International Journal of Recent Research and Review, Vol. VI, Issue 2, September 2013
ISSN 2277 – 8322

Photocatalytic Treatment of Textile Industry Effluent Using Titanium Oxide

Sharmila Pokharna[1], Rupali Shrivastava[2]
[1]*Department of Chemistry, Anand International College of Engineering and Technology, Jaipur, Rajasthan, India,*
[2]*Department of Chemistry, Rajdhani Engineering College, Jaipur, Rajasthan, India.*
E-mail: sharmilapokharna@gmail.com,rupaliargal@rediffmail.com

***Abstract* - The textile industry consumes large quantity of water and produces large volume of wastewater from printing and dyeing units which is rich in color, containing residues of reactive dyes and chemicals, and requires proper treatment before being released into the environment. Released colored organic compounds in effluent contaminate the water and are source of non-aesthetic pollution and eutrophication. In the present paper a laboratory experiment have been performed to investigate photocatalytic decolouration by using TiO_2 photocatalyst for treating textile effluent. Various operational parameters such as catalyst concentration, pH and optimum time were investigated in order to study their effect on photoreduction process using TiO_2. Results indicate that the photocatalytic decolouration process can efficiently treat textile effluent and reduce the levels of BOD , COD, turbidity, TDS and alkalinity. Experimental runs can be used to identify the operational parameters to perform wastewater degradation on large scale for recycling purpose.**

***Keywords*- Photo reduction, titanium oxide, textile effluent.**

I. INTRODUCTION

Production of dyestuffs and pigments in India is close to 80,000 tones. The textile industry accounts for the largest consumption of dyestuffs, at nearly 80% [1]. The Indian textile industries now predominantly use synthetic organic dyes like processing dyes or Cremazoles(orange 3R, brown GR and blue S1) , direct dyes (Violet , congo red, Royal blue and Bordeaux) and reactive dyes [2]. Textile dyes are structurally different molecules themselves with low or no biodegradability. The removal of color is associated with breakup of the conjugated unsaturated bonds in molecules [3]. Thus, many chemical treatment processes have been used extensively to treat textile wastewaters. Biological treatment like Activated sludge process (ASP) and Trickling Filter (TF) requires economy while oxidation ditch, aerated lagoon, stabilization ponds are low cost. These conventional treatment methods do not degrade the effluents upto the limit it can be recycled and also require detection time of several days. However, photocatalytic detoxification is a process where a semiconductor upon adsorption of a photon acts as a catalyst in producing reactive radicals, mainly hydroxtyl radicals, which in turn can oxides organic compounds and totally neutralize them. It completely destroy the organic and inorganic compounds in the water instead of simply removing or displacing them. Since the photocatalytic decolouration process is driven by light, outdoor facilities can be constructed that make use of free sources of energy supplied by the sun. The combination of light and catalysts has proven very effective for water purification. Work has been done in this field by M.K. Pal and K.K. Mazumdar [4] , who carried out photoreduction of ethylene blue in the presence of various organic and bimolecular, spectrophotometrically and potentiometrically. Also, Kang Shyh-Fang *et. al.* [5] treated the textile effluents by H_2O_2/ UV oxidation combined with RO separation for reuse. The use of solar radiation for the photocatalytic oxidation of organic contaminants in waste water is fast developing application. In fact for removal of colour and reduction of chemical oxygen demand (COD) in industrial waste water, photocatalytic oxidation is the only environmentally benign, effective treatment available [6].

The main challenge for the textile industry today is modify production methods, so they are more ecologically friendly at a competitive price, by using safer dyes and chemicals and by reducing cost of effluent treatment/ disposal. This paper explores the feasibility of using solar radiations for treating textile effluent by photocatalytic reduction. Various operational parameters affecting the reduction such as catalyst concentration, pH and optimum time were investigated. The catalyst itself is unchanged during the process. Additionally microamounts of reagent are 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.

