



## Treatment of textile Industry Waste water using Solar photo Catalysis

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### Abstract

*The present study investigated the application of solar photo catalysis in the treatment of textile industry wastewater using zinc oxide (ZnO) and Titanium dioxide (TiO<sub>2</sub>) as photo catalysts. Thin films of nanometer precision were prepared by coating chitosan and catalyst inside the glass tubes by Layer-by-layer (L-b-L) technique. A recirculation reactor set up was fabricated using the coated glass tubes and the experimental studies were carried out under solar irradiation. The experimental results indicated an appreciable decrease in Total Organic Carbon (TOC), Chemical Oxygen Demand (COD) and turbidity within two hours of exposure under solar radiation.*

**Keywords:** Chemical oxygen demand, photo catalyst, solar radiation, total organic carbon, titanium dioxide, waste water, zinc oxide.

### Introduction

In recent years, the waste water discharged into receiving waters has become a serious environmental problem. The uncontrolled disposal of the waste water not only results in deterioration of health and environment but also wastage of raw materials and energy. World is facing challenges in meeting rising demands of clean water due to extended droughts, population growth, more stringent health based regulations and competing demands from a variety of users. The contamination of water sources and pollutants of carbon compounds arising from the discharge of waste water from the chemical industries, power plants, landfills, and agricultural fertilizers remains the issue of global concern<sup>1,2</sup>. Effluent discharged from textile industry causes serious environmental threats due to its high contamination of color and organic matter. A variety of naturally available low cost adsorbents such as natural clay, bagasse pith and maize cob were used for the treatment of dye waste water. The cost of treatment is higher for bagasse and maize cob compared to activated carbon<sup>3</sup>.

In the recent years, semiconductor photo catalysis has played a major role in wastewater treatment to overcome these environmental issues. The most commonly used semiconductor materials are ZnO and TiO<sub>2</sub> which are the ideal photo catalysts in several respects such as low price, high photo catalytic activity, antibacterial activity and non-toxic in some extend. ZnO has almost the same band gap energy (3.2 eV) as TiO<sub>2</sub> and its photo catalytic capacity is predicted to be similar to that of TiO<sub>2</sub>. However, ZnO has more efficiency than TiO<sub>2</sub> in photo catalytic degradation of some dyes and textile wastewater<sup>4-8</sup>. Titanium dioxide (TiO<sub>2</sub>) Nano-particles and films were prepared by the sol-gel method and zinc oxide (ZnO) films were synthesized by sputtering method<sup>9</sup>. Reduction of pollutants by solar energy can be an economically acceptable solution in

tropical countries where solar radiation is most abundant available renewable energy sources.

The preliminary investigation on the extraction of heavy metals from produced water using *M. oleifera* leaves and seeds as adsorbents was carried out with a view of sourcing for local or natural adsorbents that can be used to treat waste water<sup>10</sup>.

Textile industries consume large quantity of fresh water and discharges almost same amount of waste water. The effluent contains wide range of chemicals including various dye stuffs. These dyes are highly structured organic compounds and are difficult to be broken down biologically. Several experiments have focused on the treatment of textile wastewater to reduce total suspended solids (TSS), chemical oxygen demand (COD), total dissolved solids (TDS) and turbidity<sup>11-15</sup>. Coagulation and flocculation methods are effective on dye removal, but the main problems of these methods are high cost, and generation of large amounts of mud which lead to environmental and health issues<sup>16-19</sup>.

The commonly used method for the treatment of textile mill effluent are photo catalysis in which the particles are dispersed in liquid medium and thin films are formed on the supported materials. The Layer-by-Layer coating method is one of the simple and low-cost techniques for preparing thin films on supported materials such as glass plates; steel fibers; perlite granules and aluminum foil<sup>20-23</sup>. The phosphate and alumina based materials have vast catalytic applications<sup>24-28</sup>.

