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# Photocatalytic Degradation of a Real Textile Wastewater using Titanium Dioxide, Zinc Oxide and Hydrogen Peroxide

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**----------ABSTRACT----------**

*In this study, the photocatalytic degradation of textile wastewater from Gul Ahmad textile industry in Karachi, Pakistan, using $TiO_2$, ZnO, and $H_2O_2$as photocatalyst was investigated. The experiments were carried out at 38 $^oC$ in astirrerbath reactor by using Ultra-Violet photo oxidation process. The degradation of wastewater using $TiO_2$ and ZnO under various pH and using $TiO_2$ and $H_2O_2$ were examined. Titanium dioxideand zinc oxide proved to be very effective catalysts in photocatlytic degradation of real textile industrial water. The maximum decolorization achieved was 95.29% by using $TiO_2$ and 64.41% by using ZnO at 37 $^oC$ and pH of 9, within 150minutes of irradiations. At pH of 7.3 the maximum decolorization was 90.48%. When $TiO_2$ was combined with $H_2O_2$ the maximum decolorization was about 86% but surprisingly within 50 minutes of the irradiation time. A higher reaction rate was found for Titanium dioxide. The results indicate that for real textile wastewater, $TiO_2$ is comparatively more effective than 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, Hydrogen peroxide*

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## I. Introduction

In Pakistan most textile industries are facing water shortage. The treated water may be recycled in the same industry 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 (Kansal et al., 2007). More than 10,000 commercial dyes and pigments, under commercial names are used world wide by textile industries (Walter &Huren, 1995). 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 azodyes, and anthraquinone dyes (Walter &Huren, 1995).

The chemical and physical processes like adsorption, flocculation, reverse osmosis, and ultra filtration are suggested by many researchers for color removal from textile effluent (Robinson et al., 2001; Zamora et al., 1999; Ladakowicz et al., 2001; &Geogiou et al., 2002). However, the effluent treated by these techniques alone is not recyclable and require further treatment (Arslan et al., 2000; Chaudhuri & Sur, 2000; & Stock et al., 2000). Extensive research is conducted worldwide by many researchers on studying photo degradation of commercial dyes. Kansal (2007) carried out experiments by irradiating the aqueous solutions of dyes known as MO (MethylOrange) and RG6 (ReactiveGreen6). His results show that maximum decolorization (above90%) is achieved with ZnO. Each dye responded differently to photocatalytic system under varying pH, amount of catalyst, and initial concentration of dye. There view (The & Mohamed, 2011) confirms that performance of the catalyst can be enhanced by introducing foreign species into $TiO_2$ matrix.

The studies (Kasanen et al., 2011 &Syoufian et al., 2007) on photocatalytic activity of $TiO_2$ on photo decomposition of a dye called MB (Methylene Blue) indicate that degradation of MB by $TiO_2$ varied from 80%-92%. The photocatalytic declourisation of a dye RO4 (Reactive Orange4) by $TiO_2$ (Muruganandham &Swaminathan, 2006) reports that the dye was completely degraded in three hours at pH of 5, room

temperature, and in the presence of reaction enhancer like $H_2O_2$. The study of Qamar et al., (2005) reports that photocatalytic degradation of two dyes, chomotrope2 Bandamido black10B by $TiO_2$ is strongly influenced by pH, amount of catalyst and reactionenhancer like $H_2O_2$. They recommend further studies using real textile effluent to determine optimal degradation conditions. Bizanietal., (2006) report their findings on photodegradation of two commercial azo-dyes in the presence of $TiO_2$ and effectiveness of their system for real textile wastewater. They observed complete removal of the colour; pH and reaction enhancer $H_2O_2$ played an important role in enhancing the process. They achieved complete decolorization of real textile wastewater within six hourof irradiation.

