OPTIMIZATION FOR PHOTOCATALYTIC COLOR REMOVAL OF TURQUOISE BLUE DYE C.I. 199 IN IMMOBILIZED AC/TIO₂ AND UV - SYSTEM USING RESPONSE SURFACE METHODOLOGY

Jurex Gallo¹, Josephine Borja¹, Susan Gallardo¹, Cris Salim³, Pailin Ngaotrakanwiwat², and Hirofumi Hinode³

¹Department of Chemical Engineering, De La Salle University, Manila, Philippines, Tel: +63 02 5244611 local 215, e-mail: jurex_gallo@yahoo.com

² Department of Chemical Engineering, Burapha University, Chonburi, Thailand; e-mail:pailin@buu.ac.th ³ Tokyo Institute of Technology, Tokyo, Japan, e-mail: hinode@ide.titech.ac.jp

Received Date: January 16, 2012

Abstract

The aim of the study is to optimize the process parameters in photocatalytic color removal of Turquoise blue dye (TBD) using immobilized Titania-activated carbon (AC/TiO₂) and UVsystem. A preliminary study was performed which revealed that 5% is the best AC loading in AC/TiO₂. The immobilized AC/TiO₂ with 5% AC loading was characterized using BET, SEM, TEM and TGA techniques. The point of zero charge (pH_{pzc}) of the composite catalyst was also determined. Response surface methodology (RSM) based on Central composite design (CCD) was applied in optimization. The cummulative effect of operating parameters initial dye concentration, catalyst loading, initial solution pH, UV intensity and recirculating flow rate on the efficiency of immobilized AC/TiO₂ for Turquoise blue dye removal were evaluated. A mathematical model was proposed and the analysis of variance (ANOVA) indicated that the derived model could be used to navigate the design space. The mathematical model is correlated to the experimental value with a correlation coefficient of 0.93. The optimum operating parameters were found to be 15 ppm initial dye concentration, initial dye solution pH of 3.0, 3g/ L catalyst loading, recirculating flow rate at 100 ml/s and UV intensity of 2.5 mW/cm². The initial dye concentration has the highest influence in color removal while the recirculating flow rate is found as the least significant factor. These optimum conditions exhibited 90.0 % and 86.4 % color removal for Turquoise blue dye and textile wastewater with TBD stream respectively.

Keywords: Photocatalysis, Response surface methodology, TiO₂/AC, Turquoise blue dye

Introduction

Textile dyes and other industrial dyestuffs constitutes one of the largest group of organic compounds that represents an environmental concern [1]. About 20% of the total world production of dyes is lost in the dyeing process and eventually released in textile effluents [2]. Textile dyes are potentially toxic due to their low removal rate and if untreated would cause long term health concerns [3]. The impact and toxicity of dyes released in the environment have been extensively studied [4].

In the Philippines, local textile mills were temporarily shut down due to high color of wastewater discharges exceeding the country's regulatory standards for textile effluent [5]. Arising from the steep development of dyeing industries worldwide, the degradation of dyes in textile wastewater received an increasing attention over the years. Conventional and biological methods are ineffective for the degradation and mineralization of dye molecules [6]. Thus, a growing research has been inspired to find a selective, reliable and durable alternative treatment of heavily polluted textile effluent. In particular, photocatalysis is a promising method of treatment for its ability to completely degrade

organic pollutants in wastewater. A photocatalytic process is featured by the high reactivity of hydroxyl radicals to complete elimination of pollutants. Despite its known potential, problems still arise such as the limitations of the widely use catalyst TiO_2 and the cost prohibitive reaction medium associated with powder catalysts. The limitations of TiO_2 in photocatalysis include low surface area and low adsorption capacity. Impregnation of AC with TiO_2 is one option to address the problem. Several studies on photocatalytic degradation of dyes using AC/ TiO_2 - UV system has been described in literatures [7,8]. The synergistic effect of combined TiO_2 and AC is known to enhance the efficiency of the catalyst for pollutant degradation [7]. Immobilizing the composite catalyst. AC/ TiO_2 in a substrate is also of a worthwhile study for easy recovery of the catalyst. This technique has turned from an interesting alternative approach into a powerful method by offering a number of advantages. Although this technology is in its infancy at present, a widespread and great progress in this area can be expected in the future [8].

