Photocatalytic Treatment of Colored Wastewater

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De la Salle University

PCIEERD 4th Anniversary
EDSA Shangri-La Hotel, Ortigas Center
June 27, 2014

ERDT RESEARCH PROGRAM

- TRACK: Environment & Infrastructure
  - Dr. Benito Pacheco – chair
- DRINK: Drinking water for everyone
  - Dr. Analiza Rollon – head
- Dr. Susan Gallardo- Project Leader
  - Dr. Josephine Borja & Dr. Carmela Centeno – co-proponent
  - Dr. Anton Purnomo, Engr. Eden Mariquit & Kathleen Lansigan - Project assistants
  - Jurex Gallo (PhD scholar), Kerry Cabral & Mary Ann Mactal (MS scholars)
  - Prof. Hirofumi Hinode & Dr. Pailin Ngaotrakanwiwat
- Saffron Phils. Incorporated– industry partner

Time line of the R & D Program

RESEARCH ACTIVITY

2008 → Survey of Textile Industry, Dye Persistency Test

2009 → Preparation of Catalyst by Solgel and Catalyst Charaterization

ERDT Monitoring Visit

2010 → Effect of TiO2 Loading on Photocatalytic Decolorization of Methyl Orange

ERDT Monitoring Visit

Optimization of Parameters in photocatalytic degradation of TBD and Methyl Orange

2011 → Development of a Recirculating Reactor in Photocatalytic TBD Degradation

2012 → Pilot Scale Investigation of Solar Photodegradation of Textile Wastewater with TBD

OUTPUT

Presentation in 2nd ERDT Conference 2008

Progress Report, Dissemination Workshop, Presentation in 3rd ERDT Conference

Progress Report, Dissemination Workshop, Presentation in 5th ERDT Conference and RSCE 2010

Presentation in 7th ERDT Conference and RCCE 2011, Patent Application

Publications in AEJ and AJChE

Operation Manual, Terminal Report and Thesis

Plant Visit (Saffron Philippines Inc.) April 13, 2009

[L-R] Mr. Maca, Mr. Chu, Mr. Dacanay, Mr. Cabral, Mr. Gallo and Dr. Gallardo

Plant Visit (Saffron Philippines Inc.) April 13, 2009

Plant Visit (Saffron Philippines Inc.) April 13, 2009

List of Publications

(1) Gallo, J., Borja, J., Mariano m., and Gallardo , S., Photocatalytic Degradation of Turquoise Blue Dye Using Immobilized AC/TiO2: Optimization of Process Parameters and Pilot Scale Investigation. Accepted for Presentation in RSCE 2014.
(2) Gallo, J., Borja, J., Salim, C., Ngaotrakanwiwat, P., Hinode, H., and Gallardo S. 2012. "Optimization for Photocatalytic Color Removal of Turquoise Blue Dye C.I. 199 in Immobilized AC/TiO2 and UV System using Response Surface Methodology" Asean Engineering Journal,
(3) Mariano, M., Kho, M and Lucanas A. Pilot Scale Investigation of the Solar Photodegradation of Wastewater Containing TBD using Nanotitania- Activated Carbon Composite Catalyst, 2012. BS Thesis De La Salle University. Manila
(4) Mactal M., Optimization of Process Parameters for the Photocatalytic Removal of TBD in Water Matrix using AC/Nanotitania Catalyst. 2011. MS Thesis De La Salle University. Manila
(5) Gallo, J., Borja, J., Salim, C., Ngaotrakanwiwat, P. and Hinode, H., 2011. "Nanotitania- Activated Carbon with Enhanced Photocatalytic Activity: A Comparison Between Suspended and Immobilised Catalyst for Turquoise Blue Removal", Asean Journal in Chemical Engineering, Vol. 11, No. 2, pp. 59-69.
(6) Gallo, J., Borja, J., Gallardo, S., Salim, C., Ngaotrakanwiwat, P., & Hinode, H. Development of a Photocatalytic Reactor with Immobilized AC for Turquoise Blue Removal. Poster Presentation in the 7th ERDT Conference 2011.
(7) Gallo, J., Borja, J., Gallardo, S., Ngaotrakanwiwat, P., & Hinode, H. (2011). Photocatalytic degradation of turquoise blue dye in immobilized nanoTiO_2-AC and UV system: Optimization using response surface methodology. In the proceedings of 3rd RCCE.
(8) Gallo, J., Mactal, M., Borja, J., Gallardo, S., & Hinode, H. (2010). Nanotiitania-activated carbon with enhanced photocatalytic activity: A comparison between suspended and immobilized catalyst for turquoise blue removal. In the Proceedings of 17th RSCE.
(9) Cabral, K., Gallo, J., Salim, C., Hinode, H., Borja, J., & Gallardo, S. (2010). Optimization of process parameters using Box-Behnken experimental design for the photocatalytic decolorization of methyl orange in aqueous medium. In the Proceedings of 5th ERDT Conference: *Philippine Competitiveness through ERDT*. Manila, Philippines.
(10) Gallo, J., Cabral, K., Centeno, C., Borja, J., & Gallardo S. (2009). Characterization of nano-titania prepared by sol-gel method and photocatalytic studies in dye degradation. In the Proceedings of ASEAN RSCE: *Chemical Engineering at the Forefront of Global Challenges*.
(11) Cabral. K. P., Gallo, J. C., Borja, J. Q. & Gallardo, S. M. (2009). Effect of TiO_2 loading on the photocatalytic decolorization of methyl orange. In the Proceedings of 3rd ERDT Conference: *Post-graduate Multi-disciplinary Approach to Solving Philippine Problems*. Manila, Philippines.
(12) Cabral, K. P., Borja, J. Q., Centeno, C. R., & Gallardo, S. M. (2008). Synthesis, characterization, and activity testing on nanotitania photocatalyst calcined at 400 and 500 ^oC: *A start-up experiment. In the Proceedings of 2nd ERDT Conference: Synergy in Multi-disciplinary R&D*. Manila, Philippines.
(13) Gallo, J. C., Co, R. A. S., Mariquit, E. G., Cabral, K. P., Borja, J. Q., & Gallardo, S. M. (2008). Assessment of the colored wastewater in the Philippine textile industry and preliminary study on the color removal of wastewater using photocatalysis. In the Proceedings of 2nd ERDT Conference: *Synergy in Multi-disciplinary R&D*. Manila, Philippines.

Introduction


- The release of the synthetic dyes in textile industries in the environment, is considered to be a major environmental issue that needs to be addressed properly
- Employing Advanced Oxidation Processes (AOPs) using UV-TiO_2 provides a promising treatment of these commercial wastewaters
- The target users of these technologies would be the company involved in the textile industries
  - to meet standards of DENR,
  - prevent water pollution and degradation of aquatic life
  - foster environmental responsibility within the industry ensuring sustainable development

Objectives of the Study

- The research objective is to treat wastewater effluent containing dyestuffs by photocatalysis, particularly using the UV-TiO_2 system.
- Specific objectives are as follows:
  - To assess the color problem of a textile industry in the Philippines.
  - To prepare a composite catalyst AC/TiO_2 using the sol-gel method for photocatalytic oxidation of dye.
  - To characterize the catalysts prepared using BET, SEM- EDX, TEM, TGA , FTIR and XRD.
  - To perform adsorption and photocatalytic activity tests to determine the performance of the catalysts prepared
  - To conduct optimization of operating parameters
  - To conduct kinetic study and toxicity study
  - To facilitate transfer of technology to an industry partner

Photocatalysis

- ✓ Semiconductors need to absorb energy from light that is equal or more than its energy gap
- ✓ Electrons are promoted from valence band to conduction band leaving electron hole pair
- ✓ Electron and hole partake in redox reaction producing hydroxyl radicals and superoxide.
- ✓ Hydroxyl radicals and superoxide formed are responsible for degradation of dyes.

