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Photocatalytic degradation of Direct Yellow 12 dye using UV/TiO_2 in a shallow pond slurry reactor

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Abstract

The adsorption and photocatalytic degradation of diazo Direct Yellow 12 (Chrysophenine G), commonly used as a cotton, paper and leather dye has been investigated in aqueous suspension of semiconductor oxide TiO_2 as photocatalyst in a non-concentrating shallow pond slurry type reactor under UV light. The adsorption of dye on the semiconductor shows a strong dependence on the pH and follows a Langmuir adsorption model. The studies include dark adsorption experiments at different pH conditions and their effect on initial rate of photodegradation. The effect of initial concentration of dye, catalyst loading, pH, addition of oxidant on the reaction rate was ascertained and optimum conditions for maximum degradation was determined. The disappearance of the organic molecule follows approximately a pseudo-first kinetic order according to the Langmuir–Hinshelwood model. COD analysis of the dye under optimum conditions showed 94% reduction in COD after 2.5 h and complete decolourisation as determined by UV–vis analysis was achieved in 1.5 h.

Keywords: Direct Yellow 12 dye; Adsorption; Photodegradation; UV/TiO_2; Shallow pond photoreactor

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1. Introduction

Synthetic dyes are extensively used for dyeing and printing in textile industries. Over 10,000 dyes with an annual production over 7×10^5 metric tonnes worldwide are commercially available and about 50% among them are azo dyes [1]. It is estimated that approximately 15% of the dyestuffs are lost in the industrial effluents during manufacturing and processing operations [2]. Synthetic dyes, classified by their chromophores, have different and stable chemical structures to meet various colouring requirements. The release of these coloured wastewaters in the ecosystem causes aesthetic pollution, eutrophication and perturbations in aquatic life [3].

Color is usually the first contaminant to be recognized in wastewater. Many azo dyes may be decomposed into potential carcinogenic amines under anaerobic conditions in the environment [4]. Color removal from wastewater is often more important than the removal of soluble colourless organic substances, a major fraction of which contributes to the COD and BOD, besides disturbing the ecological system of the receiving waters.

The traditional techniques used for colour removal are activated carbon (charcoal), filtration and coagulation. Each method has few advantages and disadvantages. For example, the use of charcoal is technically easy but has high waste disposal cost. Coagulation using alums, ferric salts or limes is a low cost process, but all these methods have a major disadvantage of simply transferring the pollutants from one phase to another phase rather than destroying them. Biological treatment is a proven method and cost effective. However, it has

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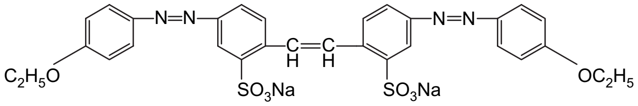
been reported that majority of dyes are only adsorbed on the sludge and not degraded, due to the biorecalcitrant nature of these dyes molecules [5,6].

There are a number of advanced oxidation processes currently being evaluated for the destruction of dyes in effluents. Among these heterogenous photocatalysis [7] in the presence of irradiated semiconductor oxides like TiO_2, ZnO and CdS have been successfully used to decolourize and mineralize many organic pollutants including several dyes and their intermediates present in aqueous systems using both artificial light and under sunlight using solar technology [8–12].

In solar photocatalytic systems, concentrating and non-concentrating photoreactors have been used. A disadvantage with concentrating reactors is that they cannot concentrate the diffused solar radiations and use only the direct component of the UV radiations, while the non-concentrating photoreactors use both the direct and diffused components of the UV radiation. The solar photocatalytic oxidation with TiO_2 as a catalyst uses only UV portion of the solar radiation, which forms about 4–6% of the total spectrum. At locations with high humidity and during cloudy or partly cloudy periods as much as 50% or more of the UV radiation can be in diffuse form [13]. Moreover, the prohibitive cost associated with solar concentrators limit their usefulness for industrial applications. Non-concentrating reactors have the potential to be simple in design and low in cost. A number of different designs of non-concentrating solar reactors have been proposed which includes trickle down flat plate [14], tubular flat plate [15], pressurized flat plate [16] and shallow solar ponds [17]. Industries which generate large amount of effluent per day already use ponds for the microbiological treatment of wastewater and similar shallow solar ponds can be used for the front or back end of a combined solar/microbiological treatment of wastewater.



