

Photocatalytic degradation of Acid Orange 7 (AO7) dye using TiO₂

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Abstract- The present study was undertaken to determine the feasibility of Advanced Oxidation Processes (AOPs) in treatment of textile dyes in wastewater. Acid Orange (AO7) is an azo dye with potential ecotoxicity to the exposed organisms. Natural attenuation by sunlight, and photo-catalytic degradation (with TiO₂) was studied for colour removal and effective degradation of AO7. The experimental results confirmed that natural attenuation under sunlight and shade is not an effective process for degradation of AO7. It was observed that a fraction of dye (5%) is degraded/transformed during the day time with exposure to sunlight but the colour was regenerated during night. Photocatalytic degradation of AO7 under UV light (30W) with TiO₂, and without TiO₂ was found to be effective in degradation of dye with an initial concentration of 50mg/L. Experiments with TiO₂ were found to be higher than without TiO₂ but the rate of degradation was quite low. The dose of photo-catalyst regulates dye degradation and it was found to be maximum at a dose of 1.0g/L of TiO₂ with the degradation efficiency of 76% in a period of about 32 hours. Complete degradation of AO7 was observed in a period of about 127 hours. The recovery of photocatalyst was found to be 62% for its reuse.

Keywords: Advance oxidation processes, photocatalysis, TiO₂, Acid Orange 7

I. INTRODUCTION

Waste water from industries like textile, paper, plastics and leather etc. contains residual dyes and is released in aqueous streams. In India, approximately 40,000 different dyes and pigments are used in industries. Out of it more than 2,000 are different azo dyes. During the year 2013 – 14 about 200.54 MT of dyes and pigments were produced, out of which 2.33 MT were azo dyes [1]. Azo Dyes constitute more than 50% of total dyes produced worldwide [2-3]. These possess lethal toxicity, mutagenicity, genotoxicity, and carcinogenicity to aquatic organisms as well as animals. Azo dyes are identified to cause tumors in urinary bladder [4]. Acute toxicity (EC₅₀) was observed at 87 mg/l of Acid Orange 7; and 0.13 mg/l of Disperse Red1 when tested against *Daphnia similis* [5]. Azo dyes are observed to be toxic with EC₂₀ value as low as 0.1 mg/l for *E. coli*. [6]. Azo Dye HC Orange 1 was observed to be 100% lethal to zebrafish at 8 mg/l and at 10 mg/l towards Goldfish with 48 hours of exposure [7]. These dyes escape conventional wastewater treatment processes and persist in the environment as a result of their high stability to light, temperature, water, detergents, chemicals, soap, and other parameters such as bleach and perspiration. Conventional treatment methods like Activated sludge process, adsorption

onto activated carbon, coagulation by a chemical agent, ozone oxidation, hypochlorite oxidation, electrochemical method etc. were found to be ineffective and complete decolourisation/degradation was not achieved [8-11]. Flocculation causes generation of large amount of sludge; and activated carbon adsorption poses the problem of adsorbent regeneration [12]. Azo dyes are highly hazardous to humans and environment and are resistant to degradation using conventional treatment methods. Hence, a suitable treatment technology needs to be identified for removal of azo dyes from wastewater. Advanced Oxidation Processes (AOPs) are reported to be efficient methods for the degradation of recalcitrant compounds. These generate hydroxyl radicals using different mechanisms. Hydroxyl radicals so generated attack the organic compounds (dyes) and cause degradation of the same. Photo – catalysis process uses light photons to generate the hydroxyl radicals. It involves band to band excitation of semiconductor particles by irradiation, to generate [•]OH radicals derived from valence band hole oxidation of terminal –OH groups and hydration water on the particle surface [13]. TiO₂ is reported to be most effective photo catalyst due to its non-toxicity, insolubility, high photoactivity and inexpensive nature. The light also helps in degradation of other simple organic compounds present. Therefore, the present work is undertaken to study the natural attenuation of AO7 dye, and to investigate the potential of TiO₂ as a photo catalyst under UV radiation towards degradation of AO7.

II. MATERIALS AND METHODS

A. Chemicals

The Acid Orange 7 is an azo dye with complex chemical structure (Fig. 1), recalcitrant nature, and reported ecotoxicity. It was obtained from Vishnu Chemicals, Ankleshwar, Gujrat 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 I ultrapure water. A stock solution (500mg/L) of AO7 was prepared for degradation experiments. The plot of absorbance (400-700nm) of AO7 against wavelength represented 490nm as the wavelength of maximum absorption.

