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# Photochemical Treatments of Textile Industries Wastewater

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## 1. Introduction

Textile industry is one of the most water and chemical intensive industries worldwide due to the fact that 200-400 liters of water are needed to produce 1 kg of textile fabric in textile factories (Correia et al., 1994 & Orhon et al., 2003). The water used in this industry is almost entirely discharged as waste. Moreover, the loss of dye in the effluents of textile industry can reach up to 75% (Couto & Toca-Herrera, 2006). The effluents are considered very complex since they contain salt, surfactants, ionic metals and their metal complexes, toxic organic chemicals, biocides and toxic anions.

Azo dyes are regarded as the largest class of synthetic. Approximately, 50–70% of the available dyes for commercial applications are azo dyes followed by the anthraquinone group (Konstantinou & Albanis, 2004). Azo dyes are classified according to the presence of azo bonds (–N=N–) in the molecule i.e., monoazo, diazo , triazo etc. and also sub-classified according to the structure and method of applications such as acid, basic, direct, disperse, azoic and pigments (Bhutani, 2008). Some azo dyes and their dye precursors are well-known of high toxicity and suspected to be human carcinogens as they form toxic aromatic amines (Gomes et al., 2003 & Stylidi et al., 2003).

Different physical, chemical and biological as well as the various combinations of pre-treatment and post-treatment techniques have been developed over the last two decades for industrial wastewaters treatment in order to meet the ever-increasing requirements of human beings for water. Though there are numerous studies published in this field, most of the techniques adopted by these researchers are uneconomical, ineffective or impractical uses (Cooper, 1995 & Stephen, 1995).

Recent studies have demonstrated that heterogeneous photocatalysis is the most efficient technique in the degradation of colored chemicals(Li et al., 2003; Vione et al., 2003; Antharjanam et al., 2003; Fernandez-Ibanez et al., 2003; Liu et al., 2003; Ohno, 2004; Chen et al., 2004; Alkhateeb et al., 2005 & Attia et al., 2008). These studies used titanium dioxide and / or zinc oxide in the photolysis processes. The large bang gap of titanium dioxide and zinc oxide (~ 3.2 eV) put a limitation of using these semiconductors in photocatalytic degradation under natural weathering conditions. Only a small part of the overall solar intensity could be useful in such photodegradation processes. However, the existence of dye on the surface of catalyst reduces the energy required for excitation and then increases the efficiency of the excitation process by extending its absorption in the visible region of the spectrum.

## 2. Methods used in treatment of textile wastewater

There are several factors to choose the appropriate textile wastewater treatment method such as, economic efficiency, treatment efficiency, type of dye, concentration of dye and environmental fate.

There is no general method for the treatment of textile industrial wastewater. Wastewaters from textile industry contain various pollutants resulting from various stages of production, such as, fibers preparation, yarn, thread, webbing, dyeing and finishing. Mainly three methods are used for the treatment of textile industrial wastewater. These are:

1.  Physico-chemical methods.
2.  Advanced oxidation methods.
3.  Biological sludge methods.

The main operational methods used for the treatment of textile industrial water involve physical and chemical processes (Shaw et al., 2002 & Liu et al., 2005). However, these techniques have many disadvantages (See Table 1, Mutambanengwe, 2006). These disadvantages include Sludge generation, high cost , formation of bi – products, releasing of toxic molecules, requiring a lot of dissolved oxygen, limitation of activity for specific dyes and requiring of long time.

In recent years, advanced oxidation processes (AOPs) have gained more attraction as a powerful technique in photocatalytic degradation of textile industrial wastewater since they are able to deal with the problem of dye destruction in aqueous systems (Konstantinou & Albanis, 2004).

## 3. Photocatalysis

Photocatalysis is defined as the acceleration of a photoreaction in the presence of a catalyst, while photolysis is defined as a chemical reaction in which a chemical compound is broken down by photons. In catalyzed photolysis, light is absorbed by an adsorbed substrate.

Photocatalysis on semiconducting oxides relies on the absorption of photons with energy equal to or greater than the band gap of the oxide, so that electrons are promoted from the valence band to the conduction band:

$$\text{Semiconductor} + \text{h}\nu \rightarrow \text{h}^+ + \text{e}^- \tag{1}$$
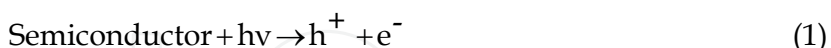
If the photoholes and photoelectrons produced by this process migrate to the surface, they may interact with adsorbed species in the elementary steps, which collectively constitute photocatalysis.

The numerous gas- and liquid-phase reactions photocatalysed by $TiO_2$ and $ZnO$ have been reviewed. There is a general agreement that adsorption is necessary since the surface species act as traps for both; photogenerated holes and electrons, which otherwise recombine.

In addition to participating in conventional surface reaction steps, adsorbed dye molecules assist in the separation of photoholes and photoelectrons, which may otherwise recombine within the semiconductor particles. A major factor affecting the efficiency of photocatalysis process is electron/hole recombination.

If the electrons and holes are used in a reaction, a steady state will be reached when the removal of electrons and holes equals the rate of generation by illumination. Recombination and trapping processes are the de-excitation processes which are responsible for the creation of the steady state, if no reaction occurs. There are three important mechanisms of recombination:

1. Direct recombination.
2. Recombination at recombination centers.
3. Surface recombination.

There are different types of semiconductors, whose band gaps range between 1.4 and 3.9 eV, i.e., it could be excited with a light of 318–886 nm wavelengths. This means that most of the known semiconductors could be excited by using visible light. However, not all these semiconductors could be used in the photocatalytic reactions. Bahnemann et al., (1994) report that the most appropriate photocatalysts should be stable toward chemicals and illumination and devoid of any toxic constituents, especially for those used in environmental studies. The authors also explaine that $TiO_2$ and $ZnO$ are the most commonly used in photocatalytic reactions due to their efficient absorbtion of long wavelength radiation as well as their stability towards chemicals. Other semiconductors like $WO_3$, $CdS$, $GaP$, $CdSe$ and $GaAs$ absorb a wide range of the solar spectrum and can form chemically activated surface-bound intermediates, but unfortunately these photocatalysts are degraded during the repeated catalytic cycles involved in heterogeneous photocatalysis.

