



## COMPARATIVE STUDY ON DECOLORIZATION EFFICIENCY OF BLUE AZO DYE-235 USING $TiO_2$ , $V_2O_5$ AND $ZnO$ AS PHOTOCATALYSIS

Dr. Riyadh Al-Anbari<sup>1</sup>, Dr. Abdul Hameed Al-Obaidy<sup>2</sup>, \*Eman Abd<sup>3</sup>

- 1) Prof., Building and Construction Engineering Department, University of Technology, Baghdad, Iraq.
- 2) Prof., Environmental Research Center, University of Technology, Baghdad, Iraq.
- 3) Assist Lecturer, Environmental Engineering Department, Al-Mustansiriyah University, Baghdad, Iraq.

**Abstract:** Decolorization of blue azo dye (Cibacron Blue FN-R) from simulated wastewater has been investigated as a function of solar photocatalysis process. The photocatalysis activity using different catalysis was compared. Different parameters affected the removal efficiency, including initial concentration of dye, pH of the solution, catalysis dosage, and  $H_2O_2$  concentration, were evaluated to find out the optimum operation conditions. The results proved that, the optimal pH value for  $TiO_2$ ,  $V_2O_5$  and  $ZnO$  were 2, 2, and 8 respectively and the best catalysis dosage was 500mg/L for  $TiO_2$ ,  $V_2O_5$  and  $ZnO$ . In addition, the most efficient  $H_2O_2$  concentration was 300,100, 100 mg/L for  $TiO_2$ ,  $V_2O_5$  and  $ZnO$  respectively. The theoretical relationships described the photocatalysis process have been predicted for the three catalysis. It can be concluded, from these experiments, that the using of  $ZnO$  as a photocatalysis was found to be more efficient than  $TiO_2$  and  $V_2O_5$  to remove blue azo dye from aqueous solution.

**Keywords:** photocatalysis, zinc oxide, titanium oxide, vanadium oxide, azo dye

### دراسة مقارنة كفاءة ازالة اللون لصبغة الازو الزرقاء- ٢٣٥ باستخدام $ZnO$ , $V_2O_5$ , $TiO_2$ كعوامل تحفيز ضوئي

**الخلاصة:** تم دراسة عملية ازالة اللون لصبغة الازو الزرقاء (Cibacron Blue FN-R) من مياه مخلفات مصنعة في المختبر باستخدام عملية التحفيز الضوئي الشمسي. تمت مقارنة كفاءة انواع مختلفة من عوامل التحفيز ومن ثم تقييم تأثير عدة عوامل مثل تركيز الصبغة الاولي، قيمة الاس الحامضي للمحلول، جرعة العامل المساعد المستخدم وتركيز بيروكسيد الهيدروجين المضاف وذلك لإيجاد أفضل قيم لهذه العوامل المؤثرة على نسبة الازالة. لقد تم التوصل الى ان أفضل قيمة للاس الحامضي للمحلول باستخدام اوكسيد التيتانيوم، اوكسيد الفناديوم و اوكسيد الخارصين هي ٢، ٢، ٨ على التوالي وأفضل جرعة للعامل المساعد المستخدم كانت ٥٠٠ ملغم/لتر لكل من اوكسيد التيتانيوم، اوكسيد الفناديوم و اوكسيد الخارصين. أفضل تركيز لبيروكسيد الهيدروجين المضاف كانت ٣٠٠، ١٠٠، ١٠٠ ملغم/لتر لهيدروكسيد التيتانيوم، اوكسيد الفناديوم و اوكسيد الخارصين على التوالي. تم ايضا" ايجاد العلاقة النظرية الخاصة بوصف عملية التحفيز الضوئي لكل نوع من انواع العوامل المساعدة. من التجارب العملية يمكن استنتاج ان استخدام اوكسيد الخارصين كعامل مساعد لعملية التحفيز الضوئي هو الاكثر كفاءة" من اوكسيد التيتانيوم و اوكسيد الفناديوم في ازالة صبغة الازو الزرقاء من المحلول المائي.

## 1. Introduction

Dyes are common industrial residues present in wastewater of different industries, ordinarily in the textile dyeing process, inks, and photographic industries, among others [1].

\*Corresponding Author [eman\\_abd2016@yahoo.com](mailto:eman_abd2016@yahoo.com)

Textile industry produces large volume of colored dye effluent, which are toxic and non-biodegradable [2].

Dyes contained two types of group, namely chromophore (chromophore is an electron withdrawing group) and auxochromes (are electron releasing groups) which are responsible for their color. The most important chromophores are the azo ( $-N = N-$ ), carbonyl ( $C = O$ ), methine ( $-CH=$ ), and nitro ( $NO_2$ ) groups [3].

Among the different types of dyes used in textile industry, 60–70% is azo compounds [2]. Reactive dyes, one of the prominent and most widely used kinds of azo dye, are typically azo-based chromophores combined with various reactive groups. These dyestuffs are designed to resist biodegradation and are barely removed from effluents using conventional wastewater treatments, such as activated sludge, adsorption, oxidation process, and coagulation [4].

