Photocatalytic degradation of Mixture of Dyes using some Composite semiconductors

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ABSTRACT - Bhilwara is known as textile city in India. It has many textile industries which drain out their colorful wastewater into nearby water bodies and land in surrounding area. The wastewater from textile industries causes serious impact on natural water bodies and land because of high discharge of synthetic dyes and chemicals in the dyeing and printing process, remained as unused materials in the wastewater from various stages of textile industry processing. High values of pH, COD and BOD, presence of particulate matter and sediments, chemicals which are dark in colour leading to turbidity in the effluents causes depletion of dissolved oxygen, which has an adverse effect on the aquatic ecological system. In this research, the photodegradation of mixture of dyes used in textile industry of Bhilwara in Rajasthan, India, using composite semiconductor TiO_2 and ZnO with different ratio as photocatalysts was investigated. The effect of amount of mixture of Dyes, pH, time, amount of catalyst, presence of salt and ratio of composite TiO_2 and ZnO was investigated for mixture of dyes and the optimized conditions for maximum amount of decolourization were determined. The maximum decolorization of 0.05g/l dye solution achieved was 91.30% 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 under UV irradiations. The results indicate that for mixture of dyes, composite TiO_2 and ZnO (90:10) ratio is comparatively more effective than only TiO_2 or only ZnO.

Keywords- Photodegradation, Wastewater treatment, Ultra Violet light, Solar light, Textile industry, Titanium dioxide, Zinc oxide.

I. INTRODUCTION

In India most textile and other industries are facing deficiency of water. It is known that textile industries discharge large volumes of toxic, coloured and non-biodegradable wastewater. The textile effluent is mostly composed of colored commercial dyes, chemicals and pigments. The textile effluent containing these dyes and pigments releases toxic substances into aqueous phase and poses environmental concerns. Many dye chemicals are difficult to degrade using conventional biological treatment processes[1-2]. It is more important to reuse this type of wastewater than to discharge it. Textile industries are one of the industries that consume large volumes of water in the processing operations including pre-treatment, dyeing, printing and finishing. The release of the treatment baths which are highly toxic and heavily coloured after the dyeing process contributes to water pollution the textile finishing industry discharged millions kg of dye due to dyeing and rinsing processes, either in the dissolved or suspended form in water 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 dyes and heavy metal (lead, Chromium, Iron and Zinc) are being discharged into water bodies[3-4]. Due to this colored waste water, quality of drinking, domestic and farming 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 badly affected. The conventional 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 ground which also creates the secondary level of land pollution [5-7].

During finishing process of textile industry 15-20% dyes are lost in effluent. Therefore, degradation of dyes by conventional methods is very difficult [11]. Other alternative method is being required to reduce the costs of treatment of effluents discharge [8-9] into water. A number of semiconductor photo catalysts have been explored for the photocatalytic redox reactions. Examples with wide band gap energies include WO3, TiO2, ZnO, and Fe2O3. Others such as CdS, ZnS, V2O5, ZrO2, SnO2, CeO2 and Sb2O4 have also been found to exhibit photocatalytic activity, but only to a very small extent, compared to Titania or ZnO. Among the possible semiconductors that can be used in heterogeneous photocatalysis, Titanium dioxide, (Eg = 3.2 eV) is most extensively used. ZnO also seems to be a

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suitable photocatalyst but it dissolves in acidic solutions and therefore, cannot be used for technical applications [10-12.]

Many other semiconductor particles like cadmium sulphide (CdS) or Gap absorb large fraction of the solar spectrum and can form chemically activated surface bond intermediates but unfortunately these photocatalyst are degraded during the repeated catalytic cycles involved in the heterogeneous photocatalysis [13-15]. Titanium dioxide's strong resistance to chemical and photo corrosion, its safety and low cost and biological harmless limits the choice of convenient alternative [Pelizzetti, 1995]. Moreover TiO2 is more stable than the other photocatalyst in ambient condition and can be recycled [Kiriakidou et al., 1999; Sun and Smirniotis, 2003] [16-18].

