

Solar Photocatalytic Degradation of Reactive Yellow 81 and Reactive Violet 1 in Aqueous Solution Containing Semiconductor Oxides

A. Giwa

P.O. Nkeonye

K.A. Bello

E.G. Kolawole

Department of Textile Science and Technology
Ahmadu Bello University
Zaria, Nigeria

A.M.F. Oliveira Campos

Department of Chemistry
Minho University
Braga, Portugal

Abstract

The textile industry consumes considerable amounts of water during the dyeing and finishing operations. Dyes are extensively used and hence wastewaters discharged in rivers or public sewage treatment plants are highly contaminated. In this work, the photocatalytic decolorization and degradation of two reactive dyes, Reactive Yellow 81 (RY81) and Reactive Violet 1 (RV1) in aqueous solution with TiO₂-P25 (Degussa) as photocatalyst in slurry form has been investigated using solar rays. The effects of various parameters such as catalyst loading, pH, and initial concentration of the dye on decolorization and degradation have been determined. Chemical oxygen demand and UV-vis spectrophotometer were used to study the mineralization and degradation of the dyes respectively. The most effective catalyst was Degussa P25, which produced decolouration of 92% for Reactive Yellow 81 (50 mg/L) and 85% for Reactive Violet 1 (50 mg/L) in 20 minutes. The results are thus promising in terms of possible application of sunlight/TiO₂ catalysed degradation to coloured waste.

Keywords: Reactive Yellow 81; Reactive Violet 1; Aminochlorotriazine; Photocatalysis; TiO₂.

1.0 Introduction

Dyes are widely used in the textile, leather, paper, printing inks, plastics, cosmetics, paints, pharmaceutical, and food industries. The total world colorant production in 2008 alone was estimated to be about 1.5 million tons [1]. It is estimated that 15% of these dyes is lost in the synthesis, processing of colorants, dyeing, printing and finishing [2]. This invariably corresponds to a release of about 615 tons per day into the environment and ecological system. Due to their toxicity and recalcitrance, these dyes are hazardous to the environment and even when they are present in very low concentrations, can present serious carcinogenic effects [3].

Degradation of dye molecules sometimes results in the formation of non-colored dye fragments which, although satisfying the requirement of decolorization, leads to the formation of environmentally unfriendly degradation products, such as aromatic amines, which are sometimes much more toxic than the parent dyes. Because of the high levels of aromatics present in these molecules and the stability of modern dyes, conventional biological treatment methods are ineffective for decolorization and degradation [4-8].

Physico-chemical methods such as coagulation/flocculation, activated carbon adsorption and reverse osmosis techniques have been developed in order to remove the color [9]. However, the latter methods can only transfer the contaminants (dyes) from one phase to the other leaving the problem essentially unsolved [10]. In general, each technique has its limitations.

The use of one individual process may often not be sufficient to achieve complete decolorization. Dye removal strategies consist therefore mostly of a combination of different techniques. Therefore, attention has to be focused on techniques that can lead to the complete destruction of the dye molecules. This had led to the study of other methods.

Photocatalysis, which is one of the Advanced Oxidation Processes, is a new method used to mineralize dye compounds [11,12]. The utilization of photocatalysis has been attracting increasing attention. It may be developed to a useful process for the reduction of water pollution caused by dyeing compounds because of their mild conditions required and their efficiency in the mineralization. It also has the potential ability to oxidize most of the organic contaminants to CO₂ and H₂O [13-16].

Advanced oxidation processes (AOPs) are therefore mostly based on the generation of highly reactive radical species (especially the hydroxyl radical HO[•]) that can react with a wide range of compounds, including compounds that are otherwise difficult to degrade, e.g. dye molecules [4]. The four AOPs that have been most widely studied are ozonation, UV/H₂O₂, Fenton's reagent (Fe²⁺/H₂O₂) and UV/TiO₂ [17].

With TiO₂ catalyzed UV treatment, a wide range of dyes can be oxidized. The dyes are generally not only decolorized but also highly mineralized [7,18-20].

Since there is no general or economical method to remove the dye materials from the wastewater, UV irradiation for color removal might be a promising process due to two reasons: no chemical sludge or toxic residue is left in the treated effluent, and UV decomposition has the potential to accomplish both color removal and toxicity reduction in one step.

The present study is therefore aimed at determining a simple, efficient and economic way of degrading textile dyes usually present in textile wastewater effluents.

2.0 Methods

2.1 Chemicals

Two Reactive dyes were examined, namely Reactive Yellow 81 (RY 81), from Sigma-Aldrich, and Reactive Violet 1 (RV 1), supplied by ICI. All dyes were used without further purification, and some of their characteristics are given in Table 1. The photocatalysts used in this experiment were technical grade TiO₂ Degussa P-25 (anatase/rutile, surface area 56 m² g⁻¹, nonporous), TiO₂ UV-100 (Hombikat, Schachtleben chemie, surface area 25 m² g⁻¹ 100% anatase) and ZnO (Merck, surface area 9.2 m² g⁻¹) [4]. Double distilled water was used in the preparation of various solutions. The pH of the solutions was adjusted with 2M HCl or 2M NaOH.

2.2 Experimental

Sunlight intensity was measured using a Digital Lux Meter (model no. LX1010B). The pH of the solution was varied by adding HCl or NaOH solution as required and measured using an ORION per Hect pH meter. The concentrations of the two dye solution samples were determined using a JENWAY 6405 UV/Vis. spectrophotometer. Samples after photocatalytic treatment were centrifuged at 2000 rpm for 15 min using a Baird & Tatlock Auto Bench Centrifuge, and finally filtered using a 0.2 μm syringe filter.

2.3 Degradation Experiment

2.3.1 Photolysis

For solar degradation, stock solutions of 200 mg/L each of RY81 (D1) and RV1 (D2) were prepared in double distilled water for all the experiments. Necessary dilutions of each stock solution were performed with double distilled water to obtain a series of dye solutions with varying concentrations. The pH of the solution was noted. 700 ml each of the respective dye solutions without catalyst were then irradiated under sunlight on a flat surface in a 1000ml beaker with constant stirring. At 1 hour intervals, the intensity of the sun (which was averagely highest at 9.50 x 10⁴ Lux (occurred between 12.00 and 2.00 pm) was measured using the Lux meter. On a daily basis and at specific times, an aliquot of 2 ml was taken from each beaker with a syringe. The pH of the final solutions were noted. These samples were analyzed for color disappearance using a UV-Vis spectrophotometer at the maximum absorption wavelength of each dye. All experiments were carried out from 10.00 am to 4.00 pm. Only the results obtained on Mondays throughout the 7 weeks were used.

2.3.2 Photocatalysis

A 100 ml solution of the required concentration of 10-100 mg/L of each dye was prepared from the stock solution and transferred into a 500 ml Pyrex beaker for solar irradiation. Before the solar irradiation, 1g of catalyst was added to the solution and stirred in the dark for 15 min so that adsorption equilibrium could be established. The solutions were then exposed to the sun for irradiation with constant stirring throughout the experiment. At 1 hour intervals, the intensity of the sun was measured using the Lux meter and samples were withdrawn and spectrophotometric measurements of the concentration of the dyes were made. The color removal of the dye solution was measured at the λ maximum of the absorption spectrum of each dye.

Decolorization efficiency was calculated from a mathematical equation adapted from measurements of decolorization [21]. From the respective absorbances obtained, percentage color disappearance was calculated using the following:

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

where $(\text{Absorbance})_0$ is the absorbance before irradiation and $(\text{Absorbance})_t$ is the absorbance at time t.

Further experiments were set to optimize the operation parameters such as initial concentration, pH and catalyst loading. Before and after photocatalytic treatment, the aliquots were centrifuged and filtered.

