of 60 minutes. The suitable equation for determining the maximum adsorption capacity of activated charcoal in the TSS absorption process of tofu industrial wastewater is the equation Freundlich with $R^2 = 1$. The maximum adsorption power of activated charcoal on the TSS absorption of tofu industrial wastewater was 51,8134 mg / L.

1. Introduction
Bananas are a tropical fruit that is very popular in almost all over the world [13]; [36], there are various types of bananas, one of which is the Raja banana. Banana peels represent 40% of the total weight of bananas, so technology is needed to process these wastes so they don't pollute the environment.

Activated charcoal is a carbon that has been through an activation process with a carbonization process at a temperature of 750 - 950 °C so that it has good absorption capacity [1] of organic and inorganic compounds, both in the form of solutions and gases [16]. The pore size of activated charcoal is divided into three categories, namely macroporous (> 25 nm in size), mesoporous (> 1 nm and <25 nm in size) and microporous (<1 nm in size) [28].

Banana peel has high efficiency and low cost so that it can be used as an alternative to reduce pollution [36]; [24]; [42]. Activated charcoal from banana peels has a specific surface area of up to 3365 m² / gram [33]. Charcoal from banana peels can be used as an adsorbent because it has a fixed carbon (C) content of 92.53% [4];[6]. The adsorption process is influenced by several factors, namely pH, contact time, adsorbent concentration and temperature. pH affects the surface of the adsorbent [3]; [35]. The contact time produces a strong force between the adsorbent to the fluid [25]; [17]; [26]; [34]. The concentration of adsorbent will affect the adsorption time [25]. A small variations of
temperature tends not to change the adsorption process so that the heating is required at high temperatures [39]; [40].

Tofu is one of the traditional foods in Indonesia that is made with soy ingredients [15]; [17]. Tofu industrial liquid waste contains very high Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), and Total Suspended Solid (TSS) [7]. COD can be used as a parameter of the efficiency of the anaerobic digestion process [10]; [5]; [19]. BOD indicates that there is an activity of microorganisms [7].

Total Suspended Solid (TSS) is the residue of total suspended solids with a diameter of less than 62 µm [41]; [14]; [31] can be in the form of mud, clay, to heavy metals [12]; [23]; [29]. High TSS will block the entry of sunlight into the water, it can be disrupting the photosynthesis process and causing a decrease in dissolved oxygen released into the water by plants [30]; [8].

There are several kinds of equations in the adsorption isotherm process, but because the adsorption of molecules or ions on a solid surface is generally limited to a layer of one molecule, the adsorption follows the Freundlich and/or Langmuir adsorption equations [20]; [18]. This research aims to determine the adsorption isotherm model for the adsorption process in reducing TSS levels of tofu industrial wastewater using the Langmuir and Freundlich equations.

2. Materials and Methods

2.1 Activated Charcoal From Banana Peel

The process of making activated charcoal consists of three stages, namely:

- **Dehydration process**
  Banana peel is cleaned of dirt that is still attached then washed thoroughly. Banana peel is cut 1-2 cm (initial weight) then put in the oven at 60 °C for 6 days after that save in a desiccator for 15 minutes. Put it in the oven again at 110 °C for 1 hour then weigh the end.

- **Delignification process**
  Dried banana peels from the dehydration process were soaked in a solution of sodium hydroxide (NaOH) 1M for 12 hours and then filtered and washed the banana peels with aquadest. Put it in the oven at 60 °C for 24 hours, then save it in a desiccator for 15 minutes and calculate the weight of dry banana peels until it is constant.

- **Carbonization process**
  Weigh 10 grams of dried banana peels then carbonized in the furnace with a temperature of 700 °C for 2 hours. After that, the size reduction is done to get the size of 80 mesh.

2.2 Tofu Industrial Liquid Waste

Tofu liquid waste contains a lot of water, protein, fat, and high carbohydrates so that decomposition by microorganisms is very easy to occur [38]; [21]; [27]; [37]. From the research of Wulandari et al., (2016) has been conducted decreased levels of COD, BOD and TSS in the tofu industry wastewater using Moringa seed powder as a natural coagulant using the coagulation-flocculation method. After the coagulation-flocculation process, the COD and BOD values have met the quality standards while the TSS value is still high. Before carrying out the further research process, a preliminary analysis test was carried out on the tofu industrial liquid waste sample as follows Table 1. From Table 1. It seen that tofu industrial liquid waste is considered unworthy to be disposed of because it does not meet standards quality of wastewater for the tofu industry according to the regulation of the Minister of Environment No. 5 the year 2014 so that the adsorption process is carried out with activated charcoal.
Table 1. Comparison of preliminary analysis test results with standard quality

| Parameters | Preliminary analysis test results (mg/L) | Coagulation flocculation process (mg/L) | Standard quality /SNI (mg/L) |
|------------|------------------------------------------|----------------------------------------|-----------------------------|
| COD        | 4180                                     | 128                                    | 300                         |
| BOD        | 821,0                                    | 114                                    | 150                         |
| TSS        | 773,0                                    | 546                                    | 200                         |

2.3 The Adsorption Process In The Adsorber Column

Preparing tofu industrial wastewater and adsorption equipment then measure the volume of tofu industrial liquid waste 1L in the container tank. Weigh the activated charcoal according to the variable then put it in the adsorption column. Turn on the pump and open the raw material valve then run according to the variable time (20, 40, 60, 80, 100) minutes and the mass of activated charcoal (100, 200, 300) gram. The product flowed into the storage tank until the specified time. After the time is reached according to the variable, the samples are taken for the final TSS analysis.