Jainand Shrivastava (2008) reports that photodegradation of a dye, cyanosine by $TiO_2$ is faster at pH of 8, temperature of +30 $^oC$, and in the presence of $H_2O_2$. Other studies [2 and 17] show that degradation of commercial dyes like Rhodamine B, Acid Blue 40, Basic Yellow 15, Direct Blue 160, and Reactive Red 120 by UV-$TiO_2$ is effective under optimum conditions but addition of $H_2O_2$ does not have significance influence on degradation efficiency. Other researchers (Sivakumar et al., 2011; Aguedach et al., 2005; Tang & Chen, 2004; &Qamar et al., 2004) report that photo degradation of azodyes like RB5 (Reactive Black5), RY145 (Reactive Yellow 145, and Chrysoidine is effective at low pH. However the results of Qamar et al., (2004) and Zayaniet al., (2009) show kinetic dependency on catalyst loading, pH, and presence of $H_2O_2$; and the degradation rates are strongly influenced by these parameters. The results of Chenand Cao (2005) on role of additives indicate that addition of $H_2O_2$ does not accelerate the photocatlytic degradation, rather it inhibits. Bansal and Sud (2011) studied photodegradation of Procion Blue dye from real textile wastewater using $TiO_2$ and ZnO. They report that ZnO is more efficient catalyst at pH 7, which is discharge pH of industrial effluents.

During last two decades, photodegradation of organic and inorganic pollutants of dyes by titanium dioxide, zinc oxide and hydrogen peroxide as photocatalyst has been studied by many researchers (Prieto et al., 2005) and it is predicted that in the near future, photocatalysis technique will be considered most effective in treating textile wastewater. Many researchers attempted to study photocatalytic activity of semiconductors like $SnO_2$, CdS and ZnO (Vinodgopal & Kamat, 1995; Neppolian et al., 2002); Lathasree et al., 2004; Lizama et al., 2002; &Akyol et al., 2004). However, there are contradicting reports on the suitability and effectiveness of semi-conductors. For some commercial azo-dyes, ZnO is reported suitable and for some $TiO_2$ (Daneshvar, 2003). 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 waste water.

Still not enough is known about effectiveness of semiconductors like $TiO_2$, ZnO, $H_2O_2$ 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. For this study sample wastewater was collected from Gul Ahmad Textile Company and it was confirmed by the sample provider that they used azo and anthraquinone dyes while dyeing cotton, silk, and polyester fabric during the time of sample collection.

According to Grezechulska and Morawski (2002) removal of color from wastewater is often more important than the removal of other organic colorless chemicals. Xiaobo and Samuel (2007) focused on the most important photocatalytic applications of titanium dioxide and zinc oxide. Alkhateeb et al., (2005) and Abbas et al., (2008) have reported that titanium dioxide and zinc oxide have good photocatalytic properties and nominated both catalystst to be promising substrates for photodegradation of water pollutants. Hence this study was focused on decolorization of selected samples of effluent from a local textile industry using $TiO_2$, ZnO, and $H_2O_2$ with irradiation with Ultra-Violet light under constant temperature but at different pH.

## II. Sampled TextileWastewaterCharacteristics

At the time of sampling, GulAhmad Textile Company was processing cotton and synthetic fabric. This composite textile wastewater was analyzed for biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total dissolved solids (TDS). The results of these analyses are presented in Table 1. The variation in results was due to dyeing and processing of different batches of the fabric during sampling period. The BOD/COD ratio was between 0.71 and 0.84.

## III. Ultraviolet Energy

The selection of ultraviolet energy depends on the absorption capacity of the molecules of the contaminant in the sample water. The Ultraviolet (UV) energy not only advances the oxidation process but sterilizes the wastewater by destroying five major group of micro-organism. Previous research (Al-Kdasi et al., 2004) has indicated that UV light at wavelength 200-678 nm, and 50-150W is adequate for composite water (textile wastewater of cotton and synthetic fabric)with an irradiation time of 1-3 hour. Hence is the reason for selecting of the parameters for this study.

## IV. Experimental instruments andscope ofstudy

The UV lamp selected for this study was 8.0 inches long with an UV output of 11 W. A total number of eight UV lamp tubes, manufactured by Jiangsu Shen Xing PhotoelectricityAppparatus Co., Ltd. China, were submersed in the specially designed reaction vessel (diameter 8 inches, volume 5 liter) to produce 88 W of energy. The sample wastewater was placed in a 5 liter glass cylinder acting as a photoreaction cell. The catalyst powder was suspended in the sample and the solution in the cell was kept homogeneous by constant stirring with a top mounted stirrer and aeration by using an air pump as shown in the figure 1 (actual experimental rig). The schematic diagram of the experimental setup is shown in figure 2. The aerial view of the geometrical arrangement of the UV tubes is shown in figure 3. The passing of the air facilitated the wastewater circulation around the reaction vessel in order to maintain the reaction temperature at the desired value. This cell was placed in a constant temperature bath. The PH meter and temperature probe was inserted in to cell to monitor PH and temperature of the wastewater. The photocatalytic degradation was carried out over suspension of Titanium Oxide, Zinc Oxide and $TiO_2/H_2O_2$ under ultraviolet irradiation.