Due to their synthetic nature and structure mainly aromatic, most dyes are non-biodegradable, having carcinogenic action or causing allergies, dermatitis, skin irritation or different tissular changes. Moreover, various azo dyes, mainly aromatic compounds, show both acute and chronic toxicity. High potential health risk is caused by adsorption of azo dyes and their breakdown products (toxic amines) through the gastrointestinal tract, skin, lungs, and also formation of hemoglobin adducts and disturbance of blood formation [5].

There are several available methods to treat this wastewater such as: adsorption, coagulation and precipitation, aerobic and anaerobic process, and others [6]. One difficulty with these methods is that they are not destructive but only transfer the contamination from one phase to another. Therefore, a new and different kind of pollution is faced and further treatments are deemed necessary [7, 8]. An alternative to conventional methods, “advanced oxidation processes” (AOPs) have been developed based on the generation of very reactive species such as hydroxyl radical. The generated hydroxyl radical can oxidize a broad range of organic pollutants quickly and non-selectively [9, 10]. Among the (AOPs), heterogeneous photocatalysis appears as an emerging solution to the environmental pollution of aquatic system [10].

A photocatalyst is defined as a substance, which is activated by adsorbing a photon and is capable of accelerating a reaction without being consumed; these substances are invariably semiconductors [11]

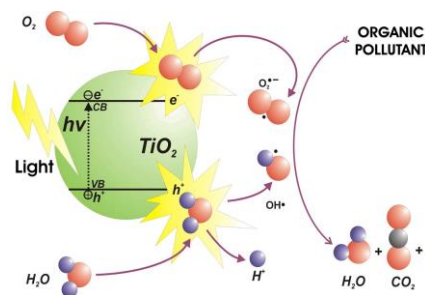
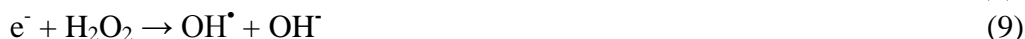


Figure 1. Schematic of semiconductor excitation [12]

The photocatalytic reaction mechanism shown in Fig.1 can be described by (4) to (10) as shown below [13]:



Several compounds such as metal oxides ( $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}$ ) and metal sulfides ( $\text{CdS}$ ,  $\text{ZnS}$ ) have been studied as potential semiconductor photocatalysts [11, 14]. Among these semiconductors,  $\text{TiO}_2$  is more applicable because of its low cost, consistency, self-reduction, and good performance in atmospheric condition [15]. The main problem with  $\text{TiO}_2$  is that it can absorb only a small portion of solar spectrum in the UV region, and has a high recombination rate of photoinduced electron-hole pairs at or near its surface [16, 14, 17].

The present study was concerned to monitor the decolorization of the reactive blue dye (Cibacron Blue FN-R) and the variation in ORP (oxidation-reduction potential) in solution by using  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  and  $\text{ZnO}$  as a photocatalysis under solar light irradiation instead of UV-lamp. In addition, different oxidation processes including UV,  $\text{H}_2\text{O}_2$  +UV,  $\text{H}_2\text{O}_2$ +UV+catalysis were conducted for optimization of the best method. The effects of important parameters such as pH, initial concentration of reactive dye, catalyst loading and volume of  $\text{H}_2\text{O}_2$  were examined with respect to the highest efficiency of decolorization of reactive blue dye.

## 2. Experimental Set-up and Materials

### 2.1. Materials

The blue reactive dye RB had been supplied from AL-Kut textile factory south of Baghdad, (Department of Dying and Printing). Simulated solutions were prepared by dissolving a defined amount of dye in the required volume of distilled water. The chemical formula for this dye is  $\text{C}_{29}\text{H}_{23}\text{CuFN}_9\text{O}_{12}\text{S}_3 \cdot 3\text{Na}$  and the colour index number is CI Reactive Blue 235[18- 21].

Analytical grade reagents of  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{ZnO}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NaOH}$  and  $\text{H}_2\text{O}_2$  were used as such without further purification.

### 2.2. Experimental set-up

Different oxidation processes were carried out by preparing a suspension of simulated synthetic solution containing blue reactive dye and the selected photocatalysis, this suspension was transferred to 1000ml Pyrex beaker on a magnetic stirrer. This suspension was kept in dark for about 15 min to achieve the equilibrium of

adsorption after that the degradation was accomplished under sunlight and the average intensity of sunlight was measured by using UV-radiometer (UV-340A, Lutron, USA). The heat up of the solution was not much and the temperature varied within  $\pm 6$  °C between starting and ending point of reaction.

Samples were withdrawn from beaker at regular time interval and filtered by using 0.45  $\mu\text{m}$  membrane filter then the dye concentration was measured by UV-spectrophotometer (UV-1800 Shimadzu) at a spectrum length of 410nm.

