Study of Organic Photocatalytic Degradation Mechanism in Textile WWTP Effluent Treatment by Using Immobilized TiO_2 Nanofibers Composite Catalyst

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Outlines

1. Background, Objectives
2. Methods
3. Results and Discussion
4. Conclusion
5. Outputs

Team Members

Researchers:

1. Dr-Ing. Marisa Handajani, ST., MT.
2. Prof. Suprihanto Notodarmajo, Ph.D

Students:

1. Doni Sugiyana, ST., M.Eng. (Doctoral program)
2. Wulan Saprihatini (Master Program)

Background

Textile Industy in West Java

(Indonesia : 2699; West Java : 1500}*

Direct discharge

Organic, color,
salt ions, metals

33% Garment

1% Fiber

8% Spinning

58% Weaving &
Dyeing Finishing

Dyeing wastewater:
100 – 1000
m^3/day/company

Treated

WWTP

Excessive:
Organic,color
& salt ions

Recycle, reuse

POST-TREATMENT

*Indonesian Textile Assc. 2010

Background

Photocatalytic Treatment UV/TiO_2

TiO_2 + UV(λ 254 nm) → TiO_2 (e^-_{CB} + h^+_{VB})

$TiO_2(h^+_{VB})$ + H_2O → TiO_2 + H^+ + **OH•**

$TiO_2(h^+_{VB})$ + OH^- → TiO_2 + **OH•**

$TiO_2(e^-_{CB})$ + O_2 → TiO_2 + **O_2^-•**

O_2^-• + H^+ → **HO_2•**

Organic + **OH•** → degradation products

Organic + h^+_{VB} → oxidation products

Organic + e^-_{CB} → reduction products

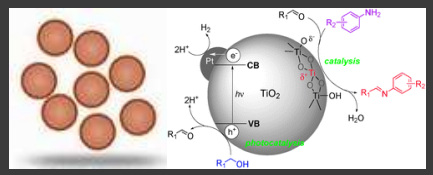
Potential for Treatment of Textile WWTP Effluent:

- Effective degradation of organic & color
- No excess sludge
- Rapid treatment process
- Reusable
- Low process cost

Background

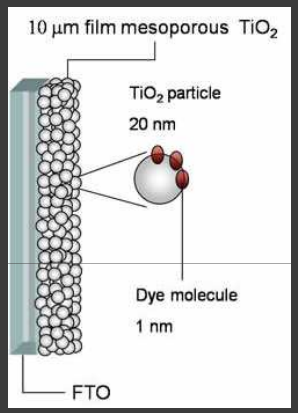
Development of Immobilization Technique for Photocatalytic Treatment of Wastewater

Suspended particles



Catalyst separation problem

Immobilized particles



- Practical for application
- Lesser contact area
- Attachment strength problem

Improvement of immobilized particles in this research:

Composite
(fiber-based)

Catalyst size
(nano-sized particle)

Mechanism of Organic Degradation??..

Objectives

To Investigate..

The mechanism of organic degradation during **photocatalytic process** of **textile WWTP effluent** treatment by using **immobilized TiO_2 nanofibers composite** catalyst

Methods

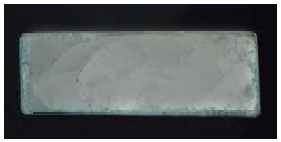
TiO_2 Nanofiber-Nanoparticles Composite

Annealing
(550°C, 60 min)

Before Annealing *After Annealing*

TiO_2 Nanofibers Immobilized on Glass Plates

As-spun Nanofiber (Electrospinning)



Nanofiber+Nanoparticles (Sol-gel, Dip-coating)

Annealing
(550°C, 60 min)

TiO_2 Nanofibers-Nanoparticles Immobilized on Glass Plates

Methods

SEM images

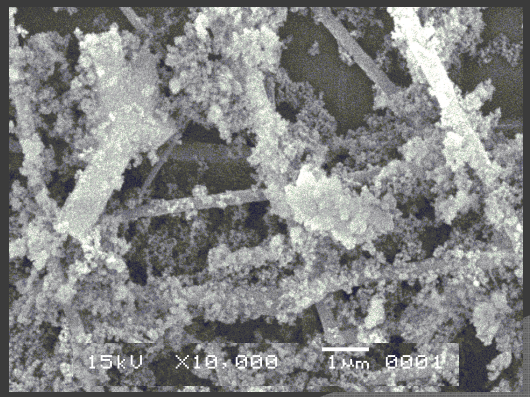
Nanofibers

5000x

10000x

Composite

5000x

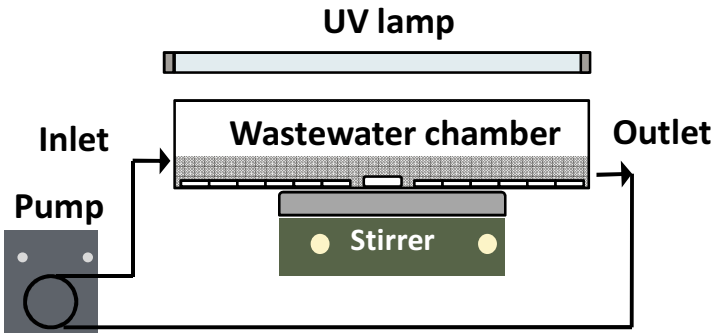


10000x

Catalyst distribution: 4.26 mg-TiO_2/cm^2

Methods

Photoreactor



UV Lamps:

UV-C, 3 x 15 W, λ 254 nm

Catalyst:

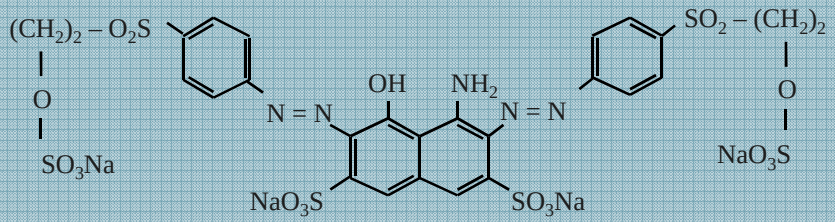
Glass plates in chamber (500 mL)

TARGET WASTEWATER

Simulated Wastewater Containing Reactive Black 5 (azo dyes)

Reactive Black 5 (RB5)

- $(C_{26}H_{21}N_5Na_4O_{19}S_6)$
- Molecular weight: 991.8
- Dye concentration: 10 mg/L
- Molecular structure:



Real Textile WWTP Effluent

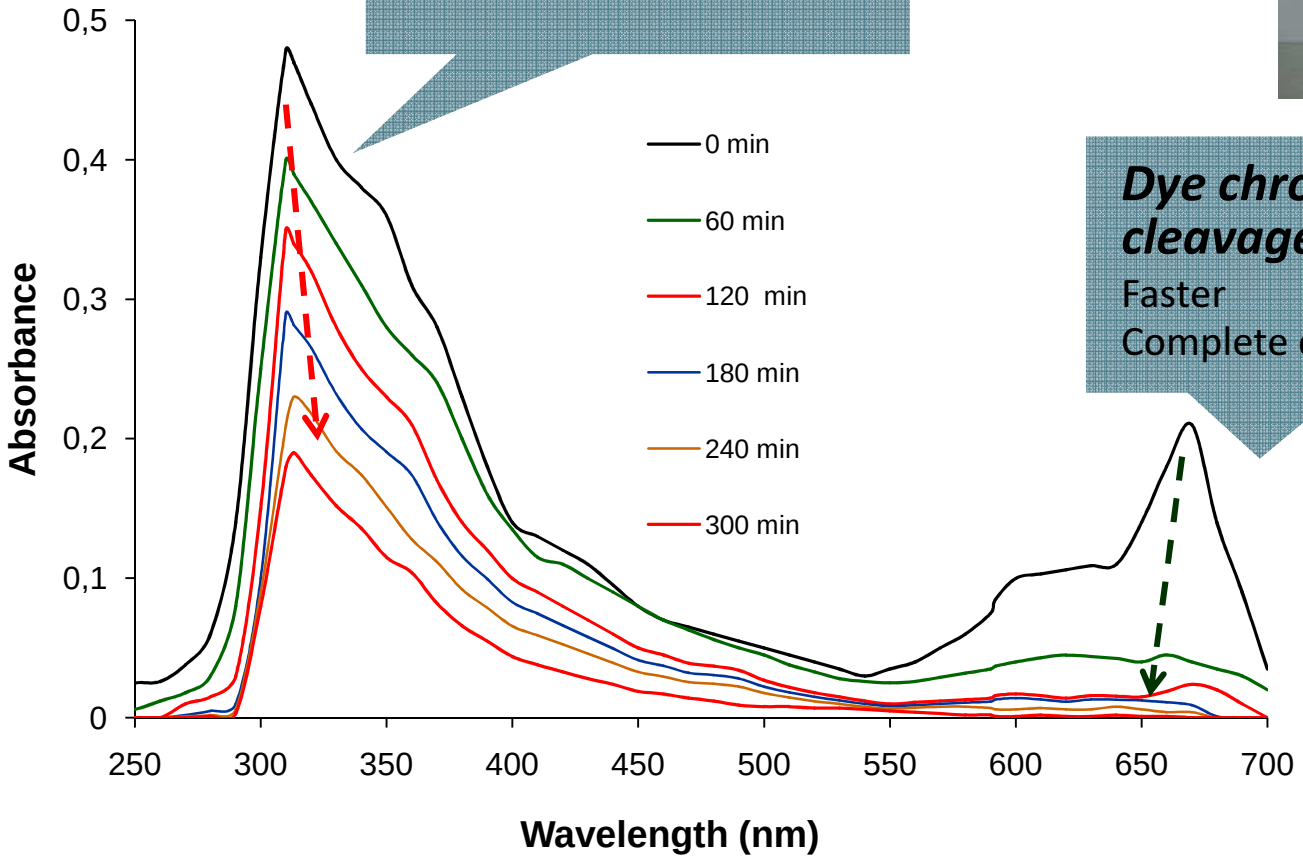
Characteristics:

- Company : Rancaekek, Bandung
- Process : Cotton Dyeing Finishing
- Wastewater discharge : 345 m^3/d
- WWTP Process:
  - Coagullation-Flocculation
  - Activated sludge

