NOVEL EFFLUENT TREATMENT TECHNIQUE IN TEXTILE INDUSTRY

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Abstract

The textile industry consumes large quantity of water and produces large volume of wastewater which is rich in color, containing residues of dyes and chemicals, and requires proper treatment before being released into the environment. These dyes are resistant to biological as well as physical treatment technologies and advanced oxidation processes (AOPs), involving photo-catalyzed degradation is considered as an efficient cure for dye pollution. Photocatalytic degradation technique with semiconductors such as TiO_2 and ZnO is generally applied for treating wastewater containing contaminants due to its ability to achieve complete mineralization of the organic contaminants under mild conditions such as ambient temperature and ambient pressure. In the present study a laboratory experiment is to be performed to investigate photocatalytic degradation by using TiO_2 and ZnO photocatalyst for treating textile effluent. Operational parameters such as type of catalyst, catalyst concentration, irradiation time were investigated in order to study their effect on photodegradation process and the COD reduction.

Keywords: *Textile effluent, dye-degradation, Photocatalysis, TiO_2, ZnO-photocatalyst, type of catalyst, catalyst concentration, irradiation time, COD reduction.*

1. Introduction to Photocatalytic Degradation

The word photocatalysis is of Greek Origin and composed of two parts: The prefix **"**Photo" (phos: Light) and the word "Catalysis**"** (Katalyo: brake apart, decompose). The term can be generally used to describe a process in which light is used to activate a substance, the photocatalyst which modifies the rate of chemical reaction without being involved itself in chemical transformation. So basically a photocatalyst is a substance that generates catalyst activity using energy from light. Thus the main difference between a conventional thermal catalyst is that it is activated by heat and a photocatalyst is that it is activated by photons of appropriate energy. Photocatalytic reactions occur homogeneously and heterogeneously.

1.1 For homogeneous photocatalysis [35]: In homogeneous photocatalysis, the reactants and the photocatalysts exist in the same phase. Acid base catalysis, enzyme catalysis etc. are examples of homogeneous catalysis. The most commonly used homogeneous photocatalysts include ozone and photo-Fenton systems (Fe+ and Fe+/H_2O_2). The reactive species is the •OH which is used for different purposes. Some of the examples of homogenous photocatalysis: Ultraviolet lamp (UV), O_3/H_2O_2/UV, Photo-fenton process.

1.2 For heterogeneous photocatalysis [35]: Heterogeneous catalysis has the catalyst in a different phase from the reactants.Catalysis by metals and semiconductors are examples. Here reactions occur at the interface between the phases.

1.3 Beginning: [36, 37]

The enormous efforts to the research on TiO_2 material begins with the discovery of photocatalytic splitting of water on a TiO_2 electrode under ultraviolet (UV) light by Fujishima and Honda in 1972.

1.4 Photocatalyst [36]:

A photocatalyst (or catalyst) is a solid material, need to satisfy the following events: (i) the molecule is adsorbed on the particle surface; (ii) the molecule undergoes chemical transformation while visiting several reaction surface sites by surface diffusion and (iii) the intermediate or product molecule is subsequently desorbed to the gas phase or to the condensed phase.

The catalyst may accelerate the photoreaction by interacting with the substrate(s) either in its ground state or in its excited state or with the primary product (of the catalyst), depending on the mechanism of the photoreaction.

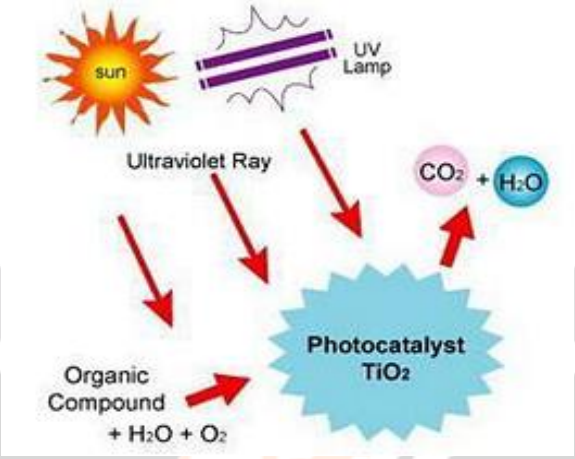


Figure 1: Schematic diagram of photocatalysis treatment.

