

## Deposition of TiO<sub>2</sub> on Macroporous Cordierite Substrate for Wastewater Treatment

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**ABSTRACT.** In this paper, the titanium dioxide (TiO<sub>2</sub>) which act as the photocatalyst was synthesized and deposited on macroporous cordierite (MC) (carrier substrate) by using sol-gel and dip-coating method. The TiO<sub>2</sub>/MC in this study were characterized by XRD, SEM, densitometer and UV-Vis spectrometer. The effect of calcination temperature at 700 °C, dipping cycles of TiO<sub>2</sub>/MC and UV light irradiation on photodegradation of organic pollutant (methyl orange (MO)) were studied. The results showed that TiO<sub>2</sub>/MC with 5 cycles of dipping parameter have the highest removal efficiency after 7 hours while without drop-off present in wastewater treatment process. Conversely, further increasing the dipping cycles at 7 reduced the photocatalytic activity. Under UV light irradiation, all samples have been photo-activated to decolorized MO except sample MC which do not have photocatalyst.

**Keywords:** Titanium dioxide, Photocatalyst, Sol-gel method, Dip-coating method, Cordierite;

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## 1. INTRODUCTION

Nowadays, the rate of environment pollutants is increasing sharply. Water pollution is one of the main concern of human health. Azo dyes, one type of the most concerned contaminants in refractory wastewater treatment due to carcinogenic and mutagenic properties. Moreover, the azo bonds (-N=N-) in the dye are difficult to be removed as they are adherent and long lasting. Heterogeneous photocatalysis, a classification from photocatalysis is belonged to advanced oxidation processes (AOPs) which works at near-ambient temperature and pressure. Powerful oxidizing radical species such as •OH were produced through AOPs for complete decomposition of organic contaminants into non-toxic products like H<sub>2</sub>O, CO<sub>2</sub> and inorganic salts [1,2]. Photocatalyst materials such as titanium dioxide (TiO<sub>2</sub>) can be a good candidate in photocatalytic activity due to its strong oxidizing power of its holes, high photostability and redox selectivity [3,4]. However, conventional TiO<sub>2</sub> powder gives disadvantages of agglomeration and difficulty to separate between final particles and fluid for the catalyst recycling [5]. In addition, the small size of titania particles would make photocatalytic slurry reactors impractical and caused the difficulty in separation stage such as filtration [6]. There are a few types of carriers or catalyst supports such as alumina (Al<sub>2</sub>O<sub>3</sub>) and zirconia (ZrO<sub>2</sub>) which used for water treatment process. Cordierite ceramics (2MgO·2Al<sub>2</sub>O<sub>3</sub>·5SiO<sub>2</sub>) have been found to be alternative catalyst support due to high mechanical strength, good thermal stability and low thermal expansion coefficient [7,8]. In addition, it has lower sintering temperature than Al<sub>2</sub>O<sub>3</sub> which give advantages of reducing processing time and cost. In order to accelerate the degradation reaction, porous ceramic cordierite is promoted due to its higher photocatalytic surface area. Furthermore, good performance in higher contact area with fluid required high fraction of open porosity. In this study, the deposition of high amount of photocatalyst TiO<sub>2</sub> on macroporous cordierite were prepared by sol-gel method and it was further deposited by dip-coating method.

## 2. MATERIALS AND METHODS

Titanium (IV) isopropoxide (purity: >98%) and MO were purchased from ACROS as a precursor in the synthesis of TiO<sub>2</sub> and dye in this study. Acetic acid (purity: 99.8%), absolute ethanol (purity: 95%) and deionized water were used to prepare the TiO<sub>2</sub> sol. Hydrochloric acid (Fisher Scientific) and deionized water

were used to pre-wash substrate. Macroporous cordierite (MC) (96.4 wt.%  $\alpha$ -cordierite) was used as a photocatalyst support in this study.

### 2.1 Synthesis of $TiO_2$ and Deposition Method

In this study,  $TiO_2$  sol was prepared by sol-gel method with volume ratio of  $Ti(OC_3H_7)_4:H_2O:C_2H_5OH:CH_3COOH$  is 1:2:1:0.53. The  $TiO_2$  sol was stirred vigorously at 80 °C for 30 min followed by aging process for 3 hours. Then, the MC samples were pre-washed with HCl and  $H_2O$  with ratio 1:25 and dried in hot oven at 70 °C for 10 min. Sample C0 was prepared in the absent of  $TiO_2$  while sample C1, C2, C3 and C4 of  $TiO_2$ /MC were prepared by the dip-coating method in different dipping cycles of 1, 3, 5 and 7 respectively. Each dipping cycle process was carried out by dipping cordierite in  $TiO_2$  sol for 3 min then dried in a hot oven at 70 °C for 10 min. After that, the  $TiO_2$ /MC samples were calcined at 700 °C for 4 hours.

