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APPENDICES

APPENDIX A

Publications Resulting from This Research Work

PUBLICATIONS

National Proceedings

1. **Thongprachan, N., Viriya-empikul, N., Charinpanitkul, T., and Tanthapanichakoon, W.** Initial Intrinsic Rates of Photocatalytic Decomposition of Organic Dyes and Compounds Using Titanium Dioxide Nanoparticles. Proceedings of Thailand Materials Science and Technology Conference 4th, pp. 218-220. March 31 to April 1, 2006, Thailand, 2006.

Initial Intrinsic Rates of Photocatalytic Decomposition of Organic Dyes and Compounds Using Titanium Dioxide Nanoparticles

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Abstract

Two titania with different average crystallite sizes (T1: 30, and N1: 400-500 nm) and specific surface areas (50-250 m²/g) were investigated in this work. To examine decomposition performance, an equal amount (2 mg) of each titania is dispersed in 10 ppm of four different simulated wastewater (20 mL) contaminating: Black 5, methylene blue, lignin, and phenol. Adsorption of each pollutant on the two titania was investigated in darkness. T1 can adsorb more methylene blue (8.32 %) and phenol (4.21 %) than N1. While Black 5 and lignin were not observed. It was found that T1 provided the best decomposition efficiency of all organic compounds with irradiation by two 30-Watt UV lamps. Its decomposition efficiency with respect to Black 5, methylene blue, lignin, and phenol was 92.5, 96.22, 90.24, 19.72 % after 60 minutes, respectively.

1. Introduction

At present, water pollution has been recognized as a serious environmental problem. The major sources of pollutants are manufacturing processes, especially in chemical industry. In recent years, many researchers are interested in applying the “photocatalytic decomposition process” to the treatment of hard-to-biodegrade organic pollutants in industrial wastewater [1,2]. The advantages over other traditional methods are its high potential for high-level degradation of organic compounds under ambient condition within a short period with negligible formation of undesirable by-products. TiO₂ is the most popular photocatalyst employed in practical applications due to its relatively low price, non-toxicity, high chemical stability, etc [3]. Titania exists in three crystalline structures (anatase, rutile, and brookite phases) which behave differently [4]. Even titania of the same morphology and phase could show different performances which depend on the specific surface area, crystallite size and porous structure.

In this work, the intrinsic decomposition rate and adsorption efficiency of two different titania samples against four aqueous organic substances -- Black 5, methylene blue, lignin, and phenol -- were

investigated experimentally and the results were discussed with respect to the crystalline phase and average crystallite size of the titania samples.

2. Experimental

2.1 Experimental procedure

The experiments consisted of dispersing 2 mg of the titania samples (see Table 1) in 20 ml of 10 ppm organic solution and the samples were irradiated with two 30-Watt UV-C lamps (Philips G30T8), while they were mechanically shaken to ensure good dispersion of the titania in each sample (Fig.1) [5]. The experiments were carried out at room temperature. For comparison, the selected titania was also suspended in a organic solution with shaking but without UV-C light irradiation.

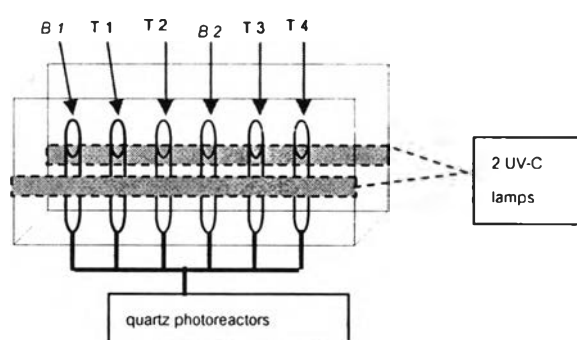


Fig.1. Arrangement of reactors and lamps in the shaker (T1, T2, T3, and T4 are test tubes having organic solution and titania, B1 and B2 are test tubes having only organic solution).

Table 1 Physical characteristics of titania sample.

Code name	T1 ^a	N1 ^o
Crystal phase	Anatase	Anatase
TiO ₂ content (wt.%)	98	Apatite coated
Avg. crystallite size (nm)	30	400-500
Particle shape	Sphere	Sphere, cylinder
Specific surface area (m ² /g)	56-59	64

^aTitania samples and their properties are provided by Prof. Yasushige Mori, Doshisha University.