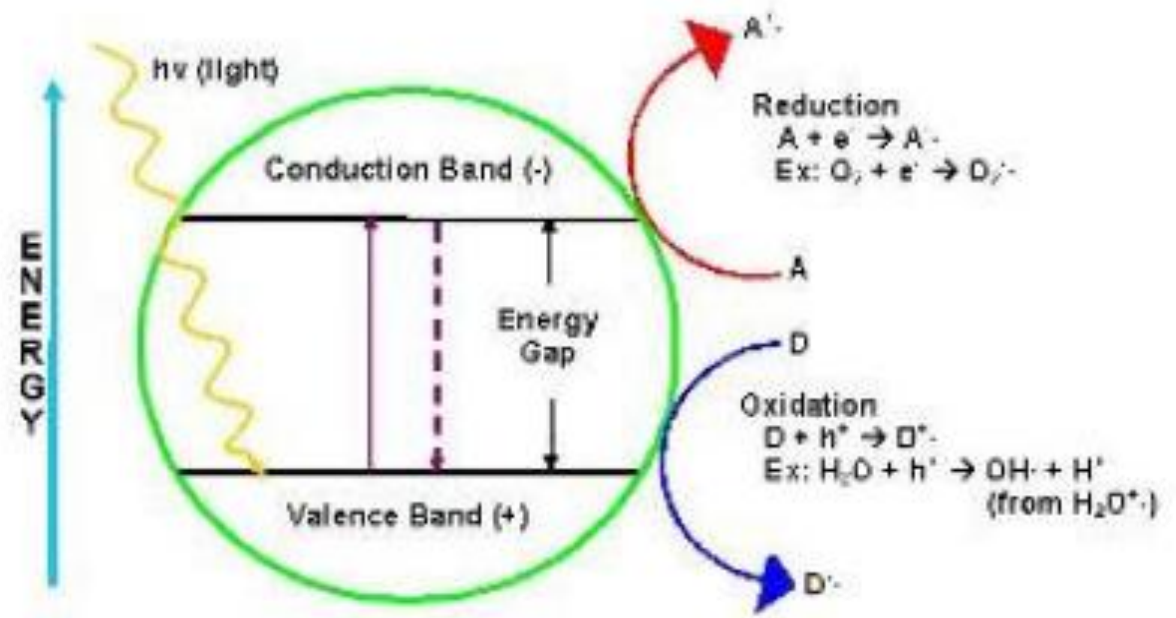
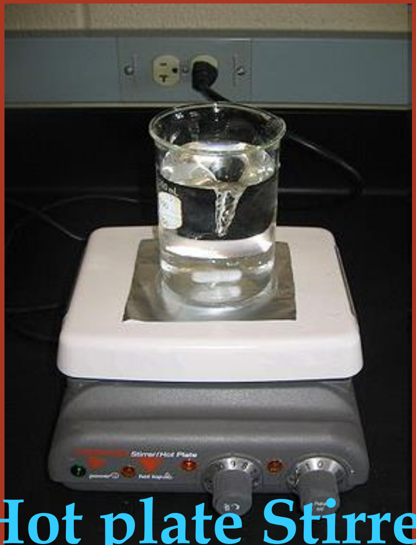


Fig. 3.5 Photocatalysis (http://dev.nsta.org/evwebs/1952/home.htm)

LABORATORY INVESTIGATIONS

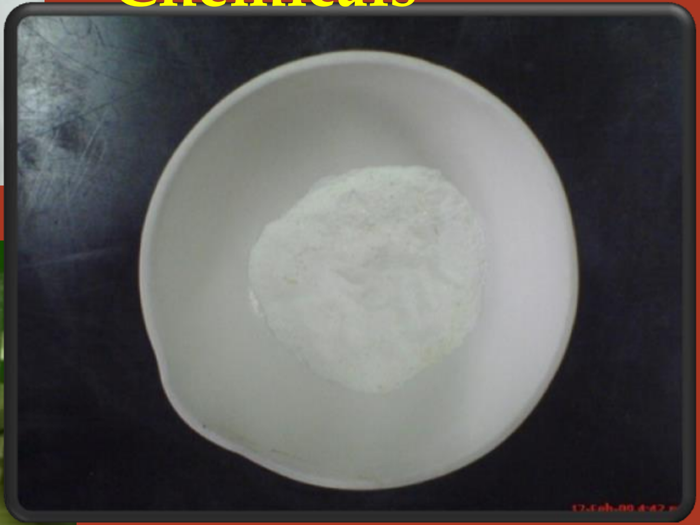
Methods: Scientific Equipment and Laboratory Facilities



Hot plate Stirrer

Ultrasonicator

Chemicals



Prepared Catalyst

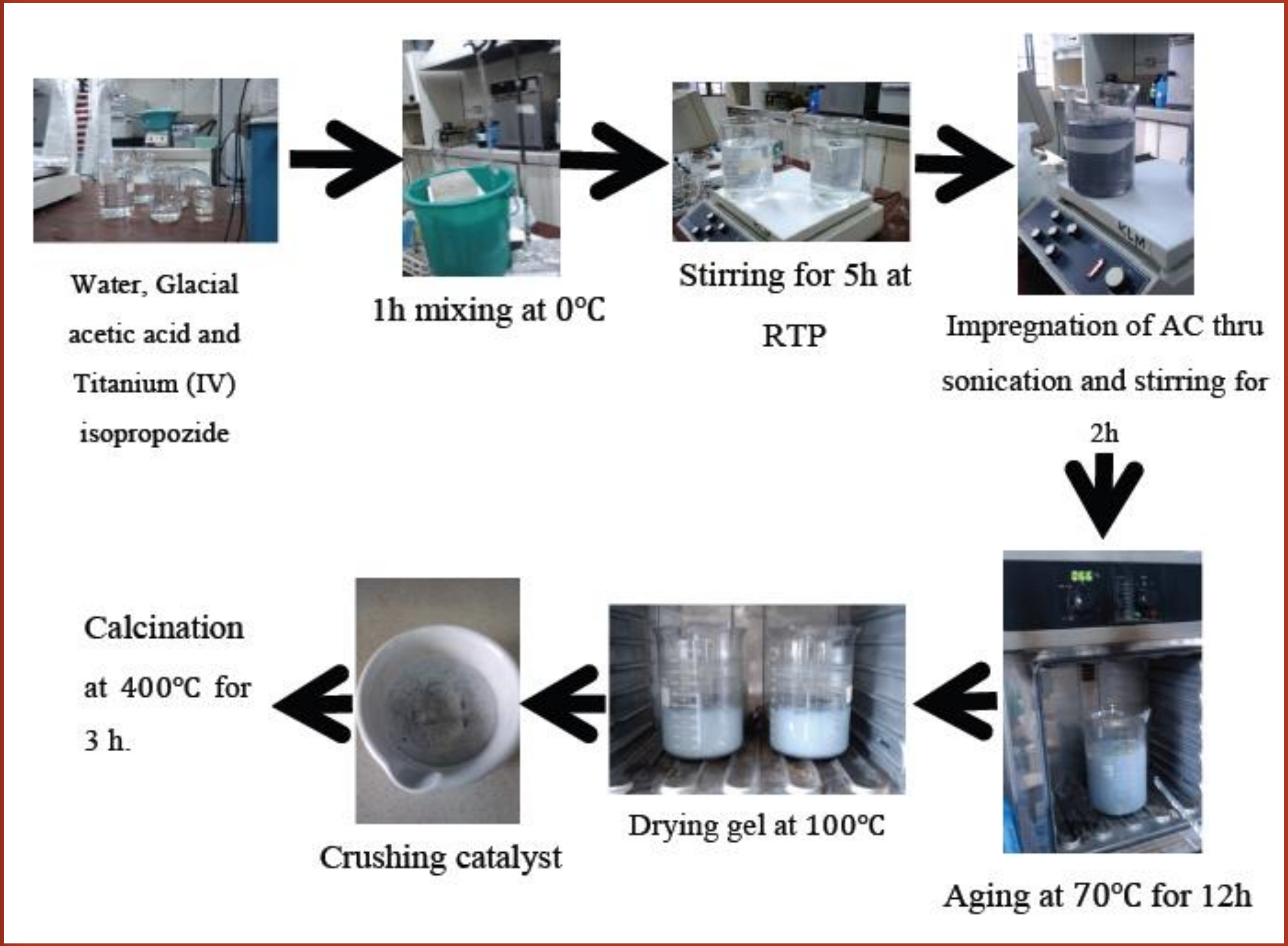
Oven

Furnace

Nano-Titania Catalyst Preparation by Solgel

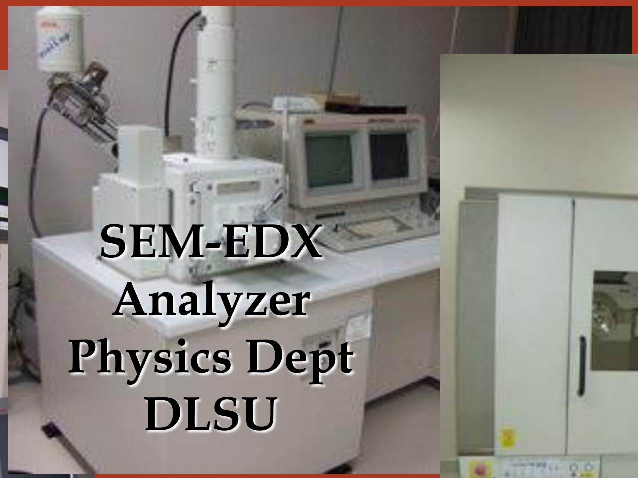
Methodology:

