Methylene Blue and Methyl Orange Dyes Removal using Low-Cost Composite of Banana Peel-TiO₂ Adsorbent

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Abstract. Composite banana peel activated carbon-TiO₂ is a photocatalyst used to degrade complex compound. In this research, peel of banana was activated using NaOH activator. The aims of this study was to compose biomass wastes (banana peels) with TiO₂ catalyst using photocatalytic process to solve Methylene Blue and Methyl Orange dye waste problems. Sample were calcined at 300°C and activator concentration of NaOH varied (1:0; 1:1; 1:2; and 1:3) to obtain optimal results. The quality of activated carbon of banana peel was compared to SNI 06-3730-1995. There parameter measured were moisture content, ash content, adsorption of iodine, adsorption capacity of Methylene Blue and surface area of activated carbon. The results showed that the highest banana peel activated carbon compares to NaOH concentration of 1: 3 were 0.65%; 4.88%; 774.09 mg/g; 24.90 mg/g and 92.43 m²/g, respectively. It indicates that the optimal results are obtained in the preparation of activated carbon with 1:3 of activator composition. This activated carbon banana peel was combined with titanium dioxide P25. The composites were characterized by FTIR (Fourier Transform Infrared) and SEM (Scanning Electron Microscopy). FTIR spectrum showed that the absorption appeared in the region of Ti-O-C at wave number 1009 cm⁻¹ and C=C at wave number 1620 cm⁻¹. SEM showed that TiO₂ spread on activated carbon surfaces. Based on analysis of Infrared presents the functional group of Ti-O and C=O of the composite. Morphology of the composite banana peel activated carbon-TiO₂ showed that TiO₂ spreads on active carbon surfaces. Based on analysis which have done showed that the composite activated carbon of banana peel-TiO₂ formed. Optimum Methylene Blue and Methyl Orange degraded were 94.61% and 84.30%, respectively.

1. Introduction
One alternative for treating dye wastes is the photocatalytic processes. The dyes will be degraded by positive holes (h⁺) in the band valence reduced by electrons in conduction band. Among the many types of semiconductors, TiO₂ powders were chosen as semiconductor because it has larger photocatalytic activity, stable to light, non-toxic, the ability to oxidize is high and not dissolve under experimental conditions (Adriana, 2008). To overcome the shortcomings of the process of photocatalysis, it is necessary to combine the photocatalytic method with adsorption processes. Activated biomass as adsorbent has been widely used. The efficiency of adsorption in textile waste purification as has been studied to adsorb Congo Red dyes (Foroughi-Dahr et al., 2014), Direct Yellow 12 (Ghaedi, et al., 2012).

The use of TiO₂ photocatalysis which serves as a catalyst in the degradation of organic pollutant compounds. The process of photocatalysis can solve a large number of variations of organic
compounds into CO₂, water and mineral salts as a product of degradation products (Subramani, 2006). TiO₂ photocatalyst has long been known as a promising compound because of its low price and high effectiveness. The photocatalytic activity of TiO₂ can be increased by modifying the structure, surface area and particle size (Adriana, 2008; Rajagukguk et al., 2019). According to Chanakya, et.al., (2006), activated carbon is an appropriate adsorption medium to be composed of TiO₂ catalyst because it can capture and absorb very fine particles other than that it is non-toxic, easily obtained and economics.

Banana peels can be chemically and physically more economical by being used as an adsorbent. The use of banana peels as an adsorbent is due to the content of pectin and cellulose. Basrafshan, et.al., (2016) stated that the banana peel content of about 80% is composed by cellulose, hemicellulose and pectin. Banana peel has a starch content of around 11.48% and crude fiber of about 1.52%. Cellulose and pectin have hydroxyl groups which cause banana peels to have a pretty good potential as an adsorbent. Based on preliminary study, banana peel waste activated with 3M HCl has the best absorption of methylene blue. The NH₂ group protonates to NH₃⁺, OH group protonates to H₃O⁺. Therefore, the aim of this study to combine banana peel activated carbon waste with TiO₂ to get the best solution in dealing with textile dye wastes such as Methyl Orange and Methylene Blue which are low-cost and environmentally friendly.

2. Method
This study conducted to use biomass (banana peel) become valuable material. Then, it composed to TiO₂ catalyst because it can capture and absorb very fine particles become non-toxic, easily obtained and economics. The material can be used to solve the problems of textile dye wastes, for example, Methylene Blue and Methyl Orange. It is also low-cost and environmentally friendly.

2.1. Reagents and Materials
The materials used in this study were banana peels, TiO₂, CaSO₄.2H₂O, distilled water, deionized water, NaOH, I₂, Na₂S₂O₃, K₂Cr₂O₇, KI, 10% H₂SO₄, starch, Methylene Blue and Methyl Orange. The instruments used in this study were sieve (Shaker Laboratory (USA) size 100 and 120 mesh, desiccator, oven (Gallenkamp Hotbox Oven Size1), furnace (Gallenkamp Muffle Furnace Size1), centrifuge, mortar and pestle, crucible porcelain, measuring flask, burette, Erlenmeyer, Beaker glass, analytical balance (Metlller type AE200), Whatman 42 filter paper, Scanning Electron Microscope and UV-Vis Spectrophotometer (Thermo Scientific Genesys 20) and FTIR.