The doses of catalysis taken were 100, 200,300,400,500 and 600  $\text{mg.L}^{-1}$  and the concentrations of  $\text{H}_2\text{O}_2$  added were 0, 100, 200, 300 and 400  $\text{mg.L}^{-1}$ . The initial concentration of reactive blue dye chosen were 25, 50, 75 and 100  $\text{mg.L}^{-1}$ . To study the effect of pH, the values of 2,4,6,8 and 10 were selected as initial pH value of the solution.

### 2.3. Kinetic analysis

The most suitable model used to describe photocatalytic processes is the Langmuir–Hinshelwood (LH), which is described by the following mathematical relationship:

$$r = -\frac{dc}{dt} = k_{\text{LH}} \frac{KC}{1+KC} \quad (11)$$

Where:  $r$  ( $\text{mg L}^{-1}\text{s}^{-1}$ ) represents the reaction rate,  $C$  ( $\text{mg L}^{-1}$ ) the pollutant concentration at time  $t$  during degradation,  $K$  ( $\text{mg}^{-1}\text{L}$ ) the equilibrium constant for pollutant adsorption onto catalyst and  $k_{\text{LH}}$  ( $\text{mg L}^{-1}\text{s}^{-1}$ ) the reaction rate constant at maximum coverage. Under certain experimental conditions,  $KC \ll 1$ , so that the LH model is usually closer to first-order reaction kinetics and (11) will simplified to:

$$r = \frac{dc}{dt} = -k_{\text{LH}} \cdot KC = -K_0 C \quad (12)$$

Where,  $K_0$  ( $\text{min}^{-1}$ ) =  $k_{\text{LH}} K$  is the pseudo-first-order rate constant [22].

The intensity of solar irradiance was never constant and could not be controlled due to multiple environmental influences (i.e., time of day or atmospheric conditions) and in order to normalize data collected at different solar light intensity and exposure time (13) was used[23]

$$t_{30W,n} = t_{30W,n-1} + (t_n - t_{n-1}) \frac{UV}{30} \frac{V_i}{V_T} \quad (13)$$

In eq. (13),  $t_n$  is the experimental time for each sample,  $UV$  the average solar ultraviolet radiation measured during  $t_n$ , and  $t_{30W}$  is the “normalized illumination time”. In this case, time refers to a constant solar UV power of  $30 \text{ W/m}^2$  (typical solar UV power on a perfectly sunny day around noon),  $V_i$  is the irradiate volume and  $V_T$  the total volume [24]. In that way, photocatalytic process could be evaluated as a function of time taking into account environmental conditions [23]

### 3. Results and Discussion

#### 3.1. Effect of pH

The pH value of the aqueous solution is a key parameter for photocatalytic process. The aqueous solution of dye having  $25\text{mg.L}^{-1}$  concentration and  $100\text{mg.L}^{-1}$  of catalysis ( $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  or  $\text{ZnO}$ ) were treated by varying the initial pH of solution from  $\text{pH}=2$  to 10. The pH value was justified by using  $0.1\text{N H}_2\text{SO}_4$  or  $0.1\text{N NaOH}$  as required.

Fig.2 shows the effect of pH on the removal efficiency of blue reactive dye and on the ORP value. It can be concluded from this figure that the photocatalytic process was higher in acidic media ( $\text{pH}=2$ ) for both  $\text{TiO}_2$  and  $\text{V}_2\text{O}_5$ . On the other hand, the most proper pH for photocatalytic process by utilizing  $\text{ZnO}$  as a photocatalysis was 8.