Catalyst Preparation



Methods: Scientific Equipment and Laboratory Facilities

BET Surface Analyzer
Chem Eng DLSU

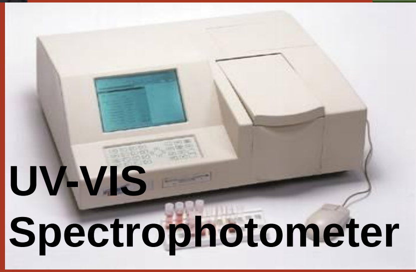


SEM-EDX Analyzer
Physics Dept
DLSU

XRD Equipment
Tokyo Tech

TEM Equipment
Tokyo Tech

FTIR Equipment
Physics Dept DLSU



UV-VIS
Spectrophotometer

TG-DTA Equipment
borrowed from UPD

Catalyst Characterization

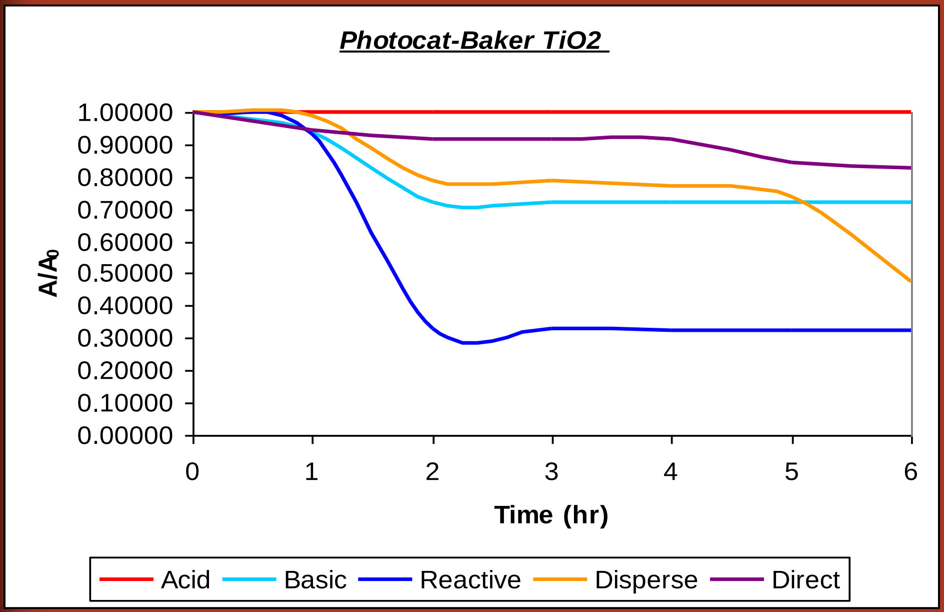
Methods: Scientific Equipment and Laboratory Facilities

Photocatalytic Reactors

Photocatalytic activity testing

Overview of Preliminary Results

Dye Persistency Test



Acid Dye	• Telon orange • Source: PTRI
Direct Dye	• Turquoise blue • Source:
Basic Dye	• Astrazone blue • Source: PTRI
Disperse Dye	• Dianix orange • Source: PTRI
Reactive Dye	• Reactive blue • Source: PTRI

ORDER OF PERSISTENCY

Acid dye ➡ Direct dye ➡ Basic dye ➡ Disperse dye ➡ Reactive dye

- ✓ **Acid dye is the most persistent dye followed by direct dye, basic dye, disperse dye and reactive dye**
- ✓ **TBD which belongs to direct dye generates high colored wastewater which is difficult to degrade**

Turquoise Blue Dye – generates high colored wastewater in a local textile mill

Turquoise blue CI 199	
Chemical formula	$C_{32}H_{16}N_8S_2O_6CuNa_2$
Molecular weight	781.8 g/mol
Solubility in water at 80degC	60g/L

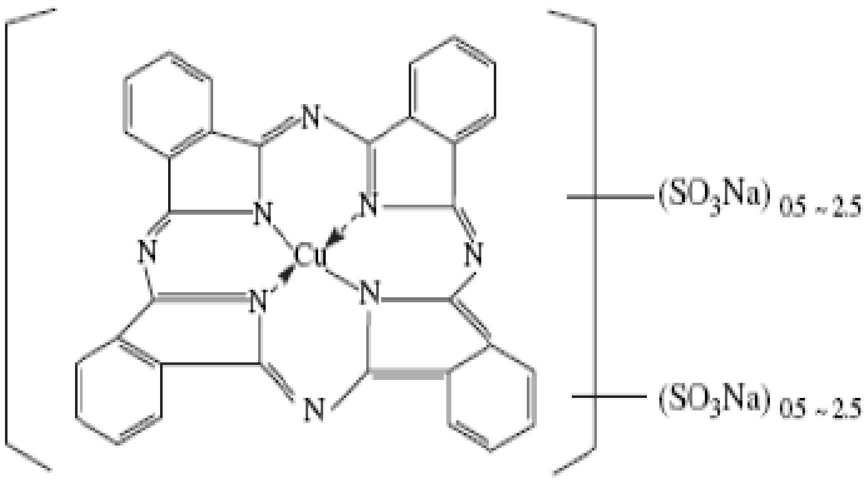


Fig. 3.1 Chemical Structure of Turquoise Blue CI 199 (Liu *et al.*, 2007)

TBD solution

✓ TBD is a direct dye

Overview of Preliminary Results

Nanotitania synthesized using sol-gel method

		TiO_2 Photocatalyst Samples		
		J. T. Baker TiO_2	nTiO_2 Calcined at 400 ºC	nTiO_2 Calcined at 500 ºC
Characteristics	Surface Area (m^2)	2.59	126.17	106.14
	Crystallite Size (nm)	44.3 - >100.0	9.6 – 17.0	12.5 – 17.9
	Crystal Structure	Anatase, Rutile, & Brookite	Anatase & Brookite	Anatase & Brookite
	Energy Band Gap (eV)	3.36	3.25	3.21
% Decolorization in 120 min	50 ppm T.O.	27.45	72.92	77.66
	60 ppm T.O.	14.53	70.19	75.70
	80 ppm T.O.	15.32	60.26	56.73
	100 ppm T.O.	6.73	41.26	35.71

Nanotitania (TiO_2) photocatalyst tested for photoactivity towards Telon Orange

Nanotitania calcined at 400 degC has the highest surface area and also showed the highest photocatalytic activity

Results and Discussions

Catalysts Synthesized by Solgel

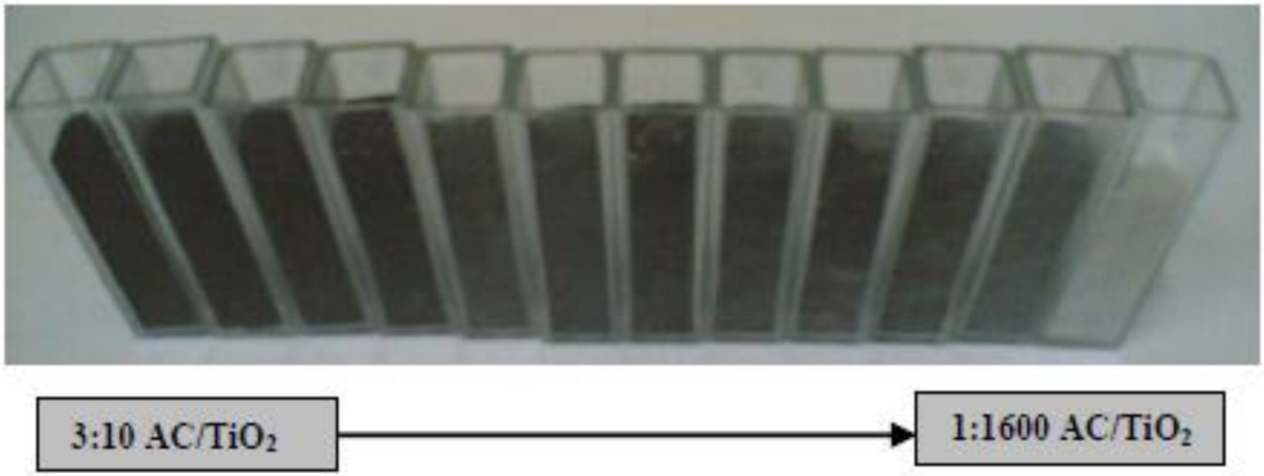
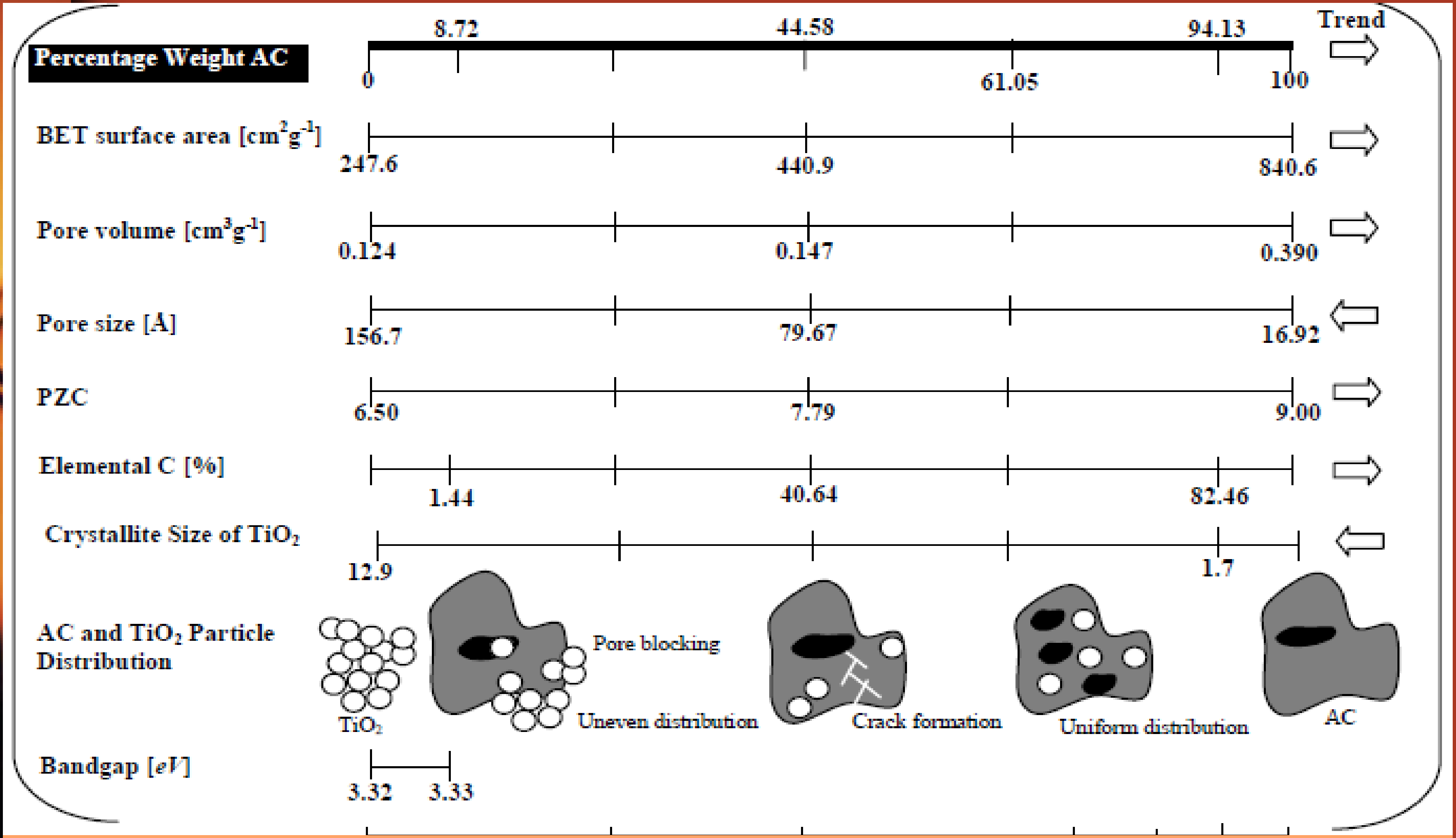


