A Comparison Study of Photocatalytic Activity of TiO_2 and ZnO on the Degradation of Real Batik Wastewater

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***Abstract*—**Dye wastewater from textile industries are reported to be a major river pollutant. Commercially available photocatalysts, TiO_2, ZnO in micrometer size and ZnO in nanometer size were selected to use for removing dye contaminants in wastewater. Photocatalytic degradation of real Batik wastewater under UV light irradiation was monitored for up to 2 hours duration. It was found that TiO_2 having a better optical absorption spectrum shows a similar degradation efficiency as compared with the micron sized ZnO, attributed to the surface defects of ZnO, while nanosized ZnO show a slightly lower degradation efficiency due to it accompanied with high percentage contaminants (20%). To ensure the robustness upon using the photocatalysts in a high pH level wastewater (pH 11.5), we monitored the stability of the catalysts for 5 hours and the catalysts were found to be stable over the observation period.

***Keywords*—**Photocatalysis, Textile wastewater treatment, Degradation efficiency.

I. Introduction

TEXTILE industries traditionally use a huge amount of water and approximately two percent of dyes that are discharged directly in industrial effluent of which, about 10% are lost during the dying process [1]. The dyes are therefore released into the environment that can lead to adverse effects on the ecosystem due to the toxicity [2]. In addition, the wastewater generated from the textile industry is generally high in both biochemical oxygen demand (BOD) and chemical oxygen demand (COD) because it comprises spent textile dyes, suspended solids, mineral oils, electrolytes, surfactants, etc [3], [4].

Photocatalysis has attracted a lot of attention as effective process in the mitigation of environmental pollution. Photocatalysis is a light induced catalytic process that reduces or oxidize organic molecules through redox reactions activated through the electron-hole pairs generated on the surface of metal oxide semiconductors upon beyond band gap light irradiation [5]. Zinc oxide (ZnO) is a promising candidate as a solar light photocatalytic material since it demonstrates high photocatalytic efficiencies for the degradation of organic pollutants [6]-[11] in comparison to other metal oxides included TiO_2 [12], [13]. Surface area and surface defects of metal oxides are important factors for enhanced photocatalytic activity [9], [14], [15]. The higher effective surface area leads to higher adsorption of organic molecules, while enhanced photocatalytic activities lead to its efficient degradation. Nanoparticles have been a very much attention as they have high surface to volume ratio that can enhance the catalytic activity.

The aim of this research is to study the degradation efficiency of the commercially available photocatalysts in the market in term of percentage of dye removal from real textile wastewater of ZnO as compared with TiO_2. In addition, effect of particles size on photocatalytic activity was also reported and discussed.

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II. Experimental

A. Materials

The reactive dyes wastewater used in this research was obtain from Batik textile entrepreneur in Prachuap Khiri Khan Province, Thailand. Physical properties of the real textile wastewater were measured using EC meter (EUTECH: PCSTestr 35) and reported in Table I.

TABLE I
PHYSICAL PROPERTIES OF BATIK WASTEWATER

	Wastewater	Effluent Standard*
pH	11.73-11.80	5.5 - 9.0
Color	Dark red	Not objectionable

Remark:*From pollution control department (2004) [16].

TiO_2 (Aeroxide™ P25, ACROS Organics™) obtained from Fisher Science, ZnO micron size (< 5μm), named ZnO-Micro and nano size (<100nm), named ZnO-Nano procured from Sigma-Aldrich were used in this research without any purification.

B. Characterization

Each photocatalyst was investigated using field emission scanning electron microscope (FESEM, Hitachi: SU8030)

working at 2.0 kV to record the morphology and size of catalysts. X-ray diffraction (XRD) of as-received ZnO and TiO_2 photocatalyst samples were performed on a PAnalytical X'Pert PRO X-ray diffractometer with Cu K_α radiation with 0.5 second of count time and 0.02 degree of step angle. Specific surface areas (SSA) of catalysts were determined using N_2 gas adsorption technique (Autosorb-1C; Quantachrome Ins.) while Zetasizer (Malvern Instruments) used to determine average particle size and particle size distribution of the photocatalysts.