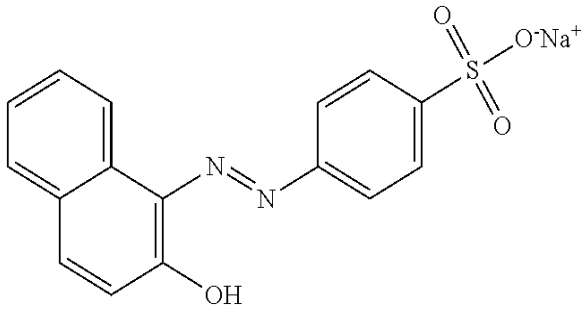


Fig. 1. Structure of AO7 dye

The standard curve of AO7 was plotted in the concentration range of 10 to 100mg/L with regular intervals of 10mg/L. In order to study natural degradation of dye under sunlight 500mL of the stock solution was placed in transparent glass bottles in sunlight and under shade conditions separately. An average exposure of 8 hours of sunlight was given to the dye solution. A volume of 10ml was expected from the flasks placed in sunlight and shade was taken before and after the exposure to sunlight. The concentration was obtained reading absorbance at 490nm over Labtronics make LT 290 model spectrophotometer. The photo catalytic degradation of AO7 was studied at an initial concentration of 50mg/L with TiO₂ as catalyst under UV light. A 30W UV lamp with a flux of 3.17×10^{19} photons/s was used for photo exposure. Degradation of AO7 was studied at different doses of (0.5, 1.0, 2.0g/L) of TiO₂ and the absorbance was monitored at regular interval of 60 minutes. The extracted samples were centrifuged at 5000rpm for 20min to separate TiO₂ particles from the solution. A blank with no dosing of TiO₂ was also run to compare the degradation. The percent degradation of AO7 was calculated using the formula given below:

$$\text{Percent degradation \%} = \frac{(C_i - C_f)}{C_i} \times 100$$

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

The recovery of photo-catalyst TiO₂ was also attempted to determine the possibility of its reuse. The treated dye solution was centrifuged at 5000rpm for 20 minutes to separate TiO₂, dried at 104°C and weighed to determine final weight.

III. RESULTS AND DISCUSSION

A. Natural attenuation of AO7

Since the study aimed at removal of color of the dye the dye/its breakdown under natural sunlight, and photo catalytic (TiO₂) degradation under UV light, the experiments were conducted separately. To study the natural attenuation under sunlight and shade to separate transparent glass flasks containing solution were used, and the samples were extracted before sunrise and after the sunset with a difference of 8 hours. It was observed that there was no significant change in the dye concentration even after 5 days of exposure. During the period, only 5% degradation was observed for both the experiments. There was slight decrease in dye concentration for the solution kept under sunlight during day time owing to photo-transformation of AO7, but

the levels were regenerated during night time. Almost similar trend (Fig. 2a, b) was observed for the experiment under shade and the transformation resulting in reduction in color may be attributed to exposure to daylight, but limiting direct exposure to sunlight. Similar observations have been reported [14] by other researchers with only 2% decrease even at an initial dye concentration of 20 ppm. It may be concluded that direct sunlight is not an effective dye-degrading agent for AO7 at high concentration.