II. THEORY OF SOLAR PHOTO REDUCTION

A wide range of semiconductors may be used for photocatalysis, such as TiO_2 ZnO, MgO, WO_3, Fe_2O_3, CdS. The ideal photocatalyst should be photoactive, biological and chemical inert, stabile toward photocorrosion, suitable towards visible or near UV light, low cost, and non-toxic [7].

TiO_2 is known to have and excellent pigmentary properties, high ultraviolet absorption and high stability which allow it to be used in different applications, such as electroceramics, glass and in the photocatalytic degradation of chemicals in water and air. It has been used in the form of a suspension, or a thin film in water treatment. Degussa P25 is commercially available form of TiO_2 and has been used in many studies of photocatalytic degradation [8]. Studies employing P25, have been widely reported because of its chemical stability, ready availability, reproducibility, and activity as a catalyst for oxidation processes.

When a photon with an energy to or more than the band gap of TiO_2 is absorbed on its surface, it causes excitation of an electron from the valence band (vb) to conduction band (cb) , forming a 'positive hole' in the valence band and valence band holes can then migrate to the surface and participate in interfacial oxidation-reduction reactions. The oxidation degradation of an organic pollutant is attributed to direct reaction at the positive hole where adsorbed water or hydroxyl groups are oxidized to hydroxyl radicals which then react with the pollutant molecule [9].

III. EXPERIMENTAL

For the present study of assessment of water quality, Sanganer industrial area, Jaipur, Rajasthan state was selected (longitude $95^0 24$ E; latitude $27^0 18$ N). This area is principally involved in manufacturing and trade of textile products principally cotton for more than 50 years. The area lack proper drainage system and as a result of this, all the industrial waste water effluents are drained into the Amanisha canal which effects the nearby irrigation agricultural products and the quality of ground water due to high level of BOD, COD , pH , temperature etc.

Water samples from these areas were collected and designated S_1 –S_4. Samples were collected from the source point outlet of finishing unit at Sanganer industrial estate(S_1), 100 m away from source point(S_2), 200m away from source point(S_3) and 400m away from source point (S_5). Standard procedure (spot sampling) were followed during sampling. All the samples of the effluent were collected in sterile, dry and properly stopper polypropylene bottles. Temperature of the effluent was determined at the spots, whereas, the rest of physiochemical parameters were determined instantly after bringing the samples in the research lab. Various methods used for analysis are summarized in Table I.

TABLE I

Methods for Analysis of Parameters

Parameters	Instrument	Method
P^H	P^H Meter	Direct
Electric Conductivity	Conductivity Meter	Direct
Total suspended solid	Hot air oven	Filtration and drying in oven
Total dissolved solids	Hot air oven	Evaporation in oven at 110^oC
Chemical oxygen Demand	Volumetrically	In laboratory
Biological oxygen demand	BOD meter	Wrinkler method
Turbidity	Turbidity meter	Direct
Colour intensity	UV spectrophotometer	Intensity on λ max
Temperature	Thermometer	Direct on spot
Alkalinity	Volumetrically	In laboratory

IV. RESULT AND DISCUSSION

A. *Study of parameters*

Physiochemical status of colored effluent samples collected from AMANISHA NALA showed a considerably high load of pH, TSS, TDS, BOD, COD, Turbidity, Color Intensity, Alkanity and Temprature compared to prescribe National Environmental quality Standards(NEQS). However there was observed a significant decline in the values of the physiochemical parameters from source to sink.

Apparently, the effluent sample collected during dyeing and washing operation were Blue to Black in color, giving pungent smell and varying temperature[28-51^0C]. Close to source the pH of the effluent was highly alkaline in nature [11.9] but it reduces towards neutrality [S5= 7.7] at sink. Electric Conductivity of the effluent (average 3.57± 1.37 µs/m) was quite low and there was observed a decline in it away from source of effluent emission (S1). TSS in the effluent was quite high in the sample S4(1148 mg^{-1}) as compared to the first sample S1(415mg^{-1}) . TDS decreased in sample S5(457 mgL^{-1}).Overall, there was observed a significant high values of COD (Average 1632 mg L^{-1}) than BOD (Average 548 mg L^{-1}) though both followed a same decreasing pattern after considerable increase at S2 towards sink (S5). The variance in values is shown in Table II.

