

## PHOTODEGRADATION OF REACTIVE GOLDEN YELLOW R DYE CATALYZED BY EFFECTIVE TITANIA (TiO<sub>2</sub>)

(Fotodegradasi **Pewarna Golden Yellow R Reaktif** Dimangkinakan oleh Titania (TiO<sub>2</sub>) yang Efektif )

Edmand Andrew Bedurus<sup>1\*</sup>, Marinah Mohd Ariffin<sup>1</sup>, Mohd Hasmizam Razali<sup>2</sup>

<sup>1</sup>*School of Marine and Environmental Sciences,*

<sup>2</sup>*School of Fundamental Sciences,*

*Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu*

\*Corresponding author: edmand\_andrew@yahoo.com

Received: 8 February 2015; Accepted: 11 June 2015

### Abstract

In the present research, Microwave Assisted Synthesis (MAS) method was applied to synthesize titania (TiO<sub>2</sub>) at 150 °C in a range of 2-6 hours heating time. Each prepared TiO<sub>2</sub> were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and nitrogen gas (N<sub>2</sub>) sorption analysis (Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) calculation) techniques. The TiO<sub>2</sub> prepared by MAS 150 °C (4 hours) has emerged with the highest photocatalytic activity. Within 4 hours, the TiO<sub>2</sub> managed to catalyze the degradation of Reactive Golden Yellow R dye up to 98.51 %. This is because of the TiO<sub>2</sub> possessed high crystallinity of anatase phase, small crystallite size and high pore volume compared to other prepared TiO<sub>2</sub>.

**Keywords:** Titania (TiO<sub>2</sub>), Microwave Assisted Synthesis (MAS), Reactive Golden Yellow R dye, photodegradation

### Abstrak

Dalam kajian ini, kaedah Sintesis Bantuan Gelombang Mikro (MAS) telah digunakan untuk mensintesis titania (TiO<sub>2</sub>) pada suhu 150 °C dalam tempoh masa pemanasan 2 ke 6 jam. Setiap TiO<sub>2</sub> yang disintesis telah dicirikan menggunakan teknik Mikroskopi Imbasan Elektron (SEM), Pembelauan Sinar-X (XRD), dan analisis serapan gas nitrogen (pengiraan menggunakan formula Brunaeur-Emmett-Teller (BET) dan Barrett-Joyner-Halenda (BJH)). TiO<sub>2</sub> yang disintesis dengan kaedah MAS pada suhu 150 °C (4 jam) mempunyai aktiviti fotokatalitik yang tertinggi. Dalam masa 4 jam, TiO<sub>2</sub> tersebut telah berjaya memangkinakan degradasi pewarna Reactive Golden Yellow R sebanyak 98.51 %. Hal ini adalah disebabkan oleh TiO<sub>2</sub> tersebut mempunyai fasa hablur anatase yang tinggi, saiz hablur yang kecil dan isipadu liang yang tinggi berbanding dengan TiO<sub>2</sub> yang lain.

**Kata kunci:** Titania (TiO<sub>2</sub>), Sintesis Bantuan Gelombang Mikro (MAS), Pewarna *Reactive Golden Yellow R*, Fotodegradasi

### Introduction

Recently, heterogeneous photocatalysis has attracted many researchers, whereby this technique was discovered and proved to eliminate pollutants, especially organic compounds, in water and air by using solar or artificial light radiation [1-4]. Titania (TiO<sub>2</sub>), one of the heterogeneous photocatalyst has shown its tremendous ability to decompose organic compound such as pesticides [5-7] and dyes [8-13]. Focus has been given to TiO<sub>2</sub> as it is non-toxic, available at low cost, high chemical resistant, low energy consumption and low operation temperature. The basic principle of photoreaction of organic pollutants with light illumination catalyzed by TiO<sub>2</sub> can be described as follows: upon illumination of TiO<sub>2</sub> with the light in which contained energy higher than the TiO<sub>2</sub> band gap (3.2 eV for anatase), the electrons in valence bands become excited and jump to the conduction bands, creating electron-

hole pairs within the TiO<sub>2</sub>. The holes will absorb water to create hydroxyl radicals ( $\bullet$ OH). The hydroxyl radicals are very reactive and quickly oxidize the organic pollutants into carbon dioxide, water and some mineral acids [14].