UV-vis absorbance spectra (WWTP effluent)

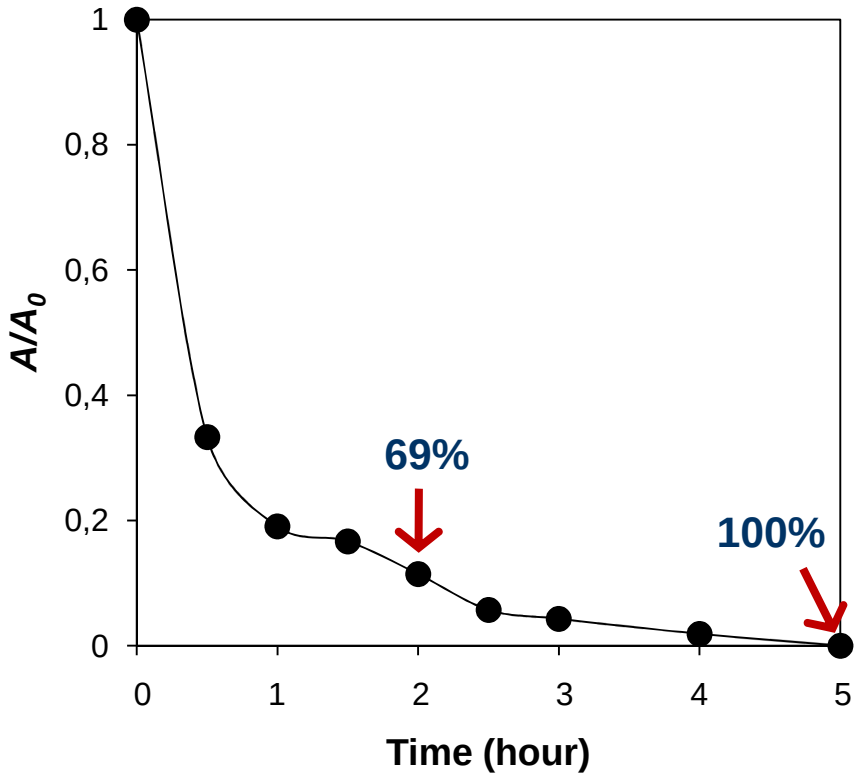
Organic compounds cleavage
Slower

Dye chromophore cleavage
Faster
Complete decolorization: 5 hrs

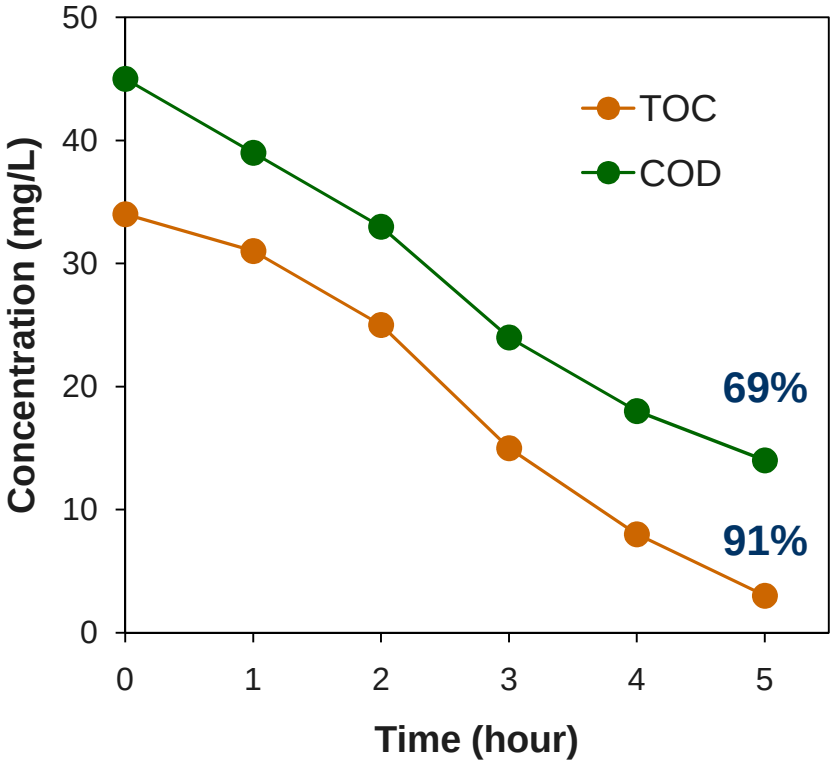


Decolorization – Mineralization (WWTP effluent)

Decolorization (λ_{max} 664 nm)

