

Reduction of textile dye by using heterogeneous photocatalysis

Omprakash Sahu¹, Karthikeyan. M. R²

¹Department of Chemical Engineering, KIOT, Wollo University, Ethiopia

²Department of Textile Engineering, KIOT Wollo University, Ethiopia

Email address:

ops0121@gmail.com(O. Sahu)

To cite this article:

Omprakash Sahu, Karthikeyan. M. R. Reduction of Textile Dye by Using Heterogeneous Photocatalysis. *American Journal of Environmental Protection*. Vol. 2, No. 3, 2013, pp. 90-94. doi: 10.11648/j.ajep.20130203.13

Abstract: Dye waste water pollutants are the major sources of environmental pollution. Textile waste water introduces intensive color and toxicity to aquatic system. Dyes possess complex aromatic structure. Hence conventional biological treatment methods are ineffective for decolourisation and degradation. Now a day's Heterogeneous photocatalysis method is used for the treatment of textile waste water. Due to the high photo catalytic activity and stability of Zinc oxide, it is generally used as a photo catalyst for the removal of organic pollutants. Therefore the study has been made to determine the amount of decolourisation of the Napthal ASG dye using the catalysts ZnO with the combination of UV irradiation by Batch process. The influence of parameters such as catalyst loading, reuse of catalyst and initial concentration of the dye has been studied. In Batch process, the optimum dosage of catalyst for the concentration of 41600 mg/L was about 20g/L and the efficiency was about 83.90%. The dye was completely degraded in 30 min. After the first usage of catalyst it is dried in the sunlight and then it is used for the second time, its efficiency is 80.25% and 71.34% for the third time reuse of dosage.

Keywords: Photocatalysis, Napthal, Zinc Oxide, Ultraviolet Light

1. Introduction

Advanced oxidation processes (AOPs) have been efficiently applied on the degradation of a variety of organic contaminants [1]. These processes include technologies such as O₃, O₃/UV, H₂O₂/UV, Fenton, photo-Fenton, TiO₂/UV, etc. which are characterized by a common factor: the generation of hydroxyl radicals. These radicals show little selectivity of attack and are able to oxidize a variety of organic compounds due to their high oxidative capacity (reduction potential of OHEo = 2.8 V) [2]. The versatility of the AOPs is also enhanced by the fact that they can offer different possible ways for OHradicals production, thus, allowing a better compliance with the specific treatment requirements.

Heterogeneous photocatalysis is a very promising technique as it has already been applied with success on the degradation of different categories of organic compounds combining the low cost, the mild conditions and the possibility of using sunlight as the source of irradiation [3, 4]. This technique is based on the illumination of semiconductor particles usually suspended in aqueous

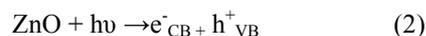
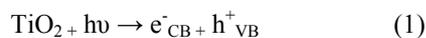
solutions. The illumination of these particles with light energy greater than the band gap energy leads to the production of high energy electron-hole pairs (e^-/h^+), which can migrate to the surface of the photo catalyst and can either recombine producing thermal energy or participate in redox reactions with the compounds that are adsorbed on the photocatalyst's surface, thus, leading to complete mineralization of the organic compounds [5].

The textile dyeing industry consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes. Wastewater from printing and dyeing units is often rich in color, containing residues of reactive dyes and chemicals, and requires proper treatment before being released into the environment [6]. The main challenge for the textile industry today is to modify production methods, so they are more eco-friendly at a competitive price, by using safer dyes and chemicals and by reducing cost of effluent treatment/disposal [7]. The wastewater from the dye house is generally multi-colored. A total of 15% of the total world production of dyes is lost during the dyeing process and is released in textile effluents [8]. The dye effluent

disposed into the land and river water reduces the depth of penetration of sunlight into the water environment, which in turn decreases photosynthetic activity and dissolved oxygen (DO). The adverse effects can spell disaster for aquatic life and the soil. Many dyes contain organic compounds with functional groups, such as carboxylic (-COOH), amine (-NH₂), and azo (-N=N-) groups, so treatment methods must be tailored to suit to the chemistry of the dyes [9]. Therefore it is necessary to find an effective method for waste water treatment to remove color from textile effluents. Therefore there are three methods for treatment of colored materials, which include [10]

- Physical methods employing precipitation, adsorption and reverse osmosis
- Chemical methods via oxidation and reduction and
- Biological methods including anaerobic and aerobic treatment.

