

## Characterization and Investigation on Photocatalytic Activities of TiO<sub>2</sub>/Coconut Shell-Based Activated Carbon

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### Abstract

Coconut shell-based activated carbon-supported TiO<sub>2</sub> catalyst had been prepared with a sol-gel method using titanium tetraisopropoxide acting as TiO<sub>2</sub> precursor. TiO<sub>2</sub>/activated carbon photocatalyst was characterized with X-Ray Diffraction (XRD), Fourier Transform-Infrared (FT-IR), Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), and surface area analysis using Brunauer-Emmett-Teller (BET) adsorption-desorption isotherm. Photocatalytic activities of TiO<sub>2</sub>/activated carbon were investigated through the degradation of indigo carmine using UV light. The highest degradation percentage (%D) obtained for the indigo carmine was 91.79% at pH 3 and an initial concentration of 5 mg L<sup>-1</sup> after 25 min radiation. TiO<sub>2</sub>/activated carbon showed higher photocatalytic activities when sunlight was used, in comparison to that of UV light.

*Keywords: TiO<sub>2</sub>/activated carbon, sol-gel, indigo carmine, photodegradation*

### Abstrak (Indonesian)

Katalis TiO<sub>2</sub> yang disangga oleh karbon aktif berbasis tempurung kelapa telah dipreparasi melalui metode sol gel menggunakan titanium tetraisopropoksida yang bertindak sebagai prekursor TiO<sub>2</sub>. Fotokatalis TiO<sub>2</sub>/karbon aktif dikarakterisasi dengan X-Ray Diffraction (XRD), Fourier Transform-Infrared (FT-IR), Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX), dan analisis luas permukaan menggunakan isotherm adsorpsi-desorpsi Brunauer-Emmett-Teller (BET). Aktivitas fotokatalitik dari TiO<sub>2</sub>/karbon aktif diuji melalui degradasi zat warna indigo carmine menggunakan sinar UV. Persentase degradasi (%D) tertinggi dihasilkan pada indigo carmine sebesar 91,79% pada pH 3 dan konsentrasi awal 5 mg L<sup>-1</sup> setelah diradiasi selama 25 menit. TiO<sub>2</sub>/karbon aktif menunjukkan aktivitas fotokatalitik lebih tinggi saat menggunakan sinar matahari dibandingkan saat menggunakan sinar UV.

*Kata Kunci: TiO<sub>2</sub>/karbon aktif, sol-gel, indigo carmine, photodegradation*

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### INTRODUCTION

The textile industry is one of the most rapidly developing industries in Indonesia, recently. Other than contributing to the benefits for mankind, the development of the textile industry also gives negative impacts on the environment. It is due to the fact that the textile industry produces environmentally harmful wastewater, including dye wastewater. Dyes are organic compounds that are hardly-biodegradable, resistant, and toxic. If released into waters without properly treated, it can pollute the environment.

Methods for textile-produced wastewater management have been widely developed, one of which is adsorption. However, this method has a

weakness where it is not able to degrade and remove the pollutant; only removing the pollutant from one phase to the other. As an alternative, photodegradation using a photocatalyst has been proposed. It is the most effective method stem from the fact that it can degrade the hazardous organic compounds to become non-toxic and more simple and environmentally friendly.

TiO<sub>2</sub> has been reported to be one of the most commonly used photocatalysts for photodegradation. It is a semiconductor material that can be used as a photocatalyst associated with its ability in intensifying the reaction of dye photodegradation with high stability [1,2]. Nonetheless, TiO<sub>2</sub> also contains some drawbacks such as low adsorption ability resulting in a

weak photocatalytic degradation process [3]. Furthermore,  $\text{TiO}_2$  powder is difficult to remove from water and tends to form aggregates. To overcome those,  $\text{TiO}_2$  can be modified or supported on a material with a higher surface area such as zeolite, activated carbon, bentonite, etc.

The application of  $\text{TiO}_2$  in zeolite as a photocatalyst in methylene blue degradation has been reported. The results revealed that the  $\text{TiO}_2$  concentration affects the reaction rate constant.  $\text{TiO}_2$  impregnated on commercial activated carbon has also been used as a photocatalyst in indigo carmine degradation. The results showed that photodegradation efficiency using  $\text{TiO}_2$ /activated carbon was higher as opposed to neat  $\text{TiO}_2$  [4,5].