C. Degradation Test

Photocatalytic activity was evaluated under UV irradiation with a real textile wastewater. A 100 cm^3 wastewater was put in a laboratory-scale reactor (5 cm x 5 cm x 5 cm) and each photocatalyst sample was dispersed inside the reactor facing UV light (5 lamps of UV light source at 254 nm: 6 W each) with continuously stirred during the degradation test. Optical absorption spectra were determined upon different light exposure durations using a UV/Vis spectrophotometer (Shimadzu: UV mini 1240) in order to monitor the rate of degradation by recording the reduction in absorption intensity of wastewater at the maximum wavelength (λ_{max} = 520 nm). The degradation efficiency (DE) was calculated as in equation 1 [17].:

$$DE = \frac{I_0 - I}{I_0} \times 100 \quad (1)$$

where I_0 is the initial absorption intensity of wastewater at λ_{max}= 520 nm and I is the absorption intensity after photo-degradation.

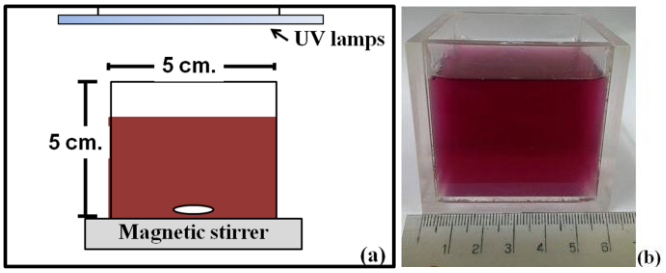

Fig.1 (a) Schematic representative of a dark photocatalysis reactor composing 5 UV lamps and (b) A photograph of photocatalytic reactor that was put in a dark UV chamber during the degradation test

Effect of photocatalyst concentrations (0.005, 0.01, 0.05, 0.0625, 0.075, and 0.1%(w/v)), effect of photocatalyst types (TiO_2, ZnO-Micro particle, and ZnO-Nano particle) were studied and discussed in term of %degradation efficiency.

III. Results and Discussion

A. SEM (Morphology)

Fig. 2(a-c) are SEM images of the as-received TiO_2 and ZnO photocatalyst samples at 50,000× that all samples having hexagonal shape of particles. Average particle size of the photocatalyst samples were determined by measuring particle dimension from 5 SEM images. It was found that average particle size of TiO_2 sample was about 210±1.05 nm, while ZnO-Nano presented a very similar in size and shape as compared with TiO_2 sample (200±0.88 nm). The ZnO-Micro presented a bigger average particle size of about 525±3.27 nm (Fig. 2c).

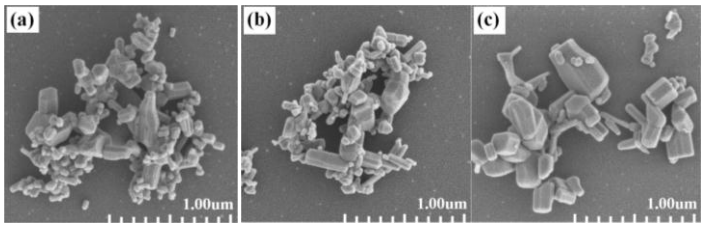

Fig. 2 The morphology of the as-received photocatalyst samples (a) TiO_2, (b) ZnO-Nano, and (c) ZnO-Micro

B. X-ray Diffraction (XRD)

Fig. 3 shows XRD patterns of the as-received photocatalysis. It can be observed that TiO_2 composed of mixed phases of anatase and rutile (Fig. 3a) while both of ZnO samples showed only zincite structure phase (Fig. 3b)