2.4 Biodegradability of organic pollutants

To investigate the biodegradability of the dye solutions, COD analysis was done by the standard acid dichromate method, while BOD was measured after 5 days of incubation at 20 °C [22].

3.0 Results and discussion

3.1 Photodegradation effects on the dye solutions

3.1.1. Photolysis experiment

The influence of solar light on the color removal of the dyes was investigated for 7 weeks. One experiment was performed in the absence of any catalyst under direct sunlight. The degradation performance of the process was assessed in terms of decolorization efficiencies defined as shown in equation 1:

$$\text{Removal Efficiency of Dye (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 and C are the initial and remaining dye concentrations at given time t respectively.

From Figure 1, it was observed that there was no decolorization of any dye after the first and second day. At the end of 4 weeks, both the dyes showed less than 20% decolorization, but at the end of 7 weeks, the percentage decolorization of D1 was 22.40% while that of D2 was 31.68%.

However, in view of the analysis of degradation using the Langmuir-Hinshelwood (L-H) Kinetic Model, the removal efficiency of the dyes in percentages was not used. Instead, the fraction of color remaining (equation 2) was used for plotting the graphs.

Hence:

$$\text{Fraction of Colour Remaining} = \frac{C}{C_0} \quad (2)$$

Therefore:

$$\text{Percentage Colour Remaining (\%)} = \frac{C}{C_0} \times 100 \quad (3)$$

[i. e 100 – Removal Efficiency of Dye (%)]

Decolorization efficiency estimates the extent of the azo bond cleavage of the dye which is the first step of the degradation [23].

3.3.2. Effect of catalyst concentrations

The results obtained for photocatalytic degradation of samples under solar light using 0.5–2.0 g/L TiO_2 are shown in Fig. 2. A series of experiments were carried out to assess the optimum amount of catalyst by varying the amount of catalyst from 0.5 to 2.0 g/L for the commercial dye solution (50 mg/L).

The results clearly show that increasing the amount of catalyst from 0.5 to 1.0 g/L increases the dye decolorization sharply from 32% to 47% for D1, 38% to 52% for D2 at 60 min. According to [24], the enhancement of removal rate could be ascribed to:

- the increase in the amount of catalyst weight which increases the number of dye molecules adsorbed
- the density of particles in the area of illumination.

But at concentrations of 1.5–2.0 g/L, (Fig. 2) the decolorization efficiencies are almost constant. This may be due to the enhancement of light reflectance by the catalyst and decrease in light penetration. Particle–particle interaction becomes significant as the number of particles in the solution increases. This reduces the site density for surface holes and electrons. Many authors have investigated the reaction rate as a function of catalyst loading under different experimental conditions [25,26]. The results obtained in this work, are in good agreement with reported values in the literature.

Figure 3 showed the reaction rate for the effects of catalyst concentration on the decolorization of the dye samples. Some studies [24,27] have provided a possible explanation for the remarkable rate of reaction behavior obtained. The increased loading of the catalyst increases the quantity of photons adsorbed and consequently the degradation rates. Hence it is essential to determine the optimum amount of catalyst required in order to avoid unnecessary excesses and also to ensure total absorption of photons for efficient mineralization. The optimum concentration of the catalyst for efficient solar photodecolorization and degradation was found to be 1 g/L. Hence 1 g/L was used as the catalyst dosage for the photocatalytic reaction.

3.3.3. Effect of pH on dye degradation

The most important parameter that influences the photocatalytic degradation is solution pH. The effects of pH from 3 to 11 on the photocatalytic decolorization are shown in Fig. 4 and 5. The desired pH level was achieved by the addition of (2M) HCl/(2M) NaOH to the solution. Increase in pH of the dye solution from 3 to 11 increased the decolorization for both dyes. The photocatalytic removal of color was observed to be fastest in alkaline pH for D1 and D2. Similar results were reported in literature for acidic dyes bearing sulphonate group [28]. At acidic pH range the removal efficiency is minimum for D1 and D2. This could be ascribed to two reasons [29,30]: at low pH value, TiO₂ particle agglomeration reduces the dye adsorption as well as photon absorption, and the azo linkage (-N=N-) is particularly susceptible to electrophilic attack by hydroxyl radicals. But at low pH the concentration of H⁺ is in excess and H⁺ ions interact with azo linkage decreasing the electron densities at azo group. Consequently, the reactivity of the hydroxyl radical by the electrophilic mechanism decreases. The percentage removal of the dye increases with the increase in pH from 7 to 11, though dye adsorption on the photocatalytic surface of TiO₂ decreases from pH 7 to 11. This indicates that the effect of dye adsorption on photocatalytic activity is limited. Hence dye adsorption may not be the only determinant for the photocatalytic degradation. The photocatalytic degradation of dyes is mainly due to the hydroxyl radical attack on the dye molecule. The production of hydroxyl radicals in an acidic medium is different from what occurs in a basic medium. In an acidic medium, photogenerated holes react with water molecules to produce hydroxyl radicals as given in Eq. (4). At alkaline pH the negative surface of the TiO₂ with OH⁻ ions acts as an efficient trap for the photogenerated holes and hydroxyl radicals are produced (Eq. (5)).



At pH > TiO₂ point of zero charge (pzc), the hydroxyl radicals and O₂⁻ radical can easily diffuse from the negative surface of TiO₂ into the bulk of reaction solution. Hence hydroxyl radicals are responsible for dye degradation.

The degradation rate for the decomposition of the dyes as a function of reaction pH is shown on Fig. 6. The interpretation of pH effects on the efficiency of the dye photodegradation process is a very difficult task because of its multiple roles. First, it is related to the ionization state of the surface according to the following reactions (equation 6 and 7), as well as to that of reactant dyes and products such as acids and amines.



The pH changes can thus influence the adsorption of dye molecules onto the TiO₂ surfaces, an important step for the photocatalytic oxidation to take place [31].

The point of zero charge (pzc) of the TiO₂ (Degussa P25) is at pH 6.8 [19]. Thus, the TiO₂ surface is positively charged in acidic media (pH<6.8), whereas it is negatively charged under alkaline conditions (pH>7). Secondly, hydroxyl radicals can be formed by the reaction between hydroxide ions and positive holes. The positive holes are considered as the major oxidation species at low pH, whereas the hydroxyl radicals are considered as the predominant species at neutral or high pH levels [32].

3.3.4. Effects of different catalysts on photodegradation of the dyes

The effects of various photocatalysts such as TiO₂-P25 (Degussa), TiO₂ (anatase), and ZnO on decolorization have been investigated at 1 g/L catalyst concentration, 50 mg/L dye concentrations and at solution pH of each dye. The results are shown in Fig. 7. The results show that TiO₂-P25 and ZnO are more efficient than TiO₂ (anatase) photocatalyst. The decolorization efficiency of TiO₂-P25, ZnO, and TiO₂ (anatase) photocatalysts are shown in Fig. 7 at the time of 30min. The order of activities of the photocatalysts are TiO₂-P25 > ZnO > TiO₂ anatase. The high photoreactivity of TiO₂-P25 has been attributed to two factors: the slow recombination of the electron-hole pair, and its large surface area [33]. ZnO has the disadvantage of undergoing photocorrosion under illumination.

Titanium dioxide is known to be the semiconductor with the highest photocatalytic activity. It has the advantage of being non-toxic, relatively inexpensive and stable in aqueous solution. Several reviews have been written regarding the mechanistic and kinetic details as well as the influence of experimental parameters [6,7,34]. And it has also been demonstrated that degradation by photocatalysis can be more efficient than by other wet-oxidation techniques.

