
ASSESSMENT OF PHOTOOXIDATION PROCESS USING DIFFRENT CATALYST IN TEXTILE EFFLUENT

Chavan T.P*., Harshad R. Kakade and S.R.Thorat

*Department of Chemistry, Amolakchand Mahavidyalaya, Yavatmal

School of Environmental and Earth Sciences, North Maharashtra University, Jalgaon

ABSTRACT

In the present investigation, wastewater samples containing acid dye from textile industries were used to remove COD and Colour by using photo-fenton oxidation process in a batch reactor. The result obtained for COD and Colour was rapidly removed during the first 6-9 minutes and that can be reborn at very long operating time due to photo-reduction of ferric ion in the system. The removal of COD and Colour was at the same time, the optimum condition under the study which was undertaken found to be $70\text{mg Fe}^{2+}\text{Xl}^{-1}$, UV power=60W, initial pH=3, $100\text{mg H}_2\text{O}_2\text{Xl}^{-1}$ and 6-9 minutes operating time. The result obtain approximately *i.e.* 50 and 80% of COD and Colour respectively. By employing the photo-fenton oxidation process, in this work we have observed that this process is more suitable for Colour removal than COD. It was also observed that during the treatment process, a small amount of sludge *i.e.* $4.8\text{X}10^{-5}\text{ kg X kg COD}^{-1}$ was generated. The presence of heterogeneous photo-catalyst such as TiO_2 in the structure accelerated the removal percentage of COD and Colour.

Keywords: COD, Colour, Photo-Oxidation Process, TiO_2 and Textile Effluent.

INTRODUCTION:

The textile wastewater is characterized by high content of dyestuff, salts, high COD deriving from additives, suspended solid (SS) and fluctuating pH depending on the process. The conventional process used to treat wastewater from textile industry is chemical precipitation with alum or ferrous sulfate. The drawbacks of this process are the generation of a large volume of sludge leading to the discarding problem, the pollution of chemical substances in the treated wastewater etc. For a more practical application, different processes were developed to treat wastewater from textile industry such as filtration process²⁷, biological process^{5, 10,25}, adsorption process⁶, electrochemical process^{1,19,31,14} and ozone process⁹ etc. The processes of advanced oxidation (AOP) involving corona discharge process (CDP), hydrogen peroxide (H_2O_2), ozone (O_3), and/or Fenton reagent both with and without a source of UV light have been investigated for many years in numerous research centers due to their high reactivity but low selectivity.

The results indicated that a flow stirred tank reactor was more effective than a tubular one and the rate controlling variable in the system was the photon flux. The Fenton process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) was well represented by the first order reaction kinetics. The reaction rate was strongly dependent on temperature, H_2O_2 and FeSO_4 dosages²⁷. Compared with other conventional processes such as electrochemical oxidation, ozone oxidation or hypochlorite oxidation the fenton process was more effective^{28,14} demonstrated that the fenton process was suitable to be used as a decolourization agent whereas the COD was primarily removed by fenton coagulation rather than by fenton oxidation.

In the present investigation, instead of using synthetic wastewater as in many previous works, the treatment of real effluent from a textile plant was carried out here by using the photo-oxidation process. Effects of initial pH, dosage of Fe^{2+} , UV power and dosages of H_2O_2 on the COD and colour removal were carried out in a batch reactor at room temperature.

MATERIAL AND METHODS:

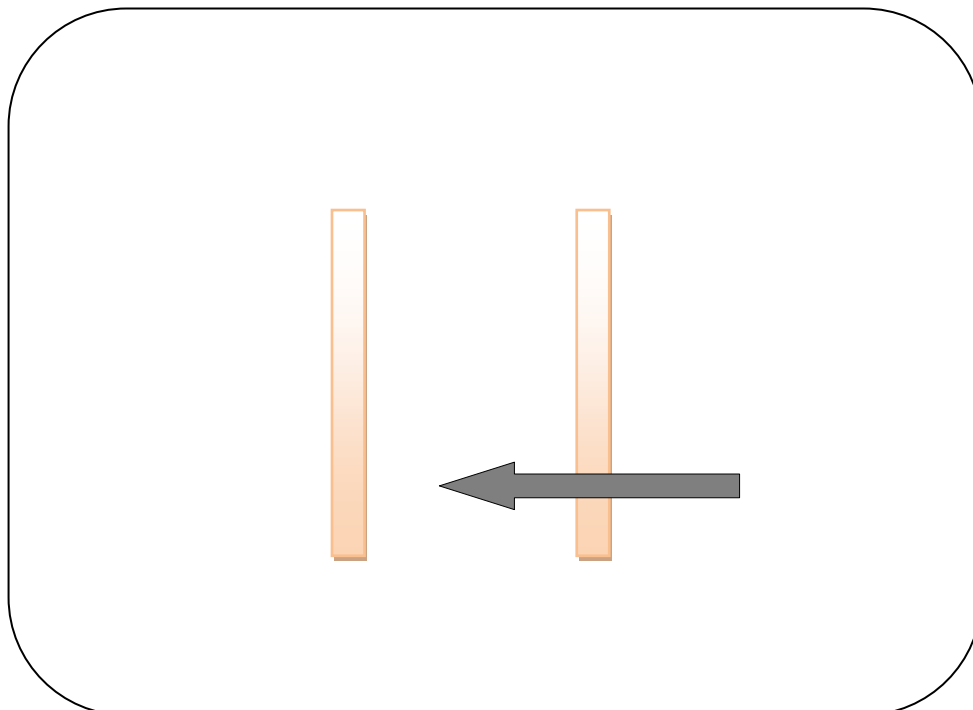
Wastewater samples containing acid dye from a textile plant in Jalgaon were used in this study. The characteristics of the effluent are presented in table 1. In each batch, a glass jar filled with 1 liter of wastewater placed in the middle of the UV-protected box having a dimension of $0.68 \times 0.68 \times 0.78 \text{ m}^3$ and surrounded by 2 UV lamps (30 W) as shown in Figure 1. The solution was agitated by using a stirrer at 420 rpm to achieve a complete mixing. As the experiment progressed, 20 ml of sample were collected at different time intervals to measure the COD and colour. Prior to chemical analysis, the sample was adjusted to pH value above 11 by using 12 M NaOH to terminate the reaction and then readjusted to pH value of 4. For all experiments, the operating time was fixed at 60 minutes. The data reported in this experiment were the average values obtained from the duplicate of experiments and the acceptable error in this work was 3%. The results obtained from the study has been presented in graphical way.

RESULTS AND DISCUSSION:

Generally the effluents characteristics need to be properly monitored for better environmental protection. Though all the textile industry had their effluent temperatures between 26°C and 35.7°C as shown in table 1. The pH range (10 – 11.5) calls for more attention. These textile wastewater is fundamental in character. Though the total suspended solids levels in the effluent is also high, Both measured BOD and COD levels also exceed the set limit by central pollution control board in India (as per National Environmental Quality Standards). Nutrients and micro-nutrients (nitrate, iron, calcium and manganese) were all below the limit. With the exception of copper, heavy metals

concentrations were below the set limits in the effluents of textile industry which is quoted in table 2. Copper levels were 2.10mg/l which is above the permissible limit. Chromium and cadmium were not detected in the textile effluents. Manganese ranges from 1.70mg/l, zinc was assess in small fraction *i.e.* 0.40mg/l. Nickel concentration was not detected in the textile effluent which was assessed for certain parameters and to know the value of textile dyeing effluent, so that we can used this wastewater for further process to carry out experiments for reduction of COD and removal of colour using UV, H₂O₂, Fe²⁺ catalyst by photo-oxidation process.