In this study, the TiO<sub>2</sub> powder was prepared and the photocatalytic activity was investigated upon degradation of Reactive Golden Yellow R dye aqueous solution. Reactive Golden Yellow R dye is classified as monoazo dye. The greater demand for brilliant hues has increased the demand for reactive dyes worldwide. This dye appears in the washwater in its hydrolyzed or unfixed form at levels that depend upon the degree of fixation on the fabric and the type of dyeing process applied, and end up in the dyehouse effluent. However, there is lack of information and research regarding this dye. Normally, the azo reactive dye is resistant to conventional biological treatment [15]. Therefore, it was considered worthwhile to make systematic progress to remove Reactive Golden Yellow R from the textile wastewater prior discharge.

The TiO<sub>2</sub> was prepared by Microwave Assisted Synthesis (MAS) technique since not much knowledge was expanded regarding this technique. Generally, this technique is quite fast, simple, and very energy efficient [16-18].

### Materials and Methods

#### Synthesis of Effective TiO<sub>2</sub> Photocatalyst

The TiO<sub>2</sub> photocatalyst were synthesized via MAS method. 1.0 g of commercial TiO<sub>2</sub> powder (SIGMA) was suspended in 50 ml of 10 M sodium hydroxide (NaOH) aqueous solution in a Teflon vessel. This suspension was ultrasonicated for 30 min at 40 °C. Then, the mixture was reacted in a microwave reactor (Milestone Microwave Laboratory Systems) at constant temperature (150 °C) with various heating time ranged from 2 hours to 6 hours. After that, each sample was washed with 0.1 M acid hydrochloric (HCl) solution for an hour, followed by distilled water until pH value became nearly 7. Then, the washed TiO<sub>2</sub> was filtered and dried at 60 °C overnight. Each dried TiO<sub>2</sub> was calcined in furnace at 450 °C for an hour in order to remove impurities as well as to crystallize the TiO<sub>2</sub>.

#### Characterization of the Synthesized TiO<sub>2</sub>

Morphology and elemental composition of commercial and synthesized TiO<sub>2</sub> powder were examined using scanning electron microscope (SEM, JEOL JSM-6360 LA). An X-ray diffractometer (XRD, Rigaku Miniflex II) with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) was applied to characterize the crystalline phase of the samples. The samples were spread on a glass slide specimen holder and the scattered intensity was measured between 20° and 80° at a scanning rate of 2 $\theta$  = 5 °/min. Specific surface area for each prepared TiO<sub>2</sub> photocatalyst was measured based on Brunauer-Emmett-Teller (BET) multilayer nitrogen gas sorption method (Quantachrome autosorb 1C – Volumetric Technique) at 77.3 K. The pore size and pore volume were estimated using Barrett-Joyner-Halenda (BJH) model. The samples were degassed at 100 °C before sorption experiment.

#### Photodegradation of Reactive Golden Yellow R Dye

In this study, each prepared TiO<sub>2</sub> was tested to catalyze the degradation of Reactive Golden Yellow R dye within 4 hours. The photodegradation was carried out inside a homemade photoreactor. Mixture of 100 ml of 10 mg/L dye solution and 0.1 g of synthesized TiO<sub>2</sub> powder was stirred for 10 min in the dark condition so that an adsorption-desorption equilibrium could be established between dye and catalyst surface [16; 19]. Then, the mixture solution was irradiated with UV light (302 nm, 15 watt). During the illumination, 5 ml sample solution was withdrawn from the suspension at fixed intervals (30 min) and filtered to separate the catalyst particles. Each collected sample solution was analyzed via UV-Vis spectrophotometer (UV-1601PC, Shimadzu). The same photocatalytic procedure was applied on commercial TiO<sub>2</sub> powder (SIGMA) for comparison.

### Results and Discussion

#### Scanning Electron Microscopy (SEM)

The SEM technique was carried out in order to investigate the surface morphology of the prepared TiO<sub>2</sub> photocatalysts. Figure 1 showed the aggregated of nearly-spherical shape with reasonably uniform size, distributed homogeneously throughout the surface of commercial TiO<sub>2</sub> (SIGMA). The precursor powder, thus, consists of typical particulate morphology.