Fig. 5.1 AC/TiO_2 with Various AC Loadings

- ✓ AC/TiO_2 with high AC loading [3:10 AC/TiO_2] showed a dark color while AC/TiO_2 with low AC loading [1:1600 AC/TiO_2] is whitish in color

Results and Discussions

Summary of Characterization Results



- ✓ BET Surface area increases with more AC loading.
- ✓ Uniform distribution of AC and TiO_2 as more AC is added
- ✓ No significant change in band gap.

Results and Discussions

Performances of AC/TiO2 with Various AC Loading

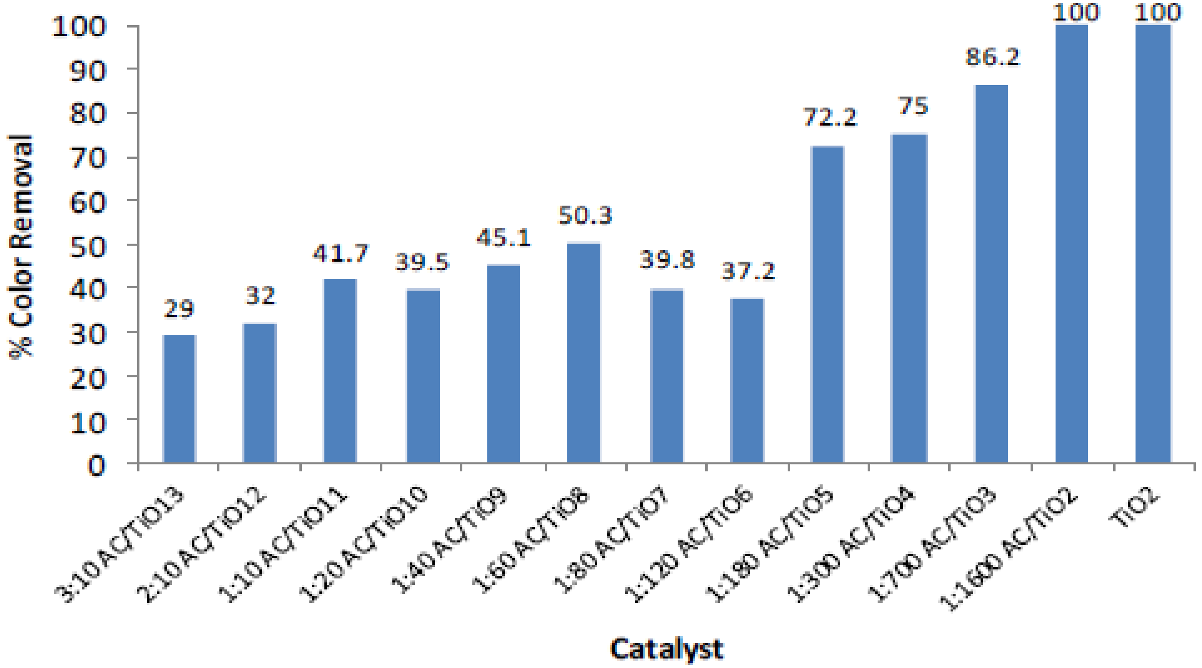
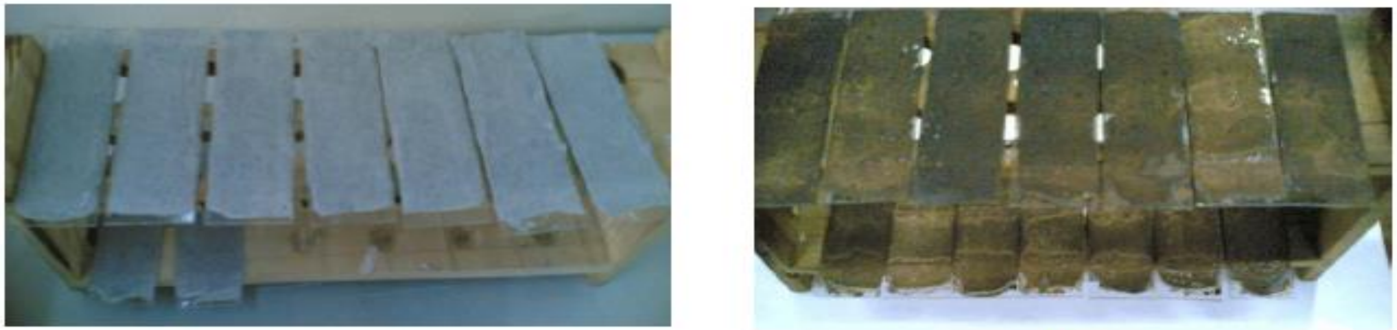


Fig. 5.17 Efficiencies of AC/TiO_2 with Various AC Loading in Photocatalytic Degradation of TBD

- ✓ **Using 1:1600 AC/TiO_2 (8.72% AC loading), a total color removal for TBD was observed in 120 minute – irradiation while it took longer for bare TiO_2 to completely degrade TBD in 150 minute – irradiation.**

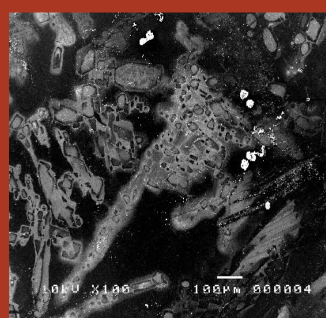
Results and Discussions

Immobilized Catalyst [1:1600 AC/TiO_2]



(a) (b)

Fig. 5.18 Glass Plates Coated with PEG-AC/TiO_2 (a) Before Heating (b) After Heating



SEM Image of Etched Glass Plate

Immobilized Catalyst Installed in Glass Holder

- ✓ **Using 1:1600 AC/TiO_2 (8.72% AC loading) was successfully immobilized in glass plate using PEG as binder.**