Activated carbon is a material containing organic or inorganic carbons originated from plants, animals, or mining materials that are obtained from the activation process. The materials include various types of wood, rice husk, bones, coal, coconut shell, or coffee cascara. The process of activated carbon preparation includes two steps, they are carbonization (charring) and activation. The activation aims to open the pores to give access to adsorbate and enhance the surface area, pore distribution, and pore size [6].

Carbon activation can be conducted in two ways; chemically and physically. Chemical activation is conducted by the addition of chemicals such as acids, basics, or salts. Meanwhile, physical activation can be done through heating at a particular temperature. Activation is a very important process as it determines the quality of the produced activated carbon, including its surface area or the adsorption ability [1]. Chemical activation offers some benefits including the enhancement of surface area and porosity that can facilitate better adsorption. The physical activation of coconut shell, rice husk, used coffee grounds, and their use to support Cu catalyst have been reported. However, the surface area of the activated carbon only reached  $356.22 \text{ m}^2 \text{ g}^{-1}$  contributing to weak catalytic activities on the dehydrogenation of ethanol into acetaldehyde [7].

Activated carbon produced from chemical or physical activation has been massively applied as an adsorbent. In the Adsorption process, the surface area of an adsorbent has a significant role. Activated carbon can also be used to adsorb gases, pollutants, and dyes which highlight its importance in handling environmental pollution. Nakamura et al [8] has reported the use of coffee ground-based activated coffee on acid orange 7 adsorptions.

In this research, the investigation on  $\text{TiO}_2$  photocatalyst supported with coconut shell-based

activated carbon using the sol-gel method. The given  $\text{TiO}_2$ /activated carbon photocatalyst will be tested for its photodegradation ability on indigo carmine with several parameters (pH, contact time, and dye concentration) to obtain optimum conditions for photodegradation. The synthetic dye, indigo carmine, was chosen because of its massive use in the textile industry, especially in a color coating of jeans (denim) and polyester fibers.

## MATERIALS AND METHODS

### Materials

Materials used included coconut shell charcoal (prepared in this research), distilled water, HCl 1 M,  $\text{AgNO}_3$  solution, indigo carmine, NaOH, titanium tetraisopropoxide ( $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ ), and isopropyl alcohol were manufactured by Merck. All chemicals were used without any further purification.

### Methods

#### Preparation of coconut shell-based activated carbon

Coconut shell (2.5 kg) was charred in an open barrel to obtain coconut shell-based charcoal. Then, it was ground, filtered using sieve 100 mesh, and activated using HCl 1 M (ratio of 1:10 for 12 h at room temperature). It was filtered and washed to neutralize the pH using distilled water to obtain activated carbon. The neutral pH was confirmed by the absence of AgCl precipitates after the administration of  $\text{AgNO}_3$  into the filtrate. The activated carbon was oven-dried at  $100 \text{ }^\circ\text{C}$  for 6 h. The percentages of yield, water content, and ash content were calculated based on [9].

#### Impregnation of $\text{TiO}_2$ onto activated carbon

The synthesis of  $\text{TiO}_2$ /activated carbon photocatalyst was carried out with sol-gel method by drop-wising 15 mL titanium tetraisopropoxide ( $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ ) into 100 mL isopropyl alcohol at 250 rpm for 3 h to reach homogeneity. Into the solution, 10 g coconut shell-based activated carbon was slowly added for 14 h and followed by filtration. The solid was oven-dried at  $100 \text{ }^\circ\text{C}$  for 5 h and calcinated in a furnace at  $350 \text{ }^\circ\text{C}$  for 5 h to obtain  $\text{TiO}_2$ /activated carbon [10].

### Characterization

Activated carbon and  $\text{TiO}_2$ /activated carbon were characterized using Shimadzu XRD-700 Series X-Ray Diffractometer (Kyoto, Japan), Shimadzu FT-IR 8400 (Kyoto, Japan), and Scanning Electron Microscope – Energy Dispersive X-Ray Spectrometer (SEM) (Jeol. Jsm-6510 LA, Tokyo, Japan). As for surface area analysis was carried out using QuadraSorb Station 1 (ver. 5.06) based on the Brunauer-Emmett-Teller (BET) isotherm of nitrogen adsorption-desorption.

