

## Catalytic Study on TiO<sub>2</sub> Photocatalyst Synthesised Via Microemulsion Method on Atrazine

(Kajian Pemangkinan Fotopemangkin TiO<sub>2</sub> Disintesis Melalui Kaedah Mikroemulsi Terhadap Atrazina)

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### ABSTRACT

*Titanium dioxide photocatalyst was synthesised by microemulsions method under controlled hydrolysis of titanium butoxide, Ti(O(CH<sub>2</sub>)<sub>3</sub>)CH<sub>3</sub>. The synthesised TiO<sub>2</sub> photocatalyst was compared with Sigma-commercial TiO<sub>2</sub> by carrying out the investigation on its properties using scanning electron microscopy (SEM), x-ray diffraction (XRD) analysis and thermal gravimetric analysis (TGA). The photocatalytic activities for both photocatalysts were studied for atrazine photodegradation.*

*Keywords: Atrazine; microemulsions; photodegradation; TiO<sub>2</sub>*

### ABSTRAK

*Titanium dioksida telah disintesis melalui kaedah mikroemulsi hidrolisis terkawal titanium butoksida, Ti(O(CH<sub>2</sub>)<sub>3</sub>)CH<sub>3</sub>. TiO<sub>2</sub> yang disintesis telah dibandingkan dengan TiO<sub>2</sub> Sigma-komersial berdasarkan kajian terhadap sifat fizikal dan kimianya dengan menggunakan mikroskop elektron imbasan (SEM), pembelauan sinar-X (XRD) dan analisis gravimetri terma (TGA). Aktiviti fotopemangkinan bagi kedua-dua fotomangkin telah dikaji dengan menjalankan fotodegradasi terhadap atrazina.*

*Kata kunci: Atrazina; fotodegradasi; mikroemulsi; TiO<sub>2</sub>*

### INTRODUCTION

Titanium dioxide photocatalyst attracted great attention as a promising photocatalyst for photocatalytically degrading organic pollutants due to their unique and outstanding properties such as environmental friendly, safe to use, low cost and high photocatalyst activity (Yesodharan & Devipriya 2004). Photocatalytic is a process which involves reaction between solid catalyst and a light source responsible for producing •OH radicals which will be degraded to achieve complete mineralization of a wide variety of organic compounds. Photocatalytic activity of TiO<sub>2</sub> is influenced by their microstructure, crystal structure, shape and particle size, crystalline size, crystallinity behaviour, specific area, low band gap and preparation method condition (Janus et al. 2008; Li et al. 2009).

There are numerous techniques to synthesise TiO<sub>2</sub> including chemical precipitation, sol gel, chemical vapor deposition and hydrothermal crystallinity including microemulsions (Hong et al. 2005). Microemulsion is the most preferable method to synthesise TiO<sub>2</sub>. This method is believed to give nanosized TiO<sub>2</sub> particle with less agglomeration and flocculation. In addition, the surfactant in the microemulsions acts to stabilise micro cavities to provide a cage-like effect that limits particle nucleation, growth and agglomeration (Lee et al. 2005).

Therefore, the aim of this study was to synthesize TiO<sub>2</sub> by microemulsions method which in turn was used to degrade 2-chloro-4-(ethylamino)-6 (isopropylamino)-S-triazine or widely known as atrazine.

### EXPERIMENTAL DETAILS

#### INSTRUMENTS

In the synthetic stage, ultrasonicator (JAC Ultrasonic Cleaner, JAC 2010, 240~50Hz/30 A) was used to stir and vibrate the microemulsion homogeneously. Then, the product which is in the powdered form was calcined by using a furnace to grow it in the form of nanostructure and to remove any organic residues.

The physical properties including the morphology of the synthesized and Sigma-commercial TiO<sub>2</sub> was characterised by scanning electron microscopy, SEM (JEOL JSM-6360 LA). Nitrogen adsorption/desorption isotherms by BET (Brunauer-Emmett-Teller) method was carried out by using Quantasorb (Quantachrome Autosorb Automated Gas Sorption) to determine the specific surface area. The samples were degassed by liquid nitrogen at 150°C for 15 h. Meanwhile, the phase transition of TiO<sub>2</sub> powder was analysed by using thermal gravimetric analysis, TGA (Thermogravimetric Analyzer Pyris 6 TGA). Furthermore,

the particle size of both TiO<sub>2</sub> powders were determined by X-Ray diffraction method, XRD (Rigaku, Miniflex II Desktop X-Ray Diffractometer).