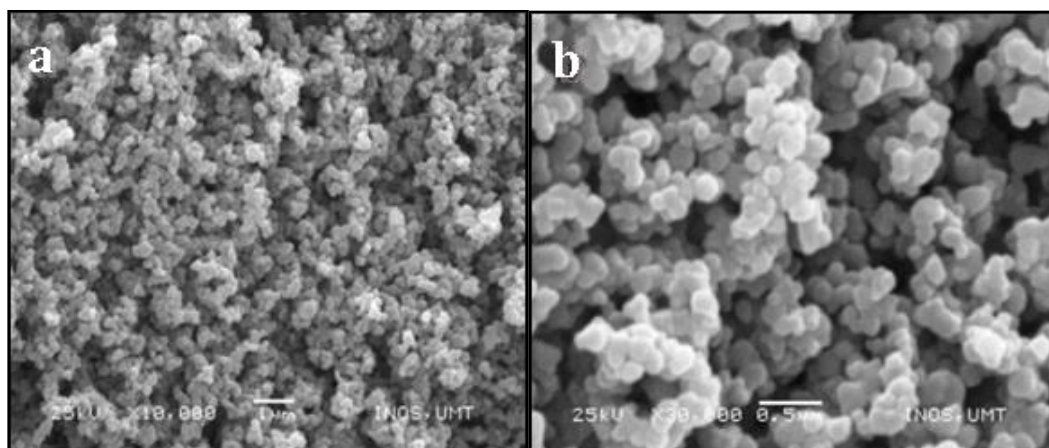
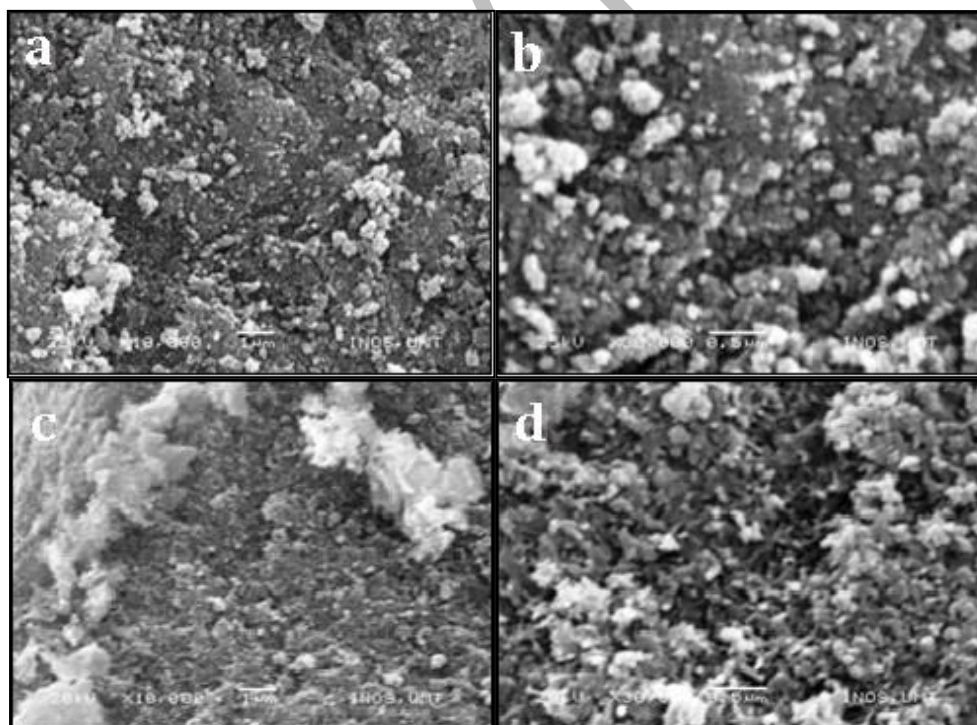


Figure 1. Scanning electron micrographs of commercial  $\text{TiO}_2$  (SIGMA) with 2 magnification a) X10000 and b) X30000

Figure 2 depicted the micrographs of surface morphology of  $\text{TiO}_2$  prepared by MAS 150 °C with various heating time. After treated with MAS 150 °C for 2 hours, the  $\text{TiO}_2$  was agglomerated and formed several large bulky structures. Small packed agglomerates with various shapes and sizes were distributed non-homogeneously on the large bulky surface. When the MAS heating time was prolong to 4 hours, many elongated structure were formed on the large bulky surface. However, the small packed agglomerates were still existed. As the heating time was kept prolong to 6 hours, the elongated structure continue to grow and distributed thoroughly on the bulky surface.



