Effect of Sample Separation Processing Techniques on Particle Size and Photocatalytic Activity of TiO_2 from Microwave-Assisted Synthesis

N. Pijarn, S. Jiemsirilers, and S. Jinawath

***Abstract*—Techniques for sample separation from chemical reaction is an important step in a synthesis process. Two techniques, filtration and centrifugation, were used for separating the synthesized TiO_2 precipitates in this study. Photocatalytic activities of the synthesized TiO_2 and P25 were evaluated through the degradation of methylene blue (MB). The results show that the MB degradation of the TiO_2 powder obtained from the centrifugation technique is higher than that from the filtration technique due to its smaller particle size and larger content of anatase.**

***Index Terms*—Titanium dioxide, Filtration, Centrifugation, Microwave-assisted synthesis, Photocatalytic activity**

I. Introduction

Separation technique is very important in fine powder preparation from solution. Filtration is basically the physical technique which is commonly used for the separation of solids from liquids. According to the reports of several researchers [1]-[5], this technique does not give a complete separation, the solid can be contaminated with some liquid and filtrate contain fine particles since the limitation depends on opening size of filtration paper**.** Another common technique is centrifugation which is a process related to the use of the centrifugal force for the sedimentation of mixtures with a centrifuge. The lasting solution is called the "supernatant liquid". The supernatant liquid is then either rapidly decanted from the tube without disturbing the precipitate, or withdrawn with a Pasteur pipette. The limitation of this technique is depending on the type of separation**.** Some reports of centrifugation technique have been published online [6]-[10]. However, there have been many reports on comparison of conventional filtration (using filter paper) and centrifugation of the solid sample from the solution [11]-[15] but not in the case of TiO_2. A comparative study between conventional filtration and centrifugation techniques of TiO_2 separation is very rare. Most experiments involved with TiO_2 used sophisticated membrane filtration [16]-[18].

Consequently, in this work, the properties of TiO_2 powders obtained from microwave-assisted synthesis followed by either conventional filtration or centrifugation were determined in terms of particle size (ZetaPaLs (Brookhaven Instruments Corporation, New York, USA), specific surface area (BET) mineral phase content and photocatalytic activities were evaluated by observing the degradation of methylene blue (MB), using TiO_2 (P25) as reference.

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The authors are with Department of Materials Science, Faculty of Science, Chulalongkorn University (e-mail: nuchtennis@ gmail.com, sirithan.j@chula.ac.th, supatra.j@chula.ac.th).

II. Materials and Method

A. Materials

TiO_2 was synthesized from titanyl sulfate ($TiOSO_4$) and sodium hydroxide (NaOH). $TiOSO_4$ is analytical reagent grade from Riedel-deHa ën® Co., Ltd., Country of Origin Germany, Germany. NaOH is analytical grade from Ajax finechem Pty. Ltd, Auckland, New Zealand. Methylene blue dye for photocatalytic study is analytical reagent grade from FLUKA Chemika/Biochemika Fluka Chemie AG, CH-9470 Buchs Switzerland. Reverse osmosis (RO) water was used for dilution of solution from the Siam drink.Co.Ltd., Pathumthani, Thailand. Titanium dioxide (P25) used in this study was purchased from Degussa Co., Ltd., Shanghai, China.

B. Microwave Synthesis of TiO_2

3.2 g of $TiOSO_4$ was dissolved in 200 cm^3 of RO water followed by vigorous stirring for 30 min to yield a clear solution. The pH of the solution was adjusted to 14 by adding 1.0 M of NaOH solution drop by drop into the solution with stirring. The forming suspension was then heated in a microwave oven (M181GN TDS, SAMSUNG) at a power of 200W and duration of 10 minutes, then aging for precipitation 18 h, and separated from the solution by filtration or centrifugation techniques, washed to neutrality, dried, and gently ground to fine powder. Then the powder was calcined at 700^{o}C for 2h to enhance crystallinity [19].

Separation of solid sample from liquid medium by filtration was done in Buchner funnel (9 cm ø) with a filter paper (9 cm ø) no.5, Whatman, England) using a vacuum pump (GAST Manufacturing, Inc., a unit of IDIX Corporation MICH. USA).

Centrifugation was done in a centrifuge (Universal 320 Centrfugen, Andreas Hettich GmbH & Co.KG, Tuttlingen, Germany) at 6000 rpm for 5 min with PE centrifuge bottles. After centrifugation, the supernatant was poured, and the slurry was subjected to suction for a minute to pre-dry solid sample. The centrifugation procedure was repeated four times to completely eliminate Na_2SO_4 from the reaction as in previous research [20].