In addition, the collected sample was irradiated for 4 h under UV-light 302 nm 230 V~50 Hz and then analysed by using UV-Vis spectrophotometer (UV-1601 PC, UV-Visible Spectrophotometer, Shimadzu).

#### REAGENTS

The reagents used were hexadecyl trimethyl ammonium bromide, HTAB (Sigma-Aldrich), titanium butoxide (purity 97%, Sigma-Aldrich), cyclohexane (Hamburg Chemical), NaCl (Merck Schuchardt) and ammonium hydroxide, NH<sub>4</sub>OH (Mallinckrodt). Meanwhile, as a comparison to the synthesised titanium dioxide, TiO<sub>2</sub> Sigma-Aldrich was used as the commercial photocatalyst to degrade atrazine from. In addition, for catalytic studies, atrazine Sigma-Aldrich was used as a standard. All of these chemicals were used as received without further purification. In addition, no special precautions were taken at any stage during the experimental task.

#### GENERAL EXPERIMENTAL PROCEDURES

Microemulsion A and B which consist of 60 mL cyclohexane as oil phase and 30 mL surfactant phase which is hexatrimethyl ammonium bromide, HTAB (0.5 M) were prepared according to 6:3:1 proportion as carried out by previous report (Wang et al. 2004). Then, 10 mL of titanium (IV) butoxide, Ti(O(CH<sub>2</sub>)<sub>3</sub>)CH<sub>3</sub> was added in microemulsion A. Ammonium hydroxide solution, NH<sub>4</sub>OH 2 M (as reducing agent) was added in reagent B. Both microemulsions were mixed in a 250 mL beaker and were stirred and vibrated homogeneously in ultrasonicator (JAC Ultrasonic Cleaner, JAC 2010, 240~50Hz/30 A) for 1 h to prevent the agglomeration of TiO<sub>2</sub> pigment in water. Next, 10 mL of 5 M solution of sodium chloride, NaCl was added to these microemulsions, followed by continuous stirring and vibrated constantly in an ultrasonicator for another 1 h to ensure that the mixture

was completely mixed. Then, the microemulsion was washed with 30 mL acetone before the product was annealed (Nabertherm, HTC 08/16, 400 V, 50/60 Hz) at 600°C for 4 h, respectively. The powder obtained was washed with 30 mL distilled water to remove any excess NaCl, followed by drying in an oven at around 90°C for approximately 12 h to remove any excess water.

For the photocatalytic degradation of atrazine, the activity was performed by using 100 mL aqueous solution of atrazine (5 mg L<sup>-1</sup>) and 0.2 g of TiO<sub>2</sub> catalyst. As a control, the observations involving the degradation by Sigma-commercial TiO<sub>2</sub> and synthesised TiO<sub>2</sub> were carried out as well. The degradation mixture were stirred magnetically and irradiated by UV-light (302 nm, 230 V~50 Hz) for 1 h to ensure their optimum thermodynamic stability. Every 5 mL of the aqueous suspension was collected at each 30 min interval during the irradiation and then filtered on 0.20 μm millipore syringe filter (Advantec) to remove the catalyst. Sample was exposed for 4 h under UV-light and analyzed by using UV-Vis spectrophotometer (UV-1601 PC, UV-Visible Spectrophotometer Shimadzu).

#### RESULTS AND DISCUSSION

##### CHARACTERISATION OF TiO<sub>2</sub> PHOTOCATALYST

Figure 1(a) shows the SEM micrographs of synthesized TiO<sub>2</sub> by microemulsion method while Figure 1(b) shows the Sigma-commercial TiO<sub>2</sub> particles. It can be observed in Figure 1(a), that there were plenty of elongated fibrous-like structures with 50-60 nm average diameter which are closely arranged together. The Sigma-commercial TiO<sub>2</sub> particles size was between 65 and 85 nm in diameter. The Sigma-commercial TiO<sub>2</sub> particles had spherical shape and has a uniform size distribution. From these observations, although the synthesised particles were physically larger than the Sigma-commercial TiO<sub>2</sub>, the fibrous-like shape of synthesised TiO<sub>2</sub> particle determines the high specific surface area, as suggested by Lu et al. (2008) and Murugesan et al. (2007). Moreover, this observation were