In photocatalytic degradation of dyes, operating conditions such as initial dye concentration, catalyst loading, initial dye solution pH, UV intensity and recirculating flow rate were known to affect the efficiency of photocatalyst. Conventional and classical methods of studying a process by maintaining other factors involved at an unspecified constant level does not depict the combined effects of all factors involved. This method is also time consuming and requires large number of experiments to determine optimum level, which are unreliable [9]. These limitations of the classical method can be eliminated using RSM by optimizing all affecting parameters collectively [10]. RSM is a mathematical and statistical technique for designing experiments, building models, evaluating relative significance of several independent variables and determining optimum conditions for desirable responses [11].

The present work is aimed at optimization of the process parameters in photocatalytic degradation of Turquoise blue dye as follows: initial dye concentration, catalyst loading, initial dye solution pH, UV intensity and recirculating flow rate. The immobilized AC/TiO₂ prepared by sol-gel method was characterized and the results of characterization were also presented in this paper. Turquoise blue dye used as the target pollutant is an azo dye which also belongs to direct dye. This particular type of dye ranked next to acid dye in terms of persistency when subjected to photocatalytic treatment using JT. Baker TiO₂ and UV system [5].

Methodology

Materials

Titanium (IV) isopropoxide (Sigma Aldrich), glacial acetic acid and bi-distilled H_2O were used in the synthesis of TiO₂ via sol-gel [11]. The AC (minimum surface area = 1100 g/m², particle size = 2.36 mm) used to impregnate with TiO₂ was acquired from CarboKarn Co. Ltd. in Thailand. AC/TiO₂ was immobilized in glass plates (microscope slides) using Polyethylene glycol (MW = 10,000 g/mol) as binder with further heating in 3 hours at 300° C. Turquoise blue dye C.I. 199 (Everdirect Supra Turquoise Blue FBL) shown in Table 1 was acquired from Saffron Philippines Inc.. Actual textile wastewater with Turquoise blue dye streams was also collected from the textile mill. The initial pH of the dye solution was adjusted using 0.1 N H₂SO₄ and the dye solution pH was not controlled in the course of reaction.

Name	Molecular Formula / Molecular Weight	Color Index	Solubility in H ₂ 0	Chemical Structure	$\lambda_{max}(nm)$
Ever Direct Supra (FBL)	C ₃₂ H ₁₆ N ₈ S ₂ O ₆ CuNa ₂ / 781.5 g/mol	C.I. 199	60 g/L		605

Table 1. Turquoise Blue Dye

Experimental Set-up

The evaluation of photocatalytic activity was performed using a batch recirculating reactor shown in Figure 1. This reactor has a 254-nm UV lamp and equipped with a quartz sleeve. The volume of the reaction solution is 1.5-L. The temperature of the solution is maintained at 32 °C by a cooling water that passed inside the sleeve of the UV lamp. Heterogeneous photocatalytic reactions are usually not very temperature – sensitive because the band-gap energy of TiO₂ (~ 3.2 eV) is too high to be overcome by the thermal activation energy of kT = 0.026 eV at room temperature [13]. Increased temperature may increase oxidation rate but also reduces the adsorptive capacities associated with organics and dissolved oxygen [13]. Air was blown into the dye solution at 100 ml/s using an air pump to maintain the solution saturated with oxygen. The catalyst immobilized in glass plates was placed in a sample holder and inserted inside the reactor. The distance from the UV lamp to the immobilized AC/nanoTiO₂ composite catalyst is approximately 25 mm.