Figure 1 shows the experimental set-up of the photo-fenton oxidation process which includes a UV box as at the left side. UV lamp was fitted at right side of the pilot plant. The stirrer was fitted at the middle of the equipment and the sample port was fixed to pour the sample in reactor. The pilot bioreactor was assembled to reduced the pollution load of colour and COD but the results obtained was not satisfactory for COD reduction hence, the work on treatment of textile dyeing effluent was limited up to colour level. Use of heterogeneous catalyst such as TiO₂ can expedite the removal of COD and colour from textile effluent and it can be reused in the system by using a simple filtration. By applying the oxidation process with photo-fenton was found that this process is more suitable for removal of colour than COD.



The effect of initial pH of the solution was investigated in acidic solution from pH = 1 to pH = 7 with 100 mg H₂O₂×l⁻¹, 20 mg Fe²⁺×l⁻¹, 60 W UV power. The removal of colour occurred rapidly and reached the maximum point, around 76-80%, at the initial pH = 3-5 within 5 minutes as shown in G -1. On the

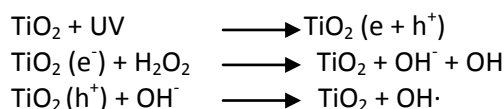
contrary, the COD reached the maximum removal, around 23-36%, within 5-10 minutes at the initial pH between 1 & 3 and remained constant after 20 minutes. In neutral condition (pH = 7), the removal percentage was reduced because the generation of OH· had considerably slowed down due to the decomposition of H₂O₂ to H₂O and O₂. In order to remove the COD and colour simultaneously, the optimum initial pH for treatment of textile wastewater by the Photo-Fenton oxidation process was pH = 1-3 (G-1) and this pH was consistent with some previous works carried out by ^{4,7,23,24,30}

The effect of Fe²⁺ dosage in the Photo-Fenton oxidation process on the treatment of textile wastewater was investigated under different Fe²⁺ dosages (0-100 mg×l⁻¹) and under controlled condition (100 mg H₂O₂×l⁻¹, UV power of 60 W, pH = 3). The sharp removal of COD and colour was observed in the first 5-10 minutes and remained constant as the operating time proceeded as shown in G-2. The results indicated that the removal of colour and COD was maximum *i.e.* 89 and 44% respectively with Fe²⁺ concentration was 80 mg×l⁻¹ whereas less COD removal observe at starting point *i.e.* at 20 mg×l⁻¹ and colour removal at 40 mg×l⁻¹. The increase of Fe²⁺ dosage significantly affected the colour removal but only slightly affected the COD removal. The removal of colour required relatively low Fe²⁺ dosages. However, much higher dosages of Fe²⁺ are necessary to obtain a high level of COD removal because a large amount of Fe²⁺ can promote the formation of OH· through the Fenton reaction. To treat the COD and colour simultaneously, the optimum Fe²⁺ dosage was 80 mg×l⁻¹. The effect of UV light was explored at different UV powers ranging from 0-120 W under the controlled condition of 80 mg Fe²⁺×l⁻¹, 100 mg H₂O₂×l⁻¹, and pH=3. The results shown in G-2 indicated that the removal of COD was strongly observed in the first 5 minutes (20-44%) and remained constant after 10 minutes, while the colour removal of 77-89% progressed rapidly within 5-7 minutes.

G-3 display the removal of COD and colour as a function of UV power in the first 5 minutes. The removal of COD and colour was maximum 48% and 92% respectively in presence of ninety watt. As the UV power increased, the removal of colour increased slightly whereas that of COD did not show considerable change. From the result and quoted in graph, it is clear that to remove COD and colour simultaneously, the optimum UV power used was ninety watt and the colour and COD removal was minimum at 30 W conditions. Use of higher UV power only resulted in slight different removal of COD and colour. G-4 displayed the removal percentage of the COD and colour at different H₂O₂ dosages by using 80 mg Fe²⁺×l⁻¹, 60 W and initial pH of 3. As the H₂O₂ dosages increased from 100 to 250 mg×l⁻¹, the removal percentage of colour increased very slightly from 89% to 92% whereas that of COD increased from 40% at H₂O₂ dosages of 100 mg×l⁻¹ and reached its maximum removal percentages of 53% at H₂O₂ dosages of 250 mg×l⁻¹. Excess H₂O₂ could not achieve a higher percentage of COD removal. Furthermore, it can interfere the measurement of COD. In addition, the

