

การบำบัดสีย้อมเมทิลีนบลูโดยไททาเนียมไดออกไซด์ที่ยึดเกาะบนถ่านจากซังข้าวโพด

## TREATMENT OF METHYLENE BLUE BY TITANIUM DIOXIDE SUPPORTED CHARCOAL FROM CORNCOB ( $\text{TiO}_2/\text{C}$ )

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**บทคัดย่อ:** ไททาเนียมไดออกไซด์ที่ยึดเกาะบนถ่านจากซังข้าวโพด ( $\text{TiO}_2/\text{C}$ ) สามารถเตรียมได้จากวิธีโซล - เจลของไททาเนียม (IV) ไอโซโพรพอกไซด์ในสภาวะที่มีถ่านอยู่ และนำไปเผาที่อุณหภูมิ  $300^\circ\text{C}$  ถึง  $500^\circ\text{C}$  เป็นเวลา 1 ชั่วโมง การตรวจสอบลักษณะของ  $\text{TiO}_2/\text{C}$  โดยเครื่อง Thermal Gravimetric Analyzer (TGA) พบว่าน้ำหนักของ  $\text{TiO}_2/\text{C}$  คงที่ ที่อุณหภูมิ  $300-450^\circ\text{C}$  จากเทคนิค X-ray power diffraction (XRD) พบว่าโครงสร้างของ  $\text{TiO}_2$  จะอยู่ในรูป anatase ในกรณีของ  $\text{TiO}_2/\text{C}$  ที่ผ่านการเผาที่อุณหภูมิ  $400^\circ\text{C}$  และ  $500^\circ\text{C}$  ดังนั้นจึงใช้  $\text{TiO}_2/\text{C}$  ที่ผ่านการเผาที่อุณหภูมิ  $400^\circ\text{C}$  ไปใช้บำบัดเมทิลีนบลูเข้มข้น 20 ppm ในน้ำที่ pH 2 ภายใต้รังสีอัลตราไวโอเลต พบว่า  $\text{TiO}_2/\text{C}$  สามารถบำบัดเมทิลีนบลูได้ร้อยละ 77.88 ภายในเวลา 4 ชั่วโมง ซึ่ง  $\text{TiO}_2/\text{C}$  มีประสิทธิภาพในการบำบัดเมทิลีนบลูดีกว่า  $\text{TiO}_2$

**Abstract:** Titanium dioxide supported on charcoal from corncob ( $\text{TiO}_2/\text{C}$ ) was prepared by the sol-gel method. The method was performed by mixing titanium (IV) isopropoxide with charcoal from corncob. The  $\text{TiO}_2/\text{C}$  was calcined at different temperature from 300 to  $500^\circ\text{C}$  for one hour. From the Thermal Gravimetric Analysis (TGA) result, weight of  $\text{TiO}_2/\text{C}$  was constant at  $300-450^\circ\text{C}$ . X-ray powder diffraction (XRD) data showed anatase phase of  $\text{TiO}_2$  in the  $\text{TiO}_2/\text{C}$  calcined at  $400^\circ\text{C}$  and  $500^\circ\text{C}$ . Specifically, the  $\text{TiO}_2/\text{C}$  calcined at  $400^\circ\text{C}$  was used for treatment of 20 ppm of methylene blue in aqueous solution at pH 2 under UV irradiation. The removal efficiency was 77.88% within 4 hours, which is higher than that of  $\text{TiO}_2$ .

**Introduction:** Recently, environmental pollution by various organic compounds in natural water has been concerned as they can pose a high threat to human health. There are so many methods developed for pollutant detoxification and photocatalytic degradation.  $\text{TiO}_2$  is widespreadly introduced in photocatalytic degradation to completely remove such poisonous substance because many organic compounds can be decomposed and mineralized by the proceeding oxidation and reduction processes on  $\text{TiO}_2$  surface [1]. The most commonly tested compounds for decomposition through the photocatalysis are phenol, cholophenol, methylene blue etc., which are carcinogenic agents [2].

