ISSN 214-453-2

PHOTO-DEGRADATION OF DIRECT YELLOW 96 IN UV/TIO$_2$ AND UV/H$_2$O$_2$ USING FACTORIAL DESIGN

A. C. OKEME[1], A. A. KOGO[2], N. YUSUF[3] AND A. GIWA[2]
[1]Entrepreneural Development Centre, Federal Polytechnic Idah, Kogi State
[2]Department of Polymer and Textile Science, Ahmadu Bello University, Zaria, Nigeria
[3]Department of Chemical and Petroleum Engineering, Bayero University, Kano, Kano State
[challyok@yahoo.com, 08037459185]

ABSTRACT

In this research, factorial design have been employed to study the influence of four important factors; pH, catalyst dosage, irradiation time and dye concentration in the treatment of C.I. Direct Yellow 96 dyestuff using UV/TiO$_2$ and UV/H$_2$O$_2$ photo-degradation processes. The results indicate that the adsorbent dosage and irradiation time exhibit a significant positive effect on the efficiency of decolourization, whereas the initial dye concentration and pH of dye solution show a significant negative effect in UV/TiO$_2$ for the dye. Under UV/TiO$_2$, maximum degradation of 73% was obtained at dye concentration of 5mg/l, pH 4, reaction time of 90min and catalyst dose of 2g/l. Under UV/H$_2$O$_2$ the irradiation time and initial dye concentration exhibit a significant positive effect on the efficiency of decolourization, whereas the pH of dye solution and adsorbent dosage show a significant negative effect for the dye. However, the UV/H$_2$O$_2$ gave a maximum degradation of 58% at dye concentration of 5mg/l, pH 4, reaction time of 90min and H$_2$O$_2$ catalyst dose of 25mM. Hence, both methods can be adopted as a preliminary treatment process for dye wastewaters.

Keywords: *Photo-degradation, dye, photoreactor, UV/TiO$_2$ and UV/H$_2$O$_2$*

INTRODUCTION

Coloured industrial effluent is the most obvious indicator of water pollution and the discharge of highly coloured synthetic dye effluents is aesthetically displeasing and cause considerable damage to the aquatic life. Over 700,000 tons of approximately 10,000 types of dyes and pigments are produced annually worldwide (Giwa *et al.,* 2012). From this amount, about 20% are discharged as industrial effluents during the textile dyeing and finishing processes without pre-treatment (Carneiro *et al.,* 2007).

Dyeing wastewater causes serious environmental problems due to its high colour, large amount of suspended solids (SS), and high chemical oxygen demand (COD) (Kim *et al.,* 2004). The impact of these dyes on the environment is a major concern because of the potentially carcinogenic properties of the chemicals (Parsons. 2004). Also, some dyes can undergo anaerobic decolouration to form potential carcinogens (Alam et al. 2010). Consequently, there is a considerable need to treat these coloured effluents before discharging them into various water bodies. The increase of public concern as well as tighter regulations has challenged the environmental research community to explore new lines in reducing environmental problems associated with such wastewater.

At present, the industrial methods for dye waste treatment include adsorption, precipitation, electrical remediation, oxidation, and biological degradation. But all these ways cost much money, and/or create secondary contamination. Currently, chemical methods such as advanced oxidation processes (AOPs) seem more promising. AOPs predominantly involve the generation of very powerful and non-selective oxidizing species, the hydroxyl radicals (OH) for the destruction of refractory and hazardous pollutants observed in industrial wastewaters, surface waters and ground waters. The photo catalytic method such as TiO$_2$ photo catalysis has been shown to be efficient for degradation and mineralization of various organic pollutants in water at room temperature and normal pressure. The method has potential to be used for treatment of industrial or domestic wastewater on a large scale (Alfano *et al.,* 2000) and also ultraviolent photolysis combined with hydrogen peroxide (UV/H$_2$O$_2$) is one of the most appropriate AOP technologies for removing toxic organics from water because it may occur in nature itself. This process involves the production of reactive and non-selective hydroxyl radicals (OH) and can initiate the decolourisation reactions by reacting with the dye molecules.

The objective of this study is to investigate the effect of UV/TiO$_2$ and UV/H$_2$O$_2$ in the treatment of C.I. Direct Yellow 96 textile dyestuff. The effects of the key operating variables, such as pH, catalyst dosage, irradiation time and dye concentration on photo degradation process. Interactions between these factors were also studied.