The disadvantage of precipitation methods is sludge formation. The disadvantage of adsorption is that the adsorbent needs to be regularly regenerated. This is associated with additional costs and sometimes with very time consuming procedures. Biological treatment is ineffective in cases where complicated aromatic compounds are present. Industries generally adding NaOCl in the final polishing steps to remove effluent color from chlorinated by products, which severely damage the surface water and ecological environments [11-15]. Photocatalytic oxidation by UV/TiO₂ or ZnO involves the oxidation of TiO₂ /ZnO particles by UV light from valence band of the solid to the conduction band [16-20].



When a semiconductor such as catalyst absorbs photons the valence band electrons are excited to the conduction band. For this to occur, the energy of photon must match or exceed the band gap energy of the semiconductor. This excitation results in the formation of an electronic vacancy or positive hole at the valence band edge.

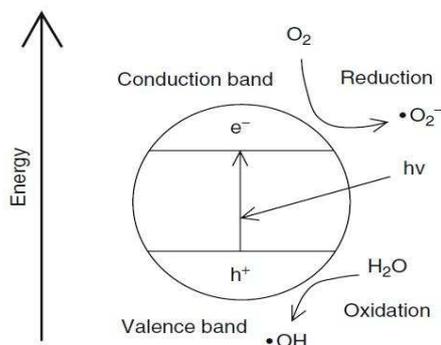
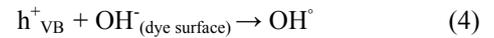


Fig 1. Excitation of Electrons from valence band to conduction band

This hole has a positive charge and reacts with the adsorbed water molecules on the surface of the solid

producing the radical OH[•] which has great potential oxidation of organic molecules.

The simplified mechanism is as follows:



hν - photons that initiates the reaction.

OH[•] - hydroxyl radical

ads - molecules that are adsorbed on the catalyst.

Once the reaction has begun the molecules generated by the oxidation of the dye (products) can be adsorbed on the catalyst and oxidized again due to the constant formation of OH[•] during the irradiation periods [21]. Zinc oxide is an inorganic compound with the formula ZnO. The powder is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g., car tires), lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, first aid tapes, etc. ZnO is present in the Earth's crust as the mineral zincite; however, most ZnO used commercially is produced synthetically [22]. ZnO is a catalyst in the photo catalytic degradation of organic pollutants due to its suitable band gap energy of 3.3 eV over a wide range of pH. Hence it is a great challenge for industry to find the effective solving technology meeting the environmental protection requirement.

2. Material and Methods

2.1. Effluent

The effluent was collected from Grasim Industries Ngada (M.P.) India, and freeze at 20°C before using for experiment.

2.2. Reagents

The real textile dye effluent (Naphthal ASG) was taken for the study. The catalyst used for the photo catalytic degradation was Zinc Oxide (ZnO). Distilled water was used in all experiments [22]. The structure of Naphthal ASG Dye is shown in Fig. 2.

2.3. Method (Batch Process)

2.3.1. Photo Reactor System

Photo catalytic tests were performed in a Pyrex glass cylinder batch photo reactor with a volume of 1000 ml. The UV light source was powered with medium pressure UV lamp of 15watt. An electrical magnetic stirrer with magnetic bar was used continuously so that catalyst can be uniformly dispersed in the solution when the sample was degraded by UV light. The entire reactor was kept inside the UV inoculation chamber in order to guarantee

maximum use of the radiation, to prevent the effects of external radiation and to maintain the temperature of the reactor system. The reactor system temperature was monitored periodically and kept constant. Samples were collected periodically using a micro-pipette[23].

