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PHOTODEGRADATION OF REACTIVE GOLDEN YELLOW R DYE CATALYZED BY EFFECTIVE TITANIA (TiO_2)

(Fotodegradasi Pewarna Reactive Golden Yellow R Dimangkinkan oleh Titania (TiO_2) yang Efektif)

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Abstract

In the present research, Microwave Assisted Synthesis (MAS) method was applied to synthesize titania (TiO_2) at 150 ^oC in a range of 2-6 hours heating time. Each prepared TiO_2 were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and nitrogen gas (N_2) sorption analysis (Brunaeur-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) calculation) techniques. The TiO_2 prepared by MAS 150 ^oC (4 hours) has emerged with the highest photocatalytic activity. Within 4 hours, the TiO_2 managed to catalyze the degradation of Reactive Golden Yellow R dye up to 98.51 %. This is because of the TiO_2 possessed high crystallinity of anatase phase, small crystallite size and high pore volume compared to other prepared TiO_2.

Keywords: Titania (TiO_2), 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_2) pada suhu 150 ^oC dalam tempoh masa pemanasan 2 ke 6 jam. Setiap TiO_2 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_2 yang disintesis dengan kaedah MAS pada suhu 150 ^oC (4 jam) mempunyai aktiviti fotokatalitik yang tertinggi. Dalam masa 4 jam, TiO_2 tersebut telah berjaya memangkinkan degradasi pewarna Reactive Golden Yellow R sebanyak 98.51 %. Hal ini adalah disebabkan oleh TiO_2 tersebut mempunyai fasa hablur anatase yang tinggi, saiz hablur yang kecil dan isipadu liang yang tinggi berbanding dengan TiO_2 yang lain.

Kata kunci: Titania (TiO_2), 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_2), 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_2 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_2 can be described as follows: upon illumination of TiO_2 with the light in which contained energy higher than the TiO_2 band gap (3.2 eV for anatase), the electrons in valence bands become excited and jump to the conduction bands, creating electronhole pairs within the TiO_2. The holes will absorb water to create hydroxyl radicals (•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_2 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 formed 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 to 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_2 was prepared by Microwave Assisted Synthesis (MAS) technique since not much knowledge was expand regarding to this technique. Generally, this technique is quite fast, simple, and very energy efficient [16-18].

Materials and Methods

Synthesis of Effective TiO_2 Photocatalyst

The TiO_2 photocatalyst were synthesized via MAS method. 1.0 g of commercial TiO_2 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 ^oC. Then, the mixture was reacted in a microwave reactor (Milestone Microwave Laboratory Systems) at constant temperature (150 ^oC) 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_2 was filtered and dried at 60 ^oC overnight. Each dried TiO_2 was calcined in furnace at 450 ^oC for an hour in order to remove impurities as well as to crystallize the TiO_2.

Characterization of the Synthesized TiO_2

Morphology and elemental composition of commercial and synthesized TiO_2 powder were examined using scanning electron microscope (SEM, JEOL JSM-6360 LA). An X-ray diffractometer (XRD, Rigaku Miniflex II) with Cu Kα radiation (λ = 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^o and 80^o at a scanning rate of $2\theta = 5$ ^{o}/min. Specific surface area for each prepared TiO_2 photocatalyst was measured based on Brunauer-Emmett-Teller (BET) multilayer nitrogen gas sorption method (Quantachromeautosorb 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 ^oC before sorption experiment.

Photodegradation of Reactive Golden Yellow R Dye

In this study, each prepared TiO_2 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_2 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_2 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_2 photocatalysts. Figure 1 showed the aggregated of nearly-spherical shape with reasonably uniform size, distributed homogeneously throughout the surface of commercial TiO_2 (SIGMA). The precursor powder, thus, consists of typical particulate morphology.