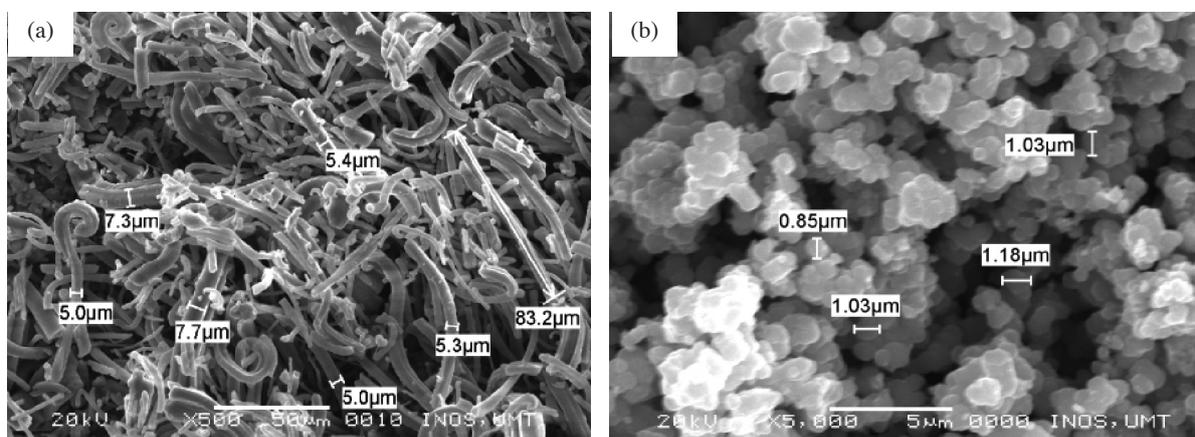


FIGURE 1. SEM micrographs of (a) synthesised and (b) Sigma-commercial TiO<sub>2</sub> photocatalysts

strongly supported by result obtained from XRD and BET surface analyzer.

Figure 2 shows the BET plot of the synthesized and Sigma-commercial  $\text{TiO}_2$  which corresponds to the total specific area of both photocatalyst. The specific surface area was slightly different between the Sigma-commercial and synthesised  $\text{TiO}_2$  photocatalyst, which is  $18.75 \text{ m}^2/\text{g}$  for Sigma-commercial, and  $60.53 \text{ m}^2/\text{g}$  for the synthesised  $\text{TiO}_2$ . This high specific area resulted from the nanometer grain size of the modified  $\text{TiO}_2$  powder. Thus, the high specific surface area greatly depends on the size and shape of the particles (Lu et al. 2009). Hence, the difference of surface area are closely related to the morphological images observed by SEM. Even though the morphological size of the Sigma-commercial  $\text{TiO}_2$  is smaller than the

synthesized  $\text{TiO}_2$ , it has elongated, fibrous-like and less aggregate structure which mean it exhibits larger surface area to react with atrazine during photodegradation process compared to the Sigma-commercial  $\text{TiO}_2$ .

Thermal gravimetric results of synthesized and Sigma-commercial  $\text{TiO}_2$  are shown in Figure 3. The thermo gravimetric curves for synthesized  $\text{TiO}_2$  can be divided into three regions. The first weight loss occurred at  $0-100^\circ\text{C}$ , and it is associated with the desorption of chemically adsorbed water molecules on the  $\text{TiO}_2$  surfaces. The second weight loss corresponds to the volatilization and decomposition of HTAB surfactant, alkoxy group and residual OH group, which occurs at  $200-600^\circ\text{C}$  (He et al. 2009). The final weight loss was due to the decomposition of surfactant molecules trapped in the  $\text{TiO}_2$  fibrous structure.