The aim here was to determine the best photocatalyst among different commercially available materials and find further means to accelerate the efficiency of the photocatalytic process. Therefore, the photocatalytic activity of three different commercially available catalysts (namely TiO₂ Degussa P25, ZnO, and TiO₂ anatase) on the degradation kinetics of the dyes was investigated. The differences in the photocatalytic activity are likely due to differences in the Brunauer-Emmett-Teller (BET)-surface (TiO₂ Degussa – 56 m²/g; ZnO – 9.2 m²/g and TiO₂ Anatase – 25 m²/g), and the density of hydroxyl groups on the catalyst's surface, since these may affect the adsorption behavior of a pollutant or intermediate molecule and also the lifetime and recombination rate of electron-hole pairs. Earlier studies have shown that Degussa P25 proved more effective in the photocatalytic degradation of a large number of organic compounds [35].

It has also been argued that the greater photo-effectiveness of TiO₂ Degussa photocatalyst can be attributed to three factors:

- i. the smaller band gap of rutile extends the useful range of photoactivity into the visible region;
- ii. the stabilization of charge separation by electron transfer from rutile to anatase slows the recombination;
- iii. the small size of the rutile crystallites facilitates the electron transfer [36].

3.3.5. Effect of dye concentration on photodegradation

Dye concentration is another very important parameter in wastewater treatment. The effect of various dye concentrations on photocatalytic decolorization has been investigated from 10 – 100 mg/L. The results shown in Figs. 8 and 9 illustrated that an increase in the dye concentration will lower the removal rate. Similar results have been reported for the photocatalytic oxidation of other dyes [20]. Efficient degradation is observed for both dyes with concentrations up to 50 mg/L, the dye D1 being slightly easier to decolorize. Increase in the concentration of dye from 10 mg/L to 50 mg/L reduces the decolorization in 20 min from 100% to 92% for D1 and from 100% to 88% for D2.

When the dye concentration increases, the amount of dye adsorbed on the catalytic surface increases. This affects the catalytic activity of TiO₂. The increase in dye concentration also decreases the path length of photons entering the dye solution. The rate of degradation is related to the formation of OH radicals, a critical species in the degradation process. The equilibrium adsorption of reactants on the catalyst surface and the rate of reaction of OH radicals with other chemicals are also significant in the rate of degradation. Hence k' can be expressed as shown in equation 8:

$$k' = k_o P_{OH} P_{dye} \quad (8)$$

where k' is the overall rate constant, k_o is the reaction rate constant, P_{OH} is the probability of generation of OH radicals on the catalyst surface and P_{dye} is the probability of OH radicals reacting with dye molecules. The reaction rate k_o is independent of the dye concentration $[dye]_o$ whereas P_{OH} and P_{dye} will be affected by the dye concentration.

This reaction follows pseudo-first-order kinetics. Previous researchers suggested that the photocatalytic degradation of aromatic compounds happens through the hydroxylation by hydroxyl radicals [37]. In addition, it was [38] pointed out that the rate-determining step of the reaction could be the formation of OH radicals, since they react very rapidly with aromatic ring compounds. The hydroxyl radicals are formed through the reaction of holes with adsorbed OH^- and water.

If we assume that the positions of adsorbed OH radicals are replaced by dye ions (dye^-) which are generated from the dissociation of the sodium salt in dye molecules, then the generation of OH radicals will be reduced due to the reduced number of active sites available for the generation of OH radicals. Therefore, P_{OH} is adversely affected by the catalyst site, the coverage fraction of dye and its oxidation intermediates. Another important aspect of this behavior is that as the initial concentration of dye increases, the path length of photons entering the solution decreases, and in low concentration the reverse effect is observed [20]. This shows that the rate of degradation decreases considerably with the increase in the concentration of dye.

3.3.6. Analysis of degradation using the Langmuir-Hinshelwood (L-H) Kinetic Model

Several experimental results that the destruction rates of photocatalytic oxidation of various dyes over illuminated TiO_2 fit the Langmuir–Hinshelwood (L–H) kinetics model [39], equation 9:

$$r = \frac{dC}{dt} = \frac{kKC}{1+KC} \quad (9)$$

where r is the oxidation rate of the reactant (mg/L min), C the concentration of the reactant (mg/L), t the illumination time, k the reaction rate constant (mg/L min), and K is the adsorption coefficient of the reactant (l/mg).

When the chemical concentration C_o is a millimolar solution (C_o small), the equation can be simplified to an apparent first-order equation [39] equations 10 and 11:

$$\ln\left(\frac{C_o}{C}\right) = kKt = k_{app} t \quad (10)$$

Or

$$C_t = C_o e^{-k_{app} t} \quad (11)$$

A plot of $\ln C_o/C$ versus time represents a straight line, the slope of which upon linear regression equals the apparent first-order rate constant k_{app} , as shown in Figures 10 and 11. The decrease of the k' values with the increase in the initial concentration of the dye can be ascribed to the decrease in the path length of photons entering the solution due to the impermeability of the dye solution (Table 2). At low concentrations the reverse effect was observed, thereby increasing the number of photon absorption by the catalyst [20]. This decreasing phenomenon can further be explained in terms of the increase in the requirement of the catalyst surface for the increased concentration of the dye. Generally first-order kinetics are appropriate for the entire concentration range up to few mg/l and the findings of several studies fit this kinetic model reasonably well [26,40,41].

All isotherms showed a linear shape which means there is no strong competition between the water and the dye molecules to occupy the TiO_2 surface sites [42,43]. The adsorption isotherms correspond well to the Langmuir type, implying a monolayer adsorption model [39,44,45]. When the dye concentration increases, the amount of dye adsorbed on the catalytic surface increases. This affects the catalytic activity of TiO_2 [13-16]. The increase in dye concentration also decreases the path length of photons entering the dye solution. At high dye concentration, a significant amount of solar light may be absorbed by the dye molecules rather than the catalyst and this may also reduce the catalytic efficiency [40].

The photocatalytic decolorization of dyes containing TiO_2 obeys pseudo-first-order kinetics. At low initial dye concentration, the rate expression is given by equation 12:

$$\frac{-d[C]}{dt} = k'[C] \quad (12)$$

where k' is the pseudo-first-order rate constant. The dye is adsorbed onto the TiO_2 surface until adsorption-desorption equilibrium is reached. After adsorption, the equilibrium concentration of the dye solution is determined and it is taken as the initial dye concentration for kinetic analysis. Integration of Eq. (12) (with the limit of $C=C_0$ at $t=0$ with C_0 being the equilibrium concentration of the bulk solution) gives equation 13:

$$\ln \left[\frac{C_0}{C} \right] = k' t \quad (13)$$

where C_0 is the equilibrium concentration of dye and C the concentration at time t . A plot of $\ln C_0/C$ versus t for photo-decolorization is shown in Figs. 10 and 11. A linear relation between dye concentration and irradiation time has been observed.

3.4. Biodegradability

In order to assess the degree of mineralization reached during the photocatalytic treatment, the formation of CO_2 [30,41], is generally determined. However, in this case, the determination of total organic carbon (TOC) and/or the measurement of the chemical oxygen demand (COD) or the biological oxygen demand (BOD) of the irradiated solution are generally used for monitoring the mineralization of the dye [46-47].

To determine the COD removal in TiO_2 -sensitized photo-oxidation, the dye samples were tested as follows. Reaction conditions included: concentration of dyes = 50 mg/L, concentration of TiO_2 = 1000 mg/L, light intensity = 95000 lux, reaction period = 6 h. For each dye chemical, a test was carried out at the optimum pH for the dye chemical in question over 6 hours and analytical samples were collected during the tests for COD and BOD determination. The results of the tests (shown in Table 3 and Fig. 12) indicated that BOD increased after treatment for both dyes, while the COD decreased during the reaction. The increase in BOD may imply that the biodegradability of the dyes can be increased by the sensitized photo-oxidation reaction due to the conversion of non-biodegradable organics (do you mean organic?) dyes to degradable forms. A ratio of BOD/COD in wastewater is normally used to express the biodegradability of the wastewater. When the ratio of BOD and COD is more than 0.3, the wastewater has a better biodegradability, whereas if the ratio is less than 0.3, it is difficult to degrade the impurities by biological methods [48].