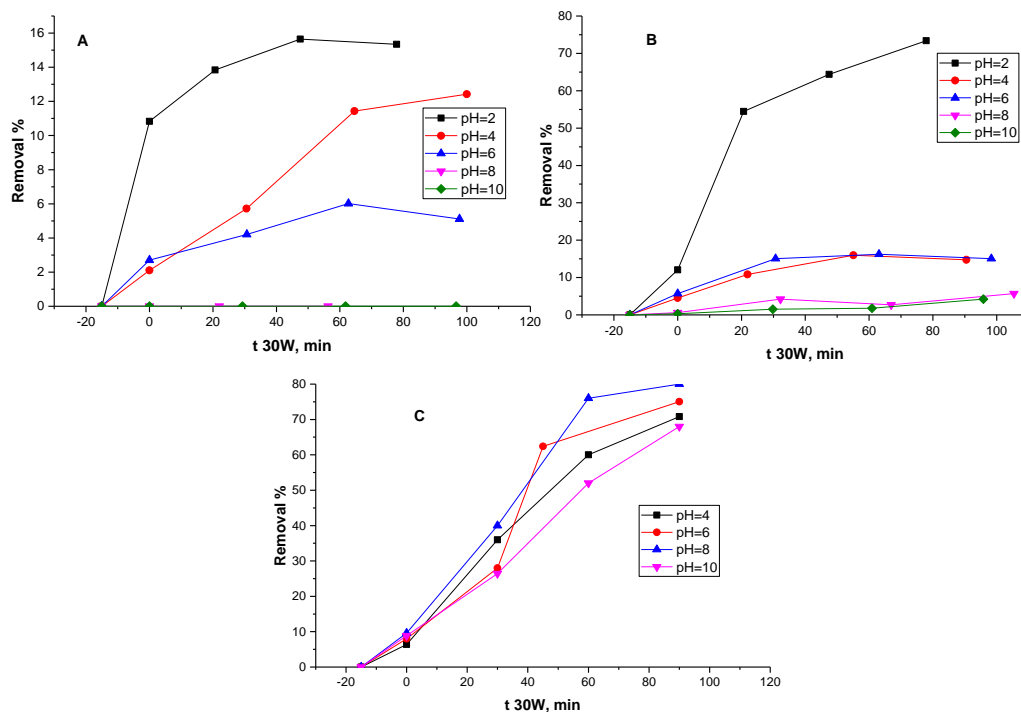


Figure 2. Change of the removal efficiency of pollutant at different initial pH by using (a)  $\text{TiO}_2$ , (b)  $\text{V}_2\text{O}_5$  and (c)  $\text{ZnO}$

This catalyst behavior can be explained by the surface charge of catalyst. Each catalyst have point of zero charge ( $\text{pH}_{\text{pzc}}$ ) at this pH where the net charge on catalyst surface is equal zero [25] and catalyst surface is positively charged at  $\text{pH} < \text{pH}_{\text{pzc}}$  whereas it is negatively charged for  $\text{pH} > \text{pH}_{\text{pzc}}$  [26].

The point of zero charge (pzc) of the  $\text{TiO}_2$  is approximately at  $\text{pH} 6.5$ . In acid media ( $\text{pH} \leq 6.5$ ) the  $\text{TiO}_2$  surface is positively charged, whereas under alkaline conditions ( $\text{pH} \geq 6.5$ ) it is negatively charged. A negative charge excess promotes the repulsion of the dye by the titanium surface, diminishing the catalytic activity of this

semiconductor[27] In same way,  $V_2O_5$  and ZnO have  $pH_{pzc}$  about 2.5 and 8.2 respectively.

### 3.2. Effect of photocatalysis loading

The photocatalyst dose has an evidential effect on the photocatalysis process of reactive blue dye. The dose of the photocatalyst ( $TiO_2$ ,  $V_2O_5$  and ZnO) used was changed from 100 to 600  $mg.L^{-1}$ .

Fig. 3 showed that the decolorization processes was increased when the dose of catalyst increased up to 500 $mg/L$ . This increment in decolorization can be attributed to the increment in the active sites on the catalyst surface, which accelerated the removal process [9].

Further increases in photocatalyst loading over 500  $mg.L^{-1}$ , the decolorization percent decrease. These results can be rationalized with the increasing of solution turbidity when increasing the photocatalyst load, which subsequently reduces the penetration of the light into the solution [2].

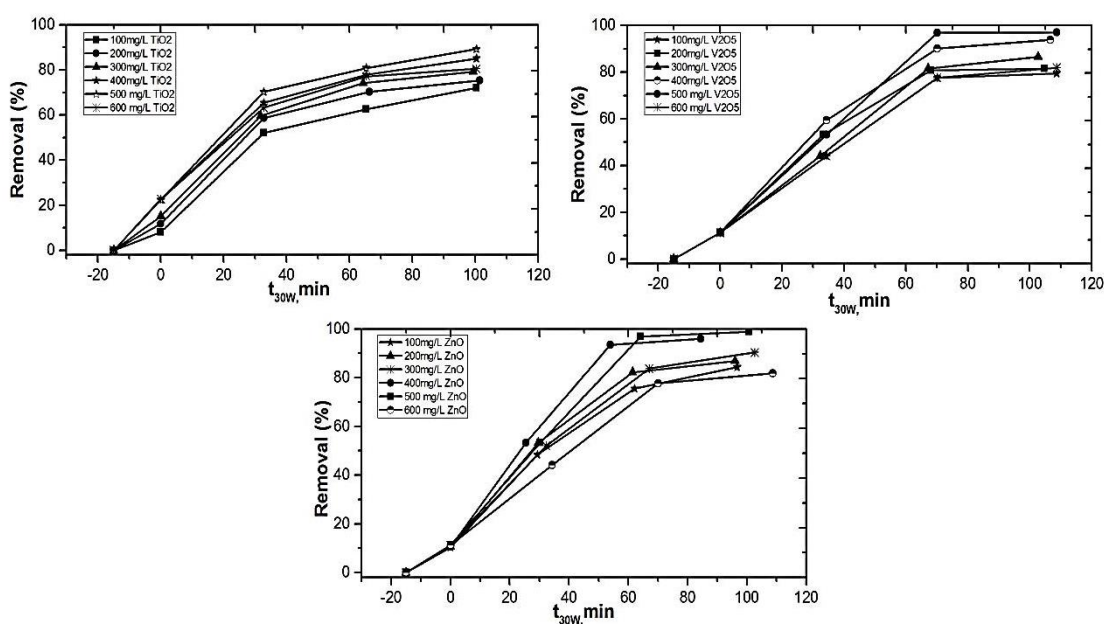


Figure 3. The effect of photocatalyst load on the removal efficiency of pollutant by using (a)  $TiO_2$ , (b)  $V_2O_5$  and (c) ZnO

Table 1 listed the summary to the effect of photocatalysis mass on the removal efficiency of reactive blue dye and it is clearly observed from this table that the best removal efficiency of dye was achieved at photocatalysis mass of 500  $mg/L$ .