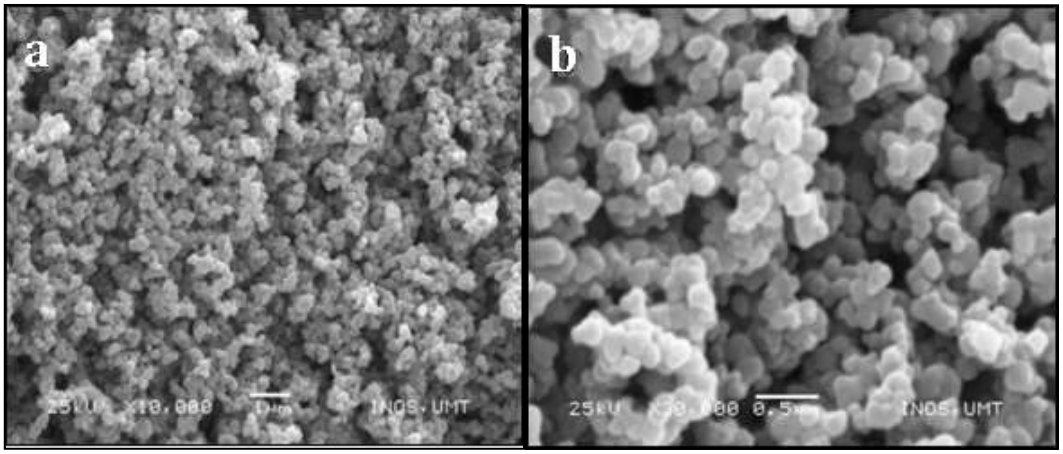
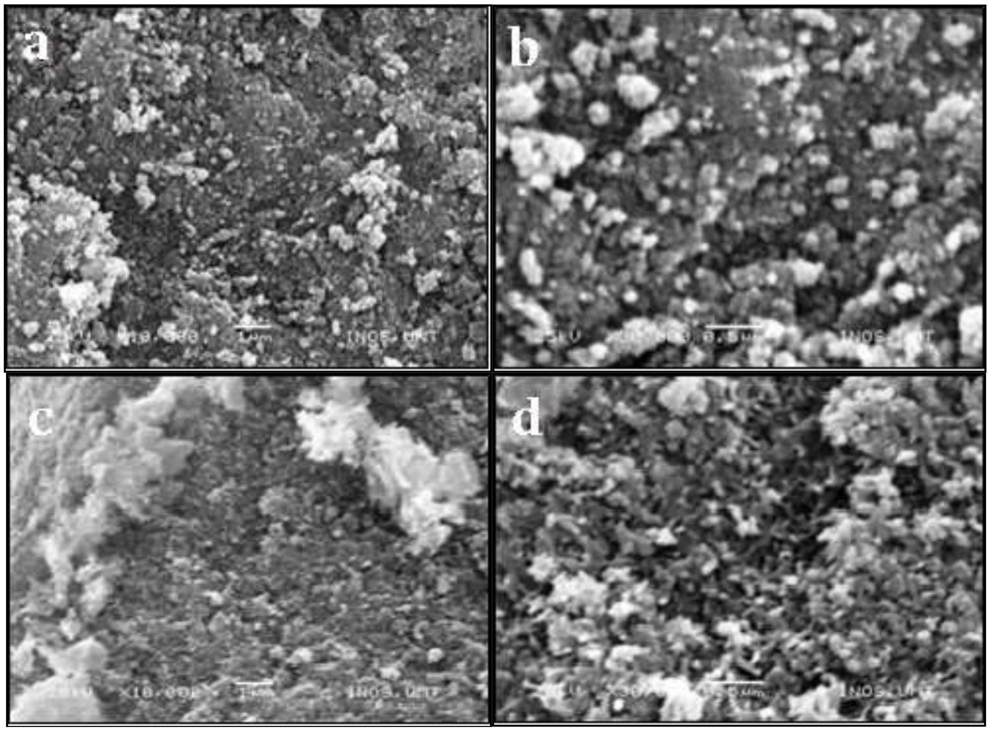


Figure 1. Scanning electron micrographs of commercial TiO_2 (SIGMA) with 2 magnification a) X10000 and b) X30000

Figure 2 depicted the micrographs of surface morphology of TiO_2 prepared by MAS 150 ^oC with various heating time. After treated with MAS 150 ^oC for 2 hours, the 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.