![Figure 1. Adsorption Column](https://example.com/figure1.png)

Description:
1. Tofu industrial liquid waste container
2. Pump (to flow liquid waste into adsorber column).
3. Valve (to regulate the flow rate of liquid waste).
4. Flowmeter (to determine the flow rate of liquid waste).
5. Adsorber column (the place of contact between activated charcoal and liquid waste).
6. Valve (to regulate the wastewater output after the adsorption during the specified time).

2.4 The Adsorption Experimental Study

In the adsorption isotherm, the amount of adsorbate that can be absorbed by the adsorbent is a function of the adsorbate concentration and temperature. The characteristics of the adsorbate include solubility, molecular structure, molecular weight, polarity, and hydrocarbon saturation [20]; [18]. The equation
that is often used to describe experimental isotherm data was developed by Freundlich, Langmuir, and others. The Freundlich isotherm model is generally used most often to demonstrate the adsorption characteristic of activated carbon used in water treatment and wastewater. This Model is heterogeneous in the process of absorption [22]; [9]. The Freundlich isotherm is described as follows:

$$\frac{x}{m} = K_f C_e^{1/n}$$  \hspace{1cm} (1)

Where \(x/m\) is the adsorbate mass adsorbed per unit mass of adsorbent, (mg adsorbate/gram activated carbon). \(K_f\) is the Freundlich capacity/constant factor, (mg absorbate/gram activated carbon) (L water/mg adsorbate). \(C_e\) is the equilibrium concentration of the adsorbate in solution after adsorption, (mg/L) and \(1/n\) is Freundlich's intensity parameter. If the value of \(1/n\) is in the range 0.1-1, the adsorption process is considered good [11]; [2]. The constant in the Freundlich isotherm can be determined by plotting \(\log(x/m)\) versus \(\log C_e\) so it can be rewritten as follows :

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (2)

The Langmuir adsorption isotherm is developed by assuming:
1. Several sites on the adsorbent surface which all have the same energy.
2. Adsorption is reversible [28].

The Langmuir isotherm model is described as follows:

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e}$$  \hspace{1cm} (3)

Where \(x/m\) is the adsorbate mass adsorbed per unit mass of adsorbent, (mg adsorbate/gram activated carbon). \(a, b\) is the empirical constant and \(C_e\) is the equilibrium concentration of the adsorbate in the solution after adsorption, (mg/L). The constant in the Langmuir isotherm can be determined by plotting \((C_e/x/m)\) versus \(C_e\) so that it can be rewritten into:

$$\frac{C_e}{(x/m)} = \frac{1}{ab} + \frac{1}{a} C_e$$  \hspace{1cm} (4)

3. Results and Discussion

3.1 Effect of Mass and Adsorption Time on TSS Values

From the TSS analysis test, the following results were obtained:

| Mass       | TSS analysis test results |
|------------|---------------------------|
|            | Time | 20 min | 40 min | 60 min | 80 min | 100 min |
| 100 gram   | 100 gram | 270 | 250 | 210 | 220,5 | 225 |
| 200 gram   | 200 gram | 175 | 120 | 100,5 | 110 | 130 |
| 300 gram   | 300 gram | 172 | 130 | 130,5 | 140 | 143,5 |

Based on the results of research on the variable adsorption time (20, 40, 60, 80, 100) minutes and the mass of activated charcoal (100, 200, 300) grams, the optimum contact time is 60 minutes with the optimum adsorbent mass of 200 grams. It can be concluded that the longer the contact time will be
better in the adsorption process until the optimum time is obtained. After the optimum time is obtained, the absorption process tends to decrease, this is due to the small probability of the adsorbent is carried by the solution so that the absorption ability reduced. Besides, it is also caused by the adsorbent that has reached its saturation point in the adsorption process, so that the absorption process becomes decreased after optimum time is reached as attached in Figure 2. After being tested by SEM, the surface area of activated charcoal was obtained 3,167 m²/g.

