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# Comparative Analysis of Methyl Red Adsorption on NaOH- and HCl-Activated Carbon from Bintaro Fruit: Kinetics and Isotherm Studies

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**Abstract.** Pollution caused by synthetic dye waste poses a significant environmental challenge, especially in the textile industry. This study aims to develop activated carbon from bintaro fruit (Cerbera manghas) activated with HCl and NaOH, to function as a bio adsorbent in eliminating methyl red from water-based solutions. The activated carbon was synthesized through pyrolysis at 400°C, followed by chemical activation with HCl and NaOH solutions. Characterization of the activated carbon revealed that NaOH activation resulted in a larger surface area and porosity compared to HCl activation. Adsorption kinetics tests revealed that the adsorption mechanism was better represented by the pseudo-second order model, with higher $R^2$ values for both adsorbents (0.951 for HCl and 0.985 for NaOH). Adsorption isotherm results demonstrated that Langmuir model provided a better fit for describing methyl red adsorption, with highest adsorption capacities were 13.18 mg/g for NaOH-activated carbon and 8.65 mg/g for HCl-activated carbon. Thus, NaOH-activated bintaro fruit carbon exhibited higher adsorption efficiency than HCl-activated carbon, making it a potential alternative for environmentally friendly dye waste treatment.

**Keywords** : Activated carbon, Bintaro fruit, Methyl red, Kinetics, Isotherm

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## Introduction

Bintaro fruit (*Cerbera manghas*) is known for its toxic properties due to the presence of harmful glycosides and alkaloids [1]. Despite its toxicity, this plant thrives in tropical regions such as Indonesia, particularly in Central Kalimantan, producing abundant biomass waste that remains underutilized. Managing toxic biomass waste like Bintaro fruit poses significant challenges, especially in mitigating its negative environmental and public health impacts [2]. In this regard, utilizing Bintaro fruit biomass for activated carbon production presents a promising approach, not only reducing waste but also creating a functional material with added value. Recent studies have highlighted the potential of utilizing biomass waste, including Bintaro fruit serves as a potential raw material for producing activated carbon with a high adsorption capacity for organic pollutants, particularly synthetic dyes [3]. Synthetic dyes such as methyl red (MR) are commonly found in textile, paper, and printing industry effluents, posing a risk of water pollution if not properly treated. Therefore, utilizing activated carbon obtained through local biomass, specifically derived from Cerbera manghas, offers a novel and sustainable approach.

Dye waste from industries significantly contributes to water pollution, as synthetic dyes are generally toxic, stable, and resistant to biological degradation. The presence of these dyes in aquatic environments can modify the water's physical and chemical properties, resulting in elevated organic pollutant levels and dissolved solid concentrations [4]. Consequently, water quality deteriorates, rendering it unsuitable for domestic or industrial use. Methyl red (MR), an azo dye with a complex aromatic structure, is particularly resistant to natural degradation in aquatic environments. The accumulation of such dyes not only disrupts water aesthetics but also reduces sunlight penetration, hindering photosynthesis in aquatic organisms [5]. Moreover, some azo dyes are reported to be carcinogenic and mutagenic if they accumulate in the food chain. Therefore, effective and environmentally friendly treatment methods, such as adsorption using bio-adsorbents, are essential.

Chemical activation using acids and bases is known to enhance the surface area, porosity, and number of active sites in activated carbon, thereby improving its adsorption capacity for dyes. Acid activation typically removes impurities and increases the surface acidity of activated carbon, enhancing its affinity for positively charged molecules [6]. In contrast, base activation tends to form hydroxyl groups on the carbon surface, making it more effective in adsorbing negatively charged dyes such as azo dyes [7]. Previous studies have demonstrated the effectiveness of chemical activation in improving the adsorption performance of bio-adsorbents derived from various biomass sources. For instance, Fitriansyah et al. (2021) reported that phosphoric acid activation of coconut husk carbon increased its adsorption capacity for Indigosol Blue 04-B dye to 19.8 mg/g [8]. Similarly, Jawad et al. (2021) found that KOH-activated dragon fruit peel carbon demonstrated a removal efficiency of 195.2 mg/g for methylene blue dye [9]. These results highlight the crucial role of chemical activation in improving the adsorption efficiency of bio-based adsorbents, warranting further investigation into its application for Bintaro fruit-based activated carbon.

