Photochemical Treatments of Textile Industries Wastewater

Anuradha Teotia[1], Dr. M. S. Baghel[2]

Department of Chemistry, Integral University, Kursi Road, Lucknow, India

Abstract:
        Chemical compounds that raise the rate of a reaction by lowering the activation energy mandatory are termed the catalyst and it is used to range the transition state. A catalyst is not inspired as part of the reaction method, unlike reactants. By using a catalyst, the method of speeding up a reaction is so-called Catalysis. With instances of each kind this page looks at the dissimilar kinds of catalyst (heterogeneous and homogeneous), and clarifications of how they work. You will also find a description of instance - autocatalysis - a reaction which is catalysed by one of its products.

Keywords — **Photochemical, Textile Industries, Wastewater treatment, oxidation process, mineralization.**

INTRODUCTION

Textile industry is one of the most water and chemical intensive commerce globally due to the fact that 200-400 litres of water are required to produce 1 kg of textile fabric in textile factories. The water used in this industry is more or less completely discharged as waste. Furthermore, the losses of dye in the seepages of textile industry can extent up to 75%. The effluents are considered very compound since they comprise salt, surfactants, ionic metals and their metal complexes, toxic organic chemicals, biocides and toxic anions. Azo dyes are observed as the largest class of synthetic. Roughly, 50–70% of the available dyes for commercial applications are azo dyes tailed by the anthraquinone group. Azo dyes are categorized according to the presence of azo bonds (–N=N–) in the molecule i.e., monoazo, diazo , triazo etc. and also sub-classified agreeing to the structure and technique of applications such as acid, basic, direct, disperse, azoic and pigments. Some azo dyes and their dye antecedents are well-known of high toxicity and alleged to be human carcinogens as they form toxic aromatic amines.

Dissimilar physical, chemical and biological as well as the several combinations of pretreatment and post-treatment techniques have been established over the last two decades for industrial wastewaters treatment in order to meet the ever-increasing necessities of human beings for water. However there are several studies issued in this field, most of the methods adopted by these investigators are uneconomical, ineffective or impractical uses.

Recent studies have established that heterogeneous photo catalysis is the most effectual method in the degradation of colored chemicals. These studies used titanium dioxide and / or zinc oxide in the photolysis methods. The large bang gap of titanium dioxide and zinc oxide (~ 3.2 eV) put a limitation of using these semiconductors in photocatalytic degradation under natural surviving conditions. Only a small part of the complete solar intensity might be useful in such photodegradation methods. Though, the existence of dye on the surface of catalyst decreases the energy vital for excitation and then upsurges the competence of the excitation method by prolonging its absorption in the visible region of the spectrum.

2. Methods used in treatment of textile wastewater

There are numerous factors to choose the appropriate textile wastewater treatment technique such as, economic efficiency, treatment efficiency, kind of dye, concentration of dye and environmental fate.

There is no general technique for the treatment of textile industrial wastewater. Wastewaters from textile industry comprise numerous pollutants resultant from many stages of production, such as, fibers preparation, yarn, thread, webbing, dyeing and finishing. Chiefly three approaches are used for the treatment of textile industrial wastewater. These are:
1. Physico-chemical approaches.
2. Advanced oxidation approaches.
3. Biological sludge approaches.

The chief operational approaches used for the treatment of textile industrial water include physical and chemical processes. Though, these methods have several drawbacks (See Table 1, Mutambanengwe, 2006). These difficulties comprise Sludge generation, high cost, formation of bi – products, releasing of toxic molecules,

needing a lot of dissolved oxygen, limitation of activity for specific dyes and needful of long time.

In recent years, advanced oxidation processes (AOPs) have gained more attraction as a powerful method in photocatalytic degradation of textile industrial wastewater as they are capable to deal with the problematic of dye destruction in aqueous systems.

3. Photocatalysis

Photocatalysis is well-defined as the acceleration of a photoreaction in the existence of a catalyst, while photolysis is well-defined as a chemical reaction in which a chemical composite is broken down by photons. In catalysed photolysis, light is captivated by an adsorbed substrate.

Photocatalysis on semiconducting oxides trusts on the absorption of photons with energy equal to or greater than the band gap of the oxide, so that electrons are endorsed from the valence band to the conduction band:

$$Semiconductor + h\nu \rightarrow h+ + e-$$
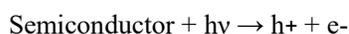
If the photoholes and photoelectrons formed by this procedure migrate to the surface, they could interact with adsorbed species in the elementary steps, which jointly create Photocatalysis.