The ratio of BOD/COD was initially low and increased significantly after treatment. The ratio of BOD/COD had changed from 0.0438 to 0.3423 for D1 and 0.0712 to 0.3409 for D2 as shown in Table 3. From the results, it was found that BOD increased after photo-oxidation. This implies that the biodegradability of the dye samples can be enhanced by photo-oxidation. The sensitized photo-oxidation process could be one of the alternatives for decolorization and will enhance COD removal in dye samples after conventional biological treatment. It is obvious that decolorization of dye solutions is not followed by the same extent of mineralization. This means that the dye decomposes to smaller organic intermediates that are still present in the solution, suggesting that prolonged illumination can probably lead to complete mineralization.

4.0 Conclusion

Reactive Yellow 81 and Reactive Violet 1 dyes were degraded by solar irradiation in the presence of a catalyst. The most effective catalyst studied was Degussa P25, which produced decolouration of 92% for Reactive Yellow 81 (50 mg/L) in 20 minutes and 85% for Reactive Violet 1 (50 mg/L) in 20 minutes. Reactive Yellow 81 was easier to degrade than Reactive Violet 1. The variables studied included the effect of pH and the amount of catalyst and dye on decolouration. It was observed that in basic medium, a lower concentration of dye and 1 g/L of catalyst were the optimum conditions. The degradation included not only the loss of colour of the solution with irradiation, but also an increase in biodegradability as shown by the BOD/COD ratio. The results are thus promising in terms of the possible application of sunlight/ TiO_2 catalysed degradation to coloured waste.

Acknowledgement

The authors acknowledge the financial support of Ahmadu Bello University Zaria, Nigeria Board of Research Grant and the Nigerian Educational Trust Fund (ETF) Staff Training and Development Intervention Grant.

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Table 1: Description of the dyes

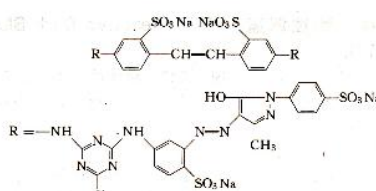
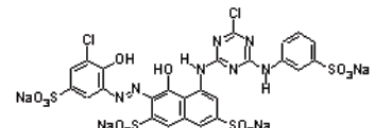
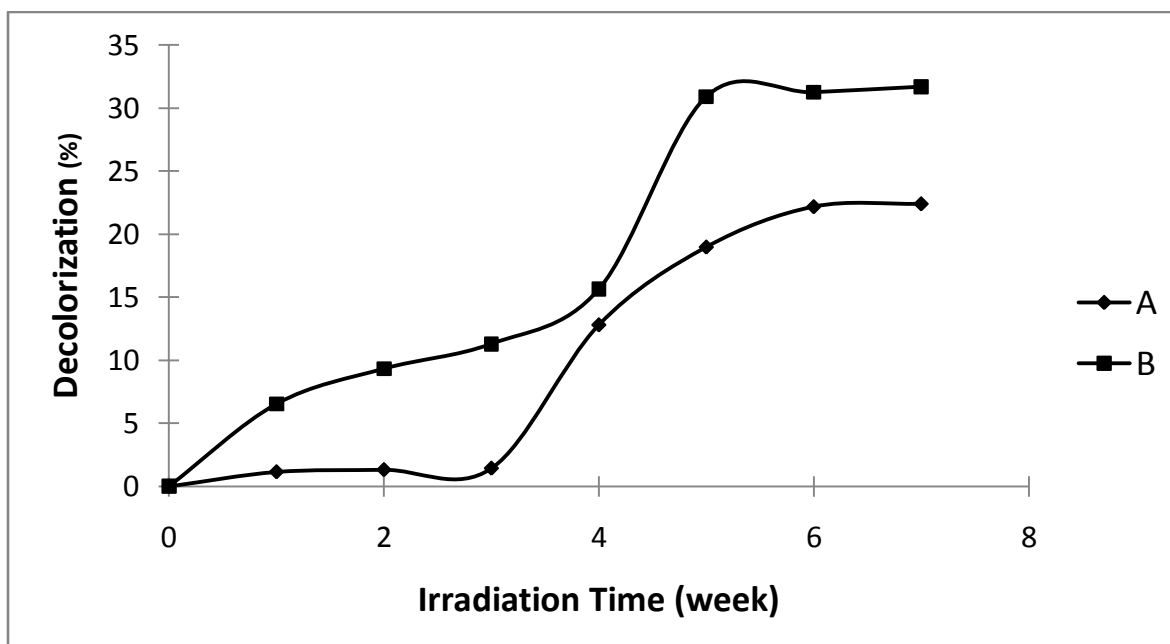
PROPERTY	DYE 1	DYE 2
C. I. Name	Reactive Yellow 81	Reactive Violet 1
Commercial Names	Cibacron Yellow G-E Procion Yellow H-E 3G	Procion Violet H3R Procion Brilliant Purple H3R
Functional group	bifunctional bis(aminochlorotriazine)	monofunctional aminochlorotriazine
CAS Number	59112-78-6	12239-45-1
Chemical Formula		
Lambda max (nm)	410	555

TABLE 2: k' and t_{1/2} values for various initial concentration of the dye

Concentration (mg/l)	K'		R ²		t _{1/2} (min)	
	RY81	RV1	RY81	RV1	RY81	RV1
10	0.03640	0.03112	0.9841	0.9879	19.04	22.27
20	0.03239	0.01586	0.9968	0.9869	21.40	43.69
50	0.02799	0.01234	0.9643	0.9912	24.76	56.16
100	0.01049	0.00696	0.9574	0.9866	66.06	99.57

TABLE 3: Variation of BOD and COD during photodegradation

Dye Samples	Initial BOD ₅ (mg/l)	Final BOD ₅ (mg/l)	Initial COD (mg/l)	Final COD (mg/l)	pH	Initial BOD/COD	Final BOD/COD
D1	5	19	114.1	55.5	9	0.0438	0.3423
D2	7	21	98.3	61.6	9	0.0712	0.3409