### Investigation of photocatalytic activities

Into each of five glass containers 100 mL (designed to block any light exposure), 25 mL indigo carmine solution at particular concentrations, and 25 mg photocatalyst were added. The containers were inserted into a radiation box, where the cover was removed afterward to allow the light exposure. It is stirred for 30 min to reach adsorption equilibrium. Afterward, UV light was used to irradiate the mixture at room temperature, and followed by centrifugation at 4,000 rpm for 10 min for separation. Indigo carmine concentration in the supernatant was determined using Shimadzu UVmini-1240 UV/Visible Scanning Spectrophotometer (Kyoto, Japan) at 610 nm. This procedure was conducted to study the optimum pH (ranged from pH 3-11), irradiation time (0 – 25 min), and initial concentration of indigo carmine (5 – 25 mg L<sup>-1</sup>). To confirm the photocatalytic activities, the results will be compared with those without the addition of photocatalyst.

### Photocatalytic degradation using sunlight

Photocatalytic degradation of indigo carmine under the sunlight was investigated at the optimum parameters (pH, the weight of photocatalyst, and initial concentration of indigo carmine). Samples were irradiated under the sunlight for 0, 5, 10, 15, 20, and 25 min between 11.00 AM – 02.00 PM Jakarta Time.

## RESULT AND DISCUSSION

### Coconut Shell-Based Activated Carbon

The activated carbon used in this research is derived from coconut shells. The coconut shells were priorly charred in an open barrel to produce coconut shell charcoal. The charcoal was activated chemically using HCl 1 M to yield activated carbon. The yield percentage, water content, and ash content were then determined. The results showed that the activated carbon satisfied the Indonesian national standard (SNI 06-3730-1995), where the yield, water content, and ash content were 16.4%, 15%, and 2.55%, respectively.

### Impregnated TiO<sub>2</sub> on activated carbon

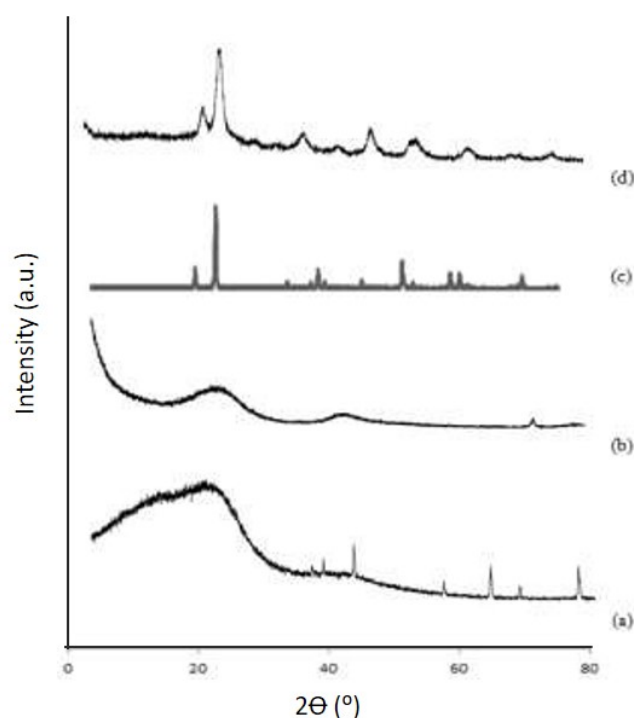
The preparation of activated carbon-supported TiO<sub>2</sub> (TiO<sub>2</sub>/activated carbon) was conducted using impregnation, where the support (activated carbon) was contacted with the feed metal solution (Ti(OCH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>), followed by drying and calcination processes to convert the feed into an active species (TiO<sub>2</sub>). Ti metal acts as the active center, meanwhile, the activated carbon facilitates the dispersion of the active centers. Impregnation used in this research is a wet impregnation. To understand the characteristics of

the produced photocatalyst, XRD, FT-IR, SEM-EDX, and surface area analysis were carried out.

### Characterization

#### X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of coconut shell-based activated carbon, commercial activated carbon, TiO<sub>2</sub>, and TiO<sub>2</sub>/activated carbon were presented in Figure 1.