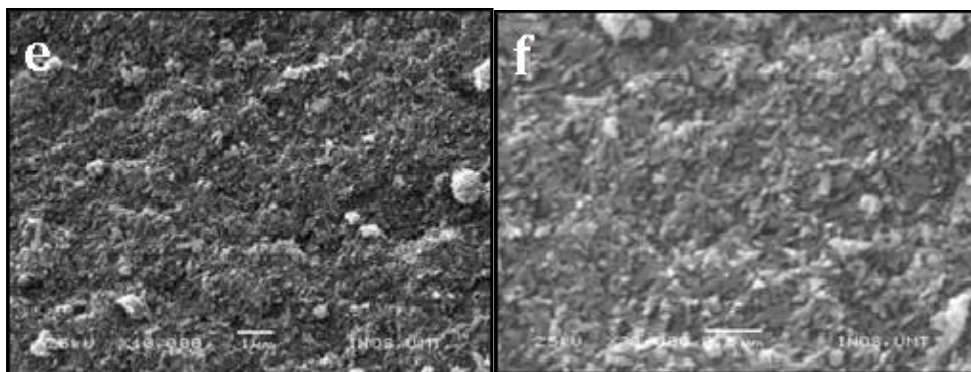


Figure 2. Scanning electron micrographs of TiO<sub>2</sub> prepared by MAS treatment at 150 °C for 2 hours (a and b), 4 hours (c and d), and 6 hours (e and f) with 2 magnifications (X10000 and X30000).

### X-ray Diffraction XRD

XRD was applied to determine crystalline phase composition and to estimate crystallite size of the prepared TiO<sub>2</sub> photocatalyst. Figure 3 depicted the XRD diffractograms of MAS 150 °C with various MAS heating time. From the result, all peaks have been assigned to anatase crystalline phase (PDF Card No.: 00-021-1272) when MAS heating time was less than 5 hours. However, the TiO<sub>2</sub> with 4 hours treatment showed smoother peaks. This showed that the TiO<sub>2</sub> possessed high crystallinity. Upon prolong the MAS heating time to 6 hours, the XRD pattern of the prepared TiO<sub>2</sub> comprises two type of peaks which were assigned to sodium titanium oxide (N<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>) and anatase crystalline phase. The existence of N<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> in the lattice structure deteriorated the crystalline structure of the MAS 6 hours prepared TiO<sub>2</sub>. Meanwhile, the crystalline sizes were obtained using Scherrer's equation in Equation 1 [19]:

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where d was the average crystallite size (nm),  $\lambda$  was the wavelength of Cu K $\alpha$  radiation applied ( $\lambda = 0.154$ ),  $\theta$  the was the Bragg's angle of diffraction,  $\beta$  was the full-width at half maximum intensity (FWHM) of observation at 101 hkl diffraction (converted to radian) and K was the constant (usually applied as ~0.94). The crystallite size was decreased as the MAS heating time was prolong from 2 hours to 6 hours. Table 1 summarized the crystalline phase and crystallite size of all prepared TiO<sub>2</sub>.

Table 1. Anatase crystallite size for TiO<sub>2</sub> prepared via MAS 150 °C at various heating time

| Type of Photocatalyst               | Crystallite size (nm) | Peak assignment                                                                                         |
|-------------------------------------|-----------------------|---------------------------------------------------------------------------------------------------------|
| Commercial TiO <sub>2</sub> (SIGMA) | 43.76                 | Anatase (TiO <sub>2</sub> )                                                                             |
| MAS 150 °C 2 hours                  | 29.90                 | Anatase (TiO <sub>2</sub> )                                                                             |
| MAS 150 °C 4 hours                  | 13.62                 | Anatase (TiO <sub>2</sub> )                                                                             |
| MAS 150 °C 6 hours                  | 8.94                  | Anatase (TiO <sub>2</sub> ) and sodium titanium oxide (N <sub>2</sub> Ti <sub>6</sub> O <sub>13</sub> ) |