cost of H_2O_2 is expensive. Therefore, in actual operation, the dosage of H_2O_2 should be minimized. According to above results, it seems that the increased amount of H_2O_2 was not enough to remove the COD in wastewater to a level greater than 53% and colour also *i.e.* 92%.

In order to get a higher percentage of COD and colour removal, a large quantity of $\text{OH}\cdot$ radicals in the system should be produced. One way to produce the $\text{OH}\cdot$ radicals is the utilization of heterogeneous photo-catalyst. In this study, TiO_2 was considered as a candidate catalyst because it can accelerate the reaction according to the following reactions.



G-5 shows the results of the COD and colour removal in the presence and absence of TiO_2 by using $100 \text{ mg}\cdot\text{l}^{-1} \text{H}_2\text{O}_2$, $80 \text{ mg}\cdot\text{l}^{-1} \text{Fe}^{2+}$, UV power = 90 W and initial pH = 3. For both with and without TiO_2 , the very rapid removal of COD and colour was observed within the first 5-10 minutes. During this time, in the absence of TiO_2 , the removal of COD and colour was 52% and 85%, respectively. On the other hand, with TiO_2 (7.99 g/l), the COD and colour were removed respectively around 62% and 95%.⁹ The results indicated that the presence of TiO_2 could promote the COD removal by about 16%. It had, however, a slight effect on colour removal.

Figure 2 shows the example of textile wastewater before and after treatment by the Photo-Fenton oxidation process. The colour of wastewater after treatment is clear and not objectionable in comparison with that before treatment. When the treatment process finished, a small amount of sludge was generated ($5.8 \times 10^{-5} \text{ kg} \times \text{kg COD}^{-1}$) compared with the conventional anaerobic process ($0.611 \pm 0.33 \text{ kg} \times \text{kg COD}^{-1}$). This sludge was the $\text{Fe}(\text{OH})_3$ occurring during the process.

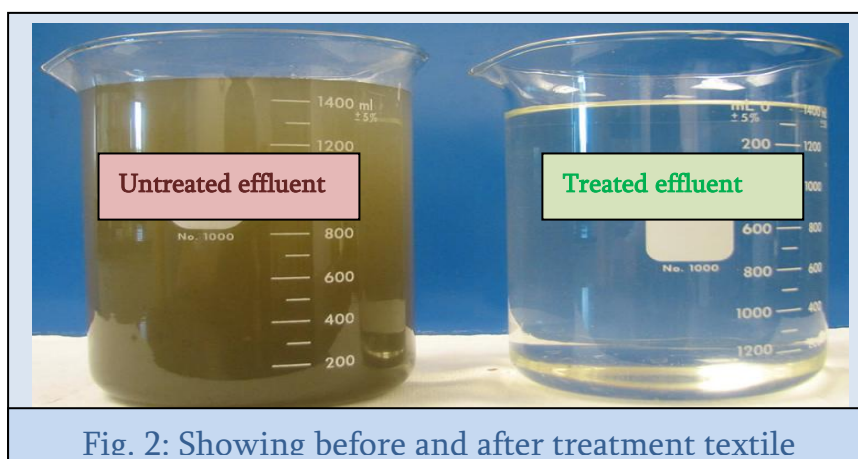


Fig. 2: Showing before and after treatment textile

The cost of this treatment process was not estimated because this work was carried out as a batch-mode reaction at a bench-scale. So, it is difficult to estimate the real treatment cost in this situation. Many investigators have carried out their work in relation to degradation of dyes from wastewater

i.e. ^{2,3,16,20,21,15,14,29,22,18,25,8,11,12,13} and many more have studied the related work on photo-oxidation process for textile effluent.