## 4. Photosensitization

The illumination of suspended semiconductor in an aqueous solution of dye with unfiltered light (polychromatic light) leads to the possibility of the existence of two pathways (Hussein et al., 2008):

1. In the first pathway, the part of light with energy equal to or more than the band gap of the illuminated semiconductor will cause a promotion of an electron to conduction band of the semiconductor and as a result, a positive hole will be created in the valence band. The formed photoholes and photoelectrons can move to the surface of the semiconductor in the presence of light energy. The positive hole will react with adsorbed water molecules on the surface of semiconductor producing $^{\bullet}OH$ radicals and the electron will react with adsorbed oxygen on the surface. Moreover, they can react with deliquescent oxygen and water in suspended liquid and produce perhydroxyl radicals ($HO_2^{\bullet}$) with high chemical activity (Zhao & Zhang, 2008). The processes in this pathway can be summarized by the following equations:

$$h^+ + OH^- \rightarrow \overset{\bullet}{O}H \tag{2}$$

$$h^+ + H_2O \rightarrow H^+ + \overset{\bullet}{O}H \tag{3}$$

$$e^- + O_2 \rightarrow \overset{\bullet}{O}_2^{\,-} \tag{4}$$

$$\overset{\bullet}{O}_2^{\,-} + H^+ \rightarrow \overset{\bullet}{HO}_2 \tag{5}$$

$$\overset{\bullet}{HO}_2 + \overset{\bullet}{O}_2^{\,-} \xrightarrow{\;H^+\;} H_2O_2 + O_2 \tag{6}$$

$$H_2O_2 \rightarrow 2\overset{\bullet}{O}H \tag{7}$$

$$Dye + Semiconductor\,(h^+_{VB}) \rightarrow Dye^{\cdot\,+} + Semiconductor \qquad (8)$$

$$Dye^{\cdot\,+} + O_2^{\cdot\,-} \rightarrow DO_2 \rightarrow degradation\ products \qquad (9)$$
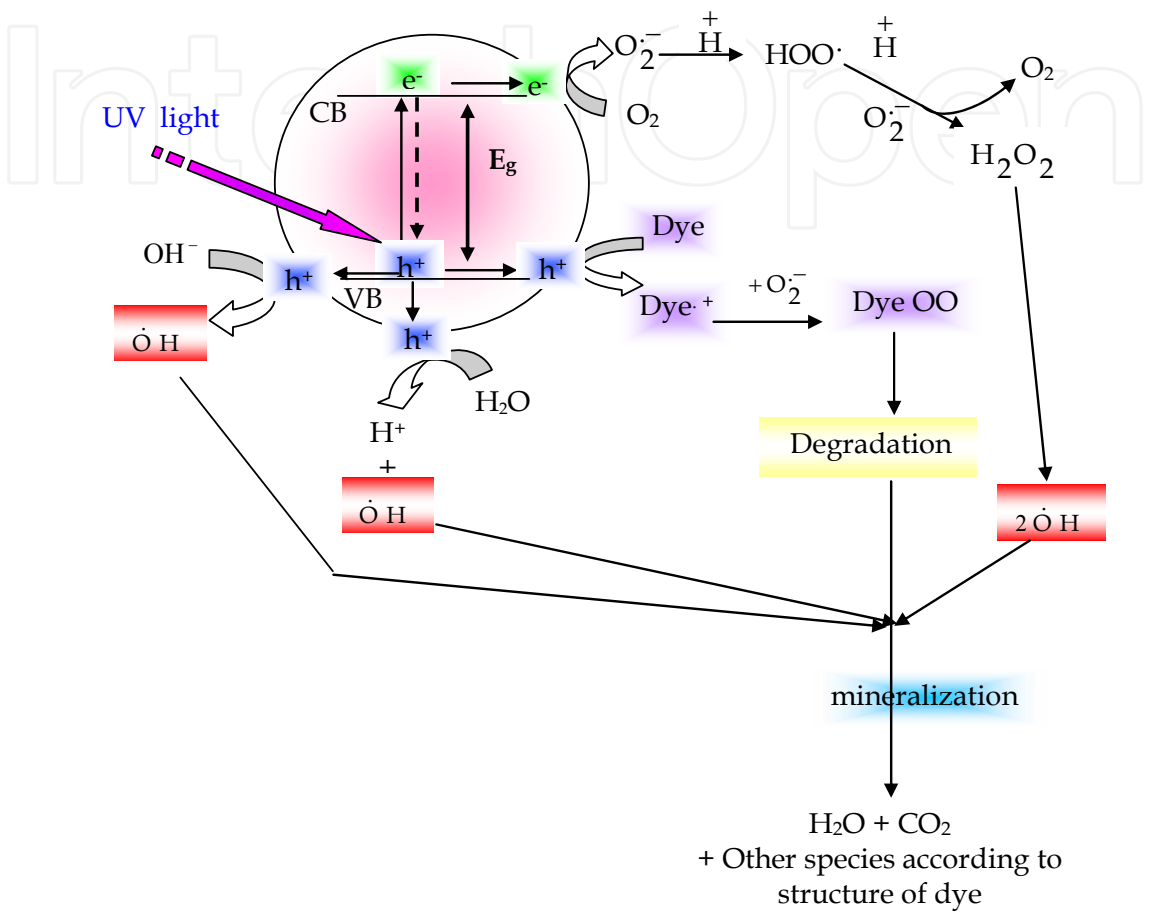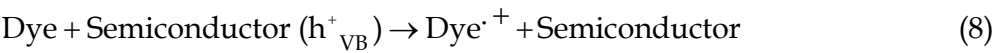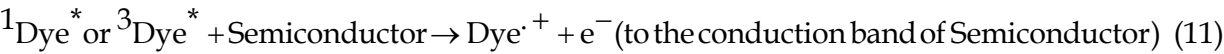