^oApatite-coated titania samples and their properties are provided by Nonami Science (Thailand) Co., Ltd.

There are two types of experiments as follows:

Type 1. Tests to find out the adsorption efficiency of each of the nano-titania against organic solution without any exposure to light for either 10 and 60 min.

Type 2. Tests to find out the efficiency of photocatalytic decomposition plus adsorption of each of the nano-titania against organic solution after exposure to UV light for either 10 or 60 min.

2.2 Analysis

Prior to each residual concentration analysis, TiO₂ powder suspended in the aqueous sample will be separated by centrifuging (3800 rpm, 15 min). Then residual concentration of Black 5, methylene blue, or lignin in the supernatant liquid will be analysed by a UV-Vis spectrophotometer (Jan Way, 6405 UV/Vis) at wavelength 595 nm, 660 nm or 280 nm, respectively. While the residual concentration of phenol in the supernatant liquid will be analyzed by a high-pressure liquid chromatography (HPLC) using a Shimadzu column (Class VP), with 60% methanol: 40% water as the mobile phase and the UV-Vis detector using a wavelength of 270 nm.

3. Results and Discussion

3.1 Adsorption

In Table 2 the values of % removal of organic compounds by adsorption are the averages of those observed at 10 min and 60 min which were found to differ only slightly. This means that adsorption equilibrium was essentially reached after only 10 min. from the start. Table 2 shows the adsorption capacity of organic compounds by each titania samples. Between the two types of titanias, it is considered that T1 can adsorb more methylene blue and phenol than N1 because the effective specific surface area of T1 is much higher than N1 whose surface is partially coated with apatite. For black 5 and lignin, we observe that the titania powder separated out by centrifugation retained its white color. This phenomenon is consistent to the finding that the adsorption of Black 5 on the 2 nano-titania is negligible because Black 5 and lignin molecules are much more bulky than MB and phenol.

Table 2 Adsorption of organic compounds by each titania sample.

Organic compounds	Avg. adsorption efficiency (%)	
	T1	N1
Black 5	0	0
Methylene blue	8.32	8.28
Lignin	0	0
Phenol	4.21	1.77

3.2 Intrinsic photocatalytic decomposition

Table 3 shows that T1 is the most active for all compounds. The photocatalytic decomposition of phenol was most different because its molecular structure is much smaller and only one single bond, thereby requiring more energy for breaking the weakest bond. The decomposition of organic compounds by T1 is much higher than N1 because the effective metal surface area of nano-sized T1 is higher than the micro-sized N1. Furthermore, a part of incidental photons are obstructed by the apatite particles on N1 before contacting the TiO₂ surface.

Table 3 Intrinsic photocatalytic decomposition of organic compounds by each titania sample.

Organic compounds	Avg. decomposition efficiency at 60 min (%)		Initial rate constant (min^{-1})	
	T1	N1	T1	N1
Black 5	92.50	26.78	0.79	0.009
Methylene blue	96.22	31.77	0.30	0.0073
Lignin	90.24	*	0.06	*
Phenol	19.72	2.87	0.0179	0.0106

* Concentration of lignin could not be measured.

4. Conclusions

T1 is more effective than N1 as photocatalyst and adsorbent because the effective specific metal surface area of T1 is higher than N1. The initial reaction rate of T1 in degrading organic compounds can be approximated as first-order reaction. However, the problem of catalyst particle loss from elutriation during catalyst recycle is still unsolved. A suitable continuous reactor for the photocatalytic decomposition process is desirable, such as a simple rotary drum filtering reactor. The design and operation of such a catalyst will be reported.

Acknowledgement

The author is grateful to Prof. Mori Yasushige of Doshisha University and Nonami Science (Thailand) Co., Ltd. for providing nanotitania samples and New Energy and Industrial Technology Development Organization (NEDO) for financial support.

