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PHOTOCATALYTIC TREATMENT OF TEXTILE INDUSTRY EFFLUENT HAVING DYES USING SOME COMPOSITE SEMICONDUCTORS

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ABSTRACT

In this research, the photocatalytic degradation of textile wastewater from Bhilwara textile industry in Rajasthan, India, using composite TiO_2 and ZnO with different ratio as photocatalysts was investigated. The experiments were carried out at 36^{o}C in a stirrer bath reactor by using Ultra-Violet photo oxidation process. The effect of pH, time, amount of catalyst and ratio of composite TiO_2 and ZnO was investigated and the optimized conditions for maximum amount of degradation were determined. The progress of reaction was observed spectrophotometrically. Titanium dioxide and zinc oxide proved to be very effective catalysts in photocatalytic degradation of real textile industrial water. The maximum decolorization achieved was 88 by using composite TiO_2 and ZnO 1gm/l with (90:10) ratio at 36^{o}C and pH of 8.5, within 180 minutes of irradiations. The results indicate that for real textile wastewater, composite TiO_2 and ZnO (90:10) ratio is comparatively more effective than only TiO_2 or only ZnO. This study proves that real textile wastewater reacts differently to catalysts than aqueous solution of azo-dyes, which is associated with surface steps and sensitization of the reaction rate by presence of other contaminants in real textile wastewater.

KEYWORDS: Photocatalytic degradation, Wastewater treatment, Ultra Violet light, Textile industry, Titanium dioxide, Zinc oxide.

INTRODUCTION

In India most textile, leather and other industries are facing shortage of water. The treated water may be recycled or reused in other applications in other industries that require low quality water. Hence recycling of water is considered an excellent approach for saving huge volume of water. It is known that textile industries discharge large volumes of toxic and non-biodegradable wastewater. The textile effluent is mostly composed of colored commercial dyes, chemicals and pigments. Many commercial dyes and pigments, under commercial names are used worldwide by textile and other industries. The textile effluent containing these dyes and pigments releases toxic substances into aqueous phase and poses environmental concerns. The most common classes of commercial dyes are azo dyes, Vat dyes, Reactive Dyes. Most of the reported studies are on aqueous solution of the dyes prepared in labs and only a few studies are done on real textile industries waste water. Still not enough is known about effectiveness of semiconductors like TiO_2, ZnO, H_2O_2, SnO_2, CdS or their combine effect on real textile wastewater. The real textile wastewater is the result of use of dyes commonly used for dyeing cotton, silk, viscose, flex, wool, jute and polyester.

Bhilwara, Rajasthan India has more than 300 textile manufacturing units which export their production to whole world. This region is called Indian textile town which constitutes many dyeing and bleaching units. Bhilwara serves as one of the major exporters of textiles and is the second largest producer of polyester fiber in India.[1] Textile dyes are main source of coloured organic compounds in water bodies. During dye production and textile manufacturing process a large quantity of waste water containing tons of organic dyes and heavy metal (lead, Chromium, Iron and Zinc) are being discharged into water bodies every year. Due to this colored waste water, quality of drinking, domestic and agricultural water in this region is not safe because water is contaminated with high levels of chlorides and fluorides. Agriculture practices of villages located downstream of textile processing unit are seriously affected.[2] The physiochemical methods to treat textile industry effluents are very difficult and also expensive. Therefore, continues the accumulation of large amount of sludge and toxic material in soil which also creates the secondary level of land pollution.[3-4]

The impact of these dyes on the environment is a major concern because of the potentially carcinogenic properties of the chemicals.[5] The wastewater which is coloured in the presence of these dyes and chemicals can block both sunlight penetration and oxygen dissolution that are very essential for aquatic life.[6] Consequently, there is a considerable need to treat these coloured effluents before discharging them into various water bodies. Various approaches on handling and decontaminating such effluents have been reported in the literature. Typical techniques include the classical methods such as adsorption[7], coagulation, ion flotation, sedimentation and others. Moreover the cost effectiveness and ease in synthesis, azo dyes are much more used in textile industries compared to natural dyes. Usually dyes are aromatic and heterocyclic compounds and are poisonous and carcinogenic especially azo dyes.[8-9] Azo bonds (N=N) present in these compounds are opposed to break, with the potential for the determination and accumulation in the environment.[10] Therefore, degradation of dyes by conventional methods is very difficult.[11] Other alternative method is being required to minimize the costs of treatment of effluents discharge.[12]