In adsorption studies, kinetic and equilibrium analyses play a vital role in elucidating the interaction processes between adsorbents with adsorbates. Kinetic studies are conducted to assess the adsorption rate and identify the most appropriate kinetic model, such as the Pseudo-First Order or Pseudo-Second Order model [10], which represent specific characteristics of dye-surface interactions. Selecting the appropriate kinetic model is crucial for enhancing adsorption efficiency, particularly in large-scale applications. Additionally, equilibrium analysis through isotherm models, including Langmuir and Freundlich, offers valuable insights into adsorption behavior, provides insights into the distribution of adsorbates on the adsorbent surface at equilibrium [11]. This study provides an in-depth analysis of the adsorption potential and performance of carbon-based adsorbents synthesized from Bintaro fruit, contributing to its advancement as a highly effective material for dye waste remediation.

This research aims to enhance the understanding of the adsorption properties of activated carbon derived from Bintaro fruit, particularly regarding the effects of HCl and NaOH activation on its capacity and efficiency in adsorbing methyl red (MR). Furthermore, the findings may expand the potential applications of toxic biomass waste like Bintaro fruit as valuable adsorbent materials, promoting more sustainable environmental management practices. The utilization of locally sourced

biomass for activated carbon aligns with circular economy principles, encouraging the conversion of waste into valuable resources. Thus, this study not only supports the development of industrial wastewater treatment technologies but also promotes the optimal use of local resources, contributing to improved environmental management.

## Experimental

**Materials**. The equipment used in this study included 100-mesh sieve, oven, furnace, centrifuge, rotary shaker, mortar, and UV-Vis spectrophotometer (SAFAS UVmc1). The materials used were Bintaro fruit (Cerbera manghas) from Palangka Raya city, analytical-grade HCl (Merck), analytical-grade NaOH (Merck), deionized water, Whatman No. 42 filter paper, and methyl red dye.

**Preparation of Bintaro Fruit Samples**. The Bintaro fruit was thoroughly washed and dried under sunlight for 48 h. It was then finely chopped and further dehydrated in a controlled oven environment at 105°C for 4 h.

**Synthesis of Activated Carbon from Bintaro Fruit.** The dehydrated samples were carbonized within a furnace set to 400°C for 5 h. After cooling, the carbonized material was pulverized using a mortar and screened through a 100-mesh filter. The obtained carbon was then chemically activated by immersing it in a solution of 0.5 M HCl and 0.5 M NaOH, maintaining at a 1:20 (w/v) ratio for 24 hours. Finally, the activated carbon was rinsed with deionized water until reaching a neutral pH, filtered using Whatman No. 42 filter paper, and dried in an oven at 65°C for 12 hours.

**Adsorption Kinetics of Methyl Red on Bintaro Fruit Activated Carbon.** A total of 0.2 g of HCl- activated carbon (AC-A) and NaOH-activated carbon (AC-B) was added to 20 mL of a 30 ppm MR solution. The mixture was agitated using a rotary shaker at 160 rpm, with contact times varying from 30 to 180 minutes. The solid residue was separated out of the liquid phase through centrifugation. MR concentration within the remaining solution was analyzed through UV-Vis spectrophotometry, specifically wavelength at 510 nm. The amount of adsorbed MR (qt) over time (t) was determined based on Equation 1.

