



Cassava Skin Usage (*Manihot esculenta* L.) as Photocatalyst for Degradation of Methylene Blue in the River of Textile Industrial Zone

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Abstract

The progress of the textile industry can increase the amount of dyestuff waste, but often waste disposal is overlooked. The purpose of this research is to provide solution in handling river water pollution by textile industry dye waste. The degradation of textile industry dye waste can be done with TiO₂ semiconductors with UV light as a source of irradiation, but only 5% of sunlight can be utilized TiO₂ to excite its electrons, so degradation process is not effective. It needs a material that can optimize the activity of TiO₂ semiconductor, one of them C-dot coming from cassava skin. The results obtained in this research were TiO₂/C-dot composite which could degrade methylene blue where its effectiveness was tested using UV-Vis spectrophotometer instrument. TiO₂/C-dot photocatalyst activity test for methylene blue 0.0001 M showed that the concentration of 20% with the amount of degradation up to 96,99%, best type of rays was sunshine with amount of degradation up to 66,25% and longest radiation in sunshine with the amount of degradation was up to 78.77% and UV with the amount of degradation up to 75.99%.

1. Introduction

Today we know that Indonesia is experiencing rapid progress in the field of industry, one of them in the textile industry. The progress of the textile industry can increase the amount of dyestuff waste, but often waste disposal is overlooked. Disposal of dyestuffs into rivers can result in pollution and harmful to public health. Therefore, appropriate solutions are needed to deal with river water pollution by textile industry dye waste.

The photocatalytic process using TiO₂ semiconductors with UV light as a source of irradiation has shown the potential to overcome the problem of dyestuff waste by degrading the dye to a more environmentally friendly compound [1], but only 5% of sunlight can be utilized TiO₂ to excite its electrons due to the large band gap. The basic mechanism for the photocatalyst process is the formation of pairs of electron-holes on the surface of the catalyst when the corresponding photon is energized [2]. The formation of a nanocomposite which is a combination of two distinct

components of either one or both scales $\leq 10^{-9}$ m or equivalent to the size of the atom or molecule can enhance the photocatalytic activity of TiO₂, one of which is the TiO₂/C-dot composite [3]. Research conducted showed that the quantum carbon dot (CQDs) attached to TiO₂ surfaces could effectively degrade methyl blue (MB) to close to 100% [4]. Thus, the TiO₂/C-dot composite is also expected to have such photodegradation capability due to the similarity of the C-dot properties to the CQDs. With this photodegradation method, the dyestuff will be decomposed into components that are simpler and safer for the environment [5].

Only limited as staple food substitutes for rice and raw materials for various processed products, while the skin is often discarded. In fact, cassava skin contains starch compounds that can be utilized as carbon sources in the manufacture of carbon nanodot material or better known as C-dot through hydrothermal method [6].

Based on these facts, the innovation to solve the problem of river water pollution by dyestuff waste is the making of cotton-based TiO₂/C-dot nanocomposite

(*Manihotesculenta L.*) as photodegradation material of dyestuff, especially methylene blue compound. The abundance of carbon sources in cassava peel starch compounds is predicted to be engineered into carbon nanodot material which is simply known as C-dot [7]. The advantages of this innovation are the easy process of making TiO₂/C-dot composites, cheap and abundant raw material sources, and enhanced photodegradation capability against methylene blue compounds.

2. Materials and Methods

2.1. Materials and Procedures

Materials used in this study include methylene blue, TiO₂, NaOH, concentrated HCl, C-dot powder of cassava leather, aquadest, and 96% ethanol obtained from Merck.

2.2. Phase of preparation of materials

The main ingredients in this research, namely cassava leaf waste. Cassava leather as a base material luminescence material has a source of many carbon compounds. The simple synthesis of luminescence material begins with processing the cassava skin into a powder.