The photocatalysis reaction effective for the degradation of various organic and toxic impurities in waste water; however, its practical application as slurry type suspensions is limited due to the difficulty in separating the catalysts particles after the photocatalytic reaction.[13-15] Xiaobo and Samuel reviewed the broad applications of titanium dioxide as a photocatalysts.[16] These applications were comprised of photodecomposition of various industrial pollutants.[17] Semiconductor catalysts TiO_2 and ZnO have been widely used to mineralize toxic organic pollutants in wastewater into less damaging inorganic nontoxic compounds.[18] Several studies have been carried out for decolorization of industrial wastewater by using photocatalysis and bacteria treatment.[19-20] The elimination of color from wastewaters is more necessary than the removal of other colorless organic compounds.[21] Because of aesthetic and environmental concerns the decolorization of effluent from textile dyeing and finishing industry has given most importance.[22,23]

TiO_2/ZnO photocatalysis, in the presence of UV irradiation can fragment the pollutant dyes into non-toxic simple compounds like CO_2, HCl and water.[24] Nanosized TiO_2, ZnO and other photocatalysts in the form of nanorods, nanospheres, thin porous films, nanofibers and nanowires have been utilized in various applications, including photocatalysis because of their high activity, low cost and environmental safety.[25-27] Interestingly, very high surface to volume ratio of nanostructures make them efficient for photocatalysis and other application. Various studies have focused on treatment of industrial wastewater using different treatment methods; however, most of these treatments have difficulty in realistic uses.[28,29] In recent year, investigation on different systems have been carried out, such as, advanced oxidation processes (AOP), ozonation, sonolysis, gamma–radiolysis, electro-coagulation, H_2O_2/ UV, photocatalysis, photo-Fenton, biological and combined anaerobic–photocatalytic treatment. Photocatalytic oxidation processes, which involve the generation of highly reactive hydroxyl radical (HO), have emerged as a promising water and wastewater treatment technology for the degradation of organic contaminants. The photoactivated reactions are characterized by the free radical mechanism initiated by the interaction of photons of a proper energy level with the catalyst (TiO_2, ZnO semiconductor catalysts). The efficiency of a photocatalytic system is also affected by the form of TiO_2 and ZnO nanoparticle catalysts used as immobilized on surface or as colloidal suspension. Several researches proved that the recombination is prohibited by semiconductor-metal composites or by employing two different semiconductors. When a composite is prepared with a wider band gap semiconductor, which has more positive conduction band edge than that of the smaller band gap semiconductor, then the electrons from smaller band gap semiconductor can be injected into the larger band gap semi-conductor, that coupling can effectively prevent the recombination.

The main challenge for the textile industry today is 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. This study explores the possibility of using UV and solar radiations for treating textile effluent by photocatalytic reduction. Various operational parameters affecting the reduction such as effluent concentration, catalyst concentration, ratio of catalyst (TiO_2 and ZnO with different ratio), pH and optimum time will investigate. The catalyst itself is unchanged during the process. Additionally micro amounts of reagent will sufficient to carry out the process. Due to these advantages the process result in considerable saving in the water, production cost and keeping the environment clean.

MATERIALS AND METHODS

For the present study of Photocatalytic Treatment of Textile Industry Effluent having dyes and pigments Using Composite semiconductor TiO_2 and ZnO with different ratio, Bhilwara industrial area, Rajasthan is selected. Water Samples were collect from the source point outlet of finishing unit at Bhilwara industrial area. Standard procedure (spot sampling) was followed during sampling. All the samples of the effluent were collect in sterilized, dry and properly stopper polypropylene bottles. Temperature of the effluent was determine at the spots, whereas, the rest of physiochemical parameters pH and electrical conductivity (EC), Total Dissolved Solids (TDS), Hardness and Chloride were determined after bringing the samples in research lab.

