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PHOTOCATALYTIC DEGRADATION OF TURQUOISE BLUE DYE USING IMMOBILIZED AC/TIO2: OPTIMIZATION OF PROCESS PARAMETERS AND PILOT PLANT INVESTIGATION

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Abstract

AC/TiO_2 was synthesized via sol-gel method and characterized. Response Surface Methodology (RSM) based on Central Composite Design (CCD) was applied in optimization of process parameters in photocatalytic degradation of Turquoise blue dye (TBD) under UV light. The optimum conditions are 15.00 mg/L initial dye concentration, initial solution pH of 3.00, 3.00 g/L catalyst loading, recirculating flow rate of 100 ml/s and UV intensity of 2.50 mW/cm^2. A 90.01% color removal of TBD and 86.4% color removal of textile wastewater with TBD under UV light were achieved while 38.5% color removal of TBD in textile wastewater was observed under visible light in 6-hour irradiation. In pilot plant investigation using a fixed-bed reactor, a 54.8% color removal of TBD in textile wastewater in 1.5 hours of solar irradiation was observed.

Keywords: Photocatalytic treatment, AC/TiO_2, Textile wastewater, Optimization, Response surface methodology.

1. Introduction

Photocatalytic degradation of dyes using TiO_2 has been studied in the past by various researchers [1]. There are different types of dyes used by textile industries. Turquoise blue dye (TBD), an azo dye with molecular formula $C_{32}H_{16}N_8S_2O_6CuNa_2$ and molecular structure shown in Fig. 1 belongs to direct dye which ranked next to acid dye in terms of persistency and is also the most persistent compared to basic dye, disperse dye and reactive dye when subjected to

Nomenclatures

A	Final absorbance
A_0	Initial absorbance
C	Final dye concentration, ppm
C_0	Initial dye concentration, ppm
[Io]	Light intensity, mW/cm^2
[TBD]	Initial Turquoise blue dye concentration, ppm

Abbreviations

CCD	Central composite design
RSM	Response surface methodology
TBD	Turquoise blue dye

photocatalytic treatment using JT Baker TiO_2 [2]. Azo dyes can be grouped as monoazo, diazo, triazo or polyazo dyes according to the number of azo bonds (–N=N–) in the structure. The color of azo dyes is due to these azo bonds and the associated chromophores [3].

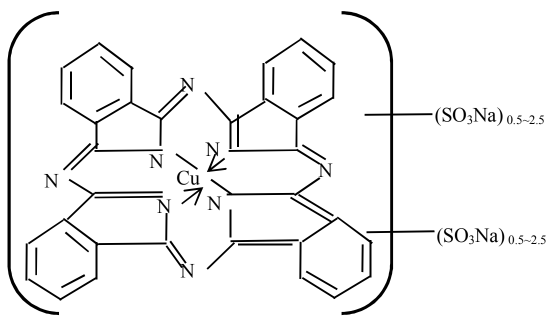

Fig. 1. Molecular structure of TBD [4].

The objective of this study is to optimize the operating parameters in photocatalytic degradation of TBD using a recirculating reactor with immobilized AC/TiO_2 and facilitate the transfer of technology to an industry partner. The TiO_2 catalyst impregnated with AC was used in this study for its known synergistic effect in photocatalysis [5]. The operating parameters which include initial dye concentration, catalyst loading, initial dye solution pH, UV intensity and recirculating flow rate have been studied by previous researchers. Optimum parameter values vary depending on the target pollutant, type of catalyst and design of reactor used; hence, there is a need to evaluate optimum operating parameter values for every new photocatalytic dye degradation study. In the present study, Response Surface Methodology (RSM) was used in determining the optimum values of operating parameters in photocatalytic dye degradation using a recirculating photocatalytic reactor. Central Composite Design (CCD) as shown in Fig. 2 is a widely used RSM being applied in optimization and is useful for building a second order model for a response variable without needing to use a complete three-level factorial experiment.

The application of photocatalysis in the treatment of textile wastewater is timely, as to date, no universal photocatalytic system that is commercially available which features high efficiency, easy catalyst activity and activates in visible light [6].