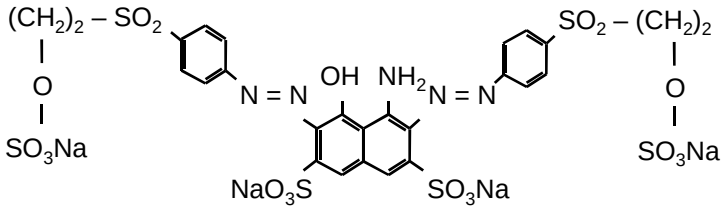


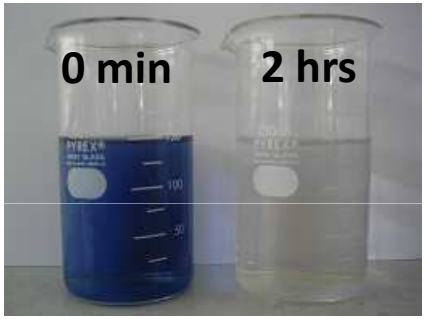
Mineralization

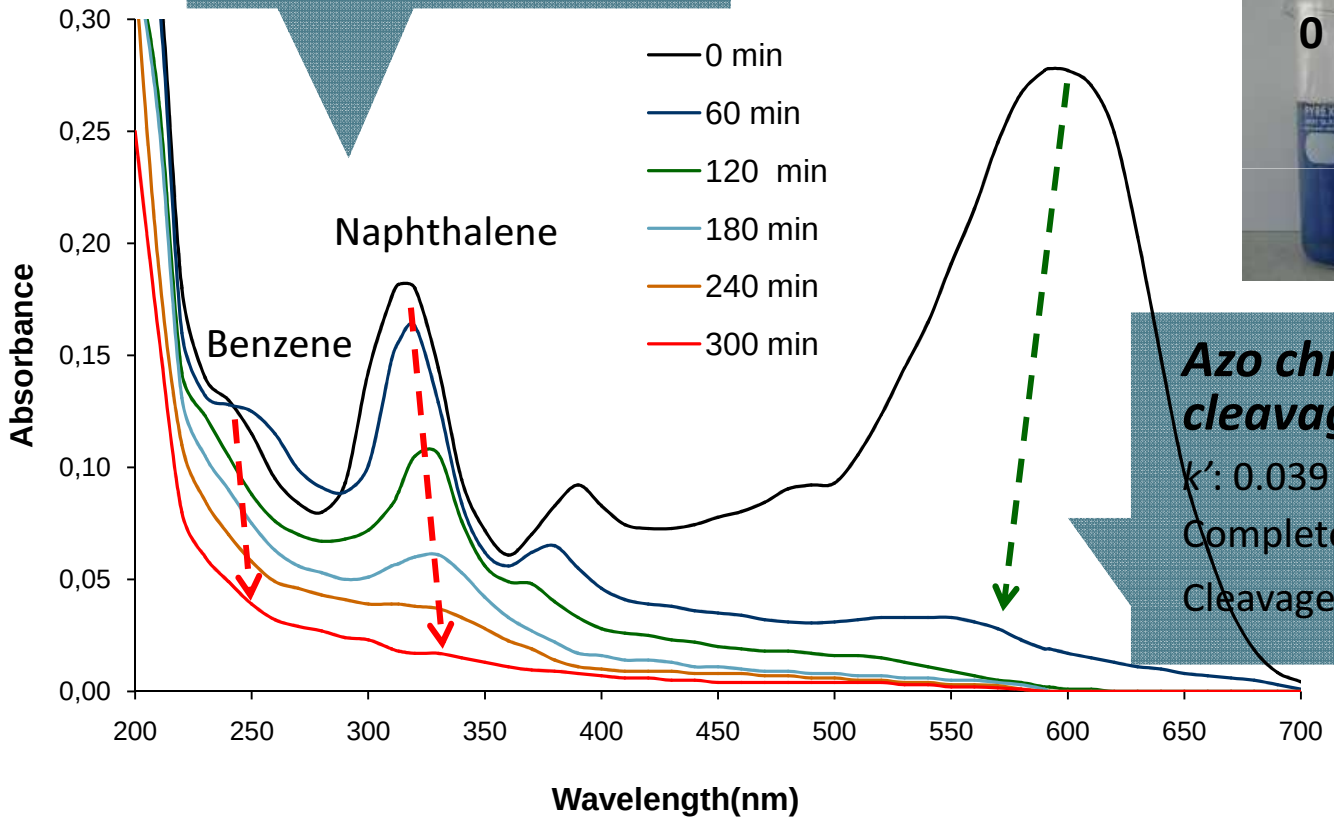


UV-vis absorbance spectra (RB5)