2.2. Preparation of activated banana peels
Fifty gram of banana peel soaked in 200 mL NaOH solution with a ratio of NaOH is 1: 0; 1: 1; 1: 2; and 1:3, then the sample was left for 24 hours at room temperature. The sample was then filtered and washed with deionized water to neutralize pH. The sample was then dried at 105°C for 24 hours until constant. The sample was then cooled in a desiccator for characterization of water and ash contents by gravimetric method. Furthermore, iodine analyzed by using titrimetric method and methylene blue absorption by UV-Vis Spectrophotometer.

As much as 5 grams of activated carbon was put into 100 mL deionized water then it is stirred and heated for 30 minutes at a temperature of 100 °C and a speed of 360 rpm. Samples were filtered and dried for 24 hours at 105°C. Composite photocatalytic TiO₂ - activated carbon was made by comparison between titanium dioxide: calcium sulfate: activated carbon is 1.7: 3.4: 0.85. The three samples were put into 100 mL deionized water then stirred and dried for 30 minutes at 100°C and 360 rpm. The sample is then cooled to room temperature. Samples were filtered using filter paper and dried in the oven for 1 hour at 105°C. The sample was calcined in a furnace temperature of 300°C for 1 hour. Samples were ground and then stored in a desiccator for subsequent analysis.

2.3. Application composites to the dye samples
Methylene Blue standard was prepared from 1 to 5 ppm as well as Methyl Orange. Then calculated by Calibration method to get the regression line. The 0.5 gram of dried composite was chemically treated
with 25 ml Methylene Blue and Methyl Orange from 10 to 50 ppm solution. The mixture was stirred for 1 hour at room temperature and analysed by UV-Vis Spectrophotometer. All experiments were repeated twice. The adsorption amount of MB and MO were calculated as follows:

Amount of adsorption as

\[ Q = \frac{(C_0 - C_t)V}{m} \] .................(1)

Co is the initial dye concentration (mg/L)

Ct is the dye concentration after adsorption,

V dye volume (mL),

m adsorbent mass (g)

3. Result and Discussion

Characterization of banana peel activated carbon-TiO\(_2\) composites using NaOH in a ratio of 1:0; 1: 1; 1: 2; and 1: 3 at 300°C based on SNI Method No. 06-3730-1995 (Indonesian National Standard) has been conducted. The parameters analysed were water content, ash content, iodine absorption capacity and adsorption capacity of Methylene Blue dyes. The characterization results can be seen in Table 1.

| Samples | Moisture Content (%) | Ash Content (%) | Iodine Adsorb. (mg/g) | MB Adsorp. (mg/g) | Surface Areas (m\(^2\)/g) |
|---------|---------------------|----------------|------------------------|------------------|---------------------------|
| 1:0     | 2.09                | 5.66           | 664.29                 | 24.84            | 92.18                     |
| 1:1     | 1.94                | 5.27           | 756.48                 | 24.84            | 92.20                     |
| 1:2     | 0.89                | 5.05           | 765.71                 | 24.89            | 92.38                     |
| 1:3     | 0.65                | 4.88           | 774.09                 | 24.90            | 92.43                     |

SNI No, 06-3730-1995

SNI: Indonesian National Standard.

Based on the Table 1, without using activator; water and ash contents, absorption of Methylene Blue and Methyl Orange as well as surface area have the lowest parameters. The characterization of ash content, namely reducing and eliminating oxide molecules and impurities in the adsorbent pore. The higher the activator concentration will cause more impurities in the form of organic and inorganic substances to dissolve and escape from the surface of carbon pores (Wei et.al., 2016).

The highest absorption of Iodine obtained in the adsorbent of banana peel which is activated by NaOH in a ratio of 1:3 was 774.09 mg/g. These data indicate that at this concentration, activators have optimum binding to impurities and open pores in the adsorbent so that more macropores are formed and open and have a greater surface area. The greater number of macropores and surface area makes the adsorbent of banana peel which has been activated with NaOH 1: 3 has the ability to adsorb Iodine better and more optimal than the adsorbent of banana peel with other concentration variations.

The highest absorption of Methylene Blue is in the adsorbent of banana peel which carbonized with NaOH activator composition of 1:3 was 24.90 mg/g. The largest surface area of the adsorbent was 92.43 m\(^2\)/g. A ratio of 1: 3 was the optimum concentration of the activator and works optimally to remove impurities in the pores of the adsorbent. The adsorbent has more pores and a larger surface area so that the absorption capacities of Iodine and Methylene Blue increased.

Mechanism formation of the composite banana peels activated carbon-TiO\(_2\) can be seen on the figure below.
Figure 1. Schematic Illustration of the formation Composite of Activated Carbon of Banana Peels-TiO$_2$ (Sun, et.al., 2019).