Table 1. Effect of photocatalysis mass on the removal efficiency of reactive blue dye

Photocatalysis mass ( $mg/L$ )	$TiO_2$	$V_2O_5$	ZnO
100	72	79.5	84.3
200	75.4	81.6	86.8

300	79.3	86.5	90.4
400	85	93.8	95.9
500	89.3	97.1	98.9
600	80.5	81.9	81.9

### 3.3. Effect of H<sub>2</sub>O<sub>2</sub> concentration

The results proved that H<sub>2</sub>O<sub>2</sub> has a positive effect because it is increased the rate of photocatalytic process by enhancement the formation of hydroxyl radical. It is due to H<sub>2</sub>O<sub>2</sub> inhibits the electron–hole recombination. A possible way of increasing the degradation of the dye is increasing the concentration of OH radicals by the addition of oxidant like H<sub>2</sub>O<sub>2</sub> [27]. Fig.4 shows that the degradation rate increases with increasing the quantity of H<sub>2</sub>O<sub>2</sub>, becomes maximum at 300, 100 and 100 mg.L<sup>-1</sup> for TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> and ZnO respectively and then starts decreasing with further increase in the concentration of H<sub>2</sub>O<sub>2</sub>.

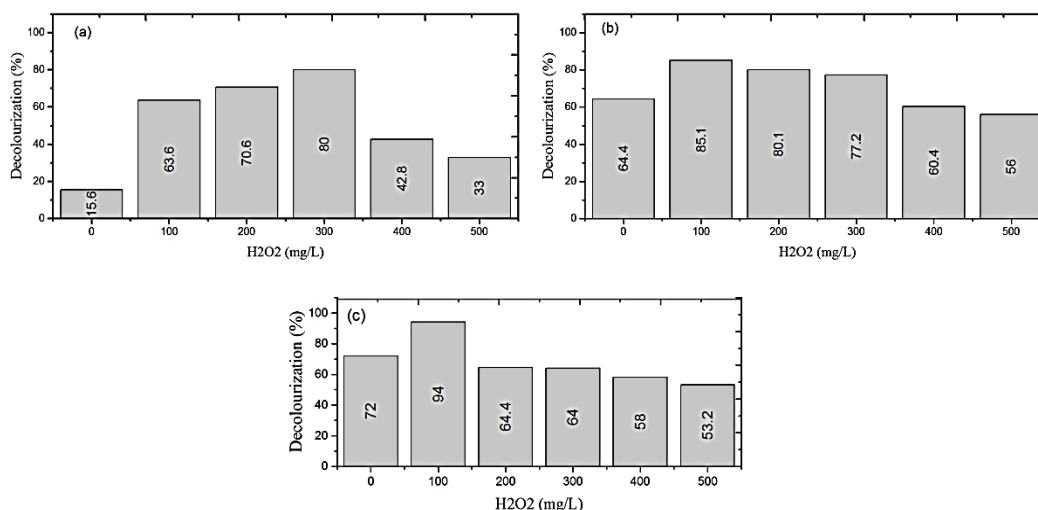


Figure 4. The effect of H<sub>2</sub>O<sub>2</sub> concentration on the removal efficiency of pollutant and on ORP value by using (a) TiO<sub>2</sub>, (b) V<sub>2</sub>O<sub>5</sub> and (c) ZnO

This effect is due to the fact that at a higher H<sub>2</sub>O<sub>2</sub> concentration, scavenging of OH radicals will take place, which can be expressed by eq. (14). The result is the formation of perhydroxyl radicals which are significantly less reactive than hydroxyl radicals and thus influence the degradation of dyes [35- 37].



### 3.4. Kinetic studies and the effect of initial concentration of dye

The effect of initial concentration of reactive dye was evaluated by using different values of initial concentration (25, 50, 75 and 100 mg.L<sup>-1</sup>) and the others operation conditions (optimum pH, optimum photocatalyst load, contact time) were kept constant.

As the concentration of reactive dye was increased, the percentage of photodegradation decreased, as shown in Fig.5. The possible explanation for this behavior is that: increase in the initial concentration of dye can lead to increase molecules that occupy and/or block all the active catalytic sites present on the surface of the catalysis and lead to decrease in degradation rate. In addition, the other reason may be the decrease in the path length of photon entering the dye solution and consequently decrease in removal rate. Many researchers have reported similar results earlier [28-34].