The adsorption kinetics were examined through two different approaches: the Pseudo-First Order and Pseudo-Second Order models. The mathematical expression for the Pseudo-First Order model is provided in Equation (2) [12].

$$qt = \frac{(Co-Ct).V}{m} \quad (1)$$

$$\frac{dqt}{dt} = k_1\,(qe - qt) \quad (2)$$

The integration of Equation (3) results in:

$$\ln(qe - qt) = ln(qe) - k_1 t \quad (3)$$

A linear plot of ln (qe − qt) against t allows for the determination of k1 based on the slope. The Pseudo -Second Order model is described by Equation (4) [12].

$$\frac{1}{qt} = \frac{1}{k_2 qe^2} + \frac{1}{qe} \quad (4)$$

**Adsorption Equilibrium Analysis of Methyl Red on Bintaro Fruit Activated Carbon**. A measured amount of 0.2 g of activated carbon (AC-A and AC-B) was introduced into 20 mL of MR solutions, with initial concentrations varying between 10 and 60 ppm. The mixtures were agitated at 160 rpm for each activator, the optimal contact time was identified based on adsorption performance. The solutions were then centrifuged to separate the solid residue. The remaining MR concentration in the filtrate was assessed using a UV-Vis spectrophotometer at 510 nm. The equilibrium adsorption behavior was examined through the Langmuir and Freundlich isotherm models. The mathematical representation of the Langmuir model is given in Equation (5).

$$\frac{Ce}{qe} = \frac{1}{kL\ qmax} + \frac{ce}{qmax} \quad (5)$$

The Freundlich model is described by Equation (6) [13].

$$qe = K_F\, C_e^{1/n} \quad (6)$$

## Result and Discussion

**The Synthesis of Activated Carbon from Bintaro Fruit**. The synthesis of activated carbon from Bintaro fruit began with the preparation of raw materials, including thorough washing to remove impurities and drying to reduce moisture content. Physical activation was carried out through pyrolysis at 400°C, which enhanced the porosity and thermal stability of the material . At high temperatures, vola-

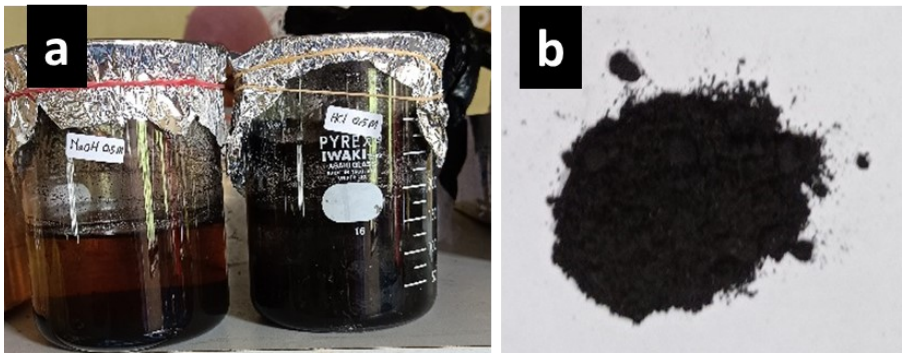


**Figure 1.** Activation process with acids and bases (a), Activated carbon from bintaro fruit (b)

tile components in the biomass decomposed, leading to a well-developed porous structure and an increased specific surface area [3].

Chemical activation was performed by soaking the carbonized material in a solution of 0.5 M HCl and 0.5 M NaOH over 24 h. This process aimed to remove inorganic compounds or residues that could interfere with the adsorption performance of the activated carbon. Acid and base treatments also modified the surface chemistry, increasing the number of functional groups that interact with the dye during adsorption [14]. After activation, the carbon was purified by rinsing with deionized water until it reached a neutral pH to ensure no residual activating agents remained that could affect adsorption performance. Figure 1 illustrates the activation process and the resulting activated carbon.