Fig. 1. Dye/semiconductor/UV light system

2.  In the second pathway, the other part of light with energy which is less than the band gap of the illuminated semiconductor will be absorbed by the adsorbed dye molecules. Dye molecules will be decolorized by a photosensitization process. The photocatalytic decolorization of dyes, which is described as photosensitization processes, is also characterized by a free radical mechanism. In this process, the adsorbed dyes molecules on the surface of the semiconductor can absorb a radiation in the visible range in addition to the radiation with a short wavelengths (Fernandez-Ibanez et al., 2003; Ohno, 2004 & Alkhateeb et al., 2005). The excited colored dye (dye*) (in the singlet or triplet state) will inject an electron to the conduction band of the semiconductor (Hussein & Alkhateeb, 2007). The processes in this pathway can be summarized by the following equations:
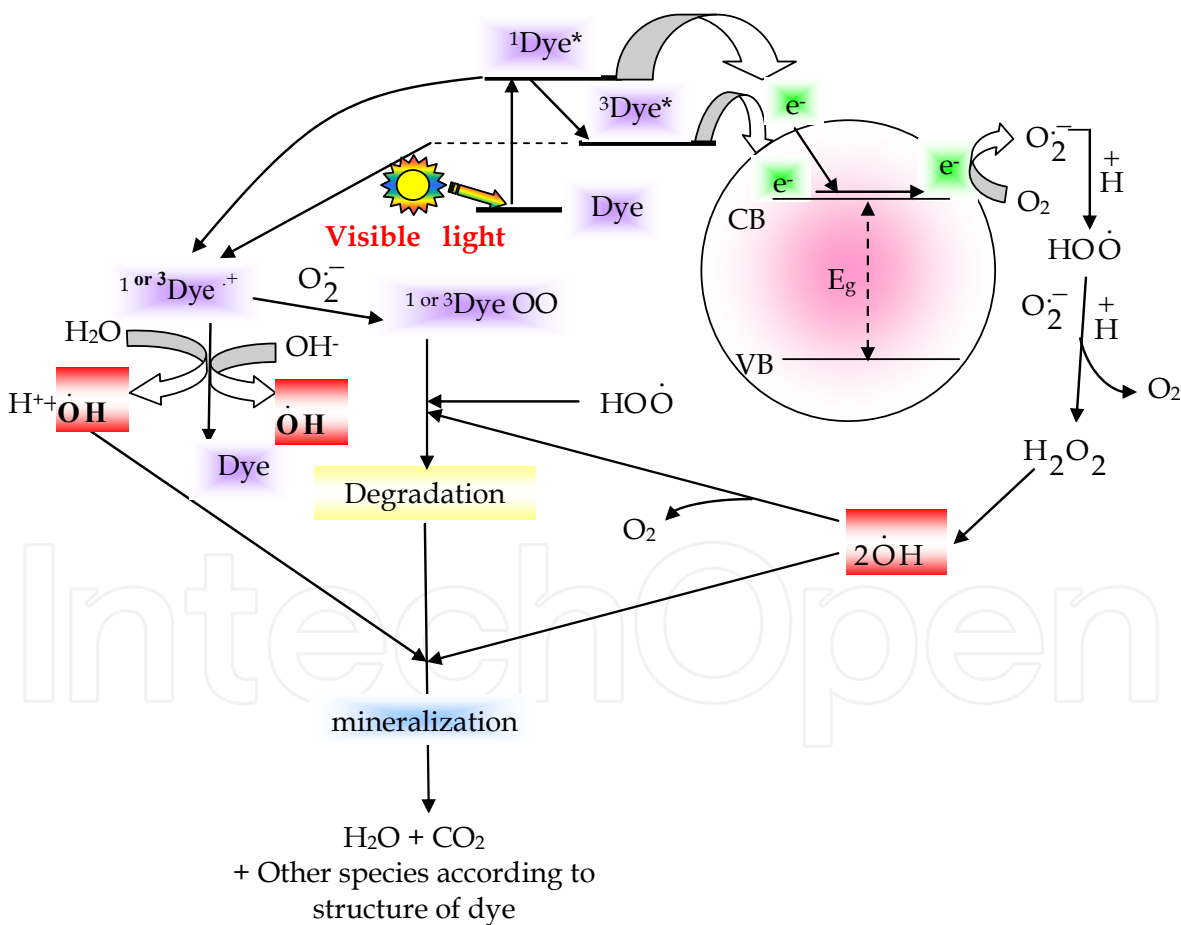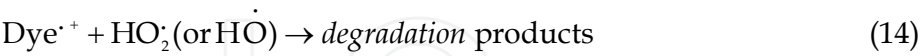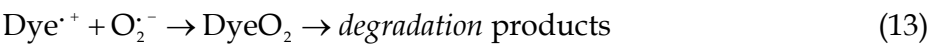
$$Dye + h\upsilon\left(VIS\ or\ UV\ reagion\right) \rightarrow {}^1Dye^* \ or\ {}^3Dye^* \qquad (10)$$

$${}^1Dye^* \ or\ {}^3Dye^* + Semiconductor \rightarrow Dye^{\cdot\,+} + e^- (to\ the\ conduction\ band\ of\ Semiconductor) \quad (11)$$

$$e^- + O_2 \rightarrow O_2^{\cdot -} + \text{Semiconductor} \tag{12}$$

$$\text{Dye}^{\cdot +} + O_2^{\cdot -} \rightarrow \text{DyeO}_2 \rightarrow \textit{degradation} \text{ products} \tag{13}$$

$$\text{Dye}^{\cdot +} + \text{HO}_2^{\cdot}(\text{or } H\dot{O}) \rightarrow \textit{degradation} \text{ products} \tag{14}$$

$$\text{Dye} + 2\dot{O}H \rightarrow H_2O + \text{oxidation products} \tag{15}$$

$$\text{Dye}^{\cdot +} + \overline{O}H \rightarrow \text{Dye} + \dot{O}H \tag{16}$$