Generally, two or more phases are involved in a photocatalytic reaction—a light source and a semiconductor material are used to initiate the photoreaction while the catalyst system can simultaneously carry out oxidation and reduction reactions using long wavelength, UV light as well as sunlight.

1.5 Why Semiconducting Material Is Used? [4, 5, 10, 14, 23, 35, 36]

A photocatalytic reaction proceeds through the excitation of electron from the valance band to conduction band by absorption of light. In metals the valance band and conduction bands are merged together, as a result there is no bandgap. So either reduction or oxidation happened depends upon band position. But insulators need a high energy for excitation process because the bandgap is very large. [36]

Semiconductors are materials with conductivity between that of metals and insulators. Their band gap (E bg), which is the energy gap between the valance band (highest occupied band) and conduction band (lowest unoccupied band), is between that of metals and insulators. [36]

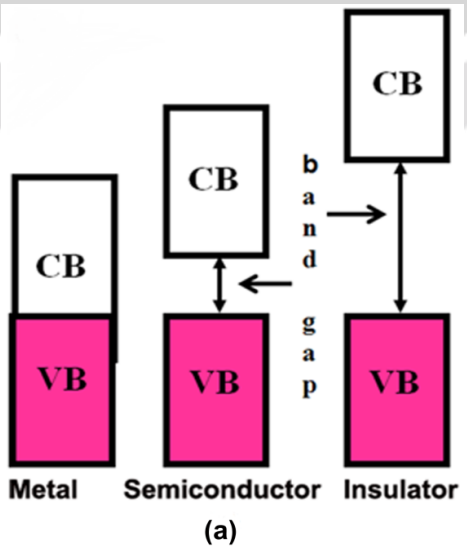


Figure 2: Valence band and Conduction band positions in metals, semiconductors, and insulators.

Unlike the metals which have a continuum of electronic states, semiconductors possess a void energy region where no energy levels are available to promote recombination of an electron and hole produced by photoactivation in the solid. The void region, which extends from the top of the filled valence band to the bottom of the vacant conduction band, is called the band gap. When a photon with energy equal to or greater than the materials band gap is absorbed by the semiconductor, an electron is excited from the valence band to the conduction band generating a positive hole in the valence band. The ultimate goal of the process is to have a reaction between the excited electrons with an oxidant to produce a reduced product, and also a reaction between the generated holes with a reductant to produce an oxidized product. Due to the generation of positive holes and electrons, oxidation-reduction reactions take place at the surface of semiconductors. In the oxidative reaction, the positive holes react with the moisture present on the surface and produce a hydroxyl radical.
An ideal semiconductor photocatalyst should be chemically and biologically inert, photo catalytically active, non-photo corrode, easy to produce and use, activated by sunlight, environmentally and economically acceptable etc. Among the various semiconductors, none of them become an ideal photocatalyst by satisfying all conditions. Thus only a few of them are effectively termed as very good semiconductor photo catalysts.

Titania (Titanim dioxide) becomes one such of candidate. Because it displays the features of an ideal semiconductor photocatalyst with the exception that it does not absorb visible light. The bandgap of titania is 3.2 eV, which corresponds to the UV range of electromagnetic spectrum. Thus the activity of titania is limited to UV region, which is around 5-10% of solar spectrum (because UV in natural sunlight is only 5-10 %). Despite this limitation, the other positive features to titania make it a prominent semiconductor material and widely studied in the field of semiconductor photochemistry. After TiO_2, ZnO too has been widely used as a very powerful photocatalyst in various applications. [36]

Various composites formed by TiO_2 and other inorganic oxides such as ZnO, SnO_2, SiO_2, In_2O_3, Cu_2O, MgO, WO_3, MoO_3, and being used. [5]

1.6 Photocatalytic Oxidation Process (Mechanism)[4, 10, 16, 38]
The principal reaction mechanism of a semiconductor photocatalyst is described as follows: When a photocatalytic surface is exposed by a radiation of energy equal to or greater than the bandgap energy (bandgap of the semi-conductor photocatalyst material), it creates a positively charged hole in the valance band and negatively charged electron in the conduction band by exciting the electrons in the valance band to the conduction band. [4] The generated electron-hole pairs must be trapped in order to avoid recombination.