EXPERIMENTAL

Materials

The dye C.I. Direct Yellow 96 (DY96) was obtained from Sigma. Titanium dioxide (Degussa P25) and H$_2$O$_2$ (30% w/w) was utilized as a photo-catalyst. Distilled water was used to prepare experimental solutions. The pH of the solutions were adjusted using H$_2$SO$_4$ and NaOH. The chemical structure, physical and chemical properties of the Direct Yellow 96 dye according to manufacturer are shown in Figure 1 and Table 1.

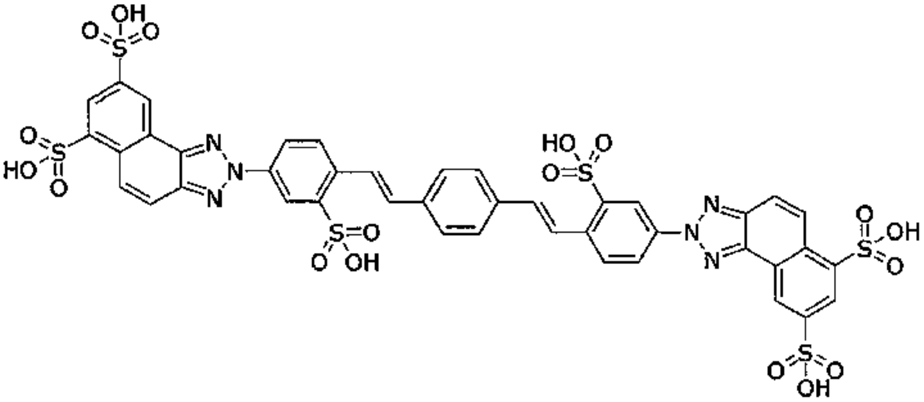

Fig. 1: C.I. Direct Yellow 96 (Diphenyl Brilliant Flavine)

Table 1: Chemical and Physical Properties of DY96

Properties	Values
Molecular Weight	1275.59 g/mol
Hydrogen Bond Donor Count	8
Hydrogen Bond Acceptor Count	23
Rotatable Bond Count	15
Exact Mass	1274.51 g/mol
Monoisotopic Mass	1274.51 g/mol
Topological Polar Surface Area	395 A^2
Heavy Atom Count	86
Formal Charge	4
Complexity	2030
Covalently-Bonded Unit Count	5

Photoreactor

The photocatalytic activities of the photocatalysts were performed in a 400 ml jacketed glass reactor fitted with a 9W 5" long Philips (PL-S 9W/10/2P Hg) bulb. The samples were centrifuged (6000 rpm, 10 min) and filtered through a millipore filter (0.45 µm) membrane and analyzed for the concentration of the C.I. Direct Yellow 96 in the solution using computer software attached to UV-Vis Spectrophotometer. Photocatalytic degradation processes were performed using a 200 ml solution containing a specified concentration of the selected dye. Samples were withdrawn from sample points and analyzed for degradation. Photo-degradation of dye solutions was checked and controlled by measuring the maximum absorbance of dyes by UV-Vis Spectrophotometer.

Design of Experiments

The experimental design consisted of four variables with two levels using MINITAB software (version 16). Because experiments from the degradation are time consuming, a half fraction design of 8 trials was used. Tables 2 and 3 display the Factors and their Uncoded Levels of low and high values of trials for the design of experiment (DOE).

Table 2: Factors and their Uncoded Levels for C.I. Direct Yellow 96 using UV/TiO_2.

Factor	Name	Low	High
A	Concentration (mg/l)	5	25
B	pH	4	8
C	Time (mins)	0	90
D	Dose (g/l)	0	2

Table 3; Factors and their Uncoded Levels for C.I. Direct Yellow 96 using UV/H_2O_2

Factor	Name	Low	High
A	Concentration (mg/l)	5	25
B	pH	4	8
C	Time (mins)	0	90
D	Dose (mM)	5	25

RESULTS AND DISCUSSION

To measure the percentage degradation which is a function of absorbance of the aqueous dye solution before and after exposure to the UV light, percentage colour disappearance was calculated using the following equation:

$$Decolorization\ (\%) = \frac{(Absorbance)_0 - (Absorbance)_t}{(Absorbance)_0}$$

where $(Absorbance)_o$ is the absorbance before irradiation and $(Absorbance)_t$ is the absorbance at time t. The results obtained are shown in Tables 4 and 5 for both UV/TiO_2 and UV/H_2O_2 processes.

