Determination of rice husk activated Carbon capacity in adsorption of Cu Metal from Sasirangan liquid waste based on isotherm model

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Abstract. The process of manufacturing Sasirangan - a traditional fabric of South Kalimantan - has an impact that affects environmental pollution, namely the dyeing process of the fabric. The synthetic dyes used contain heavy metals and one of those toxic metals is copper (Cu). This study aims to determine the adsorption capacity of rice husk activated carbon adsorbent by adjusting the adsorption pattern based on isotherm models as the treatment to sasirangan liquid waste. The method consists of three stages: preparation of adsorbent by carbonization process, chemical and physical activation, then continued by adsorption process of Cu metal with carbon from rice husks with variations of adsorbent dose (2, 4, and 6 grams). This treatment was conducted by batch process. In this research, the adsorption capacity of rice husk adsorbent towards heavy metal Cu in sasirangan liquid waste was determined from the equilibrium state with the Langmuir isotherm equation and Freundlich isotherm equation. Based on isothermal studies of adsorption data, the correlation coefficient values obtained from the isotherm model approaches are: for dose of 2 grams adsorbent, Langmuir $R^2 = 0.9991$ and Freundlich $R^2 = 0.9981$; for dose of 4 grams adsorbent, Langmuir $R^2 = 0.9992$ and Freundlich $R^2 = 0.9989$; for dose of 6 grams adsorbent, Langmuir $R^2 = 0.9990$ and Freundlich $R^2 = 0.9986$. The results of investigation indicate that adsorption data correlated well with Langmuir isotherm model.

Keywords: adsorption, Cu metal, sasirangan liquid waste, isotherm model

1. Introduction
Sasirangan is a traditional fabric from South Kalimantan which is produced by the Banjar tribe on a home industry scale. An important part of making sasirangan fabrics is making pattern by dyeing the finished fabric using synthetic dyes which are relatively stable and firmly attached [1]. The synthetic dyes used contain heavy metals, such as copper (Cu) [2]. Heavy metal contamination in ecosystems related to their accumulation in living tissues throughout the food chain as non-biodegradable pollutants potentially causing significant health problems [3]. If the heavy metal content exceeds the
threshold, then the liquid waste of Sasirangan textile industry has a high potential for contamination that it does not meet the requirements to be discharged into the environment before being treated first [4].

Traditional processing methods commonly used for metal-containing wastes are chemical precipitation and filtration, electrochemical treatment, chemical oxidation or reduction, reverse osmosis, solvent extraction, ion exchange, and evaporation. However there are several disadvantages of these methods, such as high cost, imperfect metal removal, low selectivity, high energy requirements and by-products a poisonous slurry that is difficult to remove [5]. Nowadays, adsorption methods have been widely used to remove toxic metals from wastewater. The adsorbents used are prepared from agricultural byproducts, which are cheap and widely available [6]. Agricultural wastes such as mangosteen peel [7], sawdust [8], sunflower stalks [9], peanut shells [10], and wheat husks [11] have been used to remove metal ions from wastewater.

The adsorption process is an effective technology for heavy metals removal in Sasirangan liquid waste. Adsorption is kind of attachment process of adsorbate on the surface of an adsorbent [12]. One type of adsorbent used is activated carbon made from rice husks. Currently, the existence of rice husks in Indonesia has not received proper attention. Its utilization is still only for simple purposes such as rubbing ash and as a plant medium. In certain areas, rice husks are even discarded and considered less useful. Rice husks can be used as adsorbents because they contain cellulose which can adsorb metal cations from the solution medium. Thus, rice husks have the potential to be utilized as heavy metal adsorbents from liquid medium [13]. Research about the potential of rice husk activated carbon as an adsorbent has been carried out. It was reported that the maximum adsorption capacity of rice husk activated carbon towards paraquat is 317.7 mg/g.

The relationship between the amount of adsorbed adsorbate and the concentration of adsorbate in solution at equilibrium and constant temperature can be expressed by the adsorption isotherm [14]. The amount of substance adsorbed on the surface of the adsorbent is a balanced process, because the rate of adsorption is accompanied by desorption. At the beginning of the reaction, the adsorption event is more dominant than the desorption event, so that adsorption takes place quickly. At certain times the adsorption event tends to be slow, and conversely the rate of desorption tends to increase. The time when the adsorption rate is the same as the desorption rate is often referred to as the equilibrium state [15].

Adsorption isotherm model is applied to effectively use the adsorption process in waste treatment for environmental protection purposes [16]. Adsorption isotherms is generally a curve presenting the phenomenon controlling the mobility and the retention of a substance from an aqueous porous medium or aquatic environment to a solid-phase at constant temperature and pH [17, 18]. The ratio between the amount of adsorbate and the residual in solution (adsorption equilibrium) is determined when the adsorbate-containing phase and the adsorbate concentration in the bulk solution have been contacted with the adsorbent for sufficient time [19, 20]. In this study, the adsorption capacity of rice husk activated carbon adsorbent was defined by observing the adsorption pattern at the equilibrium with Langmuir isotherm and Freundlich isotherm models.