TABLE II

Physiochemical characterization of textile effluent samples compared with National Environmental Quality Standards (NEQS)

Parameters	Units	NEQS limit	Sample(1)	Sample(2)	Sample(3)	Sample(4)	Sample(5)
PH	-	6-9	11.9	9.2	8.9	7.7	6.63
Alkalinity	-	200	640	520	430	350	230
TDS	mgL^{-1}	2000	3540	2562	1853	1448	1231
TSS	mgL^{-1}	40	76	62	53	48	42.8
BOD	mgL^{-1}	80	1088	713	503	342	160
COD	mgL^{-1}	250	1650	1420	1122	934	700
Turbidity	NTU	5	36	32	29	26	25
Electric conductivity	µs/m	0.5	3.84	2.43	1.07	1.01	0.083
Temperature	^0C	-	49.0	31.8	35.7	29.5	21.0

B. Method development for photoreduction of textile dyes Reagents:

Titanium dioxide(TiO_2 P25) 70% anatse is supplied by merck company. Standard stock solution of TiO_2 was prepared by dissolving 0.399gm of TiO_2 in 250 ml distilled water.

Dyes (direct dyes- violet and congo red, cremazoles-orange 3R and Blue S1) were obtained at random basis from local Sanganer market .They had no information regarding chemical constituents, purity and hazardous nature. Dye solutions were made by dissolving 10 mg dry powder in 100ml of distilled water. All the dyes used were water soluble.

C. Instrument

Study of treatment of textile effluent by application of photoreduction was carried out using UV-Visible double beam spectrophotometer.

D. Methodology

λ max of individual dyes were determined in the range of wavelength from 300 nm to 750 nm, the results are shown in Table III.

1 ml of each of the photocatalyst TiO_2 were separately introduced in 25ml of standard dye sample and were kept for photoreduction at room temperature in visible radiation. Table IV , represent the colour degradation of commercial dyes namely violet , congo red, blue S1 and orange 3R with respect to time with all the three types of photocatalyst titanium oxide, zinc oxide and manganese oxide.

The results also show that TiO_2 is efficient for maximum decolouration and 96 hours duration is appropriate time for decolouration. Based on the above study different concentrations of TiO_2 were used for the treatment of textile industry effluents samples S1-S4. For this 25 ml of 10 times diluted samples were mixed with 0.2 ml, 0.4 ml, 0.6 ml,0.8 ml, 1.0 ml and 1.2ml of 0.02M TiO_2 solution. Samples were kept in sunlight for photoreduction for 96 hrs. Results of photoreduction using different concentration of TiO_2 photocatalyst with all the four industrial samples can be seen in Fig. 1 to 4.

TABLE III

λ max. of Individual Dyes

Dye	**λ max.**
Violet dye	545 nm
Congo red	495nm
Blue S1	570nm
Orange 3R	490nm

TABLE IV

Photoreduction using TiO_2

Sample(1)+reagent	Initial	24 hrs	48 hrs	72 hrs	96 hrs	120 hrs
Violet dye	1.382	1.193	0.823	0.643	0.312	0.311
Congo Red	1.368	1.146	0.924	0.712	0.209	0.211
Blue S1	1.392	1.198	0.847	0.619	0.389	0.387
Orange 3R	1.400	1.196	0.912	0.743	0.204	0.200