PROCEDURE AND ANALYSIS

To carry out the photochemical reaction 200 ml of waste water effluent solution of desired concentration was taken in 250 ml round bottom flask. The mixture was then irradiated under UV light using 2 x 200 W Tungsten lamps (Sylvania Laxman) and solar light to provide energy to excite composite TiO_2 and ZnO loading. To ensure thorough mixing of catalyst, oxygen was continuously bubbled with the help of aerator. A water filter was used to cut off thermal radiation. The pH was measured with pH meter (Systronics, 106). All the experiments were performed at 36^oC.

About 3 ml aliquot of the solution was withdrawn after a specific time interval and its absorbance was measured using spectrophotometer (Schimadzu, UV-1700 pharmaspec) at 561 nm after filtered through Millipore filter of 0.45 um. The rate of decrease of color with time was continuously monitored. The rate of degradation was calculated in terms of changes in absorption spectra. The degradation efficiency (%) was calculated as:

Degradation efficiency (%) = (Co – C)/ Co x100

Where Co is the initial concentration of contaminants in the sample wastewater and C is the concentration after photo irradiation.

RESULTS AND DISCUSSION

Control experiments (in absence of photocatalyst, light) confirm the necessity of photocatalyst, light to follow the photocatalytic path for the Degradation of dyes and pigments. The photocatalytic degradation of Textile Industry Effluent having dyes and pigments was observed at 561 nm. The optimum conditions for the degradation were pH = 8.5, TiO_2 and ZnO = 1 gm/l, TiO_2 and ZnO ratio 90:10, Time = 180 Minutes.

It was observed that absorbance (Abs.) decreases with the increase in time of irradiation indicating that the dye is degraded on irradiation. The effect of variation in various reaction parameters has been studied e.g. pH, concentration of the TiO_2 and ZnO, Ratio of TiO_2 and ZnO, Time etc under UV and Solar irradiation.

Effect of variation in amount of catalyst

The amount of semiconductor TiO_2 and ZnO powder affects the process of degradation of Textile Industry Effluent having dyes and pigments. Keeping all other factors identical, the concentration of catalyst was changed from 0.0, 0.2, 0.5, 1.0, to 2 gm/l. It was observed that the degradation increases with increasing catalyst level up to 1.0 gm/l and beyond this, degradation becomes almost constant (Fig. 1).

This may be due to the fact that, initially the increase in the amount of catalyst increases the number of active sites on the surface that in turn increases the number of •OH and O2 •− radicals. As a result the rate of degradation is increased. Above a certain level (saturation point) the number of substrate molecules is not sufficient to fill the active sites of semiconductor powder and increase in turbidity of solution reduces the light transmission through the solution. Hence, further addition of catalyst does not lead to the enhancement of the degradation rate and it remains constant.

Table: 1 Effect of Catalyst (composite TiO_2 and ZnO) amount variation.

TiO2 and ZnO Amount Variation			
Composite Catalyst ratio 90:10 ,pH 8.5 , Time 150 Minutes			
S. No.	Catalyst gm/l	Degradation % Under UV	Degradation % Under Solar
1	0 gm/l	21%	19%
2	0.2 gm/l	76%	65%
3	0.5 gm/l	82%	69%
4	1 gm/l	88%	77%
5	2 gm/l	85%	74%

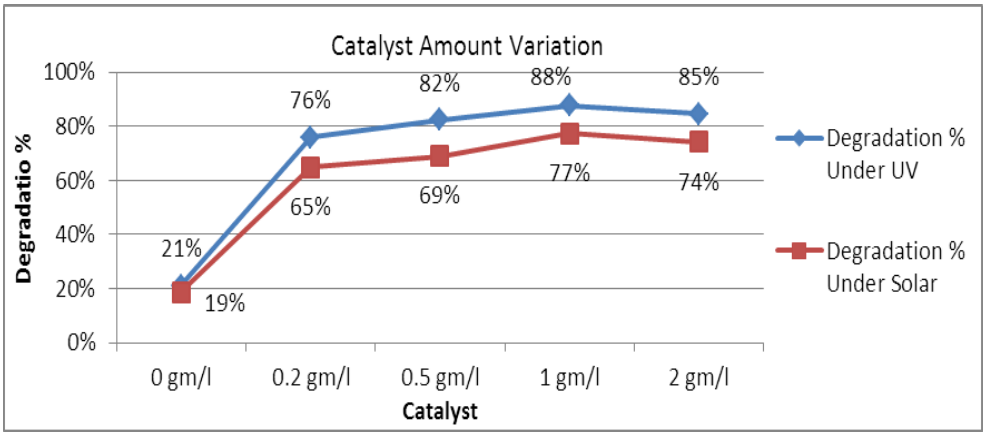

Fig: 1 Effect of Catalyst (composite TiO_2 and ZnO) amount variation.