2.3. Phase of C-dot synthesis from Cassava Skin

The independent variables used in this study are cassava powder of the material preparation stage. Cassava skin was added in 100 ml 0.1 M HCl solution and stirred in a magnetic stirrer for 1 hour with temperature controlled at 30°C. Giving the acid aims to break down polymer compounds such as cellulose, and pectin to form a more simple carbohydrate compounds (hydrolysis). The result of the hydrolysis is then neutralized pH with 100 ml of a strong base of 0.1 M NaOH. At this stage the temperature at the magnetic stirrer is raised at 100°C. The exothermic reaction to the addition of this strong base produces heat so that the carbon chain in the material can break and produce C-dot. Furthermore, characterization of C-dot material with XRD was done.

2.4. Synthesis TiO₂/C-dot Composite

The synthesis of TiO₂/C-dot composites was performed by sol-gel method. The TiO₂ nanoparticles were prepared by heating the commercial TiO₂ at a temperature of 500°C for 1 hour. The second stage, 0.1 g of TiO₂ nanoparticles and various C-dot content of cassava leather (10%, 20%, 30%, 40%, 50% dan 100% (w/w)) added 5 mL of ion free water with stirring for 10 minute and dried in 80°C vacuum oven for 12 hours. After synthesis process is done characterization with XRD and SEM.

2.5. Photodegradation Activity Test on Methylene Blue

Photodegradation of the dye was carried out by taking 25 mL methylene blue 0.0001 M and then added a c-dot photocatalyst of cassava leather, and irradiated by ultraviolet light for ± 80 min, after the photocatalysis was finished filtrate was analyzed using visible uv spectrophotometer. Photocatalyst activity test was performed by comparing with standard methylene blue 0.0001 M.

2.6. 2.6. The Effect of Light on Methylene Blue Photodegradation

Four 50 mL cups filled with 25 mL methylene blue 20 mg/L solution with different treatment, i.e. first glass containing methylene blue solution; the second glass added 50 mg C-dot. Then photodegradation process is done in photoreactor for 50 minutes using UV light. Furthermore, with the same preparation procedure illuminated by sunlight at 10:00 to 10:50 pm and left in dark conditions. The photodegradation process is done triplo. The methylene blue concentration after the treatment was measured by a UV-Vis spectrophotometer at a wavelength of 664 nm.

2.7. Influence of Irradiation on Methylene Blue Degradation using TiO₂/C-dot Composite Photocatalyst

Nine pieces of 50 mL glass of glass filled 25 mL of 20 mg/L methylene blue solution and 50 mg C-dot was added, then radiation was done by sunlight. Furthermore, with the same preparation procedure illuminated by UV light in the photoreactor. Methylene blue absorbance measurements were performed on the first glass at 5 minute irradiation and measured on the other glass at 10, 20, 30, 40, 50, and 60 minutes. The photodegradation process is done triplo. The methylene blue concentration after the treatment was measured by a UV-Vis spectrophotometer at a wavelength of 200 nm – 800 nm.

3. Results and Discussion

3.1. Synthesis of C-dot from Cassava Skin

The results obtained from hydrolysis of HCl neutralized with NaOH produce heat so that the carbon chain in the material can break and produce C-dot.



Figure 1: C-dot

3.2. Making Composite TiO₂/C-dot

The result of mixing 0.1 gram of TiO₂ nanoparticles and various C-dot grade of cassava leaf 10%, 20%, 30%, 40%, 50% and 100% of TiO₂/C-dot composite. This composite has a darker color than TiO₂ and is close to a dark brown color.



Figure 2: TiO₂/C-dot composite

3.3. Characterization of TiO₂/C-dot Composite

The synthesis results were characterized by SEM showing the composite surface morphology of TiO₂/C-dot Nanoparticles with different magnifications.