Chrysophenine G

This work presents a detailed study of the adsorption and photocatalytic degradation of Direct Yellow 12 (Chrysophenine G), a diazo dye widely used as a cotton dye and also in leather and paper industry, due its stability towards alkalies being an ethylated product. Studies in the degradation of this class of dyes are limited although a lot of work in the degradation of acid dyes is reported in literature [5,18–21]. Previously degradation of this dye has been studied using UV/H_2O_2/Fe^{2+} [22] and UV/H_2O_2 [23]. These homogenous photocatalytic processes are effective, however, they use large quantity of reagents and thus their application to industrial effluents is limited. We have therefore, undertaken to investigate the dye-sensitized degradation using TiO_2 under artificial source of UV light in a shallow pond slurry reactor at laboratory scale. Effect of parameters such as UV intensity, pH, initial concentration, oxidants, aperture to volume ratio and catalyst loading on reaction kinetics were studied to optimize the process for maximum degradation.

2. Experimental

2.1. Reagents and chemicals

The photocatalyst used in all the experiments was anatase form of titanium dioxide powder (Degussa P25 TiO_2 procured from Degussa Company, Germany having a BET surface area of $50 \pm 15\ m^2\ g^{-1}$ with average particle size of 30 nm). Direct Yellow 12 dye (98% purity) used for making coloured paper was obtained from Ballarpur Industries Ltd, paper and pulp mill, Hyderabad, India. All chemicals were used as received. In all the experiments doubly distilled water was used for preparation of stock solution.

2.2. Photoreactor

A diagrammatic representation of the experimental set up of artificial light irradiated shallow pond slurry reactor is shown in Fig. 1. The setup consist of a UV chamber made up of galvinized aluminium sheet having dimensions of 4 in. × 2.5 in. × 2.5 in. consisting of 8× 40 W UV black fluorescent lamps (Philips), fitted in parallel on the top of the chamber. An exhaust fan is fitted on the sidewall of the chamber to maintain a constant temperature. The reactor used is cylindrical in shape and made of borosil glass, which has a diameter

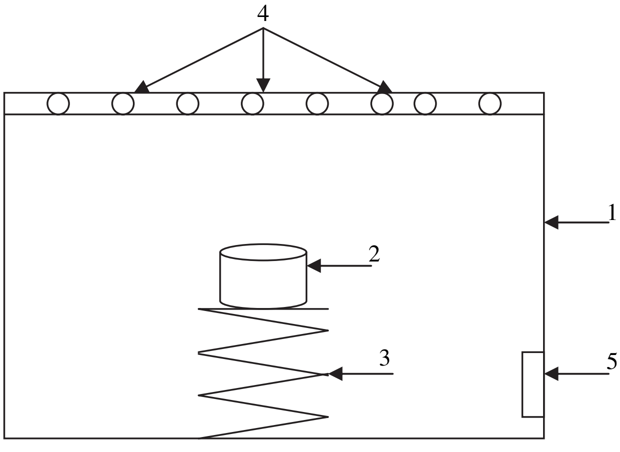


Fig. 1. Schematic diagram of lab scale set up: (1) UV chamber, (2) reactor, (3) Lab jack, (4) UV lamps, (5) exhaust fan.

of 5 cm and is 6 cm in height with a capacity of approximately 1000 ml. The reactor is placed on a lab jack so that required intensity could be attained by adjusting the distance of the reactor from the UV tubes. The UV intensity in the reactor can be varied from 25 to 50 W m^{-2} corresponding to the average intensity of UV radiation in sunlight [24]. The process is carried out in open atmosphere and oxygen purging is done from time to time.

2.3. Analysis

For the determination of concentration of dye, Hitachi U-2001 UV–Vis spectrophotometer was used. Eppley (model no. 33013) radiometer was used for measuring the UV intensity. The pH of the solution was varied by adding HCl or NaOH solution as per requirement and measured using ELICO, India LI 120-pH meter. COD analysis was done by the standard acid dichromate method [25].