The many gas- and liquid-phase reactions photocatalysed by TiO2 and ZnO have been appraised. There is an overall agreement that adsorption is essential since the surface species act as traps for both; photogenerated holes and electrons, which otherwise recombine. In totalling to participating in conventional surface reaction steps, adsorbed dye molecules help in the separation of photoholes and photoelectrons, which can otherwise recombine within the semiconductor particles. A major factor distressing the efficacy of photocatalysis procedure is electron/hole recombination. If the electrons and holes are used in a reaction, a steady state will be reached when the removal of electrons and holes equals the rate of generation by illumination. Recombination and trapping procedures are the de-excitation processes which are responsible for the formation of the steady state, if no reaction happens. There are three significant machineries of recombination:

1. Direct recombination.
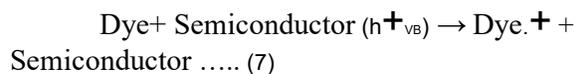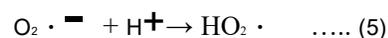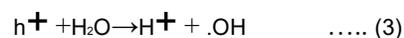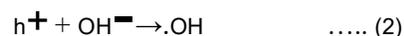2. Recombination at recombination centres.
3. Surface recombination.

There are different kinds of semiconductors, whose band gaps range among 1.4 and 3.9 eV, i.e., it could be enthusiastic with a light of 318–886 nm wavelengths. This means that most of the known semiconductors co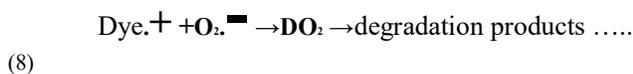uld be motivated by using visible light. Though, not all these semiconductors could be used in the photocatalytic reactions. Bahnemann et al., (1994) report that the most suitable photocatalysts should be stable toward chemicals and illumination and devoid of any toxic constituents, particularly for those used in environmental studies. The authors also elucidate that TiO2 and ZnO are the most normally used in photocatalytic reactions due to their effective absorption of long wavelength radiation as well as their stability en route for chemicals. Other semiconductors like WO3, CdS, GaP, CdSe and GaAs absorb a wide variety of the solar spectrum and can form chemically activated surface-bound intermediates, but awkwardly these photocatalysts are tarnished during the repeated catalytic cycles intricate in heterogeneous photocatalysis.

4. Photosensitization

The enlightenment of suspended semiconductor in an aqueous solution of dye with unfiltered light (polychromatic light) indications to the likelihood of the existence of two paths (Hussein et al., 2008):

1. In the first pathway, the part of light with energy equal to or more than the band gap of the lightened semiconductor will source a promotion of an electron to conduction band of the semiconductor and as an outcome, a positive hole will be formed in the valence band. The designed photoholes and photoelectrons can move to the surface of the semiconductor in the existence of light energy. The positive hole will react with adsorbed water molecules on the superficial of semiconductor creating .OH radicals and the electron will react with adsorbed oxygen on the surface. Furthermore, they can react with deliquescent oxygen and water in suspended liquid and yield perhydroxyl radicals (HO_2.) with high chemical activity (Zhao & Zhang, 2008). The procedures in this pathway can be abridged by the subsequent equations:

$$h^+ + OH^- \rightarrow .OH \quad\quad ..... (2)$$

$$h^+ + H_2O \rightarrow H^+ + .OH \quad\quad ..... (3)$$

$$e^- + O_2 \rightarrow O_2 \cdot {}^- \quad\quad ..... (4)$$

$$O_2 \cdot {}^- + H^+ \rightarrow HO_2 \cdot \quad\quad ..... (5)$$

$$H_2 O_2 \rightarrow 2OH \quad\quad ..... (6)$$

Dye+ Semiconductor ($h^+{}_{VB}$) → Dye.$^+$ + Semiconductor ..... (7)

Dye.$+$ $+O_2$.$\blacksquare$ $\rightarrow DO_2$ $\rightarrow$degradation products …..
(8)

5. Advanced oxidation processes

Glaze et al., (1987) define Advanced Oxidation Processes (AOPs) for water treatments as the procedures that happen near ambient temperature and pressure which include the generation of highly reactive radicals, particularly hydroxyl radicals (.OH), in adequate quantity for water purification. Advanced oxidation procedures can also be easily well-defined as methods of destruction of organic pollutants from wastewaters. These procedures comprise chemical oxidation methods using hydrogen peroxide, ozone, combined ozone and hydrogen peroxide, hypochlorite, Fenton's reagent, ultra-violet improved oxidation such as UV/O3, UV/ H2O2, UV/air, wet air oxidation and catalytic wet air.