$$\text{Dye}^{\cdot +} + H_2O \rightarrow \text{Dye} + \dot{O}H + H^+ \tag{17}$$



Fig. 2. Nonregenerative dye/semiconductor/visible light system

The mechanism above is favoured by nonregenerative organic dye where dye/semiconductor/visible light system and the sensitizer itself degrade. However, in regenerative semiconductor system, the following mechanism may be followed:
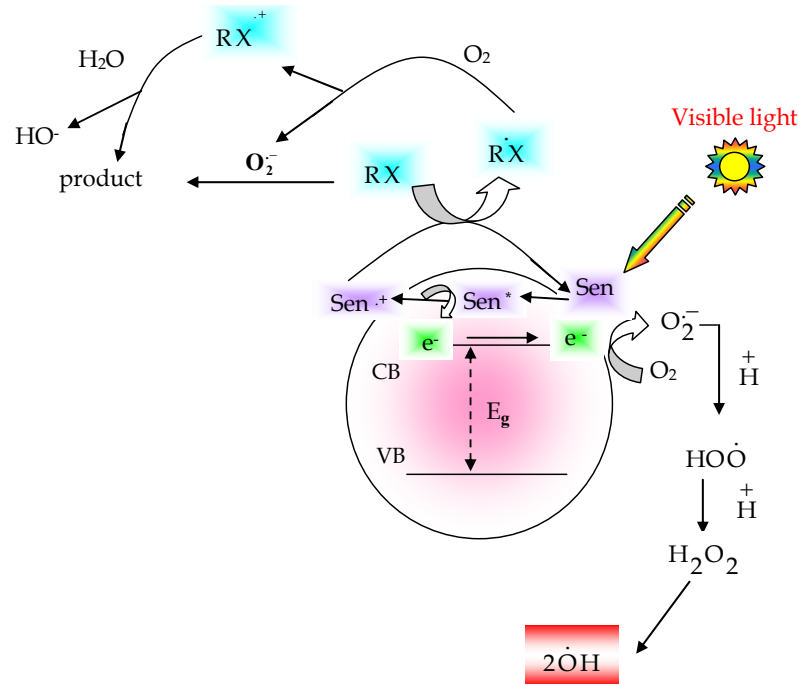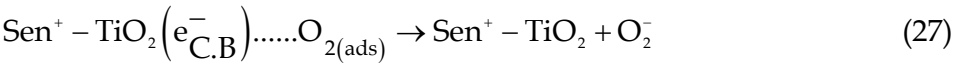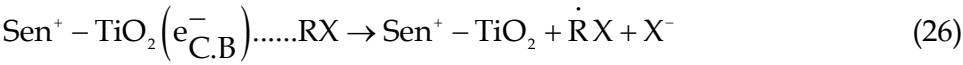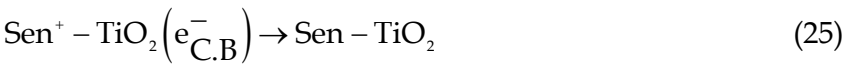
$$Sen + TiO_2 \leftrightarrow Sen - TiO_2 \tag{18}$$

$$Sen - TiO_2 + RX \leftrightarrow Sen - TiO_2......RX_{(ads)} \tag{19}$$

$$Sen - TiO_2 + O_2 \leftrightarrow Sen - TiO_2......O_{2(ads)} \tag{20}$$

$$Sen - TiO_2 \underset{h\upsilon}{\overset{h\upsilon\ visible\ light}{\rightleftharpoons}} Sen^* - TiO_2 \tag{21}$$

$$Sen^* - TiO_2......O_{2(ads)} \rightarrow Sen^+ - TiO_2 + O_2^- \tag{22}$$

$$Sen^+ - TiO_2 + O_2^- \rightarrow Sen - TiO_2 + O_2 \tag{23}$$

$$Sen^* - TiO_2 \rightarrow Sen^+ - TiO_2\left(e_{C.B}^-\right) \tag{24}$$

$$Sen^+ - TiO_2\left(e_{C.B}^-\right) \rightarrow Sen - TiO_2 \tag{25}$$

$$Sen^+ - TiO_2\left(e_{C.B}^-\right)......RX \rightarrow Sen^+ - TiO_2 + \dot{R}X + X^- \tag{26}$$

$$Sen^+ - TiO_2\left(e_{C.B}^-\right)......O_{2(ads)} \rightarrow Sen^+ - TiO_2 + O_2^- \tag{27}$$
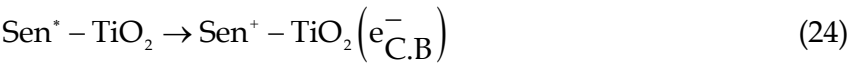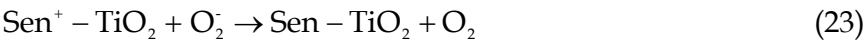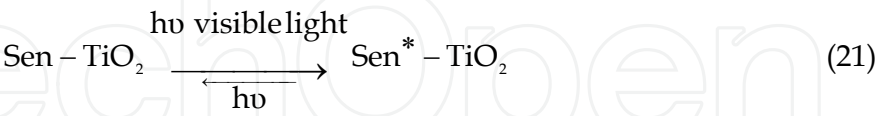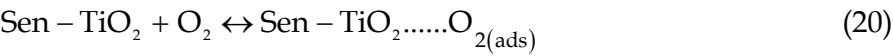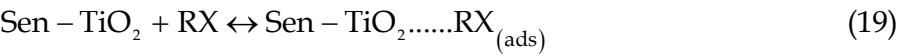


Fig. 3. Regenerative dye/semiconductor/visible light system

Cho et al., (2001) conclude that there is no direct electron transfer between an excited sensitizer and $CCl_4$ molecules, in homogeneous solution, and the existence of semiconductor is essential for sensitized photocatalysis. Platinum supported on titanium dioxide acts as an excellent sensitizer and could have practical advantages as a mild and convenient photocatalyst for selective oxidation processes (Hussein et al., 1984). The addition of Rhodamine-B, as sensitizer to $TiO_2$ dispersion system increases the rate of photooxidation properties (Hussein et al., 1991). The authors explained that due to the fact that more light absorbed by Rhodamine-B between 460-580 nm, then the energy transfer from sensitizer to $TiO_2$ or to any other active species and hence promote the photocatalytic activity of titanium dioxide.