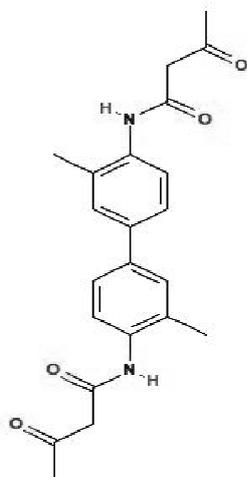


Fig 2. Structure of Napthal ASG Dye

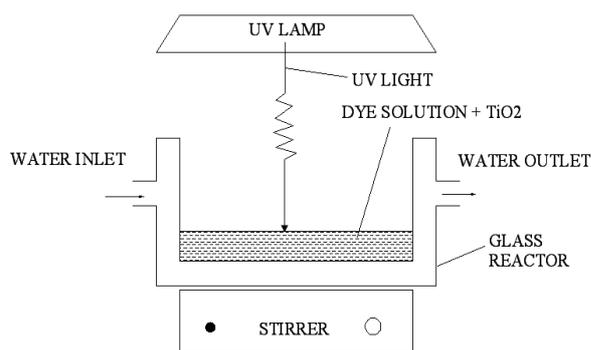


Fig 3. Photo reactor system for the Batch process

2.3.2. Effect of ZnO on the Photo Reactor System

Napthal ASG dye (250 ml, 41600ppm) with the dosage of catalyst ZnO was placed in a photo reactor. An electrical magnetic stirrer was used continuously in the reactor so that catalyst can be uniformly dispersed in the solution. After stirring the solutions for 5 minutes, 5 ml of sample was collected and labeled as sample at 0 minute. Samples were collected using 10 ml micro pipette at different time interval 5, 10,15,20,25 and 30 minutes. The concentration of dye was determined from the absorbance observed at $\lambda=388\text{nm}$ using UV-Vis spectrophotometer [24, 25].

Percentage of Degradation (%D) was calculated by using the following equation

Where

A_0 – absorbance of $t=0$ minute

A_t – absorbance at t minutes.

In order to determine the concentration of the dye after treatment, a calibration curve was drawn by measuring the absorbance of dye solution of known concentrations. The calibration curve for the dye is shown below

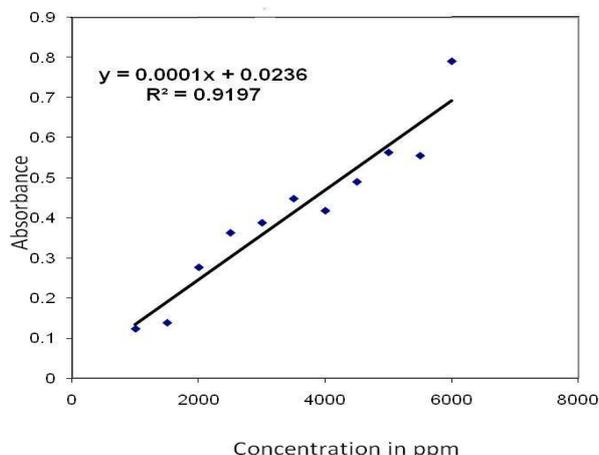


Fig 4. Calibration curve for Napthal ASG dye

3. Results and Discussions

3.1. Effect of Catalyst Dosage

The dosage of the catalyst was varied with the concentration of dye as constant to find the optimum dosage. With the concentration of dye as 41600 mg/L, the dosage of catalyst was varied as 5 g/L, 10 g/L, 15 g/L, 20 g/L, 25 g/L, 30 g/L, 35 g/L, 40 g/L, and 45 g/L. With the room temperature and irradiation time as constant, the optimum dosage was found to be 20 g/L which is illustrated in the graph below. The density of particles in the area of illumination also increases and so the rate is enhanced. Above a certain level, the substrate molecules available are not sufficient by the increased number of particles (i.e.,) although more area is available for a constant dye concentration the number of substrate molecules present in the solution is the same. Hence the additional catalyst powder is not involved in catalyst activity and the rate does not increase with an increase in the amount of catalyst beyond a certain limit.

3.2. Efficiency on Second and Third Reusage of Catalysts (ZnO)

Since the dosage for the dye treatment (20 mg/l) was very high it is advisable for reuse of the photocatalyst. Hence the zinc oxide which is used for the treatment was reused for second time and third time. The efficiency of degradation of dye on reuse are shown if Fig. 5.

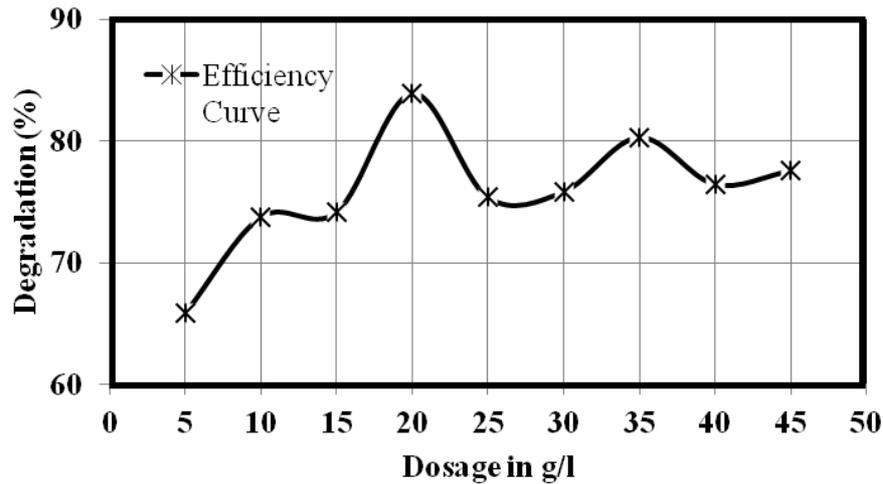


Fig 5. Decolourisation efficiency with respect to various catalyst dosages concentration of dye is 41600 mg/L