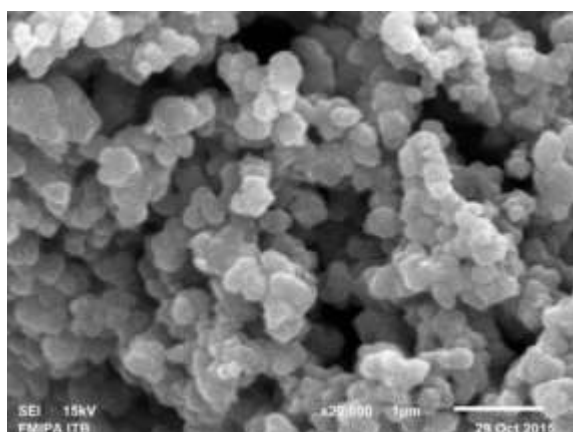


**Figure 1.** XRD patterns of (a) coconut shell-based activated carbon (b) commercial activated carbon (c) TiO<sub>2</sub> and (d) TiO<sub>2</sub>/activated carbon

The diffraction pattern of coconut shell-based activated carbon (Figure 1a) shows two broadening peaks at  $2\theta = 25.08^\circ$  and  $43.98^\circ$ , suggesting the amorphous phase (non-crystalline) of the activated carbon. A similar pattern was observed on that given by the commercial activated carbon (Figure 1b). It is in good agreement with Omri et al [9] where peak at  $2\theta = 22^\circ$  from plane (002) and  $2\theta = 43^\circ$  from plane (100). Diffraction pattern of TiO<sub>2</sub> has peaks of  $2\theta$  around  $25.28^\circ$ ,  $36.94^\circ$ ,  $37.80^\circ$ ,  $38.50^\circ$ ,  $48.04^\circ$ ,  $55.06^\circ$ ,  $62.68^\circ$ ,  $70.30^\circ$ ,  $74.02^\circ$ , and  $75.02^\circ$  which are similar to the anatase phase of TiO<sub>2</sub> (JCPDF No. 21-1272). The diffraction pattern of TiO<sub>2</sub>/activated carbon shows the peak appearances at  $2\theta$  around  $25.3^\circ$ ,  $37.8^\circ$ ,  $48^\circ$ ,  $53.9^\circ$ , and  $55^\circ$ , which is similar to Omri et al [9]. This analysis revealed the successful impregnation of TiO<sub>2</sub> onto the activated carbon surface.

### Scanning Electron Microscope-Energy Disperse X-Ray Spectrometer (SEM-EDX)

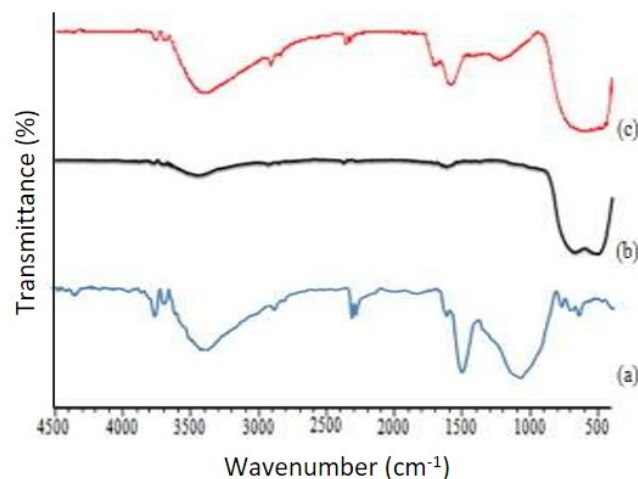
Characterization of TiO<sub>2</sub>/activated carbon with Scanning Electron Microscope (SEM) and Energy Disperse X-Ray Spectroscopy (EDX) aimed to study the surface morphology and elemental composition of TiO<sub>2</sub>/activated carbon, respectively. The SEM images reveal the ununiform shape of TiO<sub>2</sub>/activated carbon, which is more likely to form a spherical shape with agglomeration (Figure 2). Meanwhile, from EDX analysis, it was found that the carbon and titania contents in the photocatalyst were 15.81% and 85.19%, respectively.