In the present experimental studies, the L-b-L method was used for catalyst coating inside the glass tubes and then a recirculation reactor set up was fabricated using a peristaltic pump. The main aim of the study was to investigate the

effectiveness of using ZnO/TiO<sub>2</sub> nanoparticles thin film for the treatment of textile industry waste water in an efficient and environmental friendly way. The research was carried out during March 2013 and the effluent was collected from a leading textile industry in the sultanate of Oman. The composition of textile mill effluent is shown in table-1<sup>29</sup>. The main purpose of this study was to harness solar energy through photo catalysis and to remove contaminants that exist in nano scale in wastewater using semiconductor nanoparticles for useful recycling applications.

**Table-1**  
**Typical composition of textile mill waste water**<sup>29</sup>

Parameters	Range of Values
pH	7-9
Biochemical Oxygen Demand (mg/L)	80 – 6,000
Chemical Oxygen Demand (mg/L)	150 – 12,000
Total Suspended Solids (mg/L)	15 – 8,000
Total Dissolved Solids (mg/L)	2,900 -3,100
Chloride (mg/L)	1000 – 1600
Total Kjeldahl Nitrogen (mg/L)	70 – 80
Colour (Pt-Co)	50-2500

## Material and Methods

ZnO nano powder (99.9%, APS: 20 nm) was purchased from mk NANO, TiO<sub>2</sub> (Mwt: 79.90) from VWR PROLABO, high molecular weight Chitosan (Mwt 500 kDa) from Molekula, Acetic acid (100%) from Mervick and COD HR Reagent EPA (HI 93754C-25) from Hanna instruments. 0.1 N NaOH and 0.1 N HCl are used for pH adjustment. Distilled water was used throughout for all experiments. Textile industry wastewater was collected from Oman Textile Mills and pretreated using desert sand column before applying the solar photo catalysis treatment. The pretreated sample was transferred and stored in the laboratory under room condition. Total Organic Carbon was analyzed using TOC analyzer (The characterizations of the sample were analyzed before treatment and are shown in table-2).

The experiments were carried out with the textile industry effluent and the effluent samples were allowed to settle before characterization. The samples were preserved at 4°C in order to avoid bacterial contamination. To ensure the accuracy, reliability and reproducibility of the collected data, all batch experiments were carried out in triplicate and the mean values of three data sets are presented.

**Preparation of coating solution:** Two polymer solutions were prepared as follows: Coating solution (1): 2 g of chitosan powder was dissolved in 100 ml of 1% acetic acid and stirred until the polymer dissolved completely and then, 0.2 g of ZnO catalyst was added to the prepared solution and kept under stirring for 5 hours with constant heating at 60°C.

**Table-2**  
**Characteristics of pretreated Textile Mills wastewater**

Parameters (unit)	Value
pH	8.71
Conductivity (μS)	4.847
TDS (ppm)	3.1
COD (ppm)	2780
TOC (ppm)	119.4
DO (ppm)	0.16
Turbidity (NTU)	26

Coating solution (2): 2 g of chitosan and 0.2 g of TiO<sub>2</sub> catalyst were added to 100 ml of 1% acetic acid and kept for stirring and heating at 60°C for 5 hours to get proper consistency.

**L-b-L Coating process:** The glass tube used as reactor has 60 cm length, 1.1 cm inner diameter and 0.1 cm thickness. The coating process was performed by pouring the prepared solution into the glass tube until the inner surface is uniformly coated. The excess polymer solution is rinsed followed by drying using forced circulation of hot air. The process was repeated for 10 times in order to get proper thin film.

**Experimental setup:** The schematic diagram of the experimental reactor set up is shown in Figure-1. Two glass tubes, one coated with ZnO solution and the other one with TiO<sub>2</sub> solution were used as reactor. Two sets of experiments were conducted with 1.5 litre of wastewater. A peristaltic pump was used for the recirculation at a constant speed of 85 rpm.

**Photo catalytic experiments:** The experiments were conducted under solar radiation from 9 AM to 3 PM in the month of March - April. During this period a maximum UV-index of 11 was selected for the solar radiation. The first set of experiments was carried out with 1.5 litre of wastewater using ZnO catalyst coated reactor. The discharge was re-circulated through the reactor system for a period of 4 hours. The samples were collected every 1 hour and filtered for further parametric analysis. The second set of the experiments were carried out in similar conditions using TiO<sub>2</sub> coated reactor. The schematic representation of the experimental set up is shown in figure-1.