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APPENDIX B

Experimental Results

Shaker---photoreactor

Adsorption of phenol on TiO₂ powder

Average residual concentration of phenol and TOC using TiO₂ powder without exposed to UV-C

Time (min)	C _i (ppm)	C _b (ppm)	C _f (ppm)	TOC _i (ppm)	TOC _b (ppm)	TOC _f (ppm)
10	9.1968	9.0016	8.6140	8.1910	8.8615	8.9005
60	9.4903	9.2260	8.7826	8.2310	8.2820	8.6568

Total removal efficiency of phenol by TiO₂ powder

Average residual concentration of phenol and TOC using TiO₂ powder with exposed to UV-C

Time (min)	C _i (ppm)	C _b (ppm)	C _f (ppm)	TOC _i (ppm)	TOC _b (ppm)	TOC _f (ppm)
10	9.2486	7.2884	6.9155	8.6230	8.5460	8.5140
30	9.2424	6.3334	4.3488	9.4510	9.1170	7.8980
60	9.5247	4.8658	2.5869	8.8270	8.4615	7.1920
90	9.1525	3.9428	1.7398	9.0810	8.1140	6.3208
120	8.9855	2.7958	1.1531	8.7370	8.6760	6.0605

Rotary drum filtering reactor---photoreactor

Effect of rotating speed of the drum on phenol removal

Phenol and TOC change with irradiation time at various rotating speeds of the drum using filtration velocity 0.73 cm min⁻¹.

Time (min)	5 rpm		10 rpm		20 rpm		30 rpm	
	C/C ₀	TOC/TOC ₀	C/C ₀	TOC/TOC ₀	C/C ₀	TOC/TOC ₀	C/C ₀	TOC/TOC ₀
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
15	0.9259	0.9676	0.9940	0.9965	*	0.9946	*	*
30	*	0.9653	0.9798	0.9848	0.9697	0.9811	0.9865	*
45	0.9131	0.9419	0.9626	0.9783	*	*	*	0.9825
60	0.9015	0.9368	0.9447	0.9679	0.9672	0.9625	*	*
90	0.8921	*	0.9381	0.9566	0.9558	0.9778	0.9640	0.9729
120	0.8717	0.9229	*	*	0.9199	0.9699	*	0.9449
150	*	*	0.9149	*	0.8948	0.9448	0.9166	*
180	0.8533	*	0.8909	0.9449	0.8857	0.9428	0.9059	0.9409
240	0.8214	0.9120	0.8780	0.9380	0.8850	0.9387	0.9007	*
300	0.7898	0.8895	0.8461	0.9184	*	0.9457	*	0.9252
360	0.7853	0.8510	0.8154	0.8768	0.8776	0.9045	0.8999	0.9068

* refers to the error data from the analyzer.

Effect of filtration velocity on phenol removal

Phenol and TOC change with irradiation time at various filtration velocities and rotating speed of the drum.

Time (min)	0.73 cm min ⁻¹				0.84 cm min ⁻¹				0.52 cm min ⁻¹			
	5 rpm		10 rpm		5 rpm		10 rpm		5 rpm		10 rpm	
	C/C ₀	TOC/TOC ₀	C/C ₀	TOC/TOC ₀	C/C ₀	TOC/TOC ₀	C/C ₀	TOC/TOC ₀	C/C ₀	TOC/TOC ₀	C/C ₀	TOC/TOC ₀
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
15	0.9259	0.9676	0.9940	0.9965	*	0.9826	*	*	0.9907	0.9932	*	0.9846
30	*	0.9653	0.9798	0.9848	*	*	*	*	0.9782	*	*	*
45	0.9131	0.9419	0.9626	0.9783	*	0.9794	*	0.9840	0.9756	0.9871	0.9648	0.9672
60	0.9015	0.9368	0.9447	0.9679	0.9409	0.9753	0.9699	0.9837	0.9480	0.9776	*	0.9618
90	0.8921	*	0.9381	0.9566	*	0.9632	0.9599	0.9599	*	*	0.9498	0.9611
120	0.8717	0.9229	*	*	*	0.9555	*	*	0.9298	0.9745	0.9389	*
150	*	*	0.9149	*	*	0.9393	0.9371	*	0.9204	0.9628	0.9256	0.9468
180	0.8533	*	0.8909	0.9449	*	0.9368	*	0.9477	0.8829	0.9559	*	0.9414
240	0.8214	0.9120	0.8780	0.9380	0.9113	*	*	0.9384	*	0.9498	*	0.9279
300	0.7898	0.8895	0.8461	0.9184	0.8927	*	0.9147	0.9246	0.8478	0.9304	0.8967	0.9168
360	0.7853	0.8510	0.8154	0.8768	0.8510	0.9065	0.8741	0.9180	0.7813	0.9217	0.8857	0.8863

* refers to the error data from the analyzer.