Results and Discussions

Photolysis using Recirculating Reactor

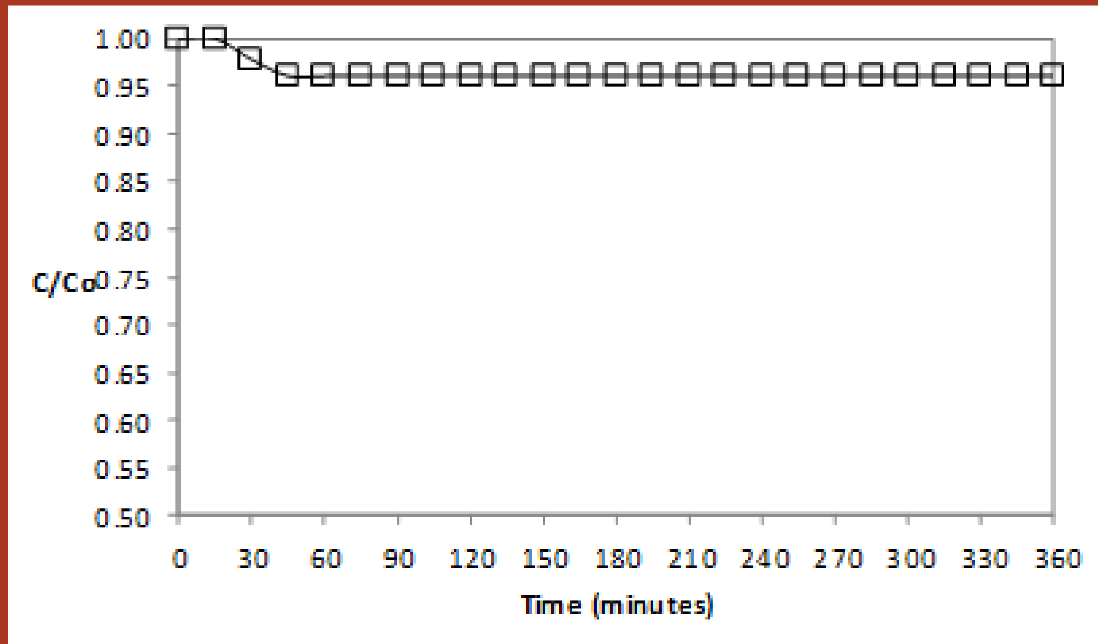


Fig. 5.35 Photolysis using a Recirculating Reactor. [TBD$_0$] = 15, mgL^{-1}, pH$_0$ = 3.0, AC/TiO$_2$ Loading = 3.0 mgL^{-1}, Io = 2.5 W/cm^2, Recirculating Flow Rate = 100ml/s

- ✓ Photolysis effect 3.93% color removal of TBD

Results and Discussions

Dark Adsorption using Recirculating Reactor

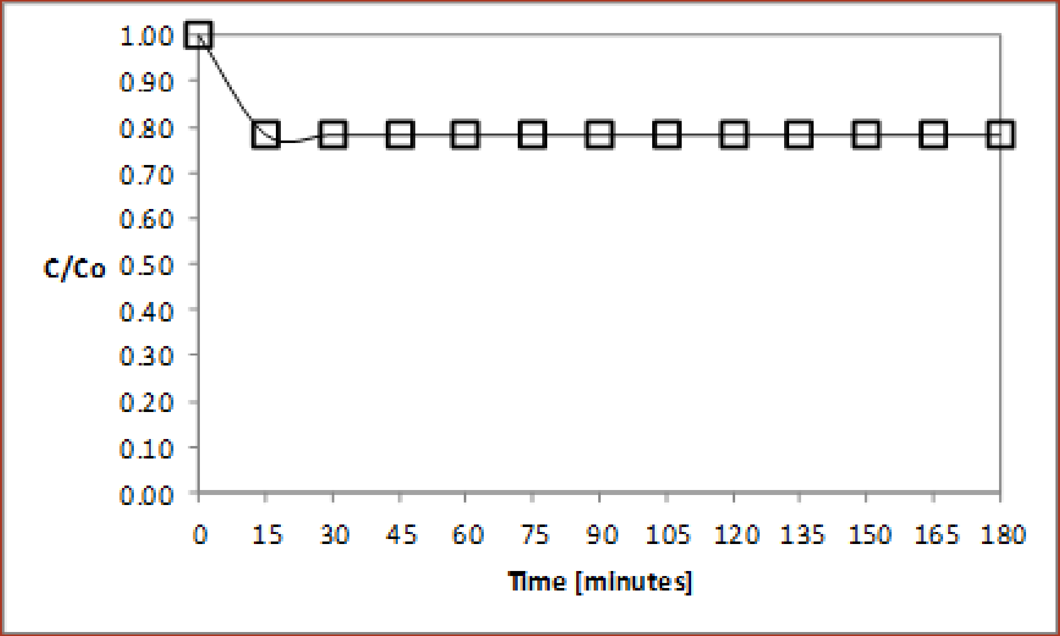


Fig. 5.36 Dark Adsorption Using a Recirculating Reactor. [TBD_o] = 15, mgL^{-1}, pH = 3.0, AC/TiO_2 Loading = 3.0 mgL^{-1}, Io = 2.5 W/cm^2, Reciculating Flow rate = 100ml/s

- ✓ **Dark experiment showed a TBD color removal of 21.7% due to adsorption.**

Results and Discussions

Optimum Operating Conditions under AC/TiO2-UV system

Table 5.7 Optimum Operating Conditions of the Process Variables in Photocatalytic Degradation of TBD under Immobilized AC/TiO_2 and UV System

Parameter	**Value**
Initial dye concentration	15 ppm
Catalyst loading	3.00 gL^{-1} dye solution
Initial solution pH	3.00
UV intensity	2.50 mW cm^{-2}
Recirculating flow rate	100 mls^{-1}

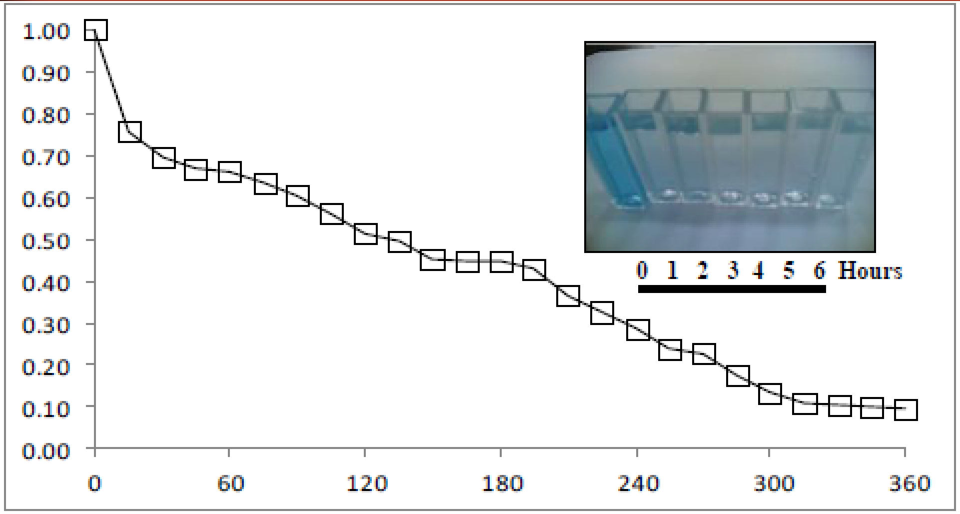


Fig. 5.43 Efficiency of AC/TiO_2 under UV light for Photocatalytic Degradation of TBD in Optimum Conditions. $[TBD_O]$ = 15, mgL^{-1}, pH = 3.0, AC/TiO_2 Loading = 3.0 mgL^{-1} , Io = 2.5 W/cm^2, Flow rate = 100ml/s, 2.50 mW cm^{-2}

- ✓ **90.01 % color removal for TBD at optimum conditions**

Results and Discussions

COD Removal

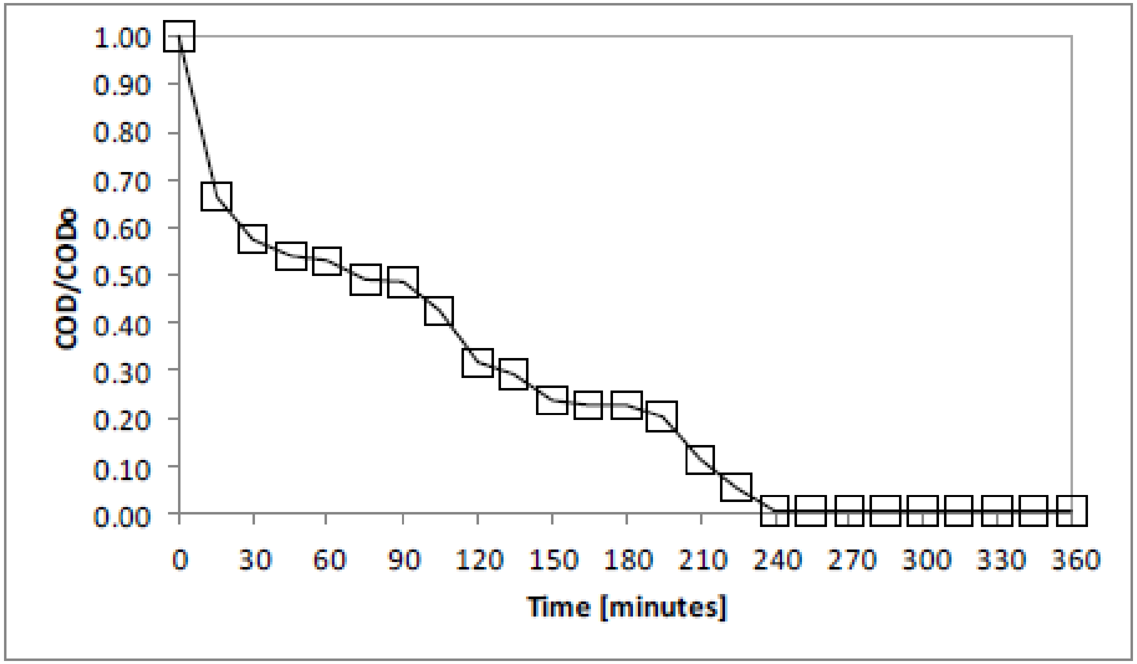


Fig. 5.44 Percentage COD Removal in Photocatalytic Degradation of TBD under Optimum Conditions. $[TBD_O]$ = 15, mgL^{-1}, pH = 3.0, AC/TiO_2 Loading = 3.0 mgL^{-1} . *Io* = 2.5 W/cm^2. Recirculating Flow rate = 100ml/s