C. Characterization

The mineral phases of the samples were observed using a

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Bruker AXS Diffractometer (D8 Advance, Bruker Company, Germany) the average particle size was estimated from the particle size distribution curve.

The morphology of the TiO_2 powder obtained was observed by scanning electron microscopy (SEM) using a JEOL Scanning Electron Microscope (JSM-6400 SEM, Japan) with Cu Kα radiation. For observation by SEM, the sample was dissolved in ethanol and sonicated for a minute and then dropped on a glass slide. After that it was coated with gold employing a standard sputtering technique.

The specific surface area of the samples was observed using a Quantachrom Autosorb -1.

D. Photocatalytic Experiment

Standard solutions of methylene blue were prepared at 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 ppm. The concentration of MB was measured by a UV/Vis spectrophotometer, Lambda 35 1.23, PerkinElmer Instrument, USA, at the maximum absorption wavelength (λ_{max}= 663.5 nm) and calibration curve was plotted. The photocatalytic activities of TiO_2 samples were evaluated by observing the photodegradation of the MB in the presence of TiO_2 powder. The initial concentration of the MB solution in this experiment was 10 ppm. The volume of the aqueous MB solution was 20 cm^3, to which 100 mg of TiO_2 powder was added. The sample was taken at 90 min in a UV reactor and the solution with the residual MB was removed from the photocatalyst by centrifugation. The operating intensity of UVA is 1.0 mw/cm^2 measured by UV Radiometer, UVR-2 Topcon Techno house Corporation, Japan.

III. Results and Discussion

Selection of an effective separation technique is important in a preparation of fine powder from solution. In this study, filtration technique (vacuum pump with Buchner funnel filter) and centrifugation technique (6000 rpm, 5 min) are compared. Both techniques are performed with neutral (pH 7) solutions.

A. Mineral Phase Present

The XRD results (Fig.1) show little significant difference between patterns of TiO_2 from two techniques. This figure illustrates the XRD patterns of the TiO_2 from different separation technique. As seen in the figure, TiO_2 profiles show a characteristic peak of TiO_2 mixed phase (anatase, rutile and brookite, JCPDS number of 21-1272, 21-1276 and 29-1360, respectively). The TiO_2 from centrifugation technique has the intensity of anatase peak (2θ~25.2 °) higher than the TiO_2 from filtration technique, whereas the TiO_2 from filtration technique has the intensity of brookite peak (2θ~25.3 °) higher than the TiO_2 from centrifugation technique. Normally, the intensity of the peak at 2θ~30° (h k l plane 2 0 0) is small and rarely observed so it is not clearly shown in TiO_2 from the filtration technique (Fig. 1a). On the contrary that of the TiO_2 from centrifugation technique (Fig.1b) was clearly split into two peaks of 1 2 1 and 2 0 0 planes. These results may be due to the preferred orientation of this sample [21].

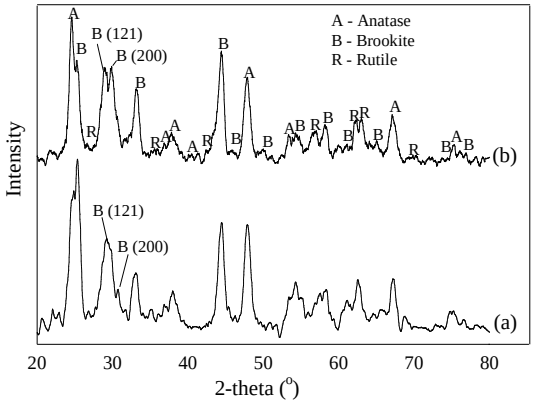

Fig. 1. XRD patterns of TiO_2 from different separation techniques: (a) Filtration technique and (b) Centrifugation technique (both calcined at 700°C for 2h)

B. Particle Size and Specific Surface Area

The particles size distributions of TiO_2 is shown in Fig. 2. The results show that TiO_2 sample from centrifugation technique has smaller size than the TiO_2 from filtration technique. The particle sizes of TiO_2 are shown in TABLE I. The particle size of TiO_2 obtained from centrifugation technique and filtration technique is 22.60 nm and 36.12 nm, respectively and the specific surface area of the TiO_2 obtained from centrifugation technique and filtration technique is 151.81 and 147.99 m^2/g, respectively (TABLE 1).