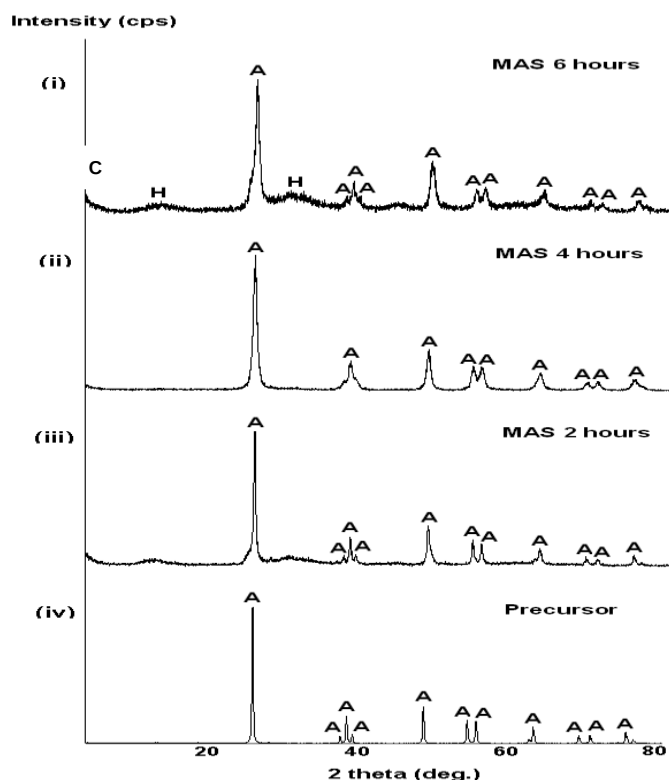


Figure 3. X-ray diffractogram (XRD) patterns of prepared  $\text{TiO}_2$  by MAS treatment at  $150\text{ }^\circ\text{C}$  for (i) 6 hours, (ii) 4 hours, (iii) 2 hours and subsequently calcined at  $450\text{ }^\circ\text{C}$  for 1 hour, respectively. XRD pattern for (iv) commercial  $\text{TiO}_2$  (SIGMA) was included for comparison. (A: Anatase ( $\text{TiO}_2$ ); C:  $\text{Na}_2\text{Ti}_6\text{O}_{13}$ )

#### Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) multilayer nitrogen gas sorption

Textural characteristics of the samples derived from  $\text{N}_2$  sorption analysis were presented in Table 2. The BET total surface area ( $A_{\text{BET}}$ ) and BJH pore diameter ( $d$ ) of MAS 4 hours was almost identical with the MAS 2 hours prepared  $\text{TiO}_2$ . However, the  $A_{\text{BET}}$  of the  $\text{TiO}_2$  increased to  $139.07\text{ m}^2/\text{g}$  after treated with MAS 6 hours. Regardless of  $A_{\text{BET}}$  increment, the pore size of MAS 6 hours  $\text{TiO}_2$  was almost identical with the MAS 2 hours and MAS 4 hours treated  $\text{TiO}_2$ , which was  $24.77\text{ nm}$ . The commercial  $\text{TiO}_2$  (SIGMA) has a specific surface area of  $39.36\text{ m}^2/\text{g}$ . However this data was invalid since its BET constant ( $C$ ) was in negative value. Incorrect incorporation of points during BET plot due to weak energy adsorption of this  $\text{TiO}_2$ , has contribute to the negative value of  $C$  [20]. Meanwhile, the pore volume of the prepared  $\text{TiO}_2$  has increased from  $0.6670\text{ cm}^3/\text{g}$  to  $0.8254\text{ cm}^3/\text{g}$  when the treatment time was prolong from 2 hours to 4 hours. However, the pore volume was slightly reduced to  $0.7935\text{ cm}^3/\text{g}$  after underwent MAS 6 hours treatment.

Figure 4 showed the representative  $\text{N}_2$  adsorption-desorption isotherms of the MAS  $150\text{ }^\circ\text{C}$  prepared  $\text{TiO}_2$  with various heating time. All the  $\text{TiO}_2$  showed the similar type IV isotherms, which represented the mesoporous (pores  $2\text{--}50\text{ nm}$  in diameter) materials according to the IUPAC classification [20]. Additionally, the loop observed was ascribed to type H3 loop, indicating the presence of mesopores with non-uniform or disordered slit-shaped pores [20]. At the same time, the hysteresis loop approaches  $P/P_0 = 1$ , indicating the presence of macropores (pores  $> 50\text{ nm}$  in diameter) in the photocatalyst [20]. Overall, the adsorption capacities of all MAS  $150\text{ }^\circ\text{C}$  prepared  $\text{TiO}_2$  were much higher than that of  $\text{TiO}_2$  commercial (SIGMA). The results were summarized in Table 3.

