



Photocatalytic Degradation of Commercial Textile Dye in Aqueous Buffer Solution using Anatase Titania

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ABSTRACT

Textile dyes present in waste water requires remover due to their hazardous and negative impacts on the environment. In this paper, the photocatalytic degradation of Vat Green 8 on anatase titania at a buffer pH of 7, 8 and 9 had been investigated. The effect of various operational parameters such as catalyst loading, pH, and initial dye concentration and irradiation time of the photocatalytic degradation was studied on a laboratory scale photoreactor containing 100 W mercury bulb. Varying concentrations of the dye solution such as 5 mg/l, 12.5 mg/l and 20 mg/l was prepared and ran in the photoreactor and the dye removal was monitored using UV-Vis spectrophotometer. The results obtained revealed that much of the dyes were removed at an optimum pH of 9 and catalyst dose of 1 mg/l. The percentage efficiency of the colour remover reached a maximum of 99% at dye concentration of 12.5 mg/l and irradiation time of 90 minutes.

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INTRODUCTION

Textile industry is one of the top industries that consumes large volume of water and at the same time generate large amount of wastewater in the form of effluents. These effluents are heavily coloured and contains an amalgam of different dyes, surfactants and additives most of which are biorecalcitrant thus constituting threat to human life and that of the aquatics [1, 2]. It became very imperative to ensure the treatment of this effluents before discharge into water bodies as the influx of the untreated wastewater not only introduces aesthetic concerns, but far more importantly, it promotes eutrophication which adversely affects the environmental health of the region by reducing light penetration which affects aquatic life and limit utilization of the water media [3]. Industrial development and its association with discharge of organic matter into the aquatic systems demands the technological development to solve the environmental problems related to organic effluents [4]. Many practices have been widely applied in the treatment of organic effluent

such as biological treatment, reverse osmosis, ozonation, and filtration, adsorption on solid phases, incineration and coagulation [5]. However, the effluent treated by these techniques alone is not recyclable and require further treatment thus indicating the limitation of the process.

In recent era, advanced oxidation processes (AOPs) have been found as an effective and alternative way for the treatment of organic effluent in aqueous system [6, 7, 8]. The recent research demonstrates that AOPs based on photocatalyst are valuable and this method ensures complete mineralization of organic molecules into nontoxic CO₂ and H₂O at the atmospheric conditions [9, 10, 11, 12]. Further, AOPs result in the generation of hydroxyl radicals (-OH) as main oxidizing agents which can remove even non biodegradable organic compounds from wastewater stream [13, 14]. Photocatalytic degradation of organic effluent emerged as one of the best methodologies for the treatment of toxic organic effluents which uses the semiconductor as catalyst such TiO₂,

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ZnO, ZnS, WO₃, CdS and Fe₂O₃, and SrTiO₃ [15, 16, 17, 18]. Amongst the semi-conductor catalyst, TiO₂ and ZnO have been widely applied as photocatalyst due to their high activity, nontoxicity, chemical stability, lower costs, optical and electrical properties and environment friendly characteristics [19, 20, 21, 22, 23].

This paper represents the photocatalytic degradation of Vat Green 8 in the presence of Anatase titanium dioxide using aqueous buffer solution. The influence of various operational parameters such as the initial concentration of the dye, initial pH, catalyst loading and irradiation time was evaluated and the photocatalytic efficiency was examined.

MATERIALS AND METHODS

Materials

Reagents: Vat Green 8 was purchase from Zigma Aldrich. TiO₂-P25 Anatase with surface area 50 ± 10 m² g⁻¹ and average size = 21 nm was purchased from Degussa Company. All other chemicals used in the study were of analytical grade and were bought from Sigma Aldrich. Double distilled water was used in the preparation of the buffer solution corresponding to the various pH and in preparing the dye solution after dissolution of the dye in dimethyl formamide (DMF).

Apparatus: A laboratory scale Photoreactor equipped with 100 W mercury bulb was used for the photodegradation. UV-visible spectrophotometer of model number Jenway-6305, was used for spectral monitoring and analyses of dye concentrations. A Whatman filter

was used for separation of photocatalyst from solution while digital pH meter, Jenway-3505 model was applied for controlling of buffer solution pH.