### 2.2 Materials Characterization

The samples were analyzed with X-ray diffractometer (XRD) model D/max-III, Rigaku using  $Cu-K\alpha$  radiation in the range of  $2\theta = 5-80^\circ$  at a scan speed of  $2^\circ/\text{min}$  and step size of  $0.02^\circ$ . Rietveld refinement was performed by Xpert HighScore Plus software. The sample's morphologies were observed by scanning electron microscopy (SEM) from JEOL (Model: JSM 6460 LA). Auto fine coated from JEOL (Model: JFC 1600) was used to coat the surface of the samples with a thin platinum layer. The conductive layer formed coating process is required to improve the imaging of the samples and reduce thermal damage. Bulk density and total porosity of  $TiO_2$ /MC were measured by densitometer.

### 2.3 Experiments of Photocatalytic Degradation of MO Dye

In this study, 10 ppm of MO dye solution with pH 7.5 was used for photodegradation. Samples  $TiO_2$ /MC are prepared in dimension of 1.5 cm  $\times$  1.5 cm  $\times$  1.5 cm and 8 pieces in each dipping parameter. Set of different dipping parameter cordierites was immersed into a beaker which contains 200 ml of MO solution and placed under UV light. The 5 ml of dye solution was sampled every hour and analyzed by UV-Vis spectrometer (Perkin Elmer Lambda 35). The absorption and reduction in wavelength were evaluated according to the absorbance at a maximum wavelength of 465 nm. The removal efficiency was measured by Eq. 1.

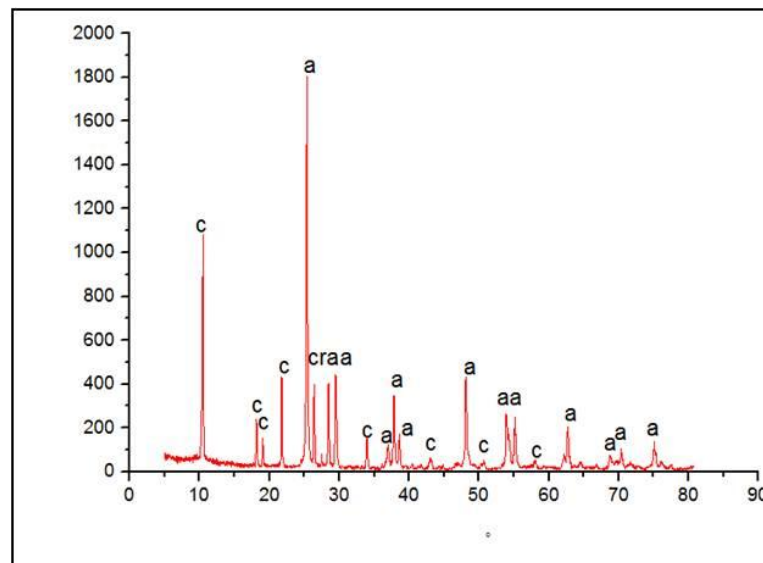
$$\text{Removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where  $C_t$  is the final concentration at reaction time (t) in hours and  $C_0$  is the initial concentration.