2. Materials and Method

2.1. Materials

The materials used in this research were sasirangan liquid waste obtained from Banjarmasin, chloric acid (HCl), nitric acid (HNO₃), and distilled water.

2.2. Method

This study consists of three stages. The first is preparation of adsorbent by carbonization process. The second stage is chemical activation with HCl solution and physical activation by burning processing in the the furnace. Meanwhile, the third stage was testing the ability of activated carbon from rice husks...
to adsorb Cu metal with variables of adsorbent doses (2, 4 and 6 gr). The treatment was conducted by batch process using a rotary shaker. The sample volume of Sasirangan liquid waste used was 200 ml.

Then the experiment was conducted to determine the ability of activated carbon of rice husk as an adsorbent. The test results were analyzed descriptively to describe the decrease in heavy metal Cu concentrations at various adsorbent doses. The reduction of Cu content is determined by Equation 1 as follows:

\[ E = \frac{C_0 - C_e}{C_0} \times 100\% \]  

Where:
- \( E \) = Decrease percentage of Cu concentration (%)  
- \( C_0 \) = Initial concentration of Cu (mg/L)  
- \( C_e \) = Final concentration of Cu (mg/L)

The relationship between the amount of adsorbed adsorbate and the concentration of adsorbate in solution at equilibrium and constant temperature can be expressed by the adsorption isotherm. The Langmuir isotherm is expressed in Equation 2 as follows:

\[ Q = \frac{b \cdot K \cdot C_e}{1 + K \cdot C_e} \]  

Where:
- \( Q \) = the amount of adsorbate per adsorbent mass (mg/g)  
- \( b \) = maximum capacity of adsorbent (mg/g)  
- \( K \) = adsorption equilibrium constant (L/mg)  
- \( C_e \) = solute concentration at equilibrium (mg/g)

Meanwhile, the mathematical expression of Freundlich isotherm is defined in Equation 3 as follows:

\[ \frac{x}{m} = k \cdot C^{1/n} \]  

Where:
- \( x \) = amount of solute adsorbed (mg)  
- \( m \) = adsorbent mass (mg)  
- \( C \) = concentration of the same adsorbent (mg/g)  
- \( k \) = adsorbent constant  
- \( n \) = adsorbent constant

3. Result and Discussion

The adsorption capacity of rice husk activated carbon can be determined by observing the adsorption pattern of adsorbent interacted with sasirangan liquid waste, with variations in its dose. In this study, the adsorption capacity of the adsorbent towards heavy metal Cu in Sasirangan liquid waste was defined by adsorption isotherm model. Two common isotherm models were established in equilibrium state: the Langmuir and Freundlich isotherm models. The applicability of the isotherm equation was judged by the determination of correlation coefficients, \( R^2 \) [23]. The adsorption isotherm has the ability to describe the relationship between the adsorbate molecule and adsorbent surface well and highlight distribution adsorbate molecules between the liquid and the solid phase [24]. Following are the results of capacity calculations with the Langmuir isotherm and Freundlich isotherm equations as can be seen in Table 1.
**Table 1.** The adsorption capacity of rice husk activated carbon with by isotherm equation

| Contact time (min) | Adsorbent dose (gr) | C₀ (mg/l) | Ce (mg/l) | x/m | Ce/(x/m) | Log Ce | Log (x/m) | R²         |
|-------------------|---------------------|-----------|-----------|-----|----------|--------|-----------|------------|
| 30                | 2                   | 0.047     | 0.028     | 0.002 | 14.737   | -1.553 | -2.721    | 0.9991     |
| 60                | 2                   | 0.047     | 0.029     | 0.002 | 16.111   | -1.538 | -2.745    | 0.9993     |
| 120               | 2                   | 0.047     | 0.027     | 0.002 | 13.500   | -1.569 | -2.699    | 0.9985     |
| 30                | 4                   | 0.047     | 0.019     | 0.001 | 13.571   | -1.721 | -2.854    | 0.9991     |
| 60                | 4                   | 0.047     | 0.018     | 0.001 | 12.414   | -1.745 | -2.839    | 0.9991     |
| 120               | 4                   | 0.047     | 0.013     | 0.002 | 7.647    | -1.886 | -2.770    | 0.9991     |
| 30                | 6                   | 0.047     | 0.021     | 0.001 | 24.231   | -1.678 | -3.062    | 0.9990     |
| 60                | 6                   | 0.047     | 0.022     | 0.001 | 26.400   | -1.658 | -3.079    | 0.9991     |
| 120               | 6                   | 0.047     | 0.017     | 0.001 | 17.000   | -1.770 | -3.000    | 0.9987     |

Where:
- C₀ = initial concentration of Cu (ppm)
- Ce = final concentration of Cu (ppm)

Recently, linear regression analysis has been one of the most widely applied tools to determine the best fitting adsorption models because it quantifies the distribution of adsorbate, analyzes the adsorption system, and verifies the consistency of hypothesis of the adsorption isotherm model [25]. The comparison of linear plot between Langmuir and Freundlich Isotherm model of 2 grams adsorbent is presented in Figure 1.