Table 4: Design of Experiment for C.I. Direct Yellow 96 using UV/TiO_2

Run Order	Dye Conc. (mg/l)	pH	Time (mins)	Dose (g/l)	Initial Abs	Final Abs	Degradation (%)
1	5	4	90	2	0.74	0.20	72.97
2	5	4	0	0	0.70	0.70	0.00
3	5	8	90	0	0.20	0.20	0.00
4	25	8	0	0	0.38	0.38	0.00
5	25	4	90	0	0.40	0.40	0.00
6	5	8	0	2	0.75	0.75	0.00
7	25	8	90	2	0.40	0.26	35.00
8	25	4	0	2	0.28	0.28	0.00

Table 5: Design of Experiment for C.I. Direct Yellow 96 using UV/H$_2$O

Run Order	Dye Conc. (mg/l)	pH	Time (mins)	Dose (mM)	Initial Abs	Final Abs	Degradation (%)
1	5	8	90	5	0.32	0.30	6.25
2	25	8	0	5	0.48	0.48	0
3	25	4	0	25	0.46	0.46	0
4	25	4	90	5	0.48	0.20	58.33
5	5	4	0	5	0.32	0.32	0
6	25	8	90	25	0.46	0.32	30.43
7	5	4	90	25	0.42	0.20	52.38
8	5	8	0	25	0.32	0.32	0

The Normal Plot displays whether the effect of the factor is positive or negative on the response. The Normal Plots for the responses are shown as Figures 2 and 3. A positive effect means that as factors increases, degradation percentage increases. Whereas a negative effect indicates that as factor increases, the degradation in percent decreases.

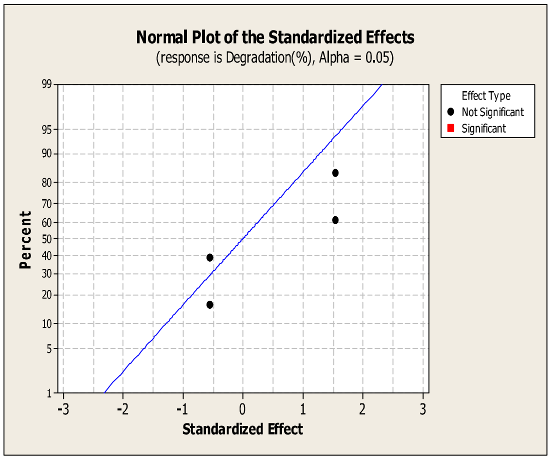

Fig 2: Normal Plot of DY96 degradation (%) under UV/TiO$_2$

The Normal Plot in Fig. 2 shows Time and Dose with a positive effect and pH and Concentration having a negative effect this implies that as Time and Dose increases, degradation percentage increases. Whereas a negative effect indicates that as pH and Concentration increases, the degradation in percent decreases.

The Normal Plot in Fig 3 shows Time and Concentration with a positive effect and Dose and pH having a negative effect.

A main effect is the difference in the mean response between two levels of a factor as shown in Figures 4 and 5.

The main effect plot fig 4 also shows that as concentration increases from 5mg/l-25mg/l there is decrease in degradation, pH in acidic region favours increase in degradation, the more the time of loading, the higher the degradation and increase of dosage from 0g/l-2g/l leads to increase in degradation.

The main effect plot Fig 5 also shows that as concentration increases from 5mg/l - 25mg/l there is increase in degradation, pH in acidic region favours increase in degradation, the more the time of loading, the higher the degradation and increase of dosage from 5mM - 25mM leads to decrease in degradation.