Aromatic Rings Cleavage
Naphthalene, Benzene



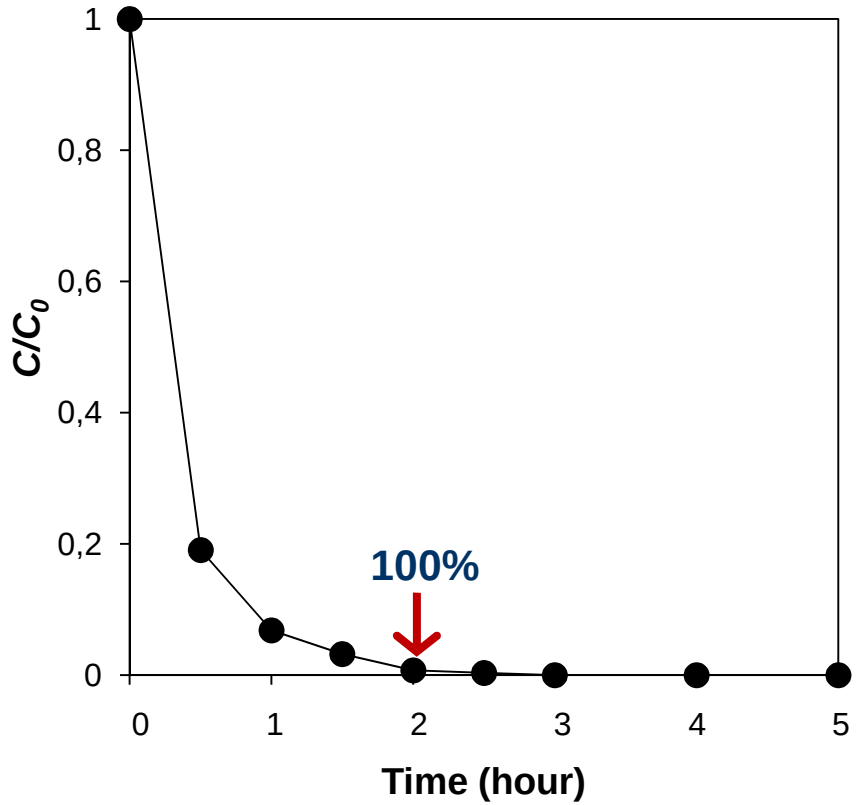




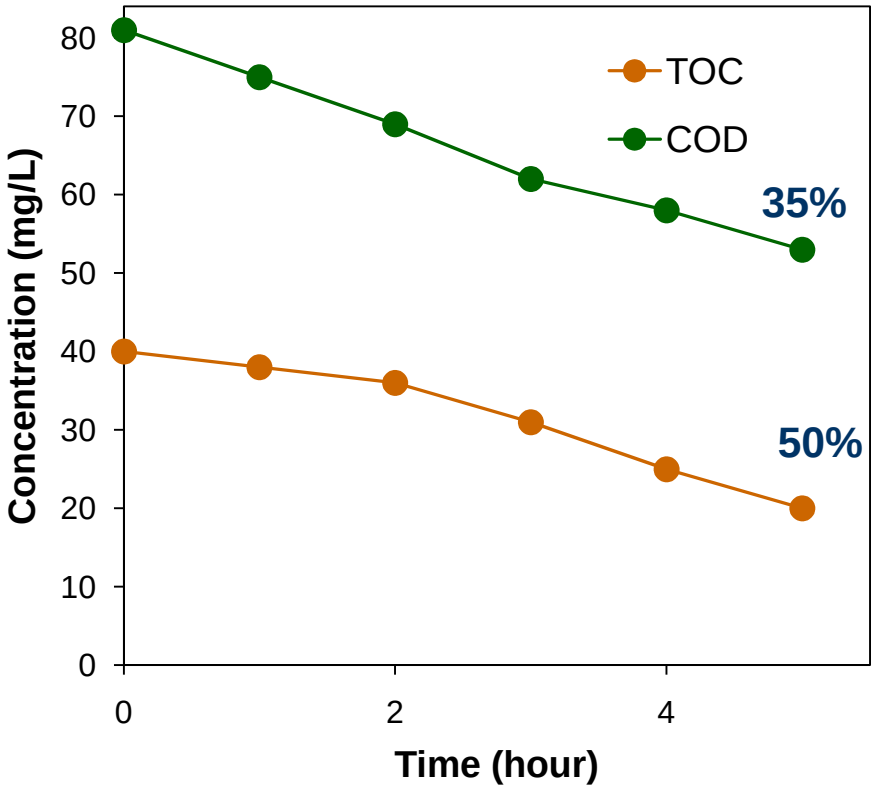
Azo chromophore cleavage
k′: 0.039 min^{-1} (1^{st} order)
Complete decolorization: 2 hrs
Cleavage of azo bonds

Decolorization – Mineralization (RB5)

Decolorization (λ_{max} 592 nm)