Table 2. Nitrogen sorption analysis for TiO<sub>2</sub> prepared by MAS 150 °C

| Type of photocatalyst               | A <sub>BET</sub><br>(m <sup>2</sup> /g) | C        | V <sub>p</sub><br>(cm <sup>3</sup> /g) | d<br>(nm) |
|-------------------------------------|-----------------------------------------|----------|----------------------------------------|-----------|
| MAS 150 °C 2 hours                  | 101.99                                  | 96.19    | 0.6670                                 | 24.53     |
| MAS 150 °C 4 hours                  | 101.98                                  | 137.10   | 0.8254                                 | 24.29     |
| MAS 150 °C 6 hours                  | 139.07                                  | 86.38    | 0.7935                                 | 24.77     |
| Commercial TiO <sub>2</sub> (SIGMA) | 39.36                                   | -3002.00 | 0.1480                                 | 22.43     |

A<sub>BET</sub> = BET total surface area, C = BET constant, V<sub>p</sub> = BJH pore volume, d = BJH pore diameter

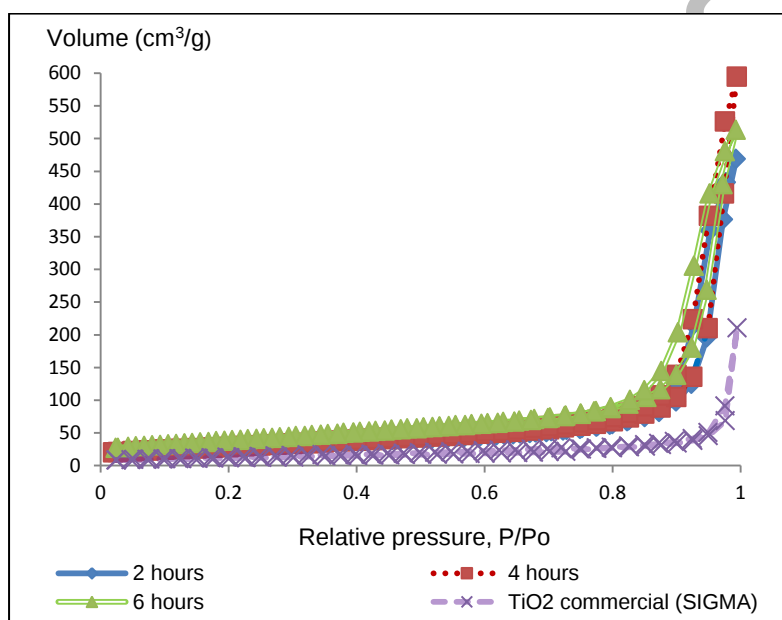


Figure 4. Nitrogen (N<sub>2</sub>) adsorption-desorption isotherms plot of MAS 150 °C prepared TiO<sub>2</sub> with various heating time. TiO<sub>2</sub> commercial (SIGMA) was plotted for comparison.

Table 3. Types of isotherms and porosity for TiO<sub>2</sub> prepared by MAS 150 °C

| Type of photocatalyst               | Type of Isotherms | Type of Hysteresis | Type of Pores          | Shape of Pores                |
|-------------------------------------|-------------------|--------------------|------------------------|-------------------------------|
| MAS 150 °C, 2 hours                 | IV                | H3                 | Mesopore and Macropore | Disordered slit- shaped pores |
| MAS 150 °C, 4 hours                 | IV                | H3                 | Mesopore and Macropore | Disordered slit- shaped pores |
| MAS 150 °C, 6 hours                 | IV                | H3                 | Mesopore and Macropore | Disordered slit- shaped pores |
| Commercial TiO <sub>2</sub> (SIGMA) | IV                | H3                 | Mesopore and Macropore | Disordered slit- shaped pores |

### Photodegradation of Reactive Golden Yellow R dye

The MAS 4 hours prepared  $\text{TiO}_2$  contributed to the highest catalytic degradation which was up to 98.51 % after 240 minutes irradiation. The degradation declined significantly to 53.83 % for MAS 6 hours treated  $\text{TiO}_2$ . Meanwhile, the MAS 2 hours prepared  $\text{TiO}_2$  was insufficient to increase the photocatalytic activity when the percentage of dye degradation collapsed to 39.34 % after 240 minutes of UV light irradiation. Commercial  $\text{TiO}_2$  (SIGMA) showed competitive performance with 91.75 % of dye degradation. The results of catalytic performances of  $\text{TiO}_2$  prepared by MAS 150 °C with various heating time were depicted in Figure 5.