Figure 1. Recirculating photocatalytic reactor

Analytical Methods

Quantachrome Autosorb-1 was used for BET analysis and the morphology of the catalyst was evaluated using Scanning Electron Microscopy (Jeol JSM-5310). Transmission Electron Microscopy (Jeol JEM-2010F) was used to estimate the crystallite size by a high resolution image of the catalyst. The percentage weights of AC, TiO_2 and PEG in the composite catalyst was determined using Thermogravimetric Analyzer (Rigaku Thermo Plus TG - 8120). UV-vis spectrophotometer (Pharmaspec UV-1700, Shimadzu) was used to determine the dye concentration based on a calibration curve

(absorbance vs. concentration). Samples were withdrawn from the reactor at 15 minute – interval. The absorbance of Turquoise blue dye solution before and after photocatalytic treatment were measured and the percentage color removal was calculated using Equation 1.

where,

 $C_O =$ initial dye concentration C = final dye concentration at 360 minute - irradiation

 $C_0 - C \ge 100$

 C_0

Experimental Design and Optimization

RSM based on Central Composite Design was applied to optimize the experimental conditions in photocatalytic degradation of Turquoise blue dye. The selected parameters considered as independent variables are initial dye concentration, catalyst loading, initial dye solution pH, UV intensity and recirculating flow rate. Levels of each parameter (Table 2) used in optimization were chosen based on results of preliminary investigation. Design Expert 7.1.5 software was used to model and optimize experimental results. A total of 50 batch runs with 8 central points were performed in this optimization study.

Independent Variable	Factor	Range Levels			
		-1.00	0.00	+1.00	
Initial dye concentration (ppm)	А	15	20	25	
Catalyst loading (g/L dye solution)	В	2.00	2.50	3.00	
Initial solution pH	С	3.00	3.50	4.00	
UV intensity (mW/cm^2)	D	1.50	2.00	2.50	
Recirculating flow rate (ml/s)	E	100	150	200	

Table 2. Experimental Range and Levels of Independent Variables

Results and Discussion

Absorption Spectrum of Turquoise Blue Dye

The absorption spectra of Turquoise blue dye during photocatalytic degradation using immobilized AC/nanoTiO₂ was monitored and the result is presented in Figure 2. The actual image of Turquoise blue dye solution at various irradiation times is also presented (Figure 2 - inset). Turquoise blue dye is characterized by a single band in the visible region at maximum absorbance at 605 nm and three bands (210nm, 260nm and 320nm) at the UV region. Reduction observed in these peaks indicates the degradation of these molecules to smaller intermediates. No appearance of new absorption bands was observed in the UV and visible region as irradiation time is increased which suggests that intermediate products formed were also successfully degraded.



Figure 2. UV-vis absorption spectrum of TBD at various irradiation times

Selection of AC/TiO2 with Various AC Loading

A preliminary study was conducted to determine the best AC loading in composite catalyst AC/TiO₂. Powder catalysts were used at same conditions (20ppm initial TBD concentration, pH 3 of initial dye solution, 1 g catalyst per L of dye solution) to evaluate their respective performances in the color removal of Turquoise blue dye. Results as presented in Figure 3 showed the superior activity of AC/TiO₂ with 5% AC loading. Using AC/TiO₂ with 5% AC loading, a total color removal for Turquoise blue dye was observed in 120 minute – irradiation while it took longer for bare TiO₂ at 150 minute – irradiation. This result clearly showed the synergistic effect of TiO₂ combined with AC as found by various authors [15, 16] This result further suggests the use of AC/TiO₂ with 5% AC loading in optimization study.