- ✓ **99.42% COD removal was observed after 240 minute – photocatalytic treatment.**

Results and Discussions

Photocatalytic Degradation of Textile Wastewater under AC/TiO2 –UV System

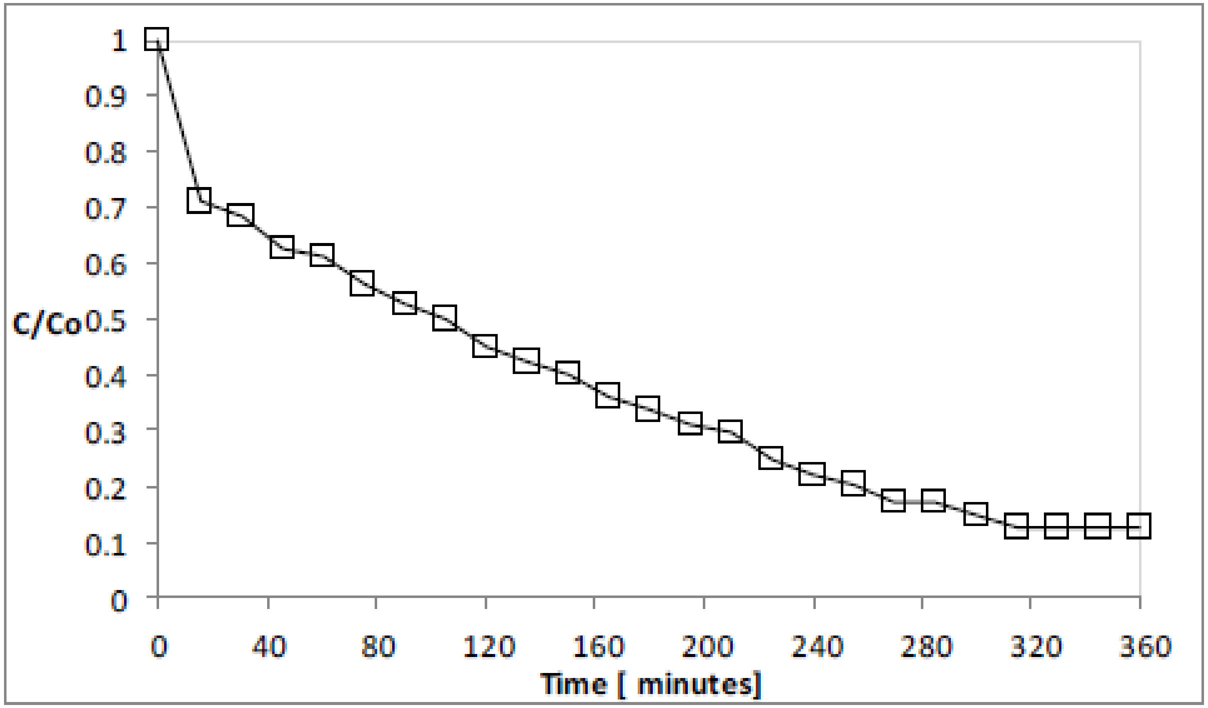


Fig. 5.44 Efficiency of AC/TiO_2 under UV light for Photocatalytic Degradation of Textile Wastewater with TBD Stream in Optimum Conditions. $[TBD_O] = 15$, mgL^{-1}, pH = 3.0, AC/TiO_2 Loading = 3.0 mgL^{-1} , $Io = 2.5$ W/cm^2, Flow rate = 100ml/s

✓ 86.40% color removal in 6-hour irradiation.

Results and Discussions

Photocatalytic Degradation of TBD under Visible Light

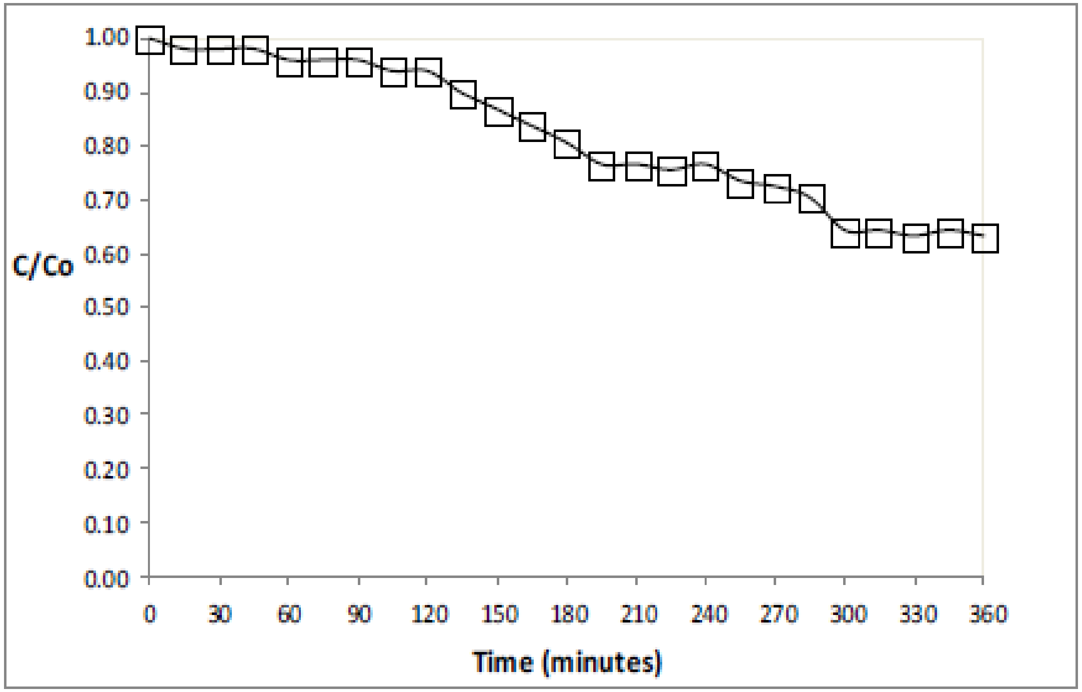


Fig. 5.45 Efficiency of AC/TiO_2 in Photocatalytic Color Removal of TBD using **Visible light** [TBD_O] = 15, mgL^{-1}, pH = 3.0, AC/TiO_2 Loading = 3.0 mgL^{-1} , I_o = 2.5 W/cm^2, Flow rate = 100ml/s

✓ 38.50 % color removal for TBD under Visible Light.

