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Modification of Iron Oxide Catalysts Supported on The Biomass Based Activated Carbon for Degradation of Dye Wastewater

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Abstract

Methylene blue is one of the dyes in the textile industry which has a negative impact on the environment. This compound is very stable, so it is difficult to degrade naturally. Methylene blue can be harmful to the environment if it is in a very large concentration, because it can increase the value of Chemical Oxygen Demand (COD) which can damage the balance of environment ecosystem. Adsorption method by using activated carbon as the adsorbent is one of the most efficient and effective techniques in dye removal due to its large adsorption capacity. However, the adsorption method using activated carbon only removes the pollutant compounds to other media or phases. Other method that can be used includes Advanced Oxidation Processes (AOPs). This method has the advantage of being able to degrade harmful compounds in the waste through oxidation (oxidative degradation) processes. One method of AOPs is the process by using Fenton reagents. This study was aimed to prepare and characterize iron oxide/porous activated carbon catalyst. The type of porous activated carbon used was carbon from biomass derived carbon with microporous character. This biomass carbon is obtained from renewable natural products, namely coconut shell.The kinetics and adsorption models in the material will be derived and evaluated from the research data. Based on the research, it can be concluded that catalytic degradation is very effective for degradation of dye wastewater. Methylene blue degradation increases with the use of Fe_2O_3/activated carbon catalyst and the addition of hydrogen peroxide as the Fenton reagent. In addition, the pore structure difference in the catalyst also had a significant effect on the methylene blue degradation reaction resulting in increased capacity of methylene blue degradation reactions.

INTRODUCTION

Methylene blue is one of the dyes in the textile industry which has a negative impact on the environment. This compound is very stable so it is difficult to be degraded in nature and dangerous for the environment in large concentrations because it can increase the value of Chemical Oxygen Demand (COD) which can damage the balance of the ecosystem of the environment. Up until now, the adsorption method with the adsorbent in the form of activated carbon remains the most efficient and effective technique in removing dyes due to its relatively large adsorption capacity (Hameed et al., 2007). However, the adsorption method using activated carbon generally only transfers pollutants to other media or phases. Another alternative method that can be used is Advanced Oxidation Processes (AOPs). This method has the advantage of being able to degrade hazardous compounds in waste through oxidative degradation (Malato et al., 2003). One of the AOPs methods is the process of

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using Fenton reagents. Oxidation with the Fenton reagent is an oxidation method that uses hydrogen peroxide as its oxidizer and iron nanoparticles as catalysts. The Fenton method that has been developed is the homogeneous Fenton method, where the bond and catalyst are in one phase, namely the liquid phase. However, the homogeneous Fenton reaction has disadvantages in terms of separating the catalyst from the system / mixture. To overcome this problem, a heterogeneous reaction system can be used, namely by developing an active iron catalyst in a porous material, such as alumina, activated carbon, and zeolite. In its function as a catalyst carrier, carbon itself has affinity for dyes. In addition, because of its good physical and chemical stability and high surface area (500-2000 m^2 / g), porous carbon is a very potential support catalyst (Prasetyo et al., 2013). Therefore the actual physical adsorption process and Fenton degradation reaction occur simultaneously in the heterogeneous catalyst system.

In this study, the preparation and characterization of iron oxide / porous activated carbon catalysts will be carried out. The type of porous activated carbon used is biomass carbon with microporous characters. This biomass carbon is obtained from renewable natural products, namely coconut shell. Coconut shell is used to make activated carbon because it is a renewable and environmentally friendly raw material. The kinetic and adsorption models in the material will be derived and evaluated from the research data. Process speed parameters will be evaluated and related to the characteristics of the catalyst obtained.

METHODS

Process of Impregnation of Iron Oxides on Porous Carbon Surfaces

As much as 2 grams of activated carbon that has been vented were included in the sample bottle. The Fe $(NO_3)_3.9H_2O$ salt solution was added according to the variable loading Fe (0.5%, 1%, or 2%) into the sample bottle that had contained activated carbon. Mixture of Fe $(NO_3)_3.9H_2O$ salt solution with activated carbon then stirred for 1 hour with ultrasonicator. After the evaporation process at room temperature the carbon was then heated at 60^0C. The calcination process was then carried out at 300^0C for 3 hours with inert N_2 flow.

Fenton Adsorption and Reaction Process

200 ml of methylene blue solution with a concentration of 20 ppm was prepared in a beaker glass. The solution was stirred with a magnetic stirrer at a constant speed of 450 rpm and room temperature of 30^0C. Five ml of H_2O_2 was then added to the solution. Furthermore, 0.025 grams of Fe_2O_3 / activated carbon catalyst with variable loading were put into a glass beaker containing a solution of methylene blue and H_2O_2. A total of 2 ml of sample solution was taken every specific time interval for 3 hours. Furthermore, the concentration of methylene blue in solution (C) at any given time interval was analyzed by UV-VIS spectro-photometer at a wavelength of 663 nm.