Effect of variation in ratio of catalyst

The ratio of composite semiconductor TiO_2 and ZnO powder affects the photocatalytic degradation of Textile Industry Effluent having dyes and pigments. Keeping all other factors identical, the ration of catalyst was changed from 100:00, 90:10, 80:20, 50:50 and 00:100. It was observed that the degradation increases with increasing catalyst ratio up to 90:10 and beyond this, degradation becomes decrease (Fig. 2).

Table: 2 Effect of TiO_2 and ZnO Ratio variation.

TiO2 and ZnO Ratio Variation			
Composite Catalyst amount 1.0 g/l ,pH 8.5 , Time 150 Minutes			
S. No.	**TiO2 and ZnO Ratio**	**Degradation % Under UV**	**Degradation % Under Solar**
1	T:Z '100:00	84%	72%
2	T:Z '90:10	88%	77%
3	T:Z '80:20	82%	75%
4	T:Z '50:50	78%	72%
5	T:Z '00:100	75%	70%

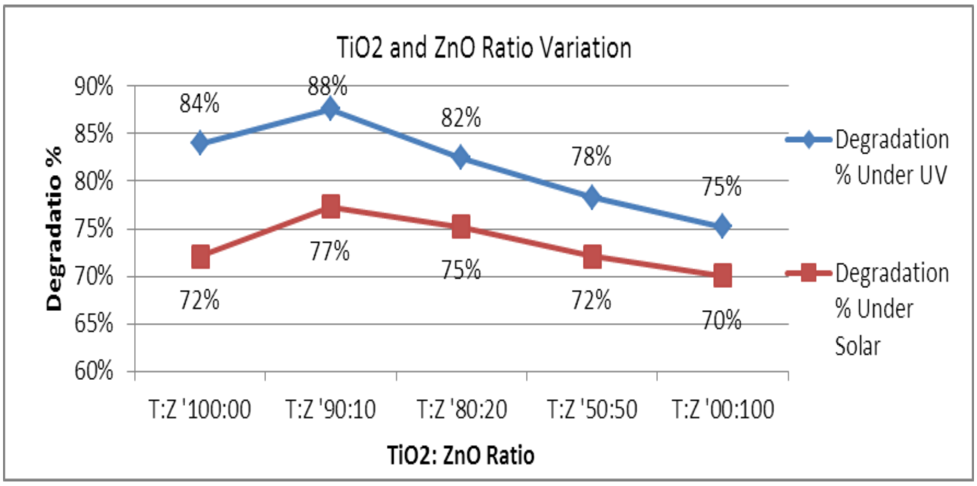

Fig: 2 Effect of TiO_2 and ZnO Ratio variation.

Effect of variation in pH

The pH of the reaction medium has a significant effect on the surface properties of composite semiconductor TiO2 and ZnO (90:10 ratios) catalyst. The effect of pH on photocatalytic degradation of Textile Industry Effluent having dyes and pigments with semiconductor TiO2 and ZnO (90:10 ratios) was investigated in the pH range of 7.0, 7.5, 8.0, 8.5 and 9.0 under visible light source.

It was observed that the photocatalytic degradation of Textile Industry Effluent increases with an increase in pH up to 8.5. This observation can be explained on the basis that as the pH of solution increases, more OH- ions are available. These OH- ions will generate more •OH radicals by combining with the positive holes of the semiconductor. These hydroxyl radicals are responsible for degradation of dye. After a certain pH value i.e. above pH 8.5 the rate of degradation of dye decreases due to columbic repulsion between the negatively charged surface of photocatalyst and hydroxide anions. This fact could prevent the formation of hydroxyl radicals. This results into a decrease in rate of photocatalytic degradation of dye.