**Fig. 1: Decolorization (%) of 50 mg/L dye samples under direct solar light without catalyst.**

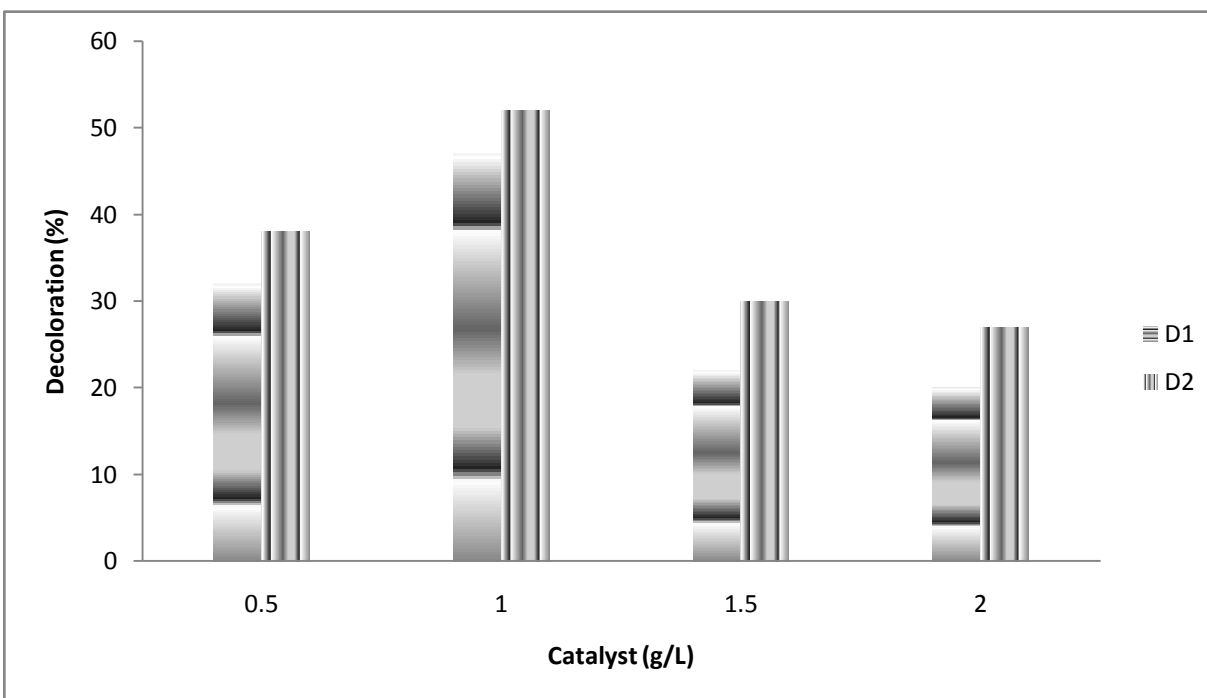


Fig. 2: Change in % decolouration of D1 and D2 with varying concentration of TiO₂. (Dye concentration = 50 mg/L; Time of irradiation = 60 min; and at natural pH of each dyes)

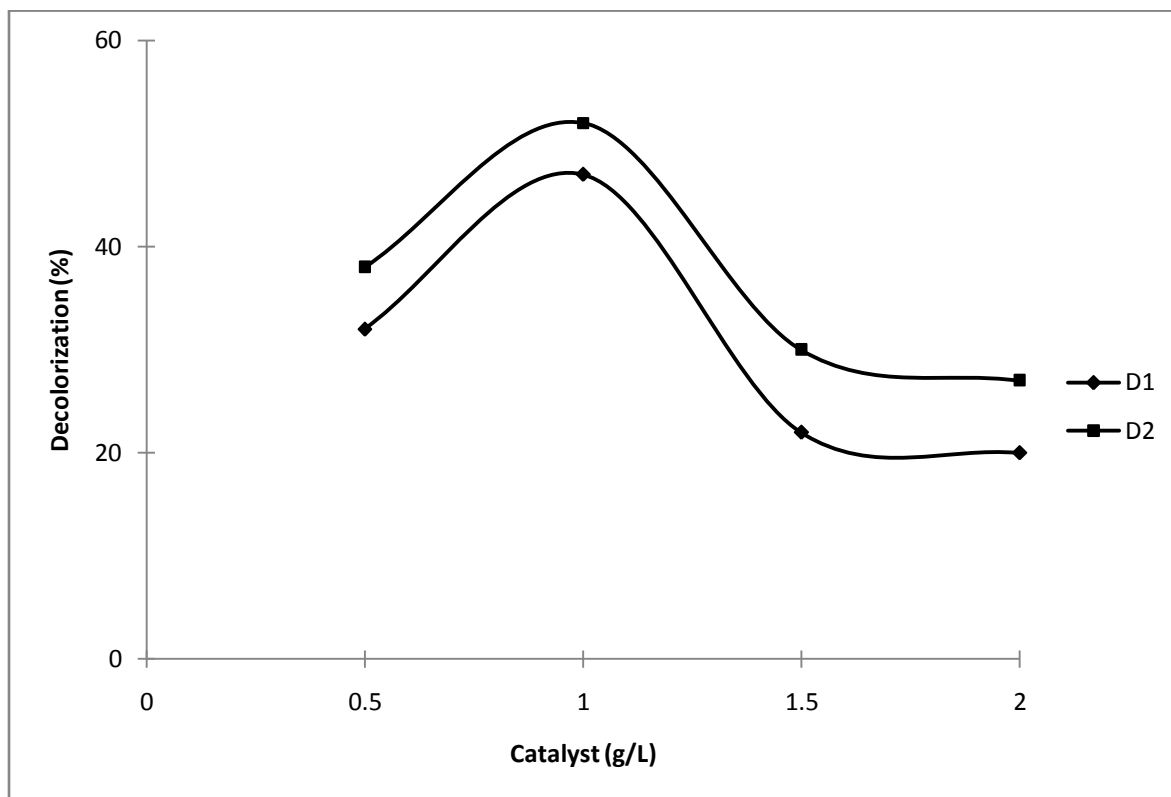


Fig. 3: Percentage decolorization with increasing catalyst concentration at 30 min.

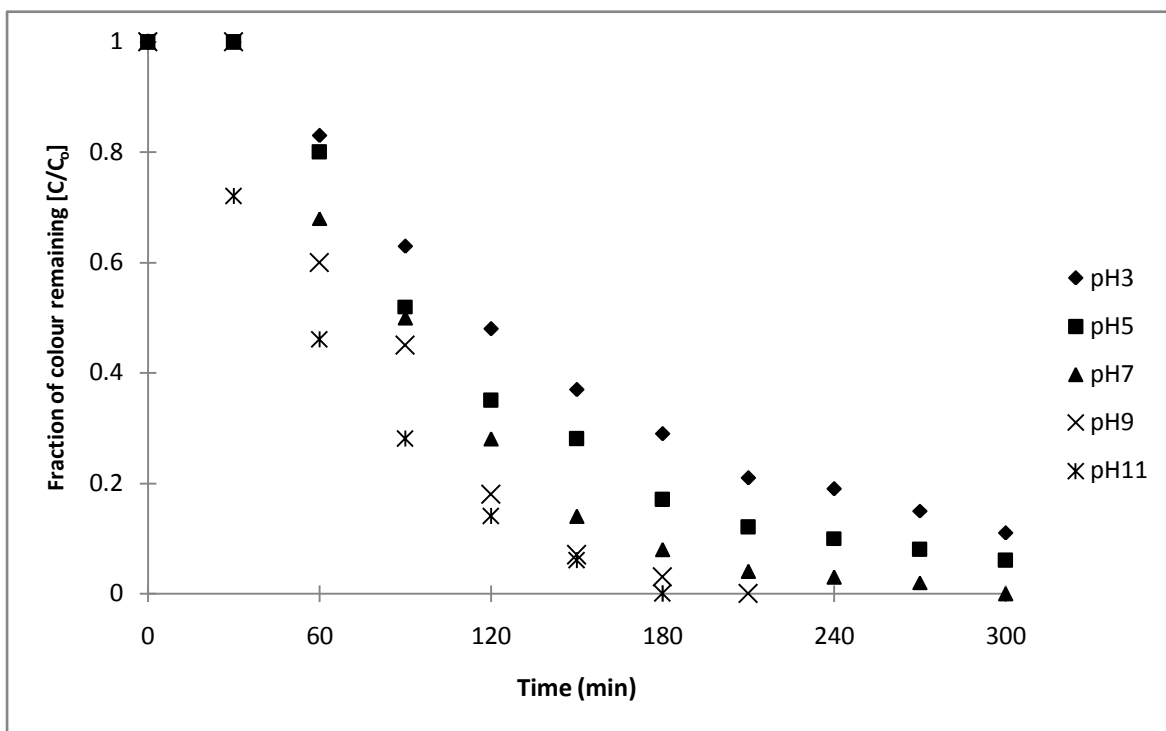


Fig. 4: The effect of pH on photocatalytic degradation of dye 1 (D1) using TiO₂ P25 [Dye sample = 50 mg/L, TiO₂ = 1 g/L]