The samples were filtered using filter paper (Dia: 4.25 cm, pore size, 20-25 $\mu$ m) and then different analyses have been done. The most important parameters analyzed are Total Organic Carbon (TOC), Chemical Oxygen demand (COD), Dissolved Oxygen (DO) and Total suspended solids (TDS)<sup>24</sup>. Figure-1 represents the experimental set up of TOC Analyzer.

## Results and Discussion

**Effect of variation of pH:** The effect of variation of pH on exposure time for the degradation of pollutants was studied by

varying the exposure time from 0 to 4 hours. It was noticed that there was a slight decrease in pH in both treatments but the variation of pH in the wastewater is more when treated with ZnO rather than treated with TiO<sub>2</sub>. The graphical representation of the effect of variation of pH with exposure time for ZnO and TiO<sub>2</sub> catalysts are shown in figure-3. After photo degradation experiment, the samples were analysed for total organic carbon (TOC), chemical oxygen demand (COD), total dissolved solids (TDS) and turbidity

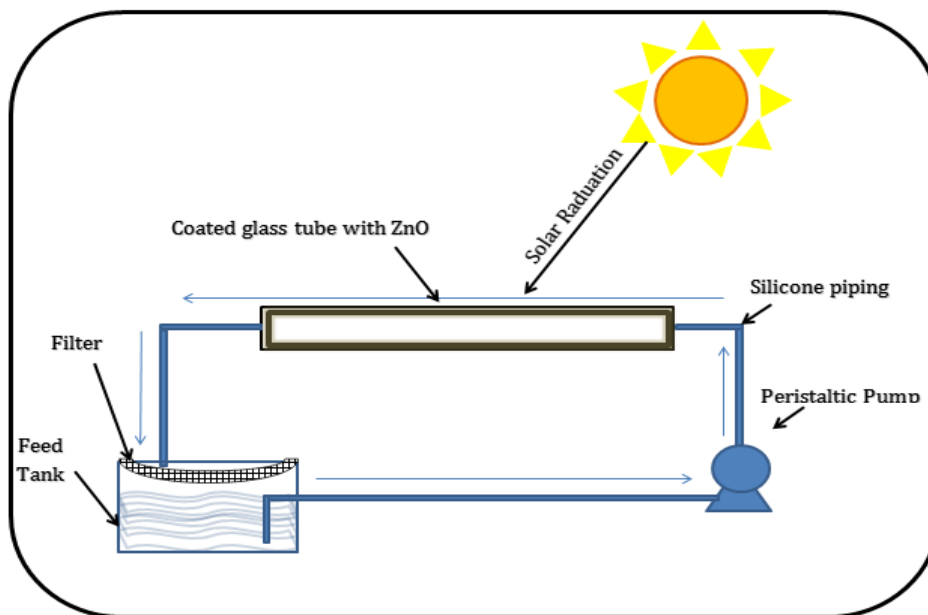


Figure-1  
Schematic representation of the reactor setup

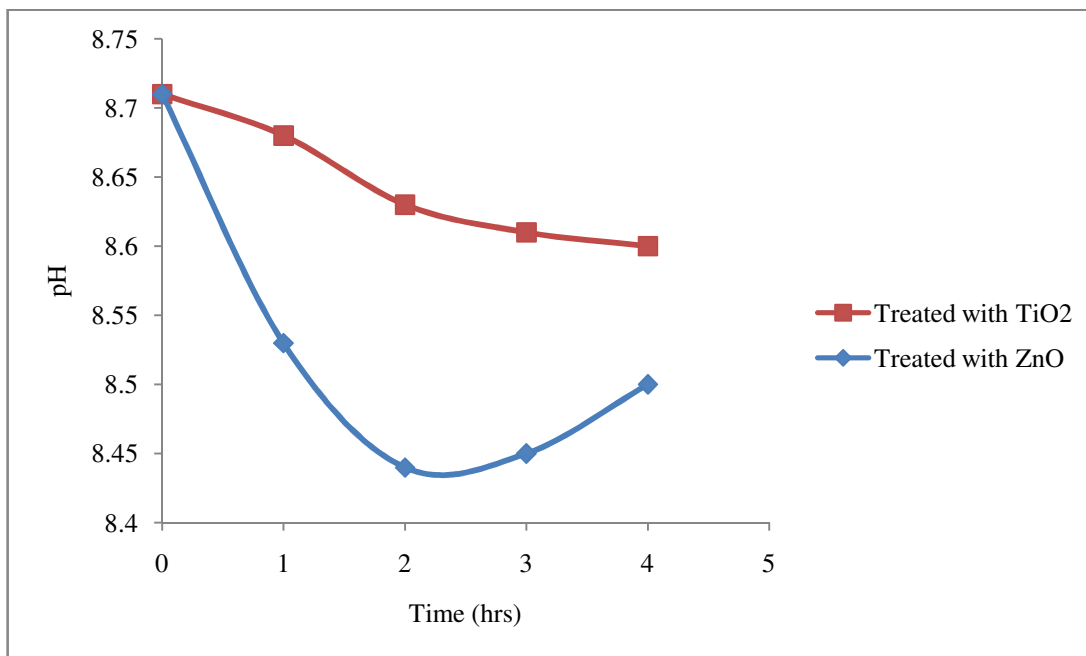


Figure-2

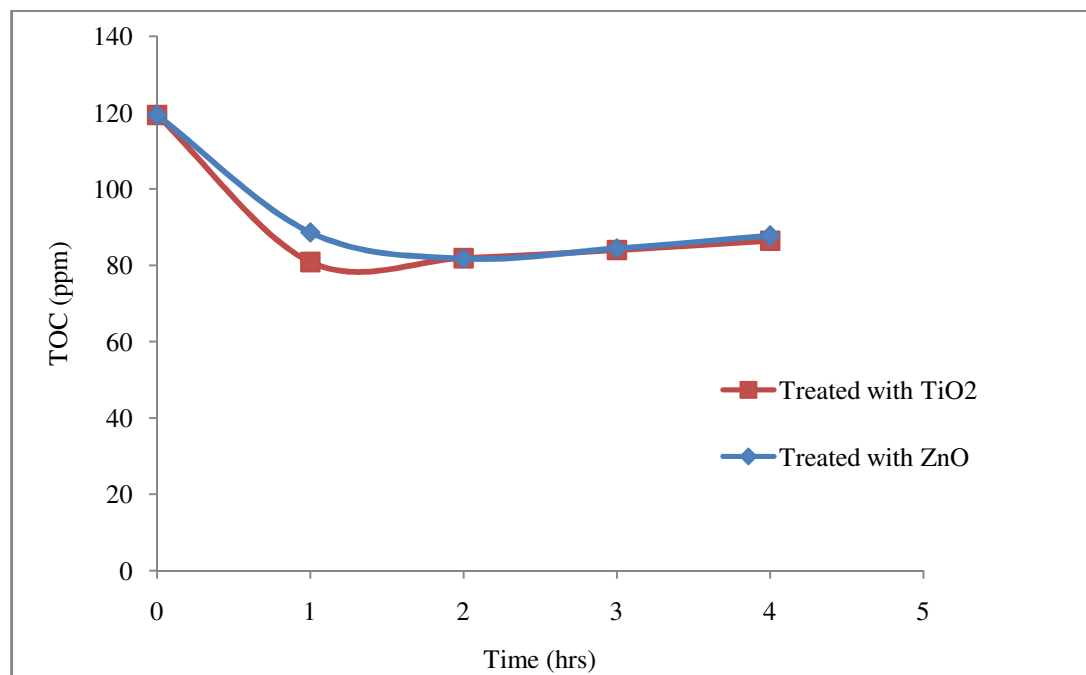
**TOC Analyzer** The first experiment was done for the wastewater treated with ZnO polymer solution, which was coated in glass tube. The characteristic of the effluent before treatment is presented in table-1