**Figure 2.** Surface morphology of TiO<sub>2</sub>/activated carbon with 20,000x magnification

### Fourier Transform-Infrared (FT-IR)

The FT-IR spectra of coconut shell-based activated carbon, TiO<sub>2</sub>, and TiO<sub>2</sub>/activated carbon are presented in Figure 3. The three spectra have broadening absorbance bands at 3406-3411 cm<sup>-1</sup> were assigned to the vibration of hydroxyl groups (-OH) from water molecules absorbed by the activated carbon. An observable broadening spectral peak at 3448 cm<sup>-1</sup> in the FT-IR spectrum of TiO<sub>2</sub>/activated carbon indicated the presence of -OH from H<sub>2</sub>O molecules. Meanwhile, a broad peak at around 486-646 cm<sup>-1</sup> was attributed to the presence of Ti-O-Ti groups in TiO<sub>2</sub>. It is in line with Omri et al [5] that the typical vibration of Ti-O-Ti was observed at around 680-850 cm<sup>-1</sup>. It further suggested that TiO<sub>2</sub> has been successfully impregnated into the activated carbon. However, the FT-IR spectrum of TiO<sub>2</sub>/activated carbon did not exhibit the presence of an absorbance band at 1200-1600 cm<sup>-1</sup> which is associated to the Ti-O-C bond. It was owing to the fact that the interaction between activated carbon and TiO<sub>2</sub> in our photocatalyst was based on physical interaction.



**Figure 3.** FT-IR spectra of (a) coconut shell-based activated carbon (b) TiO<sub>2</sub> and (c) TiO<sub>2</sub>/activated carbon

### Surface area analysis

To determine the surface area, total pore volume, and average pore diameter of activated carbon and TiO<sub>2</sub>/activated carbon Brunauer-Emmett-Teller (BET) isotherm analysis was conducted based on the adsorption-desorption of N<sub>2</sub>. Based on the results presented in Table 1, the BET surface area (S<sub>BET</sub>) of TiO<sub>2</sub>/activated carbon was smaller than activated carbon. It was ascribed to the impregnation of TiO<sub>2</sub> onto the pores of activated carbon, resulting in the blockage of the pores. It is in line with the previous report [10].

**Table 1.** BET isotherm parameters of N<sub>2</sub> adsorption-desorption

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Pore diameter (nm)	Total pore volume (cc g <sup>-1</sup> )
Activated carbon	291.611	2.56	0.186
TiO <sub>2</sub> /activated carbon	286.364	3.84	0.275

### Photocatalytic Activities

#### Effect of pH

The efficiency of photocatalytic degradation is dependent on the pH of the dye solution, as it affects the adsorption [11]. The effect of pH on the indigo carmine photodegradation can be observed in Figure 4, where it shows that the highest degradation percentage (90.94%) was obtained at pH 3 after 25 min irradiation time. It was in line with the previous reports that the optimum pH of the photodegradation of indigo carmine was pH 3 [12,13]. The irradiation time was

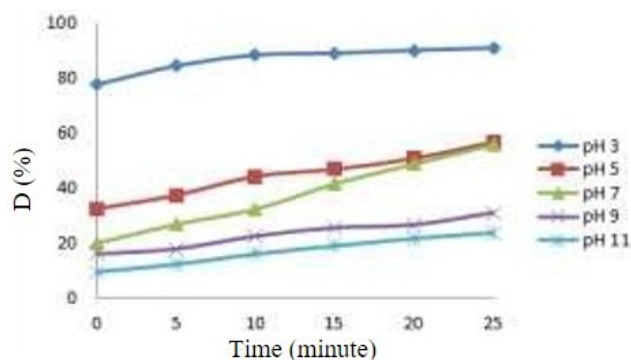


also capable of increasing the dye degradation due to the higher formation of radical hydroxyl ( $\text{OH}\cdot$ ) that was responsible in degrading the indigo carmine.

The pH increase causes a decrease in dye degradation. It was ascribed to the amphoteric properties of  $\text{TiO}_2$ , where it gave the positive charge in acidic condition and negative charge in basic condition on the surface. The reaction can be presented as follows:

- Acidic pH ( $\text{pH} < 7$ ):  $\text{Ti-OH} + \text{H}^+ \rightarrow \text{TiOH}_2^+$
- Basic pH ( $\text{pH} > 7$ ):  $\text{Ti-OH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O}$

Indigo carmine is an anionic dye with a negative charge which can be easily adsorbed onto  $\text{TiO}_2$  surface in acidic condition. The increase of indigo carmine adsorption induces quicker and easier photocatalytic reaction. As reported, the early photocatalytic process is dominated by adsorption. At high pH (basic pH) indigo carmine with its negative charge will be difficult to be adsorbed due to the repulsive force with  $\text{TiO}^-$ . Therefore, the photocatalytic reaction is expected to be reduced.