Figure 3. Photocatalytic performance of AC/TiO_2 with various AC loading (Reaction time = 150 minutes)

Characterization of Immobilized AC/TiO2 with 5% AC Loading

The immobilized catalyst AC/TiO₂ with 5% AC loading was characterized using BET, SEM, TEM and TGA techniques. The point of zero charge (pH_{pzc}) of the composite catalyst was also evaluated using pH drift test. Results showed that immobilized AC/TiO₂ with 5% AC loading has a BET surface area of 164.8 m²/g and a pore size of 120.7 Å. SEM image of the catalyst (Figure 4a) showed a uniform distribution of AC and TiO₂; the catalyst is also observed porous due to the decomposition of PEG during heat treatment.

TEM image (Figure 4b) revealed that the average crystallite size of TiO₂ in composite catalyst is at nanoscale measured less than 20 nm in diameter. The TGA data (Figure 4c) revealed the presence of PEG that was not totally removed by heating in 3 hours at 300 $^{\circ}$ C which is evident in the weight reduction observed from 300 $^{\circ}$ C – 500 $^{\circ}$ C. Moreover, the pH_{pzc} of the catalyst is 7.3 (Figure 4d).



Figure 4. Characterization of immobilized AC/TiO₂ (a) SEM (b) TEM (c) TGA (d) pH_{Pzc}

Optimization Using RSM

RSM provides an empirical relationship between the response function and independent variables. In this study, the coefficients for the response function for different independent variables were determined using the Design Expert Software 7.1. Fifty (50) batch runs were performed according to CCD design and the results are presented in Table 3.

Run	Initial	Catalyst	Initial	UV	Recirculating	% Color	% Color
	Dye	Loading	Soln pH	Intensity	Flow Rate	Removal	Removal
	Conc.	U	-	·		(Actual	(Predicted
						Value)	Value)
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

 Table 3. Experimental and Predicted % Color Removal

An approximate function of percentage color removal based on experimental results is given in Equation 2.

% Color removal	= [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	
	$-0.0007375\text{DE} + 0.000214142\text{A}^2 - 0.013941\text{B}^2$	
	$-0.00687006C^{2} - 0.07051D^{2} - 0.00000245477E^{2}$](100)	(2)
where,		
	A = Initial dye concentration (ppm)	
	B = Catalyst loading (g/L)	
	C = Initial solution pH	
	D = UV intensity (mW/cm ²)	
	E = Recirculating flow rate (ml/s)	

From the derived mathematical model, it is apparent that the percentage color removal increases with the catalyst loading (B) and UV intensity (D) while decreasing with initial dye concentration (A), initial solution pH (C) and recirculating flow rate (E).

ANOVA Result

The statistical significance of the model was checked by *F*-test. *F*-test is used for comparing the model variance with residual variance. The *F*- value is the measure of the

Source	Sum of Squares	Df	Mean Square	F-value	p-value Prob>F	
Model	1.40	20	0.070	18.17	< 0.0001	Significant
(A) Initial Dye	0.74	1	0.74	191.09	< 0.0001	
Concentration						
(B) Catalyst Loading	0.15	1	0.15	37.91	< 0.0001	
(C) Initial 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	0.03	1	0.030	7.89	0.0088	
Rate						
Residual	0.11	29	3.84 E-0.003			
Lack of fit	0.11	22	5.073 E-003			
Std deviation				0.062		
Mean				0.50		
R^2				0.93		
$R^2_{\rm adj}$				0.88		
$R^2_{\rm pred}$				0.71		
Adequate precision				17.52		