The Spectronic"Genesys20" Spectrophotometer with wavelength range 325 to 1100 nm, accuracy ±2.0 nm was used to measure absorbance at λmax of 625 nm. The rate of photodegradation is calculated in percentage with time of irradiation. Tests were conducted for variables such as pH of sample wastewater, type of catalyst, and exposure time of UV light. The effect of temperature was not included to the study plan as researchers (Sahunin et al., 2006 & Chong et al., 2010) have indicated that heat energy is in adequate to activate the $TiO_2$ surface. Most of the previous studies done between the ranges of 20-80 $^{o}$C have proved that higher reaction temperature disfavour the adsorption of organic compounds on to the catalyst ($TiO_2$) surface. The optimal temperature reported by Chong et al., (2010) for photocatalytic degradation is in the range of 20-80 $^{o}$C, hence is the reason for choosing the constant temperature in the range of 37-38 $^{o}$C.

## V. Materials

In this study titanium dioxide powder (anatase) form and Zincoxide (Dentam) were used as supplied. These Chemicals are supplied by BDH with purity of 99.99%. The 30% Aqueous Solution of Hydrogen peroxide was also supplied by BDH. The pH of the sample in the reaction vessel was adjusted with calculated volume/weight of 1 N HCl or 1 NNaOH.

## VI. Procedure

In all experiments 6 g of titanium dioxide or 4 g zinc oxide is suspended in 5 litre of the real textile dyeing wastewater which is placed in a photo reaction cell. For experiments with hydrogen peroxide, 2.4 ml $H_2O_2$ with 35% purity was added to sample wastewater. The suspension was subjected to irradiation under UV light for1-2 hour. The suspension was stirred and aerated throughout the experiment.

At regular time intervals, the $2cm^3$ of irradiated sample was taken out from the reaction vessel with the help of micro syringe, and then filtered through Millipore filter of 0.45 um to separate the solid catalyst. Using a couvette the absorption spectra was measured and the absorbance of the supernatant liquid is measured at λmax of 625 nm. 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 (azo-dyes) in the sample wastewater and C is the concentration after photo irradiation. All experiments were carried out at two pH of sample with different photocatalyst. The COD analysis was done using potassium dichromate oxidizing mixture, digested for 2 hours and measured by Thermo Orion aquafast IIAQ2040 COD meter. For accuracy of results the absorbance at a given time was compared with a calibration curve. The calibration plot was obtained by using a known percentage of colored real textile wastewater.

## VII. Results andDiscussion

The results of this study are comparable to the reported finding of studies carried out using real textile water by Sahuninetal (2006), Abbasetal (2008), and Bansaland Sud (2011); and reviewed by Chongetal (2010) and Al-Kdasietal (2004). The effect of catalyst as an oxidant on degradation of real textile wastewater by photoxidation process is shown in figure 4. The wastewater was effectively decolorized using titanium dioxide or zinc oxide under pH of 9. The maximum decolorizationachieved within 150 minutes of irradiation time, was about 95.29% by using $TiO_2$ and 64.41% by using ZnO at 37 $^{o}$C. The degradation by $TiO_2$ reported by Abbas et al [34] is similar but at low temperature of 30 $^{o}$C; however, degradationby ZnO was higher (82%) at 30 $^{o}$C. The higher reactivity of $TiO_2$ is also supported by Chong et al (2010) under similar conditions and is attributed to the geometry and working conditions of the photo reactor. The saturation level of $TiO_2$ under given

operating conditions is lower than ZnO. A direct comparison cannot be made as working geometry, irradiation time, intensity and wavelength used in reported work (Chong et al., 2010) weredifferent.

The effect of pH on degradation of textile wastewater by $TiO_2$ is shown in figure 5. The maximum decolorization achieved within 150minutes of irradiation time, was about 90.48% by using $TiO_2$ at pH of 7.3. The effect of pH studied by most researchers in the range pH 1-7 shows that pH is one of the most important operating parameter that affect the photocatalytic reactivity (surface charge density) of the $TiO_2$. The effect on surface charge density of the $TiO_2$ can be understood by following water equilibrium equations.