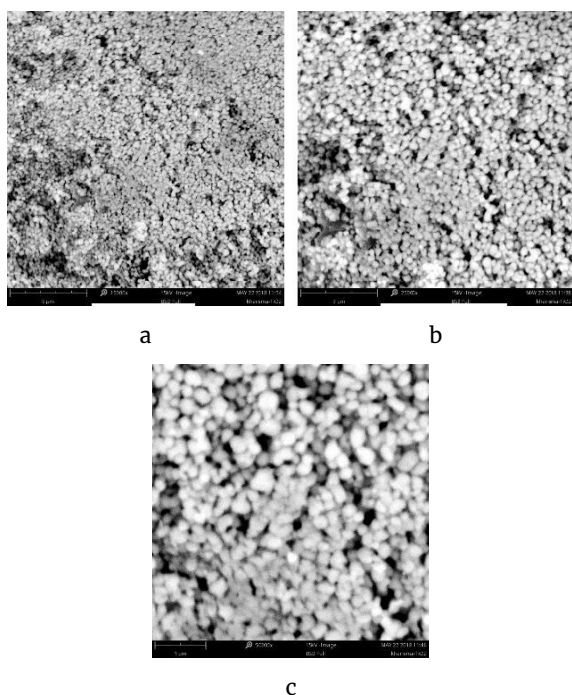


Figure 3: (a) SEM Magnification 15000x (b) SEM Magnification 25000x (c) SEM Magnification 50000x

The C-dot influence in the composite can be known from the XRD diffractogram. The intensity and crystallinity of the TiO₂/C-dot composites were less than that of TiO₂. This decrease was due to the addition of a relatively amorphous C-dot in the composite. However, there were no significant changes in the XRD pattern of the composites compared to the XRD pattern of TiO₂. All peaks on TiO₂/C-dot were similar with the diffraction angle of TiO₂, indicating that there was no new compound formed from mixing C-dot with TiO₂.

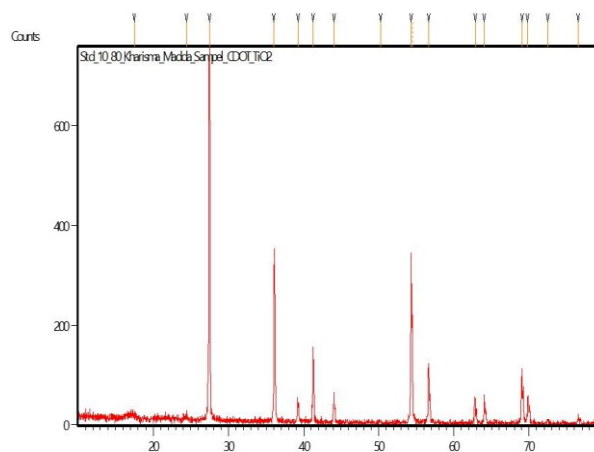


Figure 4: XRD Spectra of TiO₂/Cdot

3.4. Adsorption Test

In the analysis that has been done can be known the effectiveness of the use of TiO₂/C-dot in dyestuff degradation Methylene Blue.

3.4.1. Effect of Concentration on Photodegradation

The results of the addition of TiO₂/C-dot levels in methylene blue (25 mg/L) solution processed by the photocatalytic reactor showed color degradation as shown in the following table.

Table 2: Data of analysis of concentration variation on methylen blue degradation

Concentration	Absorption (%)	MB concentration remaining	MB concentration in degradation	Effectiveness
10	0.858	5.546	14.454	72.268
20	0.058	0.602	19.398	96.990
30	0.137	5.451	14.549	72.744
40	0.286	10.056	9.944	49.722
50	0.077	3.597	16.403	82.013
100	0.913	5.886	14.114	70.569

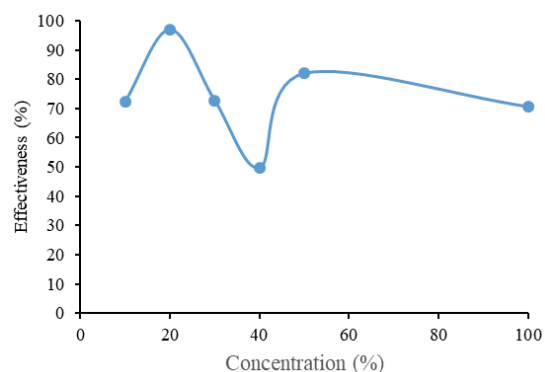


Figure 5: Diagram of the relationship between the concentration of methylen blue degradation