## 5. Advanced oxidation processes

Glaze et al., (1987) define Advanced Oxidation Processes (AOPs) for water treatments as the processes that occur near ambient temperature and pressure which involve the generation of highly reactive radicals ,especially hydroxyl radicals ($\bullet OH$), in sufficient quantity for water purification. Advanced oxidation processes can also be easily defined as techniques of destruction of organic pollutants from wastewaters. These processes include chemical oxidation processes using hydrogen peroxide, ozone, combined ozone and hydrogen peroxide, hypochlorite, Fenton's reagent, ultra-violet enhanced oxidation such as $UV/O_3$, $UV/H_2O_2$, UV/air, wet air oxidation and catalytic wet air.

Hydroxyl radicals are strong reactive species, which are capable of destroying a wide range of organic pollutants. Table 1 shows hydroxyl radical as the second strongest oxidant (Weast, 1977; Legrini et al., 1993  Domènech et al., 2001 ; & Mota et al., 2008).

| Oxidant | $E^\circ$ (V) |
|---|---|
| Fluorine ($F_2$) | 3.03 |
| Hydroxyl radical ($\bullet OH$) | 2.80 |
| Atomic oxygen (O) | 2.42 |
| Ozone ($O_3$) | 2.07 |
| Hydrogen peroxide($H_2O_2$) | 1.78 |
| Hydroperoxyl radical ($O_2H \cdot$) | 1.70 |
| Potassium permanganate ($KMnO_4$) | 1.67 |
| Hypobromous acid (HBrO) | 1.59 |
| Chlorine dioxide ($ClO_2$) | 1.50 |
| Hypochlorous acid (HClO) | 1.49 |
| Hypochloric acid | 1.45 |
| Chlorine ($Cl_2$) | 1.36 |
| Bromine ($Br_2$) | 1.09 |
| Iodine ($I_2$) | 0.54 |

Table 1. Standard reduction potential of common oxidants against Standard Hydrogen Electrode

The attack of organic pollutants by hydroxyl radicals occurs via the following mechanisms (Buxton et al., 1988; Legrini et al., 1993 & Pignatello et al., 2006):

1. Electron transfer from organic pollutants  to hydroxyl radicals:

$$\dot{O}H + RX \rightarrow RX^{\cdot\,+} + OH^{-} \qquad (28)$$

2.  Hydrogen atom abstraction from the C-H, N-H or O-H bonds of organic pollutants:

$$\dot{O}H + RH \rightarrow R^{\cdot} + H_2O \qquad (29)$$

3.  Addition of hydroxyl radical to one atom of a multiple atom compound:

$$\dot{O}H + Ph \rightarrow HOPh^{\cdot} \qquad (30)$$

## 6. Fundamental parameters in photocatalysis

In semiconductor photocatalysis of industrial wastewater treatment, there are different parameters affecting the efficiency of treatment. These parameters include mass of catalyst, dye concentration, pH, light intensity, addition of oxidizing agent, temperature and type of photocatalyst. Other factors, such as, ionic components in water, solvent types, mode of catalyst application and calcinations temperature can also play an important role on the photocatalytic degradation of organic compounds in water environment (Guillard et al., 2005 & Ahmed et al., 2011).

### 6.1 Effect of type of catalyst

Haque & Muneer (2007) observe that Degussa P25 is more reactive for degradation of a textile dye derivative, bromothymol blue, in aqueous suspensions than other commercially available photocatalysts types of titanium dioxide, namely Hombikat UV100, PC500 and TTP. They explain the high activity of Degussa P25 is due to composing of small nano-crystallites of rutile dispersed within the anatase matrix. The band gap of rutile is less than that of anatase and as a result electron will transfer from the rutile conduction band to electron traps in anatase and the recombination of electrons and holes will be reduced. Hussein, (2002) reported that anatase has higher photoactivity than rutile due to the difference in surface area.

Decolorization percentage of real textile industrial wastewater on rutile, anatase, and zinc oxide shows that the activity of different catalysts falls in the following sequence (Hussein & Abass, 2010 a):

$$ZnO > TiO_2 \text{ (Anatase)} > TiO_2 \text{ (Rutile)}$$

ZnO is more active than $TiO_2$ due to the absorption of wider spectrum light (Sakthivela et al., 2003). However, the amount of zinc oxide required to reach the optimum activity is two times more than that for titanium dioxide (anatase or rutile) (Hussein & Abass, 2010 a). In another study, Hussein et al., (2008) observed that ZnO is less active than anatase when the same weight of catalysts is used for photocatalytic degradation of textile wastewater. Akyol et al., (2004) reported that ZnO is more active than $TiO_2$ for the decolorization efficiency of aqueous solution of a commercial textile dye due to the band gap energy, the charge carrier density, and the crystal structure.

Decolorization efficiency of real textile industrial wastewater in the presence and absence of catalyst and/or solar radiation was also investigated (Hussein & Abass, 2010 b). The results indicate that the activity of different catalysts fall in the sequence:

ZnO > TiO$_2$ (Anatase) > TiO$_2$ (Rutile) > in the absence of catalyst = in the absence of solar radiation or artificial radiation = 0