Methods

A 0.1g of the dye was dissolved in 100 ml DMF to serve as stock solution of the dye. Varying concentration of the dye (5 mg/L, 12.5 mg/L and 20 mg/L) were then prepared from the stock solution using the aqueous buffer solution of varying pH. The photocatalyst was then added in different amount between 0 - 2 g/L after which it was kept in the dark for 15 minutes to establish equilibrium between adsorption and desorption. The dye solution containing the photocatalyst was then irradiated inside the photoreactor over a period of time specified by the experimental design after which an aliquot was taken and filtered in order to separate the dye solution from the photocatalyst. The absorbance value of the photolyte was determined using UV-Vis spectrophotometer. In each run, the percentage photo-degradation was calculated using the expression;

$$(\%) \text{ Photocatalytic degradation} = \frac{C_0 - C_t}{C_0} \times 100$$

Where C₀ and C_t represents the concentration before irradiation and concentration at any time of irradiation respectively. A Box Beckhen design of experiment was used in generating the experimental runs as shown in Table 1.

Table 1: Design of experiment for Vat Green 8

Run Order	Concentration (mg/L)	Catalyst Loading (g/L)	pH	Time (min.)	Degradation %
1	5.0	2	9	45	74.42
2	12.5	1	8	0	0
3	12.5	0	9	0	0
4	20.0	1	8	45	58.58
5	12.5	2	9	90	76.73
6	5.0	1	8	45	84.92
7	12.5	1	9	45	97.38
8	20.0	1	9	0	0



Run Order	Concentration (mg/L)	Catalyst Loading (g/L)	pH	Time (min.)	Degradation %
9	12.5	2	9	0	0
10	12.5	2	8	45	86.84
11	12.5	1	9	45	97.38
12	5.0	1	9	0	0
13	12.5	0	8	45	11.23
14	5.0	0	9	45	04.36
15	12.5	2	10	45	66.72
16	5.0	0	8	45	03.13
17	5.0	1	9	90	92.04
18	12.5	1	9	90	99.58
19	12.5	0	9	90	41.22
20	12.5	1	9	45	97.38
21	12.5	0	10	45	05.48
22	20.0	1	10	45	59.06
23	20.0	2	9	45	68.16
24	12.5	1	8	90	87.45
25	12.5	1	10	0	0
26	20.0	1	9	90	79.12
27	5.0	1	10	45	74.63

RESULTS AND DISCUSSION

Calibration Curves for the Standard Solutions

The standard solutions of the dye at pH of 7, 8 and 9 were prepared and the absorbance

vs. concentration at λ_{max} was plotted. The curve is linear and in agreement with the Lambert–Beer law as shown in Figure 1.

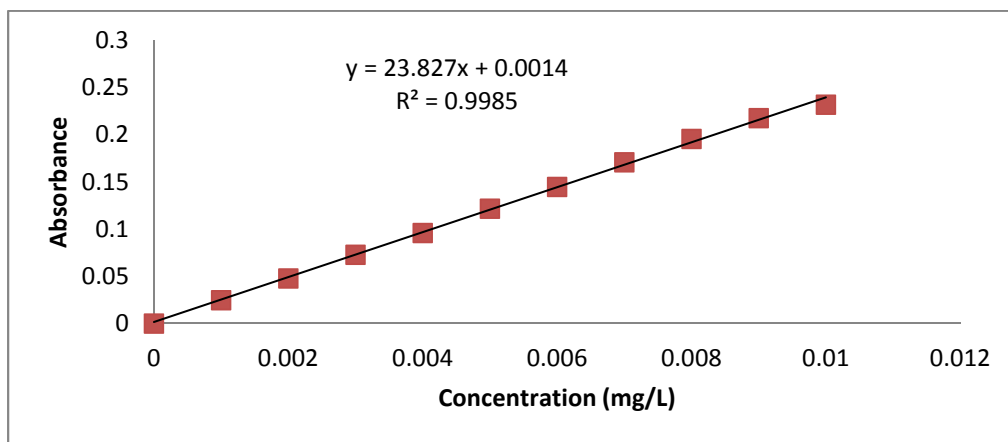


Figure 1: Calibration curve of Vat Green 8

The dye sample was dissolved in DMF so as to improve intermolecular solute-solvent interaction force which enhances the dye solubility significantly. To ensure validity of Beer-

Lambert's law, a set of 10 different calibration solutions were prepared. These dye concentration were chosen since the solution for testing absorbance correlation are best kept in

the absorbance range of 0.2 – 1.5. This procedure is similar to the one used by other researcher [42, 43].

