Physicochemical and photodegradation characteristics of hematite-biochar nanocomposite prepared from bamboo sawdust

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Abstract. This work implicates the synthesis of biochar-hematite nanocomposite from bamboo sawdust and its photodegradation characteristic for remazol brilliant blue. The nanocomposite was prepared through a one-step pyrolysis process in a tubular furnace under a flow of nitrogen and impregnation using FeSO\(_4\).7H\(_2\)O and FeCl\(_3\).6H\(_2\)O. The physicochemical properties were characterized by x-ray diffraction and Fourier transform infrared spectroscopy, which confirmed that hematite was successfully identified on the surface of the nanocomposite. The results also show that the nanocomposite is suitable for photodegradation application. The decolorization of remazol brilliant blue is suitable with the Langmuir isotherm model and pseudo-second-order kinetic model. At pH = 1, initial concentration = 200 mg/L, contact time = 60 minute and nanocomposite dosage 0.4 g/L, the decolorization efficiency reached 96.9%.

1. Introduction

Batik is one of cultural heritage, thus batik industry is growing rapidly in Indonesia [1]. According to Siregar et al. [2], Indonesia has 40,922 batik industries. As one of the mainstay export commodities, it provides many benefits to the country. However, the rapid development of the batik industry has caused environmental problems due to the high concentration of dyestuff used in the production process. Synthetic chemical dyes including azo dyes are widely used for batik coloring. Azo dyes such as Remazol brilliant blue are non-biodegradable because they contain an azo functional group attached to an aromatic ring. In addition, azo dyes are toxic and carcinogenic which can threaten the life of living things [3]. Thus far, several studies have been initiated to remove the dyes from wastewater, including electrocoagulation [4], osmosis [5], aerobic process [6], anaerobic process [7], and adsorption [8-13]. Among these methods, adsorption is the most widely used method due to its simple design and high efficiency [14]. In this sense, chitosan [15], activated carbon [16-18], zeolite [19] and biochar [20] have been utilized as adsorbents. Lately, biomass-based biochar is considered as an auspicious adsorbent due to its abundant availability. However, the adsorption performance of biochar is limited. The combination of biochar and hematite (Fe\(_2\)O\(_3\)) as a photoactive catalyst has been proven effective on the synergistic adsorption-photodegradation of dye [21].
On the other side, bamboo (Dendrocalamus asper), a member of the grass family, commonly grows in many regions, including Indonesia. Bamboo sawdust contains of 45.02% of cellulose, 10.81% of hemicellulose, and 28.35% of lignin [22], making it possible to act as raw material in the biochar preparation. To our knowledge, very few studies have explored the utilization of bamboo sawdust as a functional material in photocatalysis. Therefore, the aim of this study was to develop hematite-biochar nanocomposite from bamboo sawdust. In this sense, the physicochemical properties of the nanocomposite and its photodegradation characteristic for Remazol brilliant blue were assessed.

2. Material and Methods

2.1. Raw materials and reagents
The bamboo sawdust was obtained from Magelang, Indonesia. It was washed with distilled water and dried at 110°C for 24 h in an electric oven (Memmert type UN55, Germany). The dried sample was then sieved using a 100-mesh sieve to obtain a uniform size of less than 150 μm. Remazol Brilliant Blue (RBB) dye was obtained from Kampung Batik Semarang, Indonesia, while HCl, NaOH, FeCl₃·6H₂O and FeSO₄·7H₂O was acquired from Merck (Germany).

2.2. Hematite-biochar nanocomposite preparation
A one-step approach was performed to prepare biochar from bamboo sawdust. In this sense, bamboo was carbonized using a tubular furnace at temperature of 500°C under a stream of N₂ for 30 minutes to produce biochar. Biochar-hematite was made by coprecipitation method using FeCl₃·6H₂O and FeSO₄·7H₂O with the weight ratio of Fe²⁺ to Fe³⁺ was set at 9 (0.48 M FeSO₄ and 0.05 M FeCl₃). The mixture of FeCl₃ and FeSO₄ solutions was stirred and heated at 60°C for 30 min, then 15 g of biochar was added. The mixture was mixed properly at 30°C for 40 minutes. While stirring, NaOH solution (2M) was added drop-wise to increase pH to 11 and precipitate iron (II) hydroxides from the aqueous solution. The stirred was continued for 1 hour and allowed to stand for 24 hours. After cooling, the sample was washed with HCl and distilled water until the pH of the filtrate was around 7 and dried in an oven at 80°C to constant weight [23].

2.3. Hematite-biochar nanocomposite characterization
The crystallinity of the Hematite-Biochar Nanocomposite (henceforth called HBN) was characterized using X-ray Diffraction (XRD) merk Panalytical/X’Pert3 Powder (Netherlands) with Cu Kα radiation (λ = 1,540598 Å). The sample was scanned in the range of 2θ = 20-70°. The functional groups were examined using Fourier Transform Infrared Spectrophotometry (FTIR) merk Perkin Elmer (Ohio, United States) at a wavelength of 400-4000 cm⁻¹.