The different ideas for improving  $\text{TiO}_2$  photocatalytic properties have been widely investigated. One of methods to obtain such photocatalytic degradation is  $\text{TiO}_2$ -carbon composites, including mounting of  $\text{TiO}_2$  on activated carbon or coating of anatase with carbon layer [3].

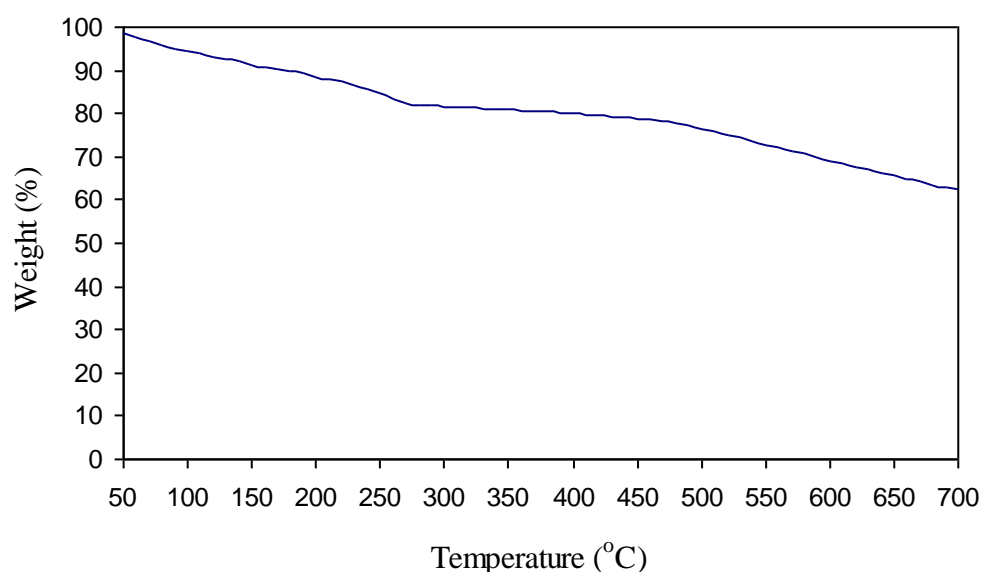
$\text{TiO}_2$  provides not only an effective photocatalytic property, but also low cost and production of less toxic substance [2]. Hence, the present research studies about preparation  $\text{TiO}_2/\text{C}$  for treatment of methylene blue in aqueous solution.

**Methodology:** Preparation of the catalyst: The titanium dioxide supported on charcoal from corncob ( $\text{TiO}_2/\text{C}$ ) was prepared from Titanium (IV) tetraisopropoxide by sol-gel method in the presence of charcoal from corncob. The charcoal (1g) was suspended in titanium (IV) tetraisopropoxide (5ml) under stirring condition. Isopropyl alcohol (20ml) was subsequently added and was stirred of the mixture for an hour.  $\text{TiO}_2/\text{C}$  was dried for an hour and was calcined for an hour at temperature at 300,400 and 500°C

Characterization of the catalyst:  $\text{TiO}_2$  was characterized by X-ray powder diffraction (XRD), Thermal Gravimetric Analysis (TGA) and Scanning Electron Microscope (SEM).