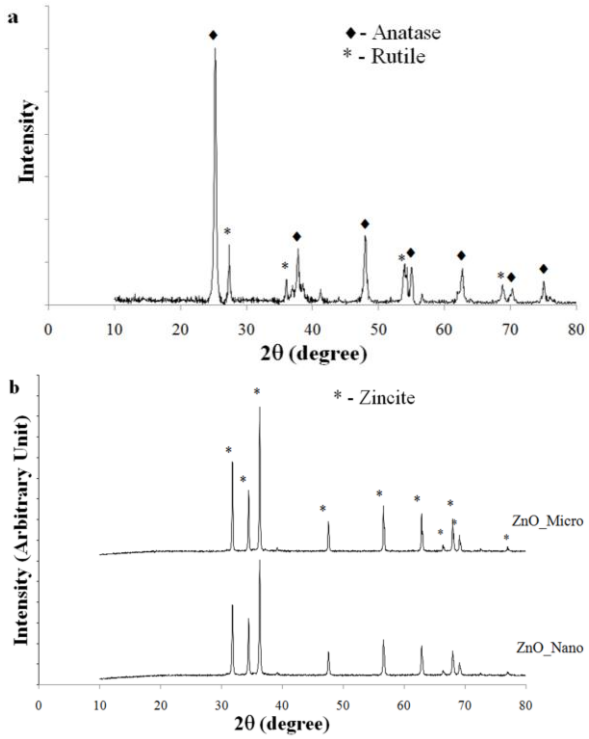

Fig. 3 X-ray diffraction diffractograms of the as-received photocatalyst samples (a) TiO_2, (b) ZnO samples

C. UV-VIS Absorption

Optical absorption spectra of the as-received TiO_2 and ZnO photocatalyst samples are shown in Fig. 4. It can be seen that TiO_2 has the greatest ability to absorb light in the observation wavelength range (250-800 nm) as compared with ZnO samples. The adsorption peak of both ZnO samples and TiO_2 were almost similar located at 371 nm.

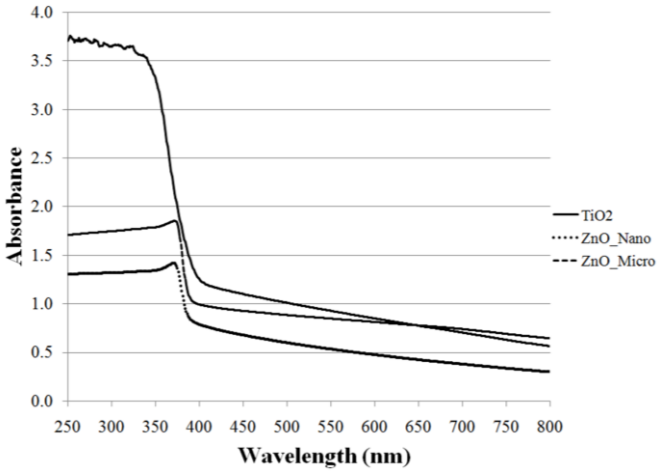

Fig. 4 UV-VIS absorption spectra of the as-received TiO_2, ZnO-Nano, and ZnO-Micro photocatalyst samples

D. Particle Size Distribution (PSD)

The average particle size of TiO_2, ZnO-Nano, and ZnO-Micro samples measured by Zetasizer were 449.1, 441.8, and 725.9 nm, respectively while their particle size distribution were monomodal as shown in Fig. 5. By comparing of particle size obtained from Zetasizer with SEM technique, it can be seen that the particle size obtained from Zatasizer were bigger size than that obtained by SEM technique that because of an agglomeration effect of the nanoparticles.

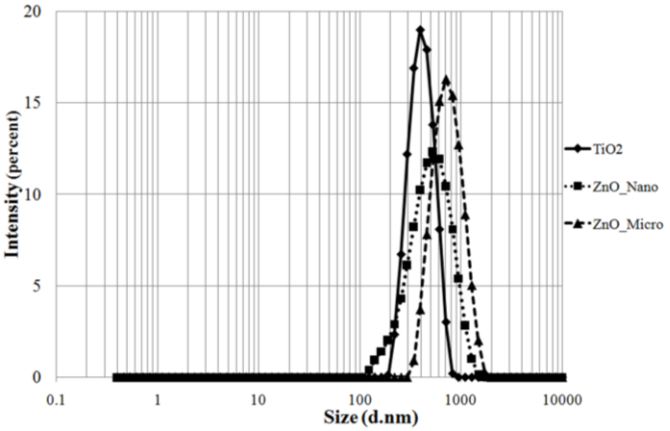

Fig. 5 The particle size distribution of the as-received TiO_2, ZnO-Nano, and ZnO-Micro photocatalyst samples