Table: 1 Effect of pH variation.

pH Variation			
Composite Catalyst ratio 90:10, Amount 1.0 g/l, Time 150 Minutes			
S. No.	pH	Degradation % Under UV	Degradation % Under Solar
1	pH 7	79%	70%
2	pH 7.5	81%	72%
3	pH 8	83%	74%
4	pH 8.5	88%	77%
5	pH 9	82%	73%

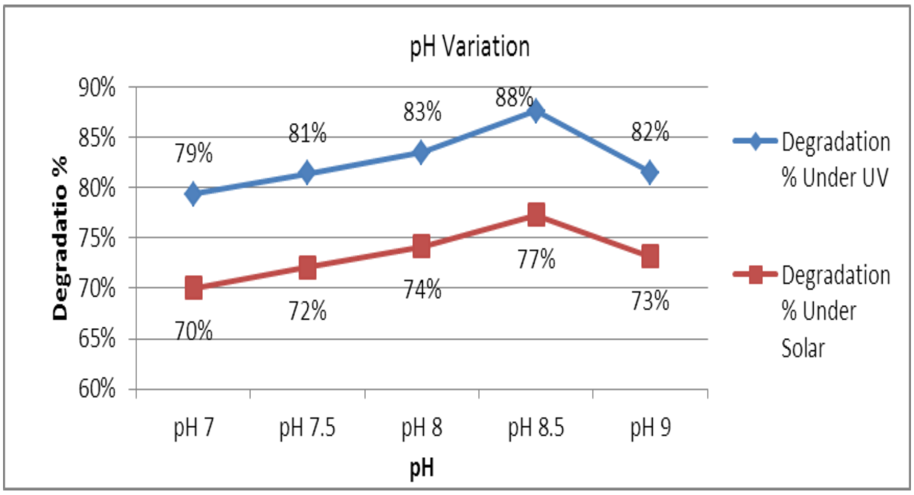

Fig: 3 Effect of pH variation.

Effect of variation in Time

The variation in time affects the photocatalytic degradation of Textile Industry Effluent having dyes and pigments. Keeping all other factors identical, irradiation time was changed from 30 to 180 Minutes. It was observed that the degradation increases with increasing time up to 180 minutes and beyond this, degradation becomes decrease.

Table: 4 Effect of Time Variation.

Effect of Time Variation in UV and solar Irradiation		
Catalyst 1.0 gm/l, Ratio 90:10, pH 8.5		
Time	Degradation % Under UV	Degradation % Under Solar
0	0%	0%
30	30%	24%
60	44%	33%
90	58%	43%
120	73%	54%
150	87%	68%
180	88%	73%

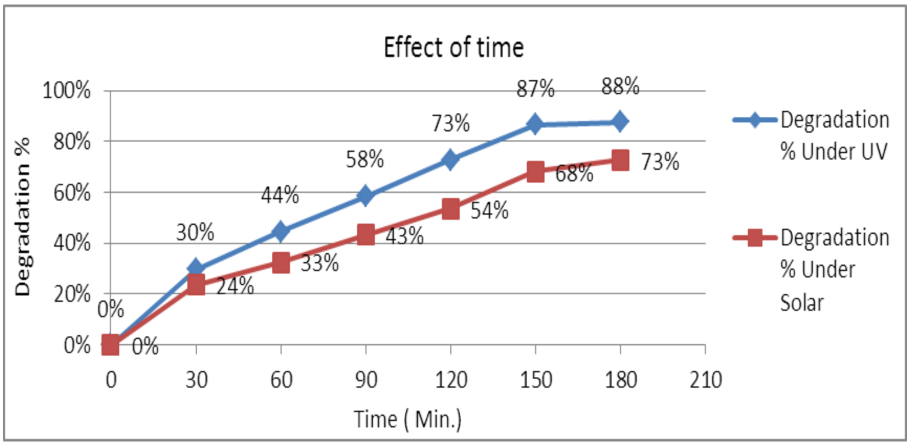

Fig: 4 Effect of Time Variation.

Effect of variation in Na_2CO_3

The Comparison study carried out between UV and Solar irradiation on the degradation of the Textile Industry Effluent by adding increasing amount of sodium carbonate. It reveals that the degradation percentage of the effluent gradually decreases with increasing carbonate ion concentration.

Table: 5 Effect of variation in Time Na_2CO_3.