The use of conventional wastewater treatment methods for the treatment of effluents from textile dyeing industries is increasingly becoming challenged. Practically many dyeing industries are unable to afford such treatments as most of the conventional treatment methods produce secondary wastes and their disposal again increases the problem and trouble of the industries. Hence there is always a need to develop new treatment methods and also to modify and test the existing methods for more effective elimination of dyes from the wastewater [19-21]. Heterogeneous photocatalysis using semiconductor oxide catalysts is a competent unconventional method currently being evaluated to a great extent to ensure the rapid and complete transformation of the toxic organic compounds in textile effluents to benign chemicals. Titanium dioxide and ZnO has essentially proved itself to be the best semiconductor oxide because of its many desirable qualities [22-23].

This study deals the possibility of using UV and solar radiations for treating dyes from textile effluent by photocatalytic reduction. Various operational parameters affecting the reduction such as dye concentration, ratio of catalyst (TiO_2 and ZnO), amount of catalyst, pH, presence of Salts and optimum time will investigate. The catalyst itself is unchanged during the process. Due to these advantages the process result in considerable saving in the water, production cost and keeping the environment clean.

II. MATERIALS AND METHODS

For the present study the commercially available dye (Reactive Blue 4, Reactive Brown 2, Reactive Orange 5, and Reactive Yellow 4 in equal amount) and composite semiconductor TiO_2 and ZnO with different ratio were used. For the preparation of stock solution, 0.05 gm of mixture of dyes was dissolved in 1.0 L of double distilled water. Aqueous solutions of desired concentrations were prepared from the stock solution.

III. PROCEDURE AND ANALYSIS

For this experiment of photochemical reaction, 100 ml of dye solution of desired concentration was taken in 250 ml round bottom flask. The mixture of dyes were then irradiated under water separated UV light using 2 x 200 W Tungsten lamps and solar light to supply energy to excite composite TiO_2 and ZnO(90:10 ratio) loading. To ensure thorough addition of catalyst, oxygen was continuously bubbled with the help of aerator. All the experiments were performed at 36 ^{o}C.
About 3 ml of the solution was withdrawn after 30 min, time interval and its absorbance was measured using spectrophotometer at 561 nm after filtered through Millipore filter of 0.45 um. Colour degradation rate 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 starting concentration of dyes in the sample and C is the concentration after photo irradiation.

IV. RESULTS

Degradation of mixture of dyes in presence and absence of light (UV and Solar) and photocatalyst were observed at 561 nm. The optimum conditions for the degradation of mixture of dyes were Dye 0.05 g/l, pH = 8.5, TiO_2 and ZnO = 1 gm/l, TiO_2 and ZnO ratio 90:10, Time = 180 Minutes.

It shows 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 Dye, concentration of the TiO_2 and ZnO, Ratio of TiO_2 and ZnO, Time etc under UV and Solar irradiation.

1. Effect of variation in concentration of mixture of Dye:-

The effect of starting concentration of the mixture of dyes solution on the degradation of the dye was investigated by varying the dye concentrations from 0.01g/L to 1.0 g/L in the presence of 1.0 g/L of TiO_2 and ZnO (90:10 ratios) under UV and Solar light. The degradation decreases with increase in initial concentration of mixture of dye. Under UV irradiation of the solutions for a period of 180 minutes 91% degradation is observed for the dye solution of 0.05 g/L whereas the dye solution of 1.0g/L exhibits only 67% degradation in the same time under UV Irradiation.