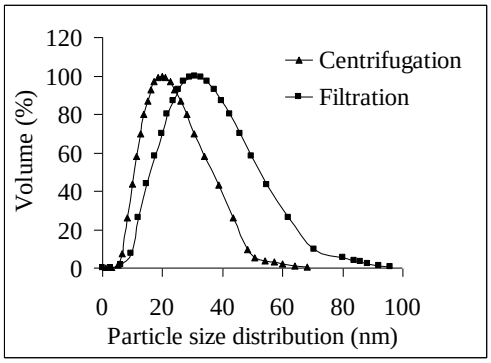

Fig. 2. Particle size distribution of TiO_2 obtained from different separation techniques

TABLE I: The Particle Size and Specific Surface Area of Samples from Different Separation Techniques

Separation technique	Particle size (nm)	Specific surface area (m^2/g)
Filtration	36.12	147.99
Centrifugation	22.60	151.81

C. Morphology

SEM images of TiO_2 samples are shown in Fig. 3. The crystal shape of rutile is rectangular (fig.3a) but those of anatase and brookite are quite spherical (fig.3b) [22]. Fig. 3a, it is possible that the sample from filtration technique may contain higher rutile phase due to its high aspect ratio. Therefore, this is a possible explanation for the reduction in the fraction of rutile phase in centrifugation technique. This finding is agreement with Murakami *et.al* report [22]

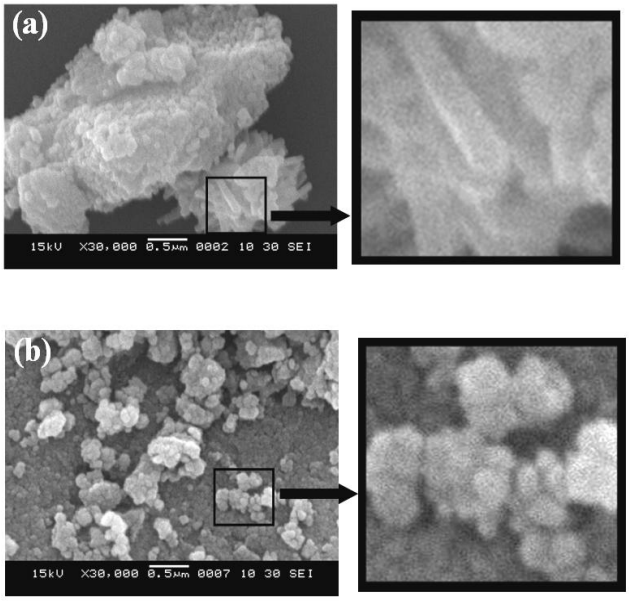

Fig. 3. SEM image of TiO_2 samples from different separation techniques: (a) Filtration technique and (b) Centrifugation technique

IV. Photocatalytic Results

Absorption Spectra and Standard Calibration Plot of Methylene Blue

The concentrations of standard solution were prepared as 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 ppm. The absorption spectra of standard MB solutions and the calibration plot are shown in Fig. 4.

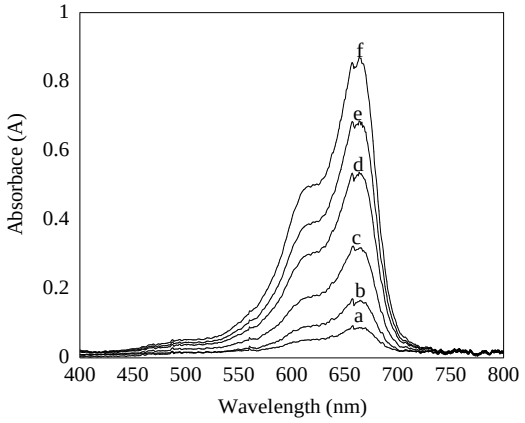

Fig. 4. Absorption spectra of methylene blue standards; a) 0.5 ppm, b) 1.0 ppm, c) 2.0 ppm, d) 3.0 ppm, e) 4.0 ppm, and f) 5.0 ppm.