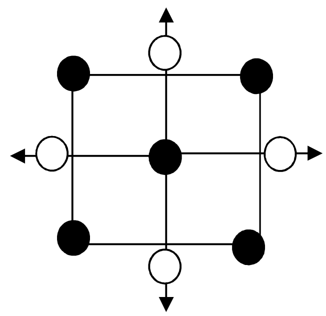

Fig. 2. Central composite design for *p* = 2 factor.

2. Methodology

2.1. Laboratory investigation

TBD is the target pollutant used in this study which was provided by the textile industry partner. The catalyst used in photocatalytic degradation of TBD is AC/TiO_2 composite catalyst with 8.72% wt AC loading synthesized via sol-gel method and calcined at 400 ^oC. In catalyst preparation via sol-gel, the materials used are Titanium isopropoxide, glacial acetic acid, double distilled water and activated carbon acquired from Carbo Karn Co. Ltd. in Thailand.

The catalyst produced was characterized for its BET surface area, pore size, pore volume, Point of zero charge (PZC), particle size, TiO_2 crystal structure and band gap. AC/TiO_2 was immobilized in glass plates using Polyethylene glycol (MW = 10,000 g/mol) as binder with further heat treatment for 3 hours at 300 ^oC. The photocatalytic reactor used in this study is the recirculating batch reactor shown in Fig. 3.

The reactor has a 254-nm UV lamp and equipped with a quartz or a pyrex glass sleeves. The effective volume of the reactor is 1 L. The temperature of the solution is maintained at 32.0 ± 0.5 ^oC by cooling water that flows inside the sleeve of the UV lamp. Air was supplied into the dye solution by an air pump at 100 ml/s which maintained the solution saturated with oxygen.

The catalyst-coated glass plates were installed in a sample holder designed to fit exactly at the bottom of the reactor hence prevents movement during photocatalytic reaction. The UV lamp is installed in a vertical position and the distance from the lamp to the surface of immobilized AC/TiO_2 is approximately 25 mm.

The body of the reactor was totally covered with aluminum foil to maximize the use of light within the vessel. The % color removal was calculated using Eq. (1):

$$\%\ \text{Color removal} = \frac{C_o - C}{C_o} \times 100 \qquad (1)$$

where C_o= initial dye concentration and C = final dye concentration at 6 hours irradiation.

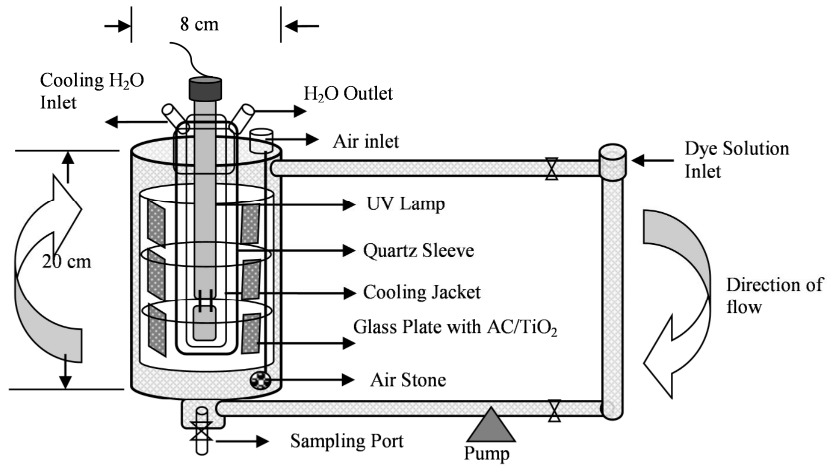

Fig. 3. Recirculating batch photocatalytic reactor.

2.2. Pilot plant investigation

The pilot plant reactor (see Fig. 4) is a fixed bed, thin film type solar photocatalytic reactor adopted from Noguiera and Jardim [7]. In this reactor, the textile wastewater was pumped and allowed to flow along the fixed bed of photocatalyst. The reactor used solar light to activate the AC/TiO_2 film. The exposure of wastewater to sunlight was carried out from 9 AM until 3 PM. The parameters evaluated are shown in Table 1.