Under pH less than 4.5-7:

$TiOH + H^+ \leftrightarrow TiOH_2^+$ (1)

Under pH more than 7:

$TiOH + H^- \leftrightarrow TiO^- + H_2O$ (2)

The results of studies (Bansal & Sud, 2011) on wastewater containing azo-dyes report that the lesser degradation of dye occurs in basic solution and higher in acidic with $TiO_2$; and in case of ZnO the maximum degradation occurs at pH 7. The degradation observed in this study proves that surface charge density distribution for $TiO_2$ is highly dependent on the pH of thereactor system.

Figure 6 shows the degradation of textile wastewater by combined dosing of $TiO_2$ and $H_2O_2$. A maximum decolorization (about 85.71%) was achieved at pH of 4 and within 50 minutes of the irradiation time. The degradation of the textile wastewater with hydrogen peroxide under UV irradiation is reported (Al-Kdasi et al., 2004) more effective which is contributed to the fact that under UV, $H_2O_2$ are photolyzed to form two hydroxyl radicals (OH-) that react with organic contaminants. This study confirms that the complete destruction of azo-dyes in real textile water is achievable in 50 minutes; which is agreement with findings of Adel Al-kdasi et al., (2004). Based on the findings of Sahuninetal (2006), $TiO_2$ was considered as most suitable to combine with $H_2O_2$, because in the presence of $H_2O_2$ the reaction is accelerated as per following (Sahunin et al., 2006).

$TiO_2 + UV \rightarrow TiO_2 (e- + h+)$ (3)

$TiO_2 (e-) + H_2O_2 \rightarrow TiO_2 + OH + OH$ (4)

$TiO_2 (h+) + OH \rightarrow TiO_2 + OH$ (5)

The over all mechanism of enhanced photo decolorization of real textile industrial wastewater byan additive like $H_2O_2$ was widely postulated and presented by following equations (Akpan& Hameed, 2009).

$TiO_2$ or ZnO $+ hv$ (energy> 3.2 ev) $\rightarrow e^- + h^+$ (6)

$e^- + O_2$ (ads) $\rightarrow .O_2^-$(ads) (7)

$h^+ + OH^-_{(s)} \rightarrow .OH_{(s)}$ (8)

The highly reactive hydroxyl radicals oxidize the dye molecules as follows:

$OH$ + dye $\rightarrow$ degradation (9)

In the other route where a UV irradiation is used a photo sesitization process occurs, in which the sensitizer (the dye) absorbs radiation in the visible range to yield an excited state of the sensitizer. The dye radicals inject electrons to the conduction band of the $TiO_2$ or ZnO and convert to $dye^{-+}$.

The formed species oxidize the dye molecule, as follows:

dye + visible light $\rightarrow$ dye (10)

dye + semiconductors $\rightarrow dye^{-+} + e^-$ (11)

The formed $dye^{-+}$ radical ions acts react with dye molecules in the same way of the reaction of hydroxyl radicals.

$dye^{-+}$ + dye $\rightarrow$ degradation (12)

Figure 7 shows the effect of pH on the performance of the catalyst. The maximum degradation of 90.48% was achieved by $TiO_2$ at pH of 7.3. A similar pattern in the effect of pH on commercial dyes in aqueous solution by UV/$TiO_2$ is reported by Walter and Huren (1995). The pH has the greatest effect on the oxidation kinetics of azo-dyes at comparatively less irradiation time. The findings of Bansal and Sud (2011) show that occurrence of lesser degradation of basic dye solution and higher in acidic dye solution with $TiO_2$. Until now there is no comprehensive study conducted that encircles the comparison of the effect of $TiO_2$ and ZnO photocatalytic degradation under different operating parameters. Therefore, in order to commercialize the photocatalytic wastewater technology, several key parameters like catalyst development, reactor design and process optimization need to further investigated.