Adsorption Kinetics of Methyl Red on Activated Carbon. Adsorption of MR results in Table 1 indicate that AC-B exhibited a greater capacity for MR compared to AC-A. At 30 minutes, AC-B adsorbed 51.30% of MR, while AC-A adsorbed only 26.44%. This difference is attributed to the increased porosity and surface area resulting from NaOH activation, which tends to produce larger mesopores compared to the microporous structure formed by HCl activation [7]. As adsorption time increased, the efficiency of AC-B decreased to 40% at 120 minutes, while AC-A reached only 30.96%. This trend indicates a decrease in accessible binding sites on the adsorbent's structure and a gradual weakening of the adsorption forces between the material and the target molecules over time [15].

**Table 1**. Adsorption of MR by AC-A and AC-B with time variation

| Time (m) | Adsorption (%) | | Adsorbed MM (mg/g) | |
|---|---|---|---|---|
| | AC-A | AC-B | AC-A | AC-B |
| 30 | 26.44 | 51.30 | 7.77 | 15.07 |
| 60 | 29.83 | 53.56 | 8.76 | 15.73 |
| 90 | 33.22 | 50.17 | 9.76 | 14.73 |
| 120 | 40.00 | 47.91 | 11.75 | 14.07 |
| 150 | 35.25 | 42.26 | 10.35 | 12.41 |
| 180 | 30.96 | 40.00 | 9.09 | 11.75 |

In addition to differences in pore structure, the surface chemistry of activated carbon plays a crucial role in determining its adsorption capacity. Activation with NaOH increases the number of hydroxyl (-OH) and carbonate groups on the carbon surface, which enhances the electrostatic interactions between the negatively charged MR molecules and the adsorbent. In contrast, activation with HCl tends to promotes the formation of acidic functional groups on the carbon surface, which may reduce its affinity for anionic dyes such as MR [16]. This pattern suggests that the adsorption mechanism likely follows a pseudo-second order kinetic model, where the rate of adsorption is governed by the presence of unoccupied active sites and the chemical affinity between the adsorbent and the adsorbate [17].

Based on Figure 2 and Table 2, the analysis of MR adsorption kinetics on AC-A and AC-B revealed that the pseudo-second order model provides a more accurate representation of the adsorption mechanism than the pseudo-first order model. The findings suggest that the pseudo-second-order model better represents the adsorption process, as indicated by its higher R2 values of 0.951 for AC-A and 0.985 for AC-B. In contrast, the pseudo-first-order model showed lower accuracy, with R2 values of 0.382 for AC-A and 0.947 for AC-B, reinforcing its weaker fit to the adsorption behavior. The high $R^2$ values indicate that the adsorption kinetics are primarily governed by chemical interac-

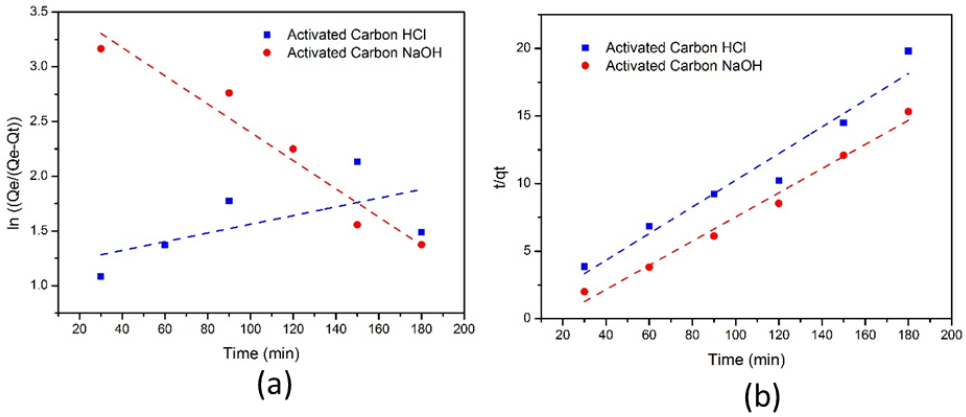


**Figure 2.** (a) Pseudo-First order Model, (b) Pseudo-Second order Model for adsorption of MR by bintaro fruit activated carbon

tions between the activated carbon and MR, rather than mere molecular diffusion [3].