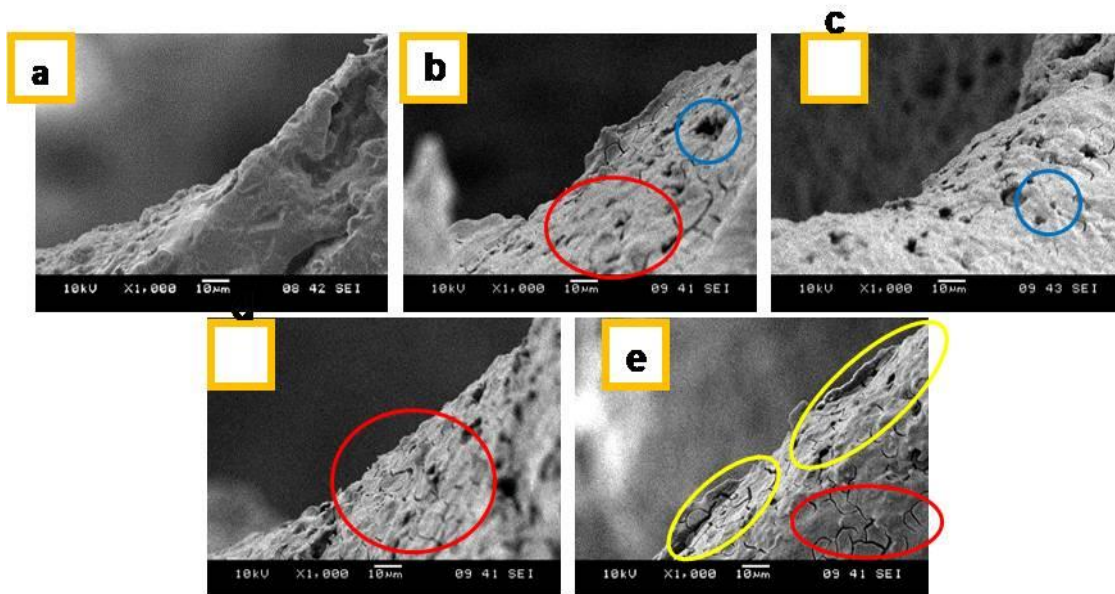
## 3. RESULTS AND DISCUSSION

Fig. 1 demonstrates the XRD pattern of  $TiO_2$ /MC. It has shown that the cordierite ceramic with the present of anatase and a small fraction of rutile phase which indicates  $TiO_2$  has been successfully coated on the MC. The highest intensity anatase was located at  $25.3368^\circ$  at (011) crystal plane with d-spacing of 3.5124. This indicates that  $TiO_2$ /MC have a high concentration of anatase phase or availability of active  $TiO_2$  compound [9,10].

For uncoated cordierite, C0 (Fig. 2(a)), it has large surface area but with an uneven and rough surface with a low percentage of shrinkage in the substrate. While after dipping process and heat treatment, the  $TiO_2$  was successfully deposited on the substrate as shown in Fig. 2(b-e). However, the  $TiO_2$  thin films have uneven rough surfaces and contain some cracks on the surface of the substrate (spotted by the red circle). According to Yao et al. [11], the crack happened due to the difference in heat dissipation between the cordierite substrate and the  $TiO_2$  coating. Moreover, the relieve stress after the calcination process was one of the reasons the coated foam were struck. In addition, there are some holes in the thin film for each substrate (labelled by the blue circle). This is due to the insufficient amount of  $TiO_2$  coated or the high viscosity of  $TiO_2$  sol during dip coating process. For Fig. 2(e), there are some excess  $TiO_2$  coated on the surface of the substrate (spotted by the yellow circle). The higher the dipping cycles resulted in severe agglomeration of particles, thus higher the content of  $TiO_2$  coated on the substrate [9]. However, too many dipping cycles such as sample T4 have caused the excess  $TiO_2$  to attach weakly at the surface. Furthermore, the bulk density of sample C4 is lower than samples C2 and C3 by bulk density of  $0.0191 \text{ g/cm}^3$  and  $0.0371 \text{ g/cm}^3$  as shown in Fig. 3.