## VIII. Kinetic Analysis

The kinetics of decoloration of textile wastewater with $TiO_2$ and ZnO is shown in figures 8 and 9 respectively. The plotted data produced a straight line that indicates that the decolorization of the textile wastewater can be described by the following first-order kinetic model equation.

$$\ln (C_O/C) = kt \quad (13)$$

The linear regression analysis for correlation constants for $R^2$= 0.999 for $TiO_2$ and 0.981 for ZnO; whereas the slope values for $TiO_2$ and ZnO are 0.032 and 0.029 respectively. The closeness in two rate constant values in this study is similar to the closeness of the rate constant values reported by Bansal and Sud ( 2 0 1 1 ) . It should be noted that the Bansal's data is for disappearance of a commercial dye and this study is carried out on real textile wastewater. The rate constant depends on a number of process operating parameters and geometry and working conditions of the reactor. A small difference in rate constant values for $TiO_2$ and ZnO is associated with the transport of photo electron through the catalyst to the adsorbed oxygen on the surface; and suggests that the rate controlling process is associated with surface steps. Therefore, a different type of sensitization produces a different reaction rate. More precise rate of reaction can be calculated if effects of photon absorption are included to the kinetic model equation. Figure 10 shows the real textile wastewater before and after the photocatalytic irradiation with $TiO_2$.

## IX. Conclusions

Titanium dioxide and zinc oxide proved to be very effective catalysts in photocatlytic degradation of real textile industrial water. The maximum decolorization achieved was 95.29% by using $TiO_2$ and 64.41% by using ZnO at 37 $^oC$ and pH of 9, within 150 minutes of irradiations. At pH of 7.3 the maximum decolorization was 90.48%. Similar to most researcher's findings, the decolorization at lower pH supports the notion that pH is one of the most important operating parameter that affect the photcatalytic reactivity of the catalyst. When $TiO_2$ was combined with $H_2O_2$ the maximum decolorization was about 86% but surprisingly within 50 minutes of the irradiation time. A higher reaction rate was found for Titanium dioxide. The results indicate that for real textile wastewater, $TiO_2$ is comparatively more effective than ZnO. This study proves that real textile wastewater reacts differently to catalyst than aqueous solution of azo-dyes; that is related to the rate controlling process, which is associated with surface steps and accordingly, presence of other contaminants sensitizes the reaction rate.

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Table 1. Characteristics of sampled textile water (from Gul Ahmad)

| Characteristics | Value |
|---|---|
| COD ($mgxl^{-1}$) | 250-650 |
| BOD ($mgxl^{-1}$) | 350-550 |
| TDS ($mgxl^{-1}$) | 1060-1780 |
| $P^H$ | 6.57-2.57 |
| Conductivity ($mSxcm^{-1}$) | 1.72-2.57 |
| Colour (pt-Co unit) | 586-1182 |
| Turbidity (NTU) | 104-136 |