E. Photocatalytic Activity Test

Photocatalytic activities on the degradation of textile wastewater using TiO_2 photocatalyst at different concentrations, 0.005, 0.01, 0.05, 0.0625, 0.075, and 0.1%wt were carried out under the UV irradiation for 120 min as detailed in experimental section as shown in Fig. 6. From the degradation results in Fig.6, it can be observed that the degradation efficiency gradually increased with an increase TiO_2 concentrations from 0.005% to 0.05% and become decrease after 0.05%. The optimum amount of TiO_2 powders in the wastewater was 0.05% exhibiting the degradation efficiency of 34.92% after 2 hours of UV irradiation. It was also found that too clouded TiO_2 dispersion could be an adverse effect for wastewater treatment as the particles can block the UV light path resulting in the reduction of the degradation efficiency.

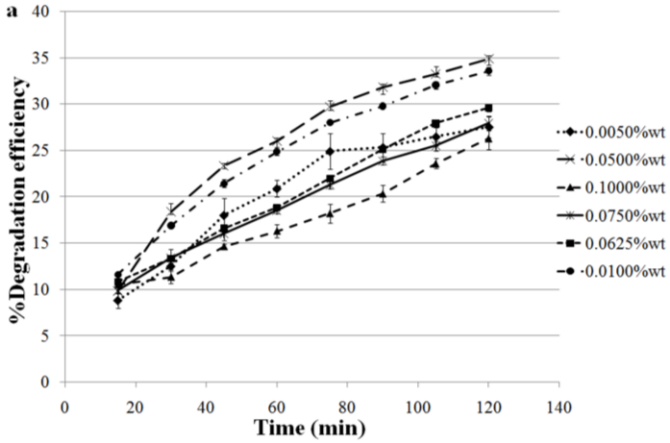

Fig. 6 Plot of %degradation efficiency of textile wastewater treatment using TiO_2 photocatalyst against degradation time at different concentrations (TiO_2 concentration = 0.005, 0.01, 0.05, 0.0625, 0.075, and 0.1%wt., degradation time = 120 minutes under UV irradiation)

The comparison study of the photocatalyst activity of TiO_2, ZnO-Micro, and ZNO-Nano on the degradation of textile wastewater was carried out using 0.05%wt catalyst for up to 120 min as shown in Fig. 7. It can be clearly observed that the ZnO-Nano exhibited a lower photocatalytic activity as compared with ZnO-Micro and TiO_2 that can be attributed to ZnO-Nano having only 80% purity that could be a reason to obtain a lower catalytic activity. When considering the photocatalytic activity of ZnO-Micro and TiO_2, it can be seen that TiO_2 showed a better degradation efficiency than that ZnO-Micro, while after 90 min degradation time ZnO-Micro showed a slightly better degradation efficiency.

To confirm the effect of particles size of the photocatalysts on the degradation efficiency, we conducted separated experiments to determine the effective surface area by examining surface adsorptions. The surface adsorption of the photocatalyst samples were examined by measuring the change of the absorption intensity (at 520 nm) after dispersing the samples into the textile wastewater in the dark for a 30 min period prior to the degradation test.

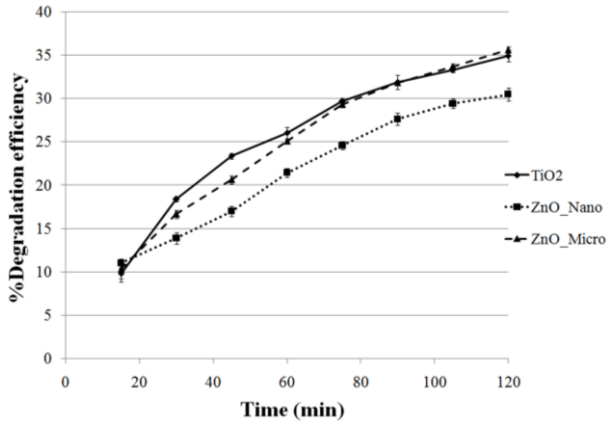

Fig. 7 The photocatalyst activity of TiO_2, ZnO-Micro, and ZnO-Nano on the %degradation efficiency of textile wastewater (photocatalyst concentration = 0.05%(w/v), and time = 120 minutes)