2.3.1. Adsorption experiments in dark – TiO_2 suspensions

The adsorption tests were performed using 200 ml aqueous solution of dye at different concentrations and at different pH values put in contact with 2.0 gm l^{-1} of TiO_2 for 3 h, at 25 °C till equilibrium is attained. The adsorption of dye was monitored by filtering the solution through Millipore filter (0.45 μm) membrane. The amount of dye adsorbed was determined by mass balance.

2.3.2. Photocatalytic experiments – TiO_2 suspensions

Stock solution of dye at different concentration was prepared in distilled water with natural pH 6.8 and mixed with TiO_2 used as photocatalyst and dispersed in a batch of 200 ml aqueous suspension in the photoreactor as shown in Fig. 1. An aliquot of 5 ml was taken from the reactor at regular interval of time. The catalyst was filtered from the solution by Millipore filter (0.45 μm) and the filtrate was analyzed for determing concentration of dye at λ_{max} of 395.2 nm and COD changes were also monitored.

The reaction kinetics was studied by varying different parameters like UV intensity, initial pH of the solution, addition of oxidant, aperture to volume ratio (A/V ratio), catalyst loading and initial concentration of the dye. Except for the study on the effect of intensity, effects of all the other parameters were studied at UV intensity of 35 Wm^{-2}. The optimum catalyst loading was 2.0 g l^{-1} for studying all parameters in the same shallow pond type reactor with stirring and purging of the oxygen from time to time. All experiments were carried out in triplicate for reproducibility of results.

3. Results and discussion

3.1. Equilibrium of adsorption in dark conditions

Adsorption tests in dark conditions were carried out in order to study the adsorption of dye on the TiO_2 surface at different pH and different initial concentrations and to calculate the equilibrium constants. All isotherms showed a type of L-shape as shown in Fig. 2. The equilibrium constants were determined by fitting the experimental data to the Langmuir equation (Eq. (1)) to describe the adsorption of the dye on the homogeneous surface of TiO_2:

$$q_e = (q_m b C_e)/1 + bC_e \qquad (1)$$

where q_m is the maximum amount of dye adsorbed forming a complete monolayer, b the equilibrium parameter, C_e the concentration of dye in aqueous solution, and q_e the concentration of dye in the solid. The Langmuir equilibrium constants ($K_a = q_m b$) are shown in Table 1. According to the classification of Giles et al. [26] the L-shape of the isotherms means that there is no strong competition between the solvent and the adsorbate to occupy the adsorbent surface sites.

It is observed that the yellow azo dye adsorbs in acidic media (pH < 6.8) and negligible adsorption is observed in the alkaline media (pH > 7.0). This can be explained because the point of zero charge of the TiO_2 is at pH 6.8. The TiO_2 surface is positively charged in acid media (pH < 6.8), whereas it is negatively charged under alkaline conditions (pH > 6.8) [6]. At pH greater than 6.8 the solid surface is negatively charged, and the anionic yellow dye is repulsed and so it is scarcely

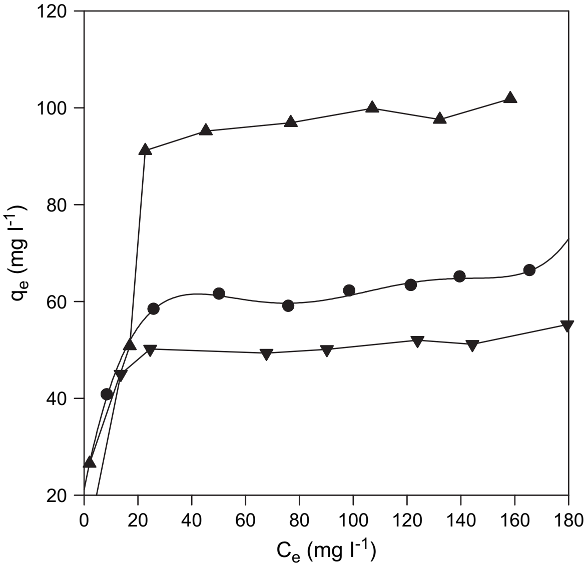


Fig. 2. Adsorption isotherms of dye on TiO_2 surface at different pH; ▲ = pH 4.5, ● = pH 6.8, ▼, = pH 8.