The positive-hole of titanium dioxide breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available. [38]

Absorption of efficient photons by titania ($h\nu \geq Ebg = 3.2$ eV) [4]

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb}$$

$Photocatalysts\ (TiO_2/ZnO) + h\nu \rightarrow e^- + h^+$	(1)
$h^+ + H_2O \rightarrow H^+ + OH^•$	(2)
$h^+ + OH^- \rightarrow OH^•$	(3)
$e^- + O_2 \rightarrow O_2^-$	(4)
$2e^- + O_2 + 2H^+ \rightarrow H_2O_2$	(5)
$e^- + H_2O_2 \rightarrow OH^• + OH^-$	(6)
$Organic + •OH\ [\ O_2 \rightarrow CO_2 + H_2O + other\ degradation\ productions$	(7)

Formation of superoxide radical anion:

$$O_2 + e^-_{cb} \rightarrow O_2^{\bullet -}$$

Neutralization of OH- group into OH by the hole:

$$(H_2O \Leftrightarrow H_+ + OH.)_{ads} + h_{vb+} \rightarrow .OH + H_+$$

It is seen that the hydroxyl radical (.OH) and superoxide radical anions (O_2^-) are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would results in the degradation of the pollutants.

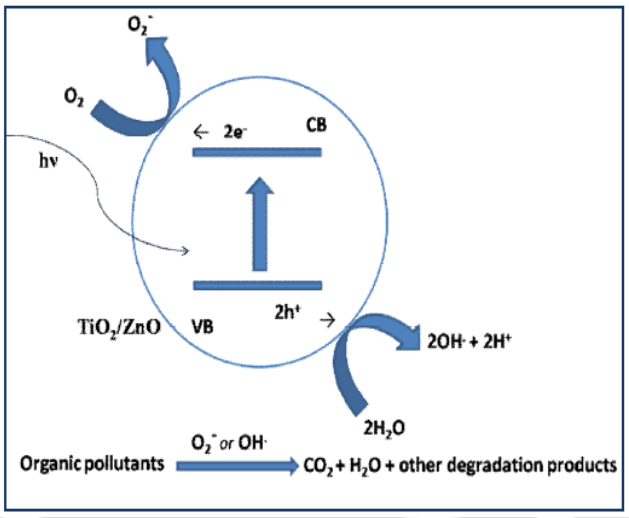


Figure 3: Schematic of the photocatalytic mechanism for TiO_2/ZnO photocatalysts [4]

1.7 Factors affecting the degradation –performance:

1) Effect of Catalyst loading
2) Effect of pH on Photocatalytic Degradation
3) Effect of Reaction temperature
4) Effect of Dye Concentration and nature of pollutants
5) Effect of Inorganic ions
6) Effect of Light Source on Photocatalytic Degradation
7) Effect on type of Catalysts used
8) Effect of Size and structure of the photocatalyst
9) Effect of H_2O_2 concentration
10) Activity enhancement by Doping

2. Experimental Setup

MATEIALS AND METHODS:

The materials and methods used during this research, including the chemicals, glassware instrument like the UV photo reactor, COD digester and the procedures used to treat the dye and effluent solutions with the UV/TiO_2; ZnO catalysis and using H_2O_2. TiO_2 and ZnO dosages and the varying UV contact times for different samples of textile effluents from the industry make up the experimental matrix.