Effect of pH

The influence pH on dye degradation cannot be over emphasized as it does not only determine chemical properties of the photocatalyst, but also influences adsorption behavior of the pollutants [35, 36]. It plays an important role in the photocatalytic reaction on the catalyst surfaces, where it affects the surface charge properties of the photocatalyst and the oxidation potential of the valence band [37]. The effect of pH on degradation of textile effluent containing Vat Green 8 was studied at varying

pH of 7, 8 and 9. The results obtained as shown in Figure 2 indicates that increasing the pH of the dye solutions leads to increasing degradation and adsorption. The possible reason for this behavior is that alkaline pH range favours the formation of more OH^\ominus due to the presence of large quantity of OH^\ominus ions [38]. Further increase in pH beyond the optimum value of 9 for Vat Green 8 results in decrease in the rate of degradation and this could be as a result of columbic repulsion between the negatively charged surface of the photocatalyst and the hydroxide anions [39]. This could prevent the formation of the hydroxyl radicals which in turn reduces the rate of degradation.

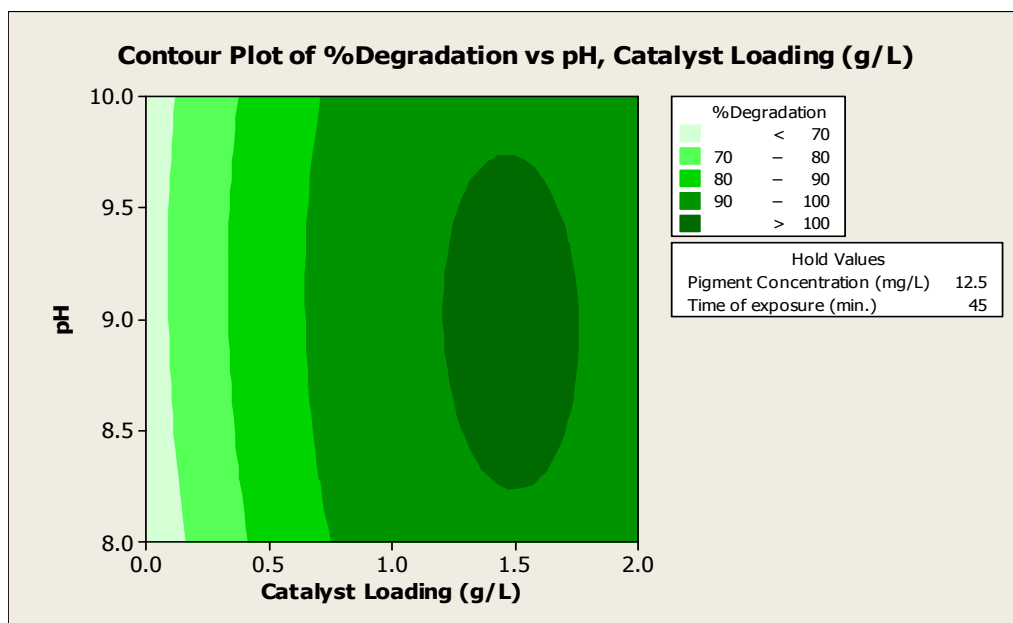


Figure 2: Contour Plot of %Degradation vs pH, Catalyst Loading (g/L)

Effect of Initial Dye Concentration:

The effect of various dye concentrations on photocatalytic degradation has been investigated from 5 mg/L – 20 mg/L. The results shown in Table 1 and Figure 3 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 [40]. The possible explanation for the decrease in removal rate is that as the initial concentration of the dye increases, the path

length of the photons entering the solution decreases. Furthermore, when the dye concentration increases, the amount of dye adsorbed per molecule of the catalyst increases. This affects the active sites of the catalyst and thereby decreases the efficiency of the catalyst. Moreover, at high dye concentration, a significant amount of radiation may be absorbed by the dye molecules rather than the catalyst and this may also reduce the efficiency of the catalyst.