**Effect of variation of exposure time:** The effect of variation of TOC with respect to time is shown in figure-4. It was noticed that ZnO and TiO<sub>2</sub> both reduced the pollutant concentration within 2 hours of exposure of solar radiation. However, there is slight increase in TOC after 3 hours of treatment and this may be due to formation of by-product which leads to this variation. There is a sharp decrease in COD reading when treated with

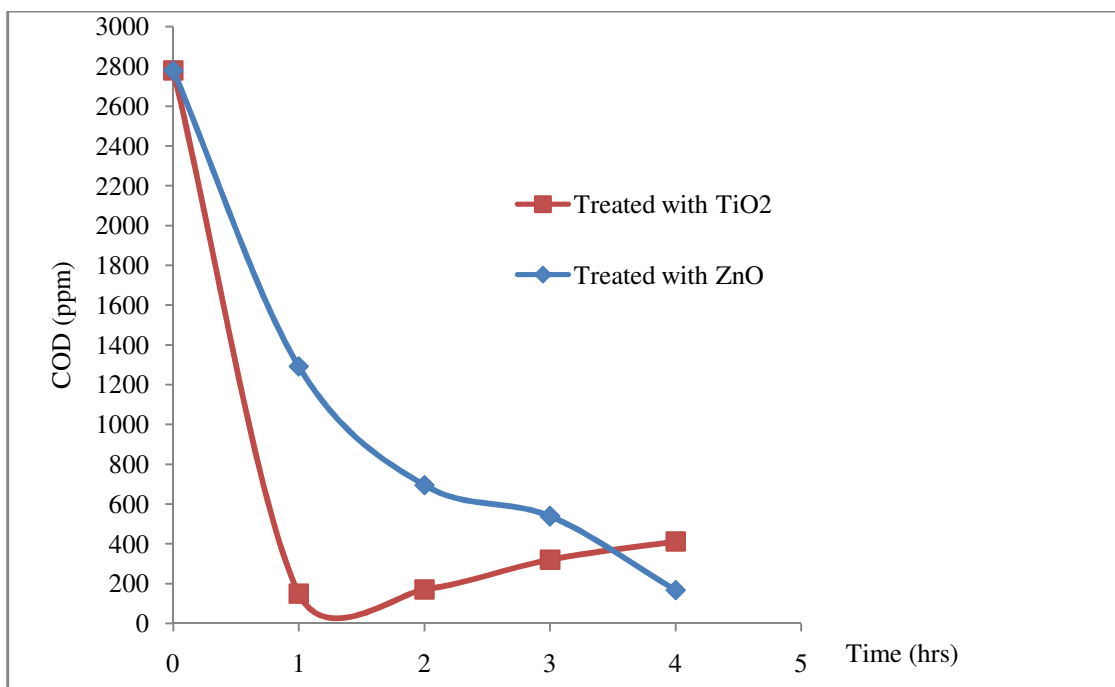
ZnO whereas TiO<sub>2</sub> shows slight increase after 2 hours of treatment as shown in Figure-5. Both ZnO and TiO<sub>2</sub> indicate dye degradation which can be observed via turbidity values. An increase in exposure time results in decrease in COD for both the catalysts as indicated in figure-5. The effect of variation of TDS on exposure time on ZnO and TiO<sub>2</sub> is shown in figure-6.