2.4. Photodegradation test
Photodegradation test was performed in a batch photoreactor equipped with three UV lamp (Phillips). The experiments were conducted by mixing the nanocomposite as photocatalyst and RBB in a certain catalyst dosage (0.4 g). The photodegradation test was carried out using three variation condition, namely pH (1, 3, 5, 7, 9, 11), initial concentration of RBB solution (2, 4, 6, 8, 10, 20, 30, 40, 50, 100, 200, 300, 400, 500 mg/L), and contact time (5, 10, 15, 20, 30, 40, 50, 60, 120, 180, 240 minutes). The suspended solid was filtered and the filtrate was analyzed to determine methyl violet concentration using a UV-visible Spectrophotometer (Model Genesys 10 uv, Thermo Scientific, USA) at wavelength (λmax) of 592 nm.

3. Result and Discussion

3.1. Characterization of hematite-biochar nanocomposite
The XRD patterns of HBN (Fig.1) showed that biochar was approaching amorphous-like structure with the presence of some crystal structure. The peaks at 2θ = 31.2918°, 35.6255°, 43.3158°, 45.668°, 57.3°,
and 63.1° are indexed as (104), (110), (113), (024), (116), and (124) planes. They are identified as hematite phase according to the Joint Committee on Powder Diffraction Standards (JCPDS No.79-1741) [24].

![XRD pattern of HBN](image)

**Figure 1.** XRD pattern of HBN

In order to investigate the chemical properties of the biochar, FT-IR analysis was performed. The result is presented in Fig. 2. The bands around 3699-3410.89 cm\(^{-1}\) is ascribed to O-H stretching vibrations from alcohol functional groups, while the band at 1,586.81 cm\(^{-1}\) can be attributed to C-H vibration of alkyl functional group [25]. The bands at 872.06 cm\(^{-1}\) indicates the presence of C-O vibration [26].

![FT-IR spectrum of biochar](image)

**Figure 2.** FT-IR spectrum of biochar

Meanwhile, the FT-IR spectrum of HBN is shown in Fig. 3. Based on Fig. 3, it can be seen that an increase or a decrease of peaks intensity related to the surface functional groups existing in the HBN is observed, as well as the appearance of new functional groups. The band at 3,433.78 cm\(^{-1}\) indicates the presence of O-H vibrations from alcohols [23]. The band at 1,105.98 cm\(^{-1}\) can be attributed to C-O vibration from carboxylate functional group while the band at 1,688.25 cm\(^{-1}\) probably due to the C-H vibration of alkyl. The bands at 582.75 cm\(^{-1}\) indicates the existence of Fe-O bending mode [27].
result indicates that there is a difference in the FT-IR spectrum between biochar and HBN where Fe-O vibration is only found in HBN [25], according to Eq. (1) [28].

\[
\text{Fe}^{2+} + \text{Fe}^{3+} + 4\text{OH}^{-} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} + 2\text{H}^+ + \text{e}^{-} \tag{1}
\]

**Figure 3.** FT-IR spectrum of HBN

FT-IR spectra of HBN before and after adsorption is shown in Fig. 4. There is a decrease in intensity at the wavenumber of 1,105.98 cm\(^{-1}\) from 54.1 to 50.0 % which indicates the binding of the RBB molecules by C-O group. On the other hand, there is an increase in intensity at the wave number of 1,688.25 cm\(^{-1}\) from 51.8 to 53.7% due to the addition C-H groups from RBB molecules [8].

**Figure 4.** FT-IR spectra of HBN before and after adsorption
3.2. Photodegradation characteristic

The existence of Fe₃O₃ (hematite) in the biochar can facilitate the photocatalytic degradation of RBB dye under UV light. As a result, the adsorption and photocatalytic degradation occur simultaneously. The photodegradation begins with the formation of reactive oxidative species (ROS) such as holes (h⁺), hydroxyl radicals (•OH) and superoxide anion radicals (O₂•⁻). Furthermore, the dye degradation may occur through the successive attack of •OH or through hole transfer to form aromatic intermediate. This compound will be self-degraded or degraded by ROS to final product such as SO₂⁺, NO₃⁻, NH₄⁺, CO₂, and H₂O according to the following reaction [21, 29]:

\[
\begin{align*}
RBB + \text{hv} & \rightarrow RBB^* \\
RBB^* + \alpha-\text{Fe}_3\text{O}_3 & \rightarrow RBB^\ldots^* + \alpha-\text{Fe}_3\text{O}_3(e^\ldots_{CB}) \\
\alpha-\text{Fe}_3\text{O}_3 + \text{hv} & \rightarrow \alpha-\text{Fe}_3\text{O}_3(e^\ldots_{CB} + h^\ldots_{CB}^+) \\
e^\ldots_{CB} + O_2 & \rightarrow O_2^• \\
O_2^• + H^+_{aq} & \rightarrow HO_2^• \\
HO_2^• + HO_2^• & \leftrightarrow H_2O_2 + O_2 \\
h^\ldots_{CB}^+ + OH^+_{aq} & \rightarrow OH^• \\
RBB^\ldots^* + (O_2^•, HO_2^•, H_2O_2, OH^•) & \rightarrow \text{degradation product} \\
RBB^\ldots^* + (O_2^•, HO_2^•, H_2O_2, OH^•) & \rightarrow \text{degradation product}
\end{align*}
\]