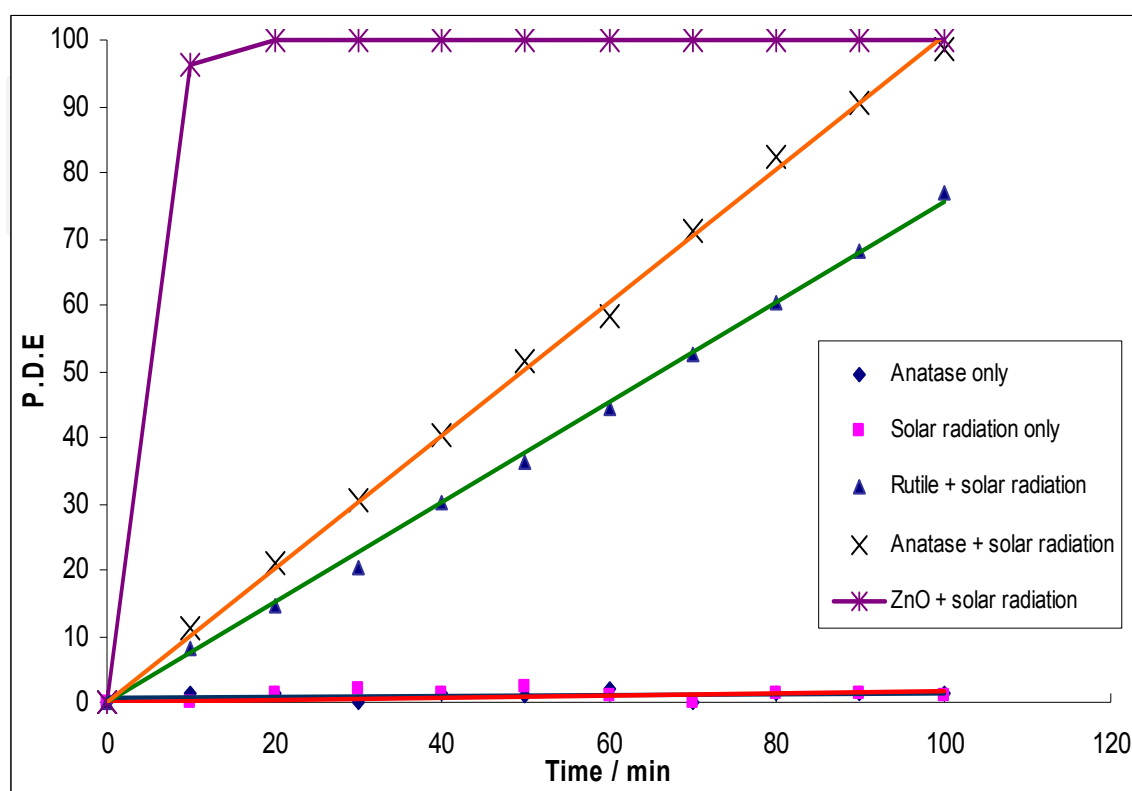The results are plotted in Figure 4.



Fig. 4. Photocatalytic decolorization of real textile industrial wastewater at different conditions.

These results also indicate that there has been no dark reaction. Incubations of colored industrial wastewater without solar radiation and/or without catalyst has been performed to demonstrate that decolorization of the dye is dependent on the presence of both; light and catalyst.

## 6.2 Effect of mass of catalyst

Photocatalysts dosage added to the reaction vessel is a major parameter affecting the photocatalytic degradation efficiency (Dong et al., 2010). Photocatalytic degradation efficiency increases with an increase in catalysts mass. This behavior may be due to an increase in the amount of active site on surface of photocatalyst particles. As a result, an increasing the number of dye molecule adsorbed on the surface of photocatalyst lead to an increase in the density of particles in the area of illumination (Kim & Lee, 2010). The extrapolation of Hird's data (Hird, 1976) indicates that only 7.5 mg of TiO$_2$ was sufficient to absorb all incident 366 nm radiation. It follows that the mass effect must be caused by changes in the effective utilization of the absorbed radiation rather than by the increased absorption.

Photocatalyst with small particles are more efficient than larger particles. This behavior may be due to (Hussein, 1984):

1. Photoholes and photoelectrons generated in the bulk would have fewer traps and recombination centers to overcome before reaching the surface.
2. A greater proportion of material would be within the space charge arising from depletive oxygen chemisorptions, which favor exciton dissociation and photohole migration to the surface.

Hence, increasing the catalyst's mass will increase the concentration of the efficient small particles within the illuminated region of the reaction vessel. The direct proportionality between photocatalytic degradation efficiency and catalyst loading is real within low concentrations of photocatalyst where there are excess active sites reaching plateau reign. The plateau is reached when this effect can no longer increase the overall efficiency of utilizing incident radiation. Moreover, after the plateau region is achieved, the activity of photocatalytic decolorization decrease with increase of catalyst concentration for all types of catalysts. This behavior is more likely to emanate from variation in the intensity of radiation entering the reaction vessel and the way the catalyst utilizes that radiation. Light scattering by catalyst particles at higher concentration lead to decrease in the passage of irradiation through the sample leading to poor light utilization (Gaya et al., 2010; Kavitha & Palanisamy, 2011). Deactivation of activated photocatalyst molecules colliding ground state molecules with increasing the load of photocatalyst may be also cause reduction in photocatalyst activity (Kim & Lee, 2010).

Photocatalytic decolorization efficiency (PDE) % of real textile industrial wastewater has been investigated by employing different masses of $TiO_2$ (anatase or rutile) or ZnO under natural weathering conditions for 20 minutes of irradiation (Hussein & Abass, 2010 b). The results are plotted in Figure 5.
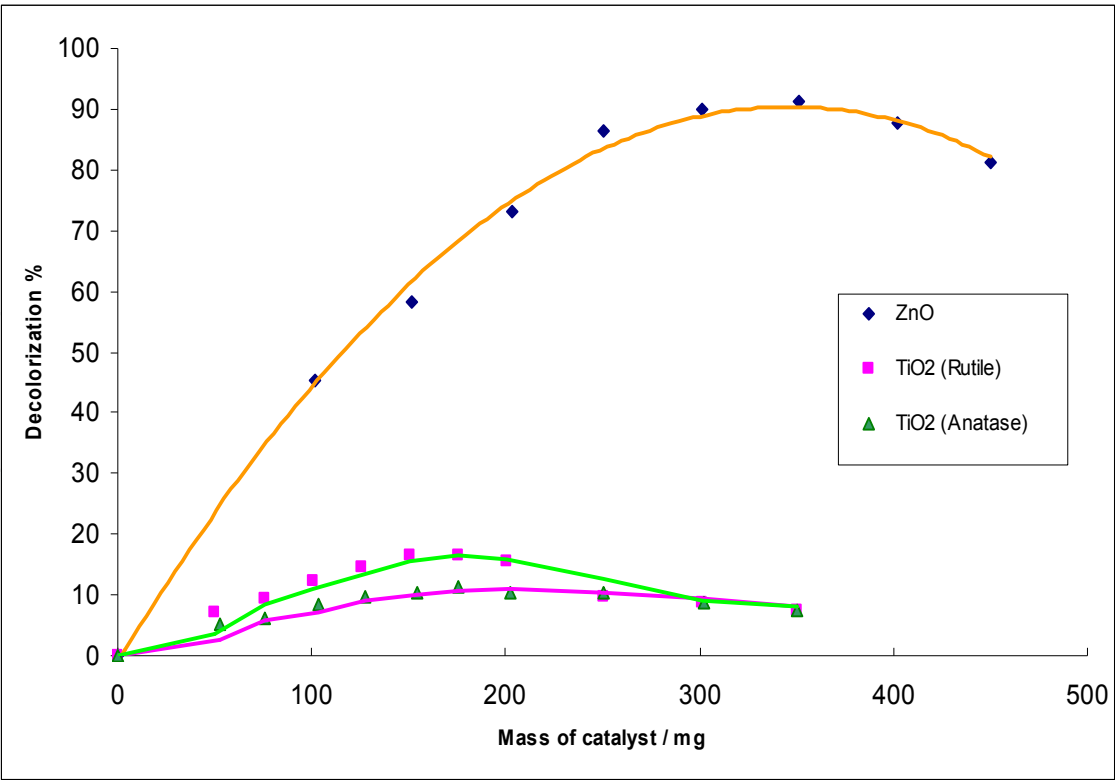