2.1 Materials:

1. Textile Wastewater

Textile wastewater was collected from the industry Bharat Vijay Mills (BVM) situated at Kalol. Textile wastewater is analyzed and treatment was done by photo catalytic treatment. Total 5 samples of different ranges of COD are collected from the industry and their degradation is carried out.

2. *Reagents and Chemicals Used*

The photocatalyst TiO_2 (Anatase grade) was procured from Ajanta Chemicals, Kalupur and Zinc Oxide (ZnO) was procured from Astron Chemicals, Ahmedabad. Hydrogen peroxide was used as an oxidant. For the determination of COD of industrial effluent and treated sample was determined by using

a) Standard Potassium Dichromate, 0.25 N
b) Sulphuric Acid
c) Standard ferrous ammonium sulphate 0.25N

d) Ferroin indicator
e) Mercuric Sulphate

HCl and NaOH were used for adjustment of pH of dye solution and textile wastewater.

3. *Instrument Used*

Magnetic Stirrer:
Magnetic stirrer was used during experimentation to solve the problem of mixing and titanium dioxide and zinc oxide that remains in suspension.

Photo Reactor:
Photo catalytic treatment of dye and effluent were performed in batch experiments. For photocatalytic UV reactor was used which was rectangular having dimensions of 250 mm length, 300 mm width and 380 mm height and made up of Mild Steel- Gauge 24. Three UV tubes (11 Watt each) were attached with the roof. A magnetic stirrer was fitted in the reactor to carry out the photo catalytic reaction in slurry mode. Different views of photocatalytic recator are shown below.

Figure 4: Photocatalytic reactor

Temperature sensor:
A digital thermometer is used to measure the reaction temperature. And it is maintained between 50-60^{o}C

Filtration:
After photo catalytic treatment by photo reactor dye and effluent sample were filtered through filter paper.

COD Digester:
COD digester was used for the digestion of samples in the process of COD determination.

Reaction vessel:
Volumetric flask were used for the photo catalytic reactions having a capacity of 500ml.

2.2 METHOD:

Preparation of solution
a) Effluent dye samples:
A total of 100ml of effluent is taken in the volumetric flask of 500ml.
b) Catalyst loading/ Catalyst concentration:
TiO_2 and ZnO are taken as catalyst.
Catalyst concentration is varied at 1g/l, 2g/l, 3g/l, 4 g/l for both TiO_2 and ZnO
c) Hydrogen Peroxide:
Hydrogen peroxide (30% w/v) was obtained from Astron Chemicals, Ahmedabad. It implies that 100 ml of solution contains 30 g or 1 ml contains 300 mg. Amount of H_2O_2 is kept as fixed. 4ml of H_2O_2 is taken in 100ml of effluent sample.
e*) PHOTOCATALYTIC TREATMENT:*
Photocatalytic treatment was for done different samples of textile effluent. The effluent of textile industry were treated and the various parameters like

1) Types of catalyst
2) Weight of Catalyst
3) Irradiation time were varied and optimized.

Degradation of textile effluent:
100 ml of sample taken in reaction vessel (500ml capacity).Wastewater collected from the homogenous tank of effluent treatment plant (ETP) of BVM textile industry.Initial pH of sample was checked and the value of pH is fixed at 7 H_2O_2 is taken fixed as 4 ml per 100 ml of effluent sample.

Types of catalyst:
2 types of catalyst that will be varied: TiO_2 and ZnO.

Weight of catalyst:
TiO_2 and ZnO will be taken as 1g/L, 2g/L, 3g/L, 4g/L.

Irradiation Time:
Time taken to irradiate the sample is fixed to 4 and 6 hours. Sample was withdrawn after every 4, 6 hrs and the COD of samples was measured as per the standard methods.
f) Estimation of COD

3. Results:

Initially some trial experiments had been carried out with catalyst concentration 0.125 to 1 and irradiation time of 2 and 4 hrs to determine the optimal range of concentration of catalysts and irradiation time.