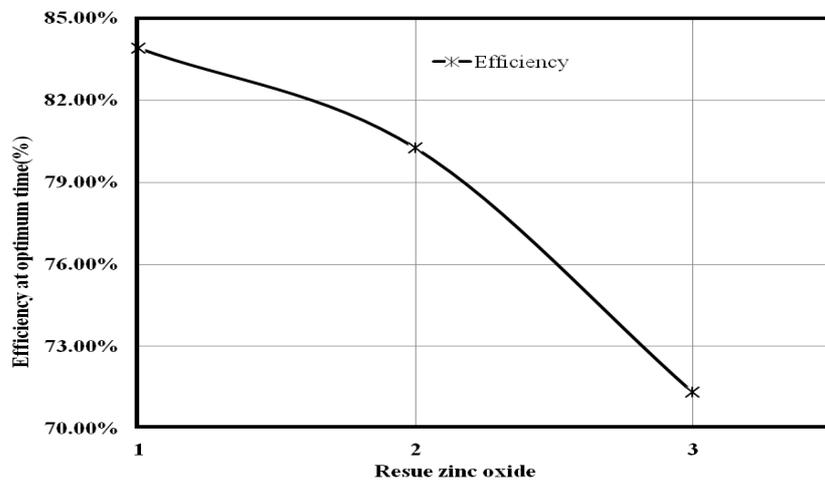


Fig 6. Effect of repeated using of ZnO

4. Conclusion

Photocatalysis has large capability for the water treatment. It can be utilized for the decomposition of organic and inorganic compounds. It can be used also to decompose natural organic matter, which has many environmental and industrial impacts. Complete decolourisation of the Napthal ASG dye was achieved in an irradiation period of 30 minutes. Degradation efficiency of 83.90% was observed for the dye concentration of 41600mg/L. An optimum catalyst dosage of 20g/L has been determined. Degradation efficiency was obtained at reuse of catalyst was 80.25%, 71.34% at second and third time reuse respectively. The drawback of this method is that of being slow compared with traditional methods but it has the advantage not leaving toxic by product or sludge to be disposed.

Acknowledge

Author acknowledge to Ministry of Higher Education Ethiopia for providing funding and facilities.

References

- [1] European Parliament and Council: Directive 2008/50/EC of 21 May 2008 on ambient air and cleaner air for Europe, OJ L 152, p. 1-44, 2008.
- [2] Bundesanstalt für Straßenwesen (BASt): Bericht über die Messungen der Luftqualität an BAB durch die Bundesanstalt für Straßenwesen - Kalenderjahr 2010 -, Bergisch Gladbach, 2011.
- [3] Rauterberg-Wulff, A.; LUTZ, M.: Impact Assessment of the Low Emission Zone Berlin, UMID: Umwelt und Mensch – Informationsdienst (4), p. 11-18, 2011.
- [4] Lorenz, J.: Particulate Matter: Immission Control Concerns Us All – Experience with Low Emission Zones in Munich,