The optimum degradation occurs at 20%. The degradation of each dye is not significant, so it takes longer to reach the desired descent percentage. This is because no catalyst plays a major role in dye reduction. The use of UV light without the use of a catalyst can

decrease the dye even if the percentage obtained is very small. This is due to the double bond in the reduced dye compound with the help of hv, but the dyestuff compound can not be substantially reduced from the large absorbance value so that the percent value of degradation obtained is very small.

When photocatalysts are exposed to ultraviolet radiation that has the appropriate energy or even exceeds the bandit energy of the oxide titan, the electrons in the valence band of the photocatalyst will be attracted to the conduction band which will produce the ekb and vacancies or holes (hvb) acting as positive charges. Furthermore, hvb will react with the metal hydroxide i.e. the titan hydroxide oxide present in the solution to form a metal hydroxide radical which is a strong oxidizer to oxidize the compounds present in said liquid waste. For electrons present on the semiconductor surface will be trapped in the metal hydroxide and can react with H₂O or O₂ present in the solution to form hydroxy radical (-OH) or superoxide (-O) which will oxidize the compounds contained in said liquid waste. This radical will be formed continuously as long as TiO₂/C-dot is still exposed to UV radiation and will attack the compound contained in the liquid waste located on the surface of the catalyst so that it will be degraded to produce a harmless compound. So the more photocatalyst is added then the active side that will produce (-OH) more and more [8].

3.4.2. Effect of Light on Photodegradation

The results of the analysis of the type of light in the methylene blue solution (25 mg/L) processed by the photocatalytic reactor show the color degradation as shown in the following table.

Table 3: Data analysis of the type of rays on methylen blue degradation

Variable	Absorption	MB concentration remaining	MB concentration in degradation	Effectiveness (%)
Sun	0.179	6.749	13.251	66.255
UV	0.205	7.553	12.447	62.237
Dark	0.217	7.923	12.077	60.383

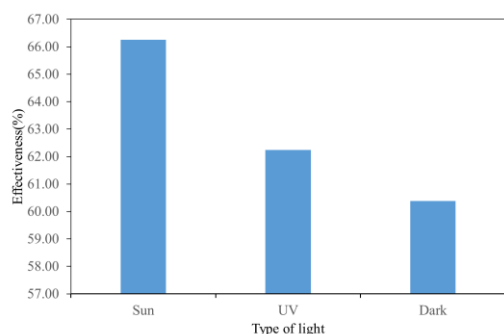


Figure 6: Diagram of the relation between the variation of rays to degradation of methylen blue

The diagram above shows that the degradation value of methylene blue increases in dark conditions, UV rays into sunlight with various photocatalysts. In dark conditions, the degradation value is low because there is

no light source so that the photon energy to produce the radical ·OH is weak, therefore methylen blue is only adsorbed on the catalyst surface and its degradation becomes not optimal. This degradation process is due to increasing time which is proportional to increasing UV radiation [9]. In sunlight conditions obtained sunlight results higher than UV light. This is because sunlight has the intensity and wavelength between (310-2300 nm) greater than the wavelength of UV light (200-380 nm). In addition, sunlight is a combination of ± 45% visible light and ± 5% of UV light so that sunlight has a relatively large energy and can provide a lot of photon energy on the photocatalyst. Photocatalysts TiO₂/C-dot increase photocatalytic activity up to ± 66.25% UV radiation to sunlight resulting in the most optimum degradation of methylene blue. When the photocatalyst is irradiated with greater energy than the bandgap, a strong oxidizing hole is generated to form an OH radical and the radical degrades the blue methylene into a simpler compound. From these light effects data, the sun can be used as a potential light source for photocatalysts in degrading methylen blue dyes. Photodegradation of dyes is carried out in the open space (exposed to sunlight). UV light radiation acts as a photon that can produce OH radicals. which has a large oxidation potential for organic molecules [10].