Hydroxyl radicals are strong reactive species, which are proficient of abolishing a wide range of organic pollutants. Table 1 shows hydroxyl radical as the second strongest oxidant (Weast, 1977; Legrini et al., 1993 Domènech et al., 2001; & Mota et al., 2008).

Oxidant	Eº (V)
Fluorine (F2)	3.03
Hydroxyl radical (.OH)	2.80
Atomic oxygen (O)	2.42
Ozone (O3)	2.07
Hydrogen peroxide(H2O2)	1.78
Hydroperoxyl radical (O2H·)	1.70
Potassium permanganate (KMnO4)	1.67
Hypobromous acid (HBrO)	1.59
Chlorine dioxide (ClO2)	1.50
Hypochlorous acid (HClO)	1.49
Hypochloric acid	1.45
Chlorine (Cl2)	1.36
Bromine (Br2)	1.09
Iodine (I2)	0.54

Table 1: Standard reduction potential of common oxidants against Standard Hydrogen Electrode

6. Fundamental parameters in photocatalysis

In semiconductor photocatalysis of industrial wastewater treatment, there are diverse parameters upsetting the efficacy of treatment. These parameters comprise mass of catalyst, dye concentration, pH, and light intensity, addition of oxidizing agent, temperature and type of photocatalyst. Other issues, such as, ionic constituents in water, solvent kinds, mode of catalyst application and calcinations temperature can also play a

significant role on the photocatalytic deprivation of organic compounds in water environment (Guillard et al., 2005 & Ahmed et al., 2011).
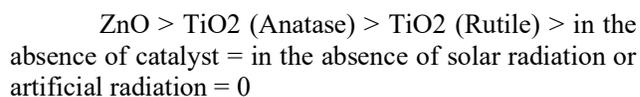
6.1 Effect of type of catalyst:

Haque & Muneer (2007) observe that Degussa P25 is more reactive for degradation of a textile dye derivative, bromothymol blue, in aqueous suspensions than other commercially existing photocatalysts kinds of titanium dioxide, i.e. Hombikat UV100, PC500 and TTP. They elucidate the high activity of Degussa P25 is due to composing of small nano-crystallites of rutile dispersed within the anatase matrix. The band gap of rutile is less than that of anatase and as an outcome, electron will transferal from the rutile conduction band to electron traps in anatase and the recombination of electrons and holes will be reduced. Hussein, (2002) stated that anatase has higher photoactivity than rutile due to the variance in surface area. Decolorization percentage of real textile industrial wastewater on rutile, anatase, and zinc oxide shows that the activity of dissimilar catalysts falls in the subsequent order (Hussein & Abass, 2010 a):

ZnO > TiO2 (Anatase) > TiO2 (Rutile)

ZnO is more active than TiO2 due to the absorption of wider spectrum light (Sakthivela et al., 2003). Though, the amount of zinc oxide necessary to reach the optimum activity is two times more than that for titanium dioxide (anatase or rutile) (Hussein & Abass, 2010 a). In alternative study, Hussein et al., (2008) detected that ZnO is less active than anatase when the same weight of catalysts is used for photocatalytic degradation of textile wastewater. Akyol et al., (2004) reported that ZnO is more active than TiO2 for the decolorization efficacy of aqueous solution of a profitable textile dye due to the band gap energy, the charge carrier density, and the crystal structure.

Decolorization competence of real textile industrial wastewater in the existence and nonexistence of catalyst and/or solar radiation was also examined (Hussein & Abass, 2010 b). The results designate that the activity of dissimilar catalysts fall in the order:

ZnO > TiO2 (Anatase) > TiO2 (Rutile) > in the absence of catalyst = in the absence of solar radiation or artificial radiation = 0

6.2 Effect of mass of catalyst

Photocatalysts dosage added to the reaction vessel is a chief parameter distressing the photocatalytic degradation efficacy (Dong et al., 2010). Photocatalytic degradation effectiveness increases with an upsurge in catalysts mass. This behavior might be due to an increase in the amount of active site on surface of photocatalyst particles. As a result, a growing the number of dye molecule adsorbed on the surface of photocatalyst lead to an increase in the density of particles in the area of illumination (Kim & Lee, 2010). The extrapolation of Hird's data (Hird, 1976) specifies that only 7.5 mg of TiO2 was enough to absorb all incident 366 nm radiation. It trails that the mass effect must be instigated by variations in the effective utilization of the absorbed radiation relatively than by the increased absorption.