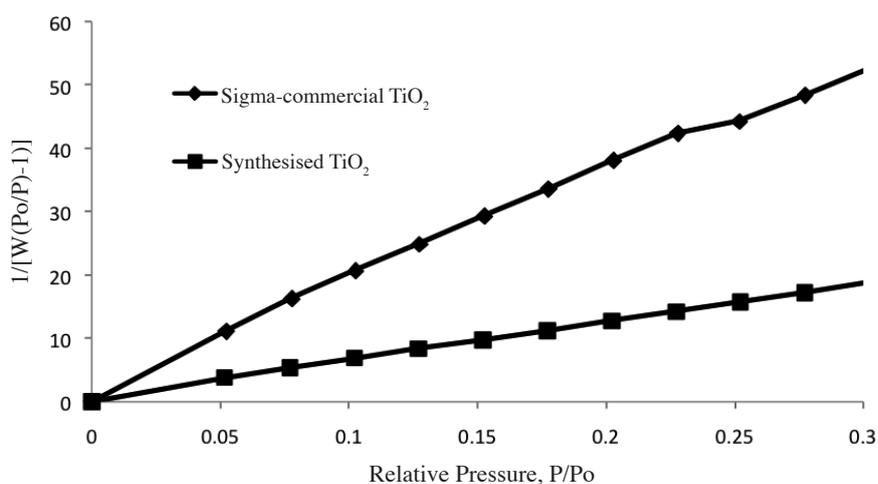


FIGURE 2. BET plot corresponding to specific surface area of Sigma-commercial  $\text{TiO}_2$  and synthesised  $\text{TiO}_2$

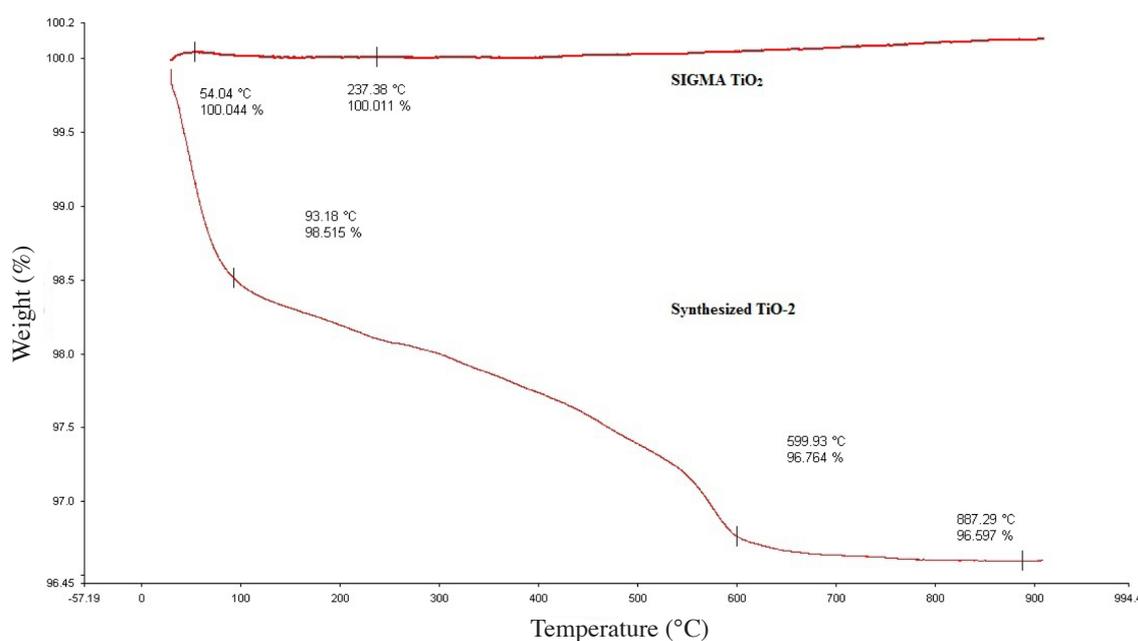


FIGURE 3. TG-DTA curves of synthesised and Sigma-commercial  $\text{TiO}_2$  powders

There was no weight loss for Sigma-commercial  $\text{TiO}_2$  due to their purity and stable form of powders. According to the TGA curves, after  $600^\circ\text{C}$  weight loss started to remain constant which is believed corresponds to the completion of transformation to anatase phase from brookite phase. From the observation,  $600^\circ\text{C}$  is an appropriate and ideal calcination temperature to synthesise  $\text{TiO}_2$  which should give better performance in the photocatalytic activities.