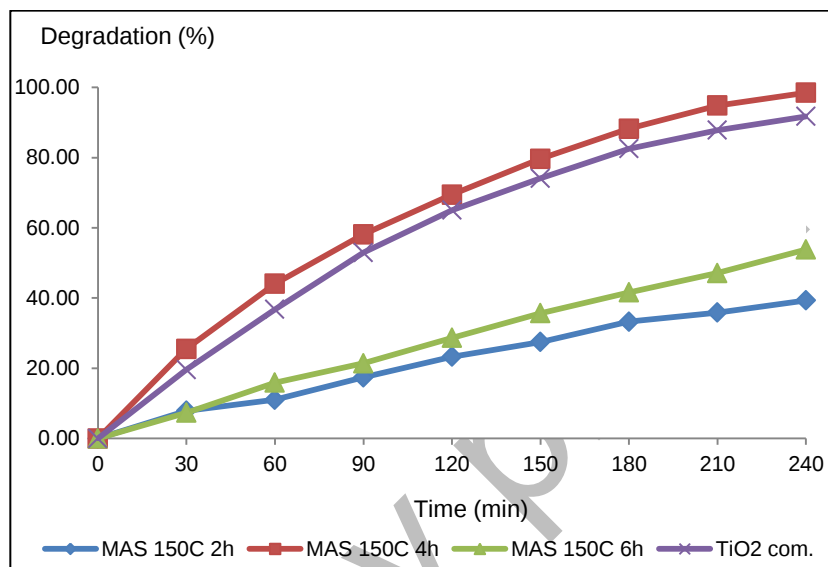


Figure 5. The plot of percentage degradation of 100 ppm Reactive Golden Yellow R dye against time of UV light irradiation in the presence of MAS 150 °C prepared  $\text{TiO}_2$  with various heating time. Performance of commercial  $\text{TiO}_2$  (SIGMA) was tested for comparison.

From the results, the highest photocatalytic activity of MAS 4 hours prepared  $\text{TiO}_2$  was due to small anatase crystallite size (13.62 nm), higher crystalline degree of anatase phase, and higher pore volume (0.8254  $\text{cm}^3/\text{g}$ ) [19]. The MAS 6 hours prepared  $\text{TiO}_2$  possessed the smallest anatase crystallite size (8.94 nm) and larger surface area (139.07  $\text{m}^2/\text{g}$ ), however, its photocatalytic activity was not effectively performed. Indeed, the existence of impurity (sodium titanium oxide) (from XRD result) in the prepared  $\text{TiO}_2$  has deteriorated its crystalline structure which led to the decreasing of its photocatalytic activity [16]. The performance of MAS 2 hours prepared  $\text{TiO}_2$  was even less effective because of its larger anatase crystallite size (from XRD result), and lower pore volume (from BJH result). As comparison, the photocatalytic activity of the commercial  $\text{TiO}_2$  (SIGMA) was lower due to its larger anatase crystallite size.

Table 4. Percentage of degradation of Reactive Golden Yellow R dye catalyzed by MAS 150 °C prepared TiO<sub>2</sub> with various heating time.

| Type of photocatalyst               | Percentage (%) of degradation of Reactive Golden Yellow R dye |
|-------------------------------------|---------------------------------------------------------------|
| MAS 150°C (2 hours)                 | 39.34                                                         |
| MAS 150°C (4 hours)                 | 98.51                                                         |
| MAS 150°C (6 hours)                 | 53.83                                                         |
| Commercial TiO <sub>2</sub> (SIGMA) | 91.75                                                         |

### Conclusion

The Microwave Assisted Synthesis (MAS) technique had produced a potential TiO<sub>2</sub> photocatalyst. The TiO<sub>2</sub> prepared by MAS 150 °C with 4 hours treatment showed promising performance with almost complete degradation of Reactive Golden Yellow R dye within 4 hours. The high performance of the TiO<sub>2</sub> was due to small crystallite size, high crystallinity of anatase phase, and high pore volume. The performance was higher than the commercial TiO<sub>2</sub> (SIGMA).

### Acknowledgement

This research was supported by Fundamental Research Grant Scheme (FRGS), vote 59121 and vote 59154, and Science Fund, vote 52027 funded by Ministry of Higher Education (MOHE) and Ministry of Science, Technology and Innovation (MOSTI) of Malaysia Government respectively.