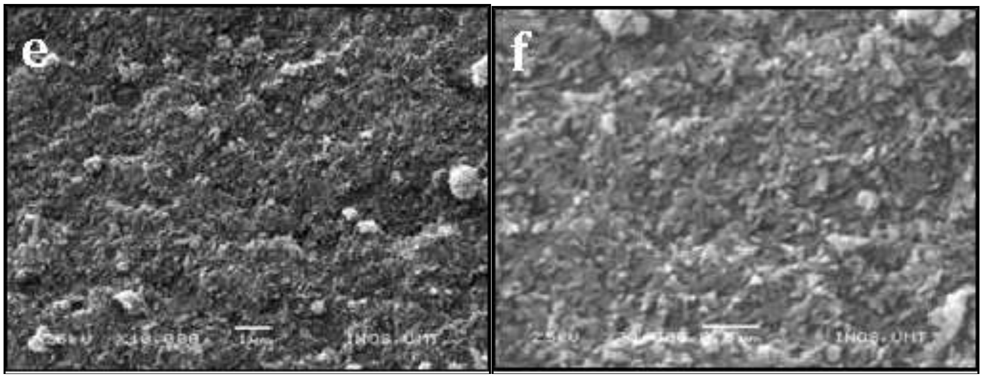


Figure 2. Scanning electron micrographs of TiO_2 prepared by MAS treatment at 150 ^oC for 2 hours (a and b), 4 hours (c and d), and 6 hours (e and f) with 2 magnifications (X10000 and X30000).

X-ray Diffraction XRD

XRD was applied to determine crystalline phase composition and to estimate crystallite size of the prepared TiO_2 photocatalyst. Figure 3 depicted the XRD diffractograms of MAS 150 ^oC 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_2 with 4 hours treatment showed smoother peaks. This showed that the TiO_2 possessed high crystallinity. Upon prolong the MAS heating time to 6 hours, the XRD pattern of the prepared TiO_2 comprises two type of peaks which were assigned to sodium titanium oxide ($N_2Ti_6O_{13}$) and anatase crystalline phase. The existence of $N_2Ti_6O_{13}$ in the lattice structure deteriorated the crystalline structure of the MAS 6 hours prepared TiO_2. Meanwhile, the crystalline sizes were obtained using Scherrer's equation in Equation 1 [19]:

$$d = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where d was the average crystallite size (nm), λ was the wavelength of Cu Kα radiation applied (λ = 0.154), θ the was the Bragg's angle of diffraction, β 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_2.

Table 1. Anatase crystallite size for TiO_2 prepared via MAS 150 ^oC at various heating time

Type of Photocatalyst	Crystallite size (nm)	Peak assignment
Commercial TiO_2 (SIGMA)	43.76	Anatase (TiO_2)
MAS 150 ^oC 2 hours	29.90	Anatase (TiO_2)
MAS 150 ^oC 4 hours	13.62	Anatase (TiO_2)
MAS 150 ^oC 6 hours	8.94	Anatase (TiO_2) and sodium titanium oxide ($N_2Ti_6O_{13}$)