Table: 1 Effect of variation in Mixture of Dyes concentration-

Amount of mixture of dyes Variation			
S. No.	Mixture of Dyes g/l	Degradation % Under UV	Degradation % Under Solar
1	0.01 g/l	86%	79%
2	0.02 g/l	89%	80%
3	0.05 g/l	91%	83%
4	0.1 g/l	82%	78%
5	0.2 g/l	77%	72%
6	0.5 g/l	71%	66%
7	1.0 g/l	67%	63%

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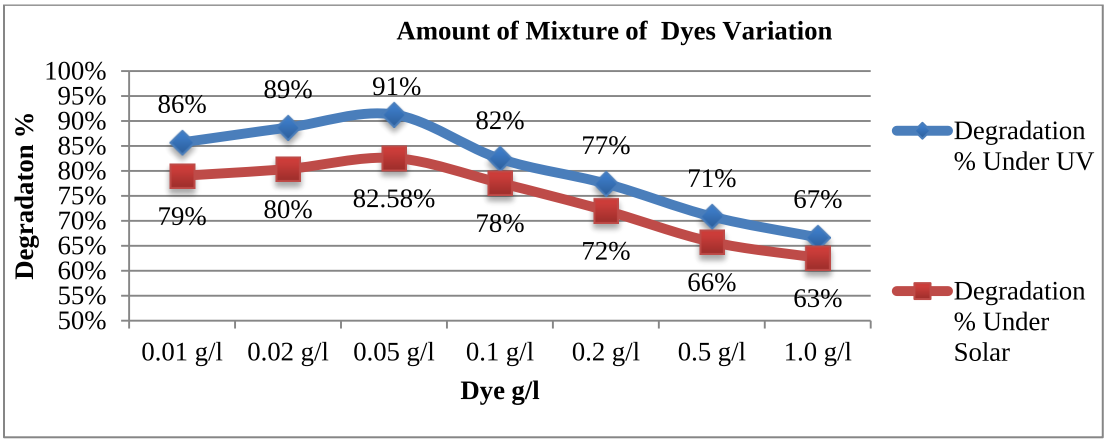
Fig: 1 Effect of variation in Mixture of Dyes concentration -



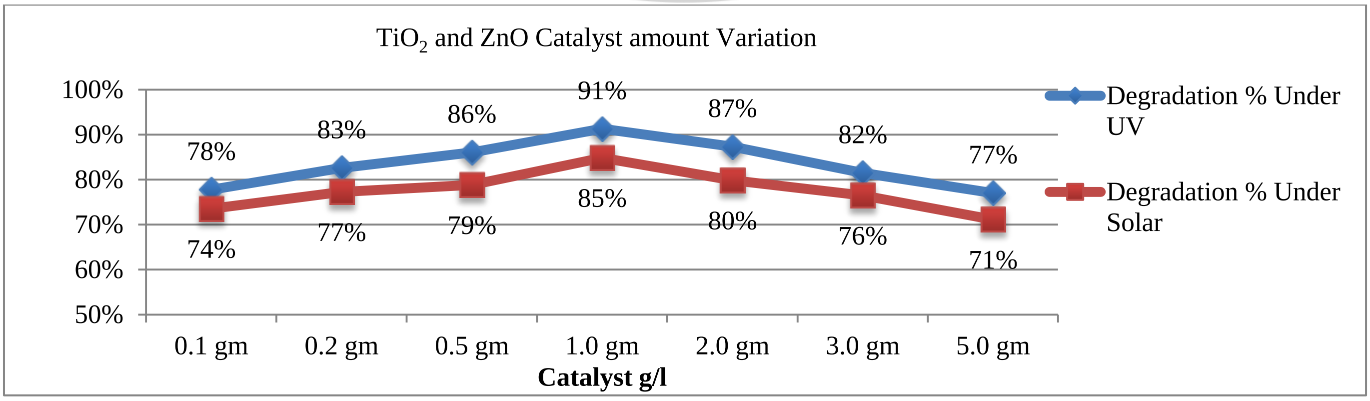
2. Effect of variation in amount of catalyst –

The quantity of semiconductor TiO_2 and ZnO powder affects the process of degradation of mixture of dyes. Keeping all other factors identical, the concentration of catalyst was changed from 0.0, 0.2, 0.5, 1.0, 2.0, 3.0 to 5 gm/l. It was observed that the degradation increases with increasing catalyst up to 1.0 gm/l and beyond this, degradation decrease. (Fig. 2).At 1.0 g/l of semiconductor and 8.5pH, we get 91 % degradation of dye under UV and 85% under solar irradiation at 180 Minutes. 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: 2 Effect of Catalyst (composite TiO_2 and ZnO) amount variation-