- UMID: Umwelt und Mensch – Informationsdienst, (4), p. 19-26, 2011.
- [5] Carp, O.; Huisman, C.L.; Reller, A.: Photoinduced reactivity of titanium dioxide, *Progress in Solid State Chemistry* (32), p. 33-177, 2004.
- [6] Chen, X.; Mao, S.S.: Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications and Applications, *Chemical Reviews* (107), p. 2891-2959, 2007.
- [7] Fujishima, A.; Rao, T.N.; Tryk, D.A.: Titanium dioxide Photocatalysis, *Journal of Photochemistry and Photobiology C* (1), p. 1-21, 2000.
- [8] Bessekhoudar, Y.; Robert, D.; Weber, J.V.: Bi₂S₃/TiO₂ and CdS/TiO₂ heterojunctions as an available configuration for photocatalytically degradation of organic pollutant, *Journal of Photochemistry and Photobiology A* 163 (3), p. 569-580, 2004.
- [9] Chen, F.; Deng, Z.; Li, X.; Zhang, J.; Zhao, J.: Visible light detoxification by 2,9,16,23-tetracarboxyl phthalocyanine copper modified amorphous titania, *Chemical Physics Letters* 415, p. 85-88, 2005.
- [10] Hodak, J.; Quinteros, C.; Litter, M.I.; San Román, E.: Sensitization of TiO₂ with phthalocyanines, *Journal of Chemical Society, Faraday Transactions* 92 (24), p. 5081-5088, 1996.
- [11] Machado, A.E.H.; Franca, D.M.; Velani, V.; Magnino, G.A.; Velani, H.M.M.; Freitas, F.S.; Müller, P.S.Jr.; Sattler, C.; Schmücker, M.: Characterization and Evaluation of the Efficiency of TiO₂/Zinc Phthalocyanine Nanocomposites as Photocatalysts for Wastewater Treatment Using Solar Irradiation, *International Journal of Photoenergy*, p. 1-12, 2008.
- [12] Mele, G.; Garcia-López, E.; Palmisano, L.; Dyrda, G.; Slota, R.: Photocatalytic Degradation of 4-Nitrophenol in Aqueous Suspension by Using Polycrystalline TiO₂ Impregnated with Lanthanide Double-Decker Phthalocyanine Complex, *Journal of Physical Chemistry C* 111, p. 6581-6588, 2007.
- [13] Amrit Pal Toor, Anoop Verma, C. K. Jotshi, P. K. Bajpai, Vasundhara Singh (2006), "Photo catalytic degradation of Direct Yellow 12 dye using UV/TiO₂ in a shallow pond slurry reactor", *Dyes and Pigments*, Vol. 68, pp. 53-60.
- [14] Behnajady M.A., N. Modirshahla, N. Daneshvar, M. Rabbani (2007), "Photo catalytic degradation of C. I. Acid Red 27 by immobilized ZnO on glass plates in Continuous mode", *Journal of Hazardous Materials*, Vol. 140, pp. 257-263.
- [15] Debabrata Chatterjee, Anima Mahata (2001), "Demineralization of organic pollutants on the dye modified TiO₂ semiconductor particulate system using visible light", *Applied Catalysis B: Environmental*, Vol. 33, pp. 119-125.
- [16] Giuseppe, Vincenzo, Alessandra, Claudio, Elisa, Vittorio, Leonardo, Edmondo and Mario (2003), "Photocatalytic oxidation of methyl-orange in aqueous suspension: comparison of the performance of different polycrystalline titanium dioxide", *Annali di Chimica*, Vol. 93, pp. 639-644.
- [17] Guillard C., D. Baldassare, C. Duchamp, M. N. Ghazzal, S. Daniele (2007), "Photocatalytic degradation and mineralization of a malodorous compound using a continuous flow reactor", *Catalysis Today*, Vol. 122, pp. 160-167.
- [18] Haque M. M., M. Muneer (2007), "TiO₂ mediated photocatalytic degradation of a textile dye derivative, bromothymol blue, in aqueous suspensions", *Dyes and Pigments*, Vol. 75, pp. 443-448.
- [19] Herrmann J. M., C. Duchamp, M. Karkmaz, Bui Thu Hoai, H. Lachheb, E. Puzenat, C. Guillard (2007), "Environmental green chemistry as defined by photocatalysis", *Journal of Hazardous Materials*, Vol. 146, pp. 624-629.
- [20] Hong, De-zhi, Gho-qing (2007), "Formaldehyde degradation by UV/TiO₂/O₃ process using continuous flow mode", *Journal of Environmental Sciences*, Vol. 19(9), pp. 1136-1140.
- [21] Jean-Marie Herrmann, Jean Disdier, Pierre Pichat, Sixto Malato, Julian Blanco (1998), "TiO₂-based solar photocatalytic detoxification of water containing organic pollutants; Case studies of 2, 4-dichlorophenoxyacetic acid and of Benzofuran", *Applied Catalysis B: Environmental*, Vol. 17, pp. 15-23.
- [22] [27] Lin, Y.-M; Tseng, Y.-H.; Huang, J.-H.; Chao, C.C.; Chen, C.C.; Wang, I.: Photocatalytic Degradation of Nitrogen Oxides over Visible Light Responsive Titania-Based Photocatalysts, *Environmental Science and Technology* (40), p. 1616-1621.
- [23] Ohno, T.; Mitsui, T.; Matsumura, M.: Photocatalytic activity of S-doped TiO₂ photocatalyst under visible light, *Chemistry Letters* 32, p. 364-365, 2003.
- [24] Asahi, R.; Morikawa, T.: Nitrogen complex species and its chemical nature in TiO₂ for visible-light sensitized photocatalysis, *Chemical Physics* 339, p. 57-63, 2007.
- [25] Sakthivel, S.; Kisch, H.: Daylight Photocatalysis by Carbon-Modified Titanium Dioxide, *Angewandte Chemical International Edition* 42 (40), p. 4908-4911, 2003.