

Removal of Yellow Acid-36 Dye from Textile Industries Waste Water Using Photocatalytic Process (UV/TiO₂)

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Received: 13 August 2019/ **Accepted:** 28 September 2019/ **Published:** 31 September

Abstract: Textile industries are the major industries which mainly use different dyes. In these industries it is estimated that 15 % of dyes are lost in wastewater during manufacturing and dying process. In this study, the photocatalytic degradation of Yellow Acid-36 dye in the presence of UV irradiation intensity has been investigated. In this experiment TiO₂ P-25 was used as catalyst and coated on the marble surface. The influence of various operation parameters, such as the initial concentration of dye, pH, time of contact, catalyst dosage and UV irradiation intensity on the degradation process was examined. The results indicated that the optimal decolorization conditions were attained with 100 g m⁻² of catalyst at pH 3, an irradiation time of 105 min, UV irradiation intensity 30 W and 5 mg L⁻¹ initial concentration of dye. The process resulted in 97.6% degradation of Yellow Acid 36. It is revealed that this method was effective in degradation of Yellow Acid 36.

Keywords: Dye degradation, Titanium dioxide, Photocatalysis, Yellow Acid 36, Advanced process oxidation.

1. Introduction

Textile industries are the major industries which mainly use different dyes. In these industries it is estimated that 15 % of dyes are lost in wastewater during manufacturing and dying process. (Natarjan et al., 2013) Dyes can be used in various industries such as fabrics, leather, paper and cosmetics. They can be grouped in to different classes: acid, basic, direct, disperses, metallic, mordant, pigment, reactive, sulphur and vat. (Ajmal et al., 2014). Dyes can be classified in several ways; each class has a very unique chemistry, structure and particular way of bonding. The contamination in wastewater due to the dyes can be recognized quite easily as a very

small amount of dye in the water (<1ppm) are highly visible. They absorb and reflect the sunlight entering water thereby interfering with the aquatic species growth and hindering photosynthesis. Additionally, they can have acute and chronic effects on organisms depending on their concentration and length of exposure. Human consumption of water contaminated with these compounds can cause a variety of adverse health effects such as wide-ranging immune suppression breathing problems, central nervous system (CNS), disorders, breathing problems, behavioral problems, allergic reactions, tissue necrosis and infections of the skin and eyes. (Pan et al 2012). So the degradation of dyes from the



wastewater is the major concern to ward environmental pollution abatement. A large wide of technologies has been developed for the removal of dyes from waters and wastewaters to decrease their environmental impact. These methods can be classified in to four categories: 1) Physical 2) Chemical 3) Biological 4) Acoustical, Radiation and Electronic processes (Gupta and Suhas, 2009). Physical methods such as membrane-filtration processes (nonofiltration, reverse osmosis electro dialysis) and sorption techniques; chemical methods such as coagulation or flocculation combined with flotation and filtration, precipitation flocculation ,electro-floitation, and electro- kinetic coagulation found to be suitable for the removal of various dye. These methods do not degrade the dye but only decrease the dye concentration in water bodies by converting it from one form to another, thereby creating secondary pollution. Also, biological methods such as aerobic and anaerobic microbial degradation, and the use of pure enzyme were also reported in literature for dye removal from wastewater. The disadvantages of the biological methods are that they are time consuming; even some dyes are resistant to aerobic treatment. It has also been reported that the production of carcinogenic compounds such as aromatic amines can occur during the anaerobic treatment of dyes (Freeman, 1989).