TiO_2 and ZnO Catalyst amount Variation			
S. No.	Catalyst TiO_2 and ZnO (90:10 Ratio) g/l	Degradation % Under UV	Degradation % Under Solar
1	0.1 gm	78%	74%
2	0.2 gm	83%	77%
3	0.5 gm	86%	79%
4	1.0 gm	91%	85%
5	2.0 gm	87%	80%
6	3.0 gm	82%	76%
7	5.0 gm	77%	71%

Fig: 2 Effect of Catalyst (composite TiO_2 and ZnO) amount variation-



3. Effect of variation in ratio of catalyst –

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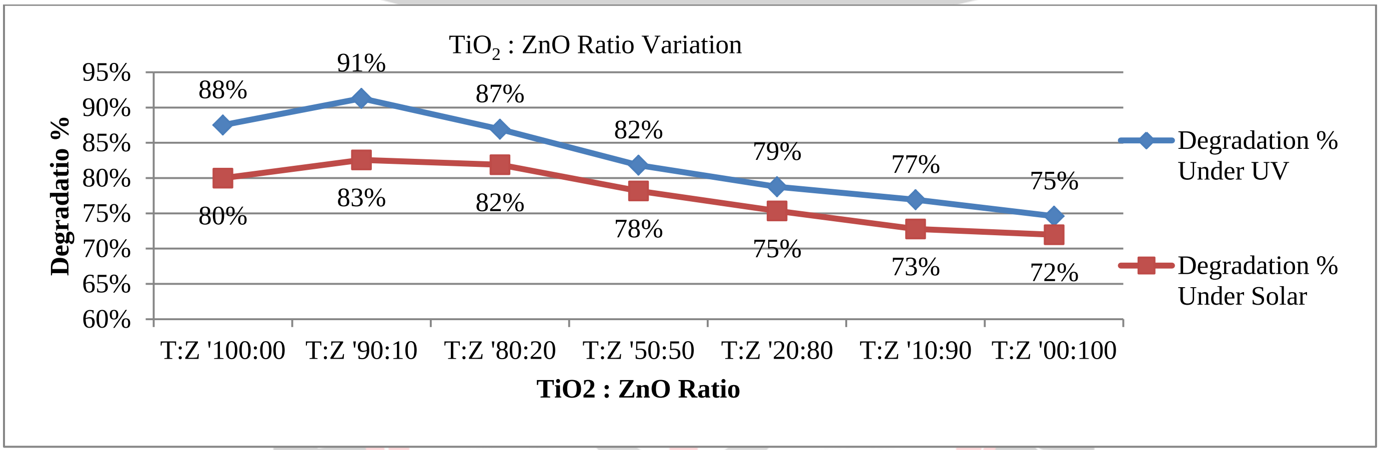
The ratio of composite semiconductor TiO_2 and ZnO powder affects the photocatalytic degradation of mixture of dyes. Keeping all other factors identical, the ration of catalyst was changed from 100:00, 90:10, 80:20, 50:50, 20:80 and 00:100. It was observed that the degradation increases with increasing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

Table: 3 Effect of TiO_2 and ZnO Ratio variation-

TiO_2 and ZnO Ratio Variation			
S. No.	TiO_2 and ZnO Ratio	Degradation % Under UV	Degradation % Under Solar
1	T:Z '100:00	88%	80%
2	T:Z '90:10	91%	83%
3	T:Z '80:20	87%	82%
4	T:Z '50:50	82%	78%
5	T:Z '20:80	79%	75%
6	T:Z '10:90	77%	73%
7	T:Z '00:100	75%	72%

Fig: 3 Effect of TiO_2 and ZnO Ratio variation-



4. Effect of variation in pH –

It was observed that the pH of the reaction medium has a significant effect on the surface properties of composite semiconductor TiO_2 and ZnO (90:10 ratios) catalyst. The effect of pH on photocatalytic degradation of mixture of dyes with semiconductor TiO_2 and ZnO (90:10 ratios) was investigated in the pH range of 7.0, 7.5, 8.0, 8.5, 9.0 and 10.0 under UV and visible light source. It was observed that the degradation of mixture of dyes increases with an increase in pH up to 8.5. 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.