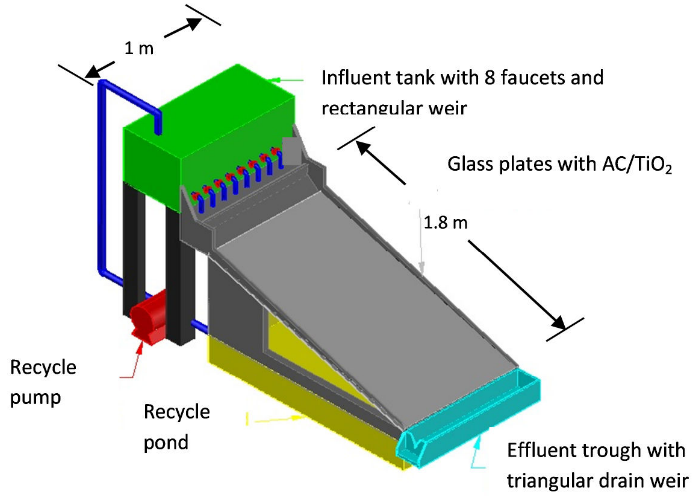

Fig. 4. Fixed bed pilot plant reactor

Table 1. Parameter values in pilot plant investigation.

Parameter (Unit)	Values
Flow rate (ml/min)	167, 222, 333
No. of recirculation passes	1, 2, 3
Residence time (hours)	1.5, 2.0, 3.0

3. Results and Discussions

3.1. Laboratory investigation

Table 2 summarizes the characterization results of immobilized AC/TiO_2. AC/TiO_2 with 8.72% wt AC loading has a BET surface area of 168.4 m^2/g and with pure anatase crystal structure of TiO_2. The AC/TiO_2 particles are in nanometer size and have a band gap of 3.33 eV which indicates that the catalyst has no visible light absorption. The PZC of the catalyst is 7.20. As TBD is anionic azo dye, effective adsorption of dye molecules onto the surface of AC/TiO_2 is expected at acidic pH of dye solution.

Table 2. Characteristics of AC/TiO_2 catalyst.

Parameter (Unit)	Value
BET surface area (m^2/g)	168.4
Pore volume (cm^3/g)	0.012
Pore size (Å)	120.7
% weight AC (%)	8.72
Particle size (nm)	9.46
band gap (eV)	3.33
Point of zero charge	7.20
TiO_2 structure	Anatase

Meanwhile, results of photolysis and dark adsorption experiments as shown in Figs. 5 and 6 show a color removal of 3.93% and 21.7% respectively. These experiments were performed to ensure that color removal in later experiment is mainly due on photocatalytic reaction.

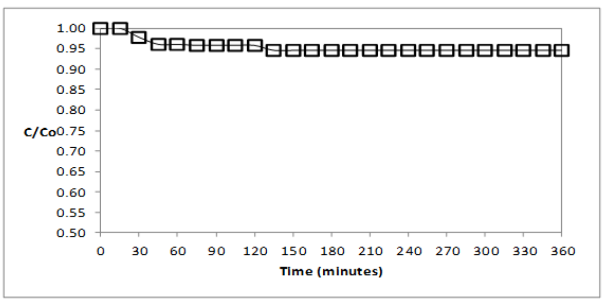

Fig. 5. Photolysis *[TBD$_O$]* = 15mg/L, pH = 3.0, *Io* = 2.5 W/cm^2.

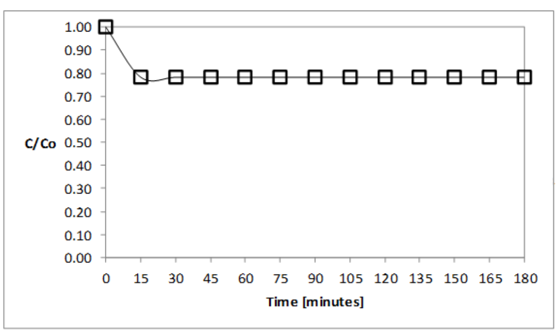

Fig. 6. Adsorption. *[TBD$_O$]* = 15 mg/L, pH = 3.0, AC/TiO_2 loading = 3.0 mg/L.