Table 1
Langmuir equilibrium constants for the adsorption of Direct Yellow dye on TiO_2 in dark

pH	K_a(g l^{-1})
4.5	1.75
6.8	0.529
8	0.1538
11	None

adsorbed. Further the relationship between photodegradation and adsorption is illustrated by studying the initial rate of degradation at different pH of the slurry as shown in Fig. 3.

With increase in pH, the initial rate of degradation and adsorption decrease while both increase with decrease in pH, indicating that pH is an important factor significantly affecting adsorption and the corresponding initial rate of degradation. Due to the electrostatic effects, the anionic dye adsorbs on the positively charged surface of the catalyst at lower pH i.e. in the acidic medium and is maximum at pH 4.5. This observation confirms the correlation between adsorption and initial rate of degradation, which is directly related and further, indicates that the degradation is a surface phenomenon.

3.2. Dye degradation and decolourisation – TiO_2 suspensions

The time dependent electronic absorption spectrum of Direct Yellow 12 dye during photoirradiation is presented in Fig. 4. Gradually after 1.5 h of irradiation time under UV light in a TiO_2 aqueous suspension the dye disappears and decolourisation of solution is observed. Besides no new bands appear in the UV–vis region due to the reaction intermediates formed during the degradation process. In parallel, the same experiments were carried out in dark in the presence of TiO_2 and in the absence of TiO_2 by UV illumination revealing in both cases no observable loss of dye molecules.

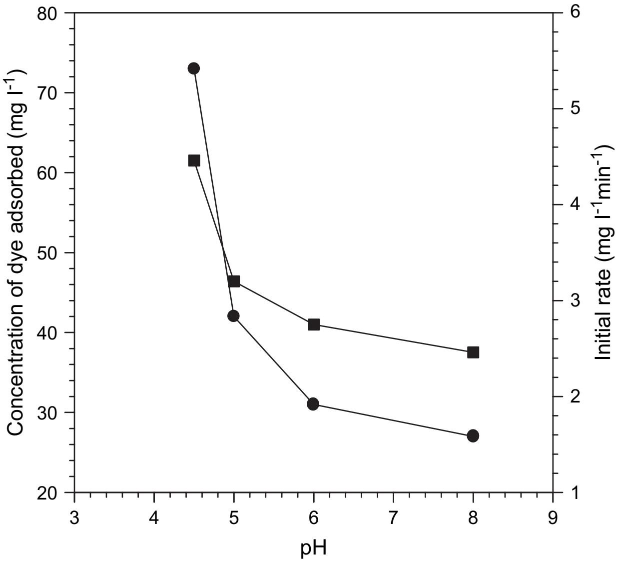


Fig. 3. Dependence of concentration of dye adsorbed (ppm) and initial degradation rate for yellow dye on pH of the solution using $[TiO_2] = 2.0$ g l^{-1}; ● = adsorption, ■ = initial rate.

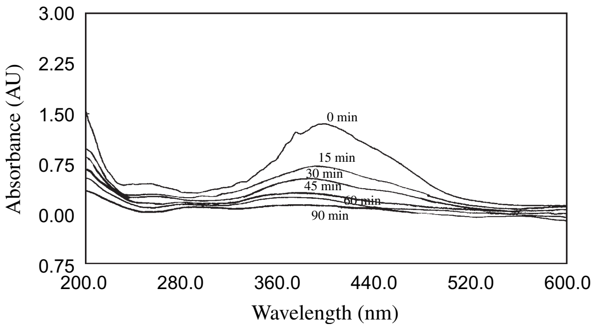


Fig. 4. Spectral changes that occur during the photocatalytic degradation of aqueous solution of Direct Yellow dye: pH = 4.5; $[TiO_2] = 2.0$ g l^{-1}; $C_0 = 100$ ppm.

It is well documented that the absorption of photons of possessing energy equal to or higher than that of the semiconductor (3.2 eV for TiO_2), causes charge separation:

$$TiO_2 + h\nu \rightarrow TiO_2\,(e^-) + TiO_2\,(h^+) \qquad (2)$$

The photogenerated holes may then react with adsorbed dye and oxidize the dye molecule by the formation of hydroxyl radicals. The photo-produced electrons in the conduction band react with the adsorbed oxygen to produce reactive radicals to yield the reactive oxygen species.