In the recent past, advanced oxidation process (AOP) has gained much attention for the removal of pollutant from wastewater. These advanced oxidation process were carried out in the presence of solar and ultraviolet irradiation. These processes are ecofriendly, economic, and capable to degrade many dyes or organic pollutants present in wastewater. These advanced oxidation processes were carried out in the presence of solar and ultraviolet irradiation. Additionally to increase the rate of degradation or adsorption of pollutant on the surface of photocatalyst, advanced oxidation process were assisted by hydrogen peroxide (H_2O_2) and ultra-sonication. (Srivastava et al., 2013; Rao et al., 2009; Sobana and Swaminathan, 2007; Aleboye et al., 2012). However, among the various advanced oxidation process, photocatalytic degradation of dyes has been mainly carried out using various semiconductor based photocatalyst such as Fe_2O_3 , ZnO , TiO_2 , V_2O_5 and ... (Huang et al., 2013; Tayade

et al., 2007; Mills and Lee 2002; Lee and Mills, 2004; Natarjan et al., 2013). Additionally, these catalysts were modified in order to enhance their photocatalytic degradation efficiency (Natarjan et al., 2015). Among semiconductor materials, titanium dioxide (TiO_2) is widely used as a photocatalyst. The photocatalytic activity of the photocatalyst materials mainly depends on the band gap, surface area, and generation of electron-hole pair for degradation dyes present in water (Li, 2019). It has been observed that the surface area plays a major role in photocatalytic degradation of dyes, by providing higher surface area, which leads to the higher adsorption of dye molecule on the surface of photocatalyst and enhance the photocatalytic activity.

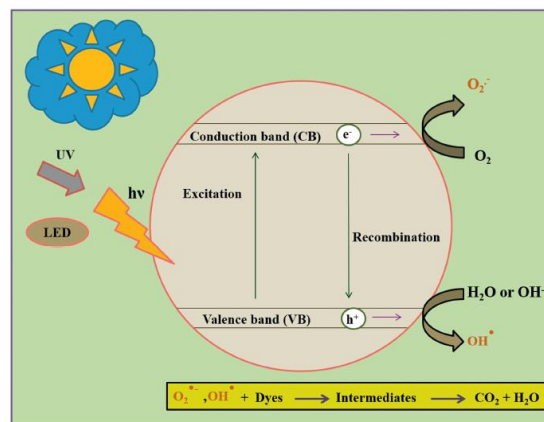


Fig.1-Photocatalytic dye degradation process

As it is shown in the Figure 1 when the semiconductor photocatalyst absorb photon energy from irradiation source (such as solar light, artificial ultraviolet light and/ or light emitting diodes (LEDs)) greater than its band gap, it generates electron and hole at conduct and valance band respectively due to the excitation of electron from valance band to conduction band upon absorption of energy. The hole generated at the valance band absorbs water molecule and create hydroxyl radical (OH^\cdot), whereas electron reacts with the oxygen to form anionic superoxide radicals ($O_2^{\cdot -}$). The mechanism described above can be represented by Eqs. 1-5 as shown below:

- 1) $\text{TiO}_2 + h\nu \rightarrow e^- + h^+$
- 2) $e^- + \text{O}_2 \rightarrow \text{O}_2^-$
- 3) $h^+ + \text{Organic} \rightarrow \text{CO}_2$
- 4) $h^+ + \text{H}_2\text{O} \rightarrow \text{HO}^\cdot + \text{H}^+$
- 5) $\text{HO}^\cdot + \text{Organic} \rightarrow \text{CO}_2$

In the photocatalytic degradation of pollutants, when the reduction process of oxygen (Eq.2) and oxidation of pollutants (Eq.3 and 4) do not proceed simultaneously, there is an electron accumulation in the conduction band, thereby causing a recombination of electrons is essential to promote photocatalytic oxidation.

The most important and fundamental elements for a successful photocatalytic system are the catalyst, the light source and the reactor configuration.

2. Materials and Methods

Reagents and materials

The Yellow Acid-36 dye used in this study which is classified as azo dyes and its chemical structure is shown in Figure2 ($\lambda=435$ nm). Synthetic solution was made of Yellow acid 36 dye and titanium dioxide P-25 Degussa used as catalyst.

Solution was prepared by dissolving a defined quantity of Yellow 36 dye in double distilled water. Then NaOH added to the solution and ultrasonic bath used. The absorbance in the maximum wavelength (λ_{max}) was measured using a UV-vis spectrophotometer. For safety and prevention of UV distribution the reactor was covered with Aluminum sheet.