An approximate function of % color removal based on experimental results was evaluated using the Design Expert software and is given below:

$$\text{Color Removal }(\%100) = 0.53217 - 0.037815A + 0.13203B - 0.26108C + 0.69065D + 0.00408192E + 0.003125AB + 0.004125AC - 0.007375AD - 0.00002875AE + 0.03125BC - 0.01875BD - 0.0005375BE + 0.00125CD - 0.0001375CE - 0.0007375DE + 0.000214142AA - 0.013941BB - 0.00687006CC - 0.07051DD - 0.00000245477EE \quad (2)$$

where,

A = Initial dye concentration, ppm
B = Catalyst loading, mg/L
C = Initial dye solution pH
D = UV intensity, mW/cm^2
E = Recirculating flow rate, ml/s

From the derived mathematical model, the ANOVA (see Table 3) showed an F-value of 18.17 which suggests that the model is significant. All model terms i.e. initial dye concentration, catalyst loading, initial dye solution pH, UV intensity and recirculating flow rate are significant with "Prob>F" values <0.05. The predicted R-squared of 0.71 is a reasonable agreement with the Adj R-squared of 0.88. This model has an adequate precision greater than 4.00 which shows that it is desirable and indicates an adequate signal. F-values implied that the initial dye concentration has the highest influence in color removal among the other parameters involved.

Table 3. ANOVA for response surface quadratic model.

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**P-value Prob>F**
Model	1.40	20	0.070	18.17	< 0.0001
A- initial dye concentration	0.74	1	0.74	191.09	< 0.0001
B- catalyst loading	0.15	1	0.15	37.91	< 0.0001
C- initial dye solution pH	0.30	1	0.30	78.15	< 0.0001
D- UV intensity	0.13	1	0.13	32.81	< 0.0001
E - Recirculating flow rate	0.03	1	0.030	7.89	0.0088
Residual	0.11	29	3.84 E -0.003		
Lack of fit	0.11	22	5.073 E - 0.003		
Standard deviation			0.062		
Mean			0.50		
R- squared			0.93		
Adjusted R- squared			0.88		
Predicted R-squared			0.71		
Adequate precision			17.53		

The effect of operating parameters showed that the color removal increases when either or both the catalyst loading and UV intensity is increased. However, the color removal decreases as the initial dye concentration, initial solution pH and recirculating flow rate increases. The increase in photocatalytic efficiency as the UV intensity is increased is due to the enhanced production of hydroxyl radicals. Also, the increase in the amount of catalyst increases the active sites on the photocatalyst surface thus causing an increase in the number of •OH radicals which can take part in the discoloration of dyes. On the other hand, as the initial concentration dye increases, the equilibrium adsorption of dyes on the catalyst surface active sites also increase, hence competitive adsorption of •OH on the same site decreases. This means a lower formation rate of •OH radical responsible for dye degradation [8]. Also, as the initial dye concentration increases, the path length of photons entering the solution decreases, which result in lower photon adsorption on catalyst particles, and consequently lower photocatalytic reaction rates [9]. Moreover, as the recirculating flow rate increases, the percentage color removal decreases. This result suggests the significance of contact time of catalyst and the target pollutant. The optimum conditions and full factorial central composite design showing the actual and predicted values are presented in Table 4 and Table 5 respectively. In Table 5, the color removal of TBD at optimum conditions in 6 hour-irradiation is 90.01%.

Table 4. Optimum conditions

Parameter (Unit)	Value
Initial dye concentration (ppm)	15
Catalyst loading (g catalyst/L solution)	3.00
Initial dye solution pH	3.00
UV intensity (mW/cm2)	2.50
Recirculating flow rate (ml/s)	100

Optimum conditions were used in photocatalytic degradation of textile wastewater with TBD under UV light and the result shows 86.40% color removal in 6-hour irradiation. This suggests that other chemicals present in actual textile wastewater may affect the efficiency of the catalyst. Moreover, photocatalytic degradation of textile wastewater with TBD was also performed under visible light and the result shows 38.5% color removal in 6-hr irradiation (see Fig. 7) with corresponding COD removal of 42.52 %.

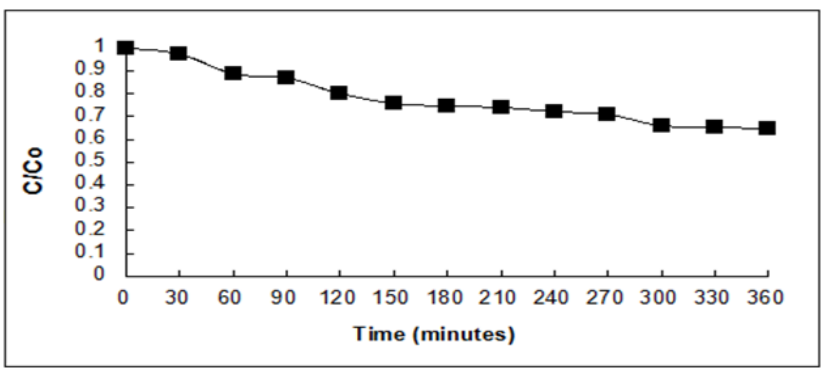

Fig. 7. Photocatalytic removal of TBD in textile wastewater under visible light.