Trial experiments and their readings:

Sample 1:
Initial COD: 780 mg/L

Catalyst	Concentration of catalyst (g/L)	Irradiation time(hours)	Final COD (mg/l)	% Reduction of COD
TiO_2	1	2	527.28	32.4
		4	465.82	40.28
	0.5	1	622.21	20.23
		2	606.53	22.24
	0.25	1	648.18	16.9
		2	631.33	19.06
	0.125	1	688.43	11.74
		2	693.27	11.12
ZnO	1	2	512.46	34.3
		4	480.48	38.4
	0.5	2	586.01	24.87
		4	552.24	29.2
	0.25	2	614.64	21.2
		4	545.14	30.11
	0.125	2	653.02	16.28
		4	631.02	19.1

Table 1: Percentage Reduction of COD using TiO_2 and ZnO for Sample 1

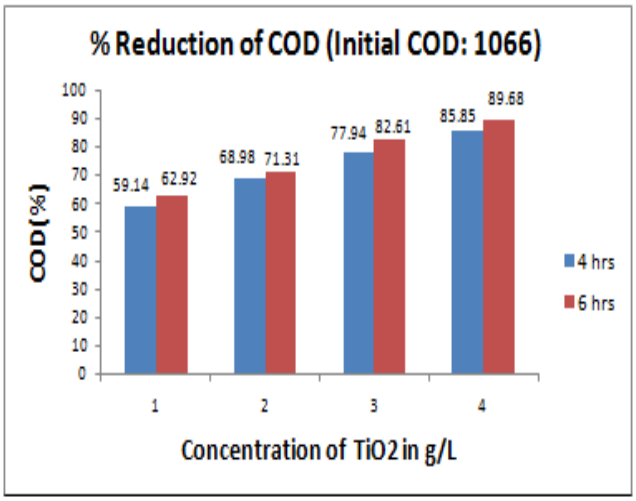
As the % reduction in COD is less than 50%, so to decrease the maximum level of COD, hydrogen peroxide is used to enhance the degradation rate and also the irradiation time and the catalyst concentration are increased. So in all the rest of effluent samples H_2O_2 is used.

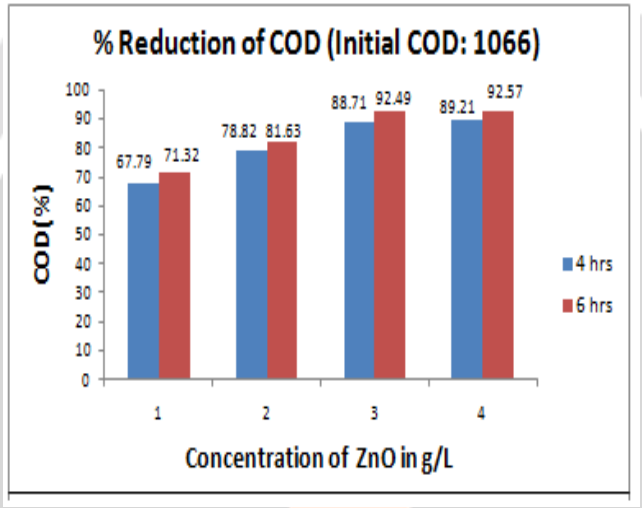
After many trial experiments to get optimum and minimum COD, Hydrogen Peroxide is used to enhance the photocatalytic degradation of dye.
A fixed quantity of 4 ml H_2O_2 (30% w/v) per 100 ml of effluent is used.