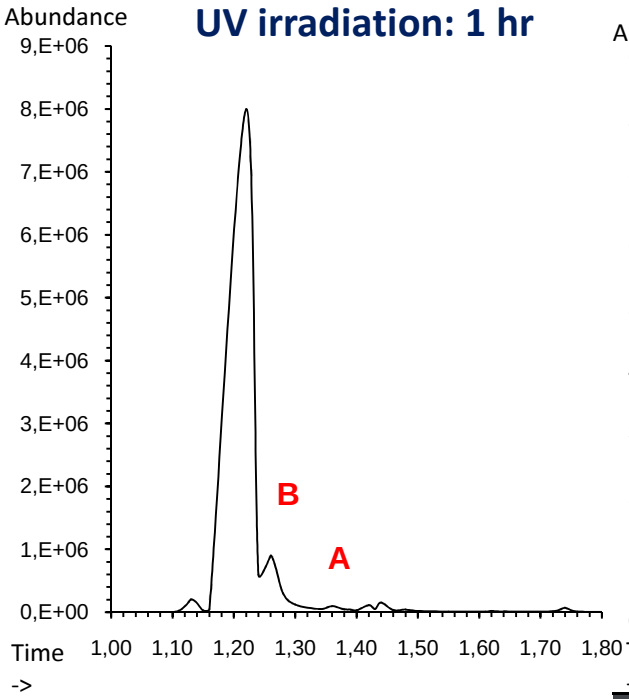
Mineralization



Results & Discussion

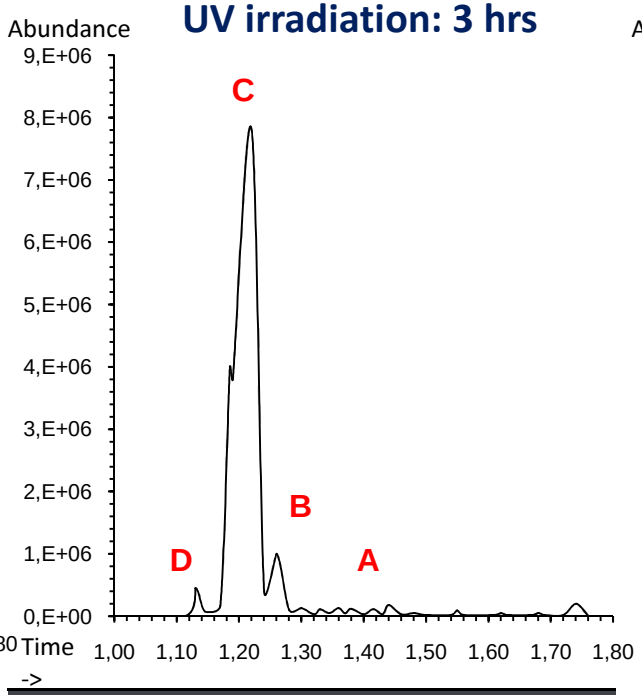
GC/MS Results for Degradation of RB5

UV irradiation: 1 hr



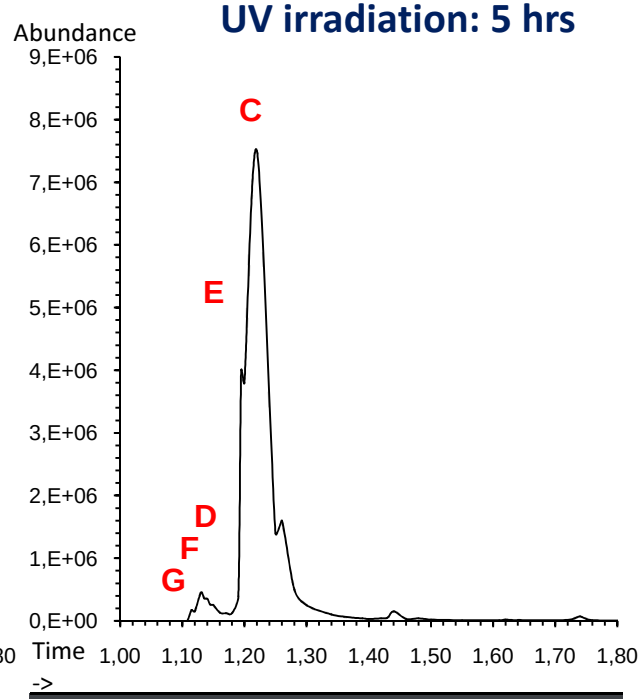
Compound /Ret. time (min)	Main fragments (m/z)
A (1.41)	45,59,73,89,96,105 ,**207**
B (1.26)	45,55,73,87,103,11 6,178,191, **281**

UV irradiation: 3 hrs



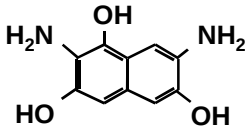
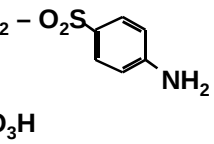
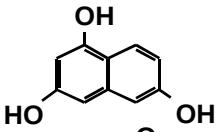
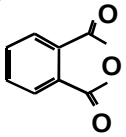
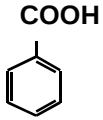
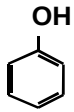
Compound /Ret. time (min)	Main fragments (m/z)
A (1.41)	45,59,73,89,96,105,**207**
B (1.26)	45,55,73,87,103,116,178, 191, **281**
C (1.22)	45,57,62,73,89,94,**178**
D(1.14)	47,65,94,**148**