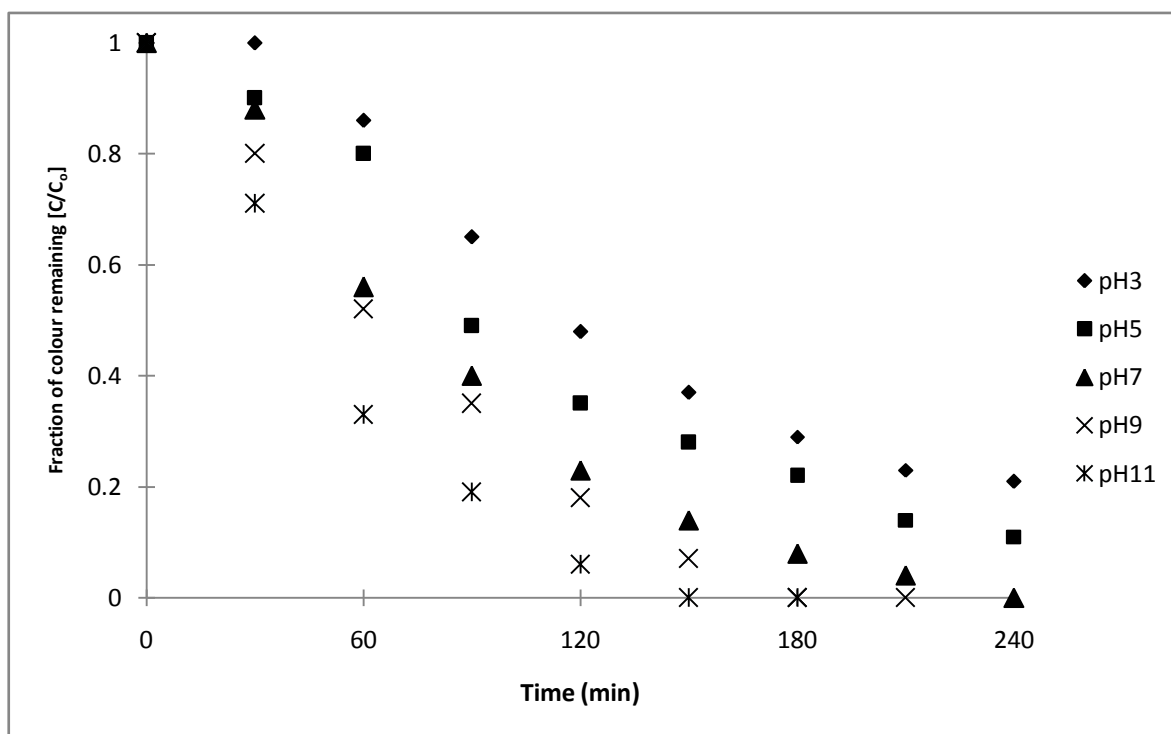


Fig. 5: The effect of pH on photocatalytic degradation of dye 2 (D2) using TiO₂ P25 [Dye sample = 50 mg/L, TiO₂ = 1 g/L]

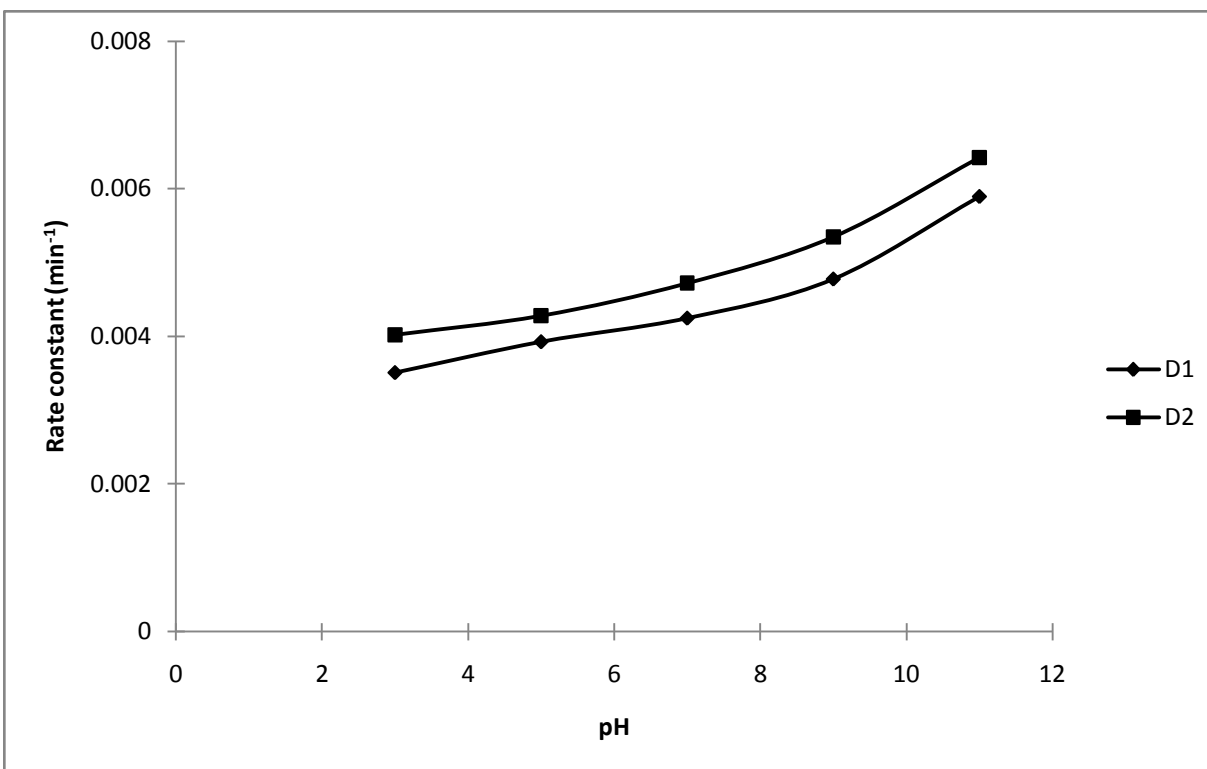


Fig. 6: The effect of pH on rate constant for the photocatalytic degradation of dyes.

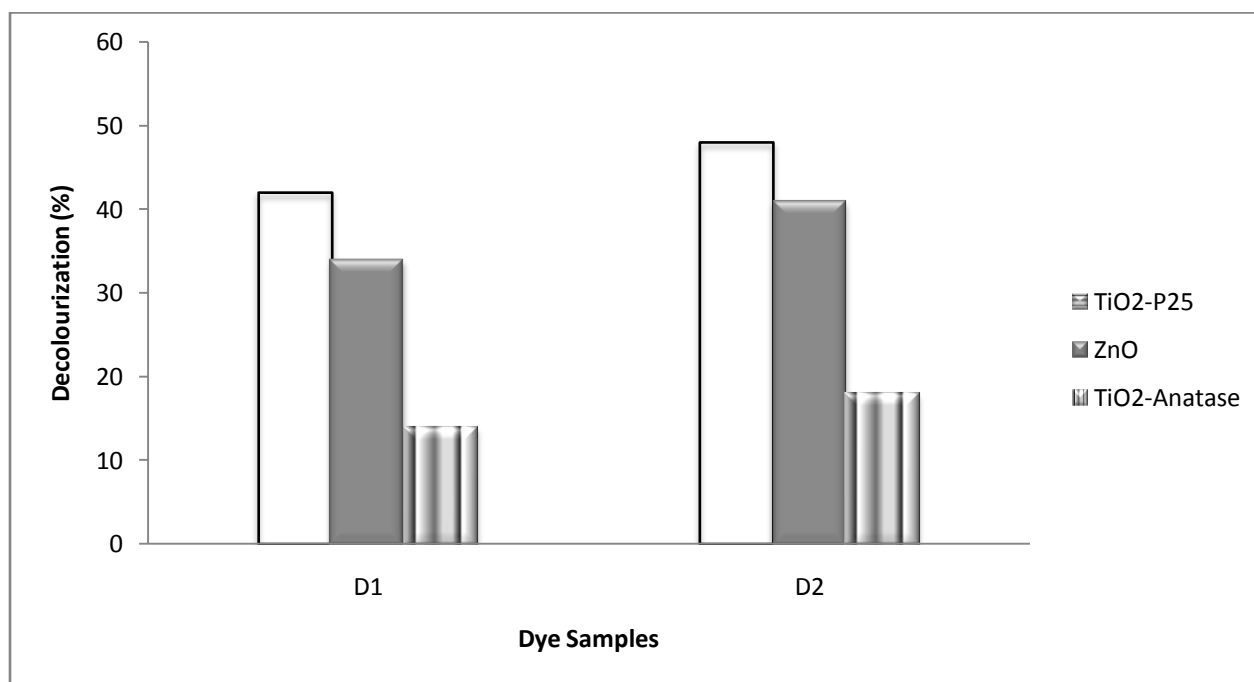


Fig. 7: The effect of catalysts on photocatalytic degradation of dyes [Dye sample = 50 mg/L, TiO₂ = 1 g/L]