Photocatalyst with small particles are more effectual than larger particles. This behavior could be due to (Hussein, 1984):

1. Photoholes and photoelectrons produced in the bulk would have fewer traps and recombination centres to overwhelm before reaching the surface.

2. A greater proportion of material would be within the space charge arising from depletive oxygen chemisorption's, which indulgence exciton detachment and photohole relocation to the surface.

Hence, growing the catalyst's mass will raise the concentration of the efficient small particles within the illumined region of the reaction vessel. The direct proportionality amongst photocatalytic degradation competence and catalyst loading is real within low concentrations of photocatalyst where there are extra active sites reaching plateau reign. The plateau is grasped when this outcome can no longer upsurge the overall efficacy of employing incident radiation. Furthermore, after the plateau region is attained, the activity of photocatalytic decolorization decline with upsurge of catalyst concentration for all kinds of catalysts. This behavior is more probable to derive from difference in the intensity of radiation inflowing the reaction vessel and the way the catalyst exploits that radiation. Light scattering by catalyst elements at higher concentration lead to decline in the passage of irradiation through the sample leading to poor light employment (Gaya et al., 2010; Kavitha & Palanisamy, 2011). Deactivation of activated photocatalyst molecules striking ground state molecules with increasing the load of photocatalyst could be also cause reduction in photocatalyst activity (Kim & Lee, 2010). Photocatalytic decolorization competence (PDE) % of real textile industrial wastewater has been examined by employing dissimilar masses of TiO2 (anatase or rutile) or ZnO under natural weathering situations for 20 minutes of irradiation (Hussein & Abass, 2010 b).

6.3 Effect of pH

Aqueous solution pH is a significant variable in the evaluation of aqueous phase arbitrated photocatalytic decolorization reactions. pH change affects the adsorption quantity of organic pollutants and the ways of adsorption on the exterior of photocatalyst (coordination). As a consequence, the photocatalytic degradation efficacy will greatly be subjective by pH changes. Zero Point Charge (pHzpc), is a notion relating to adsorption phenomenon and well-defined as the pH at which the surface of an oxide is uncharged. If positive and negative charges both exist in equal amounts, then this is the isoelectric point (iep). However, the zpc is the same as iep when there is no adsorption of other ions than the potential determining H+/OH– at the surface.

In aqueous solution, at pH higher than pHzpc, the oxide surface is adversely charged and then the adsorption of cations is favoured and as significance, oxidation of cationic electron donors and acceptors are favoured. At pH lower than pHzpc, the adsorbent surface is positively charged (See Figure 1) and then the adsorption of anions is favoured and as a significance, the acidic water contributes more protons than hydroxide groups.
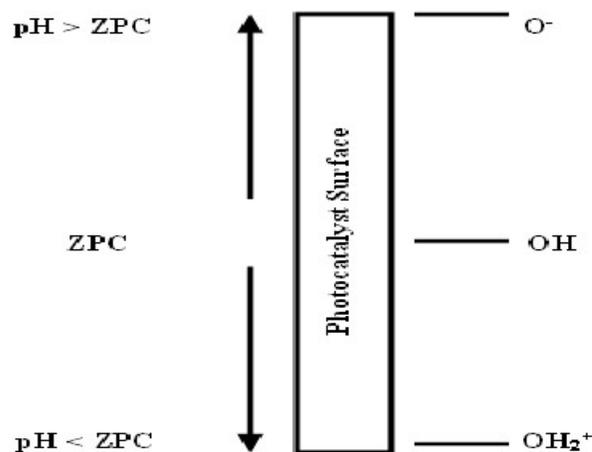

Fig 1 Effect of pH on ZPC

6.3.1 Effect of pH on photocatalytic decolorization of Bismarck brown R

Under the determined experimental condition with initial dye concentration equal to 10-4 M, ZnO dosage 3.75 gm.L-1, light intensity equal to 2.93 mW.cm-2 and temperature equal to 298.15 K, the effect of change in solution pH on decolorization percentage has been studied in the range 2-12. The decolorization percent has been found to be strongly dependent on pH of solution because the reaction takes place on the

surface of semiconductor. The decolorization proportion of Bismarck brown R will upsurge with the increase of pH displaying maximum decolorization at pH 9.