UV irradiation: 5 hrs



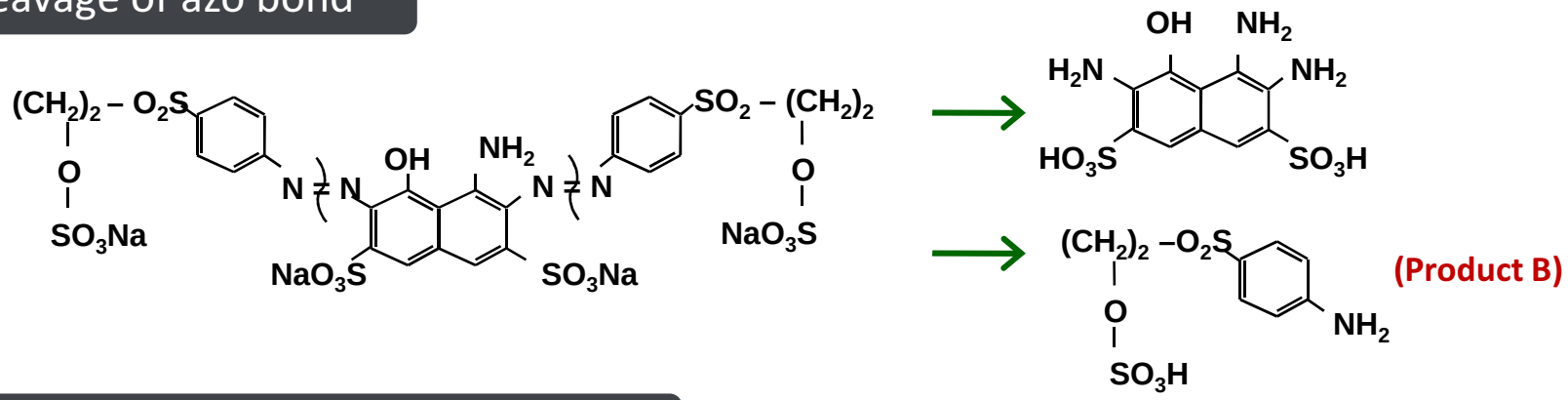
Compound /Ret. time (min)	Main fragments (m/z)
C (1.22)	45,57,62,73,89,94,**178**
D (1.14)	47,65,94,**148**
E (1.19)	45,57,73,87,94,105,116, **122**
F(1.13)	45,47,65,**94**
G (1.11)	45,57,62,73,**90**

Identification of degradation products (RB5)

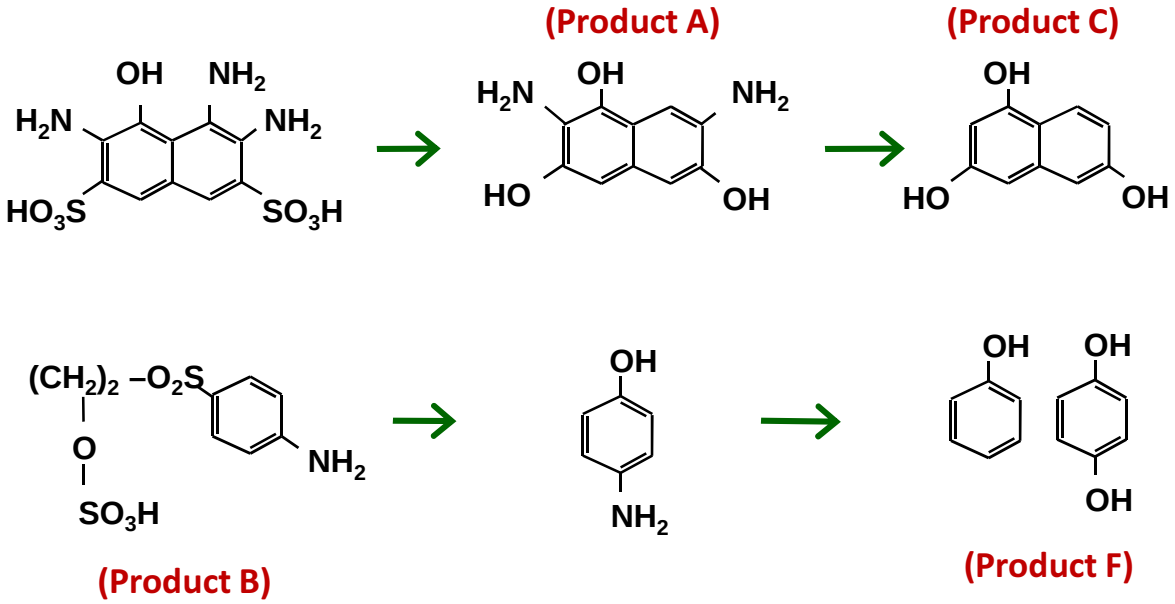
Symbol	Compound	Molecular structure	Molecular weight	Irradiation time (hour) 1	3	35
A	2,7-diamino,3,6,8-trihidroxy naphtalene		207	√	√	
B	1-sulfonat,2-(4-aminobenzenesulfonil) ethanol		281	√	√	
C	3,6,8-trihidroxy naphtalene		178		√	√
D	Phthalic anhydride		148		√	√
E	Benzoic acid		122			√
F	Phenol		94			√
G	Oxalyc acid	$(COOH)_2$	90			√

Mechanism of degradation (*pathway*) – RB5

1. Cleavage of azo bond



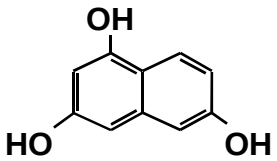
2. Cleavage of C–C, C–N and C–S bonds



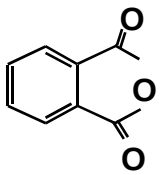
Mechanism of degradation (*pathway*) – RB5

3. Cleavage of naphtalene rings

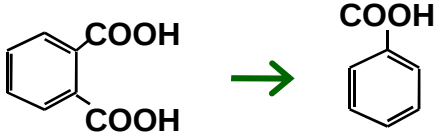
(Product C)