### References

1. Boulamanti, A. K. & Philippopoulos, C. J. 2008. Photocatalytic degradation of methyl tert-butyl ether in the gas-phase: A kinetic study. *Journal of Hazardous Materials* 160: 83-87.
2. Sharma, S. D., Saini, K. K., Kant, C., Sharma, C. P. & Jain, S. C. 2008. Photodegradation of dye pollutant under UV light by nano-catalyst doped titania thin films. *Applied Catalysis B: Environmental* 84: 233-240.
3. Kim, S. & Ehrman, S. H. 2009. Photocatalytic activity of a surface-modified anatase and rutile titania nanoparticle mixture. *Journal of Colloid and Interface Science* 338(1): 304-307.
4. Hao, H. & Zhang, J. 2009. Low temperature synthesis of crystalline mesoporous titania with high photocatalytic activity by post-treatment in nitric acid ethanol solution. *Material Letters* 63: 106-108.
5. Moctezuma, E., Leyva, E., Monreal, E., Villegas, N. & Infante, D. 1999. Photocatalytic degradation of the herbicide "Paraquat". *Chemosphere* 39 (3): 511-517.
6. Jang, S.-J., Kim, M.-S. & Kim, B.-W. 2005. Photodegradation of DDT with the photodeposited ferric ion on the TiO<sub>2</sub> film. *Water Research* 39: 2178-2188.
7. Parra, S., Stanca, S. E., Guasaquillo, I. & Thampi, K. R. 2004. Photocatalytic degradation of atrazine using suspended and supported TiO<sub>2</sub>. *Applied Catalysis B: Environmental* 51: 107-116.
8. Chen, C. C., Lu, C. S., Chung, Y. C. & Jan, J. L. 2007. UV light induced photodegradation of malachite green on TiO<sub>2</sub> nanoparticles. *Journal of Hazardous Materials* 141: 520-528.
9. Wu, J.-M. & Zhang, T.-W. 2004. Photodegradation of rhodamine B in water assisted by titania films prepared through a novel procedure. *Journal of Photochemistry and Photobiology A: Chemistry* 162: 171-177.
10. Wilhelm, P. & Stephan, D. 2006. Photodegradation of Rhodamine B in aqueous solution via SiO<sub>2</sub>@TiO<sub>2</sub> nanospheres. *Journal of Photochemistry and Photobiology A: Chemistry* 185(1): 19-25.
11. Zhang, G., Wu, J., Liu, S. & Yan, M. 2008. Fabrication of titania thin film with composite nanostructure and its ability to photodegrade Rhodamine B in water. *Frontier Chemical Engineering China*. 2 (1): 44-48.
12. Oh, H.-J., Lee, J.-H., Kim, Y.-J., Suh, S.-J., Lee, J.-H. & Chi, C.-S. 2008. Synthesis of effective titania nanotubes for wastewater purification. *Applied Catalysis B: Environmental*. 84: 142-147.
13. Yi, X., Liqin, D., Lizhen, A., Shiyang, B. & Zhibin, L. 2008. Photocatalytic degradation of Rhodamine B and phenol by TiO<sub>2</sub> loaded on mesoporous graphitic carbon. *Chinese Journal of Catalysis*. 29 (1): 31-36.

14. Tsui, K. C. K., 2007. Dye coated titania photocatalysts operating in the visible. MSc. thesis. The University of Calgary.
15. Zhang, F., Yediler, A., Liang, X. & Kettrup, A. 2004. Effects of dye additives on the ozonation process and oxidation by-products: a comparative study using hydrolyzed C.I. Reactive Red 120. *Dyes and Pigments* 60: 1-7.
16. Ribbens, S., Meynen, V., Tendeloo, G. V., Ke, X., Mertens, M., Maes, B. U. W., Cool, P. & Vansant, E. F. 2008. Development of photocatalytic efficient Ti-based nanotubes and nanoribbons by conventional and microwave assisted synthesis strategies. *Microporous and Mesoporous Materials*. 114: 401-409.
17. Rao, C. N. R., Müller, A. & Cheetam, A. K. 2004. Microwave heating. In *The Chemistry of Nanomaterials: Synthesis, Properties and Applications*, Vol. 1, pp 152-155. Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA.
18. Wu, X., Jiang, Q.-Z., Ma, Z.-F., Fu, M. & Shangguan W.-F. 2005. Synthesis of titania nanotubes by microwave irradiation. *Solid State Communications*. 136: 513-517.
19. Asiltürk, M., Sayılkan, F., Erdemoğlu, S., Akarsu, M., Sayılkan, H., Erdemoğlu, M. & Arpaç, E. 2006. Characterization of the hydrothermally synthesized nano-TiO<sub>2</sub> crystallite and the photocatalytic degradation of Rhodamine B. *Journal of Hazardous Materials*. B129: 164-170.
20. Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquérol, J. and Siemieniewska, T. (1985). Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pure and Applied Chemistry* 57: 603-619.