

# OPTIMIZED TiO<sub>2</sub>-CATALYSED UV OXIDATIVE DECOMPOSITION OF REACTIVE BLUE 13 IN AQUEOUS SOLUTION USING BOX BEHNKEN DESIGN

DAUDA BENJAMIN, BARDE ABRAHAM

**Abstract**—A photo catalytic degradation of the dye is C.I. reactive black 5 (a mono azo organic colorant) was performed in aqueous solution using TiO<sub>2</sub> as photocatalyst under UV irradiation in a laboratory scale photoreactor;. A suitable surface response experimental design, Box Behnken design, which allows adjustment of factors level to obtain an optimal response, hence, optimize process parameters in experimental analysis, was used for the optimization of colour removal. UV-Visible spectrophotometer was used to assess the absorbance of the sample solutions before and after the photocatalytic decomposition. The results for the optimization revealed that the best conditions for decolorization is as follows: initial dye concentration 12.04 mg/L, catalyst loading 1.68 g/L, pH of 3.10 and irradiation time of 85.57 min. Under these optimal conditions, the corresponding response value predicted for dye decolorization was 99.06% , which was confirmed by validation experiments. Therefore, UV/TiO<sub>2</sub> photocatalytic degradation of reactive mono dyes in aqueous solutions using Box Beckhen design has been proven to be a very viable technique for the treatment of organic colorants (specifically, reactive mono azo dyes) in aqua media since it is multivariate in approach and so allows adjustment of factor level to obtain an optimal response in experimental analysis.

**Index Terms**— Azo dye, Box-Behnken Design, Percentage Decolorization, Photocatalytic degradation, Reactive Blue 13, Titanium dioxide, Oxidative Decomposition.

## 1 INTRODUCTION

Environmental contamination and pollution by biorecalcitrant xenobiotic chemical substances is one of the most severe global problems of today's society. A major class of these xenobiotics in aqueous effluents is colourants[1]. Dyes and pigments are highly important colorants to humans globally, even from times immemorial, especially for their significant applications in the textile and fashion, printing, paints (coatings) and inks production, foods/consumables and tannery industries among others. It is obvious that the human society can no longer do away with these chemical substances even though the waste generated from their usage is a major contributor to environmental pollution "[2], [3]"-a menace that the post-modern world seek to combat and curtail. TiO<sub>2</sub>-based photocatalysis is an emerging technology capable of decolorizing, deodorizing, disinfecting and detoxifying wastewater, especially coloured based water effluents since it leads to complete mineralization of organic carbons into carbon dioxide and water , and it can be done at ambient conditions by using atmospheric oxygen as the oxidant "[4], [5]". In addition, TiO<sub>2</sub> photocatalyst is very easy to come by, very cheap and non-toxic. Many studies revealed the effects of various operating parameters and reported the range which they exert their individual influence on the photocatalytic degradation of many colorants in aqueous solution "[3], [5], [6]" Since the safe operating zone for this process has been provenly understood and known, this studies seek to used response surface design of experiment based on Box-Behnken design to examine and ascertained the operating conditions to meet specifications for optimum response (maximum

decolourizations). Hence, this work met the need for research that will adopt, adapt and advance (in the sense of optimizing) this emerging technology.

## 2 PROCEDURE FOR RESEARCH EXPERIMENTALS

### 2.1 Sourcing of Materials

A common commercial azo dye (C.I. Reactive Blue 13) was obtained from Africa Textile Manufacturer Limited (Kano, Nigeria) and the semiconductor photocatalyst, TiO<sub>2</sub> (P25) was purchased. They were used without any further purification or modification.

Reagents and solvent used were:

Distilled water (H<sub>2</sub>O)

Hydrochloric Acid (0.1M HCl)

Sodium hydroxide (0.1M NaOH)

INFORMATION OF DYES USED

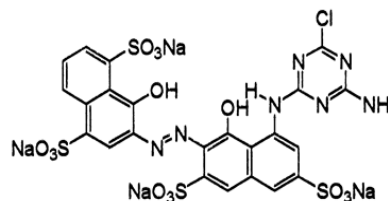


Figure 4.1: Structural formula of C.I. Reactive Blue 13

**Molecular Formula:** C<sub>29</sub>H<sub>16</sub>ClN<sub>7</sub>Na<sub>4</sub>O<sub>14</sub>S<sub>4</sub>

**Molecular Weight:** 866.06

## 2.2 DESIGN OF EXPERIMENT

A response surface design is a set of advanced design of experiments (DOE) techniques that help to better understand and optimize a response. Response Surface methodology (RSM) has been adopted to express the output parameters (responses) that are decided by the input process parameters. RSM also quantifies the relationship between the variable input parameters and the corresponding output parameters. The Box-Behnken design was used for optimization. Optimization of parameters in reaction is one of the most important stages in the development and testing of an efficient and economically viable process of high value from sustainability and chemometric perspectives. The traditional "one-factor-at-a-time approach" is time consuming, and moreover the interactions between independent variables are not considered. Response surface methodology (RSM) is an effective optimization tool wherein many factors and their interactions can be identified with fewer experimental trials [7].