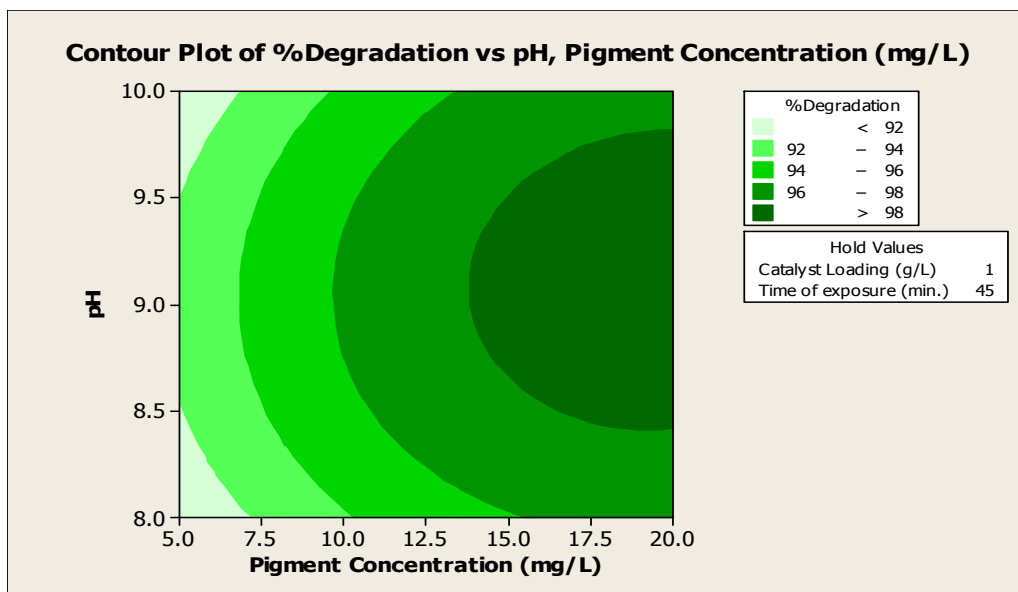


Figure 3: Contour Plot of %Degradation vs pH, Pigment Concentration (mg/L)

Effect of Irradiation Time

The effect of irradiation time on photocatalytic degradation of textile wastewater containing Vat Green 8 is shown in Figure 4. The experiments were carried out at varying concentration and catalyst loading. The initial rate of the reaction was found to be very fast and thereafter was found to decline. At the beginning, generation of OH° was very fast and a large

number of vacant surface sites were available for adsorption. After a known period of time, the remaining sites were hardly occupied due to the repulsive forces between the molecules on the surface and in the bulk phase and this is in agreement with the findings of [41]. The formation of intermediates which compete with the parent molecules decreases the reaction rate on the long run.