![Figure 2](image-url)  
**Figure 2.** TSS value in the adsorption process

![Figure 3](image-url)  
**Figure 3.** Activated charcoal from banana peel

### 3.2 Determination of Adsorption Isotherm

The determination of the adsorption isotherm is carried out by changing the Langmuir and Freundlich isotherm equations into a straight line equilibrium curve. When the adsorption isotherm is linear, the resulting curves are almost the same [40]. To determine the Langmuir and Freundlich isotherm equation, the values of \( \frac{x}{m} \), \( \frac{C_e}{x/m} \), \( \log (x/m) \), and \( \log C_e \) are calculated as shown in Table 3. Where \( m \) is mass of absorbent (gram), \( t \) is the time of adsorption (minute), \( C_a \) is initial TSS value (mg/L), \( C_e \) is final TSS value (mg/L). From Table 3, the plot is carried out to determine the Langmuir adsorption isotherm constant and the Freundlich adsorption isotherm constant by using ms Excel software.
Table 3. The value of $x/m$, $Ce/(x/m)$, log $(x/m)$ and log $Ce$

| m  | t  | Ca | Ce | $x/m$ | $Ce/(x/m)$ | Log $(x/m)$ | Log $(Ce)$ | % TSS decrease |
|----|----|----|----|-------|------------|-------------|------------|----------------|
| 100| 20 | 773| 270| 503   | 3.8821     | 69.5489     | 0.5890     | 2.4313        | 0.6507         |
| 40 | 773| 250| 523| 3.6146| 69.1629   | 0.5580     | 2.3979     | 0.6765         |
| 60 | 773| 210| 563| 3.0705| 68.3909   | 0.4872     | 2.3222     | 0.7283         |
| 80 | 773| 220,5| 552,5| 3.2145| 68.5935 | 0.5071     | 2.3434     | 0.7147         |
| 100| 773| 225| 548| 3.2760| 68.6804 | 0.5153     | 2.3521     | 0.7089         |
| 200| 20 | 773| 175| 598   | 2.5843   | 67.7153    | 0.4123     | 2.2430        | 0.7736         |
| 40 | 773| 120| 653| 1.8003| 66.6538 | 0.2553     | 2.0791     | 0.8447         |
| 60 | 773| 100,5| 672,5| 1.5163| 66.2774 | 0.1808     | 2.0021     | 0.8699         |
| 80 | 773| 110| 663| 1.6551| 66.4607 | 0.2188     | 2.0413     | 0.8576         |
| 100| 773| 130| 643| 1.9447| 66.8468 | 0.2888     | 2.1139     | 0.8318         |
| 300| 20 | 773| 172| 601   | 2.5422   | 67.6574    | 0.4052     | 2.2355        | 0.7774         |
| 40 | 773| 130| 643| 1.9447| 66.8468 | 0.2888     | 2.1139     | 0.8318         |
| 60 | 773| 130,5| 642,5| 1.9519| 66.8564 | 0.2904     | 2.1156     | 0.8311         |
| 80 | 773| 140| 633| 2.0883| 67.0398 | 0.3197     | 2.1461     | 0.8188         |
| 100| 773| 143,5| 629,5| 2.1383| 67.1073 | 0.3300     | 2.1568     | 0.8143         |

3.3 Isotherm Model of Langmuir Adsorption

In this isotherm model there is no interaction between adsorbed molecules occurs. The Langmuir isotherm equation is made by plotting the $Ce/(x/m)$ versus $Ce$ values. From Fig. 4, the Langmuir equation is obtained $Ce/(x/m) = -0.0193Ce + 56.949$ with $R^2 = 0.0034$.

![Langmuir Adsorption Isotherm Equation](image)

**Figure 4.** Langmuir adsorption isotherm equation

3.4 Isotherm Model of Freundlich Adsorption

In this isotherm model, the heat distribution of biosorption is non-uniform and affinities over the heterogeneous surface accompanied by interactions between adsorbed molecules. For the Freundlich isotherm equation, it is made by plotting log $(x/m)$ versus log $Ce$. From Fig. 5, Freundlich's equation is obtained $\log (x/m) = 0.9513 \log Ce – 1.7224$ with $R^2 = 1$. 

![Freundlich Isotherm Equation](image)
From fig. 4 and 5 it can be seen that the TSS adsorption of tofu wastewater by activated charcoal from banana peels fulfills the Freundlich adsorption equation because the value of $R^2 = 1$. This shows that the Freundlich equation can be applied to the adsorption process of activated charcoal from banana peels. Freundlich's adsorption isotherm assumes that the absorption process takes place in more than one surface layer (multilayer) and the surface side is heterogeneous so that there is a difference in binding energy on each side. From Table 4, it can be seen that the value $1/n$ is 0.5522. This shows that the absorption process is favorable because $1/n < 1$. The constant values of the Langmuir and Freundlich equations are obtained as follows:

| Table 4. Langmuir and Freundlich Constant |
|------------------------------------------|
| Isotherm       | Constant | Value  |
|----------------|----------|--------|
| Langmuir       | a        | 51.8134 |
|                | b        | 0.0003 |
| Freundlich     | k        | 1.0515 |
|                | $1/n$    | 0.5522 |

4. Conclusion

The TSS adsorption process of tofu industrial wastewater used activated charcoal from banana peels at mass variations of 100; 200; 300 grams and 20- time variations; 40; 60; 80; 100 minutes reaches the optimum contact time at 60 minutes contact time with a mass of 200 grams. The TSS adsorption process by activated banana peel charcoal fulfills the Freundlich adsorption isotherm equation. The maximum adsorption power of activated charcoal on the TSS absorption of tofu industrial wastewater was 51.8134 mg/L.

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