Table: 4 Effect of pH variation-

pH Variation			
S. No.	pH	Degradation % Under UV	Degradation % Under Solar
1	pH 7	82%	75%
2	pH 7.5	84%	78%
3	pH 8	89%	82%
4	pH 8.5	91%	85%
5	pH 9	88%	82%
6	pH 9.5	83%	77%
7	pH 10	80%	74%

Fig: 4 Effect of pH variation-

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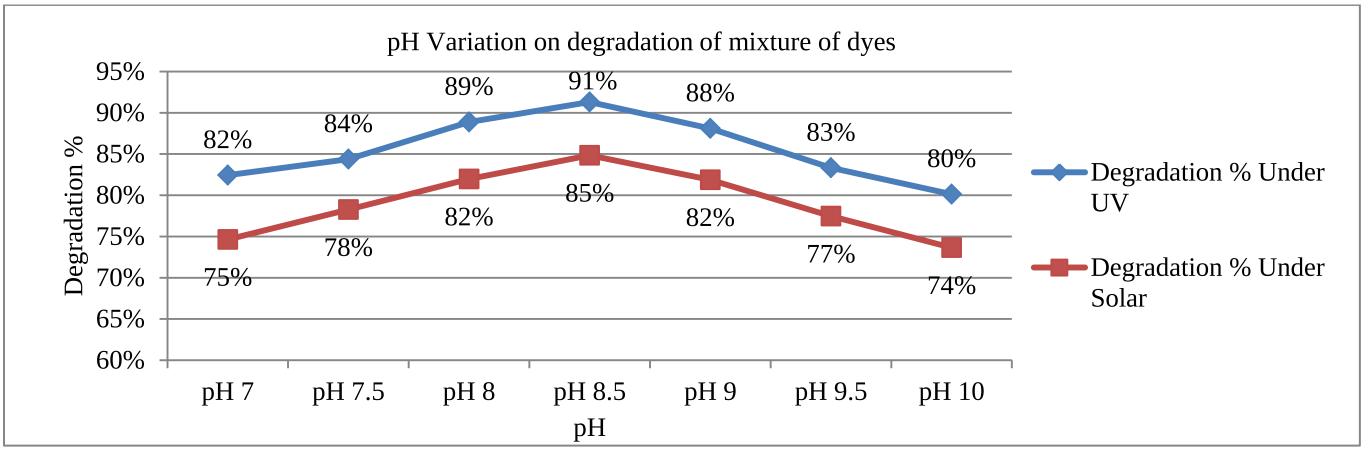