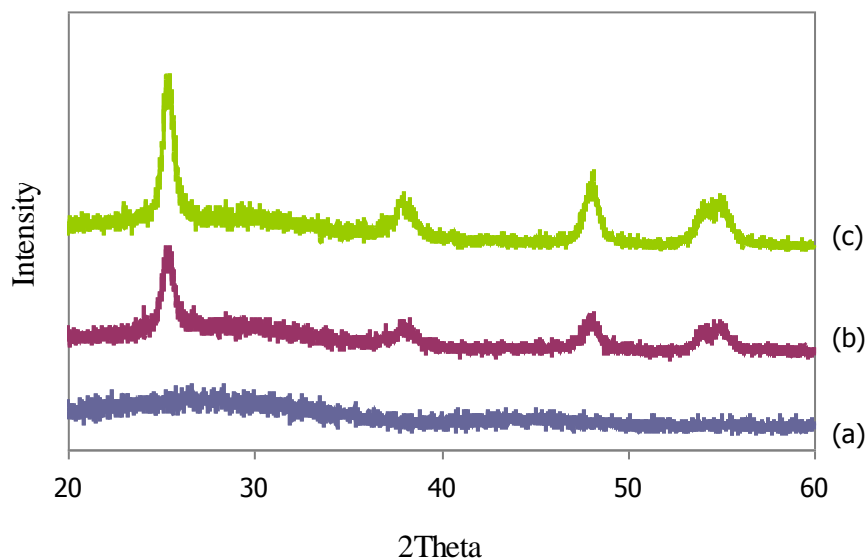
Photocatalytical degradation of methylene blue: Photoactivity of the catalyst ( $\text{TiO}_2/\text{C}$ ) was determined by methylene blue degradation under UV irradiation. The reaction was set up by adding 0.1g of catalyst into 50 ml of 20 ppm methylene blue solution at pH 2. The solution was stirred in the dark one hour after the addition of catalyst. After that the ultraviolet light was activated, 5ml of sample was collected every hour for 3 hours to determine the concentration of methylene blue by a UV-vis spectrophotometer at 664 nm. The methylene blue removal efficiency of the  $\text{TiO}_2/\text{C}$  was compared with  $\text{TiO}_2$  and charcoal from corncob. Methylene blue was also carried out in the reactor without catalyst to observe the photolysis effect of the methylene blue degradation.

## Results, Discussion and Conclusion



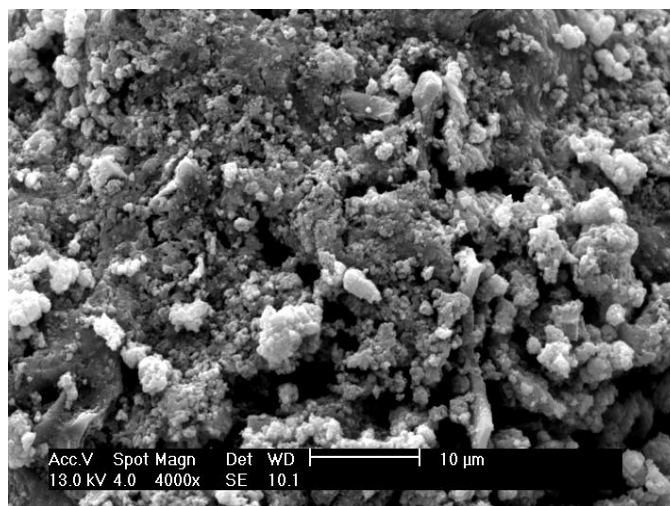
**Figure 1.** TGA diagram of  $\text{TiO}_2/\text{C}$

Figure 1 shows weight loss of  $\text{TiO}_2/\text{C}$ , which is divided into three ranges. The first drastic loss between 50-100°C is due to water evaporation. Next, the removal of organic solvent occurs between 100-250°C. After that, the weight of  $\text{TiO}_2/\text{C}$  is constant from 300 to 450°C and above 450°C the weight decreases slightly by the oxidation of charcoal.