Results and Discussions

Fit of Kinetic Data

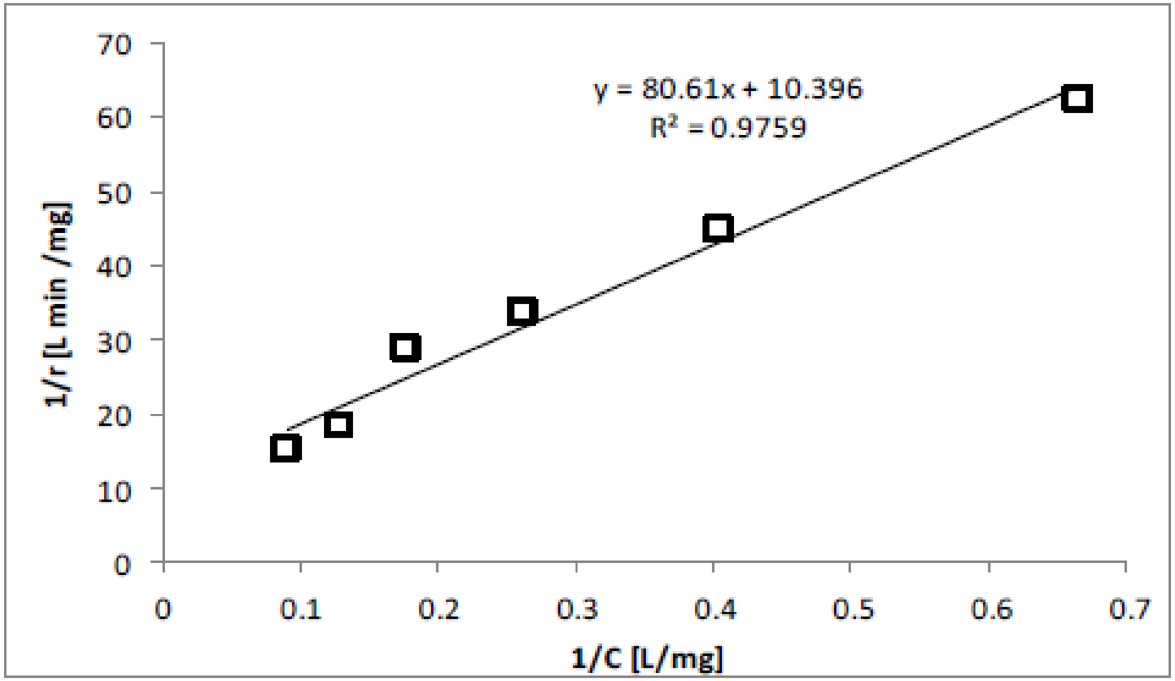


Fig. 5.46 Plot of Langmuir- Hinshelwood Kinetics in Photocatalytic Degradation of Turquoise blue dye at Optimum Conditions. $[TBD_O]$ = 15.0 mg/L, Catalyst Loading = 3.0 g/L, Initial solution pH = 3.0, Light Intensity = 2.50 mW cm^{-2}, Recirculating Flow Rate = 100ml/s

- ✓ **The kinetic data fits the Langmuir Hinshelwood model with R2 = 0.9759**
- ✓ **The kinetic parameters are *kr* = 0.096191 mg L-1 min-1 and K =0.128966 L mg-1**

Results and Discussions

Recyclability Test Results

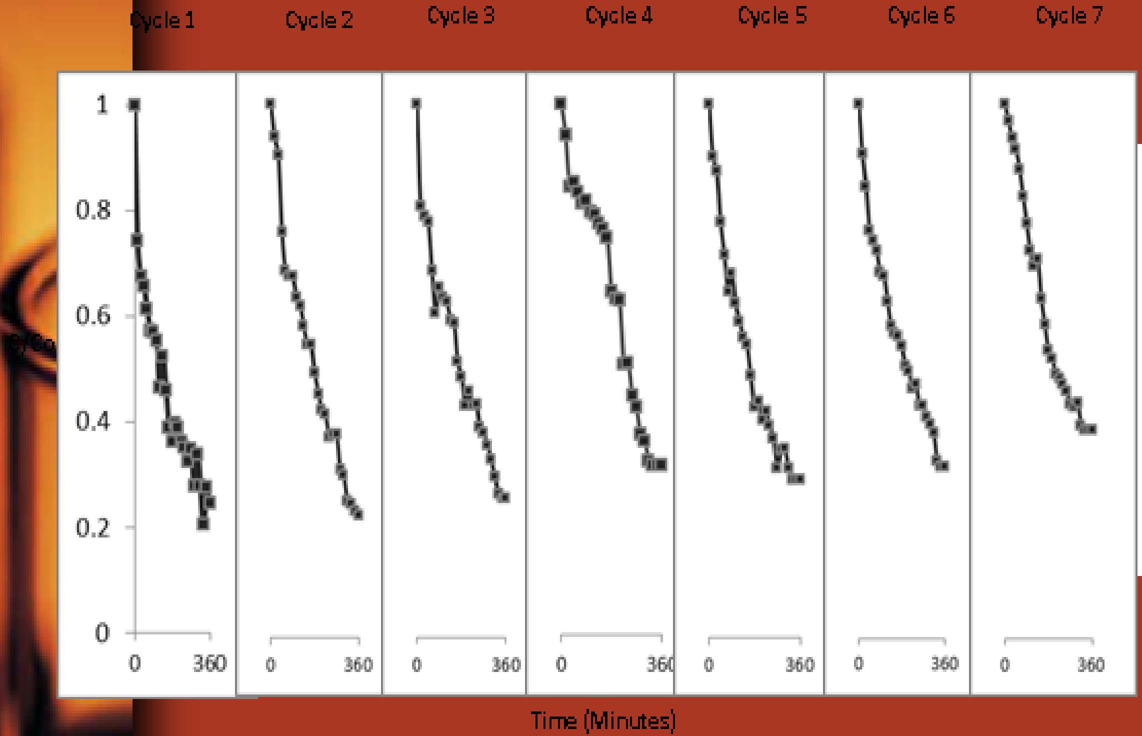


Fig. 5.54 Performance of Recycled AC/TiO_2 for TBD Degradation using UV Light

Table 5.10 Percentage Color Removal in Each Cycle

No. of Cycle (6-hr irradiation)	Percent Color Removal
1st	80.4
2nd	78.5
3rd	76.9
4th	72.4
5th	73.3
6th	67.7
7th	63.8

- ✓ **The efficiency of immobilized AC/TiO2 is not lower than 60% after 7 cycles.**

Results and Discussions

Toxicity Test Results

Table 5.9 Changes in Toxicity of Textile Wastewater with TBD Stream During Photocatalytic Degradation

	Time of Photocatalytic Reaction		
Sample	Time = 0	3 hours	6 hours
Toxicity	Toxic	Partially Toxic	Non toxic

A B C D

Fig. 5.53 Toxicity Test Results (Visual Examination after 48 Hours)

Legend

- A = Textile wastewater
- B = Textile wastewater subjected to photocatalysis in 3 hours
- C = Textile wastewater subjected to photocatalysis in 6 hours
- D = Blank

Color	Toxicity
Light Pink	More toxic
Pink	Toxic
Purple	Partially toxic
Deep Purple	Non toxic

✓ **Transformation from toxic to non-toxic after 6 hour irradiation.**

Conclusions

- The TiO_2 synthesized by **sol-gel** at **400degC is nano-sized**.
- The **addition of AC to TiO_2** has **no significant effect on the band gap energy** of the composite catalyst.
- **High photocatalytic efficiency** was observed on **AC/TiO_2 with low AC loading** [8.72 percent AC loading]
- **AC/TiO_2** was **successfully immobilized** in glass plates **using PEG** as binder.
- **TBD removal increases with catalyst loading and UV intensity** while **decreasing with initial dye concentration, initial dye solution pH and recirculating flow rate**.
- The **initial dye concentration** has the **highest influence** in TBD removal.

Conclusions

- Using **optimum conditions under UV** light, **90.0 % color removal** was observed **for TBD** while **86.4 % color removal** for **textile wastewater** with TBD stream. **38.5 % color removal for TBD** was observed **under visible light**.

- **Photocatalytic degradation of TBD** follows the **Langmuir-Hinshelwood equation**

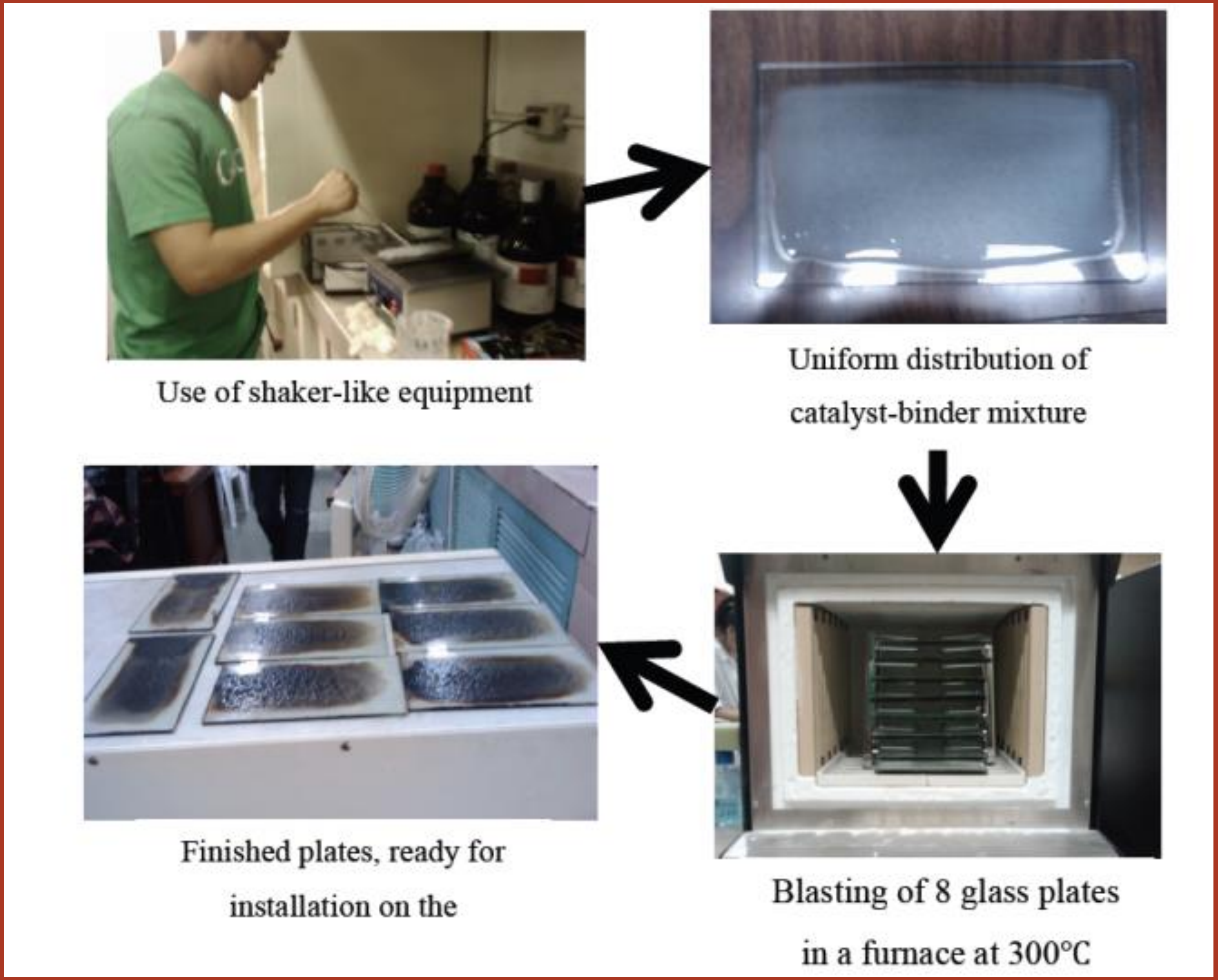
- **Textile wastewater** with TBD stream was **transformed from toxic to non-toxic** after 6-hour photocatalytic treatment.