Sample 2:
Initial COD: 1066 mg/l

Catalyst	Concentration of catalyst (g/L)	Irradiation time(hours)	Final COD (mg/l)	% Reduction of COD
TiO_2	1	4	435.5	59.14
		6	395.21	62.92
	2	4	330.59	68.98
		6	305.76	71.31
	3	4	235.11	77.94
		6	185.28	82.61
	4	4	150.82	85.85
		6	110.00	89.68
ZnO	1	4	345.00	67.79
		6	305.66	71.32
	2	4	225.72	78.82
		6	195.72	81.63
	3	4	120.29	88.71
		6	80.00	92.49
	4	4	115.0	89.21
		6	79.20	92.57

Table 2: Percentage Reduction of COD using TiO_2 and ZnO for Sample 2

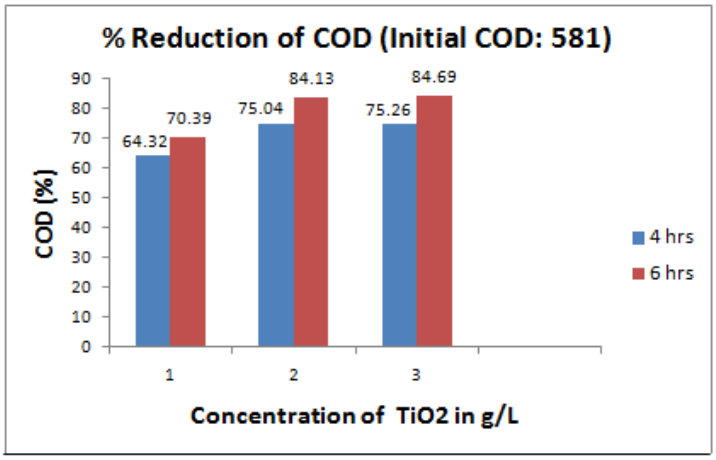


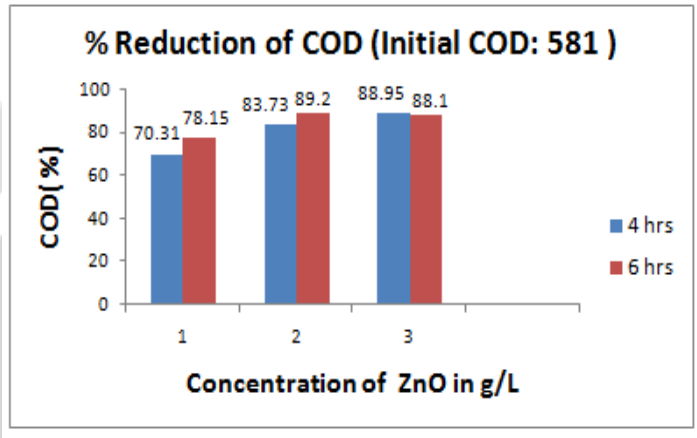


Sample 3:
Initial COD: 581 mg/L

Catalyst	Concentration of catalyst (g/L)	Irradiation time(hours)	Final COD (mg/l)	% Reduction of COD
TiO_2	1	4	207.30	64.32
		6	172.00	70.39
	2	4	145.0	75.04
		6	92.19	84.13
	3	4	143.7	75.26
		6	88.9	84.69
ZnO	1	4	172.4	70.31
		6	126.94	78.15
	2	4	94.52	83.73
		6	62.7	89.2
	3	4	64.2	88.95
		6	69.13	88.1
	4	4	101.0	82.6