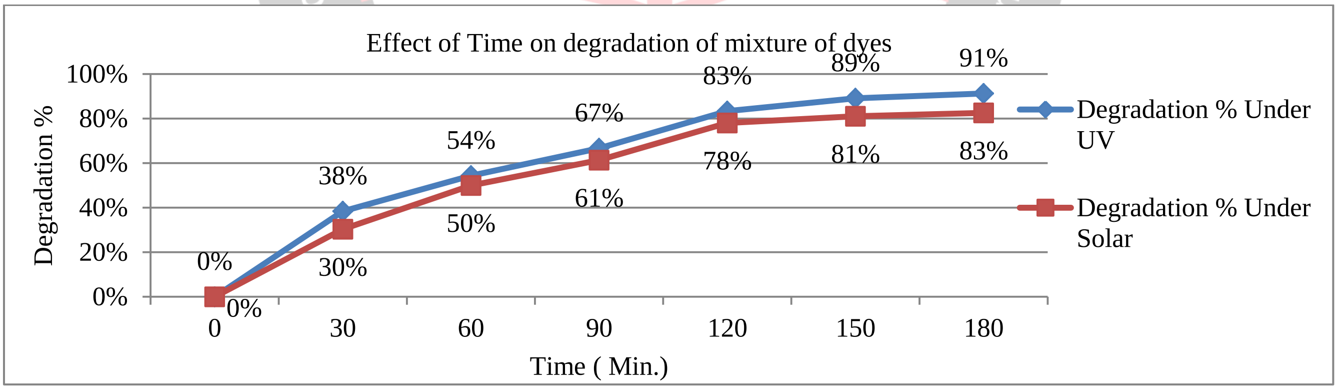
5. Effect of variation in Time –

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

Table: 5 Effect of Time Variation-

Time Variation			
S. No.	Time (Min.)	Degradation % Under UV	Degradation % Under Solar
1	0	0%	0%
2	30	38%	30%
3	60	54%	50%
4	90	67%	61%
5	120	83%	78%
6	150	89%	81%
7	180	91%	83%

Fig: 5 Effect of Time Variation-



6. Effect of variation in Na_2CO_3 –

The Comparison study between UV and Solar irradiation on the degradation of the mixture of dyes by adding increasing amount of sodium carbonate. It reveals that the degradation percentage of the mixture of dyes gradually decreases with increasing carbonate ion concentration.

Table: 6 Effect of variation in Na_2CO_3.

Effect of Na_2CO_3 on Dye Degradation			
S. No.	Na_2CO_3 g/l	Degradation % Under UV	Degradation % Under Solar
1	00 gm/l	91%	83%
2	100 gm/l	84%	75%

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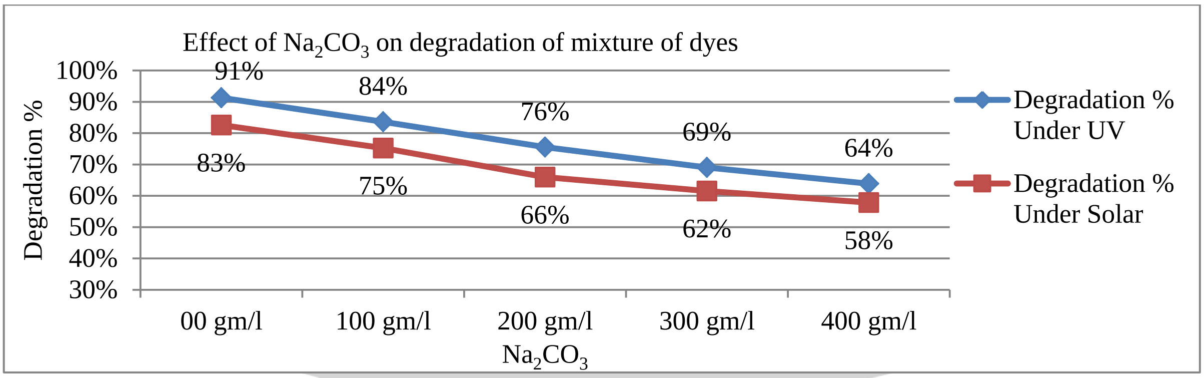
3	200 gm/l	76%	66%
4	300 gm/l	69%	62%
5	400 gm/l	64%	58%

Fig: 6 Effect of variation in Na_2CO_3.



