Catalytic Study on TiO$_2$ Photocatalyst Synthesised Via Microemulsion Method on Atrazine
(Kajian Pemangkinan Fotopemangkin TiO$_2$ 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$_2$)$_3$)$_3$CH$_3$. The synthesised TiO$_2$ photocatalyst was compared with Sigma-commercial TiO$_2$ 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$_2$

ABSTRAK

Titanium dioksida telah disintesis melalui kaedah mikroemulsi hidrolisis terkawal titanium butoksida, Ti(O(CH$_2$)$_3$)$_3$CH$_3$. TiO$_2$ yang disintesis telah dibandingkan dengan TiO$_2$ 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$_2$

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$_2$ 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).

Therefore, the aim of this study was to synthesize TiO$_2$ 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$_2$ 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$_2$ powder was analysed by using thermal gravimetric analysis, TGA (Thermogravimetric Analyzer Pyris 6 TGA). Furthermore,
the particle size of both TiO$_2$ 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$_4$OH (Mallinckrodt). Meanwhile, as a comparison to the synthesised titanium dioxide, TiO$_2$ 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 hexatrimeethyl 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$_2$)$_3$)CH$_3$ was added in microemulsion A. Ammonium hydroxide solution, NH$_4$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$_2$ 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$^{-1}$) and 0.2 g of TiO$_2$ catalyst. As a control, the observations involving the degradation by Sigma-commercial TiO$_2$ and synthesised TiO$_2$ 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 Shidmadzu).

RESULTS AND DISCUSSION

CHARACTERISATION OF TiO$_2$ PHOTOCATALYST

Figure 1(a) shows the SEM micrographs of synthesized TiO$_2$ by microemulsion method while Figure 1(b) shows the Sigma-commercial TiO$_2$ 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$_2$ particles size was between 65 and 85 nm in diameter. The Sigma-commercial TiO$_2$ 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$_2$, the fibrous-like shape of synthesised TiO$_2$ particle determines the high specific surface area, as suggested by Lu et al. (2008) and Murugesan et al. (2007). Moreover, this observation were...
strongly supported by result obtained from XRD and BET surface analyzer.

Figure 2 shows the BET plot of the synthesized and Sigma-commercial 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 TiO$_2$ photocatalyst, which is 18.75 m$^2$/g for Sigma-commercial, and 60.53 m$^2$/g for the synthesized TiO$_2$. This high specific area resulted from the nanometer grain size of the modified 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 TiO$_2$ is smaller than the synthesized 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 TiO$_2$.

Thermal gravimetric results of synthesized and Sigma-commercial TiO$_2$ are shown in Figure 3. The thermo gravimetric curves for synthesized TiO$_2$ can be divided into three regions. The first weight loss occurred at 0-100°C, and it is associated with the desorption of chemically adsorbed water molecules on the TiO$_2$ surfaces. The second weight loss corresponds to the volatilization and decomposition of HTAB surfactant, alkoxyl group and residual OH group, which occurs at 200-600°C (He et al. 2009). The final weight loss was due to the decomposition of surfactant molecules trapped in the TiO$_2$ fibrous structure.
There was no weight loss for Sigma-commercial TiO$_2$ due to their purity and stable form of powders. According to the TGA curves, after 600°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°C is an appropriate and ideal calcination temperature to synthesise TiO$_2$ which should give better performance in the photocatalytic activities.

The synthesised and Sigma-commercial TiO$_2$ photocatalysts were also analyzed by XRD method (Figure 4). The major phase of the prepared and Sigma-commercial TiO$_2$ particles was an anatase. However, the synthesised TiO$_2$ photocatalyst exhibited high crystallinity compared to the Sigma-commercial 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 TiO$_2$ at 600°C. Thus, the arrangement in the structure of titania particles exhibits the X-ray peak to be sharper and narrower compared to the commercial 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 TiO$_2$. Hence, according to the particles size, the synthesised TiO$_2$ may have a larger specific surface area compared to the Sigma-commercial TiO$_2$.

FIGURE 4. XRD patterns of (a) Sigma-commercial and (b) synthesised TiO$_2$. (A: Anatase)
These observations revealed that the synthesised TiO$_2$ has undergone modification and improvement of their chemical and physical properties to give better performance as photocatalyst compared to Sigma-commercial TiO$_2$. Hence, the photocatalytic activity was enhanced by using synthesised TiO$_2$, as suggested by Jianzhang et al. (2007), Pu et al. (2007) and Wu et al. (2008). The photocatalytic activity of 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 TiO$_2$ exhibited better results which are small crystal size, narrow size distribution, pure anatase and high degree of crystallinity compared to Sigma-commercial TiO$_2$.

CONCLUSIONS

TiO$_2$ with elongated fibrous structure (30-50 nm) and closely arranged together, high specific surface area with 60.53 m$^2$ 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 TiO$_2$ compared to the Sigma-commercial which was only 33.4% when exposed to UV-light for 4 h.

REFERENCES


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