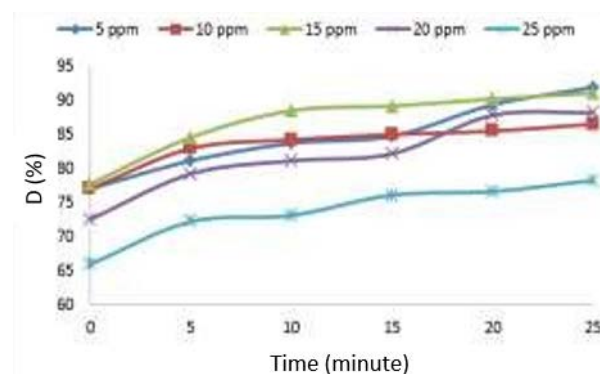


**Figure 4.** Effect of indigo carmine pH on the catalytic photodegradation (initial solution concentration =  $15 \text{ mg L}^{-1}$ ,  $25 \text{ mg}$  photocatalyst, and under UV light)

#### Effect of dye initial concentration

Figure 5 shows the correlation between the initial concentration of indigo carmine with the degradation percentage. The results showed that the highest degradation percentage was given by the  $5 \text{ mg L}^{-1}$  indigo carmine after 25 min UV irradiation. The increase in the initial concentration of indigo carmine causes a reduction in the degradation percentage. It stems from the presence of competition between the dye molecules during the adsorption and later

photodegraded. Moreover, excessive dye concentration inhibits the UV light to reach the photocatalyst surface causing less photon energy available on the  $\text{TiO}_2$  surface associated with the presence of electrons and the formation of holes.



**Figure 5.** Effect of the initial concentration of indigo carmine on the catalytic photodegradation (at pH 3,  $25 \text{ mg}$  photocatalyst, and under UV light)

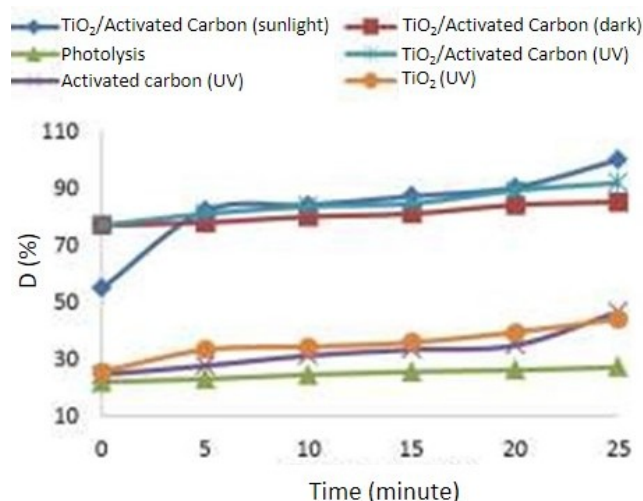
#### Photodegradation using sunlight

One of the major components in photocatalytic degradation is the use of light. The different sources of light affect the photocatalytic activities as it requires a higher or equal amount of energy with the gap energy of the photocatalyst. Figure 6 presents the effect of the source of light against the degradation of indigo carmine. The degradation percentage of indigo carmine using sunlight is higher (100%) than that of UV light (91.79%) after 25 min irradiation. It then suggests the applicability of  $\text{TiO}_2/\text{activated carbon}$  using visible light with smaller energy in comparison with UV light. The presence of carbon with black color contributes to the easier absorbance of sunlight components (the combination of visible and UV lights). Therefore, the  $\text{TiO}_2/\text{activated carbon}$  synthesized in this research can be applied in the environment.

Figure 6 also signifies the role of light in the photodegradation of indigo carmine. The degradation percentages given by the  $\text{TiO}_2/\text{activated carbon}$  without the exposure of light (in dark condition) and with the exposure of UV light were 85.12% and 91.79%, respectively. It substantiates the high adsorption ability of  $\text{TiO}_2/\text{activated carbon}$  for the indigo carmine concentration reduction up to 95.04%. Meanwhile, the combination of adsorption and

photocatalyst process resulted in a 97.26% reduction of indigo carmine concentration. Based on the data altogether, the removal of indigo carmine was dominantly due to the adsorption. It is ascribed to the smaller significantly lower content of TiO<sub>2</sub> in the TiO<sub>2</sub>/activated carbon composite.