Table 4. ANOVA for Response Surface Quadratic Model

variance of data about the mean. If the F-value departs significantly from unity, the more certain that the input variables adequately explain the variation in the mean of the data. Meanwhile, *p*-values are used to check the significance of each of the coefficients and are necessary to understand the pattern of the mutual interactions between the variables. The smaller the *p*-values, the bigger the significance of the corresponding coefficient. To validate from the statistical standpoint on any response surface model, the F-value must be as high as possible whereas the *p*-value should be as low as possible [17]. The -Prob > F" value is the p-value associated with the F-statistic which is used in testing the null hypothesis that all the model coefficients are 0. The ANOVA presented in Table 4 showed an *F-value* of 18.17 suggesting the significance of the derived model. Values of -Prob >F" less than 0.05 indicate model terms are significant. In this case, all model terms namely initial dye concentration, catalyst loading, initial solution pH, UV intensity and recirculating flow rate are significant with -Prob > F" values <0.05. All interaction terms were insignificant to the response. The predicted R^2 of 0.71 is a reasonable agreement with the adjusted R^2 of 0.88. This model has an adequate precision (17.52) greater than 4.00 which shows that it is desirable and implies an adequate signal. This also indicates that the model can be used to navigate the design space. F-values also implied that the initial dye concentration has the highest influence in color removal among the other parameters involved.

Adequacy Check of the Model

The adequacy check of the proposed model were estimated using the diagnostic plots shown in Figure 5 and Figure 6. The percentage actual color removal plotted against the predicted values as evaluated from the model was shown in Figure 5. A good agreement was obtained between the actual percentage decolorization and the predicted percentage decolorization with R^2 of 0.93 and R^2_{adj} of 0.88 which further suggests a good approximation of the proposed model with the actual percentage color removal. The internally studentized residuals measures the standard deviations that separate the actual and predicted values [18]. From Fig. 6, almost all data points lie on the straight line which indicates that neither response transformation was required for these points nor there is an apparent problem on normality.





ASEAN Engineering Journal Part B, Vol 1 No 1 (2012), ISSN 2286-7694 p.22

Response Surface Analysis

Contour plots and response surface of color removal depending on various parameters are shown in Figure 7 - 10. The response surface of initial dye concentration and recirculating flow rate on the color removal of Turquoise blue dye is presented in Figure 7. Result shows that the percentage color removal is decreased with increasing initial dye concentration. As the initial dye concentration increases, the equilibrium adsorption of dyes on the catalyst surface active sites also increase, hence competitive adsorption of OH⁻ on the same site decreases, which means a lower formation rate of OH• radical responsible for dye degradation [19]. 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 [20]. A similar effect of recirculating flow on the percentage color removal was also observed. As the recirculating flow rate increases, the percentage colorremoval decreases. This result suggests the significance of contact time of AC/TiO2 with UV illumination in photocatalytic color removal of Turquoise blue dye.



Figure 7. Effects of initial dye concentration and recirculating flow rate

Meanwhile, Figure 8 depicted the effect of UV intensity with the color removal of Turquoise blue dye. Results showed that the color removal of Turquoise blue dye increases with increasing UV intensity but this dependency was observed non linear. The increase in photocatalytic efficiency is due to the enhanced production of This result is similar to the findings of other researchers [19] who hvdroxvl radicals. conducted a study on CdS and TiO₂ photocatalysis. For TiO₂ photocatalysis, the relationship of light intensity versus reaction rate constant (k) was close to linear. It was predicted that if the intensity was continuously increased, the enhancement would decrease due to the effect of e-/h+ recombination [21]. The overall energy input to a photocatalytic process is dependent on light intensity since the UV irradiation generates the photons required for the electron transfer from the valence band to the conduction band of a semiconductor photocatalyst; and the energy of a photon is related to its wavelength. The rate of degradation increases when more radiations fall on the catalyst surface and hence more hydroxyl radicals are produced [1].



Figure 8. Effects of UV intensity and initial dye concentration

Figure 9 showed the effect of initial dye solution pH. The influence of pH in photocatalysis is due to dye particles adsorbed on catalyst surface [20]. The pH of the solution influences the surface-charge properties of the photocatalysts due to the amphoteric behavior of most semiconductor oxides [22]. As presented in Figure 9, the color removal is increasing with decreasing pH because the pH_{pzc} of immobilized AC/TiO₂ is 7.3 which favors adsorption onto more acidic dye solution.