In the present study, we have carried out the work on treatment of textile wastewater at room temperature in a batch reactor by using the Photo-Fenton oxidation process. The effects of primary pH of the solution (pH = 1-7), ferrous ion concentration (0-100 mg×l⁻¹) and UV power (0-120 W) on chemical oxygen demand (COD) and colour removal were examined. The results showed that this process was enhanced at the acidic pH range. The optimum condition was found to be at pH = 3, 80 mg Fe²⁺×l⁻¹, 5-10 minutes operating time, 60 W UV power and 100 mg H₂O₂×l⁻¹. At this condition, approximately 43% and 84% of COD and colour were removed respectively. During the treatment process, a small amount of sludge (5.8×10⁻⁵ kg × kg COD⁻¹) was generated. The presence of heterogeneous photo-catalyst such as TiO₂ in the system accelerated the removal percentage of COD and colour.

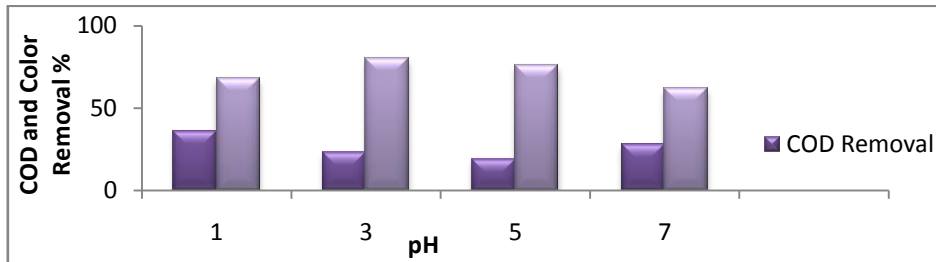
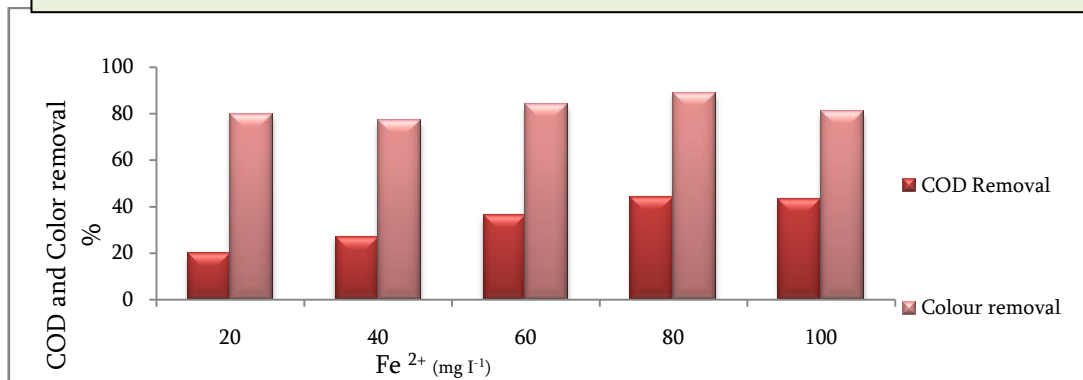
Table 1: Showing characteristics of textile effluent

Sr. No	Characteristics	Units	Values obtained
1	Temperature	⁰ C	35.7
2	pH	pH units	10.3
3	Conductivity	mS x cm ⁻¹	1.98
4	Colour	Pt-Co unit	812
5	Suspended Solids (TSS)	mg/L	240
6	Turbidity	NTU	220
7	BOD ₅	mg O ₂ /L	396
8	COD	mg O ₂ /L	1320
9	Nitrate	mg/L	1.0
10	Phosphate	mg/L	3.42
11	Calcium	mg/L	1.8
12	Magnesium	mg/L	2.42