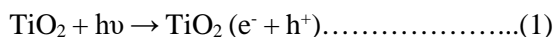
Figure 6 explains the photodegradation of indigo carmine with and without the addition of TiO<sub>2</sub>/activated carbon. The degradation percentage on the use of the photocatalyst was higher (91.79%) than that of without (27.17%). It confirms the role of TiO<sub>2</sub>/activated carbon photocatalyst in the degradation of the dye compound.



**Figure 6.** Effect of the light sources against the efficiency of photocatalytic degradation of indigo carmine (at pH 3, 5 mg L<sup>-1</sup> indigo carmine, and 25 mg photocatalyst)

**Mechanism of The Photocatalytic Degradation**

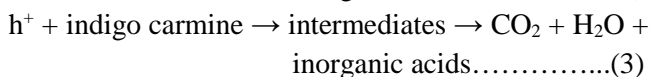
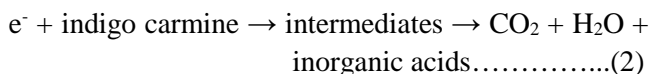
Degradation of indigo carmine facilitated by TiO<sub>2</sub>/activated carbon photocatalyst under the UV light is dependent on the photon energy (hν) that is equal or higher than the band gap energy reaching the TiO<sub>2</sub> surface. This process causes the electron in the valence band to be excited to the conduction band by leaving hole (h<sup>+</sup>) in the valence band. The reaction is represented in the following:



Electron and hole will cause the oxidation and reduction of the dye through the following 2 mechanisms:

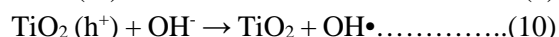
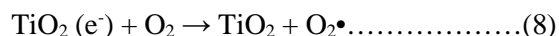
a. Direct reaction

This mechanism occurs when the electron (e<sup>-</sup>) at the conduction band reacted with indigo carmine and the hole (h<sup>+</sup>) at the valence band reacted with the indigo carmine. The reaction can be stated as:

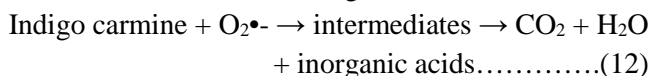
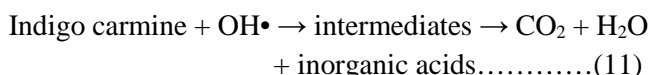


b. Indirect reaction

The electron at conduction band will react with the O<sub>2</sub> molecules in the solution yielding reactive superoxide anions (O<sub>2</sub><sup>•-</sup>) that is a reducing agent, meanwhile hole (h<sup>+</sup>) at valence band will react as an electron donor such as OH<sup>-</sup> or H<sub>2</sub>O resulting in a hydroxyl radical (OH<sup>•</sup>) that is a strong oxidizing agent. The reactions can be seen below:



Superoxide anions (O<sub>2</sub><sup>•-</sup>) and radical hydroxyl (OH<sup>•</sup>) will react with the indigo carmine molecules that have been adsorbed on TiO<sub>2</sub> surface forming oxidized intermediates. If the reaction is fully completed it will produce CO<sub>2</sub> and inorganic acids that are harmless to the environment. The reactions are presented in the following equations:



Voutier et al., [14] stated that the photocatalytic degradation of indigo carmine using TiO<sub>2</sub> will result in intermediate compounds such as benzenes, substituted benzoic acids, fumaric acid, anthranilic acid, acrylic acid, pyruvic acid, malic acid, tartaric acid, lactic acid, malonic acid, etc.

**CONCLUSION**

Based on the research and observation we had conducted, it can be concluded that the synthesized TiO<sub>2</sub>/ activated carbon had a smaller surface area (286.364 m<sup>2</sup> g<sup>-1</sup>) than activated carbon (291.611 m<sup>2</sup> g<sup>-1</sup>). The content of titania in the photocatalyst was 85.19%. The maximum degradation percentage of

indigo carmine (91.79%) was achieved at pH 3, using 25 mg photocatalyst, and an initial concentration of 5 mg L<sup>-1</sup> after 25 min irradiation time. The photodegradation percentage of indigo carmine using TiO<sub>2</sub>/activated carbon with sunlight as the source of light yielded a higher result (100%) than that of UV light (91.79%).