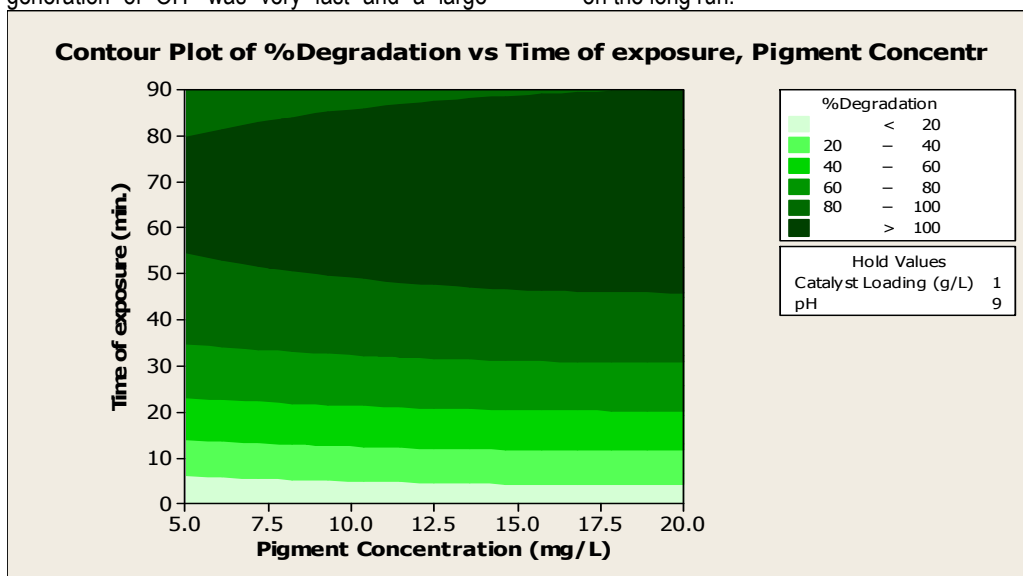


Figure 4: Contour Plot of %Degradation vs Time of exposure (min.), Catalyst Loading (g/L)

Effects of Catalyst Loading:

The effect of catalyst loading on the degradation of the dye solution had been investigated using different concentrations of TiO₂ varying from 0 to 2 g/L and the results are presented in Figure 1. From the results obtained, it was observed that dye degradation increases as the catalyst loading increases up to certain level beyond which no degradation was noticed. This is in conformity with the findings of other researchers [24, 23, and 25]. The increase in degradation as a result increase in photocatalyst amount can be attributed to increase in hydroxyl radical generated from the irradiated photocatalyst [26, 27]. At lower catalyst loading, degradation of organic molecule is low, because

more light is transmitted through the reactor and lesser transmitted radiation only will be utilized in the photocatalytic reaction [28, 29]. But beyond the optimum amount of photocatalyst, the degradation rate might be reduced due to increase in the opacity of the suspension, and thus increasing the light scattering and also the infiltration depth of the photons is diminished and less photocatalyst could be activated [30, 31, 32]. In addition to what is mentioned above, agglomeration of nanoparticles at high concentration could result to decline in the number of surface active sites available for the photocatalytic degradation [33, 34].

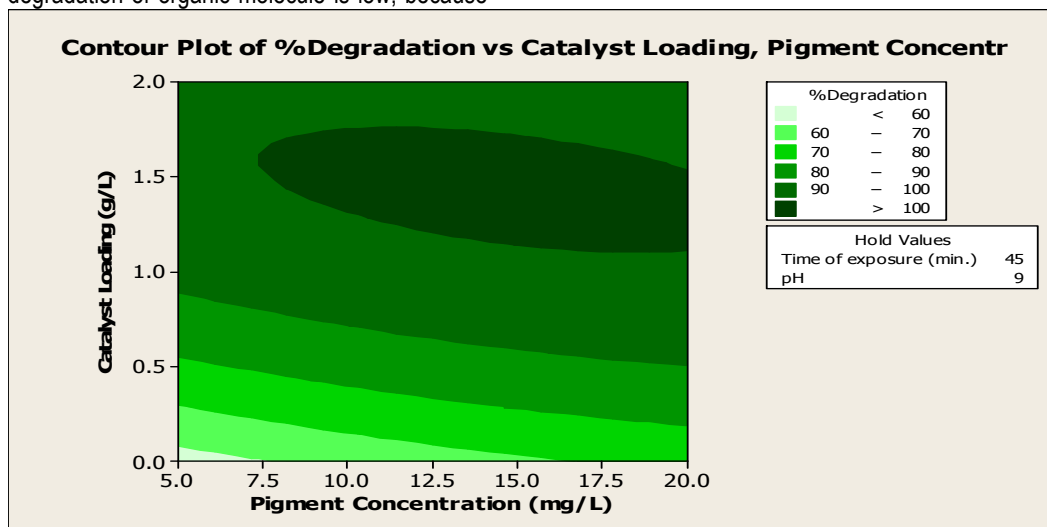


Figure 5: Contour Plot of %Degradation vs Catalyst Loading (g/L), Pigment Concentration (mg/L).

CONCLUSION

The photocatalytic degradation of Vat Green 8 was examined using Anatase TiO₂ catalyst under visible light. Some operational parameters such as irradiation time, pH of solution, catalyst loading and initial dye concentration were studied for their influence on the efficiency of the photocatalytic process. 1 g/l catalyst dosage, 25 mg/l concentration and pH of 9 were found to be the optimal conditions of the experiment. Hence, heterogeneous photocatalysis was proved to be an attractive method of removing pollutants from industrial wastewaters.

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