Figures 6 and 7 shows interaction plot of degradation for the direct dye. Each point in the interaction plot shows the mean degradation at different combinations of factor levels. If the lines are not parallel, the plot indicates that there is an interaction between the two factors

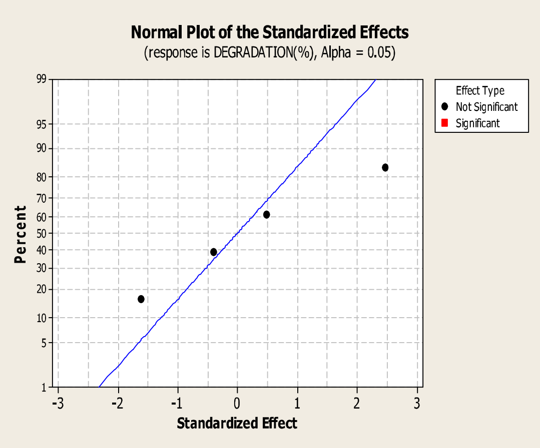

Fig. 3: Normal Plot of DY96 degradation (%) under UV/H$_2$O$_2$

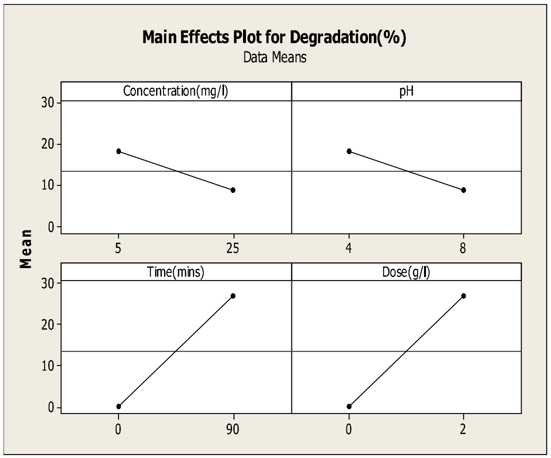

Fig 4: Main Effects Plot for Direct dye Degradation (%) (UV/TiO$_2$)

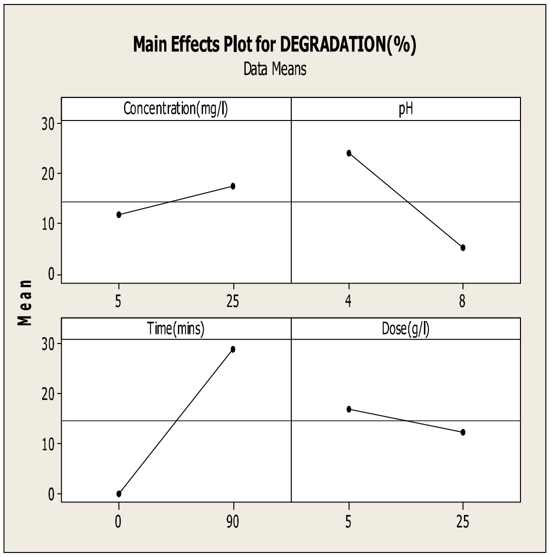

Fig. 5: Main Effects Plot for Direct dye Degradation (%) (UV/H_2O_2)

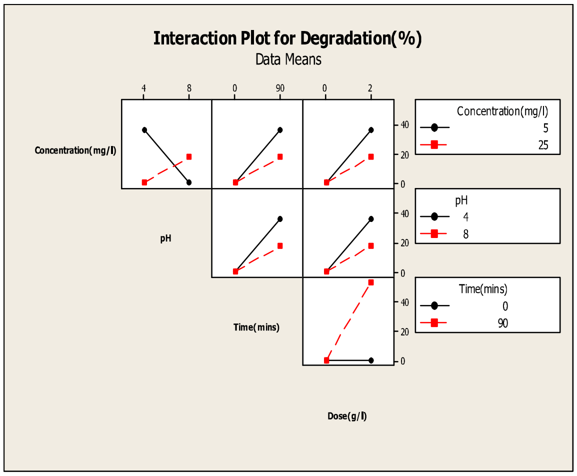

Fig. 6: Interaction Plot for Direct dye Degradation (UV/TiO_2)

For fig 6, at a concentration 5mg/l an increase of pH from 4 to 8 at 90mins with 2g/l TiO_2 leads to decrease in the adsorption efficiency by approximately 40%. At concentration of 25mg/l an increase of pH from 4 to 8 at 90mins with 2g/l TiO_2 leads to decrease in the adsorption efficiency by approximately 20%.