Na_2CO_3 Variation			
S. No.	**Na_2CO_3**	**Degradation % Under UV**	**Degradation % Under Solar**
1	0 gm/l	88%	77%
2	100 gm/l	75%	69%
3	200 gm/l	68%	63%
4	300 gm/l	56%	51%
5	400 gm/l	48%	42%

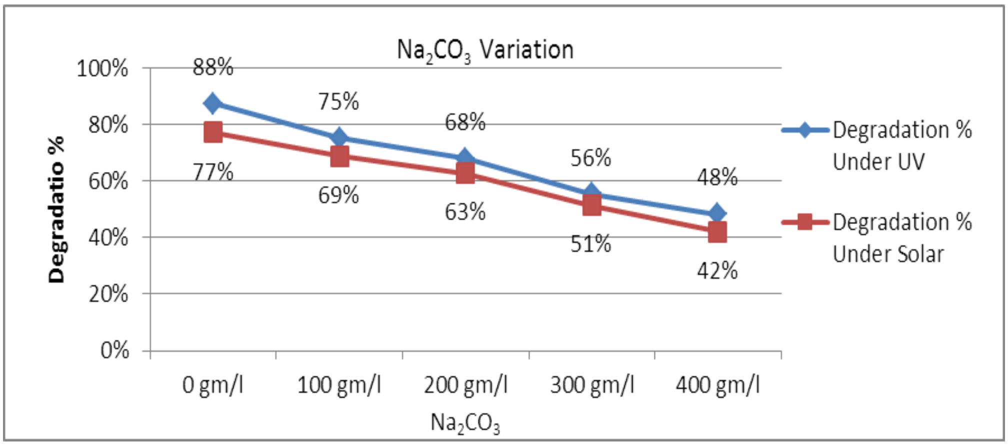

Fig: 5 Effect of variation in Na_2CO_3.

Effect of NaCl variation

Experiments were carried out by adding varying amount of NaCl to effluent solution containing 1 g/L of composite TiO2 and ZnO 90:10 ratios under UV and solar irradiation to determine the influence of NaCl. The degradation percentage of the Textile Industry Effluent decreased with increase in the amount of chloride ion.

Table: 6 Effect of variation in NaCl.

NaCl Variation			
S. No.	**NaCl**	**Degradation % Under UV**	**Degradation % Under Solar**
1	0 gm/l	88%	77%
2	100 gm/l	77%	71%
3	200 gm/l	70%	65%
4	300 gm/l	58%	52%
5	400 gm/l	52%	45%

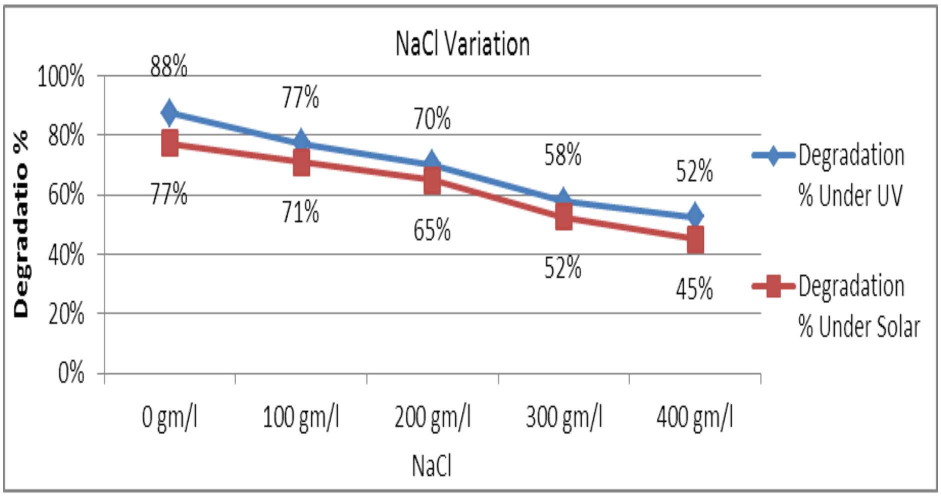

Fig: 6 Effect of variation in NaCl.