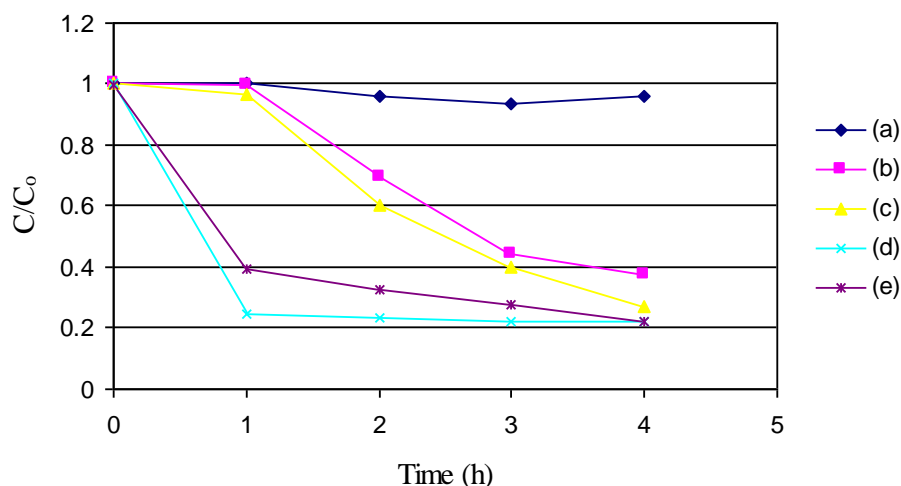
**Figure 2.** The X-ray Diffraction patterns of  $\text{TiO}_2/\text{C}$ :  
(a)  $\text{TiO}_2/\text{C}$  was calcined at  $300^\circ\text{C}$  (b)  $400^\circ\text{C}$  (c)  $500^\circ\text{C}$

Figure 2 shows the XRD pattern of  $\text{TiO}_2/\text{C}$ , which was calcined at temperature of 300, 400 and  $500^\circ\text{C}$  for one hour. The XRD pattern indicates that  $\text{TiO}_2$  in  $\text{TiO}_2/\text{C}$  exhibits anatase phase with elevating temperature up to 400 and  $500^\circ\text{C}$ . Due to the loss of the charcoal in  $\text{TiO}_2/\text{C}$  via oxidation reaction at temperature higher than  $450^\circ\text{C}$ ,  $\text{TiO}_2/\text{C}$  calcined at  $400^\circ\text{C}$  was, therefore, selected to use in the removal process of methylene blue in solution.



**Figure 3.** SEM micrograph of  $\text{TiO}_2/\text{C}$  calcined at  $400^\circ\text{C}$

SEM micrograph of  $\text{TiO}_2$  particles supported on charcoal from corncob is shown in Figure 3. The image suggests that the carbon and  $\text{TiO}_2$  are evenly distributed.



**Figure 4.** Methylene blue removal efficiency of TiO<sub>2</sub>/C at pH 2:  
(a) Photolysis, (b) TiO<sub>2</sub>-P25, (c) TiO<sub>2</sub>, (d) The charcoal, (e) TiO<sub>2</sub>/C

Percentage of Methylene blue removal by TiO<sub>2</sub>/C was compared with TiO<sub>2</sub>, TiO<sub>2</sub>-P25, the charcoal and photolysis of methylene blue are 77.88%, 72.81%, 62.63%, 78.13% and 4.12%, respectively. Which shown in Fig.4, Charcoal from corncob has the highest methylene blue removal efficiency. On the other hand, the removal of methylene blue by the charcoal due to the adsorption of methylene blue unlike TiO<sub>2</sub>/C, that has both adsorption and photoactivity.

In conclusion titanium dioxide supported on charcoal from corncob has been synthesized for removing methylene blue from aqueous solution. The catalyst is more efficiency than TiO<sub>2</sub> for the reason that it included photoactivity of TiO<sub>2</sub> and adsorption activity of charcoal from corncob. However, for the higher removal efficiency, the more suitable condition have to be investigate.

#### References:

1. T. Tsumura, N. Kojitani, I. Izumi, N. Iwashita, M. Toyoda, M. Inagaki, *J. Mater. Chem.*, 2002, **12**, 1391-1396.
2. Y. Li, X. Li, J. Li, J. Yin, *Water Research*, 2006, **40**, 1119-1126.
3. S. Mozia, M. Toyoda, M. Inagaki, B. Tryba, A.W. Morawski, *J. Haz. Mat.*, 2007, **140**, 369-375.

**Keywords:** TiO<sub>2</sub>, Charcoal, Corncob, Methylene blue

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