We observed that the ZnO-Micro exhibits the lowest dye adsorption at almost 10.81%, while ZnO-Nano and TiO_2 show significantly higher adsorption (20.66% and 17.29%, respectively), which is related to the increase in the effective surface area of the catalyst as confirmed by N_2 gas adsorption technique (BET theory) (Table II). From the optical absorption spectrum in Fig. 4, TiO_2 shows a better optical absorption spectrum than that ZnO-Micro and ZnO-Nano, however, the photocatalytic activity of ZnO-Micro was almost the same as found in TiO_2. This can be attributed to the surface defect of ZnO photocatalyst over TiO_2 enhancing its photocatalytic activity even it has a very much lower effective surface area [12], [13], [18].

As the textile wastewater are quite strong basic solution (pH 11.73-11.80), the optical absorptions of the catalyst dispersion (0.05%wt) at pH 11.5 were then monitored and plotted against the measuring time to ensure the robustness of the photocatalysts in the real condition usage (Fig. 8). It can be seen that the optical absorption (at 371 nm) of the ZnO-Nano and TiO_2 were almost stable up to 5 hours at pH 11.5, while ZnO-Micro shows a slightly decrease of an absorption peak (at 371 nm) after 2 hours. From the result, all photocatalysts could be used for treating basic range (pH>10) textile wastewater by photocatalysis under UV irradiation.

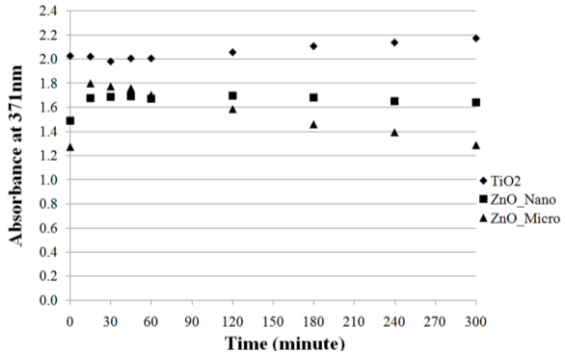

Fig. 8 A plot of optical absorptions (at 371 nm) of the dispersions of TiO2, ZnO-Nano and ZnO-Micro photocatalyst at pH 11.5 versus monitoring time

TABLE II
THE SURFACE AREA OF THE AS-RECEIVED PHOTOCATALYST SAMPLES

Catalyst samples	TiO_2	ZnO-Nano	ZnO-Micro
Dye Adsorption	17.29%	20.66%	10.81%
SSA (BET)($m^2.g^{-1}$)	52.41	9.43	5.39

IV. CONCLUSION

In summary, the commercial available TiO_2 (P25) and ZnO photocatalysts can be the attractive candidates for photocatalytic textile wastewater treatment under UV light. ZnO-Micro and TiO_2 showed a better photocatalytic activity as compared with ZnO-Nano due to ZnO-Nano having high percentage of contaminants even it has a larger effective surface area, while ZnO-Micro exhibited similar photocatalytic degradation as compared with TiO_2. The highest photocatalytic activity was found to be 34.92% upon using both ZnO-Micro that can be used in highly basic wastewater (pH 11.5) with a slightly dissolution effect during the photocatalysis treatment process.

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REFERENCES

[1] J. Easton, "The dye maker's view (Published Conference Proceedings style)," in *Proc. Colour in Dye House Effluent, In: Cooper P,editor Society of Dyes and Colourists*, Bradford, UK, 1995, pp. 11.