3.4.3. The effect of long irradiation on photodegradation

The time of radiation in the photodegradation process illustrates the length of the interaction (contact) between photocatalyst and light (hv) in generating OH radicals and contacts between OH radicals and methylen blue substrates in the degradation process. The results of long and sunlight exposure analysis of methylene shown in the following table.

Table 4: Analyzes of long irradiation data on methylen blue degradation

Variables	Absorption (%)	MB concentration remaining	MB concentration in degradation	Effectiveness (%)
M10	0.118	4.864	15.136	75.680
M20	0.098	4.246	15.754	78.770
M30	0.113	4.710	15.290	76.452
M40	0.14	5.544	14.456	72.281
M50	0.129	5.204	14.796	73.980
M60	0.136	5.420	14.580	72.899
UV10	0.165	6.316	13.684	68.418
UV20	0.224	8.140	11.860	59.302
UV30	0.129	5.204	14.796	73.980
UV40	0.118	4.864	15.136	75.680
UV50	0.116	4.802	15.198	75.989
UV60	0.137	5.451	14.549	72.744

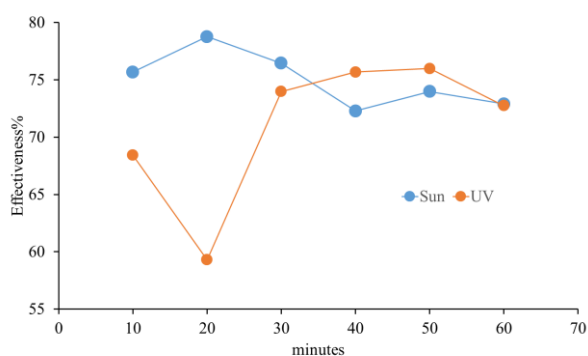


Figure 7: Diagram of the relation between the duration of sun exposure and UV radiation to methylen blue degradation

Diagram shows that degradation of methylen blue optimum at minute 20 with effectiveness equal to 78,77%. This shows that the irradiation time is 20 minutes, the solution dye becomes faded so that methylen blue is easily degraded.

While on UV rays degradation methylen blue optimum at minute 50 with effectiveness equal to 75,99%. This shows that the irradiation time is 50 minutes, the solution dye becomes faded so that methylen blue is easily degraded. Photon energy from sunlight can cause photocatalysts to produce OH radicals more than photon energy from UV light. Degradation of methylene blue increases with increasing sun exposure in the photodegradation process using TiO_2/C -dot catalyst. The longer the irradiation time, the adsorption and desorption process will run continuously, until it reaches the optimum condition where adsorption and desorption are equilibrium so that degradation tends to be stable close to 100%.

4. Conclusion

Based on the result of research, it can be concluded the photocatalyst of TiO_2/C -dot with concentration variation of 10,20,30,40,50 and 100% can be synthesized using hydrothermal method. The results of TiO_2/C -dot photocatalyst characterization using XRD and SEM show that TiO_2 has entered the external and internal parts of TiO_2/C -dot. TiO_2/C -dot photocatalyst activity test for blue methylene 0.0001 M showed that the best photocatalyst concentration to degrade methylene blue 0.0001 M at 20% level with degradation amount up to 96,99%. TiO_2/C -dot photocatalyst activity test for blue 0.0001 M methylene showed that the best type of rays to degrade methylene blue 0.0001 M is sunlight with the amount of degradation up to 66,25%. TiO_2/C -dot photocatalyst activity test for blue 0.0001 M methylene showed that the best irradiation time to degrade methylene blue 0.0001 M in sunlight with degradation amount up to 78,77% and UV with amount of degradation up to 75,99 %.

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