

Degradation of AY36 using TiO₂-UV Photocatalytic System

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ABSTRACT

This study investigates the efficacy of photocatalytic degradation process using TiO₂-UV configuration for treatment of waste water containing textile dye Acid Yellow 36 (AY36). Acid Yellow 36 dye was degraded using catalyst TiO₂ in an alkaline medium of pH 8.0. A dose of 0.25 g of TiO₂ was used for 88.4% degradation of initial concentration of 20 mg/l AY36 dye in 28 hrs. The effect of parameters such as pH, initial dye concentration, amount of TiO₂ used, and exposure to UV light/irradiation on degradation of AY36 was investigated. Further it was observed that suspended TiO₂ in dye solution shows more effective results towards dye degradation, than embedded TiO₂ in the form of alginate beads. The study concluded that photocatalytic degradation is a potential tool for degradation of azo dyes.

Keywords: TiO₂; Acid Yellow 36; Advanced oxidation process (AOPs); Photocatalysis

1. Introduction

Dyes are important raw material for industries like paper, pulp, leather, textile etc. Azo dyes have excellent coloring properties like yellow to orange so they are used in almost every industry. These dyes have colouring properties because of the presence of a chemical azo group. Other industries where dyes are used are tinting and inks, paints adhesive, polymers etc. [1] Effluents from different industries are the main source of contamination of water as they contain different fractions of residuals of dye. Azo dyes are highly resistant in nature; they are even resistant to heat temperature and weather condition.

Azo dye; R-N=N-R'

Where, R and R' can be either alkyl or aryl. The N=N is an azo group, which is only responsible for the colour of the dye and the only reason for its recalcitrant nature. It is hard to degrade dye by any biological means so chemical methods need to be applied for breakdown of double bond which turns coloured solution to colourless [2]. Industrial outlets contains huge amount of an azo dye residues which are toxic in nature and cause harmful effects on ecosystem. Dyes are not only harmful to plants and water organisms, but also show harmful Impact on human beings. There is ample evidence of the harmful effects of dyes. These are highly mutagenic and carcinogenic in nature and hence causing cancer and other dreadful disease. These are continuously being released to the environment from industries which impart ecotoxicity in aquatic ecosystems [3]. Since dyes are readily dissolved in water, they interfere with the photosynthetic activity of water organisms, and disturb the food chain of aquatic ecosystem by reducing visibility of zooplanktons. Textile dyes also cause allergies, respiratory diseases and dermatitis, irritation of skin and eyes etc. Considering the harmful effects of dyes on environment, it is important to explore an effective method for its degradation.

There are various methods of dye degradation but one of the more efficient accelerated processes is advanced oxidation process. It is a chemical treatment which reduces organic impurities of water by oxidising them to simpler forms^[4]. The hydroxyl radicals are produced during the process with the help of primary oxidants (H₂O₂, ozone) or energy sources (UV lights) or catalyst (TiO₂). These components must be precised, properly configured, and used for the study. AOPs are mainly used for non-degradable and toxic products which include photocatalysis^[5], Fenton oxidation^[6], Photofenton, ozonolysis, and ultrasonication in standalone mode or combination of two. Photocatalysis process is the acceleration of photoreaction in presence of catalyst like TiO₂ or ZnO etc. The most widely used semiconductor catalyst in photo-induced process is TiO₂ which is activated by UV light^[7]. TiO₂ is also known as heterogeneous catalyst. It is chemically and biologically inert, stable, relatively easy to produce and reuse, cheap, environment friendly, have stable electrical properties, and efficiently catalyse reactions. It exists in four mineral state anatase, rutile, brookite and TiO₂(B)^[8]. It is versatile in nature and has various application areas like paints, varnishes, paper, plastics, solar cells, glass, electrical conductors, food colouring agents etc. It is also used in immobilised form of beads and acts as an opacifier in powdered form. It is widely used as a white pigment due to its sticky nature and having very high refractive index. TiO₂ is being used in the photocatalysis process because of the following factors - inexpensive, easily available, wavelength selective, and accelerated by UV light. Photocatalytic reactions take place at room temperature and the formation of intermediate products is avoided. UV light is absorbed by TiO₂, making ground state electrons jump to excited state forming an electron hole pair. This creates a void or energy gap between lower vacant conduction band and upper filled valence band. Hydroxyl ions are generated by this process. When photons with greater or equal energy to 3.4 eV is adsorbed by TiO₂, an electron is excited from valence band to conduction band; charge carriers (OH radicals) are generated and leave a positive hole in the valence band, this photo generated electron hole pair is known as excitons.

