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 °C 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 sorption analysis (Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) calculation) techniques. The TiO$_2$ prepared by MAS 150 °C (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 °C 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 Brunauer-Emmett-Teller (BET) dan Barrett-Joyner-Halenda (BJH)). TiO$_2$ yang disintesis dengan kaedah MAS pada suhu 150 °C (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 electron-
hole pairs within the TiO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} Photocatalyst

The TiO\textsubscript{2} photocatalyst were synthesized via MAS method. 1.0 g of commercial TiO\textsubscript{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 °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\textsubscript{2} was filtered and dried at 60 °C overnight. Each dried TiO\textsubscript{2} was calcined in furnace at 450 °C for an hour in order to remove impurities as well as to crystallize the TiO\textsubscript{2}.

Characterization of the Synthesized TiO\textsubscript{2}

Morphology and elemental composition of commercial and synthesized TiO\textsubscript{2} powder were examined using scanning electron microscope (SEM, JEOL JSM-6360 LA), An X-ray diffractometer (XRD, Rigaku Miniflex II) with Cu Ka radiation (\(\lambda = 0.15418 \text{ nm}\)) 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\(^{\circ}\) and 80\(^{\circ}\) at a scanning rate of 20\(^{\circ}\)/min. Specific surface area for each prepared TiO\textsubscript{2} 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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} photocatalysts. Figure 1 showed the aggregated of nearly-spherical shape with reasonably uniform size, distributed homogeneously throughout the surface of commercial TiO\textsubscript{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 °C with various heating time. After treated with MAS 150 °C 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.
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 °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$_2$ 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$_2$Ti$_6$O$_{13}$) and anatase crystalline phase. The existence of N$_2$Ti$_6$O$_{13}$ 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]:

$$d = \frac{k\lambda}{\beta \cos \theta}$$  

(1)

where d was the average crystallite size (nm), λ was the wavelength of Cu Kα radiation applied (λ = 0.154), θ 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 °C at various heating time

<table>
<thead>
<tr>
<th>Type of Photocatalyst</th>
<th>Crystallite size (nm)</th>
<th>Peak assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial TiO$_2$ (SIGMA)</td>
<td>43.76</td>
<td>Anatase (TiO$_2$)</td>
</tr>
<tr>
<td>MAS 150 °C 2 hours</td>
<td>29.90</td>
<td>Anatase (TiO$_2$)</td>
</tr>
<tr>
<td>MAS 150 °C 4 hours</td>
<td>13.62</td>
<td>Anatase (TiO$_2$)</td>
</tr>
<tr>
<td>MAS 150 °C 6 hours</td>
<td>8.94</td>
<td>Anatase (TiO$_2$) and sodium titanium oxide (N$_2$Ti$<em>6$O$</em>{13}$)</td>
</tr>
</tbody>
</table>
Figure 3: X-ray diffractogram (XRD) patterns of prepared TiO$_2$ by MAS treatment at 150 °C for (i) 6 hours, (ii) 4 hours, (iii) 2 hours and subsequently calcined at 450 °C for 1 hour, respectively. XRD pattern for (iv) commercial TiO$_2$ (SIGMA) was included for comparison. (A: Anatase (TiO$_2$); C: Na$_2$Ti$_6$O$_{13}$)

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 °C 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 °C 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

<table>
<thead>
<tr>
<th>Type of photocatalyst</th>
<th>$A_{\text{BET}}$ (m$^2$/g)</th>
<th>C</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAS 150 °C 2 hours</td>
<td>101.99</td>
<td>96.19</td>
<td>0.6670</td>
<td>24.53</td>
</tr>
<tr>
<td>MAS 150 °C 4 hours</td>
<td>101.98</td>
<td>137.10</td>
<td>0.8254</td>
<td>24.29</td>
</tr>
<tr>
<td>MAS 150 °C 6 hours</td>
<td>139.07</td>
<td>86.38</td>
<td>0.7935</td>
<td>24.77</td>
</tr>
<tr>
<td>Commercial TiO$_2$ (SIGMA)</td>
<td>39.36</td>
<td>-3002.00</td>
<td>0.1480</td>
<td>22.43</td>
</tr>
</tbody>
</table>

$A_{\text{BET}}$ = 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

<table>
<thead>
<tr>
<th>Type of photocatalyst</th>
<th>Type of Isotherms</th>
<th>Type of Hysteresis</th>
<th>Type of Pores</th>
<th>Shape of Pores</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAS 150 °C, 2 hours</td>
<td>IV</td>
<td>H3</td>
<td>Mesopore and Macropore</td>
<td>Disordered slit- shaped pores</td>
</tr>
<tr>
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<tr>
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<td>IV</td>
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<td>Mesopore and Macropore</td>
<td>Disordered slit- shaped pores</td>
</tr>
</tbody>
</table>
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 °C with various heating time were depicted in Figure 5.

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 cm$^3$/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.

<table>
<thead>
<tr>
<th>Type of photocatalyst</th>
<th>Percentage (%) of degradation of Reactive Golden Yellow R dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAS 150°C (2 hours)</td>
<td>39.34</td>
</tr>
<tr>
<td>MAS 150°C (4 hours)</td>
<td>98.51</td>
</tr>
<tr>
<td>MAS 150°C (6 hours)</td>
<td>53.83</td>
</tr>
<tr>
<td>Commercial TiO$_2$ (SIGMA)</td>
<td>91.75</td>
</tr>
</tbody>
</table>

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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