From above explanations it can be seen that pH plays a major role in degradation of the direct yellow 96 dye. Increase in pH from the low to high point decreases the adsorption efficiency by 37.97% similar trend was reported for a direct dye by Toor *et al.*, 2006. Adsorption rate increase, as expected with increase in TiO_2 dosage. Increase of catalyst dosage from 0-2g/l increases adsorption rate. This is due to the fact that increase in absorbent dosage increases area available for adsorption. At low initial concentration adsorption in all cases are favored. The effect of TiO_2 dosage was more noticeable at lower initial concentration. These results support the previous findings related to the effect of each factor on photocatalytic degradation. Similar results were found by Ray *et al.*, 2009.

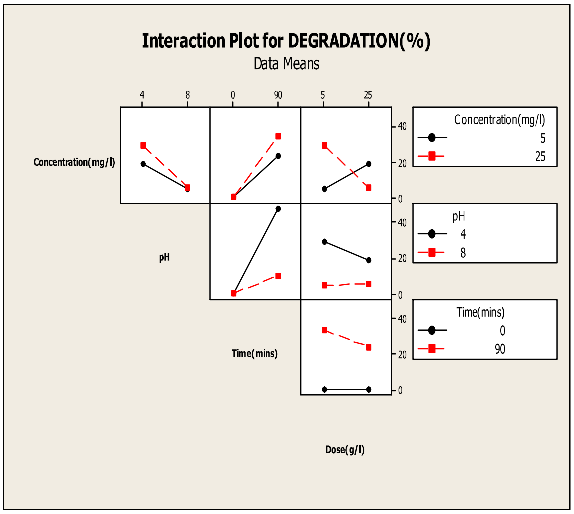

Fig. 7: Interaction Plot for Direct dye Degradation (UV/H_2O_2)

For Fig 7, which is an Interaction Plot shows that at a concentration of 5mg/l an increase of pH from 4 to 8 leads to decrease in the adsorption efficiency by approximately 5%, while an increase in time of exposure from 0-90mins increases the adsorption efficiency by approximately 40%. An increase in dosage from 5mM to 25mM H_2O_2 leads to reduction in the adsorption efficiency by approximately 20%. At 90mins time of exposure 5mM dose of H_2O_2 had an adsorption efficiency of 40% while 25mM dose of H_2O_2 had an adsorption efficiency of 20% at a concentration 25mg/l an increase of pH from 4 to 8 leads to decrease in the adsorption efficiency by approximately 10%.

For degradation of Direct Yellow 96 in this case, increase in pH from low to high point decreases the adsorption efficiency by 47.22%. According to some authors Critenden *et al.*, 1999 and Oppenlader *et al.*, 2003 the photochemical degradation rate of H_2O_2 is variable under certain pH conditions and this can affect the UV/H_2O_2 reaction to degrade different contaminants. Under alkaline conditions, hydrogen peroxide deprotonates with formation of the $H_2O_2/\,HO_2^{\,-}$ equilibrium. The $HO_2^{\,-}$ species reacts with a non-dissociated molecule of H_2O_2 according to reaction (1), which leads to dioxygen and water, instead of producing hydroxyl radicals under UV radiation. Therefore, the instantaneous concentration of 'OH is lower than expected.

$$H_2O_2 + HO_2^{\,-} \longrightarrow H_2O + OH^- + O_2 \ldots\ldots(1)$$

It was also verified that the efficiency of the processes increased at 5mM of hydrogen peroxide dosage where the remove rate were higher, after this point the efficiency decreased because of high presence of H_2O_2 in the reaction medium. When the hydrogen peroxide concentration becomes high, the excess hydrogen peroxide consumes hydroxyl radicals and it performed like hydroxyl radical scavengers. At high initial concentration adsorption in these cases was favored.

PREDICTION OF THE RESPONSE

Minitab software calculates the coefficients and constants for response equations. The response equations can be used as models for predicting responses at different operating conditions (factors). The coefficients and constants for the dye are shown in Table 6 and 7.