Dye degradation efficacy is expressed as given below:

$$\%R = (C_0 - C_t) * 100 / C_0$$

R: Dye removal efficiency

C₀: First absorption

C_t: After irradiation absorption

Photooxidation Experiments

All experiments were performed in a Plexiglas reactor equipped with UV lamps at a wavelength of 365 nm. The Catalyst coated on marble surface by slurry method. So TiO₂ powder was mixed with water-Methanol (with volume ratio of 25%). The mixed solution was stirred for 10 min in 20 degree centigrade and 1500 rpm. Then the solution was stirred for 30 min to obtain a homogenous solution and transferred into an oven heated at 105 degree centigrade for 1 h. Finally, the marble covered by slurry and dried for 24 hours and air-cooled to room temperature. The coated marble was washed thoroughly with distilled water.

Dye degradation efficacy is expressed as given below:

$$\%R = (C_0 - C_t) * 100 / C_0$$

R: Dye removal efficiency

C₀: First absorption

C_t: After irradiation absorption

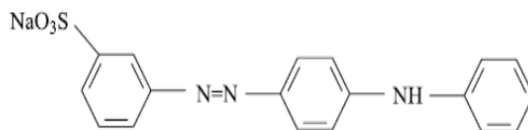


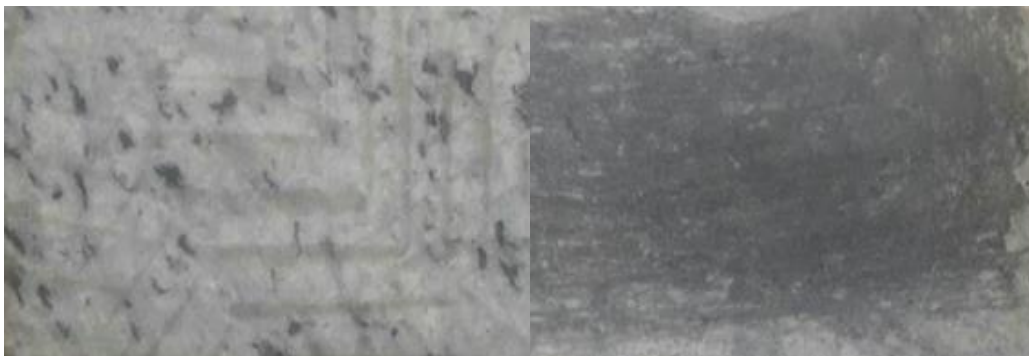
Fig.2- Structure of Yellow Acid 36

Table1: Various operation parameters used for degradation of dye are tabulated.

Variation range	Variation	No
5,25,50,75,100 (mg/l)	Dye concentration	1
35,70,105,140,180 (min)	Time contact	2
3,5,7,9,11	pH	3
20,40,60,80,100 (gr/m ²)	TiO ₂ dosage	4
10,20,30,40,50 (W)	UV irradiation intensity	5



Fig3- Reactive that be used in this study



A

B

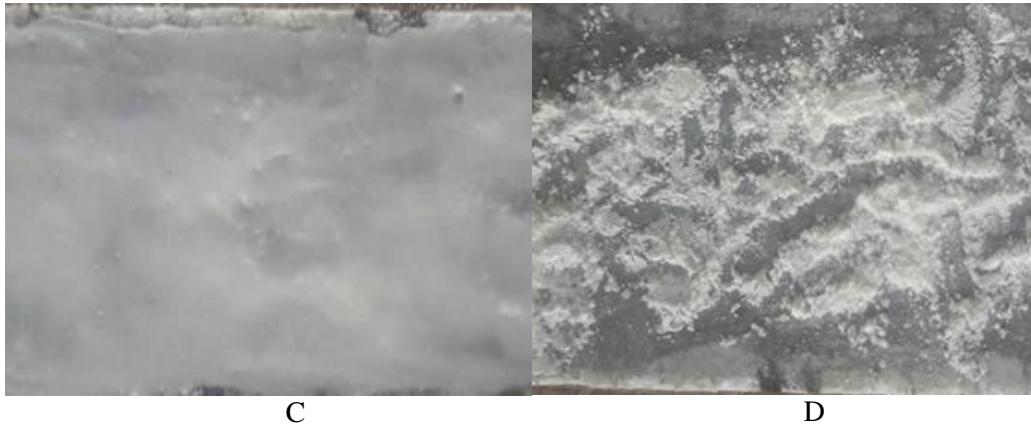


Fig.4-Coating process of TiO₂ : (a) The marble used, (b) Marble scooped, (C) Heated slurry in the oven, (D)After 24 hours