(Product D)

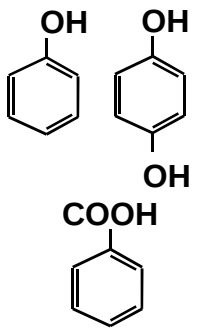


(Product E)

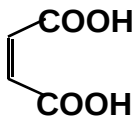


4. Cleavage of benzene rings

(Product F)



(Product E)



5. Mineralization

CH_3COO^-

, $HCOO^-$

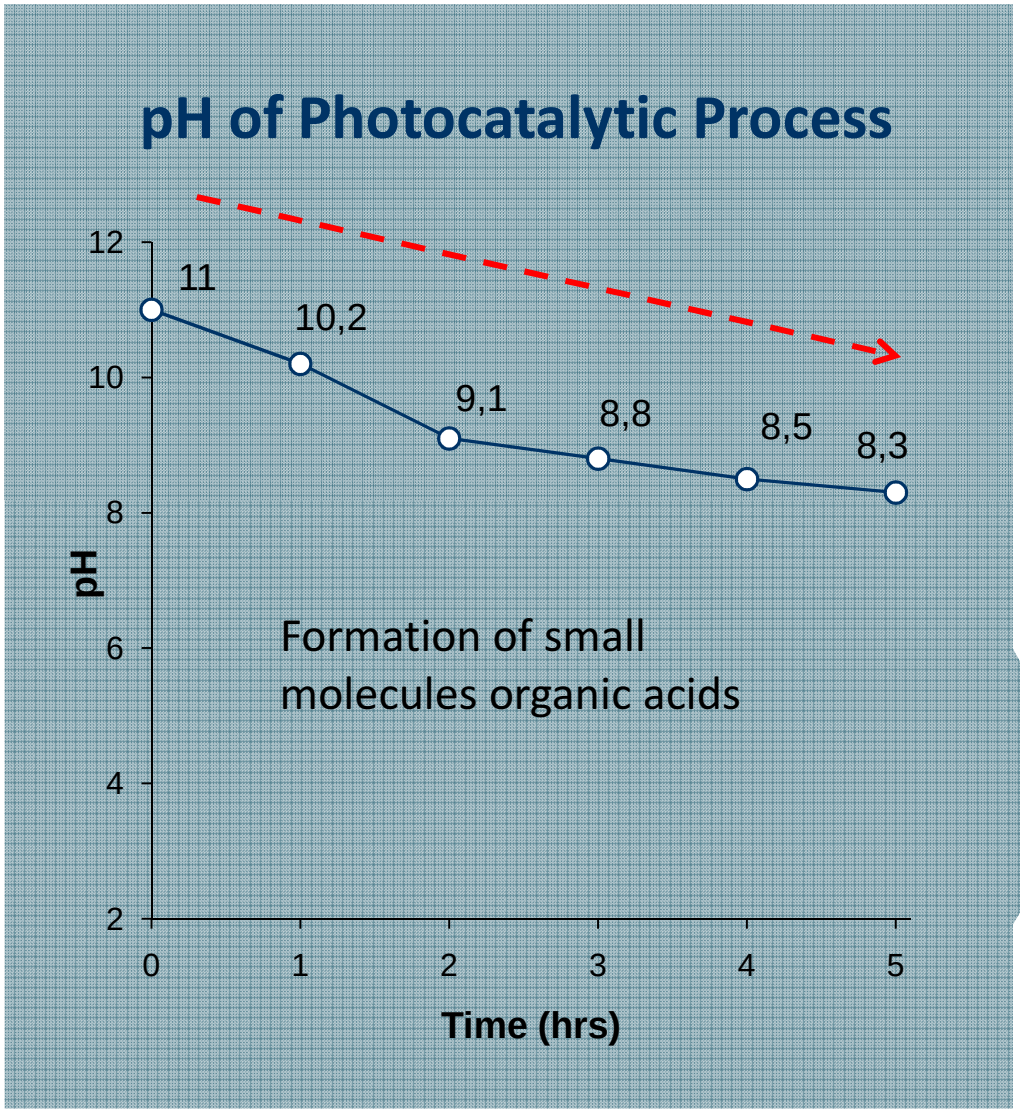
, $(COOH)_2$

(Product G)

$CO_2 + H_2O$

Results & Discussion

Degradation Pathway



Azo dyes

$OH\bullet, O_2^{-}\bullet$

Intermediates
(aromatic amines)

$OH\bullet, O_2^{-}\bullet$

Destruction of intermediates
(aliphatic acid, aromatic acid)

$OH\bullet, O_2^{-}\bullet$

Mineralization

Conclusion

- Photocatalytic treatment by using TiO_2 composite catalyst for textile wastewater contain azo dyes was accomplished through 2 steps:
  - Cleavage of azo chromophore
  - Destruction of organic intermediates
- Photocatalytic treatment could degrade intermediates (aromatic amines) to be smaller molecule organic acids.
- Photocatalytic degradation treatment by using immobilized composite catalyst was effective for mineralization of textile WWTP effluent contain azo dyes.

Thank you for your attention