Fig. 5. Effect of mass on photocatalytic decolorization efficiency of real textile industrial wastewater

The results in all cases indicate that the decolorization efficiency increases with increase in catalysts mass and then it becomes constant. It is clear from consideration of the catalyst concentrations at which the activity plateau were achieved that the mass effect does not depend upon the type of dye and source of irradiation. Moreover, plateau regions were achieved and then the activity of decolorization decreased with increasing catalyst concentration, for all types of catalysts used in this project.

## 6.3 Effect of pH

Aqueous solution pH is an important variable in the evaluation of aqueous phase mediated photocatalytic decolorization reactions. pH change effects the adsorption quantity of organic pollutants and the ways of adsorption on the surface of photocatalyst (coordination). As a result, the photocatalytic degradation efficiency will greatly be influenced by pH changes.

Zero Point Charge (pHzpc), is a concept relating to adsorption phenomenon and defined as the pH at which the surface of an oxide is uncharged. If positive and negative charges are both present in equal amounts, then this is the isoelectric point (iep). However, the zpc is the same as iep when there is no adsorption of other ions than the potential determining $H^+/OH^-$ at the surface.

In aqueous solution, at pH higher than pHzpc, the oxide surface is negatively charged and then the adsorption of cations is favoured and as a consequence, oxidation of cationic electron donors and acceptors are favoured. At pH lower than pHzpc, the adsorbent surface is positively charged (See Figure 6) and then the adsorption of anions is favoured and as a consequence, the acidic water donates more protons than hydroxide groups.
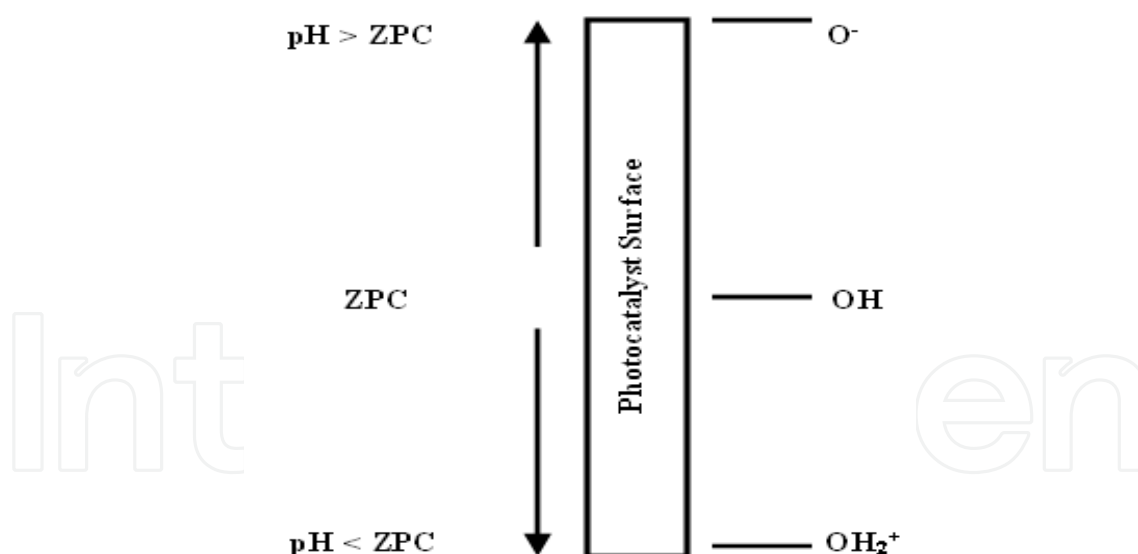


Fig. 6. Effect of pH on ZPC.

Infrared spectroscopy study of Szczepantiewicz et al., (2000) shows that the TiOH sites are the major electron traps when $TiO_2$ is illuminated. The distribution of other species ($TiOH_2^+$ and $TiO^-$) with changing pH has been proposed by Kormann & co-workers (1991) (See Figure 7). Figures 6 and 7 show that , at pH below ZPC the surface is mostly positively charged and TiOH sites increase as pH increases and reach maximum value at ZPC of semiconductor. However, $TiOH_2^+$ as pH increases and reaches zero value at ZPC. At pH