Chemical oxygen demand (COD) reflects the degree to which the degradation or mineralization of an organic species has occurred. For studying the degradation process, the percentage change in COD was studied for the dye sample having initial concentration of 100 ppm and catalyst loading 2.0 g l^{-1} as a function of irradiation time. Only small COD changes are evident within the first 60 min. However, an overall 94% reduction in COD is observed after 2.5 h as shown in Table 2. Change in COD further confirms the degradation leading to decrease in organic content.

3.2.1. Effect of catalyst loading

Experiments were performed to study the variations in the rate of degradation at different catalyst concentration ranging from 0.5 g l^{-1} to 3.5 g l^{-1} at constant UV intensity of 35 W m^{-2}, reactor with A/V ratio of 1.14 cm^2 ml^{-1}. It is observed that rate increases with increase in catalyst concentration and becomes constant above a certain level as shown in Table 3. The optimum catalyst concentration for degradation of Direct Yellow

Table 2
COD changes of Direct Yellow dye with irradiation time ($C_0 = 100$ ppm; pH = 4.5)

Irradiation time (min)	0	30	60	90	120	150
% COD removal	0	20	40	58	80	94

dye is 2.0 g l^{-1}. Our results are in good agreement with reported values in literature [27,28]. The reasons for this decrease in degradation rate are (i) aggregation of TiO_2 particles at high concentrations causing a decrease in the number of surface active sites and (ii) increase in opacity and light scattering of TiO_2 particles at high concentration leading to decrease in the passage of irradiation through the sample.

Galindo et al. [29] reported an empirical relationship between the initial decolourization rate and TiO_2 concentration, $r_0 \propto [TiO_2]^n[\text{dye}]$, where n is an exponent less than 1 for the dye studied [6]. In this work, the dependence of TiO_2 concentration on the initial decolourization rate follows a similar relationship ($r_0 \propto [TiO_2]^{0.657}$), when catalyst concentration is less than 2.0 g l^{-1} as calculated from Fig. 5.

3.2.2. Effect of initial concentration of dye

The effect of initial concentration of dye on the rate of degradation was studied by varying the initial dye concentration from 100 ppm to 500 ppm with constant intensity of 35 W m^{-2}, catalyst loading of 2.0 g l^{-1} as shown in Fig. 6. Hence, the photo-oxidation process is more suitable for low concentration of the pollutants. Our observations are in agreement with that reported by Rideh et al. [30], Chen and Ray [27] and Neppolian et al. [31] who have shown that photodegradation conversion of 2-chlorophenol, 4-nitrophenol and textile dye Reactive Red 2 decreases with increasing initial concentration. The rate of degradation relates to formation of OH radicals, which is the critical species in the degradation process. Hence an explanation to this behavior is that as initial concentration increases, more and more organic substances are adsorbed on the surface of TiO_2 but the intensity of light and illumination time are constant, so the path length of photons entering the solution decreases and in low concentration the reverse effect is observed and consequently the OH radicals formed on the surface of TiO_2 decreases, the relative number of OH radicals attacking the compound decreases and thus photodegradation efficiency decreases.

Table 3
Effect of TiO_2 load on the degradation rate during the photocatalytic oxidation (C_0 = 100 ppm; pH = 4.5)

$[TiO_2]$ (g l^{-1})	r_0 (mg l^{-1} min^{-1})
0.5	1.47
0.75	2.514
1.0	2.857
1.5	3.222
2.0	**3.819**
2.5	3.609
3.0	3.028
3.5	3.011

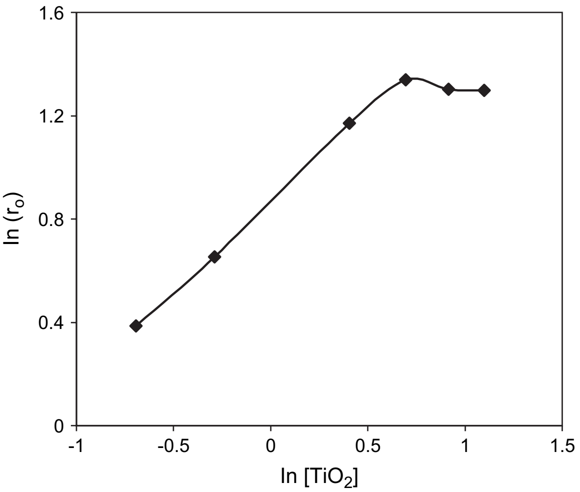


Fig. 5. Relationship between ln r_0 and the amount of TiO_2: pH = 4.5; C_0 = 100 ppm.