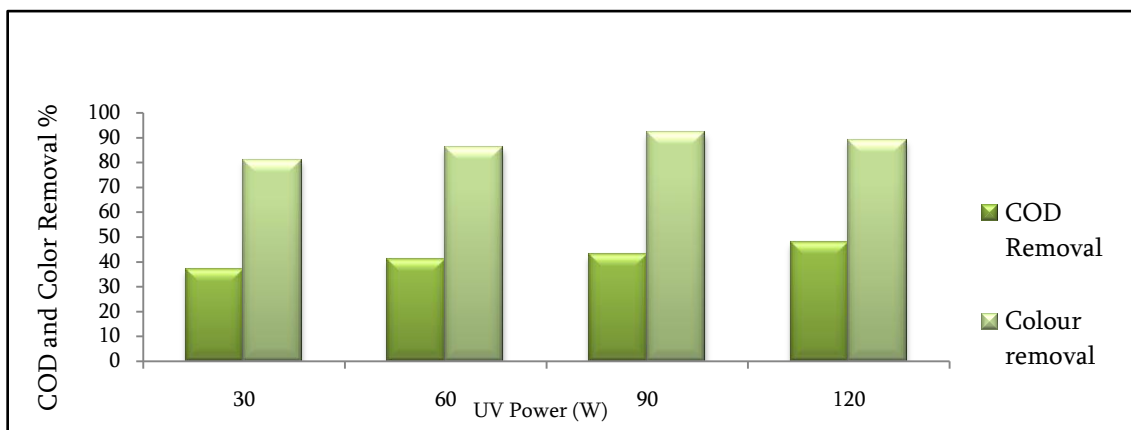
Table 2: Showing heavy metal concentrations in textile effluent

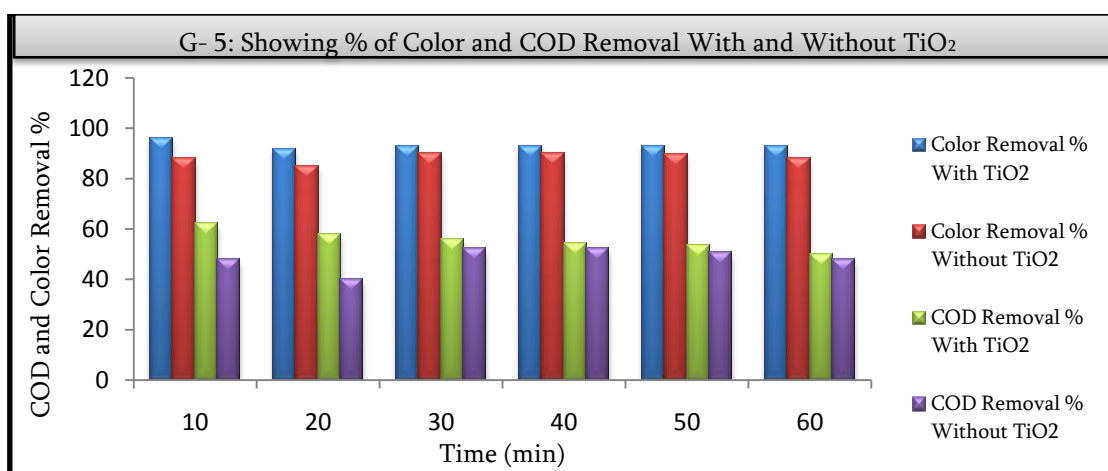
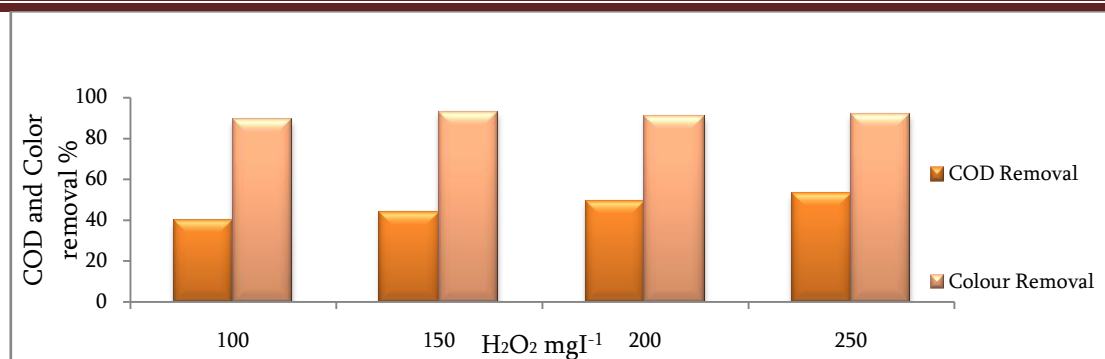
Sr. No	Parameters	Units	Values obtained
1	Aluminum	mg/L	0.11
2	Cadmium	mg/L	ND
3	Chromium	mg/L	ND
4	Copper	mg/L	2.10
5	Nickel	mg/L	ND
6	Zinc	mg/L	0.40
7	Manganese	mg/L	1.70