Figure 9. Effects of solution pH and initial dye concentration

In heterogeneous photocatalysis, dye degradation increases with increasing catalyst loading. 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. In a slurry reactor, beyond a certain limit of catalyst amount, the solution becomes turbid and thus blocks UV radiation for the reaction to proceed and therefore percentage degradation starts decreasing [23]. From Figure 10, color removal increases as the catalyst loading increases which showed that immobilized catalyst was not affected by shielding effect as described for powder catalyst suspensions.



Figure 10. Effects of catalyst loading and initial dye concentration

Optimum Conditions and Photocatalytic Color Removal of Textile Wastewater

Actual textile wastewater with Turquoise blue dye streams was tested using the recirculating photocatalytic reactor under optimum conditions presented in Table 5. Result (see Figure 11) showed 86.40% color removal in 6-hr irradiation. This discrepancy compared to the result for simulated Turquoise blue dye (90.0 % color removal) suggests that other chemicals present in textile wastewater may affect the efficiency of the composite catalyst AC/nanoTiO₂.

Parameter	Value
Initial dye concentration	15 ppm
Catalyst loading	3 g/L dye solution
Initial solution pH	3.00
UV intensity	2.50 mW/cm^2
Recirculating flow rate	100 ml/s





Figure 11. Photocatalytic degradation of actual textile wastewater using the optimum conditions

Conclusions

In photocatalytic degradation of Turquoise blue dye, AC/TiO₂ with 5% AC loading outweighed the performances of bare TiO₂ and other composite catalysts with various AC loadings. The 5% AC/nanoTiO₂ immobilized in glass plates using PEG has a BET surface area of 164.8 m^2/g . TEM observation confirmed the catalyst at nanosize with particle size less than 20 nm. In optimization study, the model derived for this system is significant with an F-value of 18.17. The adequacy check of the model with the experimental values also showed a good agreement between the actual percentage color removal and the predicted percentage color removal with R^2 of 0.93 and R^2_{adj} of 0.88. The percentage color removal for Turquoise blue dye increases with the catalyst loading and UV intensity while decreasing with initial dye concentration, initial solution pH and recirculating flow rate. The initial dye concentration has the highest influence in color removal compared to other parameters involved. The optimum conditions are 15 ppm initial dye concentration, initial solution pH of 3.0, 3g/L catalyst loading, recirculating flow rate at 100 ml/s and UV intensity of 2.5 mW/cm². Using these optimum conditions, there was 90.0 % color removal for Turquoise blue dye while 86.4 % color removal was observed for photocatalytic treatment of actual textile wastewater with Turquoise blue dye streams. RSM is found suitable in optimizing the operating conditions for photocatalytic color removal of Turquoise blue dye using AC/TiO₂ and UV system. Further, there are no new absorption bands in the UV and visible region appeared as irradiation time is increased during photocatalytic degradation of Turquoise blue dye using AC/nanoTiO₂ – UV system.

Acknowledgement

Sincere appreciation was extended to the Engineering Research and Development for Technology, Department of Science and Technology – Philippine Council for Industry and Energy Research and Development, Burapha University, Tokyo Institute of Technology, De La Salle University - Manila and Saffron Philippines., Inc. The authors are also grateful to Mr. Katsuaki Hori of the Center of Advanced Materials Analysis at Tokyo Institute of Technology for TEM observation.