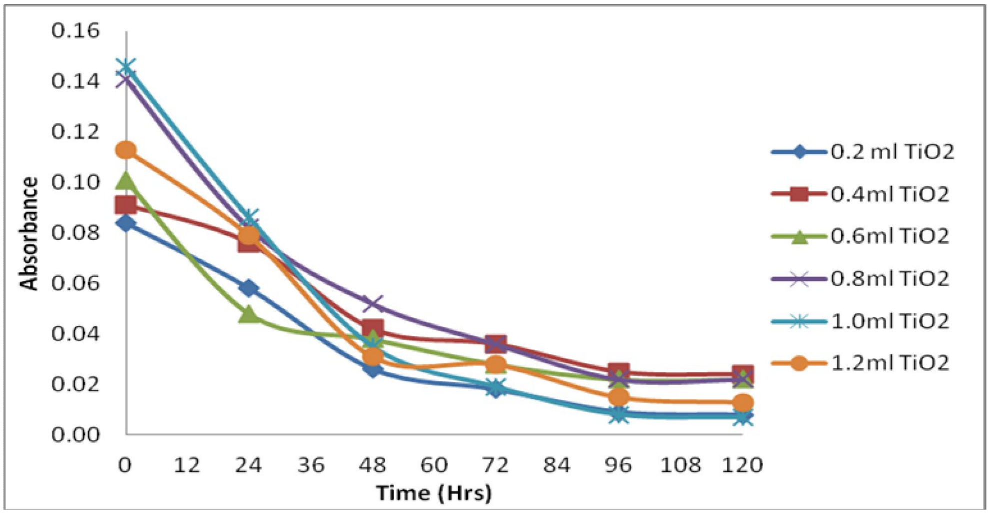

Fig. 1 : S1 Photoreduction using Titanium Oxide

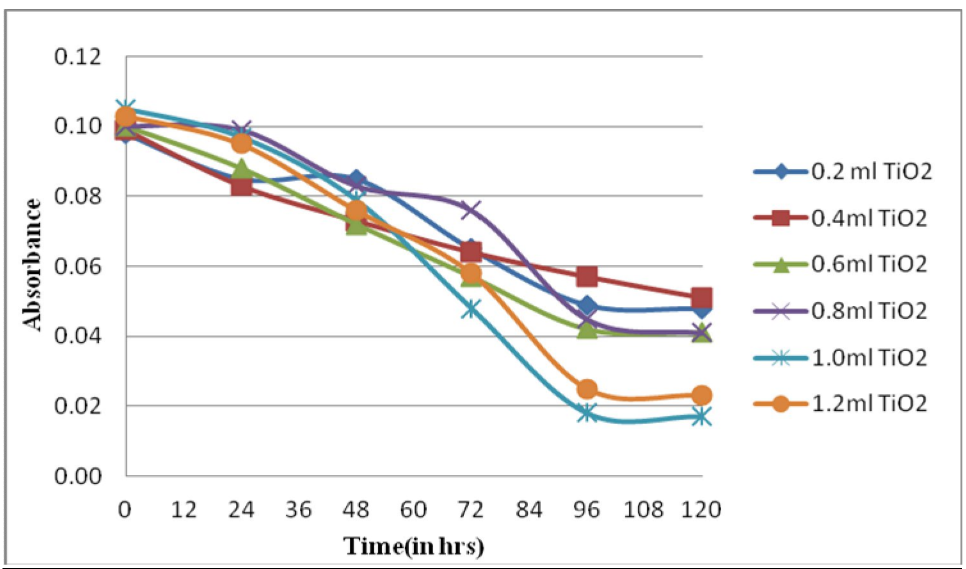

Fig. 2: S2 Photoreduction using Titanium Oxide

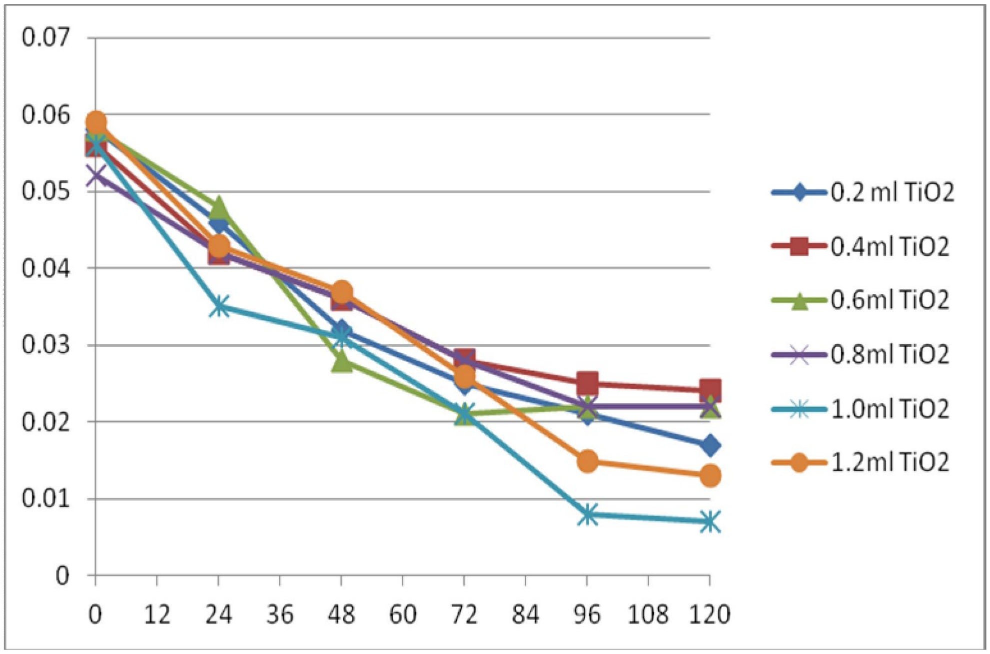

Fig. 3 : S3 Photoreduction using Titanium Oxide

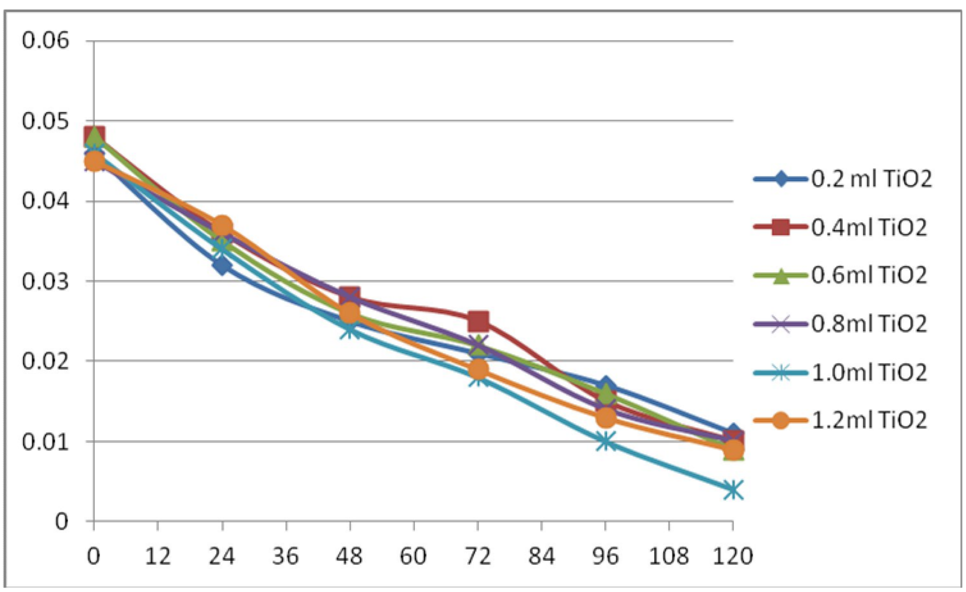

Fig. 4: S4 Photoreduction using Titanium Oxide

Results show that 88% decrease in colour intensity was observed in 96 hours and at 1.0ml of 0.02M concentration of titanium oxide. Thus titanium oxide can be successfully applied for colour removal of textile effluent by photoreduction in presence of visible light at room temperature.

Application of developed method

For this effluent sample (1) was diluted to 10 times and in 25 ml of this sample 1.2ml of 0.2M TiO_2 is added. Then it was placed in sunlight for photocatalysis for 96 hrs. After treatment different parameters were studied again by same procedure. Results of photocatalysis are summarized in Table V.