Effect of direct photolysis on the phenol removal

Phenol and TOC change with irradiation time using filtration velocity of 0.73 cm min^{-1} and rotating speed of the drum of 5 rpm.

Time (min)	C/C ₀	TOC/TOC ₀
0	1.0000	1.0000
15	0.9856	0.9729
30	*	*
45	*	*
60	0.9708	*
90	*	*
120	*	*
150	*	*
180	*	0.9406
240	0.9728	*
300	0.9526	0.9363
360	0.9504	0.9324

* refers to the error data from the analyzer.

Adsorption of phenol on TiO₂ cake

Phenol and TOC change with experimental duration using filtration velocity of 0.73 cm min^{-1} and rotating speed of the drum of 5 rpm.

Time(min)	C/C ₀	TOC/TOC ₀
0	1.0000	1.0000
15	0.9923	0.9841
30	0.9905	*
45	*	0.9663
60	0.9796	*
90	*	0.9634
120	*	0.9591
150	0.9606	0.9406
180	0.9536	*
240	*	0.9327
300	0.9458	*
360	0.9254	0.9316

* refers to the error data from the analyzer.

Calibration curve of phenol @ wavelength 254 nm

Mobile phase: 25% acetonitrile/ 75% water

Flow rate of mobile phase: 0.6 mL min⁻¹

Column temperature: 30 °C

Injection
volume: 10 µL

Phenol

(1: 254
nm, 8 nm)