References

- [1] I. Konstantinou, and T. Albanis, "TiO₂ -assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations: A review," *Applied Catalysis B: Environmental*, Vol. 49, No 1, pp. 1-14, 2004.
- [2] H. Zollinger, Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments, 2nd Revised Edition., VCH, Germany, 1991.
- [3] D. Chatterjee, V.P. Patnam, A. Sikdar, P. Joshi, R. Misra, and N. Rao, "Kinetics of the decoloration of reactive dyes over visible light irradiated TiO₂ semiconductor photocatalyst," *Journal of Hazardous Materials*, Vol. 156, No. 1-3, pp. 435-441, 2008.
- [4] E. Forgacs, T. Cserhati, and G. Oros, "Romoval of synthetic dyes from waste waters: A review," *Environment International*, Vol. 30, No. 7, pp. 953-971, 2004.
- [5] J. Gallo, E. Mariquit, A. Co, J. Borja, and S. Gallardo, "Assessment of the colored wastewater treatment in the Philippine textile industry and preliminary study on the color removal of wastewater using photocatalysis," In: 2nd Engineering Research and Development for Technology Conference, Manila, Philippines, 2008.
- [6] Z. Zhang, and H. Zheng, "Optimization for decolorization of azo dye acid green 20 by ultrasound and H₂O₂ using response surface methodology," *Journal on Hazardous Materials*, Vol. 172, No. 2-3, pp. 1388-1393, 2009.