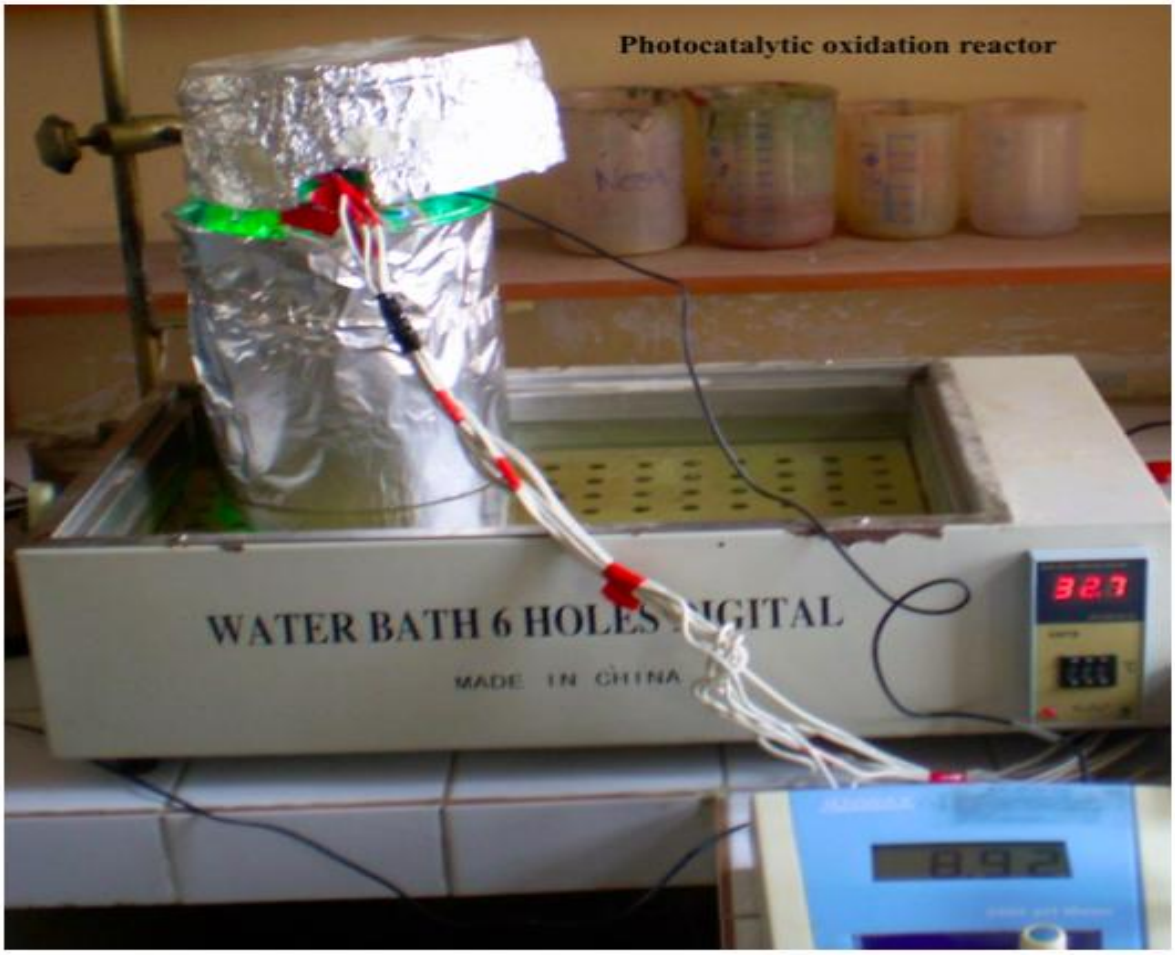


Fig 1. Photocatalytic oxidation reactor.

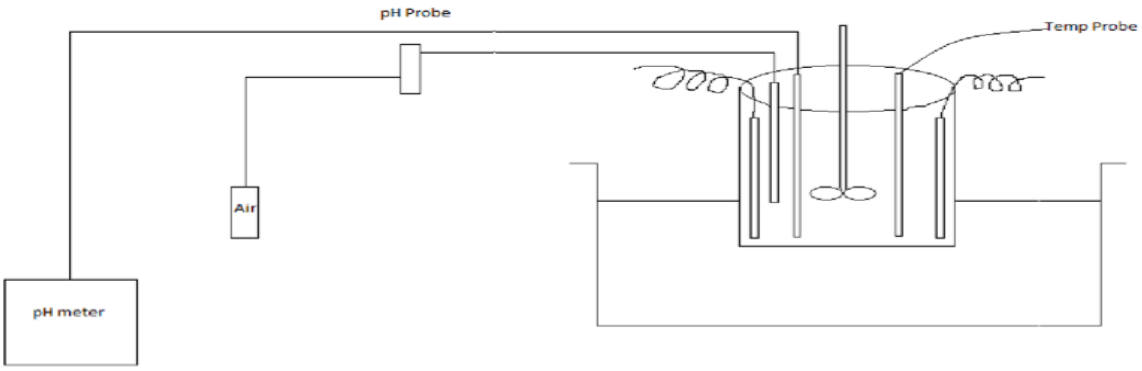


Fig 2. Schematic diagram of the experimental set-up.