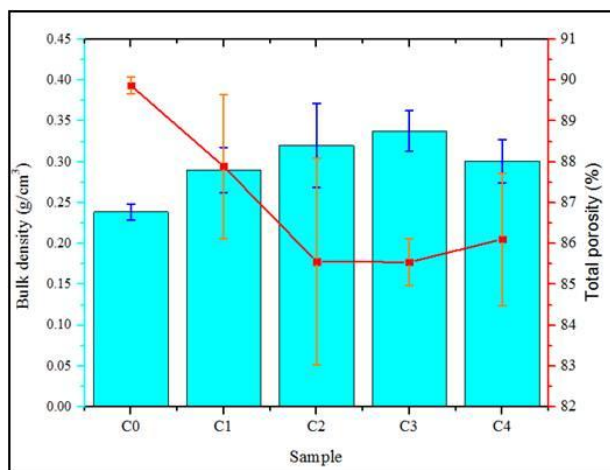


**Fig. 1** XRD diffraction pattern for TiO<sub>2</sub>/MC (c-cordierite; a-anatase; r-rutile)



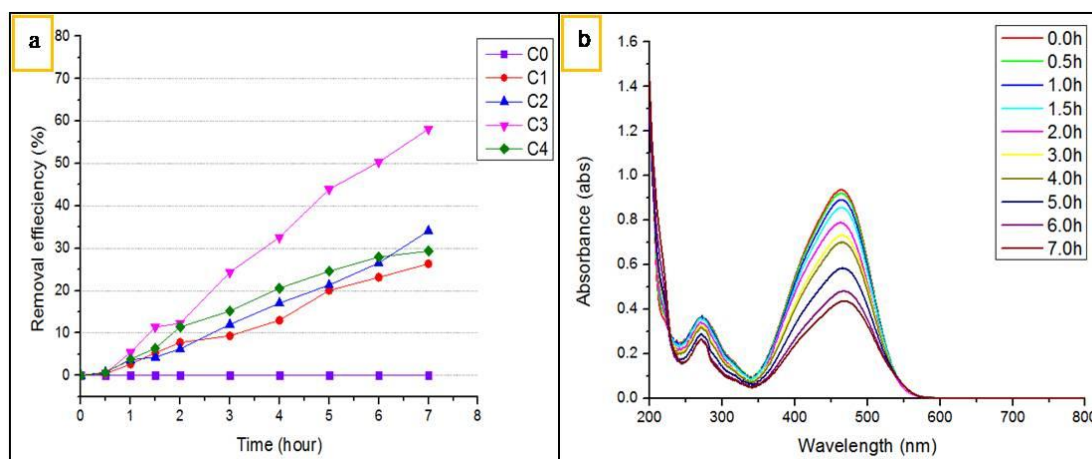
**Fig. 2** SEM morphology of TiO<sub>2</sub> deposited macroporous cordierite with different dipping cycles (a) before dip-coating, C0, (b) C1, (c) C2, (d) C3, and (e) C4 under magnification of 1000xAs shown in Fig. 3, the bulk density increased as the dipping cycles increased from 1 to 5 as more amount of TiO<sub>2</sub> coated on the cordierite. However, there was a change in the trend of the bulk density and total porosity with the increases of dipping cycle. Sample C4 with 7 dipping cycles gave the lowest bulk density of 0.3009 g/cm<sup>3</sup> and highest porosity of 86.1% as compared with C2 and C3 samples. Lowest bulk density related to the edges which made by the excess TiO<sub>2</sub> coated on cordierite not finely interlocked or mechanically bonded with cordierite. Hence, result in dropped off material and lower the bulk density of sample C4. Archimedes principle indicates that sample C3 are the best product which finely coated with a high content of TiO<sub>2</sub> in this study due to the highest bulk

density as compared to the others, no dropped off while the total porosity was in optimum pore size value of macroporous cordierite which was larger than 50 nm.



**Fig. 3** Graph of bulk density and total porosity of deposited cordierite under different dipping cycles

Fig. 4(a) showed the relationship of dipping parameters effect on removal efficiency of MO. The trend of the photodegradation of all samples was increased over irradiation time. This may due to the  $\bullet\text{OH}$  and  $\text{O}_2\bullet$  as mentioned by Ho et al. [12]. There is no photocatalytic reaction acted on sample C0 with absent of photocatalyst. Sample C3 with a value of 58.1% are higher than others. This trend was similar with the bulk density as discussed in section 3.3. The orange color of MO had been gradually changed into colorless as denotes the destruction of chromophoric group (-N=N-) and photodecomposition of organic dye. According to Guttei and Amar [13], the removing efficiency of the process strongly depended on the catalyst amount. As the amount of photocatalyst increased, the availability of the active sites such as  $\bullet\text{OH}$  radicals increased which able to remove organic compound in the MO dye and rapid attack pollutants [14,15]. From Fig. 4.4(b), there was two significant peaks located at 270 nm in UV region and 464 nm in the visible region. It can be noted that the absorption of visible bands was decreased over irradiation time. The rapid decrease in the spectrum at 464 nm indicates the decoloration of MO solution. This indicates the cleavage of azo bond (-N=N-) in this water treatment application testing [16]. In this study, the azo bond has been attacked by most of the photocatalyst active site. Although the total removal efficiency was not achieved in 100%, it was believed that the photodegradation could continuous happen even after 7 hours.



**Fig. 4.** (a) Removal efficiency of different dipping parameter over period of photodegradation activity under UV light radiation and (b) UV-Vis spectrum for photodegradation of 10 ppm MO solution by C3 upon different irradiation time



#### 4. SUMMARY

In summary, TiO<sub>2</sub>/MC with optimum dipping cycles of 5 which is C3 has the best photocatalytic performance as compared to the others. This is due to the highest photocatalyst amount whereas the higher the amount of photocatalyst, the higher the number of active sites available in the photodegradation process. Further dipping cycles which more than 5 times would result in the poor coating and TiO<sub>2</sub> dropped-off from MC. Dropped-off of photocatalyst does not achieve the objective of using photocatalyst support as the drop-offs must be filtered in a secondary process after treatment. The photodegradation was increased over UV irradiated time as increased formation of •OH and O<sub>2</sub>•-. In this study, the trend of the removal continuous increasing as a function of time and doesn't decrease in its rate of removal MO. Thus, the photodegradation process would be carry on even after 7 hours and need longer irradiation time to reach its limit.

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