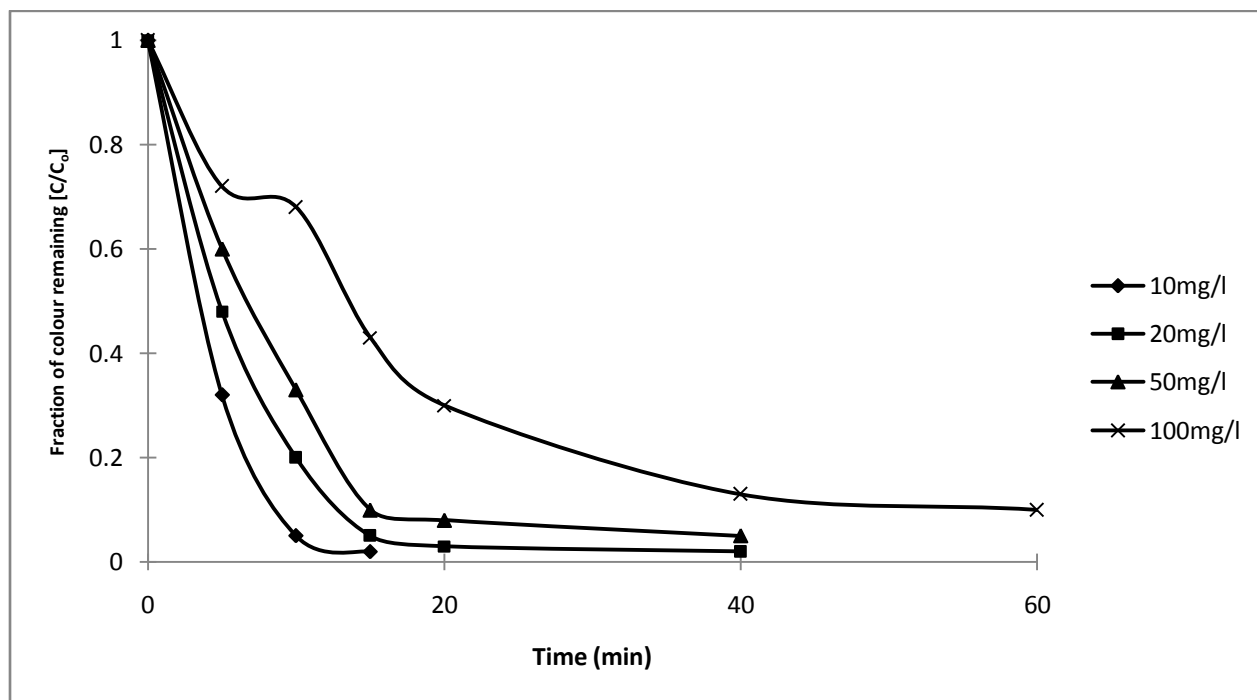


Fig. 8: The effect of dye concentration on photocatalytic degradation of D1

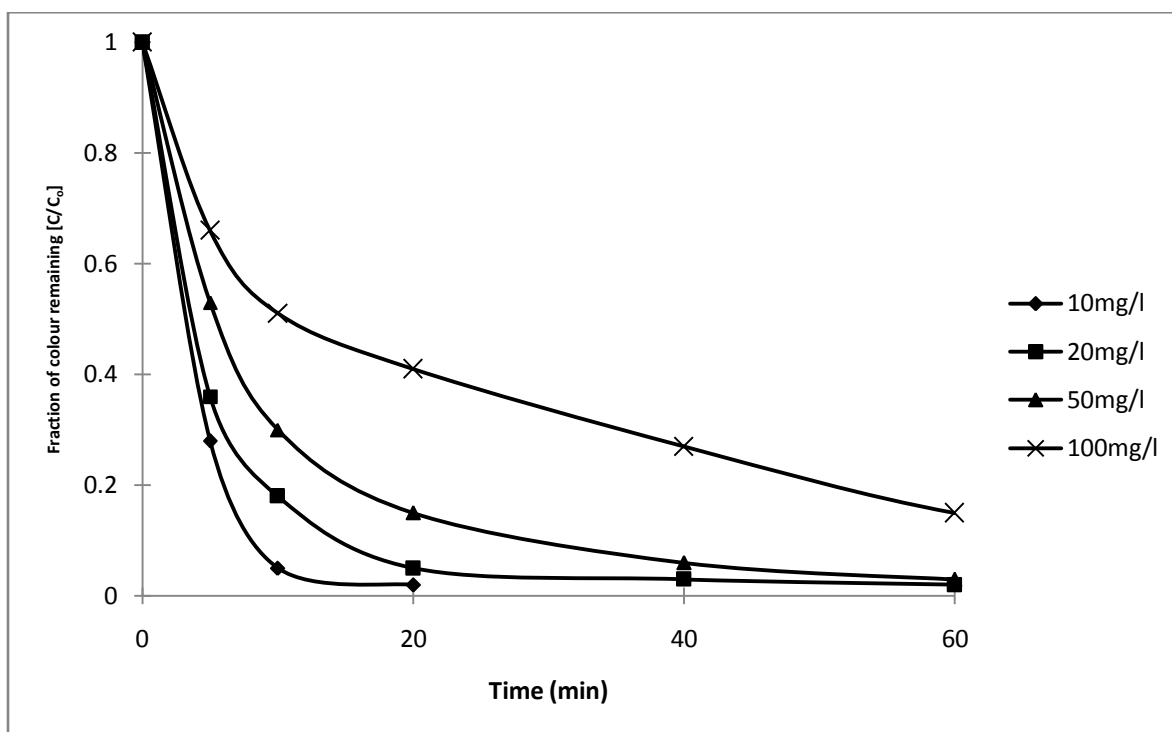


Fig. 9: The effect of dye concentration on photocatalytic degradation of D2

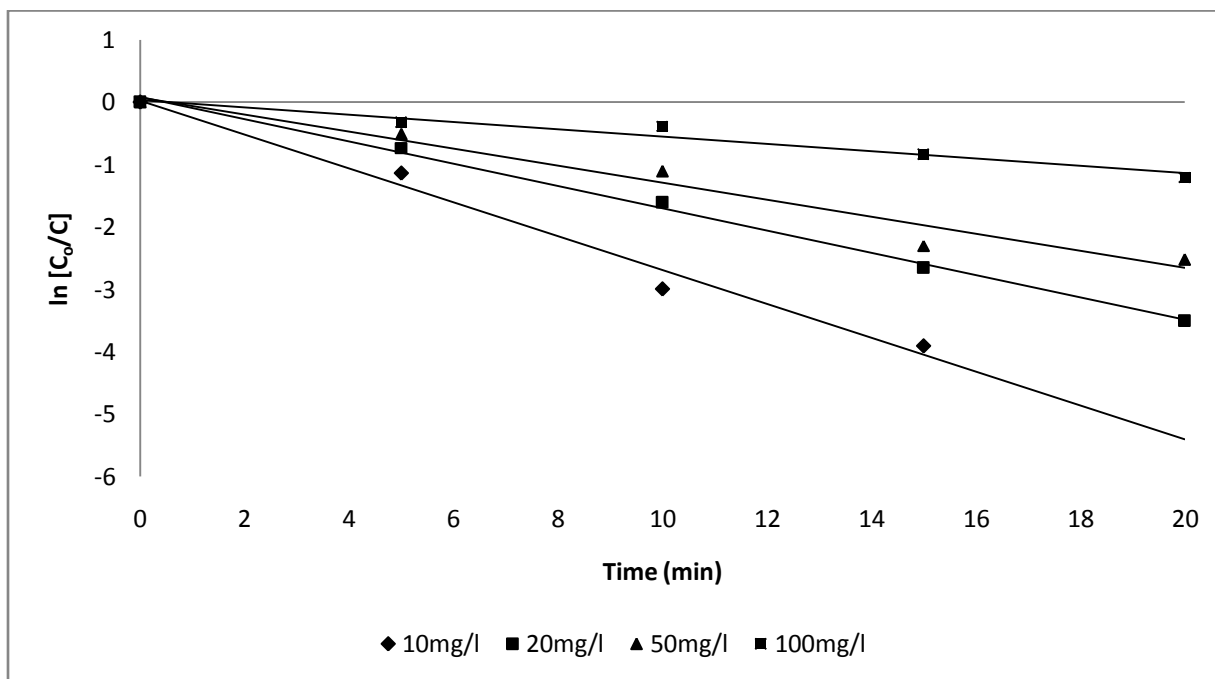


Fig. 10: Kinetics of dye 1 (D1) decolorization for different concentrations