There are various operating parameters which play a vital role in the photocatalytic degradation^[9]. One such parameter is amount of catalyst used. Greater the amount of catalyst used more will be the rate of degradation^[8].

The mechanism of photocatalytic degradation can be described by following steps:

- Absorption of photons by TiO₂ and productions of electron- hole pairs.
- Oxygen ion absorption.
- Neutralisation of OH radicals by photon holes.
- Reaction of organic pollutant with OH radical.

The first step of the reaction is carried out by photons with the energy higher than the band gap of TiO₂ i.e. 3.2 eV^[10].

2. Materials and methods

The AY36 is an azo dye with complex chemical structure, recalcitrant nature, and reported eco-toxicity. The dye was obtained from Vishnu chemicals, Ankleshwar, Gujarat having 85% minimum assay. Titanium dioxide (99% AR Grade) was obtained from High Purity Laboratory Chemicals Pvt. Ltd., Mumbai. All the experiments were performed in triplicates using Grade 1 ultrapure water.

A stock solution of 1000ppm (0.5mg/500ml) of AY36 was prepared for degradation experiments. The 20mg/l solution of dye was prepared by diluting the stock solution. A standard curve of AY36 was plotted in concentration range of 5-20 mg/L with regular interval of 5mg/L The absorption spectrum for absorbance (400-700 nm) of AY36 against wavelength reported 434nm as the wavelength of maximum absorption. The pH was adjusted at 8.0 with the help of HCl (1N) and NaOH (1N) solutions. The experiment was conducted using 150ml of the dye solution in conical flask. The solution was continuously stirred using magnetic stirrer at 150 rpm in the UV chamber fitted with three (03) lamps (λ – 254 nm) of capacity of 30 W each.

The photo-catalytic degradation of AY36 was studied at an initial dye concentration of 20 mg/L with TiO₂ as catalyst under UV light. A volume of 10 ml was extracted from the flask placed in a UV light and the absorbance was monitored first at interval of 15 minutes for first one hour; 30 minutes for next one hour; and then at regular interval of two (02) hours. The extracted sample was centrifuged at 5000rpm for 20 minutes to separate TiO₂ particles from the solution. A blank without dosing of TiO₂ was also run to compensate for the photo-degradation. The concentration was obtained observing the absorbance at 434nm over Labtronics make LT-290 model spectrophotometer. The percentage degradation of AY36 was calculated using formula given below

$$\text{Percentage degradation \%} = ((C_i - C_f) / C_i) \times 100$$

Where, C_i is the initial concentration of dye, and C_f is the final concentration of dye.

3. Results and discussion

Based on the results obtained, it was observed that photocatalytic process could degrade AY36 dye. The concentration of AY36 went on decreasing with time. It decreased from initial concentration (C_i) of 22.6 mg/l to 20.4 mg/l in first one hour. Later, the rate of degradation reduced but the degradation progressed slowly; and residual concentration of AY36 stabilised at around 2.2 mg/l after a period of 32 hours (**Figure 1**). Further degradation of AY36 was not observed, and it was concluded that Photocatalytic degradation of AY36 has an overall efficiency of about 90%. The reduced rate of degradation in later phase may be ascribed to reduction in initial dye concentration with time. The Photocatalytic degradation of AY36 might be following first order rate kinetics which is dependent over initial concentration of reactants viz. AY36 in the present study. In order to confirm it, the rate of degradation (mg/h) was calculated using the following relation

$$\text{Rate of reaction (K) (mg/h)} = (C_i - C_f) / (t_i - t_f)$$

Where, C_i is initial concentration of AY36; C_f is the final concentration; t_i is initial time; and t_f is the final time during an interval of degradation. The rate of degradation was maximum during 15 to 30 minutes (@ 2.6 mg/h) followed by the rate of 2.2 mg/h during 30 minutes to one hour. Later, the rate of degradation went on decreasing with time (**Table 1**) and it stabilised at 0.1 mg/h after a period of 32 hours with an overall decolourisation efficiency of 90.3%.