Table II shows the absorbance of methylene blue standard solutions measured by UV spectrophotometer at the maximum wavelength of 663.5 nm (λ_{max}= 663.5). The results demonstrate that the concentrations of the MB standard solutions from 0.5-5 ppm give the absorbance in a range of 0–1. The standard calibration plot (absorbance v.s. concentration) shows high linearity ($R^2 = 0.9997$). The concentration of MB in the sample is calculated from the Beer-Lambert's law [23], and the least square equation is

$$y = 0.1732x - 0.0305 \quad (1)$$

where *y* is absorbance, x is concentration of MB

TABLE II: Absorbance of Methylene Blue Standard

MB standard no.	Conc. of MB (ppm)	Absorbance (A)
Std.1	0.5	0.0567
Std.2	1.0	0.1396
Std.3	2.0	0.3196
Std.4	3.0	0.4952
Std.5	4.0	0.6684
Std.6	5.0	0.8286

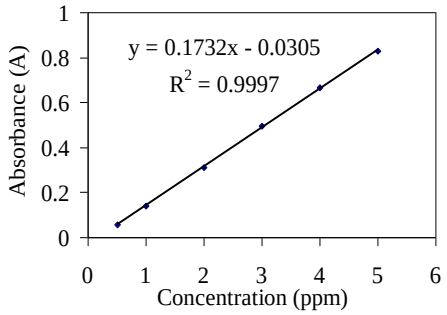

Fig. 5. Standard calibration plot of MB solution

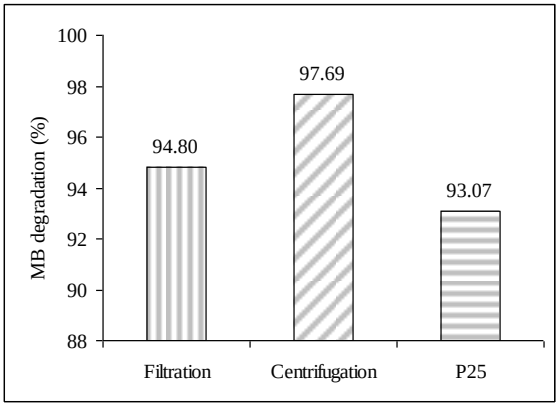

Fig. 6. MB degradation by TiO_2 from filtration and centrifugation techniques

TABLE III: Degradation of Methylene Blue by Titania Photocatalysis (at 90 Minutes Under UV Light)

Sample	Absorbance (A)	Conc. of MB (ppm)	Degradation (%)
Filtration	0.09	0.52	94.80
Centrifugation	0.04	0.23	97.69
P25	0.12	0.69	93.07

B. MB Decomposition Rate of Samples Compared with P25

10 ppm of MB solution (20 cm^3) was used as initial concentration. After 90 min in the UV reactor, the degrees of photodegradation of the MB by the TiO_2 from different sample separation techniques compared with P25 are shown in Table III and Fig. 6.

The photodegradation of MB under UV light was performed in the presence of TiO_2. The sample were set aside in the dark for 30 minutes to stabilize concentration of MB and measurement of the MB was taken in UV reactor for 20, 40, 60, 80, 100, 120, 140, 160 and 180 min. It was found that due to the nano size of the prepared TiO_2 powders, the samples highly adsorbed the MB dye in the dark (89.87 %) which resulted in a small concentration of the MB left for the UV experiment. Therefore the starting concentrations of P-25 and the prepared samples were much different as shown in Fig. 7. P-25 effectively decomposes the MB and degrades

the MB to completion at 120 min. Thus, concentration of the MB decreases with increasing UV irradiation time. Whereas the TiO_2 from filtration and centrifugation give lower C/C_0 than P25 and strongly adsorbed the MB in the dark. It is found that TiO_2 from centrifugation technique adsorbs the MB in the dark greater than the TiO_2 from filtration technique. This finding is possibly due to its smaller particle size. Consequently, agglomeration is occurred, both "intra-agglomerated" (particle with other particle agglomeration) and "inter-agglomerated" (group of particle with other group of particle agglomeration). These agglomerations can make many pores in various sizes [24].

The Total degradation of the MB (adsorption and photocatalytic degradation) by the TiO_2 from different sample separation techniques compared with P25 are shown in Fig. 7. This figure shows that the TiO_2 sample from centrifugation technique has degree of degradation (97.69%) higher than the TiO_2 from filtration technique (94.80%) and P25 (93.07%). This result relates with particle size in TABLE I because photocatalytic efficiency as well as adsorption depend on crystallinity and particle size [25]. The photocatalytic activity of the single-phase anatase sample is lower than the anatase–brookite composite [26]. Although the TiO_2 samples from both separation techniques in this work are mostly anatase-brookite composite, the TiO_2 from filtration technique may have higher rutile phase which is a stable phase and less active. For instance, a good photocatalyst should be anatase-brookite composite containing a large fraction of anatase, small fractions of brookite and rutile phases. This may be caused by hetero-junction microstructure between anatase and brookite which can enhance charge separation efficiency, therefore the photocatalytic activity is increased [27].