Average RF: 0.000166593

RF StDev:
2.57747e-006

RF %RSD:
1.54717

LSQ Weighting:
None

Force Through
Zero: On

Scaling: None

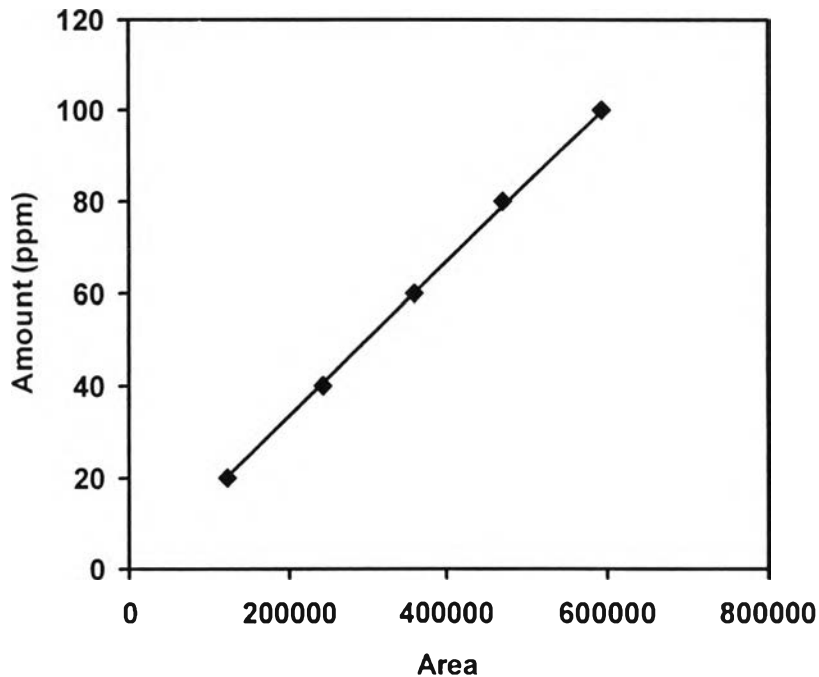
Replicate Mode: Replace

Fit Type: Linear

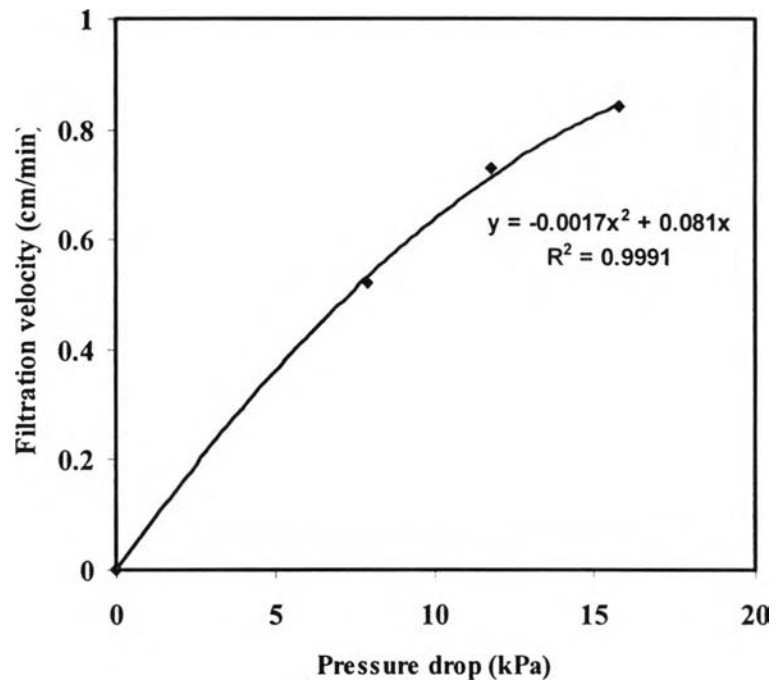
$y = 0.000168134x + 0$

Goodness of fit (r^2): 0.999604

	Level 1	Level 2	Level 3	Level 4	Level 5
Area	122487	242991	358838	472311	593542
Amount	20	40	60	80	100
RF	0.000163283	0.000164615	0.000167206	0.00016938	0.00016848



Calibration curve of filtration velocity vs. pressure drop across TiO₂ cake of 200 μm.



APPENDIX C

Experimental Procedure of Rotary Drum Filtering Reactor System

Experimental

Stage 1 Equipments checking

1. Connect the unit to the electric network.
2. Check that the motor of the rotating drum is lubricated and it has oil enough for its functioning.
3. Check that the motor of the vacuum pump is lubricated and it has oil enough for its functioning.
4. Check that the valves V-1, V-3, V-4 and V-7 are closed.
5. Check that the valves V-2, V-5, V-6, V-8, and V-9 are opened.

Stage 2 Cake forming

6. The slurry is prepared in the feeding tank T-1, mixing the TiO₂ powder in 25 L of D.I. water.
7. Switch on the feeding pump P-1 for mixing of the slurry.
8. Make the drum rotate and set a low rotation speed (approx. 15 rpm)
9. Turn on the valve V-3 and adjust the valves V-3 and V-2 at appropriate flow rate of the slurry feed.
10. Switch on the vacuum pump VP-1.
11. Slowly adjust the valves V-8 and V-10 at appropriate the vacuum degree.
12. At the same time the circulation pump P-2 has to be switched on.
13. Slowly adjust the valves V-5 and V-6 at appropriate flow rate of liquid circulation.
14. An uniform solid layer should quickly settle on the external surface of the drum.
15. The circulation pump P-2 continue draws filtered water.