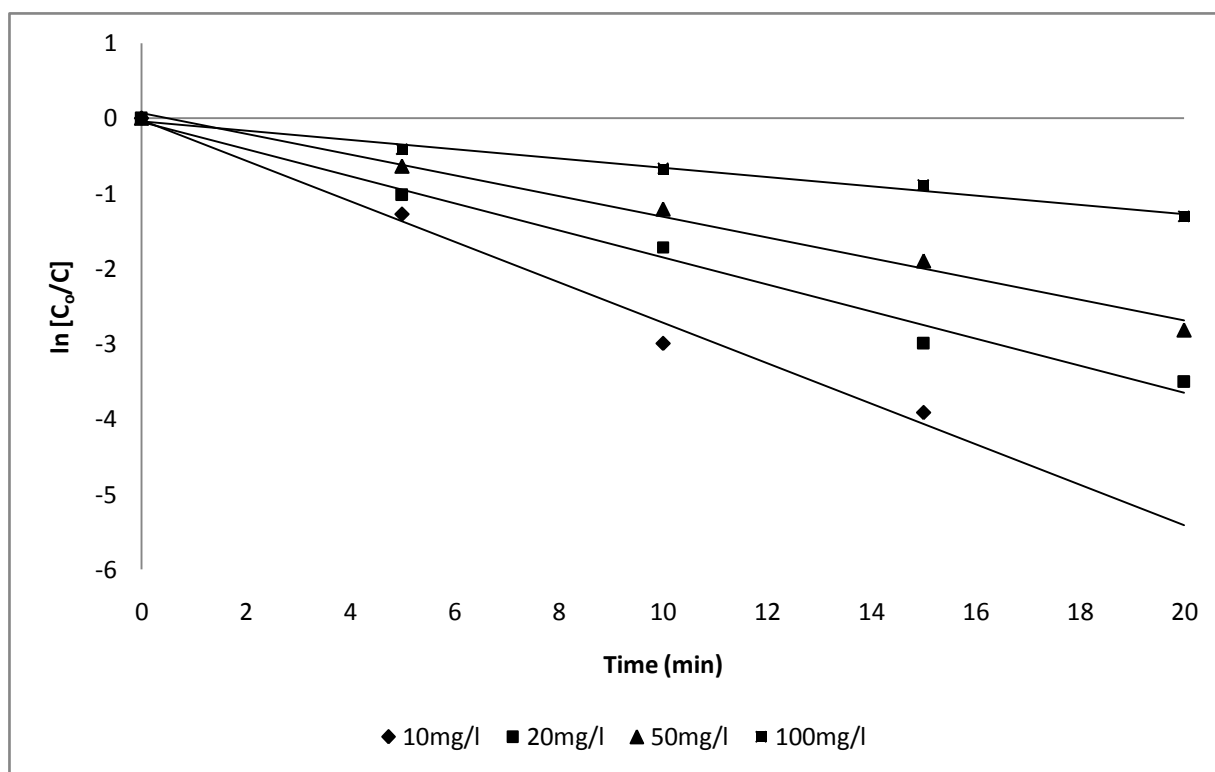


Fig. 11: Kinetics of dye 2 (D2) decolorization for different concentrations

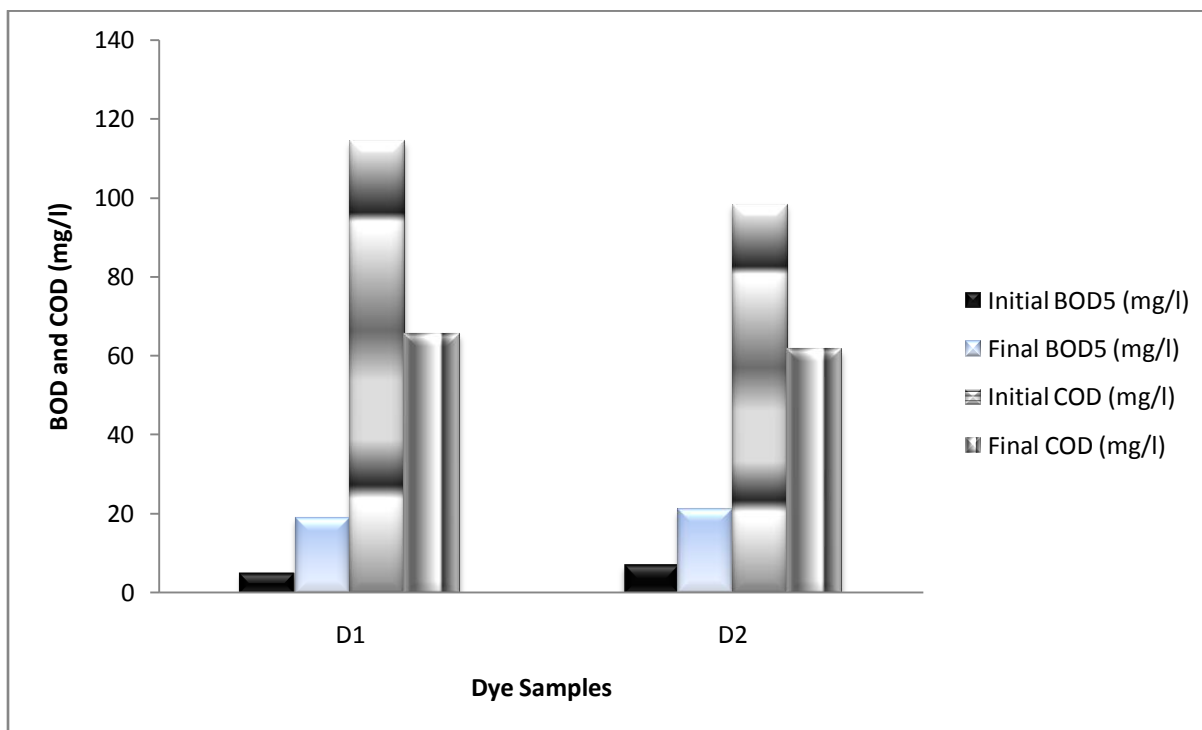


Fig. 12: Variation of BOD and COD during photodegradation [Dyes = 50 mg/l, TiO_2 = 1 g/l, light intensity (average) = 95000 lux, duration = 6 h]