The influence of initial concentration of the solute on the photocatalytic degradation rate of most organic compounds is described by a pseudo- first-order kinetics, which is rationalized in terms of the Langmuir–Hinshelwood model Eq. (3), modified to accommodate reactions occurring at a solid–liquid interface. A linear expression can be obtained by plotting the reciprocal initial rate against the reciprocal initial concentration as shown in Fig. 7.

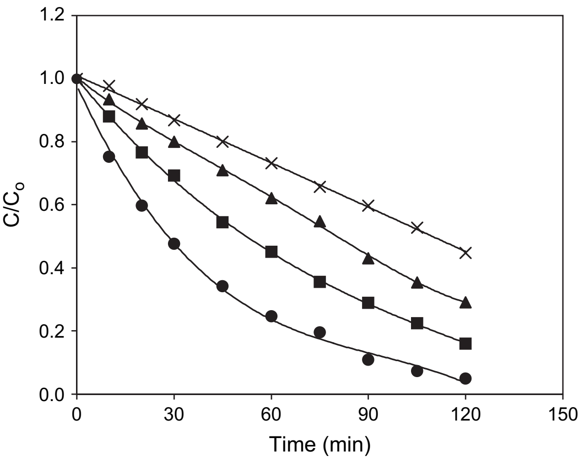


Fig. 6. Kinetics of photodegradation (λ_{max} = 395.2 nm) of dye at different initial concentrations: x = 500 ppm; ▲ = 300 ppm; ■ = 200 ppm; ● = 100 ppm.

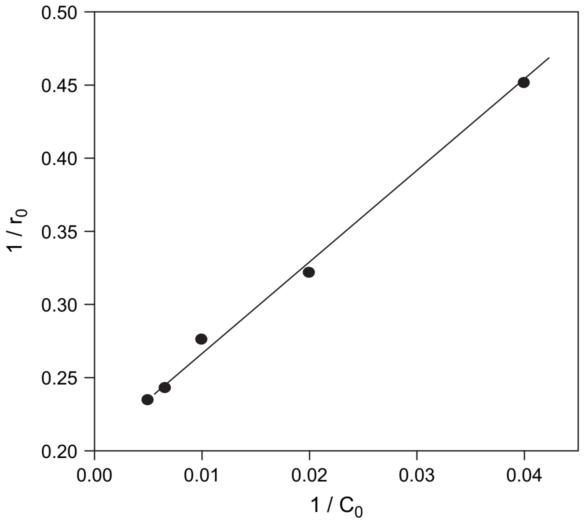


Fig. 7. Representation of Langmuir–Hinshelwood equation: pH = 4.5; $[TiO_2] = 2.0\ g\,l^{-1}$.

Now,

$$r_0 = -\mathrm{d}C/\mathrm{d}t = (k_v K_e C_0)/1 + K_e C_0 \tag{3}$$

where k_v reflects the limiting rate of the reaction at maximum coverage under the given experimental conditions. K_e represents the equilibrium constant for adsorption of dye on to illuminated TiO_2. In Eq. (3) k_v represents the apparent rate constant because it is also dependent on the source of UV light and the radiation field inside a photocatlytic reactor. The values of K_e and k_v are shown in Table 4.

3.2.3. *Effect of initial pH of the solution*

The wastewater from textile industries usually has a wide range of pH values. Further, the generation of hydroxyl radicals is also a function of pH. Thus pH plays an important role both in the characteristics of textile wastes and generation of hydroxyl radicals. Hence, attempts have been made to study the influence on the degradation of dye of initial pH in the range of 4.5–11 at different initial dye concentrations.

According to literature reports [6,32], the pH of the solution significantly affects TiO_2 activity, including the charge on the particles, the size of the aggregates it forms and the positions of the conductance and valence bands.

$$TiOH + H^+ \rightleftarrows TiOH_2^+ \tag{4}$$

$$TiOH + OH^- \rightleftarrows TiO^- \tag{5}$$

Three possible reaction mechanisms can contribute to dye degradation: hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conducting band depending on the nature of the substrate and pH [6].