Kinetics of Color Degradation in Methylene Blue

This study uses a modified model between the adsorption process and chemical reactions. This is due to the addition of H_2O_2 in methylene blue solution. The intraparticle reaction model is used to evaluate experimental data. Models are arranged based on the following mathematical equations. The balance of the methylene blue mass in the solid volume element is shown in Eq. (1).

$$\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r}\frac{\partial C_A}{\partial r} - \frac{k_r.(C_A - C_{Aeq})}{D_e} = \frac{1}{D_e'}.\frac{\partial C_A}{\partial t} \quad (1)$$

Eq. (1) can be solved by two boundary conditions and one initial condition as shown in Eq. (2) – (5).

$$C_A(r,0) = 0 \quad (2)$$

$$-D_e \frac{\partial C_A}{\partial r}(R,t) = k_c\,(C_{AL} - C_A^{\,*}) \quad (3)$$

or

$$-D_e \frac{\partial C_A}{\partial r}(R,t) = k_c \left(C_{AL} - \frac{1}{H} C_{AL}(R,t)\right) \quad (4)$$

$$\frac{\partial C_A}{\partial r}(0,t) = 0$$

(concentration of A at the center of the ball is always minimum, because while moving towards the center of the ball, A will be reacted) (5)

The parameters in the form of k_r, k_c, D_e and H are obtained by doing iterations which will produce calculated values of the equations that will be compared with the values obtained from the experimental results.

Analysis Method

The adsorption data were analyzed using a UV VIS spectrometer with a wavelength λ = 663 nm. The data from the analysis were used to calculate the concentration of methylene blue in liquids (C_{AL}). Meanwhile mathematical modeling for adsorption kinetics was done numerically using MATLAB software.

RESULT AND DISCUSSION

Fe_2O_3 / Activated Carbon Catalyst Preparation

Characteristics of porous biomass activated carbon covering specific surface area, average pore diameter and pore volume can be seen in Table 1. The table shows that biomass porous carbon is microporous carbon (IUPAC classification) with an average diameter of 1.81 nm.

Table 1. Characteristics of Biomass Carbon

Characteristic	Value
Specific surface area (S_{BET}), m^2/gram	1236
Micropore area (S_{mic}), m^2/gram	1144
% S_{mic}	92.55
Total pore volume, cm^3/gram	0.56
Micropore volume (V_{mic}), cm^3/gram	0.433
% V_{mic}	77.3
Average pore diameter, nm	1.81

Pore size distribution is calculated using the Quenched Solid State Functional Theory (QSDFT) model. In Figure 1, it can be seen that the pore distribution with a size below 2 nm is very dominant and there are two dominant peaks, which are at 0.8 nm and 2.8 nm. Based on the results of the pore distribution, it is further strengthened that the porous carbon biomass is microporous carbon (IUPAC classification).

The process of making Fe_2O_3 / activated carbon catalyst begins with impregnation of the catalyst precursor, i.e. Fe into the carbon pore surface. In terms of the size of iron ions (194 pm, hydrate), these ions can enter into the biomass's carbon-based pores. The impregnation process begins by contacting the metal solution on the carbon surface. The next process is drying and calcination for iron oxide formation. The distribution of iron oxides on the surface of carbon is an important aspect in the process of impregnation of iron oxide on the carbon surface. The distribution of metals evenly distributed on the surface of the carbon will maximize the absorption process. The results of the morphological analysis of the catalyst using Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy (SEM-EDX) can be seen in Figure 2(a). While the results of metal distribution on the carbon surface can be seen in Figure 2(b). The blue color in the figure shows the elemental mapping of the presence of Fe on the carbon surface (Han et al., 2015). From the picture it can be seen that iron oxide can spread quite well on the surface of the biomass-based carbon.

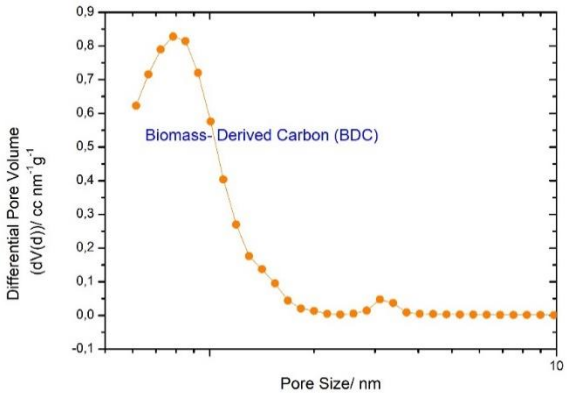
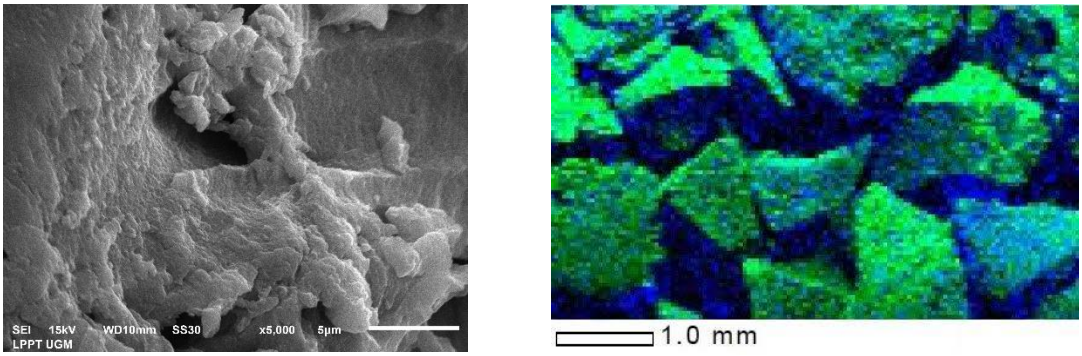