RSM has been widely used in various fields that as to do with process operations for new product development, biotechnology-media composition, improving production yield and chemical processes [7]. The RSM is a collection of mathematical and statistical techniques for designing experiments, building models, evaluating the effects of factors, and searching optimum condition of factors for desired responses. The optimization process of this methodology involves studying the response of statistically designed combinations, estimating the coefficients by fitting it in mathematical model that fits best the experimental conditions, predicting the response of the fitted model, and checking the adequacy of the model. Central composite design (CCD) and Box-Behnken design (BBD) are amongst the most commonly used in various experiments [8].

Box-Behnken design allows calculation of the response to be made at intermediate levels which were not experimentally studied. Box-Behnken designs always have 3 levels per factor. For a Box-Behnken design, the design points fall at combinations of the high and low factor levels and their midpoints. These designs allow efficient estimation of the first- and second-order coefficients, however, they can't include runs from a factorial experiment. Box-Behnken designs can prove useful most especially when the safe operating zone known for the process. Box-Behnken designs do not have axial points, thus, one can be sure that all design

points fall within the safe operating zone. Box-Behnken designs also ensure that all factors are not set at their high levels at the same time. Box-Behnken designs never include runs where all factors are at their extreme setting, such as all of the low or all of the high settings.

A three-level Box-Behnken design was employed in the present study and the optimal conditions were determined. As shown in Table 3.1, the four factors chosen for this study were designated as catalyst load, dye concentration, time of irradiation and pH. These are prescribed into three levels, coded +1, 0, -1 for high, intermediate, and low value, respectively. Response surface design methodology is often used to refine models after important factors have been determined using factorial designs; especially if you suspect curvature in the response surface. Being that the preliminary range of the parameters have been determine by single-factor experiment for the process by previous studies, here, the operation parameters were optimized using RSM. Based on one-factor-at-a-time experiments, variables such as duration of exposure to irradiation for reaction, amount of dye in solution, initial pH of solution and amount of catalyst present were identified to have strong effects on the response "[4], [5], [9]". Therefore, these factors were selected as the variables tested in the 27-run experiment of the Box-Behnken design experiment.

Table 1 Summary of experimental design

Factor Name	Low	High
Dye concentration (mg/L)	5	20
Catalyst loading (g/L)	0	2
pH	2	4
Time (min.)	0	90

Since the factors are 4 the number of experimental runs was 27.

## 2.3 PHOTODEGRADATION STUDIES OF THE REACTIVE AZO DYES

The photodegradation parameters such as dye concentration, catalyst loading, pH of the dye and the irradiation time for the dye sample were fed into the system using a Box Behnken Design of Experiment (DOE) as generated by Minitab 16 software. The photodegradation was carried out in a laboratory scale photoreactor equipped with ultraviolet light bulb of 300 W, a cooling fan to maintain steady temperature inside the reactor and a magnetic stirrer to enable swirling of the magnetic rotor placed inside the beaker containing the dye solution which stirs the solution Initially, blank experiments were performed under UV irradiation without addition of any catalyst (and negligible decolorization was obtained). Photo catalytic experiment were carried out using different catalyst at varying pH values , dye concentration and catalyst loading for some varying definite timing (as shown in Tables 2). From each the dyes used 0.1 g was dissolve in 100 ml of water in separate volumetric flask to form a stock solution. The requisite concentrations (5 mg/L, 12.5 mg/L and 20 mg/L) for each run as

generated by the design were prepared from the stock solution and other parameters such as catalyst dose, pH and irradiation time were varied as stipulated by the design. Prior to irradiation, the dye solution was equilibrated for 15 minutes in the dark to establish equilibrium between adsorption and desorption. The dye solution was irradiated inside a laboratory scale photoreactor. The absorbance for each dye sample solution was measured before irradiation. At the expiration of the exposure time for each run, the sample was brought out of the reactor after which it was filtered and the absorbance after irradiation measured. The absorbance was taken using UV-Vis spectrophotometer at the maximum absorption wavelength of 597nm. This procedure was repeated for each run of the dye samples by varying the operational parameters earlier mentioned. All experiments were carried out under ambient conditions.