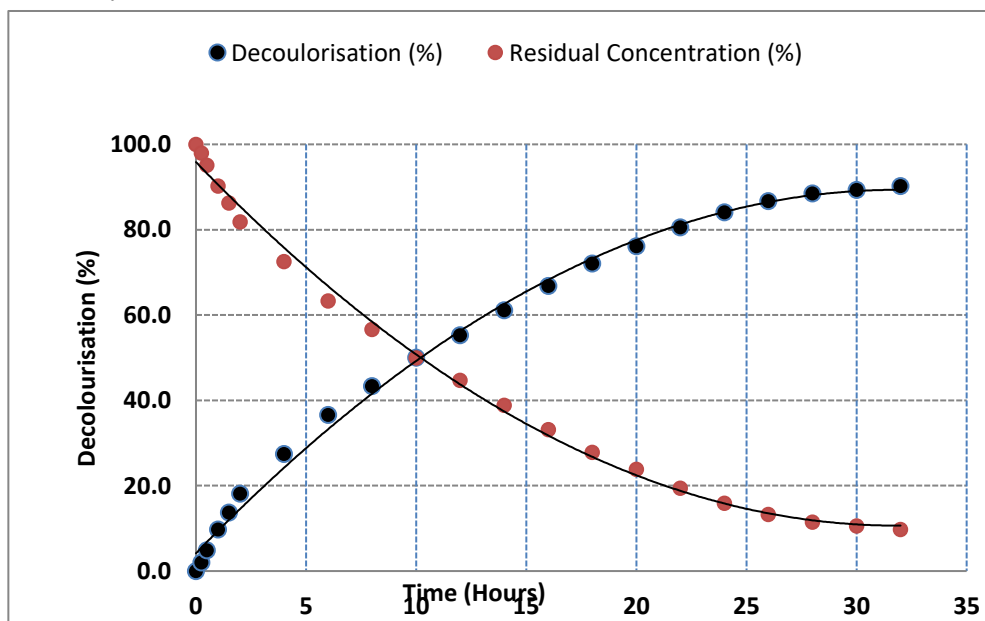


Figure 1. Degradation profile of AY36 during photocatalytic treatment

S. No.	Time (hours)	Concentration (mg/l)	Decolourisation (%)	Rate of decolourisation (mg/hour)
1	0	22.6	0.0	0.0
2	0.25	22.2	2.0	1.8
3	0.5	21.5	4.9	2.6
4	1	20.4	9.8	2.2
5	1.5	19.5	13.7	1.8
6	2	18.5	18.2	2.0
7	4	16.4	27.4	1.1
8	6	14.3	36.6	1.0
9	8	12.8	43.4	0.8
10	10	11.3	50.0	0.8
11	12	10.1	55.3	0.6
12	14	8.8	61.2	0.7
13	16	7.5	66.8	0.6
14	18	6.3	72.1	0.6
15	20	5.4	76.1	0.5
16	22	4.4	80.5	0.5
17	24	3.6	84.1	0.4
18	26	3.0	86.7	0.3
19	28	2.6	88.5	0.2
20	30	2.4	89.4	0.1
21	32	2.2	90.3	0.1

Table 1. Percent decolourisation and rate of degradation of AY36 in the present study.

4. Conclusion

Based on results obtained in the present study, Photocatalytic degradation was observed to be an effective process for decolourisation of azo dyes like AY36. The TiO₂-UV system can be used for the treatment textile industry wastewater containing toxic azo dyes. Optimisation of parameters regulating photocatalysis may be done to improve efficiency of the process to treat the industrial effluents to the level of compliance.

Conflict of interest

The authors declare no potential conflicts of interest.

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