Table 4
Langmuir–Hinshelwood constants for the photodegradation of Direct Yellow dye at different pH values

pH	K_e ($l\,mg^{-1}$)	k_v (min^{-1})
4.5	**0.005**	**18.18**
6.8	0.003	10.45
8.0	0.00075	8.524
11.0	0.00034	6.25

In our experiments, any change in the initial degradation rate with varying pH values must be ascribed to variations to the acid/base properties of the TiO_2 particle surface.

Results obtained from experiments with varying pH of dye solution from 4 to 11 are illustrated in Fig. 8.

In highly acidic medium, rate of degradation is high and decreases, as the pH of the solution is increased up to 11. The photo-oxidation process can therefore be carried out in acidic medium. These results are reflected by the k_v and K_e values of the Langmuir–Hinshelwood equation (Eq. (2)) and are given in Table 4.

3.2.4. *Effect of irradiation intensity*

The study of the effect of variation in light intensity has been done in the range of 25–50 $W\,m^{-2}$, which is close to the average light intensity of sunlight. As shown in Fig. 9, there is linear relationship between dye degradation and light intensity. It has been reported by Ollis et al. [33] that the kinetics of photocatalytic process at low light intensities shows a similar trend. The rate of degradation increases with increase in UV intensity as more radiations fall on the catalyst hence more OH radicals are produced which leads to high rate of degradation.

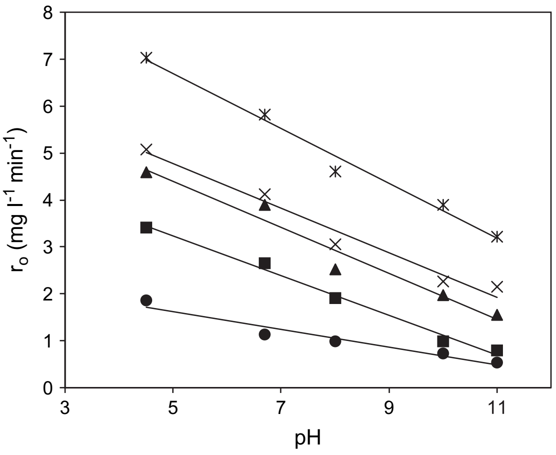


Fig. 8. Effect of the initial pH of the solution on the initial rate of degradation of the dye at different initial concentrations of solution: ⚹ = 200 ppm; × = 150 ppm; ▲ = 100 ppm; ■ = 50 ppm; ● = 25 ppm.

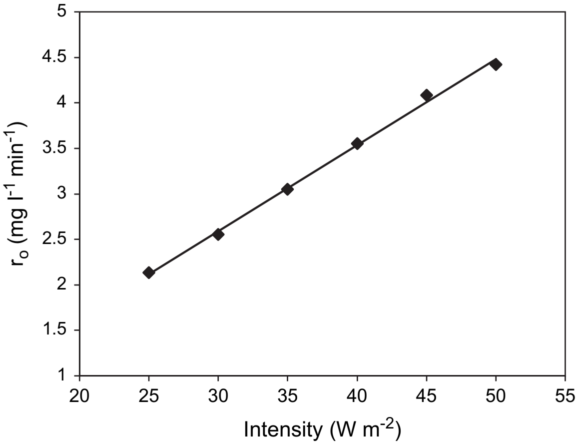


Fig. 9. Effect of light intensity on the rate of photodegradation: $C_0 = 100$ ppm; pH = 4.5; $[TiO_2] = 2.0$ g l^{-1}.

3.2.5. *Effect of A/V ratio*

If the surface area of the solution is increased the path length of photons entering the solution increases hence the formation of OH radical increases. Thus the rate of degradation increases as seen in Fig. 10. Surface area can be increased by either increasing the aperture and keeping volume constant or by keeping aperture constant and decreasing volume. Klausner and Goswami [34] have also reported that the rate of degradation of 4-chlorophenol in a shallow pond reactor depends on aperture to volume ratio (*A/V*) and it increases with increase in *A/V* ratio.