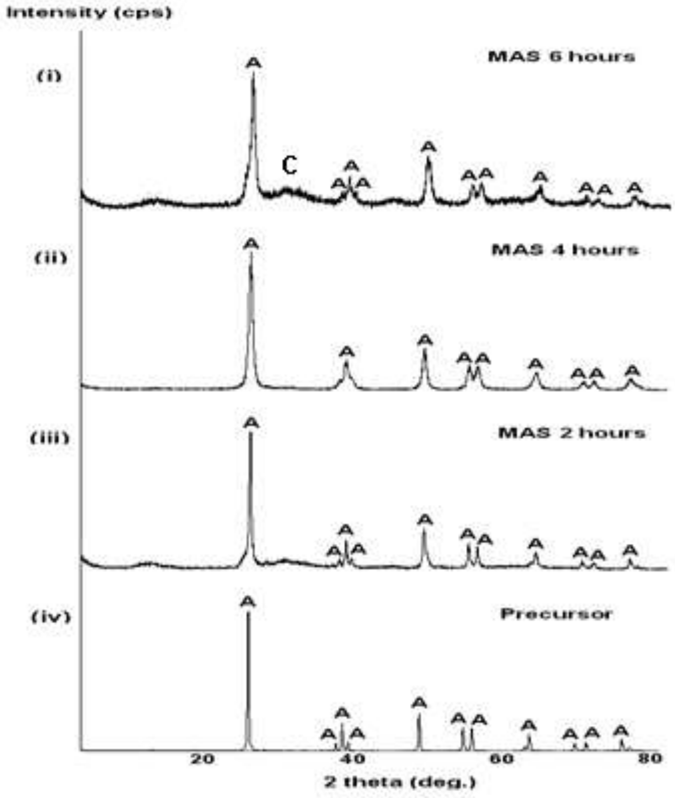


Figure 3: X-ray diffractogram (XRD) patterns of prepared TiO_2 by MAS treatment at 150 ^oC for (i) 6 hours, (ii) 4 hours, (iii) 2 hours and subsequently calcined at 450 ^oC for 1 hour, respectively. XRD pattern for (iv) commercial TiO_2 (SIGMA) was included for comparison. (A: Anatase (TiO_2); C: $Na_2Ti_6O_{13}$)

Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) multilayer nitrogen gas sorption
Textural characteristics of the samples derived from N_2 sorption analysis were presented in Table 2. The BET total surface area (A_{BET}) and BJH pore diameter (d) of MAS 4 hours was almost identical with the MAS 2 hours prepared TiO_2. However, the A_{BET} of the TiO_2 increased to 139.07 m^2/g after treated with MAS 6 hours. Regardless of A_{BET} increment, the pore size of MAS 6 hours TiO_2 was almost identical with the MAS 2 hours and MAS 4 hours treated TiO_2, which was 24.77 nm. The commercial TiO_2 (SIGMA) has a specific surface area of 39.36 m^2/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 TiO_2, has contribute to the negative value of C [20]. Meanwhile, the pore volume of the prepared TiO_2 has increased from 0.6670 cm^3/g to 0.8254 cm^3/g when the treatment time was prolong from 2 hours to 4 hours. However, the pore volume was slightly reduced to 0.7935 cm^3/g after underwent MAS 6 hours treatment.

Figure 4 showed the representative N_2 adsorption–desorption isotherms of the MAS 150 ^oC prepared TiO_2 with various heating time. All the TiO_2 showed the similar type IV isotherms, which represented the mesoporous (pores 2-50 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/Po = 1, indicating the presence of macropores (pores > 50 nm in diameter) in the photocatalyst [20]. Overall, the adsorption capacities of all MAS 150 ^oC prepared TiO_2 were much higher than that of TiO_2 commercial (SIGMA). The results were summarized in Table 3.

Table 2. Nitrogen sorption analysis for TiO_2 prepared by MAS 150 °C

Type of photocatalyst	A_{BET} (m^2/g)	C	V_p (cm^3/g)	d (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_2 (SIGMA)	39.36	-3002.00	0.1480	22.43

A_{BET} = BET total surface area, C = BET constant, V_p = BJH pore volume, d = BJH pore diameter