G – 1: Showing % of COD and colour removal at different pH

G – 2: Showing % removal of COD and Colour at different Fe²⁺ concentration

G – 3: Showing % of COD and colour removal at different UV (W)

G -4: Showing % of COD and colour removal at different H₂O₂ conc.



REFERENCES:

1. Abdo MSE and Al-Ameeri RS: Anodic oxidation of a direct dye in an electrochemical reactor. *J. Environ. Sci. Health* (1987) A 22(1), 27-45.
2. Alinsafi, A., Evenou, F., Abdulkarim, E.M., Pons, M.N., Zahraa, O., Benhammou, A., Yaacoubi, A., Nejmeddine, A.: Treatment of textile industry wastewater by supported photocatalysis. *Dyes and Pigments* (2007) 74, 439– 445.
3. Bahnemann, D.: Photo-catalytic water treatment: solar energy applications. *Sol. Energy* (2004) 77, 445–459
4. Balasaraswathy P.: Paper presented in National conference of Indian association of Dermatology. *Sunlight in India*. (2004)
5. Banat IM, Nigam P, Singh D and Marchant R: Microbial decolorization of textile dye-containing effluents: A review. *Bioresour Technol.* (1996) 58, 217-27.

6. Barlas H and Akgun T: Color removal from the textile wastewaters by adsorption Techniques. Fresenius Environmental Bulletin 9(9-10), 597-602 Venceslau PC, Tom S, and Simon JJ (1994): Characterization of textile wastewater. Environ. Technol. (2000) 15, 917-29.
7. Bhatkhande, D.S., V.G. Pangarkar, A.C.M. Beenackers,: Photo-catalytic degradation for environmental applications - A Review. J. Chem. Technol. & Biotech., (2002) 77(1)102-116.
8. Chakrabarti, S., B.K. Dutta,: Photo-catalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. J. Haz. Mat. B, (2004) 112, 269-278.
9. Chantanapha Sahunin, Jittima Kaewboran and Mali Hunsom,: Oxidation using UV/H₂O₂/Fe²⁺ Reagents. Science Asia 32 (2006): 181-186
10. Desai ID and Bhardwaj IS: Recent biotechnological trends in industrial effluent treatment. Biotech Consortium India Ltd., New Delhi. (1995)
11. Gopalakrishnan, A.N., V. Mohan,: Solar photo sensitizer technology for dyeing waste reclamation. Indian J. Environmental Protection, (1997) 17, 268-271.
12. Goswami, D.Y.,: A review of engineering developments of aqueous phase solar photo-catalytic detoxification and disinfection processes. J. Sol. Energy Engg., (1997) 119, 101-107.
13. Gupta, A.K., A. Pal, C. Sahoo,: Photo-catalytic degradation of a mixture of Crystal Violet (Basic Violet 3) and Methyl Red dye in aqueous suspensions using Ag⁺ doped TiO₂. Dyes and Pigments, (2006) 69 (3), 224-232.
14. Kang SF, Liao CH and Chen MC: Pre-oxidation and coagulation of textile wastewater by the Fenton process. Chemosphere (2002) 46(6), 923-28.
15. Los L and Perkowski J: Decoloration of real textile wastewater with advanced oxidation processes. Fibers Text East Eur (2003) 11(4), 81-5.
16. Malato, S., Blanco, J., Vidal, A., Richter, C.: Photo-catalysis with solar energy at a pilot-plant scale: an overview. Appl. Catal. B – Environ. (2002) 37, 1–15.
17. Mendonca NM, Niciura CL, Gianotti EP and Campos JR: Full scale fluidized bed anaerobic reactor for domestic wastewater treatment: performance, sludge production and biofilm. Water Sci Technol (2004) 49 (11-12) 319- 25.
18. Mendonca NM, Niciura CL, Gianotti EP and Campos JR: Full scale fluidized bed anaerobic reactor for domestic wastewater treatment: performance, sludge production and biofilm. Water Sci Technol (2004) 49 (11-12) 319- 25
19. Naumczyk L, Szpyrkowicz L and Zilio-Grandi F.: Electrochemical treatment of textile wastewater. Water Science and Technology (1996) 34 (11), 17-24.
20. Neelavannan, M.G., Ahmed Basha, C.,: Electrochemical-assisted photocatalytic degradation of textile washwater. Sep. Purif. Technol. (2008) 61, 168–174.