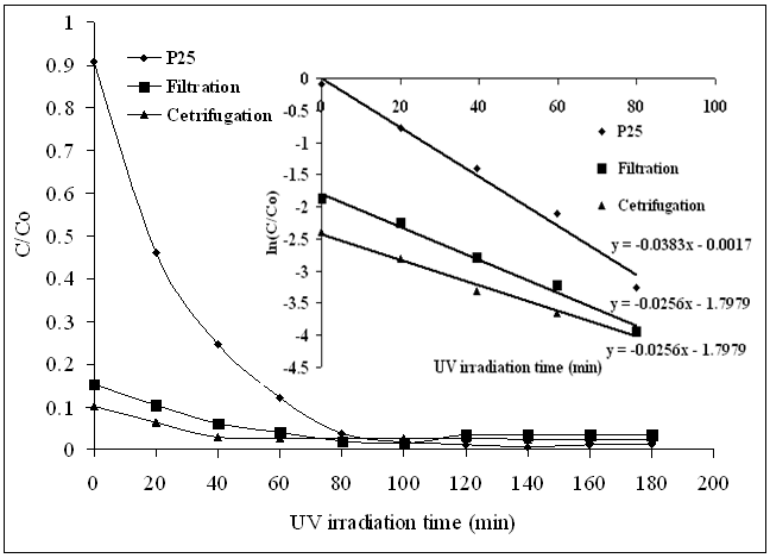

Fig. 7. Photocatalytic oxidation of MB under UV light (—◆—) P25, (—■—) TiO_2 from filtration, and (—▲—) TiO_2 from centrifugation
C/Co = concentration of MB at time t / initial concentration of MB

V. Conclusion

The TiO_2 mixed phase was synthesized successfully by the microwave assisted synthesis from $TiOSO_4$. The separation technique can affect the particle size and morphology of the TiO_2. The particle size of TiO_2 from filtration and centrifugation techniques is 36.12 and 22.60 nm, respectively. The photodegradation rate constants (k) of the TiO_2 from centrifugation technique and filtration techniques are about the same but the degree of MB degradation of the TiO_2 from centrifugation technique (97.69%) is greater than the TiO_2 from filtration techniques (94.80%) and P25 (93.07%) due to its higher adsorption which is resulted from the smaller particle size and higher surface area.

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Nuchanaporn Pijarn was born on April 15, 1978 in Ubon Ratchathani, Thailand. She received her B.Sc. degree in Chemistry from Ubon Ratchathani University in 2001 and became a lecturer at Ubon Ratchathani University. She received her M.Sc. from Mahidol University, Bangkok, Thailand in Applied Analytical and Inorganic Chemistry in 2007 and became an assistant researcher at National Metal and Materials Technology Center (MTEC), Pathumthani, Thailand. Now she is studying Ph. D. in Materials Science at Chulalongkorn University, Bangkok, Thailand.

Sirithan Jiemsililers is the head of Department of Materials Science, Faculty of Science, Chulalongkorn University. The example title of her publications: Effect of nanocrystalline χ-Al_2O_3 structure on the catalytic behavior of Co/Al_2O_3 in CO hydrogenation, and Preparation of tungsten oxide–tin oxide nanocomposites and their ethylene sensing characteristics. She is currently involved in research in developing glass and glass ceramics for glass sealants, bioglasses, chemical durability improvement, gold ruby glass and high performance glass ceramics, Utilizing of industrial wastes in geopolymer, cement and ceramic products, and photocatalytic materials for food packaging and water treatment.

Jinawath is an associate professor at Department of Materials Science, Faculty of Science, Chulalongkorn University. Her publications include: Hydrothermal synthesis of monetite and hydroxyapatite from monocalcium phosphate monohydrate, Gas/solid reaction during sintering of Si_3N_4 ceramics in an air furnace, and Visible-light-driven N–F-codoped TiO_2 powders derived from different ammonium oxofluorotitanate precursors. Her research interest is in Bioceramics: Calcium phosphates, Chemistry of Colloids: Cement Chemistry, Photocatalysts, NIR reflective pigments, Porous Materials, and Zeolite.