3. Results

The results of our experiment are shown in Figure 5 to 9. In these figures the effect of pH, contact time, initial dye concentration, UV irradiation intensity and TiO₂ concentration for efficacy of degradation were investigated. In general, increase in TiO₂ concentration, UV irradiation intensity and contact time increased the dye degradation efficiency. Also decrease in initial concentration of dye and solution pH increased the dye degradation efficiency.

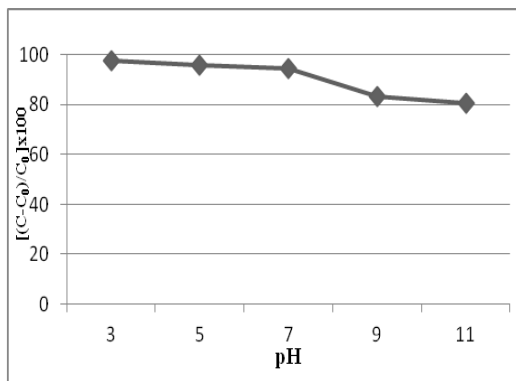


Fig.5-The effect of solution pH on dye degradation efficacy (initial Dye concentration 5=mg L⁻¹, TiO₂=100gr m⁻², contact time= 105 min, UV irradiation intensity=30W)

The experiments showed that dye degradation percentage with initial dye concentration of 5 mg/l

in presence of TiO₂ in amount of 100 mg m⁻² and 105 min with UV irradiation intensity 30 W in solution pH 3,5 ,7 , ... and 11 were in range of 97.6 , 95.9 , 84.3, 83.9 and 80.3 respectively. Results of this research showed that acidic pH is effective in accessing to maximum dye removal efficiency. Figure 5 showed it visibly.

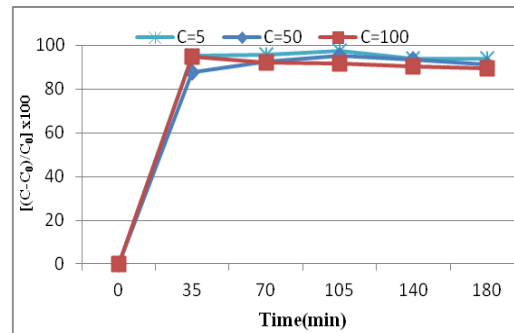


Fig.6- The effect of time on dye degradation efficacy (pH=3, TiO₂=100gr m⁻², UV irradiation intensity=30W)

As it is shown in Figure 6, the complete degradation of Yellow acid dye was obtained within 105 min and after this time, dye degradation efficiency decreased. The 105 min is the time for optimal dye degradation efficiency. The reason is that there was enough time for producing active hydroxyl radicals.

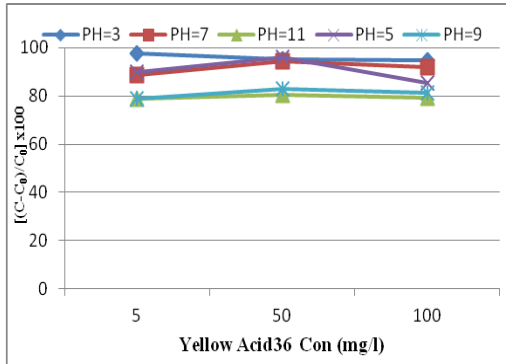


Fig.7- The effect of initial Dye on degradation efficacy (UV irradiation intensity= 30 W, TiO₂=100gr/m², concentration time= 105 min)