The synthesised and Sigma-commercial  $\text{TiO}_2$  photocatalysts were also analyzed by XRD method (Figure 4). The major phase of the prepared and Sigma-commercial  $\text{TiO}_2$  particles was an anatase. However, the synthesised  $\text{TiO}_2$  photocatalyst exhibited high crystallinity compared to the Sigma-commercial  $\text{TiO}_2$  photocatalyst as shown by standard X-ray diffraction peak PDF Card No: 00-021-1272). This characteristic is strongly due to the ideal temperature to calcine the synthesized  $\text{TiO}_2$  at  $600^\circ\text{C}$ . Thus, the arrangement in the structure of titania particles exhibits the X-ray peak to be sharper and narrower compared to the commercial  $\text{TiO}_2$  particles. It can be proven that, the suitable and ideal calcination temperature improves the crystallinity of the particles by reducing the size of the particles (Awitor et al. 2008).

In addition, the crystallite size of the particles was determined by the Debye-Scherrers equation (Li et al. 2006), which are 38 nm for synthesised and 58 nm for commercial  $\text{TiO}_2$ . Hence, according to the particles size, the synthesised  $\text{TiO}_2$  may have a larger specific surface area compared to the Sigma-commercial  $\text{TiO}_2$ .

Figure 5 shows the degradation percentage of atrazine when treated with synthesised and commercial  $\text{TiO}_2$  after 4 h of UV irradiation. After 4 h exposure to UV light, the degradation of atrazine obtained of the synthesised  $\text{TiO}_2$  was 70.6%, whilst degradation by Sigma-commercial catalyst was 33.4%. These degradation may due to their specific surface area. BET specific surface area and SEM micrograph, clearly indicated that specific surface area of the synthesised  $\text{TiO}_2$  was higher than Sigma-commercial  $\text{TiO}_2$ .

In turn, all these observations were taken into consideration in the photodegradation of atrazine by applying the synthesised and Sigma-commercial  $\text{TiO}_2$ . It was found that the photodegradation of synthesised  $\text{TiO}_2$  was higher than the commercial  $\text{TiO}_2$ . Apparently, the limit of specific surface area plays significant role to act as adsorption surface to reduce molecular oxygen on the Ti (III) sites to the superoxide radical anion. The surface to bulk ratio for synthesised  $\text{TiO}_2$  nanoparticles was much greater than Sigma-commercial  $\text{TiO}_2$  with larger grains, which yields large interface interaction between the solid, gaseous and liquid medium as well (Zhanqi et al. 2007). In the presence of synthesised  $\text{TiO}_2$ , the degradation of atrazine increased slightly in the first 30 min, which indicate the existence of a large number of active sites on the synthesised  $\text{TiO}_2$  surface at the 28% degradation. In contrast for the Sigma-commercial  $\text{TiO}_2$ , only 10% of atrazine was degraded in the first 30 min of photocatalytic activities.