The degradation performance of the process was assessed in terms of decolorization efficiencies or percentage decolorization as defined by equation 1 "[10], [11]".

$$\text{Decolorization (\%)} = \frac{A_0 - A_t}{A_0} \times 100\% \text{ -----1}$$

Where  $A_0$  and  $A_t$  are the initial and final absorbance at a given time 't' respectively.

### 3.0 RESULT AND DISCUSION

Table 2:  
RESULT

Run Order	Dye Concentration (mg/L)	Catalyst Loading (g/L)	pH (±0.1)	Time (min.)	Declorization
					Efficiency %
1	5	0	3	45	34.48
2	12.5	2	3	90	99.14
3	20	1	3	0	0
4	12.5	1	4	90	98.31
5	5	0	2	45	35
6	12.5	0	2	45	31.73
7	12.5	0	3	90	39
8	12.5	0	3	0	0
9	12.5	2	3	0	1.01
10	12.5	1	3	45	96.36
11	5	1	3	90	98.11
12	12.5	0	4	45	31.25
13	5	1	3	0	0
14	20	1	4	45	89.19
15	12.5	1	2	0	0.97
16	5	1	4	45	95.12
17	12.5	1	3	45	98.92
18	20	1	3	90	99.06
19	5	1	2	45	97.78
20	20	1	2	45	98.91
21	5	2	3	45	94.34
22	12.5	2	4	45	97.25
23	12.5	1	4	0	0

- Dauda Benjamin Ph.D., is currently a senior lecturer in the premier military university of sub-sahara Africa-Nigeria Defence Academy, Nigeria, PH-+2348161351694. E-mail: bendauda@gmail.com
- Barde Abraham, masters degree in Materials and Explosives Science in the Department of Chemistry, Nigeria Defence Academy, Kaduna, Nideria. PH-+2348065338258. E-mail: abraham-barde@nda.edu.ng

24	20	2	3	45	98.92
25	12.5	1	2	90	99.11
26	12.5	1	3	45	98.25
27	12.5	2	2	45	87.62

degradation process with resultant increase, at the point when overcrowding of the catalyst sets in a diminishing returns is experienced.

However it is pertinent to note here that those experimental processes whose settings of experimental variables are generated as in the case of Box-Behnken design are not well explained as a matter of trend change in the tables of results like the conventional approach.

### 3.2 DISCUSSION

The highest percentage decolorization was found to be 99.14; from the decomposition of reactive blue 13 with experimental setting of 12.5mg/L catalyst load, pH of 3, and 90 minute irradiation time.). The nitrogen to nitrogen double bonds (-N=N-) are characteristic of azo dyes molecules. Azo bonds are the most active bonds in azo dye molecules and can be easily oxidized either by positive holes or hydroxyl radicals. The high percentage decolorization is as a result of high decrease in the absorbance. This indicates that photocatalytic degradation not only destroys azo group and the conjugate system, but also destroys the benzene and naphthalene rings in molecules[12]. Highest degradation being record is in agreement with the report of "[3], [12], [13]" who all observed maximum degradation of some azo dyes ( such as reactive yellow 124 and, acid orange 10 and acid red 114) at the pH of about 3. This may be attributed to the electrostatic interactions between the positive catalyst surface and dye anions leading to strong adsorption of the latter on the metal oxide support. Similar behaviour has also been reported for the photocatalytic efficiency of TiO<sub>2</sub> for decolorization of azo dyes "[14], [3]". Moreover, the positive holes are considered as the major oxidation species at low pH which react with hydroxide ions forming hydroxyl radicals, thus the efficiency of process is enhanced. At increased pH, there is a columbic repulsion between negatively charged surface of catalyst and the hydroxide anions which prevent the formation of OH<sup>•</sup> and decrease the photocatalytic degradation. This catalyst behavior can be explained by TiO<sub>2</sub> surface charge density. The point of zero charge (pzc) of the TiO<sub>2</sub> (Anatase) is at pH 6.8. In acid media (pH ≤ 6.8) the TiO<sub>2</sub> surface is positively charged, whereas under alkaline conditions (pH ≥ 6.8) it is negatively charged TiO<sub>2</sub> (Saggiaro *et al.*, 2011). Considering the structure of the Reactive azo dyes (Figure 1), a positive charge excess in the TiO<sub>2</sub> surface promotes a strong interaction with SO<sub>3</sub><sup>-</sup> groups of the dye. A negative charge excess promotes the repulsion of the dye by the titanium surface, diminishing the catalytic activity of this semiconductor. These results suggest that the influence of the initial pH of the solution on photocatalysis kinetics is due to the amount of the dye adsorbed on TiO<sub>2</sub> [14]. This hypothesis agrees with a reaction occurring at TiO<sub>2</sub> surface and not in the solution, close to the surface. The decolorization percent has been is dependent on pH of solution most likely because the reaction takes place on the surface of the semiconductor photocatalyst. The highly oxidizing effect of TiO<sub>2</sub> makes it suitable for decomposition of organic and inorganic compounds at very low concentrations. Therefore even though increase in catalyst influence the