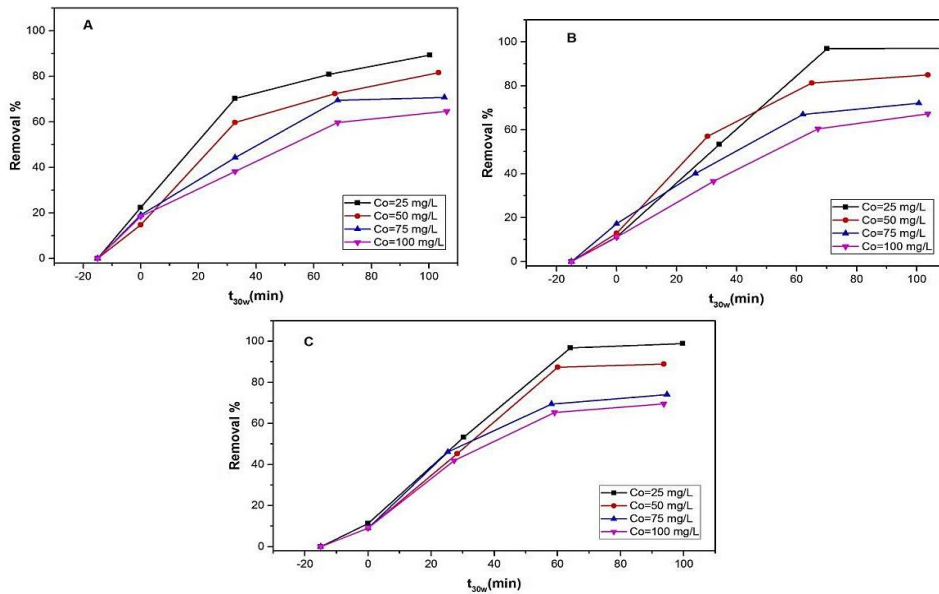


Figure 5. Removal efficiency at different values of dye initial concentration using (A)  $\text{TiO}_2$ , (B)  $\text{V}_2\text{O}_5$  and (C)  $\text{ZnO}$

The kinetics of photodegradation at various dye concentrations (25, 50, 75, and 100 mg/L) under solar light irradiation was performed after an adsorption period of 15 min in the dark, and the data were fitted with LH model (Fig.6).

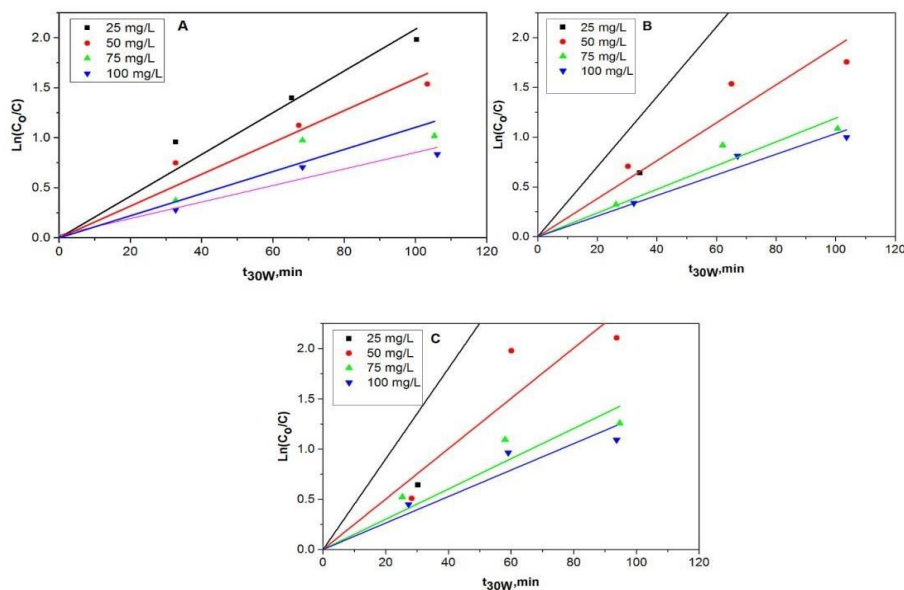


Figure 6. The LH models for three catalysis (A)  $\text{TiO}_2$ , (B)  $\text{V}_2\text{O}_5$  and (C)  $\text{ZnO}$



The rate constant ( $K$ ) for different catalysis was calculated from the slopes of the linear plots of  $\ln(C_0/C)$  vs.  $t_{30W}$ . The variation of  $(1/K_0)$  as a function of initial concentration of reactive dye are given in Fig. (7). The regression coefficients and the kinetic constants were estimated and tabulated in Table (2).

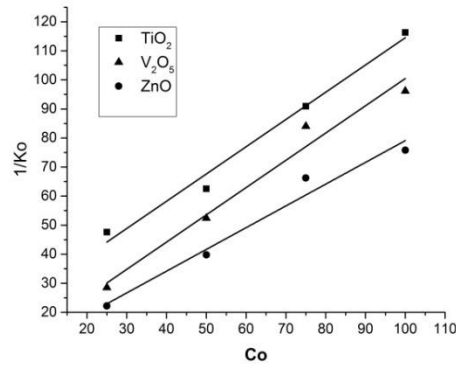


Figure 7. Variation of  $1/K_0$  vs.  $C_0$  of reactive dye

Table 2. The kinetic analysis data

Catalysis	Equation for linear fitting	$k_{LH}$ [ $\text{mg L}^{-1}\text{min}^{-1}$ ]	$K$ [ $\text{mg-1L}$ ]	Coefficient of determination $R^2$
TiO <sub>2</sub>	$Y^a=20.7+0.938X^b$	1.066	0.045	0.978
V <sub>2</sub> O <sub>5</sub>	$Y=6.625+0.938X$	1.066	0.142	0.962
ZnO	$Y=4.2+0.749X$	1.335	0.178	0.959