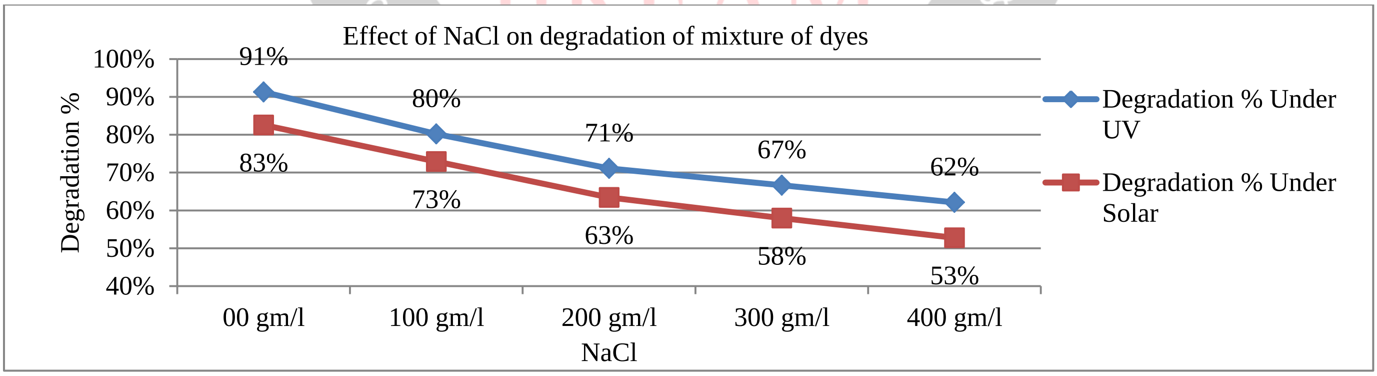
7. Effect of NaCl variation:-

Experiments were carried out by adding varying amount of NaCl to mixture of dyes containing 1 g/L of composite TiO_2 and ZnO 90:10 ratios under UV and solar irradiation to determine the influence of NaCl. The degradation percentage of the mixture of dyes was 91 % under UV and 85% under solar irradiation in absence of NaCl and 62 % under UV and 43% under solar irradiation in presence of 400 g/l of NaCl. Degradation percentage decreased with increase in the amount of chloride ion.

Table: 7 Effect of variation in NaCl

Effect of NaCl on Dye Degradation			
S. No.	NaCl g/l	Degradation % Under UV	Degradation % Under Solar
1	00 gm/l	91%	83%
2	100 gm/l	80%	73%
3	200 gm/l	71%	63%
4	300 gm/l	67%	58%
5	400 gm/l	62%	53%

Fig: 7 Effect of variation in NaCl



8. Reuse of Catalyst:-

Reuse of catalyst composite TiO_2 and ZnO 90:10 ratios affects the photocatalytic degradation of mixture of dyes. Keeping all other factors identical, Reuse of catalyst frequency was changed from original to 1^{st} time, 2^{nd} time, 3^{rd} time and 4^{th} time. It was observed that the degradation % was decreases from 91% to 80%, 71%, 56% and 52% under UV and 83% to 69%, 60%, 49% and 44% under solar irradiation.

Table: 8 Effect of Reuse of catalyst-

Reuse of Catalyst			
S. No.	Reuse	Degradation % Under UV	Degradation % Under Solar
1	Original	91%	83%

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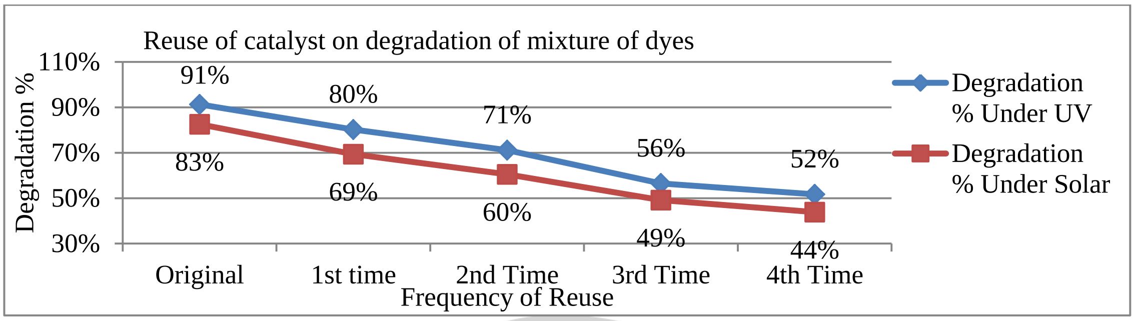
2	1st time	80%	69%
3	2nd Time	71%	60%
4	3rd Time	56%	49%
5	4th Time	52%	44%