Descriptive statistics such as mean and standard deviation were used to do preliminary evaluation of the operational parameters. However, since the study focused primarily on determining the decolourization efficiency with the specific intent to optimizing the photo-degradation process using Box-Beckhen design of experiment, these aforementioned statistical operations are not fitting or significantly informative. This process involves the varying of operational parameters like pH, dye concentration, catalyst loading, and irradiation time, for improving the efficiency of the process. Being that Box-Behnken design of experiment is employ for the two dye under study using the same factors and parametric range, the outcome of the descriptive statistical analysis would invariably the same

3.4 Table 4.3 Descriptive statistics of Operational Parameters of Reactive Blue 13 (a Mono-azo dyes)

Variable	N	Mean	SE Mean	St.Dev	Low	High
Dye Concentration (mg/L)	27	11.94	0.975	5.064	5	20
Catalyst Loading (g/L)	27	1	0.131	0.679	0	2
pH	27	2.96	0.136	0.706	2	4
Time (min)	27	45	5.88	30.57	0	90
Degradation (%)	27	63.7	8.1	42.07	0.00	99.14

Table 2 above shows the descriptive characteristics of the operational parameters and photo-degradation efficiency of the dye. The result shows mean Dye Concentration of 11.94 ± 5.064, Catalyst Loading of 1.00 ± 0.679; pH 2.96 ± 0.706; Time 45 ± 30.57. The results also shows a mean percentage decolourization of 63.7 ± 42.07.

Furthermore, stepwise regression was performed to ascertain the level of relationship between the operational parameters [i.e independent variables] and the decolourization efficiency [i.e dependent variable]. Statistical significance was set at p < 0.05 alpha level. The four (4) independent variables selected were used to form a model for each of the two dye type (i. e Dye Concentration, Catalyst Loading, pH, and Time) whereas the dependent variable of the model is Degradation efficiency.

Table 3: Regression model parameters for Di-azo dyes

Term	Coef	SE Coef	t-Value	p-Value
Constant	62.67	4.56	13.75	0.000
Catalyst Loading (g/L)	24.60	6.84	3.60	0.001
Time (min)	44.64	6.84	6.53	0.000

\*\* Statistically significant at  $p < 0.05$  alpha level

R-sq (adj) = 67.33%

Model [statistics]: F (3, 23) = 27.79, p-value = 0.000

The result (as shown in Table 4.4) indicates that of the 4 independent variables analysed, only 2 of them significantly influenced the degradation efficiency; they are Catalyst Loading, and Time.

Specifically, the result shows the Catalyst Loading yielded a coefficient of 24.60, a t-value of 3.60, and  $p = 0.001$ , which was significant since  $p < 0.05$ . This implies that [holding other variables constant] the Catalyst Loading significantly determines the degradation efficiency of Mono-azo dyes, and for every unit increase in Catalyst Loading, the degradation efficiency is affected by a factor of 24.06. The result further

## CONCLUSION

The effectiveness of  $\text{TiO}_2$ -catalyzed UV oxidative degradation of reactive mono in water has been investigated and optimized using Box-Behnken design of experiment to obtain the experimental settings of variables conditions that yielded maximum decolorization (decolorization efficiency of >95) of the dye in aqua media. Therefore, this technique could be used as a very powerful tool in the remediation of coloured wastewater, to be specific water contaminated by reactive mono azo dye, Reactive Blue 13.

**ACKNOWLEDGMENT:** WITH DEEP SENSE OF GRATITUDE, THE AUTHORS WISH TO THANK THE MEMBERS OF STAFF OF CHEMISTRY DEPARTMENT, NIGERIA DEFENCE ACADEMY, NDA KADUNA FOR THEIR SUPPORT, AND OUR FAMILIES AND FRIENDS FOR THEIR CONCERN AND CONTRIBUTIONS TOWARDS THE ACTUALISATION OF THIS GREAT WORK.