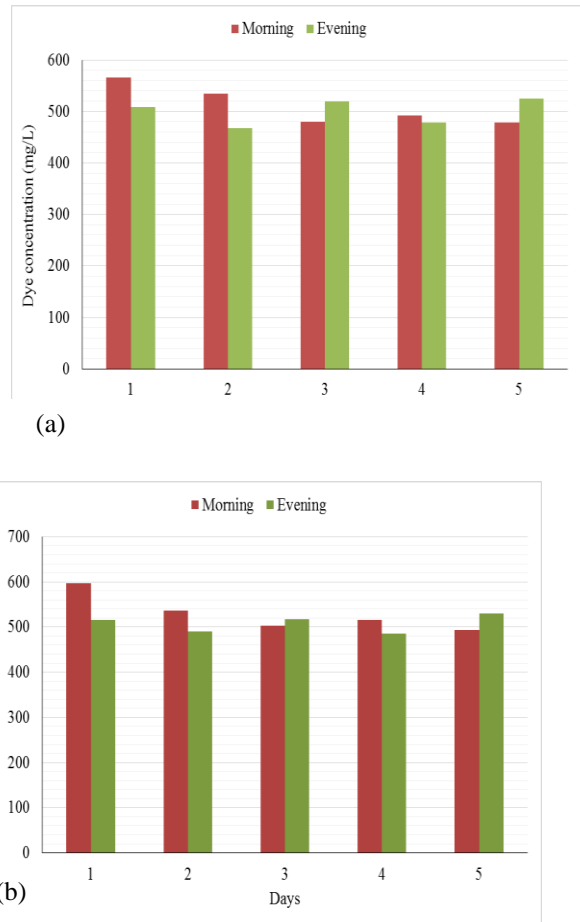


Fig. 2. To study the natural attenuation of AO7 in (a) sunlight, and (b) shade

B. Photo-Catalytic degradation of AO7

In order to ascertain the role of TiO₂ as photo-catalyst, degradation of AO7 was studied at initial concentration of 50mg/L with and without TiO₂ under UV light. There was no degradation of AO7 without TiO₂ even after 32 hours. On the other hand, 23% degradation of AO7 was observed for TiO₂ as photo-catalyst (Fig. 3). Based on the values so obtained it was concluded that the presence of photo-catalyst regulates AO7 degradation and not the UV light alone. In order to investigate the effective dose of photo-catalyst, experiments were run for varying doses of TiO₂ (0.5, 1.0 and 2.0 g/L). It was observed that maximum degradation (75.7%) was reported at TiO₂ dose of 1.0 g/L, followed by 0.5g/L (61.5%), and 2.0g/L (22.9%) in a reaction period of 32 hours (Fig. 4). Another study [15] reports 69.1% degradation of AO7 within 2.5 hours but with four times higher irradiance of UV light and at initial concentration of 25mg/L of AO7.

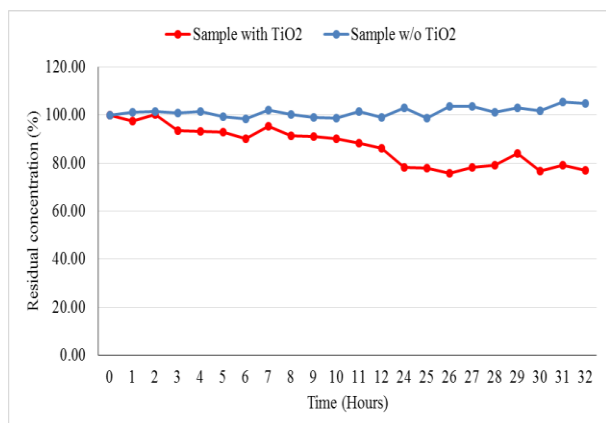


Fig. 3. Effect of photo - catalyst (TiO_2) on degradation of AO7 under UV light

It confirms the observations as obtained in our study. Lower rate of AO7 degradation at higher dose (2.0g/L) of TiO_2 could be because of reduced penetration of UV light owing to higher amount of suspended TiO_2 in the solution. Comparatively lower degradation efficiency at 0.5g/L dose of TiO_2 may be attributed to lower dose of photo-catalyst resulting in less production of $\cdot\text{OH}$ radicals responsible for AO7 degradation.

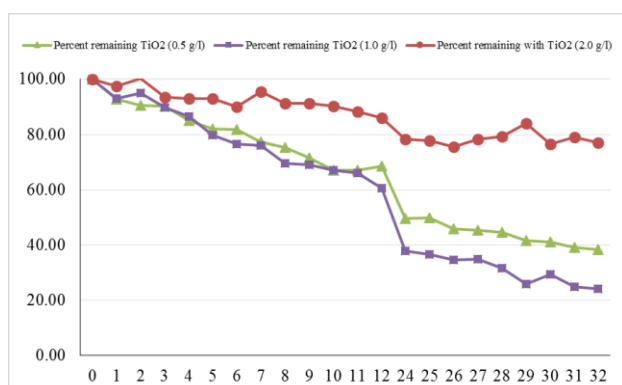


Fig. 4. Effect of different concentration of photo - catalyst on degradation of AO7

Another experiment was undertaken to determine the time required for complete photo-degradation of AO7 at a dose of 1.0 g/L of photo-catalyst. As observed in Fig. 5, complete degradation of AO7 was observed in 127 hours under the reaction conditions.

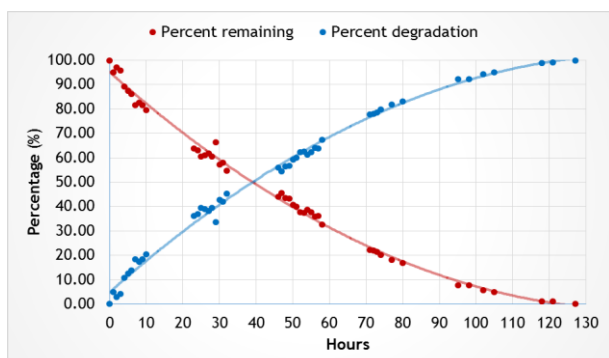


Fig. 5. Complete degradation of AO7 by photo-catalyst TiO_2 @ 1.0g/L.

IV. CONCLUSION

Based on the experimental results, it is observed that AO7 is persistent in nature and is not degraded under natural conditions. A small fraction of AO7 is photo - chemically broken down to simpler intermediate resulting in some decolourisation but the reaction is reversible and stable AO7 is formed again in dark conditions during the night. The degradation of AO7 can be facilitated using a photo-catalyst like TiO_2 which results in significant improvement in the rate of degradation of AO7. Since TiO_2 is suspended in the solution its recovery after complete degradation of AO7 is imperative, which accounts to ~ 60%.

V. REFERENCES

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