Fig: 8 Effect of Reuse of catalyst-



V. CONCLUSION

The results of the present study show that photocatalytic degradation of mixture of dyes can be efficiently carried out using composite semiconductor TiO_2 and ZnO (90:10 ratios) under UV irradiation. The degradation rate depends upon the process parameters like dye concentration, catalyst concentration, Ratio, Time and pH. The optimum catalyst dose for the degradation of 0.5 g/l concentration of mixture of dyes solution is 1.0 g/L of composite semiconductor TiO_2 and ZnO (90:10 ratios) at 8.5 pH. The addition the presence of Na_2CO_3 and NaCl and reuse of catalyst decreases the reaction rate.

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BIBLIOGRAPHY

[1] Rauf, M. and S.S. Ashraf, Radiation induced degradation of dyes—an overview. Journal of hazardous materials, 166(1): p. 6-16, 2009.

[2] Divya, N., A. Bansal, and A.K. Jana. Nano-Photocatalysts in the Treatment of Colored Wastewater-A Review. in Materials Science

[3] Forum, Trans Tech Publ, 2013.

[4] Shah, M., et al., Microbial degradation of Textile Dye (Remazol Black B) by Bacillus spp. ETL-2012. J Bioremed Biodeg, 4(180): p. 2,

[5] 2013.

[6] Salman Ashraf, S., M. Rauf, and F.H. Abdullah, A hands-on approach to teaching environmental awareness and pollutant remediation to undergraduate chemistry students. Research in Science & Technological Education, 30(2): p. 173-184, 2012.

[7] Bafana, A., S.S. Devi, and T. Chakrabarti, Azo dyes: past, present and the future. Environmental Reviews, 19(NA): p. 350-371, 2011.

[8] Mahne, D., Combination of constructed wetland and TiO2 photocatalysis for textile wastewater treatment. Unpublished Doctoral Thesis. Univerza v Novi Gorici, podiplomski študij, 2012.

[9] Wu, H., et al., Decolourization of the azo dye Orange G in aqueous solution via a heterogeneous Fenton-like reaction catalysed by goethite. Environmental technology, 33(14): p. 1545-1552, 2012.

[10] Singh, K. and S. Arora, Removal of synthetic textile dyes from wastewaters: a critical review on present treatment technologies. Critical

[11] Reviews in Environmental Science and Technology, 41(9): p. 807-878, 2011.

[12] SK Bhagat; Tiyasha, Int. J. of Chem. Tech Research, 2013, 5(3), 1289–1298.

[13] BS Chauhan; SK Sagar, In Biological Forum: An International Journal, 2013, 5(1), 113–123.

[14] Oller, I., S. Malato, and J. Sánchez-Pérez, Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. Science of the total environment, 409(20): p. 4141-4166, 2011.

[15] Mahamuni, N.N. and Y.G. Adewuyi, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation. Ultrasonics Sonochemistry, 17(6): p. 990-1003, 2010.

[16] S. Parsons, "Advanced Oxidation Processes for Water and Wastewater," IWA Publishing, London, 2004.

[17] 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, Vol. 73, No. 7, 2010, pp. 1620-1628.

[18] N. Nasuha, B. H. Hameed and A. T. M. Din, Journal of Hazardous Materials, Vol. 175, No. 1-3, 2010, pp. 126-132.

[19] B Vyas; HP Molitoris, Appl Environ Microbiol. 1995, 61, 3919–3927.

[20] HM Pinherio; E Touraud; O Tomas, Dyes and Pigments, 2004, 61, 121–39.

[21] TA Mahdavi; T Donnelly; GK Anderson, Water Res., 2001; 35, 425–432.

[22] D Wesenberg; F Buchon; SN Agathos. Biotechnol Lett., 2002, 24, 989–993.

[23] R Nagarathnamma; P Bajpai; PK Bajpai, Process Biochemistry, 1999, 34, 939–948.

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