- [7] LOCtc° c. 'LOM. Dona-Tqf t,i wg|. 'GD.T.'Tgpf qp. 'E0Garriga i Ecdq.'Q0Gonzalez-F kc|."
 IOA. Herrera'O grkcp. 'LOPerez-Rg° c.'I OEqrqp.'cpf J.A. P cxkq, "VkQ4''cevkxcvkqp''d{ 'wukpi ''
 cevkxcvgf ''ectdqp''cu'c''uwr r qtv''Rctv'K0uwthceg ej ctcevgtkucvkqp''cpf 'f gecpvcdktks{ ''uwf {," ''Applied Catalysis B: Environmental, Xqr066.''No. 2, r r 0'383-394.''42250
- [8] MDY." Hqq." cpf "DOH." J co ggf." "F geqpvco kpcvkqp" of vgzvkrg" y cuvgy cvgt" xkc" VkQ4 l'cevkxcvgf ectdqp"eqo r qukkg"o cvgtkcnu," Advances in Colloid and Interface Science, "Xqr037; . No. 2, "r r 0 130-143, 2010.
- [9] MO'Tcxknwo ct." UO'Tco crhpi co." UO'Mtkuj pcp." cpf "MO'Dcnw, "Crrrkecvkqp" qh" rgur qpug swthceg"mgy qlof qi {"vq"qr vko kj g"y g"r tqeguu"xctkcdrgu"hqt"Rgcevkxg"Rgf "cpf " Aekf 'Btqy p f {g'tgo qxcrl'wukpi "c''pqxgrl'cf uqtdgpv," Dyes and Pigments, Xqr092. 'No. 1, pp. 3: /48.'42280
- [10] M. Elibol, "Tgur qpug'uwthceg"o gy qf qnqi kecn'cr r tqcej 'hqt 'kpenxukqp"qh r gthuxqtqectdqp kp"'cevkpqtj qf kp"'hgto gpvcvkqp"o gf kwo,""Process Biochemistry, "Xqr05:. No. 5, 'r r 0889-995. 42240
- [11] I 0'Dqz."cpf "P0'Ftcr gt." Empirical Model Building and Response Surfaces. Y kg{. United States, '3; : 90
- [12] P0' Xgpmcvcej cmo." O0' Rcmpkej co {." cpf " X0' O wtgi gucp, "Sol-gel" rtgr ctcvkqp cpf ej ctcevgtk cvkqp" qh" pcpquk g" VkQ₄<" Ku" rj qvqecvcn{vke" rgthqto cpeg," Materials Chemistry and Physics, Xqn 326, "No. 2-3, rr0676/67; ."42290
- [13] O 0' Mquky k" KO' Rqwrlqu." MO' Uco ctc." GO' Vucwctqpk" cpf " GO' F ctcmcu,
 "Photocatalytic oxidation"qh"ekdcetqp" {gmqy "NU/T," *Journal of Hazardous Materials*, XqrO' 368. No. 3,"rr0680-685, 2007.
- [14] LO' J gto cpp, "J gygtqi gpgqws pj qvqecvcn{uku<" Hwpf co gpvcni" cpf " crr nkecvkqpu" vq y g tgo qxcn'qh'cs wgqwu'r qmwxcpvu.""*Catalysis Today*, Xqn075."No. 1, rr 0337"-34; .'3; ; ; 0
- [15] IO' O cvqu." IO' Nckpg." IO' J gtto cpp." F O' W ecvgi wk," cpf " IIL." Dtkq." "Kphrwgpeg of cevkxcvgf ectdqp" qp" cs wgqwu" r j qvqecvcn{ vke" eqpugewkxg" twpu" qh" r j gpqnr j qvqf gi tcf cvkqp," Applied Catalysis B: Environmental, "Xqr092."r r 0'683/68; ."42290
- [16] Z0' Y cpi ." [0' Nkw." \0' J w." [0' Ej gp." Y 0' Nkw." cpf "I0' \j cq." "F gi tcf cvkqp of o gy {nqtcpi g" d{" eqo r quksg" r j qvqecvcn{uv" pcpq/VkQ4" ko o qdktk gf " qp" cevkxcvgf ectdqpu" qhf khhgtgpv'r qtqukskgu," *Journal of Hazardous Materials*, Vol. 169, No. 1-3, pp. 3283/3289." 422; 0
- [17] O 0' Mj c {gv." E0' Eqloectu." cpf "O 0' Guucnj k" "Ctvkhkeken' ngwten' pgw qtm' o qf grkpi cpf tgur qpug" uwthceg" o gy qf qrqi {" qh" f gucrkpcvkqp" d {" tgxgtug" quo quku," *Journal of Membrane Science.* "Xqr0'58: . No. 1-2, 'r r 0'424/'436.'42330
- [18] J CL. Nkw." cpf" [CR. Ej kqw." "Qr vko cn' f geqrqt & cvkqp" ghhekgpe { "qh" Rgcevkxg" Rgf "45; d { WX IVkQ4" rjqvqecvcn{vke" rtqeguu" eqwrngf" y kj " tgurqpug" uvthceg o gyjqfqrqi {," Chemical Engineering Journal, Xqr0334."No. 1-3, rr 0395-39; ."42270
- [19] C0'Cm{qn"J (C."[cvo c| ."cpf "O 0'Dc{tco qi nw:""Rj qvqecvcn{vke"f geqmtk cvkqp"qh Rgo c| qnRgf "TT"kp"cs wgqwu"\ pQ" uwur gpukqpu,"" Applied Catalysis B: Environmental, Xqn0'76. No. 1, rr 0'3; /46."42260
- [20] O (H." J cdkdk" P 0' Vergdkep." cpf" L(H." Ej qk" "Vj g ethgev" qh" cppgcrkpi " qp rj qvqeeven{ vke r t qr gt vkgu" qh" pcpquvt wewt gf" vke pkwo " f kqzkf g" yj kp" hkro u," Dyes and Pigments, Xqr095, No. 1, r r 0325/332."42290
- [21] NOB."Tgwgti ctfj."cpf"O 0'Kpi r hcuwm" Rj qvqecvcl {vke"f geqnqwtk cvkqp"qh"tgcevkxg c| q f {g<"C"eqo r ctkuqp"dgw ggp"VkQ4"cpf"Ef U"r j qvqecvcn {uku," Chemosphere."Xqr0 57. No. 3, rr07: 7/7; 8."3; ; 90
- [22] O (A." Dgj pclcf {." P 0' O qf ktuj chrc." cpf " T0' J co | cxk" "Mkpgvke" uwf {" qp rj qvqecvcn{ vke f gi tcf cvkqp" qh" C(10' Aekf " Ygmqy " 45" d{" \ pQ" rj qvqecvcn{ uy,"" Journal of Hazardous Materials, Xqr0355."No. 1-3, rr 0'448/454."42260