These results favor the use of TiO_2 for photocatalytic reduction and the developed method can be applied for decolouration of textile effluent.

TABLE V
Study of Physiochemical parameters of textile effluent after photocatalysis

Parameters	**Units**	**NEQS limit**	**Sample(1)** before photocatalysis	after photocatalysis
PH	-	6-9	11.9	7.7
Alkalinity	mgL^{-1}	200	640	40
TDS	mgL^{-1}	2000	3540	51.47
TSS	mgL^{-1}	40	76	20.25
BOD	mgL^{-1}	80	1088	88.56
COD	mgL^{-1}	150	1650	89.64
Turbidity	NTU	5	36	24
Electric conductivity	µs/m	0.5	3.84	0.62
Temperature	^0C	18	49	21.6

V. CONCLUSION

Screening of effluent and sludge of AMANISHA NALA having effluent from textile mill has shown a detailed picture of physiochemical and microbial parameters. Study of five different samples collected from source to sink of effluent showed a considerable high values of temperature (49^0C), pH(11.9), electric conductivity(3.4 µs/m), BOD(1088 mg per lit), COD(1650 mg per lit), TSS(76 mg per lit), TDS(3540 mg per lit), Turbidity(36 NTU), and Color intensity(Dark black) as compared to the desired values. A method was then developed for remediation of effluent using photocatalysis. Photocatalytic activity of

TiO_2 was studied on four different commercial dye samples namely Violet, Congo red, Royal blue and Orange 3R.. Further studies were carried out using various concentration of TiO_2 and it was found that 1.0ml TiO_2 in 25 ml effluent sample and 96 hours was most effective for photoreduction. The developed method show that TiO_2 have great potential in photoreduction of dyes in effluents and was applied commercially in treatment of textile effluent. The decline in physiochemical parameter values show the effect of decolorization ability of TiO_2.

VI. REFERENCES

[1] The dye maker's view; Easton J.R.; *Journal: color in dye house effluent;* P. cooper Edu., Society of dyers and colorists: Bradford, England; vol. 89; pp 9-12; 1995.

[2] Synthetic dyes, chemical economic handbook: synthetic dyes. Will R., Ishikawa Y., Leder A.; *Journal: manlo park(CA): SRI Chemical and Health Business Services;* vol.19; pp 112-119; 2000.

[3] Optimization of the flocculation stage in a Model system of a food emulsion Swaste using chitosan as Polyelectrolyte." Pinotti,A., Bevilacqua, A. and Zaritzky, N. *Journal of Food Engineering*,32,69-81,1997.

[4] Photoreduction of dyes catalysed by organic and bio-molecules; M.K.Pal and K.K. Mazumdar*; Journal of Histochemistry and Cell Biology*, vol. 122; pp 267-274; 1974.

[5] Treatment of textile effluents by H_2O_2/UV oxidation combined with reverse osmosis (RO); KANG Shyh-Fang, YEN Hsing-Yuan, YANG Mu-Hoe; *Journal of environmental science and health. Part A, Toxic/hazardous substances & environmental engineering* ISSN 1093-4529, 1998

[6] " A review of Engineering Developments of Aqueous Phase Solar Photocatlytic Detoxification and Disinfection Process," D.Y.Goswami., *Journal of Solar Energy Engineering,*Vol 119(2), 101-107,1997.

[7] Photocatalytic degradation for environmental applications - a review; Bhatkhande, D.S., Pangarkar, V.G., Beenackers, A.A.C.M.*; Journal of Chemical Technology and Biotechnology* vol. 77; pp 102-116; 2001.

[8] Morphology of a TiO_2 photocatalyst (Degussa, P-25) consisting of anatase and rutile crystalline phases; Ohno, T., Sarukawa, K., Tokieda, K., Matsumura, M.; *Journal of Catalysis* vol. 20; pp 82-86; 2001.

[9] C.S. Turchi, D.F.Ollis, "Photocatlytic Degradation of organic water contaminants: mechanisum involving hydroxyl radical attack", *Journal of catalysis*, vol 122, 1990, pp 178-192.