[2] Y.M. Slokar, and A. Majcen Le Marechal, "Methods of Decoloration of Textile Wastewaters," DYES. PIGMENTS., vol. 7, 1998, pp. 335-356, Jul. 1997.

[3] W.-J. Lau, and A.F. Ismail, "Polymeric nanofiltration membranes for textile dye wastewater treatment: Preparation, performance evaluation, transport modelling, and fouling control — a review," Desalination., vol. 245, 2009, pp. 321-348, Dec. 2007.

[4] W.B. Group, in *Proc.* Environmental, Health, and Safety Guidelines - Textile Manufacturing, 2007.

[5] S.W. Powell, "Method for Electrocoagulation of Liquids," in US. patent no 6488835 B1.

[6] J. Strunk, K. Kaher, X. Xia, and M. Muhler, "The surface chemistry of ZnO nanoparticles applied as heterogeneous catalysts in methanol synthesis," SURF. SCI., vol. 603, 2009, pp. 1776-1783, Jan. 2009 http://dx.doi.org/10.1016/j.susc.2008.09.063.

[7] F.W. Gilmore, "Electrocoagulation Chamber and Method," in US. patent no 6613217 B1.

[8] R. Ullah, and J. Dutta, "Photocatalytic degradation of organic dyes with manganese-doped ZnO nanoparticles," J. HAZARD. MATER., vol. 156, 2008, pp. 194-200, Dec. 2007.

[9] J. Huang, X. Xu, C. Gu, W. Wang, B. Geng, Y. Sun, and J. Liu, "Effective VOCs gas sensor based on porous SnO_2 microcubes prepared via spontaneous phase segregation," SENSOR. ACTUATOR. B: Chemical, vol. 173, 2012, pp. 599-606, Jul. 2012.

[10] S. Danwittayakul, M. Jaisai, and J. Dutta, " Efficient solar photocatalytic degradation of textile wastewater usingZnO/ZTO composites," APPL. CATAL. B: Environmental, vol. 163, 2015, pp. 1–8. Jul. 2014.

[11] S. Danwittayakul, M. Jaisai, and J. Dutta, "Enhancement of Photocatalytic Degradation of Methyl Orange by Supported Zinc Oxide Nanorods/Zinc Stannate (ZnO/ZTO) on Porous Substrates," IND. ENG. CHEM. RES., vol. 52, 2013, pp. 13629−13636, Jul. 2013.

[12] A.M. Ali, E.A.C. Emanuelsson, and D.A. Patterson, "Photocatalysis with nanostructured zinc oxide thin films: The relationship between morphology and photocatalytic activity under oxygen limited and oxygen rich conditions and evidence for a Mars Van Krevelen mechanism," APPL. CATAL. B: Environmental, vol. 97, 2010, pp. 168-181, Mar. 2010.

[13] S.K. Pardeshi, and A.B. Patil, "Effect of morphology and crystallite size on solar photocatalytic activity of zinc oxide synthesized by solution free mechanochemical method," J. MOL. CATAL. A: Chemical, vol. 308, 2009, pp. 32-40, Mar. 2009.

[14] M. Mahmood, and J. Dutta, "Microwave assisted hydrothermal synthesis of zinc hydroxystannate films on glass substrates," J. SOL-GEL. SCI. TECHN., vol. 62, 2012, pp. 495-504, Jun. 2012.

[15] G.A. Tipton, H.M. Slack, "Cells and Electrodes for Electrocoagulation Treatment of Waste Water," in US. patent no 6972077 B2.

[16] Information on http://www.pcd.go.th/info_serv/en_reg_std_water 04. html.

[17] N. Modirshahla, A. Hassani, M.A. Behnajady, and R. Rahbarfam, "Effect of operational parameters on decolorization of Acid Yellow 23 from wastewater by UV irradiation using ZnO and ZnO/SnO2 photocatalysts," Desalination., vol. 271, 2011, pp. 187-192, Apr. 2011.

[18] M. Qamar, M. Muneer, "A comparative activity of titanium oxide and zinc oxide by investigating the degradation of vanillin," Desalination., vol. 249, 2009, pp. 535-540, Jan. 2009.