#### ACKNOWLEDGMENT

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#### REFERENCES

- [1] A. Eshaghi and H. Moradi, Optical and photocatalytic properties of the Fe-doped TiO<sub>2</sub> nanoparticles loaded on the activated carbon, *Advanced Powder Technology*, vol. 29, no. 8, pp. 1879-1885, 2018.
- [2] Y. Gu, J. Yperman, R. Carleer, J. D'Haen, J. Maggen, S. Vanderheyden, K. Vanreppelen, and R. M. Garcia, Adsorption and photocatalytic removal of Ibuprofen by activated carbon impregnated with TiO<sub>2</sub> by UV-Vis monitoring, *Chemosphere*, vol. 217, pp. 724-731, 2019.
- [3] X. He, A. Wang, P. Wu, S. Tang, Y. Zhang, L. Li, and P. Ding, Photocatalytic degradation of microcystin-LR by modified TiO<sub>2</sub> photocatalysis: A review, *Science of The Total Environment*, vol. 743, no. 15, pp. 140694, 2020.
- [4] A. K. Subramani, K. Byrappa, S. Ananda, K. M. L. Rai, C. Ranganathaiah, and M. Yoshimura, Photocatalytic Degradation of Indigo Carmine Dye Using TiO<sub>2</sub> Impregnated Activated Carbon. *Indian Academy of Sciences*, vol. 30, no. 1, pp. 37-41, 2007.
- [5] A. Omri, S. D. Lambert, J. Geens, F. Bennour, and M. Benzina, Synthesis, Surface Characterization and Photocatalytic Activity of TiO<sub>2</sub> Supported on Almond Shell Activated Carbon, *J Mater Sci Technol*, vol. 30, no. 9, pp. 894-902, 2014.
- [6] Z. Shayegan, C. Lee, and F. Haghghat, TiO<sub>2</sub> photocatalyst for removal of volatile organic compounds in gas phase – A review. *Chemical Engineering Journal*, vol. 334, pp. 2408-2439, 2018.
- [7] S. Lubis, and Sheilatina, Activated Carbon Supported Copper Catalyst for Ethanol Dehydrogenation. *Proceedings of the 2nd International Conference on Natural and Environmental Sciences (ICONES), Banda Aceh Indonesia*, pp. 166-170, 2014.
- [8] T. Nakamura, T. Tokimoto, T. Tamura, N. Kawasaki, and S. Tanada, Decolorization of Acidic Dye by Charcoal from Coffee Grounds, *Journal of Health Science*, vol. 49, no. 6, pp. 520-523, 2003.
- [9] S. Irmanto, Penurunan Kadar Amonia, Nitrit dan Nitrat Limbah Cair Industri Tahu Menggunakan Arang Aktif dari Ampas Kopi, *Molekul*, vol. 4, no. 2, pp. 105-114, 2009.
- [10] A. Omri, M. Benzina, and F. Bennour, Industrial Application of Photocatalysts Prepared by Hydrothermal and Sol-Gel Methods, *Journal of Industrial and Engineering Chemistry*, vol. 21, pp. 356-362, 2015.
- [11] E. Bulut, M. Ozacar, and A. Sengil, Adsorption of Malachite Green onto Bentonite: Equilibrium and Kinetic Studies and Process Design, *Microporous and Mesoporous Materials*, vol. 115, pp. 234-246, 2008.
- [12] A. Abamrane, Q. Samir, B. Nouredine, M. B. Said, A. Ali, and Y. Ait-ichou, Optimal Decolorization Efficiency of Indigo Carmine by TiO<sub>2</sub>/UV Photocatalytic Process Couple with Response Surface Methodology. *Oriental Journal of Chemistry*, vol. 28, no. 3, pp. 1091-1098, 2012.
- [13] S. Debnath, B. Niladri, N. Hlengilizwe, M. Arjun, and P. Kriveshini, Optimization and Mechanism Elucidation of the Catalytic Photo-Degradation of the Dyes Eosin Yellow (EY) and Naphthol Blue Black (NBB) by a polyaniline-coated Titanium Dioxide Nanocomposite. *Applied Catalysis B: Environmental*, vol. 163, pp. 330-342, 2014.
- [14] M. Voutier, G. Chantal, and H. Jean-Marie, Photocatalytic Degradation of Dyes In Water: Case Study of Indigo Carmine, *Journal of Catalysis*, vol. 201, pp. 46-59, 2001.