Figure 1. Pore size distribution with QSDFT-N_2 model

After the catalyst preparation is finished, the catalyst was then used for the process of adsorption of methylene blue without the Fenton reaction. This is important to show the absorption of carbon after Fe loading on the surface of a carbon biomass based catalyst. Table 2 shows the percentage of absorption of methylene blue in various catalysts with different loading Fe at 180 minutes adsorption time. The highest adsorption was obtained in samples with a concentration of Fe loading of 2% with an adsorption capacity of 85.45%. This is probably due to the large amount of Fe and contributes positively to the increase of methylene blue adsorption capacity (Mukti et al., 2015).

Degradation Test Results of Methylene Blue

Changes in the concentration of methylene blue use an iron oxide catalyst with the carrier of biomass-based activated carbon when with or without hydrogen peroxide shown in Figure 3. Adsorption using Fe_2O_3 / biomass-based activated carbon catalysts with the addition of Fenton



(a) (b)

Figure 2. (a) SEM for Fe_2O_3/biomass based activated carbon catalysts (b) *Elemental Mapping* C-Fe

Table 2. Effect of Fe loading on methylene blue adsorption capacity

Variation in Fe loading (% mass)	Adsorption Capacity (%)
0,5%	79.89
1%	83.85
2%	85.45

Table 3. The value of the methylene blue degradation reaction kinetics parameters are various variations of Fe loading

Parameters of reaction kinetics	Variation in Fe loading		
	0.5%	1%	2%
k_c, mass transfer coefficient (m/s)	0.0032	0.0038	0.0036
H, Henry's constant	14.06	14.73	14.81
D_e, diffusivity constant (m/s^2)	4.168×10^{-10}	4.346×10^{-10}	4.065×10^{-10}
k_r, reaction speed constant (m^3/s)	0.0409	0.0536	0.0743

reagents (H_2O_2) gives more significant results when it compared with the adsorption of catalysts without the addition of Fenton reagents (H_2O_2). This is due to the very strong oxidative properties of hydroxyl radicals (OH^*) produced from hydrogen peroxide. The hydroxyl radical will react with Fe ions to decompose the methylene blue compound (Hudaya et al., 2011). So that the adsorption and degradation process takes place simultaneously in one system.

Degradation Reaction Kinetics of Methylene Blue

Based on experimental data as shown in Figure 3, an evaluation using the kinetics and adsorption model was carried out in accordance with Equation 1. Process speed parameters were evaluated and related to the characteristics of the catalyst obtained based on experimental data. The parameter values for the methylene blue degradation reaction kinetic model are presented in Table 3.

Based on the data in Table 3 it can be seen that the difference in Fe loading concentration significantly influences the reaction speed constant (k_r). The constant value of the reaction speed is directly proportional to the increase in the concentration of Fe loading. This indicates that the greater the loading of Fe, the faster the reaction of methylene blue degradation. Whereas the other parameter values, namely, k_c, H and De did not significantly change with increasing concentration of Fe loading.

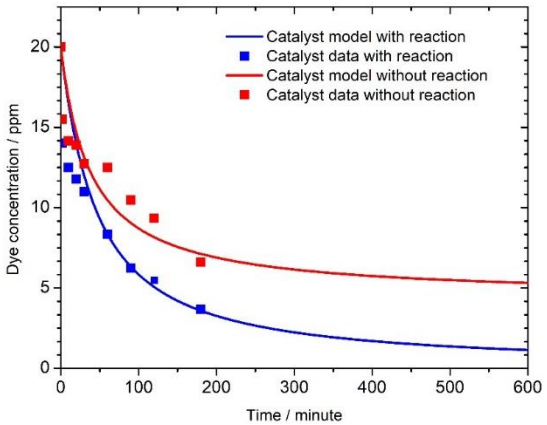


Figure 3. Changes in the concentration of Methylene Blue in solution during the Fenton catalytic reaction process using a 1% Fe_2O_3 catalyst / biomass-based activated carbon in fitting with the intraparticle reaction model

CONCLUSION

Based on the research that has been done, it can be concluded that a highly effective catalytic reaction is applied to the degradation of dyestuff waste. Degradation of methylene blue increased with the increase of catalyst loading concentration and the result of degradation percentage at 180 minutes of reaction was 85.45% with catalyst loading of 2% iron oxide / biomass based activated carbon. In addition, from the evaluation results of experimental data using kinetics and adsorption models it can be concluded that the increase in Fe loading concentration are significantly affects the reaction speed constant (k_r).

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