21. Nigam, P., Banat, I.M., Singh, D., Marchant, R.,: Microbial process for the decolorization of textile effluent containing azo, diazo and reactive dyes. *Process Biochem.* (1996) 31, 435–442
22. Parra, S., V. Sarria, S. Malato, P. Peringer, C. Pulgarin,: Photochemical versus coupled photochemical-biological flow system for the treatment of two bio-recalcitrant herbicides: metobromuron and isoproturon. *Appl. Catal. B: Environ.*, (2000) 27, 153-168.
23. Peral, J., J. Munoz, X. Domenech,: Photosensitized CN– oxidation over TiO₂. *J. Photochem. Photobiol. A: Chem.*, (1990) 55, 251-25.
24. Saquib, M., M. Muneer,: Semiconductor mediated photocatalyzed degradation of an anthraquinone dye, Remazol Brilliant Blue R under sunlight and artificial light source. *Dyes and Pigments*, (2002) 53, 237-249.
25. Shah SS Desai JD, Ramakrishna C, and Bhatt NM: Aerobic bio-treatment of wastewater from dimethyl terephthalate plant using biomass support particles. *J. Ferment. Bioeng* (1998) 86, 215-9.
26. Sheng HL and Cho CL: Fenton process for treatment of desizing wastewater. *Water Res.* (1997) 31(8), 2050-56.
27. Sójka-L J, Koprowski T, Machnowski W and Knudsen HH: Membrane filtration of textile dyehouse wastewater for technological water reuse. *Desalination* (1998) 119, 1-9.
28. Szpyrkowicz L, Juzzolino C and Kaul SN: A Comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent. *Water Res.* (2001) 35(9), 2129-36.
29. Tang WH and An H: UV/TiO₂ Photo-catalytic oxidation of commercial dye in aqueous solution. *Chemosphere* (1995) 31, 4157-70.
30. Theron, P., P. Pichat, C. Guillard, C. Petrier, T. Chopin,: Degradation of phenyltrifluoromethylketone in water by separate or simultaneous use of TiO₂ photocatalysis and 30 or 515 KHz ultrasound. *Phys. Chem. Chem. Phys.*, (1999) 1(19)4663-4668.
31. Vlyssides AG and Israilides CJ: Electrochemical oxidation of a textile dye and finishing wastewater using Pt/ Ti electrode. *J. Environ, Sci. Health* (1998) A33 (5), 847-62.