6.5 Effect of temperature

One of the benefits of photoreaction is that it is not affected or somewhat affected by temperature variation. Temperatures reliant on steps in photocatalytic reaction are adsorption and desorption of reactants and products on the surface of photocatalyst. None of these steps seems to be rate decisive. The impact of temperature is described as the variable with the least effect on photocatalytic degradation of aqueous solution of azo dyes (Obies, 2011). Attia et al., (2008) have found that the activation energy of photodegradation of real textile industrial wastewater is equal to 21 ± 1 kJ mol-1 on titanium dioxide and 24 ± 1 kJ mol-1 on zinc oxide. The activation energy for the photocatalytic degradation of textile industrial wastewater on titanium dioxide is alike to earlier discoveries for photocatalytic oxidation of diverse types of alcohols on titanium dioxide and metalized titanium dioxide (Al-zahra et al., 2007; Hussein & Rudham, 1984, 1987). The single value of activation energy (21 ± 1 kJ mol-1) that can be connected to the calculated activation energy of photooxidation of dissimilar species of titanium oxide is related with the transport of photoelectron through the catalyst to the adsorbed oxygen on the surface (Harvey et al., 1983 a & b). Kim & Lee, (2010) described that the very small activation energy in photocatalytic reactions is the deceptive activation energy Ea, whereas the true initiation energy Et is nil. These kinds of reactions are functioning at room temperature.

6.7 Comparison between mineralization and photocatalytic decolorization

Mineralization of dyes is a procedure in which dyes are changed totally into its inorganic chemical constituents (minerals), such as carbon dioxide, water and other species conferring to the structure of dye

6.8 Effect of irradiation sources

Table 2 summarized the achieved results from the different methods used for the treatments of textile industrial wastewater and different kinds of industrial dyes (Hussein, 2010). The outcomes show that the decolorization rate of textile industrial wastewater is faster with solar light than with UV light. The outcomes specified that solar energy can be efficiently used for photocatalytic degradation of pollutants in wastewater.

Process	Type of treated waste or dye	Source of irradiation	Type of catalyst	Time for complete mineralization/hours	Reference
Photocatalytic	Textile industrial wastewater	Solar	ZnO	2.7	Alkhateeb et al., (2005)
Photocatalytic	Textile industrial wastewater	Solar	TiO2	4	Alkhateeb et al., (2005)
Photolysis	Murexide	Solar	-	7.5	Alkhateeb et al., (2007)
Photocatalytic	Murexide	Solar	ZnO	3.8	Alkhateeb et al., (2007)
Photocatalytic	Murexide	Solar	TiO2	3.3	Alkhateeb et al., (2007)
Photolysis	Thymol blue	Solar	-	7	Hussein et al., (2008)
Photocatalytic	Thymol blue	Solar	TiO2	2.7	Hussein et al., (2008)
Photocatalytic	Thymol blue	Solar	ZnO	3.3	Hussein et al., (2008)
Photocatalytic	Textile industrial wastewater	Mercury lamp	TiO2	2.6	Attia et al., (2008)
Photocatalytic	Textile industrial wastewater	Mercury lamp	ZnO	3	Attia et al., (2008)
Photocatalytic	Bismarck brown G	Mercury lamp	ZnO	1	Hussein et al., (2010a)
Photocatalytic	Bismarck brown G	Mercury lamp	ZnO	0.8	Hussein et al., (2010b)

Photocatalytic	Bismarck brown G	Mercury lamp	TiO2	1.2	Hussein et al., (2010c)
Photocatalytic	Textile industrial wastewater	Mercury lamp	TiO2	3	Hussein & Abass, (2010a)
Photocatalytic	Textile industrial wastewater	Mercury lamp	ZnO	1	Hussein & Abass, (2010a)
Photocatalytic	Textile industrial wastewater	Solar	TiO2	1.8	Hussein & Abass, (2010b)
Photocatalytic	Textile industrial wastewater	Solar	ZnO	0.33	Hussein & Abass, (2010b)

Table 3: Effect of irradiation sources on photocatalytic decolorization of textile industrial wastewater and different dyes