Table 6: Estimated Coefficients for direct dye (UV/TiO_2) Degradation (%) using data in uncoded units

Term	Coef
Constant	7.8619
Concentration(mg/l)	-0.474625
pH	-2.37312
Time(mins)	0.299917
Dose(g/l)	13.4962

Table 7: Estimated Coefficients for direct dye (UV/H_2O_2) Degradation (%) using data in uncoded units

Term	Coef
Constant	27.6037
Concentration(mg/l)	0.285625
pH	-4.72687
Time(mins)	0.322306
Dose(mM)	-0.235125

In simple or multiple linear regression, the size of the coefficient for each independent variable gives the size of the effect that variable is having on dependent variable, and the sign on the coefficient (positive or negative) gives the direction of the effect. In regression with a single independent variable, the coefficient tells how much the dependent variable is expected to increase (if the coefficient is positive) or decrease (if the coefficient is negative) when that independent variable increases by one. In regression with multiple independent variables as this, the coefficient tells how much the dependent variable is expected to increase when that independent variable increases by one, holding all the other independent variables constant.

However, since this is a first order, linear model, the coefficients can be combined with the operating parameters to determine equations. The equations from this model are shown below:

$$\text{Degradation (\%) (UV/}TiO_2\text{)} = 7.862 - 0.475(\text{Conc.}) - 2.373(\text{pH}) + 0.300(\text{Time}) + 13.496(\text{Dose})$$

$$\text{Degradation (\%) (UV/}H_2O_2\text{)} = 27.604 + 0.286(\text{Conc.}) - 4.727(\text{pH}) + 0.322(\text{Time}) - 0.235(\text{Dose})$$

CONCLUSION

This study showed that factorial experimental design approach is an excellent tool and could successfully be used to develop empirical equation for the prediction and understanding the photocatalytic degradation efficiency of the Direct Yellow 96. The results obtained indicates that UV/TiO_2 treatment gave a maximum degradation of 73% at dye concentration of 5mg/l, pH 4, reaction time of 90min and catalyst dose of 2g/l, while UV/H_2O_2 treatment gave a maximum degradation of 58% at dye concentration of 5mg/l, pH 4, reaction time of 90min and H_2O_2 catalyst dose of 25mM. The results obtained shows that degradation rate can be influence by operational parameters such as pH, irradiation time, catalyst loading and dye concentration apart from the presence of electron acceptors and other additives. This process is an efficient and environmentally friendly technique for effluent treatment of industrial wastewater containing dye solution from textile industry since the dyes were mineralized into sampled and eco-friendly compounds of carbon (IV) oxide and water.

REFERENCE

Alam M.Z., Ahmad S., Malik A. and Ahmad M., (2010). “Mutagenicity and Genotoxicity of Tannery Effluents Used for Irrigation at Kanpur, India,” *Ecotoxicology and Environmental Safety*, Vol. 73, No. 7, pp. 1620-1628.

Alfano OM, Bahnemann D, Cassano AE, Dillert R (2000) “Photocatalysis in water environments using artificial and solar light”Catalysis today,– Elsevier Volume 58, Issues 2–3, 12, pp 199–230

Patrıcia A. Carneiro, Maureen K. Sakagami, Maria and Valnice B, (2007) “Chemical characterization of a dye processing plant effluent—Identification of the mutagenic components,” Mutation Research 626 pp135–142

Critenden J.C, Hu S, Hand D. W. and Green S. A. (1999). A kinetic model for UV/H_2O_2 process in a completely mixed batch reactor, water Res. 33 p1543-1548.

Giwa A., Nkeonye P. O., Bello K. A. and Kolawole E. G. (2012). Photo catalytic decolourisation and degradation of CI Basic blue 41 using TiO_2 Nanoparticles. Journal of Environmental Protection 3: p1063-1069.

Kim H, Hao O J, and Chiang PC (2004) – “Decolorization of wastewater” Critical reviews in environmental - Taylor & Francis Journal 30 p 123

Oppenlander T. (2003).Photochemical purification of water and air, advanced Oxidation processes (AOPs) principles, reaction mechanisms, reactor concepts, wiley-VCH verlag, weinheim, Germany, p 368

Parsons S. “Advanced Oxidation Processes for Water and Wastewater,” IWA Publishing, London, 2004.

Ray S., Lalman J. A., and Biswas N. (2009). Using the Box-Benkhen technique to statistically model phenol photocatalytic degradation by titanium dioxide nanoparticles. *Chem. Eng. J.*, 150, 15–24.

Toor A.P., Verma A., Jotshi C.K., Bajpai, P.K. and Singh V. (2006). “Photocatalytic degradation of Direct Yellow 12 dye using UV/TiO 2 in a shallow pond slurry reactor” Dyes and pigments 68 (1), p 53-60.