**Figure 1.** Chart of Langmuir and Freundlich isotherm linearization for 2 grams adsorbent dose

The linearity pattern formed from the Langmuir isotherm equation has the value of correlation coefficient $R^2 = 0.9991$ and for the Freundlich isotherm, $R^2 = 0.9981$. Then the adsorption process of heavy metal Cu in sasirangan liquid waste with activated carbon from rice husk follows the Langmuir isotherm model, because its $R^2$ value is more approached to linearity.

The comparison between concentrations of Cu adsorbed by rice husk activated carbon with a dose of 4 grams is presented in Figure 2.
Figure 2. Chart of Langmuir and Freundlich isotherm linearization for 4 grams adsorbent dose

Figure 2 shows the difference in the linearity pattern between two isotherm models. The linearity pattern formed from the Langmuir isotherm equation has the value of $R^2 = 0.9992$ and for the Freundlich isotherm, $R^2 = 0.9989$. Then the adsorption process of heavy metal Cu in sasirangan liquid waste with activated carbon from rice husks with activation follows the Langmuir isotherm model, because of its higher approach to linearity.

The comparison between concentrations of Cu adsorbed by rice husk activated carbon with a dose of 6 grams is presented in Figure 3.

Figure 3. Chart of Langmuir and Freundlich isotherm linearization for 6 grams adsorbent dose

Figure 3 displays the difference in the linear plot between two isotherm patterns. The linearity pattern that is formed from the Langmuir isotherm equation shows the value of $R^2 = 0.9990$ and for the Freundlich isotherm, $R^2 = 0.9986$. It is considered that the adsorption process of heavy metal Cu in sasirangan liquid waste with activated carbon from rice husks with activation follows the Langmuir isotherm model.

The adsorption capacity by the adsorbent is number of groups that can be exchanged in the adsorbent. The adsorption exchange capacity of an adsorbent is the number of ions that can be exchanged for each gram of dry adsorbent or the number of ions that can be exchanged per 1 ml of wet adsorbent. Determination of the adsorption capacity of the rice husk adsorbent can be determined through an adsorption isotherm model approach, by observing the adsorption pattern of the two adsorbents interacted with sasirangan liquid waste with optimum weight concentration and contact time. Adsorption isotherm is the relationship between the amount of substance adsorbed by the weight of the adsorbent with the concentration of solute at a certain temperature. Adsorption equilibrium occurs when the amount of adsorbate absorbed by the adsorbent (on the surface phase) and the adsorbate remaining in solution (in the bulk phase) remains relatively constant with respect to the shaking time [26].

The adsorption isotherm is used to characterize the equation between the amount of adsorbate accumulated in the adsorbent and the concentration of the adsorbate solution. Based on previous research that has been conducted in determining the most appropriate correlation for balance data in
the adsorption system design, there are two isotherm models used, namely Langmuir and Freundlich [23]. Based on the calculation for the adsorption pattern of rice husk activated carbon adsorbent towards heavy metal Cu in Sasirangan liquid waste using the Langmuir and Freundlich isotherm model approach, the value of the isotherm model is obtained. The most suitable correlation value for adsorption equilibrium data is the R² value which is closer to linearity. From the three doses of rice husk adsorbent, the R² value for the 2 grams dose is R² Langmuir = 0.9991 and R² Freundlich = 0.9993, for the 4 grams dose the value of R² Langmuir = 0.9991 and R² Freundlich = 0.9985 and for the adsorbent dose 6 grams of R² Langmuir = 0.9990 and R² Freundlich = 0.9987. The linearity of the curve that is formed indicates that the adsorption pattern follows the Langmuir isotherm model. This shows that on the surface of the rice husk activated carbon adsorbent, adsorption process occurs in the outer layer.

Adsorption isotherm describes the relationship between the adsorbed substances in a certain amount of adsorbent weight in equilibrium units [27]. Freundlich isotherm model is an empirical equation describing the nonideal and reversible adsorption. The model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [28]. Meanwhile, Langmuir isotherm is an adsorption model where on the adsorbent surface there are homogeneous active sites which are proportional to the surface area. Each active site can only adsorb one adsorbate molecule, so that the adsorption will only be limited to the formation of a single layer [22]. If every active site has adsorbed the adsorbate, the adsorbent can no longer adsorb. Chemical adsorption occurs because of the interaction between the active site of the adsorbent and the adsorbate which involves chemical bonds, chemical interactions only occur in the single absorption layer on the surface of the adsorbent cell wall. The applicability of the Langmuir model isotherm in this study means that the adsorption process occurs in a mono-layer with each molecule having the same enthalpy and activation energy. The results also show that no interaction and transmigration of dyes on neighboring surface areas [23].

4. Conclusion
This study demonstrated that rice husk activated carbon could be used as an effective adsorbent for the treatment of Sasirangan liquid waste containing heavy metal Cu. Isothermal study indicated that Langmuir adsorption isotherm model is better fits than the Freundlich model based on the values of corresponding linear correlation coefficients (R²). The highest regression values of 0.9992 obtained from 4 grams of adsorbent dose. It is therefore in conclusion that different models should be used to fit adsorption experimental data to evaluate the best model to explain the adsorption.

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