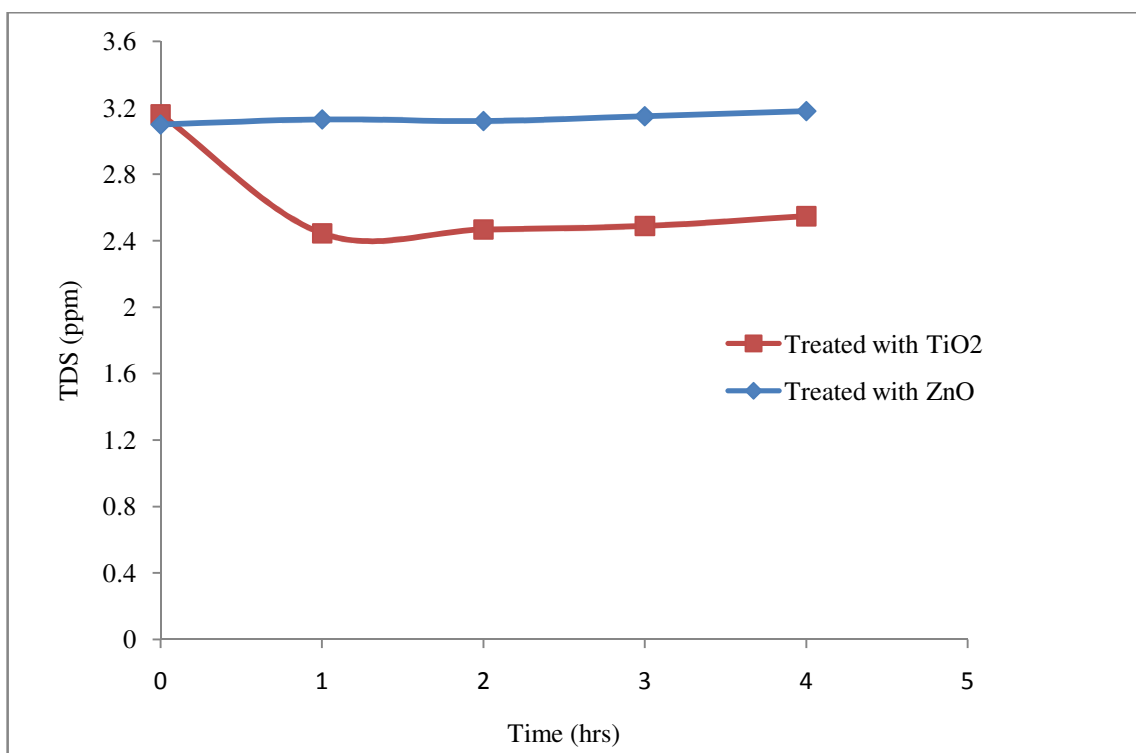
**Figure-3**  
Effect of variation of pH with exposure time for ZnO and TiO<sub>2</sub> coated reactor



**Figure-4**  
Variation of TOC with exposure time for ZnO and TiO<sub>2</sub> coated reactor



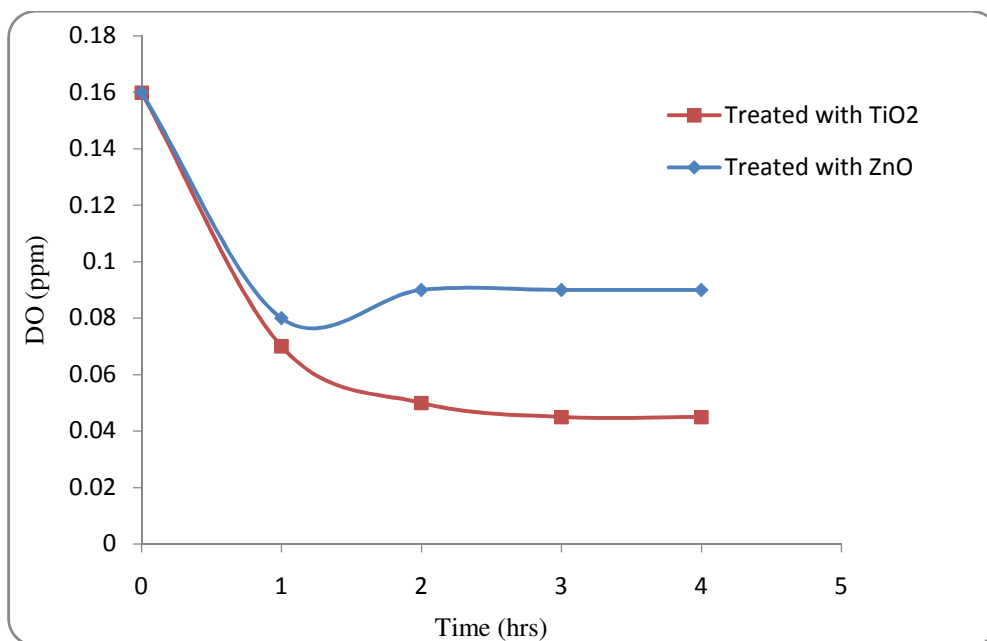
**Figure-5**  
Variation of COD with exposure time for ZnO and TiO<sub>2</sub> coated reactor