Stage 3 Photocatalytic experiments

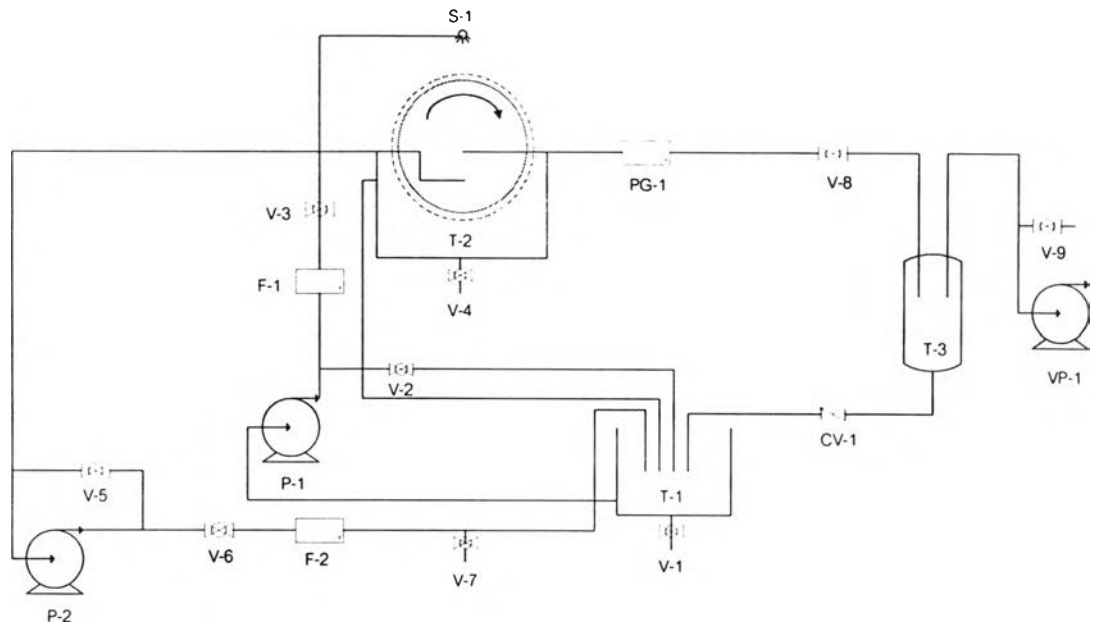
16. Close the valve V-3.
17. Dissolve 1250 mg of phenol in the feeding tank T-1 for preparing the 50 ppm of phenol solution.
18. Stir the phenol solution in the feeding tank T-1 for 5 min (well-mixing).
19. Circulate the system with phenol solution and take the sample for initial conc.
20. Switch on the UV lamp (set t = 0 at this time).
21. Open the valve V-3 and adjust this valve at appropriate flow rate of feed.
22. Take the sample at the valve V-7 every 15 min.
23. The residual phenol concentration is analysed by HPLC.
The residual total organic carbon (TOC) in phenol solution is analysed by TOC analyzer.

Stage 4 Shut down

24. Switch off the UV lamp.
25. Switch off the feeding pump P-1 and the circulation pump P-2.
26. Drain the solution in the experiment system at the valves V-1 and V-4.
27. Switch off the motor of rotating drum.
28. Switch off the vacuum pump VP-1.

Stage 5 TiO₂ Activation

29. Repeat stages 1 and 2, excepting steps 6 and 7.
30. Switch on the UV lamp, activating TiO₂ cake for 90 min.
31. Repeat stages 3 and 4.



A schematic diagram of the setup of TiO₂ cake-covered rotary drum filtering reactor.

Thickness of TiO₂ cake calculation

$$\text{Weight of particles (g)} = \frac{\text{Density of particle (g cm}^{-3}) \times 10^6}{\text{Total volume of particles (m}^3)}$$

$$\text{Total volume of particles (m}^3) = \text{Volume of cake (m}^3) \times (1 - \text{void fraction})$$

$$\text{Volume of cake (m}^3) = \frac{\text{Cake thickness (mm)} \times \text{Cross-sectional area of filter (m}^2)}{1000}$$

where density of TiO₂ = 3.84 g cm⁻³

void fraction = 0.384

cross-sectional area of filter = 0.0661 m²

VITA

Ms. Napawon Thongprachan was born on July 4, 1982 in Bangkok, Thailand. In 2004, I received and got the first class honor in Bachelor's Degree of Chemical Engineering from Mahidol University. My senior project studied about the PMMA membrane synthesis by the wet phase separation technique. I had an experience in gas field at TIG company. I was a trainee engineer who study and monitor the process estimated by Toolkit program. After that, I gained admission to Graduate School of Chulalongkorn University and graduated in 2006 with the thesis entitled "A novel rotary drum filtering reactor for photocatalytic decomposition of phenol in slurry containing titanium dioxide nanoparticles".