## REFERENCE

- [1] Awomeso J. A., Taiwo, A.M., Gbadebo A.M. and Adenowo J.A. (2010). Studies on the Pollution of Water body by Textile Industry Effluents in Lagos, *Nigeria Journal of Applied Sciences I Environmental Sanitation*, 5(4):353-359
- [2] Wang, C.; Lee, C.; Lyu, M.; Juang, L. (2008) Photocatalytic degradation of C.I. Basic Violet 10 using  $\text{TiO}_2$  catalysts supported by Y zeolite: An investigation of the effects of operational parameters. *Dyes Pigm.* 76, 817-824.
- [3] Abo-Farha A. S. (2010). Photocatalytic Degradation of Monoazo and Diazo Dyes in Wastewater on Nanometer-sized  $\text{TiO}_2$ , *Researcher*, 2(9):52-71
- [4] Hussein, H. F. (2012). Comparison between Solar and Artificial

shows the irradiation Time yielded a coefficient of 44.64, a t-value of 6.53, and  $p = 0.000$ , which was significant since  $p < 0.05$ . This implies that [holding other variables constant] the irradiation Time significantly determines the degradation efficiency of Mono-azo dyes, and for every unit increase in irradiation Time, the degradation efficiency is affected by a factor of 44.64.

Narrowing this down to the regression model, the Model statistics indicates the regression model was statistically significant at  $p < 0.05$ , while the R-sq (adj) of 67.33% implies the model accounts for about 67.33% of the variation in the degradation efficiency of mono-azo dyes. Thus, the model can produce meaningful predictions for degradation efficiency of mono-azo dyes.

Response Optimization Parameters

Dye Concentration	=	12.04 mg/L
Catalyst Loading	=	1.68 g/L
Time of exposure	=	85.57 min.
pH	=	3.10

The results showed the dependence and interdependence of the decolorizing degree on the initial concentration of dye, pH and  $\text{TiO}_2$  dose.

Photocatalytic Decolorization of Textile Industrial Wastewater, *International Journal of Photoenergy*, 2012

[5] Yonar, T. (2011). Decolorization of Textile Dyeing Effluents using Advanced Oxidation Process, *Advances Treatment of Textile Effluent*, pp 704-708

[6] Nishio, J., Tokumura, M., Znad, H.T. and Kawase, Y. (2006). Photocatalytic decolorization of azo dye with zinc oxide powder in an external UV light irradiation slurry photoreactor, *Journal of Hazardous Materials*, 138(1): pp. 106-115.

[7] Box, G.E.P, Hunter W.G. and Hunter, J.S. (1987). *Statistics for Experimenters*, Wiley Interscience, John Wiley & Sons, Inc.

[8] Manohar M., Jomy J., Selvaraj T., and Sivakumar D. (2013) Application of Box Behnken design to optimize the parameters for turning Inconel 718 using coated carbide tools. *International Journal of Scientific & Engineering Research*, 4( 4)

[9] Das S. (2006). Textile Effluent Treatment –A Solution to the Environmental Pollution, *Indian Textile Journal*, 117(2):35

[10] Giwa, A., Nkeonye, P.O., Bello, K.A., and Kolawole, E.G. (2012). "Photocatalytic Decolourization and Degradation of C. I. Basic Blue 41 Using  $\text{TiO}_2$  Nanoparticles," *Journal of Environmental Protection*, 3:1063-1069.

[11] Harikumar PS, Litty Joseph and Dhanya A (2013) Photocatalytic degradation of textile dyes by hydrogel supported titanium dioxide nanoparticles. *Journal of Environmental Engineering & Ecological Science* : <http://dx.doi.org/10.7243/2050-1323-2-2>; licensee Herbert Publications Ltd

[12] Chunmei Z., Liangyan W., Linren K., Xi Y., Liansheng W., Shaojian Z., Feili C., Feng M., and Huang Z. (2000) Photocatalytic degradation of AZO dyes by supported  $\text{TiO}_2$  + UV in aqueous solution. *Chemosphere* 41 (2000) 303±309

[13] Said A., Samir Q., Mahmoud El O., Abdelhadi A., Ali A. (2014) Factors Influencing the Photocatalytic Degradation of Reactive Yellow 145 by

TiO<sub>2</sub>-Coated Non-Woven Fibers. *American Journal of Analytical Chemistry*, 2014, 5, 445-454

[14] Saggiaro M.E., Oliveira S. A., Pavesi T., Maia G. C., Ferreira V.F.L., and Moreira C. J. (2011) Use of Titanium Dioxide Photocatalyst on the Remediation of model textile wastewater containing Azo Dyes. *Molecules*, 2011, 16, 10370-10386

IJSER