Table 5. Optimization results of full factorial central composite design.

Run No.	Dye Concentration	Catalyst loading	Dye solution pH	UV intensity	Recirculating Flow rate	Actual % Color Removal	Predicted % Color Removal
1	-2.38	0.00	0.00	1.00	0.00	78	86
2	0.00	-1.00	-1.00	-1.00	-1.00	52	59
3	-1.00	-1.00	-1.00	-1.00	1.00	61	62
4	-1.00	-1.00	-1.00	1.00	-1.00	83	78
5	-1.00	-1.00	-1.00	1.00	1.00	71	73
6	-1.00	-1.00	1.00	-1.00	-1.00	41	39
7	-1.00	-1.00	1.00	-1.00	1.00	48	41
8	-1.00	-1.00	1.00	1.00	-1.00	65	58
9	-1.00	-1.00	1.00	1.00	1.00	56	52
10	-1.00	1.00	-1.00	-1.00	1.00	77	68
11	-1.00	1.00	-1.00	-1.00	-1.00	67	71
12	-1.00	1.00	-1.00	1.00	-1.00	90	88
13	-1.00	1.00	-1.00	1.00	1.00	74	78
14	-1.00	1.00	1.00	-1.00	1.00	52	51
15	-1.00	1.00	1.00	-1.00	-1.00	60	54
16	-1.00	1.00	1.00	1.00	-1.00	67	71
17	-1.00	1.00	1.00	1.00	1.00	58	60
18	0.00	-2.38	0.00	0.00	0.00	31	36
19	0.00	0.00	-2.38	0.00	0.00	80	71
20	0.00	0.00	0.00	-2.38	0.00	25	29
21	0.00	0.00	0.00	0.00	-2.38	56	55
22	0.00	0.00	0.00	0.00	0.00	52	52
23	0.00	0.00	0.00	0.00	0.00	50	52
24	0.00	0.00	0.00	0.00	0.00	52	52
25	0.00	0.00	0.00	0.00	0.00	55	52
26	0.00	0.00	0.00	0.00	0.00	52	52
27	0.00	0.00	0.00	0.00	0.00	52	52
28	0.00	0.00	0.00	0.00	0.00	52	52
29	0.00	0.00	0.00	0.00	0.00	48	52
30	0.00	0.00	0.00	0.00	2.38	41	42
31	0.00	0.00	0.00	2.38	0.00	59	55
32	0.00	0.00	2.38	0.00	0.00	22	31
33	0.00	2.38	0.00	0.00	0.00	69	64
34	1.00	-1.00	-1.00	-1.00	1.00	35	34
35	1.00	-1.00	-1.00	-1.00	-1.00	41	34
36	1.00	-1.00	-1.00	1.00	1.00	35	39
37	1.00	-1.00	-1.00	1.00	-1.00	41	46
38	1.00	-1.00	1.00	-1.00	-1.00	17	18
39	1.00	-1.00	1.00	-1.00	1.00	20	17
40	1.00	-1.00	1.00	1.00	1.00	22	22
41	1.00	-1.00	1.00	1.00	-1.00	26	30
42	1.00	1.00	-1.00	-1.00	-1.00	44	49
43	1.00	1.00	-1.00	-1.00	1.00	38	44
44	1.00	1.00	-1.00	1.00	-1.00	52	59
45	1.00	1.00	-1.00	1.00	1.00	45	47
46	1.00	1.00	1.00	-1.00	1.00	23	30
47	1.00	1.00	1.00	-1.00	-1.00	42	37
48	1.00	1.00	1.00	1.00	-1.00	46	47
49	1.00	1.00	1.00	1.00	1.00	40	33
50	2.38	0.00	0.00	0.00	0.00	31	24

3.2 Pilot plant investigation

Using the optimum conditions determined in the laboratory, results of pilot plant investigation (see Fig. 8) shows that the 1.5-hour residence time achieved the highest color removal of 54.8%. More number of circulations passes (3 passes) resulted to a higher dye degradation. The best recirculation flow rate is 222.22 mL/min in which the residence time is 1.5 hours. It can also be observed (see Table 6) that as the intensity of solar light decreases, the % color removal also decreases. Other monitoring results show that both the pH and the temperature rise in the progress of photocatalytic experiments.