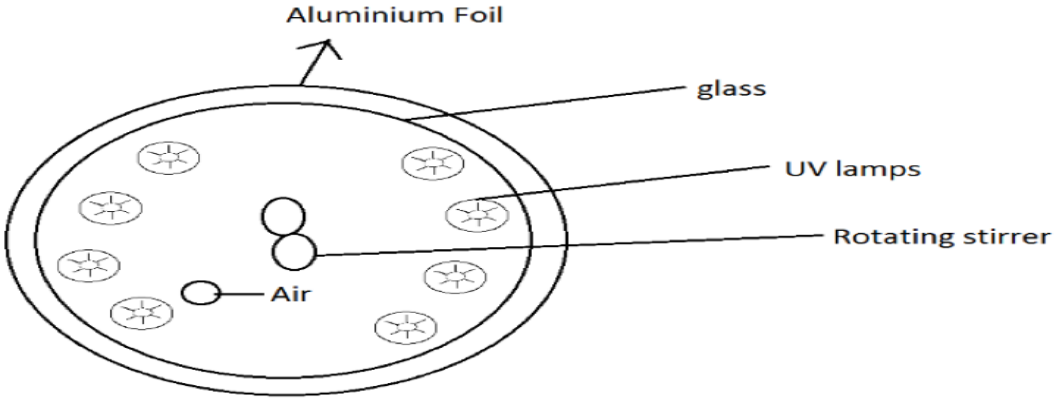


Fig 3. The aerial view of the geometrical arrangement of the UV tubes in the reactor.