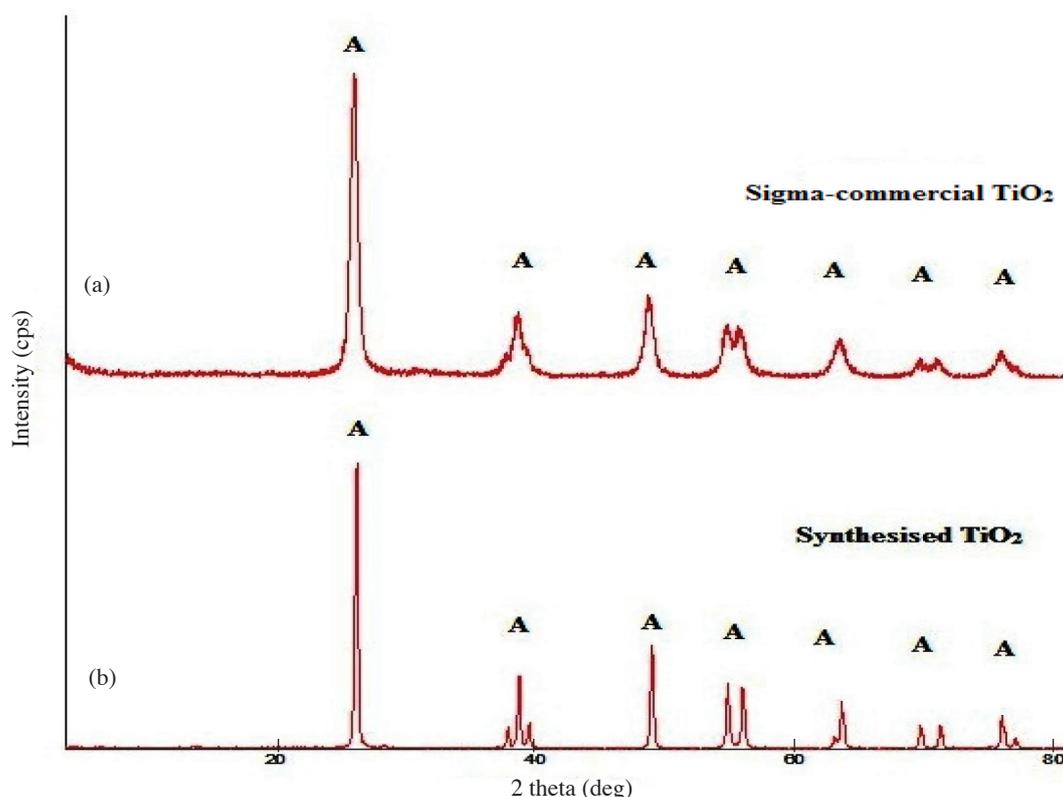


FIGURE 4. XRD patterns of (a) Sigma-commercial and (b) synthesised  $\text{TiO}_2$ . (A: Anatase)

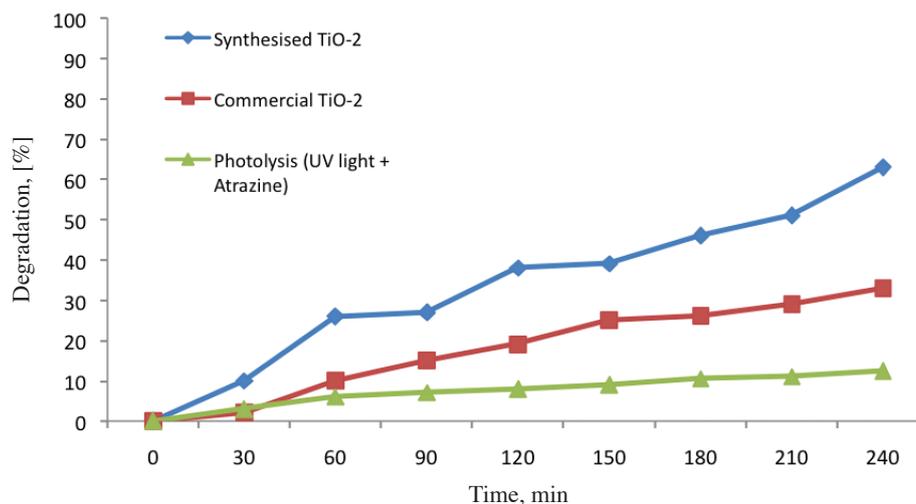


FIGURE 5. Photocatalytic degradation of 5 ppm of atrazine at 240 min illuminated with UV light

These observations revealed that the synthesised  $\text{TiO}_2$  has undergone modification and improvement on their chemical and physical properties to give better performance as photocatalyst compared to Sigma-commercial  $\text{TiO}_2$ . Hence, the photocatalytic activity was enhanced by using synthesised  $\text{TiO}_2$  as suggested by Jianzhang et al. (2007), Pu et al. (2007) and Wu et al. (2008). The photocatalytic activity of  $\text{TiO}_2$  depends on its crystal structure (anatase or rutile), surface area, size distribution, porosity, presence of dopants and surface hydroxyl group density. Thus, these factors have direct effect on the production of electron-hole pairs, surface adsorption and desorption and the reduction-oxidation process. Therefore, in this study all the findings investigated on synthesized  $\text{TiO}_2$  exhibited better results which are small crystal size, narrow size distribution, pure anatase and high degree of crystallinity compared to Sigma-commercial  $\text{TiO}_2$ .

#### CONCLUSIONS

$\text{TiO}_2$  with elongated fibrous structure (30-50 nm) and closely arranged together, high specific surface area with  $60.53 \text{ m}^2 \text{ g}^{-1}$  and anatase crystal phase was successfully synthesized by microemulsion method prior to applying both of these catalysts in photocatalytic activity on atrazine. As a result, atrazine was 70.6% degraded under the presence of synthesised  $\text{TiO}_2$  compared to the Sigma-commercial which was only 33.4% when exposed to UV-light for 4 h.

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