Table : Percentage Reduction of COD using TiO_2 and ZnO for Sample 3



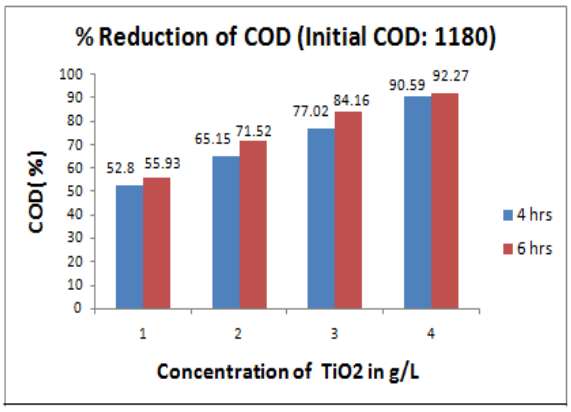


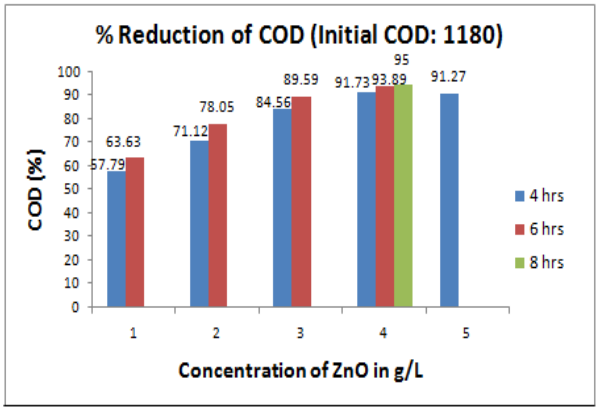
As seen from the above graph, the % reduction in COD value is almost same at 2 and 3 g/l of catalyst concentration. On further increase in the catalyst loading from 2 to 3 g/L, the degradation rate is almost constant, suggesting that an optimal level for catalyst effectiveness has been attained.

Sample 4:
Initial COD: 1180mg/l

Catalyst	Concentration of catalyst (g/L)	Irradiation time(hours)	Final COD (mg/l)	% Reduction of COD
TiO_2	1	4	556.4	52.8
		6	520.0	55.93
	2	4	411.2	65.15
		6	336.0	71.52
	3	4	271.15	77.02
		6	186.9	84.16
	4	4	111.0	90.59
		6	91.1	92.27
ZnO	1	4	498.0	57.79
		6	429.12	63.63
	2	4	340.7	71.12
		6	259.0	78.05
	3	4	182.1	84.56
		6	122.82	89.59
	4	4	97.5	91.73
		6	72.0	93.89
		8	59.0	95.0
	5	4	103.0	91.27

Table 4: Percentage Reduction of COD using TiO_2 and ZnO for Sample 4



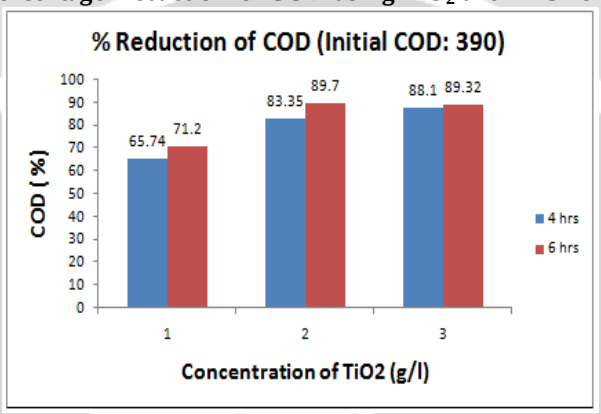


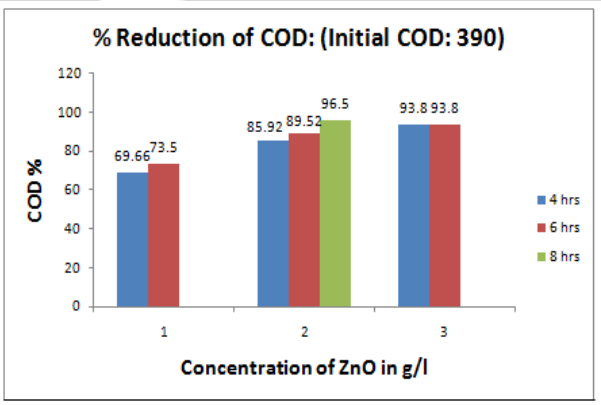
Sample 5:
Initial COD: 390mg/l

Catalyst	Concentration of catalyst (g/L)	Irradiation time(hours)	Final COD (mg/l)	% Reduction of COD
	1	4	133.6	65.74
		6	112.32	71.2
	2	4	64.93	83.35

TiO_2		6	40.17	89.7
	3	4	46.41	88.1
		6	41.6	89.32
ZnO	1	4	118.32	69.66
		6	103.35	73.5
	2	4	54.9	85.92
		6	28.47	92.7
		8	13.65	96.5
	3	4	24.18	93.8
		6	24.18	93.8

Table 5: Percentage Reduction of COD using TiO_2 and ZnO for Sample 5





3.1 Conclusion of results:

1) Effect of type of catalyst:

All the results indicate that ZnO is more effective than TiO_2 for this industry.