The percentage color removal observed in pilot plant investigation (54.80%) which exceeds the result obtained in laboratory investigation (38.50%) can be ascribed to the approximately 10% UV spectrum in solar light where the AC/TiO_2 is mainly applicable. The higher intensity of solar light (687 mW/cm^2) during pilot plant investigation compared to the light intensity used in laboratory investigation (2.50 mW/cm^2) also contributed to the increase in the efficiency of AC/TiO_2. Moreover, the improved contact between the AC/TiO_2 film and the pollutant in the fixed bed reactor also led to the better performance of the catalyst.

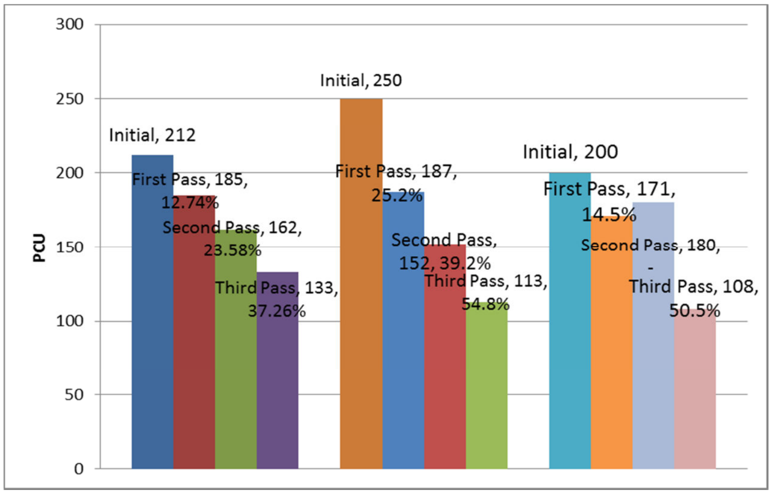

Fig. 8. Pilot plant investigation results.

Table 6. Summary of results.

Parameter (Unit)	Weather status	Average Sunlight Intensity	A/A_o	% Color Removal (Absorbance)	% PCU reduction
2 hours, 1 pass	Sunny	1090	0.70	30.00	12.74
2 hours, 2 pass	Sunny	1030	0.69	31.03	23.58
2 hours, 3 pass	Sunny/ cloudy	945	0.59	41.08	37.26
1.5 hours, 1 pass	Sunny	1101	0.75	24.55	25.20
1.5 hours, 2 pass	Sunny	1063	0.70	30.21	39.20
1.5 hours, 3 pass	Cloudy/ sunny	687	0.36	64.01	54.80
1 hour, 1 pass	Cloudy	835.6	0.88	11.67	14.50
1 hour, 2 pass	Cloudy	921	0.62	38.38	14.50
1 hour, 3 pass	Cloudy/ sunny	914	0.57	43.25	15.50

4. Conclusions

The following are the conclusions derived based from the results:

- The immobilized AC/TiO_2 with 8.72% weight AC loading has a BET surface area of 168.4 m^2/g and with pure anatase crystal nanosized TiO_2.
- In laboratory investigation, the model derived for this system is significant with an *F-value* of 18.17. The initial dye concentration has the highest influence in color removal. Moreover, 90.01% color removal for TBD while 86.40% color removal of actual textile wastewater was observed during photocatalytic treatment under UV light. However, only 38.50% color

removal in 6-hr irradiation was achieved using visible light with corresponding COD removal of 42.52%.

- In the pilot plant investigation, 54.80% color removal was observed in 1.5 hrs residence time with 3 recirculation passes. The approximately 10% UV spectrum in solar light, higher light intensity and improved contact between the catalyst and textile wastewater in the fixed bed reactor contributed to the enhanced photocatalytic efficiency of AC/TiO_2.

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