- The **efficiency of immobilized AC/TiO_2 is not lower than 60% after 7 cycles**.

PILOT PLANT INVESTIGATION

Methodology:

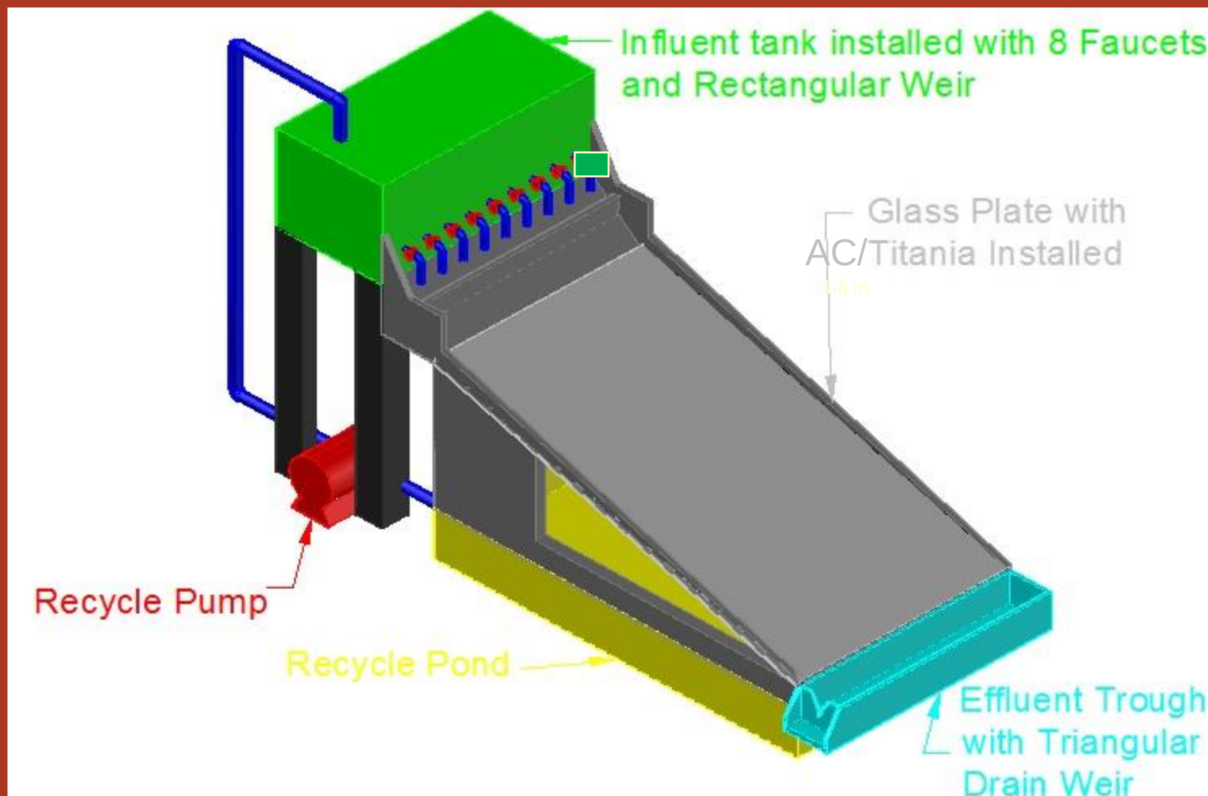
Catalyst Immobilization



Methodology:

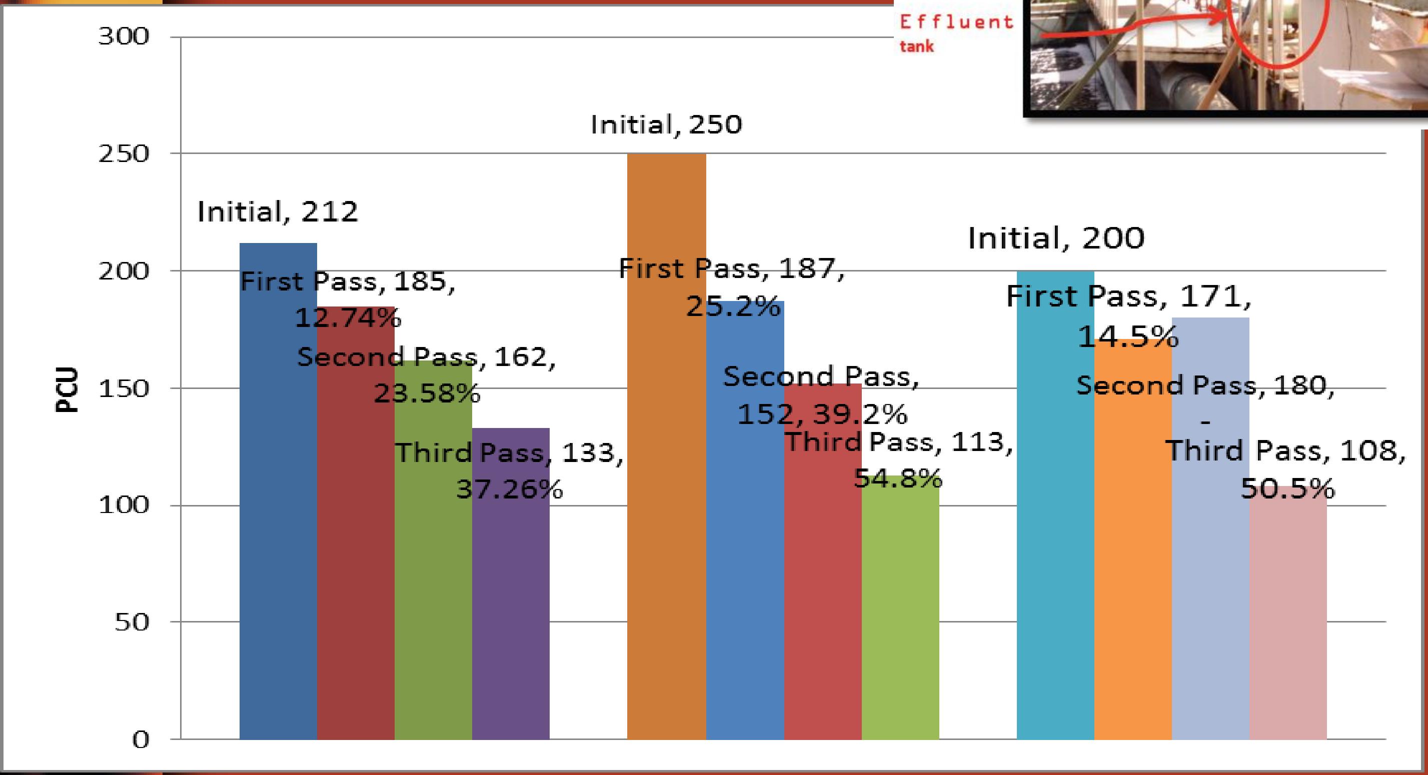
Photocatalytic Reactor

1 m



Photocatalytic activity testing

Results and Discussions: Pilot Plant Investigation



54.80% color removal was observed at 1.5 hours residence time with 3 recirculation passes.

Conclusions

- In pilot plant investigation, 54.80% color removal was observed at 1.5 hours residence time with 3 recirculation passes.

Acknowledgment

- DOST – PCIEERD
- DLSU Manila
- Saffron Philippines Inc.
- Tokyo Institute of Technology, Japan
- Burapha University, Thailand
- Martin Mariano, Michael Kho and Alton Lucanas
- PTRI

Thank you!!