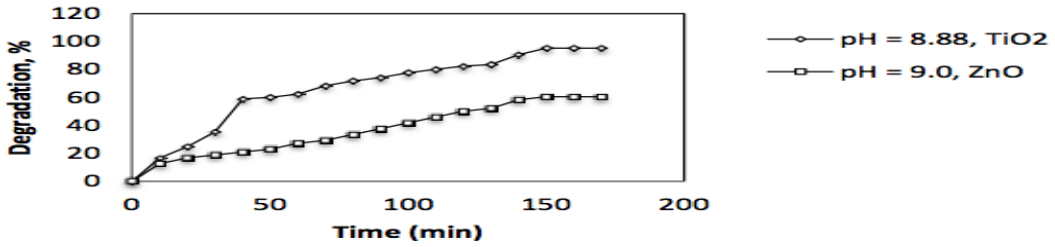


**Figure 4. Degradation of textile industry waste water by photooxidation using TiO2 and ZnO**

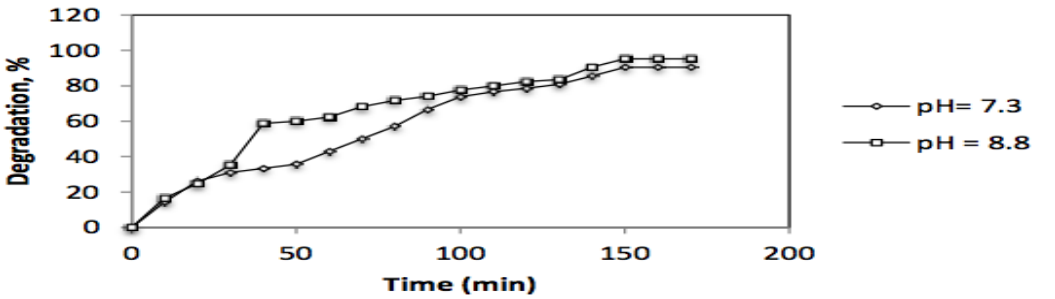


**Figure 5. Effect of pH on degradation of textile industry waste water by Photooxidation using TiO2**

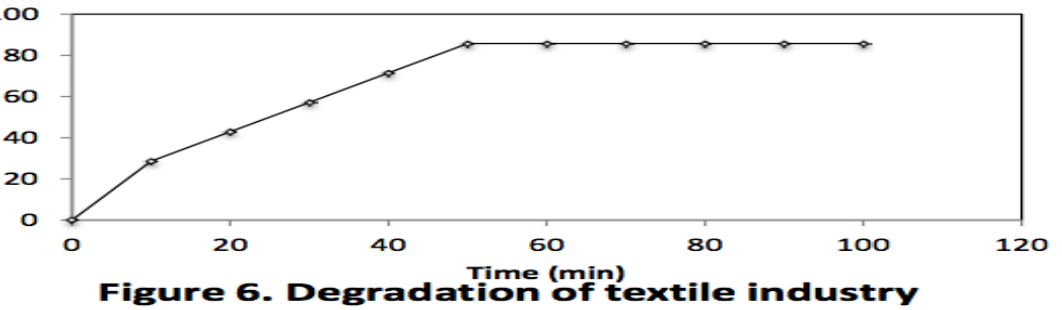


**Figure 6. Degradation of textile industry waste water by Photooxidation using TiO2/H2O2**

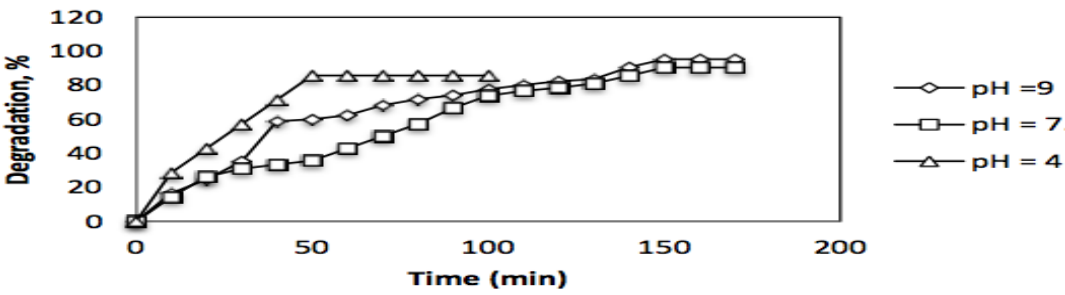


**Figure 7. Effect of pH on the Performance of Catalyst**

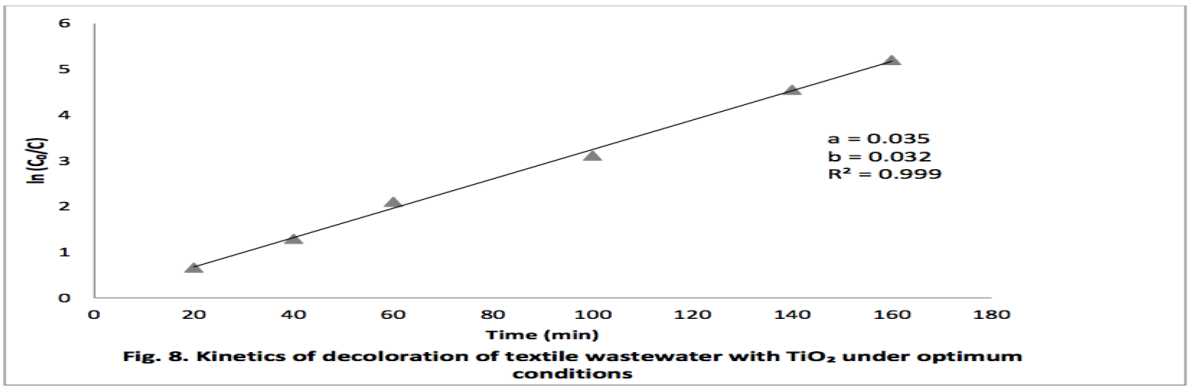


**Fig. 8. Kinetics of decoloration of textile wastewater with $TiO_2$ under optimum conditions**

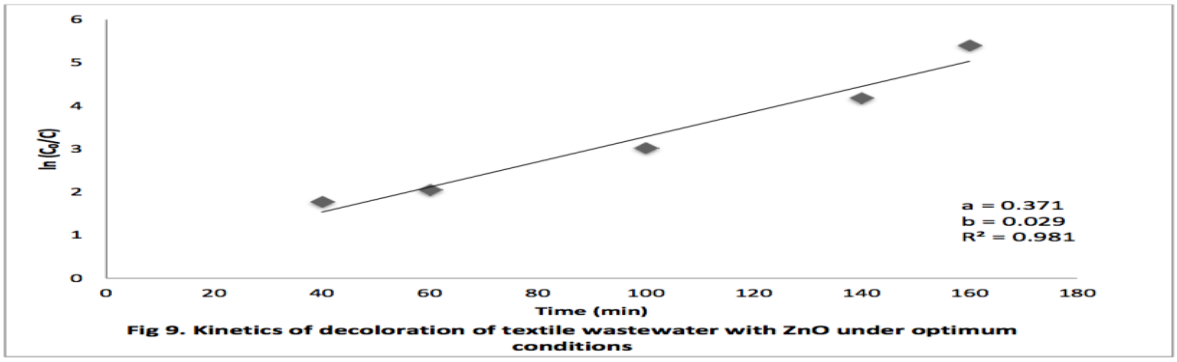


**Fig 9. Kinetics of decoloration of textile wastewater with ZnO under optimum conditions**


Fig 10. Real textile wastewater before and after photocatalytic irradiation.