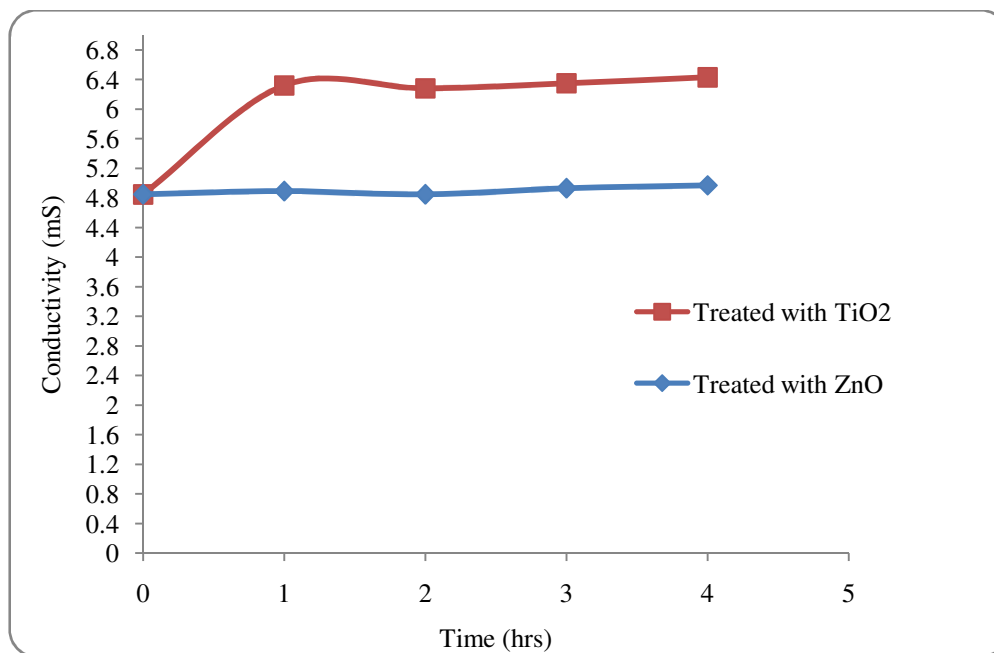
**Figure-6**  
Variation of TDS with exposure time for ZnO and TiO<sub>2</sub> coated reactor

In the case of TiO<sub>2</sub>, the Dissolved oxygen (DO) decreased with increase in exposure time up to 3 hours above which no change as seen in figure-7. There was a drastic decrease in DO for the

first hour followed by increase in time up to 5 hours of exposure time as indicated in figure-8.



**Figure-7**  
Variation of DO with exposure time ZnO and TiO<sub>2</sub> coated reactor



**Figure-8**  
Variation of conductivity with exposure time for ZnO and TiO<sub>2</sub> coated reactor

## Conclusion

In this experimental work, the effectiveness of using ZnO and TiO<sub>2</sub> nanoparticles by solar photo catalysis in removing toxic organic pollutants from textile industry waste water was investigated. Multilayer thin film using chitosan polymer and catalyst was fabricated by L-b-L method in glass tube as reactor. The effluent samples were treated with ZnO coated tube and

TiO<sub>2</sub> coated tube. Different parameters were analyzed and studied for the treated samples. The results showed ability of both photo catalysts in reduction of organics matters present in the collected wastewaters. It was found that the optimum exposure time of photo catalytic reaction under solar radiation was within 2 hours for most of the experiments. The study of treatment of effluent sample using ZnO and TiO<sub>2</sub> thin films showed that both photocatalysis process achieved good

degradation of organic matters, whereas TiO<sub>2</sub> is better than ZnO in TOC and COD degradation. Based on the above results it is seen that multilayer thin films fabricated using L-b-L method finds application in the treatment wastewater in an efficient and environmental friendly manner.

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