a: represent  $1/K_0$  ;

b: represent  $C_0$

The variation in the spectrum of the solution was monitored by measuring the absorption of light with UV-Vis spectrophotometer and Fig.8 is an example of the results from UV-Vis spectrophotometer. Fig. 8 represents the reduction in color of reactive blue dye at different time intervals at the optimum operation conditions for each type of catalyst. The same results was obtained by (Montano, 2007) when treating reactive red dye by photocatalytic process.

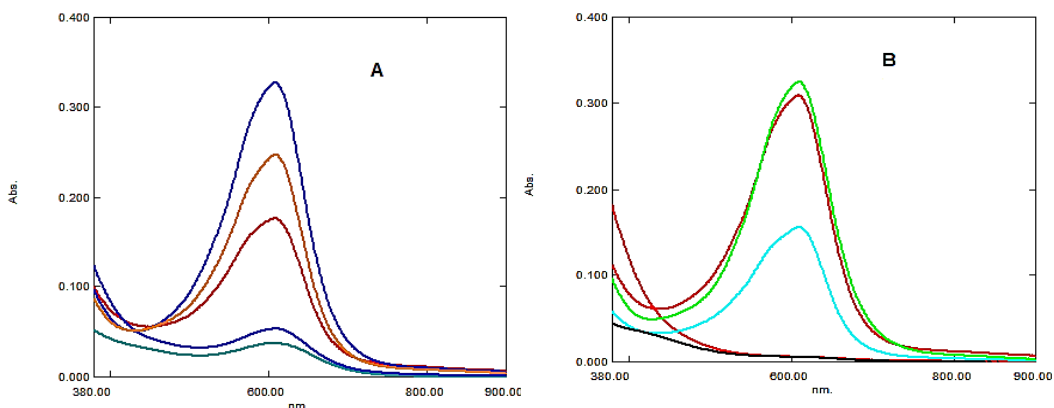


Figure 8. Variation in the spectrum of reactive blue dye for three catalysis (a) TiO<sub>2</sub>, (b) V<sub>2</sub>O<sub>5</sub> and (c) ZnO

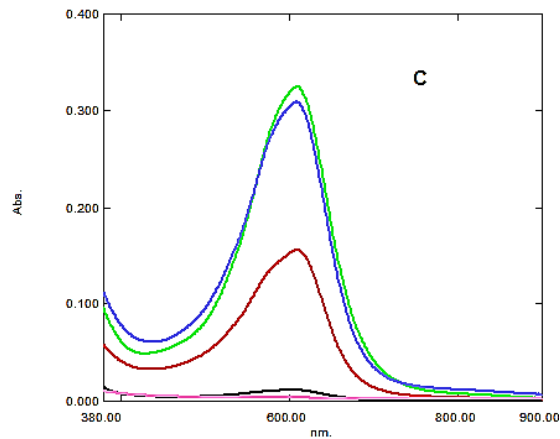


Figure 8. continued

### 3.5. Theoretical Representation

Response surface method (RSM) is a collection of mathematical and statistical techniques that are useful for modeling, analysis and optimizing the process in which response of interest is influenced by several variables and the objective.

From the experimental runs performed, mathematical relationship of the response function (Y) and influence of the independent variables is express as a general quadratic polynomial model eq. (15). The regression coefficients obtained by response surface regression analysis were achieved by fitting experimental data to the quadratic model.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_j \sum_{i=2}^k \beta_{ij} X_i X_j + \sum_{i=1}^k \beta_{ii} X_i^2 \quad (15)$$

Where:  $\beta$ 's are constants, X's are independent variables, Y is the response(the dependent variable) [38].

The mathematical models that adequately describe the photocatalytic of reactive blue dye under solar light irradiation were developed. The dependent variable of the process was the removal percentage of reactive dye and the independent variables namely  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  represent pH,  $H_2O_2$ , catalysis dosage and influent concentration of dye.