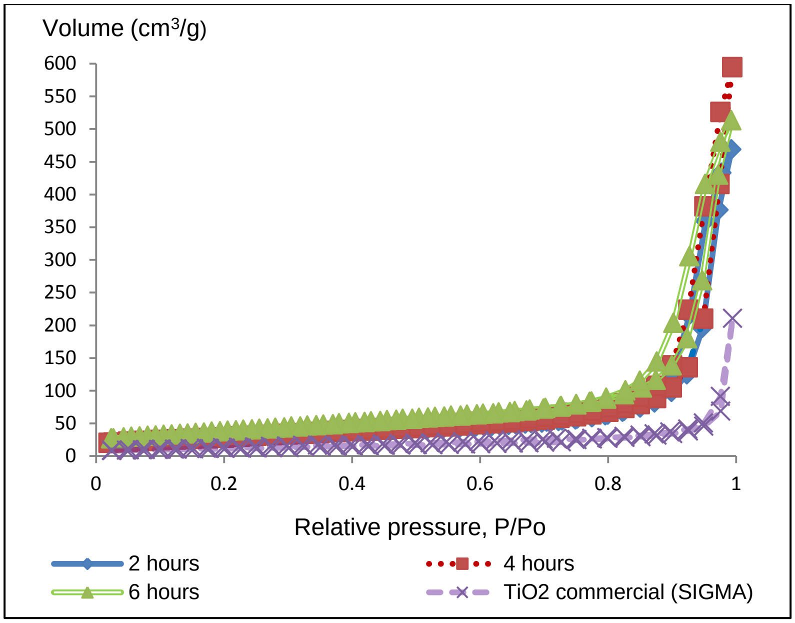


Figure 4. Nitrogen (N_2) adsorption–desorption isotherms plot of MAS 150 °C prepared TiO_2 with various heating time. TiO_2 commercial (SIGMA) was plotted for comparison.

Table 3. Types of isotherms and porosity for TiO_2 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_2 (SIGMA)	IV	H3	Mesopore and Macropore	Disordered slit- shaped pores

Photodegradation of Reactive Golden Yellow R dye

The MAS 4 hours prepared 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 TiO_2. Meanwhile, the MAS 2 hours prepared 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 TiO_2 (SIGMA) showed competitive performance with 91.75 % of dye degradation. The results of catalytic performances of TiO_2 prepared by MAS 150 ^oC with various heating time were depicted in Figure 5.

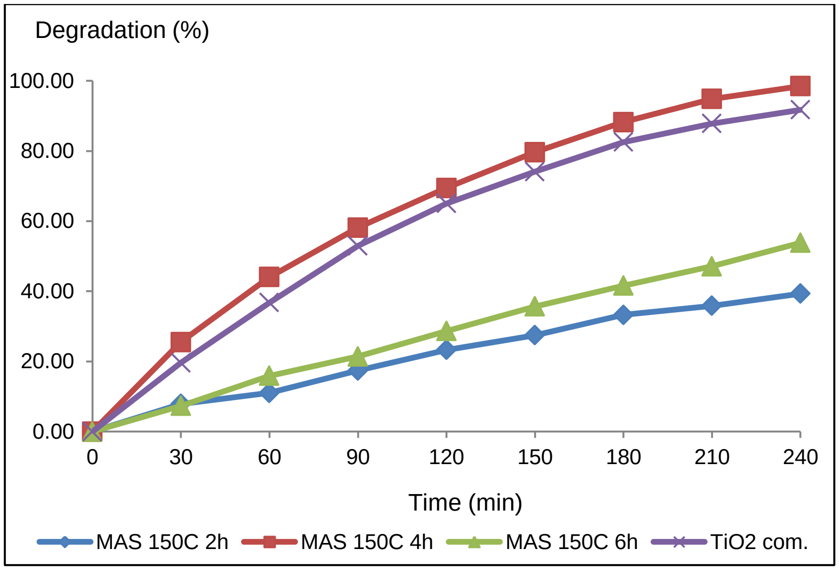


Figure 5. The plot of percentage degradation of 100 ppm Reactive Golden Yellow R dye against time of UV light irradiation in the presence of MAS 150 ^oC prepared TiO_2 with various heating time. Performance of commercial TiO_2 (SIGMA) was tested for comparison.

From the results, the highest photocatalytic activity of MAS 4 hours prepared TiO_2 was due to small anatase crystallite size (13.62 nm), higher crystalline degree of anatase phase, and higher pore volume (0.8254 cm3/g) [19]. The MAS 6 hours prepared TiO_2 possessed the smallest anatase crystallite size (8.94 nm) and larger surface area (139.07 m^2/g), however, its photocatalytic activity was not effectively performed. Indeed, the existence of impurity (sodium titanium oxide) (from XRD result) in the prepared TiO_2 has deteriorated its crystalline structure which led to the decreasing of its photocatalytic activity [16]. The performance of MAS 2 hours prepared 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 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_2 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_2 (SIGMA)	91.75

Conclusion

The Microwave Assisted Synthesis (MAS) technique had produced a potential TiO_2 photocatalyst. The TiO_2 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_2 was due to small crystallite size, high crystallinity of anatase phase, and high pore volume. The performance was higher than the commercial TiO_2 (SIGMA).

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