CONCLUSION

The results of the present study show that heterogeneous photocatalytic degradation of Textile Industry Effluent can be efficiently carried out using composite semiconductor TiO2 and ZnO (90:10 ratios) under UV irradiation. It is observed that adsorption plays an important role in the photodegradation of the dye. The degradation rate depends upon the process parameters like catalyst concentration, Ratio, Time and pH. The optimum catalyst dose for the degradation of solution is 1.0 g/L of composite semiconductor TiO2 and ZnO (90:10 ratios) at 8.5 pH. The addition the presence of Na2CO3 and NaCl decreases the reaction rate.

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BIBLIOGRAPHY

1. SK Bhagat; Tiyasha, Int. J. of Chem. Tech Research, 2013; 5(3): 1289–1298.
2. BS Chauhan; SK Sagar, In Biological Forum: An International Journal, 2013; 5(1): 113–123.
3. P Anjali; S Poonam; I Leela, Int. Biodeterior Biodegradation, 2007; 59: 73-84.
4. IM Banat; P Nigam; D Singh; R Marchant, Bioresour. Technol., 1996; 58: 217–227.
5. S. Parsons, "Advanced Oxidation Processes for Water and Wastewater," IWA Publishing, London, 2004.
6. M. Zubair Alam, S. Ahmad, A. Malik and M. Ahmad, "Mut- agenicity and Genotoxicity of Tannery Effluents Used for Irrigation at Kanpur, India," Ecotoxicology and Environ- mental Safety, 2010; 73(7): 1620-1628.
7. N. Nasuha, B. H. Hameed and A. T. M. Din, Journal of Hazardous Materials, 2010; 175: No. 1-3, pp. 126-132.
8. B Vyas; HP Molitoris, Appl Environ Microbiol. 1995; 61: 3919–3927.
9. HM Pinherio; E Touraud; O Tomas, Dyes and Pigments, 2004; 61: 121–39.
10. TA Mahdavi; T Donnelly; GK Anderson, Water Res., 2001; 35: 425–432.
11. D Wesenberg; F Buchon; SN Agathos. Biotechnol Lett., 2002; 24: 989–993.
12. R Nagarathnamma; P Bajpai; PK Bajpai, Process Biochemistry, 1999; 34: 939–948.
13. Sabin F, Türk T, Vogler A. (1992) -Acta Hydrochimica Et Hydrobilogica, 25(3): 163-7.
14. Mehrvar M, Anderson WA, Moo-Young M. (2001). International Journal of Photoenergy, 3: 187-91.
15. Khezrianjoo S, Revanasiddappa H. (2012). Chemical Sciences Journal 2012(CSJ-85); 1-7.
16. Chen X, Mao SS. (2007) Chemical Reviews, 107(7): 2891-959.
17. Attia AJ, Kadhim SH, Hussen FH. (2008). E Journal of Chemistry, 5(2): 219-23.
18. Akpan UG, Hameed BH. (2009): A review. Journal of Hazardous Materials, 170(2-3): 520-9.
19. Hussen FH, Abass TA. (2010). International Journal of Chemical Science, 8(3): 1353-64.

20. Asad S, Amoozegar MA, Pourbabaee AA, Sarbolouki MN, Dastghei SMM. (2007). Bioresource Technology, 98(11): 2082-8.
21. Ndasi NP, Augustin M, Bosco TJ. (2011). International Journal of Environmental Sciences, 1(7): 1403-19.
22. Elahee K. (2010): lessons from developing economies Journal of Energy in Southern Africa, 21(3): 9-15.
23. M. RK, K.S. (2010). International Journal on Applied Bioengineering, 4(1): 25-33.
24. Singh P, Mondal K, Sharma A. (2013). Journal of Colloid and Interface Science, 394: 208-15.
25. Hoffmann MR, Martin ST, Choi W, Bahnemannt DW. (1995) Environmental Applications of Semiconductor Photocatalysis. Chemical Reviews, 95(1): 69-96.
26. Meng Z, Juan Z. (2008). Global Environmental Policy in Japan, 12: 1-9.
27. Hernandez-Alonso MD, Fresno F, Suareza S, Coronado JM. (2009). Energy & Environmental Science, 2(12): 1231-57.
28. Vandevivere PC, Bianchi R, Verstraete W. (1998). Journal of Chemical Technology and Biotechnology, 72(4): 289-302.
29. Chan YJ, Chong MF, Law CL, Hassell DG.(2009) Chemical Engineering Journal, 155(1-2): 1-18.