3.2.6. *Effect of added H_2O_2*

One possible way to increase the reaction rate would be to increase the concentration of $OH^{\cdot}$ radicals because these species are widely considered to be promoters of photocatalytic degradation. The addition of hydrogen peroxide to the heterogeneous system increases the concentration of OH radical, since it inhibits the electron–hole recombination, according to following equation:

$$TiO_2\,(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH^{\bullet} \quad (6)$$

Hydrogen peroxide is considered to have two functions in the process of photocatalytic degradation. It accepts a photogenerated electron from a conduction band and thus promotes the charge separation, and it also forms $OH^{\cdot}$ radical, according to Eq. (6).

However, at high concentration of H_2O_2, it also acts as a scavenger as shown in Eqs. (7) and (8):

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (7)$$

$$HO_2^{\bullet} + OH^{\bullet} \rightarrow H_2O + O_2 \quad (8)$$

The optimum H_2O_2 concentration for degradation of dye with initial concentration 100 ppm at pH of 4.5 is as shown in Fig. 11.

4. Conclusion

The results presented show that a TiO_2 assisted process in aqueous dispersions under UV irradiation, can easily degrade Direct Yellow 12, an anionic diazo dye. It is observed by adsorption studies that the adsorption of dye is a prerequisite for the degradation process. Both adsorption and photodegradation is maximum in acidic medium when the pH is 4.5. The photodegradation kinetics follows the Langmuir–Hinshelwood model and also depends on the TiO_2 concentration, pH, UV light intensity, *A/V* ratio and

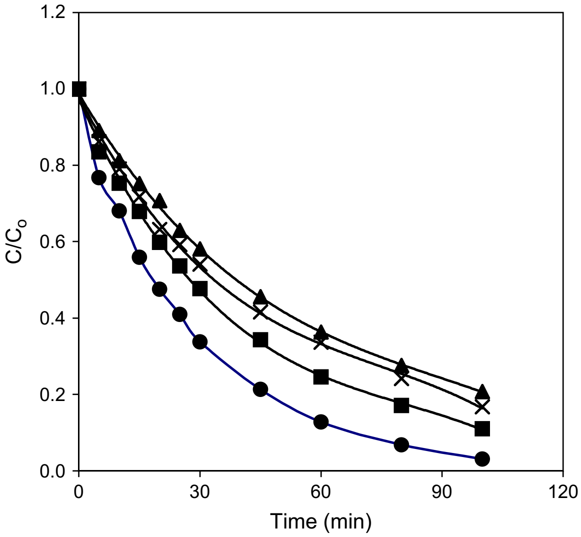


Fig. 10. Kinetics of photodegradation of dye for different *A/V* ratios: ● = 2.27 cm^2 ml^{-1}; ■ = 1.135 cm^2 ml^{-1}; × = 0.7567 cm^2 ml^{-1}; ▲ = 0.6958 cm^2 ml^{-1}.

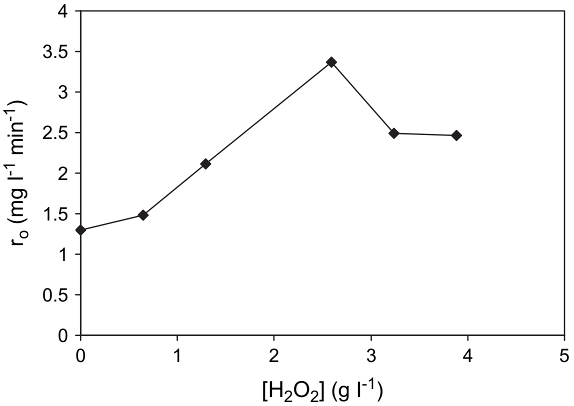


Fig. 11. Effect of H_2O_2 concentration on the initial rate at $C_0 = 100$ ppm; pH = 4.5; $[TiO_2] = 2.0$ g l^{-1}.

hydrogen peroxide concentration. The effect of these operational parameters on initial rate of degradation has been studied and the optimum conditions determined for effective degradation in a shallow pond slurry reactor. The only restriction is that the pond should be shallow as it is observed that more the aperture to volume ratio higher will be the degradation rates. This process has a potential to be used as integrated photocatalytic–biological treatment of biorecalcitrant dyes present in the effluent of various industries. This type of solar pond reactors is also suitable for industries that generates large amount of effluent per day as it is simple to design.

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