Figure 2-4 showed that the comparison spectra of function group of banana peel activated carbon (black line), titanium dioxide (red line), and composite of activated banana peel-TiO$_2$ (blue line) analyzed using FTIR (Fourier Transform Infrared).

Figure 2. FTIR Spectrum of TiO$_2$

Figure 3. FTIR Spectrum of Activated Carbon by 1:3 NaOH
Figure 4. FTIR Spectrum of Composites Banana Peels Activated Carbon - TiO$_2$

| Vibration            | Wave Numbers (cm$^{-1}$) |
|----------------------|--------------------------|
|                      | These results | Others          |
| Ti-O-Ti              | 703           | 660*            |
| OH bending           | 1302          | 1400**          |

Notes: *Sun et al., (2019) ** Foo dan Hameed (2010)

Table 2 proved that the vibration of Ti-O-Ti and OH bending existed at 703 cm$^{-1}$ and 1302 cm$^{-1}$ as seen in Figure 2. The wavelengths were closed to the other studies. Figure 3 showed that the functional groups of banana peel activated carbon as explained in Table 3. Compared to others, the wavenumber were closed.

Table 3. Functional Groups of Banana Peel Activated Carbon

| Vibration            | Wave Numbers (cm$^{-1}$) |
|----------------------|--------------------------|
|                      | These results | Others          |
| O-H streching        | 3162           | 3210*            |
| O-H bending          | 1302           | 1610*            |
| C-H alifatik         | 2929           | 3000***          |
| C=C bending          | 1577           | 1600**           |
| C-O streching        | 1071           | 1150**           |
| C=N streching        | 2219           | 2300***          |

Notes: *(Foo dan Hameed, 2010), **(Supratman,2009) ***(Orha, et.al., 2016)

Figure 4 proved that TiO$_2$ composed to the banana peel activated carbon as existing of Ti-O-Ti, O-stretching, C=C stretching , Ti-O-C and C-O.

Figure 5 explained that morphology of the adsorbent analyzed had the best characterization results of activated with NaOH 1:3. The material surface of A1 and A2 were SEM photographs of activated carbon at magnifications of 1000x and 5000x. It can be seen that carbon shaped have bars and pores. Figure B1 and B2 were SEM photographs of the composites activated carbon-TiO$_2$ at 1000x and 5000x magnification. It explained that TiO$_2$ attached and spread on the carbon surfaces. Carbon inhibited the accumulation of TiO$_2$ particles. Obstruction of the of TiO$_2$ particles is assumed to cause the surface area of TiO$_2$ particles increased. It means that the increasing photocatalytic activities of TiO$_2$.
Table 4. Functional Groups of Composites Banana Peels Activated Carbon -TiO₂

| Vibration       | Wave Numbers (cm⁻¹) | These results | Others |
|-----------------|----------------------|---------------|--------|
| Ti-O-Ti         | 597                  | 600*          |        |
| O-H stretching  | 3221                 | 3210**        |        |
| C=C stretching  | 1620                 | 1600***       |        |
| Ti-O-C          | 1009                 | 1060**        |        |
| C-O             | 1155                 | 1155**        |        |

Notes: *(Sun, et.al., 2019) ** (Foo dan Hameed, 2010) *** (Orha, et.al., 2016) **** (Supratman, 2009)

Figure 5. Morphological analysis on the surface of the adsorbent was carried out using SEM (Scanning Microscope Electron instrument. A1 and A2 were SEM photographs of activated carbon of banana peels enlarged of 1000x and 5000x. A3 and A4 were SEM photographs of the activated carbon of banana peel composites-TiO₂ at 1000x and 5000x enlarged.

Photodegradation results of Methylene Blue dan Methyl Orange dyes using activated carbon materials indicate the increasing of photodegradation. It is because of the adsorbent bound the dyes. In Figure 6, it was found that the amount of Methylene Blue dye absorbed increase from 89.75 % to 94.61%, and then decreased to 92.99%. It means that the optimum absorption was 96.81%. The percentage removal of Methylene Blue dye was also found to increase from the dye concentration 10 ppm to 30 ppm and then decreased. It also means that the maximum concentration of the dye removal was 30 ppm. At low concentrations there will be unoccupied active sites on the adsorbent surfaces. Above optimal Methylene Blue concentration.
4. Conclusion
This work showed that composite of banana peel-TiO$_2$ can be used as an absorbent of Methylene Blue dyes. The optimum preparation condition of banana peel activated carbon by using 1: 3 NaOH as an activator gives the results that moisture content of 0.53%; ash content of 4.88%; and iodine absorption of 774.09 mg/g and adsorption methylene blue of 92.43 m$^2$/g, respectively. FTIR spectrum showed the presence of functional groups Ti-O-C, Ti-O-Ti, C=C, C-O and O-H, which shows that TiO$_2$ has bind to activated carbon in the composites. In can be concluded that the composite synthesized was successfully degraded 94.61% of Methylene Blue dyes of and 84.30% of Methyl Orange dyes, respectively.

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