2) Effect of photocatalyst loading on COD:

In order to avoid the use of excess catalyst, it is desirable to find out an optimum catalyst loading for efficient COD reduction. A series of experiments was carried out by varying the amount of catalyst from 1 to 4 g/L with a solution pH of about 7, and UV irradiation time of 4 hrs and 6 hrs.

Results show that an increase in the catalyst loading from 1 to 4 g/l for higher ranges of COD decreases the COD reduction sharply. Whereas after 4 g/l the % reduction is almost constant or it the COD starts increasing.

And for low ranges of COD (<600 mg/l), the increase in the catalyst loading from 1 to 3 g/l for higher ranges of COD decreases the COD reduction sharply and after that % reduction is almost constant or it the COD starts increasing.

This can be explained on the basis that optimum catalyst loading is found to be dependent on initial solute concentration because with the increase in catalyst dosage, total active surface area increases, hence availability of more active sites on catalyst surface. At the same time, due to an increase in turbidity of the suspension with high dose of photocatalyst, there will be decrease in penetration of UV light and hence photoactivated volume of suspension decreases. Thus it can be concluded that higher dose of catalyst may not be useful both in view of aggregation as well as reduced irradiation field due to light scattering.

3) Effect of irradiation time:
The required duration for the complete photocatalytic treatment of organic pollutants in the textile waste water was studied based on the duration of catalyst irradiation to the light source. The catalysts irradiation time was varied from 4 and 6 hours under the UV light source. In the present study the results obtained represented that highest degradation efficiency when the irradiation of photocatalyst was continued till 8 h when increase in catalyst loading increase COD. Under UV light source and the organic pollutants removal efficiency reached upto 96.5% for 8 h irradiation time. The photo catalytic degradation efficiency increased with respect to irradiation time of photo catalyst and the results obtained are shown in tables.

4) Effect of H_2O_2 concentration:
To enhance the photocatalytic degradation of dye, increase in the hydroxyl radical concentration is required. The enhancement in degradation of dye by the addition of H_2O_2 increases the concentration of hydroxyl radical and it could act as an alternative electron acceptor to oxygen because hydrogen peroxide is a better electron acceptor than molecular oxygen. Moreover hydrogen peroxide also produces hydroxyl radicals via photodecomposition and it inhibits the e−, h+ recombination according to the following equations:

$$TiO_{2(e^-)} + H_2O_2 \rightarrow TiO_2 + OH^- + {}^{\bullet}OH$$

$$H_2O_2 + e^-_{(CB)} \rightarrow {}^{\bullet}OH + OH^-$$

$$H_2O_2 + h\nu \rightarrow 2\,{}^{\bullet}OH$$

$$H_2O_2 + O_2{}^{\bullet -} \rightarrow {}^{\bullet}OH + OH^- + O_2$$

4. Conclusion and Future Prospects

The results indicate that for this industry photocatalytic degradation can be carried out with ZnO being more efficient than TiO2 with catalyst concentration taken around 3-4g/l with irradiation upto 6 hrs, we can achieve around 90 % COD reduction. Advanced oxidation processes (AOPs) with UV irradiation and photocatalyst titanium dioxide (TiO_2) and Zinc Oxide (ZnO) are gaining growing acceptance as an effective wastewater treatment method. [8].

Photocatalytic degradation of organic pollutants is promising technology due to its advantage of degradation on pollutants instead of their transformation under ambient conditions. The process is capable of removing a wide range of organic pollutants such as pesticides, herbicides, and micropollutants. Although significant amount of research has been conducted on ZnO; TiO2 photocatalysis at laboratory scale, its application on industrial scale requires certain limitations to be addressed.

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