Mathematical models that represented the process are given in eqs. (16) to (18) with determination coefficients of (0.9957, 0.987 and 0.9) for  $TiO_2$ ,  $V_2O_5$  and  $ZnO$  respectively

$$Y = -496.5 - 1041.4X_1 - 862.57X_2 + 5763.8X_3 - 11588.3X_4 + 0.14X_1^2 - 6 * 10^{-4}X_2^2 - 17 * 10^{-5}X_3^2 - 10^{-3}X_4^2 - 1948.8 X_1X_2 + 6110.4X_1X_3 - 50.4 X_2X_3 - 24400.1X_1X_4 + 392.1X_2X_4 - 114.5 X_3X_4 \quad (16)$$

$$Y = -176.6 - 383.9X_1 - 1854.2X_2 + 2782.8X_3 - 3576.4X_4 + 2.4X_1^2 - 16 * 10^{-5}X_2^2 - 18 * 10^{-5}X_3^2 + 21 * 10^{-5}X_4^2 - 3781.9 X_1X_2 + 1986.68 X_1X_3 - 48.7 X_2X_3 - 7932.8 X_1X_4 + 571.5X_2X_4 - 75.4 X_3X_4 \quad (17)$$

$$Y = -52.3 - 718.4 X_1 - 215 X_2 + 4848.7 X_3 - 1035 X_4 - 0.93 X_1^2 + 85 * 10^{-6} X_2^2 - 3 * 10^{-4} X_3^2 - 2 * 10^{-3} X_4^2 - 2833.9 X_1 X_2 + 3963.8 X_1 X_3 - 319.7 X_2 X_3 - 15825.8 X_1 X_4 + 2194.2 X_2 X_4 - 183.6 X_3 X_4 \quad (18)$$

Experimentally determined responses (actual values) were plotted against responses obtained from the developed approximating function (predicted values) the plot (Fig.9) showed that, there is a good agreement between the two set of results thus, validating the model's reliability under the independent variables investigated.

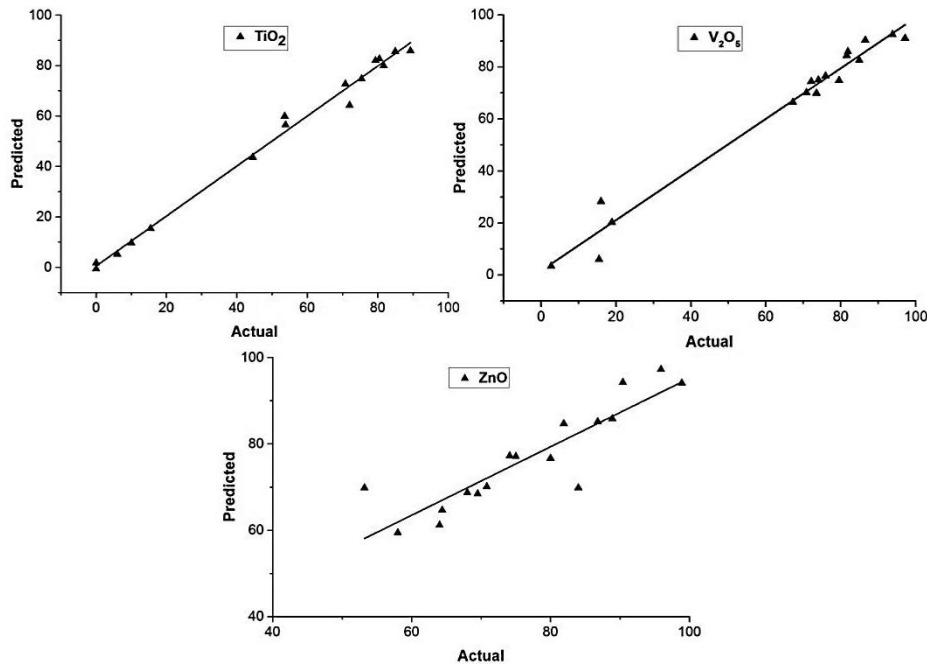


Figure 8. Plot of actual responses against predicted values of the removal percent of reactive blue dye for three catalysis

## 2. Conclusions

Photocatalytic process of reactive blue dye was carried out using different catalysis  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  and  $\text{ZnO}$  under solar light irradiation. The optimum conditions for decolorization were obtained to be: for  $\text{TiO}_2$ ; pH=2,  $\text{H}_2\text{O}_2$  concentration =300  $\text{mg.L}^{-1}$ , catalyst load=500  $\text{mg.L}^{-1}$  and initial concentration of dye=25  $\text{mg.L}^{-1}$ . For  $\text{V}_2\text{O}_5$ : pH=2,  $\text{H}_2\text{O}_2$  concentration =100  $\text{mg.L}^{-1}$ , catalyst load=500  $\text{mg.L}^{-1}$  and initial concentration of dye=25  $\text{mg.L}^{-1}$ . For  $\text{ZnO}$ : pH=8,  $\text{H}_2\text{O}_2$  concentration =100  $\text{mg.L}^{-1}$ , catalyst load=500  $\text{mg.L}^{-1}$  and initial concentration of dye=25  $\text{mg.L}^{-1}$ .

The decolorization process fitted well to L-H model and the reaction kinetics was determined for each catalysis.

An approximating theoretical relation was developed that adequately described the process. The suitability of the model was found to be satisfactory. In addition, data generated from the quadratic polynomial fitted the experimental data well

The order of activities of the photocatalysts were  $\text{ZnO} > \text{V}_2\text{O}_5 > \text{TiO}_2$  with removal efficiencies of 98.9, 97.1 and 89.3 respectively.  $\text{ZnO}$  was the most efficient catalyst.

### 3. References

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