CONCLUSION

Photocatalytic degradation methods is the most effectual and clean technology. Textile industries have become universal. Thus, this technique can be considered as a promising method for providing challenging quantities of water particularly for countries facing severe suffering from water shortage. The presence of catalyst and lights are vital for photocatalytic degradation of colored dyes. Photocatalytic degradation efficiency (PDE) of textile industrial wastewater is noticeably affected by illumination time, pH, early dye concentration and photocatalyst loading. Solar photocatalytic treatment has been showed to be an effectual method for decolorization of industrial wastewater through a photocatalytic procedure and the transformation is almost complete in a reasonable irradiation time. In the countries where, intense sunlight is presented throughout the year, solar energy could be efficiently used for photocatalytic degradation of pollutants in industrial wastewater. The zero point charge is 6.4 and 9.0 for TiO2 and ZnO, correspondingly above which the surface of photocatalyst is adversely charged by means of adsorbed hydroxyl ions; this favours the creation of hydroxyl radical, and as a result, the photocatalytic degradation of industrial wastewater rises due to inhibition of the photoholes and photoelectrons recombination.

REFERENCES

1. Ahmed,S. ; Rasul, M.; Martens W. ; Brown , R.& Hashib, M.(2011). Advances in Heterogeneous Photocatalytic Degradation of Phenols and Dyes in Wastewater: A Review. *Water Air Soil Pollut* , Vol. 215,pp.3–29.
2. Akyol, A.; Yatmaz, H. & Bayramoglu, M. (2004). Photocatalytic Decolorization of Remazol Red RR in Aqueous ZnO Suspensions. *Applied Catalysis B: Environmental*, Vol. 54, pp. 19–24.
3. Alkhateeb, A.; Hussein, F. & Asker, K. (2005). Photocatalytic Decolorization of Industrial Wastewater Under Natural Weathering Conditions. *Asian J. Chem.*, Vol. 17, No. 2, pp. 1155-1159.
4. Bhutani., S.(2008). *Organic chemistry-selected topics*, 1st ed., Ane Book India, 169- 172, New Delhi.
5. Buxton, G.; Greenstock, C.; Helman, W.& Ross, A. (1988). Critical Review of Rate Constants or Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals in Aqueous Solution, *J. Phys. Chem. Ref. Data.*, Vol. 17, No.2,pp. 513- 886.
6. Chen , Chih-Yu , (2009). Photocatalytic Degradation of Azo Dye Reactive Orange 16 by TiO2, *Water Air Soil Pollut* Vol.202,pp. 335–342.
7. Chen, D. & Ray, A. (1998). Photodegradation Kinetics of 4-nitrophenol in TiO2 Suspension, *Wat. Res.*, Vol. 32, No. 11, pp.3223-3234.
8. Chen, J.; Liu, M.; Zhang, J. ; Ying, X. & Jin, L. (2004). Photocatalytic Degradation of Organic Wastes by Electrochemically Assisted TiO2 Photocatalytic System, *J. Environ. Manage.*, Vol. 70, No. 1, pp. 43-47.
9. Galvez, J.(2003). *Solar Detoxification*, United Nations Educational, Scientific and Cultural Organization, Electronic Copy.
10. Gaya, U.; Abdullah, A. ; Zainal, Z .& Hussein, M. (2010). Photocatalytic Degradation of 2,4-dichlorophenol in Irradiated Aqueous ZnO Suspension, *International Journal of Chemistry*, Vol. 2*, No. 1,* pp.180-193.
11. Glaze, W.; Kang. J. & Chapin, D. (1987). The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. *Ozone Sci. and Eng.,* Vol. 9, pp.335-342.
12. Gomes da Silva & Cfaria, J. (2003). Photochemical and Photocatalytic Degradation of an Azo Dye in Aqueous Solution by UV Irradiation. *J. Photochem. Photobiol. A: Chem.*, Vol. 155, pp. 133-143.
13. Hachem, C.; Bocquillon, F.; Zahraa, O. & Bouchy, M.(2001). Decolourization of Textile Industry Wastewater by the Photocatalytic Degradation Process. *Dyes and Pigments*,Vol.49, pp. 117–125.

14. Haque, M. & Muneer, M. (2007). TiO2-mediated Photocatalytic Degradation of a Textile Dye Derivative, Bromothymol Blue, in Aqueous Suspensions, *Dyes and Pigments*, Vol. 75, pp. 443-448.
15. Kormann, C.; Bahnemann, D. & Hoffmann M.(1991). Photolysis of Chloroform and Other Organic Molecules in Aqueous TiO2 Suspensions, *Environ. Sci. Technol.*, Vol. 25, pp. 494-500.
16. Legrini, O.; Oliveros, E. & Braun, A. (1993). Photochemical Processes for Water Treatment, *Chem. Rev.*, Vol. 93, pp. 671-698.