The adsorption rate constant ($k_2$) for AC-B (0.0254 g/mg·min) was significantly higher than that for AC-A (0.0057 g/mg·min). This suggests that MR adsorption on AC-B occurs at a faster rate than on AC-A when following the pseudo-second-order model. The variation in k2 values can be linked to the unique physical and chemical characteristics of carbon surfaces resulting from the respective activation methods. This observation is also consistent with the higher maximum adsorption capacity (% adsorption) of 51.30% for AC-B, compared to 40% for AC-A. Furthermore, AC-B reached maximum adsorption in a shorter time (60 minutes) compared to AC-A, which required 120 minutes. This phenomenon can be explained by the increased surface area and the greater number of active sites in AC-B, which facilitate faster adsorption and enable the system to reach maximum capacity more quickly [18].

**Table 2**. Kinetic parameters of MR adsorption using activated carbon from bintaro fruit

| Materials | Pseudo-First Order | | Pseudo-Second Order | |
|---|---|---|---|---|
| | β ($min^{-1}$) | $R^2$ | $k_2$ (gr/mg.min) | $R^2$ |
| AC-A | 0.0040 | 0.382 | 0.0057 | 0.951 |
| AC-B | 0.0129 | 0.947 | 0.0254 | 0.985 |

**Adsorption Isotherms of Methyl Red on Activated Carbon.** The adsorption isotherms of MR on activated carbon were examined to gain insight into the equilibrium distribution of dye molecules across the adsorbent surface [19]. The results, as shown in Table 3, indicate that AC-B had a higher adsorption capacity compared to AC-A across all tested concentrations. At a concentration of 40 ppm, AC-B adsorbed 16.75 mg/g of MR, while AC-A adsorbed only 12.88 mg/g. This variation is due to the increased surface area and higher density of active sites generated by NaOH activation, leading to an improved adsorption capacity of the carbon (Wu et al., 2021). At high concentrations (50–60 ppm), The reduction in adsorption capacity for both activated carbons was caused by the exhaustion of available active sites, with a more pronounced decline observed for AC-A (8.01 mg/g) compared to AC -B (11.99 mg/g). This decline is associated with the full occupancy of active sites on the carbon surface, which limits the number of MR molecules that can be adsorbed. The decline also suggests that at higher concentrations, the competition among MR molecules in the solution increases, resulting in some molecules remaining in the solution without being effectively adsorbed [20].

**Table 3.** Adsorption of MR by Activated Carbon from Bintaro Fruit at Various Concentrations

| Initial Concentration Co (ppm) | Adsorbed MM (mg/g) | |
|---|---|---|
| | AC-A | AC-B |
| 10 | 5.53 | 6.08 |
| 20 | 9.62 | 11.39 |
| 30 | 11.75 | 15.73 |
| 40 | 12.88 | 16.75 |
| 50 | 10.33 | 14.31 |
| 60 | 8.01 | 11.99 |

The adsorption process is strongly influenced by the surface characteristics of the activated carbon after activation. AC-B typically carries a negative surface charge, which enhances its electrostatic affinity for MR, a cationic dye. In contrast, AC-A produces a more positively charged surface, making it less effective in attracting MR molecules [14].

The analysis of MR adsorption isotherms on AC-A and AC-B is presented in Figure 3 and Table 4. Based on Table 4, The highest adsorption capacity (B) of AC-B (13.18 mg/g) was notably greater than AC-A (8.65 mg/g), indicating that NaOH activation enhances the adsorption capability. Additionally, the Langmuir constant (KL) for AC-B (5.58 L/mol) was much greater than that for AC-B (0.41 L/mol), suggesting stronger interactions between the adsorbent and adsorbate in NaOH-activated material. The higher $R^2$ values for the Langmuir model (0.9464 for NaOH and 0.9261 for HCl) further indicate that this model provides a better representation of the adsorption mechanism than the Freundlich model. The Langmuir isotherm model suggests that MR adsorption on Bintaro fruit-derived activated carbon occurs on a homogeneous surface through monolayer interactions [21].