The results of this research showed that dye removal efficiency accelerated with dye concentration reduction. With dye concentration acceleration from 5 mg L⁻¹ to 100 mg L⁻¹, 105 min contact time and 30W UV irradiation intensity and TiO₂ in concentration of 100 gr m⁻², percentage of dye degradation decreased from 93.6 to 89.2. Therefore decrease in amount of dye had better photocatalytic efficiency degradation, it showed in Figure 7. Also in higher concentration of dye, surface area of nanoparticles decreased, that it prevented reaction between dye, free radicals and electron holes. With dye concentration acceleration light transmission decreased because light photons were absorbed with the dye before arrival to catalyst particles. Also with increase in dye concentration and making dye flocculation, the competition for absorption on substrate was increased. In other words photocatalysts were trapped in the dye flocculation.

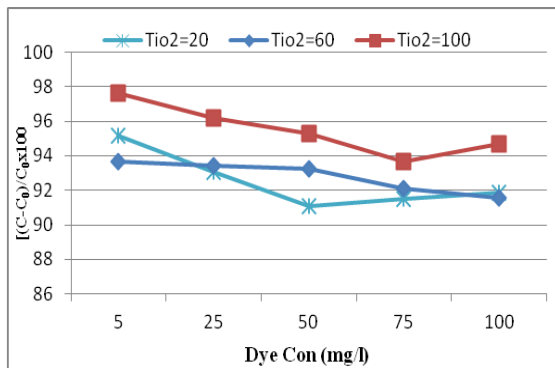


Fig.8- The effect of TiO₂ concentration on dye degradation efficacy (UV irradiation intensity= 30 W, pH=3, concentration time= 105 min)

The degradation efficiency increased with increase in TiO₂ concentration. With increase in TiO₂ dosage from 20 to 100 g m⁻² in dye concentration of 50 mg/l, contact time of 105 min and UV irradiation intensity 30 W the percentage of dye degradation increased from 91 to 95.2%. With increase in catalyst dosage more electron holes and more OH radicals produced from free electrons. Increase in active radicals increased the breakdown of dye molecule structure it is showed in Figure 8.

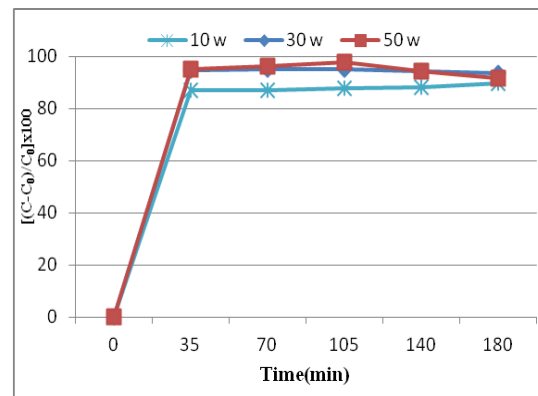


Fig.9- The effect of UV wavelength on dye degradation efficacy (UV irradiation intensity= 30 W, pH=3, concentration time= 105 min)

One of the other effective factors on photocatalytic refinement process is UV irradiance intensity. For assessment of the effect of this parameter, irradiation intensity in the range of 10, 20, 30 ... and 50 W were experimented. The results showed that higher amount of UV had better photocatalytic efficiency. The reason is that with increase in irradiation intensity more electrons are stimulated. Increase in amount of stimulated electrons makes more OH active radicals produced which accelerate photocatalytic oxidation rate. As there was no significant differences between range percentage of degradation in irradiation intensity from 30 W to 50 W, so 30 W chosen.

4. Discussion

The photocatalytic oxidation of Yellow Acid 36 dye has been studied using TiO₂ as catalyst. The results of the study could be summarized as follow:

- 1- Parameters such as concentration of dye, pH, catalyst dosage, time of contact and UV irradiation intensity play an important role on degradation rate.
- 2- In a heterogeneous photocatalytic water system, pH is one of the most important operating parameters. Acidic pH is effective in accessing to maximum dye removal efficiency.
- 3- Increase in contact time, increased the dye degradation efficiency.
- 4- The dye removal efficiency accelerated with dye concentration reduction.
- 5- Increase in UV irradiation intensity, increased the dye degradation efficiency. The reason is that with increase in UV irradiation intensity, more electrons are stimulated.