The solution pH value is important to obtain a high uptake capacity. The effect of pH was studied in the range of 1-11. The effect of pH toward the amount of RBB uptake is shown in Fig. 5. The removal of RBB by biochar and HBN is optimum at pH 1 where the efficiency reaches 68.51% and 95.75%, respectively. This result revealed that the removal of RBB increases due to the photodegradation process. This result agree with the finding of other study, in which the removal of dyes from aqueous solutions by graphene oxide-chitosan nanocomposite is optimum at pH 1 [30]. The amount of RBB uptake decreases by increasing pH. It may be due to the surface of biochar and HBN consist of O-functional group. At high acidity (low pH) the functional groups are protonated into O-H²⁺ or O-OH⁺, resulting an electrostatic interaction between O-H²⁺ or O-OH and SO³⁻ contained in RBB molecules [31, 32]. As a results, the amount of RBB uptake increases.

![Graph showing the effect of pH on the amount of RBB uptake](image)

**Figure 5.** Effect of pH toward the amount of RBB uptake
(Initial concentration = 10 mg/L, contact time = 240 minutes, dose = 0.4 g)

The effect of the initial concentration to the amount of RBB removed is presented in Fig. 6. As shown in Fig. 6, the higher initial concentration of the solution, the higher the amount of RBB uptake until
equilibrium is reached. It may be due to the higher initial concentration of the solution increases the driving force to overcome all mass transfer resistance in the adsorption process [21].

![Figure 6](image1.png)

**Figure 6.** Effect of initial concentration toward the amount of RBB uptake (pH = 1, contact time = 240 minutes, dose = 0.4 g)

Contact time greatly affects to the amount of RBB uptake [33]. Contact time is very important to determine the equilibrium time of RBB uptake [30]. The effect of contact time was studied in the range of 5 to 240 minutes at 25°C, pH 1, and initial RBB concentration of 10 mg/L. The results is presented in Fig. 7. As shown in Fig. 7, there is a significant increase in the amount of RBB uptake by biochar and HBN in the first 5 minutes due to the abundant availability of active sites [34]. The removal of RBB dyes increases from 5 to 60 minutes then relatively constant. It is in accordance with a research conducted by Torgut et al. [33] in which RBB removal by activated carbon polymer reached equilibrium after 60 minutes.

![Figure 7](image2.png)

**Figure 7.** The effect of contact time toward the amount of RBB removed (Initial concentration = 10 mg/L, pH = 1, dose = 0.4 g)

In order to evaluate the kinetics of the dye removal, pseudo-first order and pseudo-second order kinetic models are proposed. The linear form of pseudo-first order equation can be defined as follows [8]:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t$$  \hspace{1cm} (11)

where $q_e$ (maximum amount of RBB adsorbed at equilibrium) and $q_t$ (maximum amount of RBB adsorbed at any time) are expressed according to the Eqs. (12) and (13), respectively [8].
\[ q_e = \frac{(C_0 - C_e)V}{m} \]  
\[ q_t = \frac{(C_0 - C_t)V}{m} \]

with \( C_0 \) (mg/L) is the initial concentration of RBB solution, \( C_e \) (mg/L) is the concentration of RBB at equilibrium, \( C_t \) (mg/L) is the concentration of RBB at time \( t \) (min), \( m \) (g) is the dose of adsorbent, \( V \) (L) is the volume of RBB solution, and \( k_1 \) (min\(^{-1}\)) is the rate constant. The linear form of pseudo-second order equation is formulated as [8]:

\[ \frac{1}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \]

with \( k_2 \) is the rate constant (mg.g\(^{-1}\).min\(^{-1}\)). Data analysis based on the value of \( R^2 \) (Table 1) stated that the removal of RBB is in accordance with the pseudo-second order kinetic model. This finding was also reported by Reza and Ahmaruzzaman [23] where the RBB removal by hematite activated carbon followed a pseudo-second order kinetic model with \( R^2 \) of 0.9998. The kinetic parameters are presented in Table 1.

### Table 1. The kinetic parameters of pseudo-first order and pseudo-second order

| kinetics model          | parameters | value            |
|-------------------------|------------|------------------|
| pseudo-first order      | \( k_1 \) (g/mg.min) | 0.0591871        |
|                         | \( R^2 \)   | 0.902            |
| pseudo-second order     | \( k_2 \) (g/mg.min) | 0.2575908        |
|                         | \( R^2 \)   | 0.999            |

4. Conclusion

This study show that the Hematite-Biochar Nanocomposite (HBN) has been successfully prepared and used to remove Remazol Brilliant Blue (RBB) dye. In this sense, the decolorization efficiency reaches more than 95% at pH 1, the initial concentration of 200 mg/L, for 180 minutes. Based on the value of \( R^2 \), the removal of RBB is in accordance with the pseudo-second order kinetic model.

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