In contrast, the Freundlich isotherm model, which describes adsorption on heterogeneous surfaces, showed a higher n value for AC-B (11.00) compared to AC-A (6.91), indicating that adsorption on AC-B is more favorable. Additionally, the KF value for AC-B (0.31 mg/g) was higher than that for AC-A (0.25 mg/g), reflecting a greater adsorption capacity. However, the lower $R^2$ values for the Freundlich model (0.2165 for NaOH and 0.1688 for HCl) suggest that the Langmuir model provides a more accurate representation of the adsorption process compared to the Freundlich model.

## Conclusion

This study demonstrates that NaOH-activated carbon (AC-B) derived from Bintaro fruit exhibits superior adsorption performance for MR compared to HCl-activated carbon (AC-A). The higher adsorption capacity (51.30% at 30 minutes) and stronger alignment with the Pseudo-Second Order kinetic model ($R^2$ = 0.985) highlight the effectiveness of NaOH activation. The Langmuir isotherm model most accurately described the adsorption process, indicating a maximum adsorption capacity of 13.18 mg/g for AC-B. The stronger interaction between AC -B and methyl red, as indicated by the higher Langmuir constant (KL = 5.58 L/mol), further supports its potential as a sustainable solution for dye waste treatment. Thus, NaOH-activated Bintaro fruit carbon represents a promising alternative for environmentally friendly wastewater treatment.

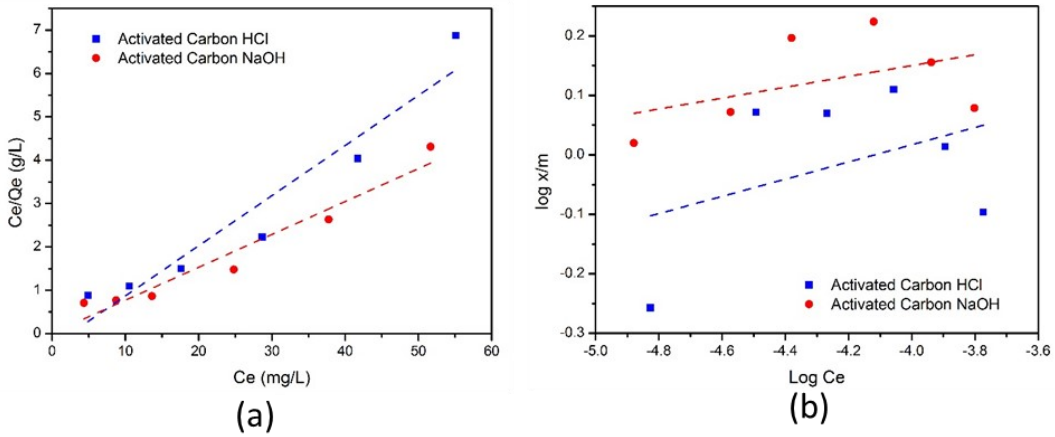


**Figure 3.** Isotherm Models for MR Adsorption onto Bintaro Fruit Activated Carbon: (a) Langmuir Isotherm, (b) Freundlich Isotherm

**Table 4.** Isotherms parameters of MR adsorption using activated carbon from bintaro fruit

| Materials | Langmuir Isotherm | | | Freundlich Isotherm | | |
|---|---|---|---|---|---|---|
| | B (mg/g) | $K_L$ (L/mol) | $R^2$ | $K_F$ (mg/g) | n | $R^2$ |
| AC-A | 8.65 | 0.41 | 0.9261 | 0.25 | 6.91 | 0.1688 |
| AC-B | 13.18 | 5.58 | 0.9464 | 0.31 | 11.00 | 0.2165 |

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