- 6- The concentration of the photocatalyst is another critical parameter that determines the degradation rate of Yellow Acid 36 dye. It has been widely observed that the degradation rate increase with an increase in catalyst loading. This is due to the availability of more active catalyst sites at higher concentrations, which results in the generation of more hydroxyl species. However, when such load is increased beyond an optimum value, there is no appreciable increase in the degradation rate.

5. Conclusions

The aqueous solution of Yellow Acid 36 dye decolorized by heterogeneous photocatalysis in the system UV/TiO₂. The best conditions found for were 100 gr m⁻² of catalyst at pH 3, an irradiation time of 105 min, an irradiation intensity 30W and 5 mg L⁻¹ of dye concentration. The process resulted in the 97.6% degradation of dye.

References

- Ajmal A, Majeed I, Malik RN, Idris H, Nadeem MA, (2014). Principales and mechanism of photocatalytic dye degradation on TiO₂ based photocatalysts: a comparative overview. *RSC Adv*, 4(70):37003-37026.
- Bizani E, Fytianos K, Poullos VI, Tsiridis V, (2006). Photocatalytic decolorization and degradation of dye solutions and wastewater in presence of titanium dioxide. *J Hazardous Materials*, 136(1):85-94.
- Freeman HM, (1989). *Standard handbook of Hazardous hazardous waste Treatment and Disposal*. 2nd ed. United states Second Edition: Mc Graw-Hill Book Company. 1168 p.
- Gupta VK, (2009). Applications of low-cost absorbents for dye removal—a review. *J Environ Manag*, 90(8):902313-2342.
- Huang H, Leung DY, Kwong PC, Xiong J, Zhandg L, (2013). Enhanced photocatalytic degradation of methylene blue under vacuum ultraviolet irradiation. *Catal Today*, 201:189-194.
- Li Y, Wang W, Wang F, Di L, Yang S, Zhu S, et al, (2019). Enhanced photocatalytic Degradation of Organic Dyes via Defect- Rich TiO₂ Prepared by Dielectric Barrier Discharge Plasma. *Nanomaterials (Basel)*, 9(5). pii: E720.
- Natarajan TS, Bajaj HC, Tayade RJ, (2014). Preferential adsorption behaviour of methylene blue dye onto surface hydroxyl group enrich TiO₂ nanotube and its photocatalytic regeneration. *J Colloid Interface Sci*, 433:104-114.
- Natarajan TS, Bajaj HC, Tayade RJ, (2018). Recent advances based on the synergetic effect of adsorption for removal of dye from waste water using photocatalytic process. *J Environ Sci (China)*, 65:201-222.
- Natarajan TS, Natarajan K, Bajaj HC, Tayade RJ, (2013). Enhanced photocatalytic activity of bismuth-doped TiO₂ nanotubes under direct sunlight irradiation for degradation of rhodamin B dye. *J Nanopart Res*, 15(5):1669.
- Natarajan, TS, Bajaj HC, Tayade RJ, (2015). Synthesis of homogenous sphere-like BiO₂ nanostructure by silica protected calcinations with high visible –light driven photocatalytic activity under direct sunlight. *Cryst Eng Comm*, 17(5):1037-1049.

- Pan H, Feng J, He GX, Cerniglia CE, Chen H, (2012). Evaluation of impact of exposure of Sudan azo dyes and their metabolites on human intestinal bacteria. *Anaerobe*, 18(4):445-453.
- Sobana N, Swaminathan M, (2007). Combination effect of ZnO and activated carbob for solar assisted photocatalytic degradation of direct blue 53. *Sol Cells*, 91(8):727-734.
- Srivastava P, Goyal S, Tayade R, (2013). Ultrasound-assisted adsorption of reactive blue 21 dye on TiO₂ in the presence of some rare earths (La, Ce, Pr and Gd). *Can J Chem Eng*, 92(1):41-51.