higher than ZPC the density of TiO⁻ groups on the surface start to form and reached 100% value at pH 14. The importance of pH during the reaction is not less than that of initial state. The formation of intermediate products, sometimes, changes the pH of aqueous solution and as a result, it affects the rate of photodegeradation (Galvez, 2003).
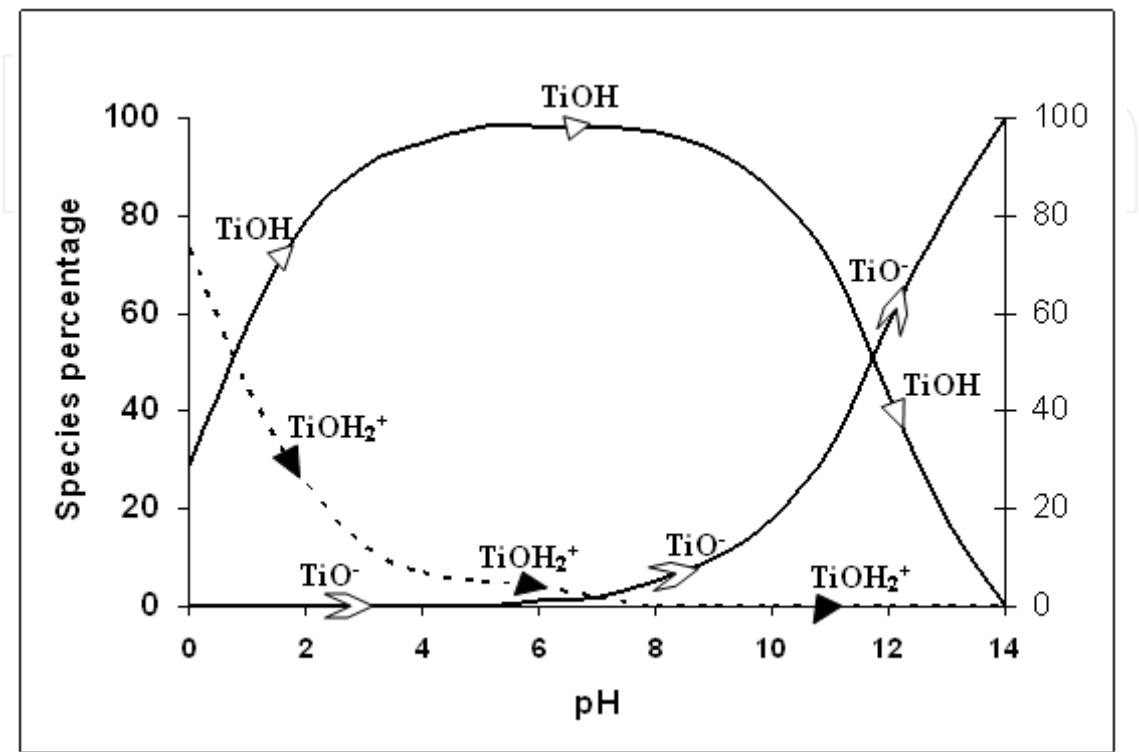


Fig. 7. The distribution of TiO$_2$ surface species at different pH

At pH above and below pHzpc, the surface of zinc oxide and titanium dioxide are negatively or positively charged according to the following equations:

$$ZnOH + H^+ \leftrightarrow ZnOH_2^+ \tag{31}$$

$$ZnOH + OH^- \leftrightarrow ZnO^- + H_2O \tag{32}$$

$$TiOH + H^+ \leftrightarrow TiOH_2^+ \tag{33}$$

$$TiOH + OH^- \leftrightarrow TiO^- + H_2O \tag{34}$$

### 6.3.1 Effect of pH on photocatalytic decolorization of Bismarck brown R

Under the determined experimental condition with initial dye concentration equal to $10^{-4}$ M, ZnO dosage 3.75 gm.L$^{-1}$, light intensity equal to 2.93 mW.cm$^{-2}$ and temperature equal to 298.15 K, the effect of change in solution pH on decolorization percentage has been studied in the range 2-12 (Figure 8). The decolorization percent has been found to be strongly dependent on pH of solution because the reaction takes place on the surface of semiconductor. The decolorization percentage of Bismarck brown R increases with the increase of pH, exhibiting maximum decolorization at pH 9.
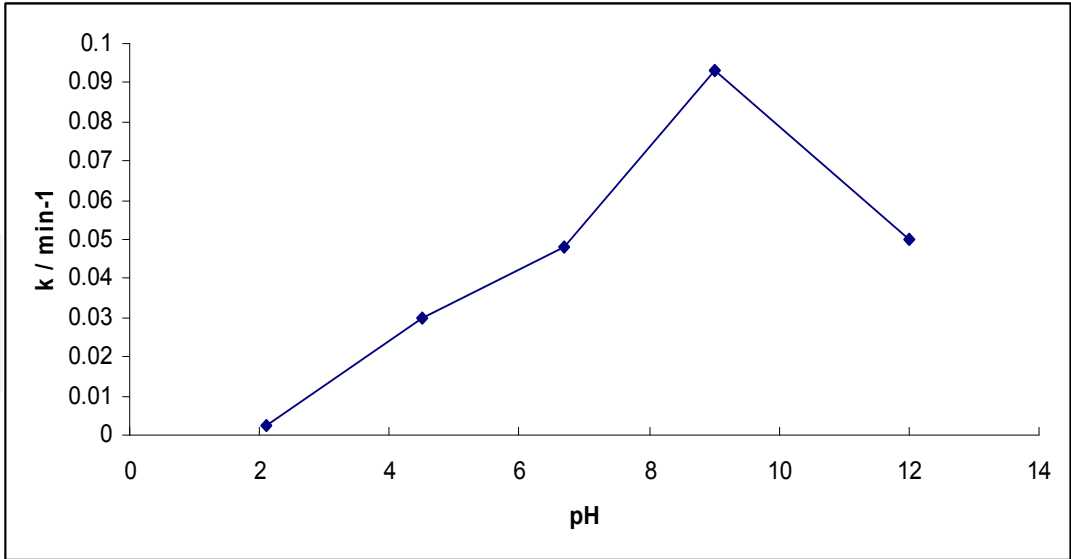
Fig. 8. Effect of pH on photocatalytic decolorization efficiency of Bismarck R brown on ZnO

Under the determined experimental condition with initial dye concentration equal to $10^{-4}M$, $TiO_2$ dosage 1.75 gm.$L^{-1}$, light intensity equal to 2.93 mW.$cm^{-2}$ and temperature equal to 298.15 K, the effect of change in solution pH on decolorization percentage has been studied in the range 2-10. The results are plotted in Figures 9, for $TiO_2$ (DegussaP25), $TiO_2$ (HombikatUV100), $TiO_2$ (MillenniumPC105) and $TiO_2$ (Koronose2073). It was observed that the decolorization percentage strongly depends on the pH of solution because the reaction takes place on the surface of semiconductor. The decolorization percentage of Bismarck brown R increases with the increase of pH, exhibiting maximum decolorization at pH that is equal to 6.61, 6.54, 6.75, 6.63 for $TiO_2$ (DegussaP25), $TiO_2$ (HombikatUV100), $TiO_2$ (MillenniumPC105) and $TiO_2$ (Koronose2073), respectively.
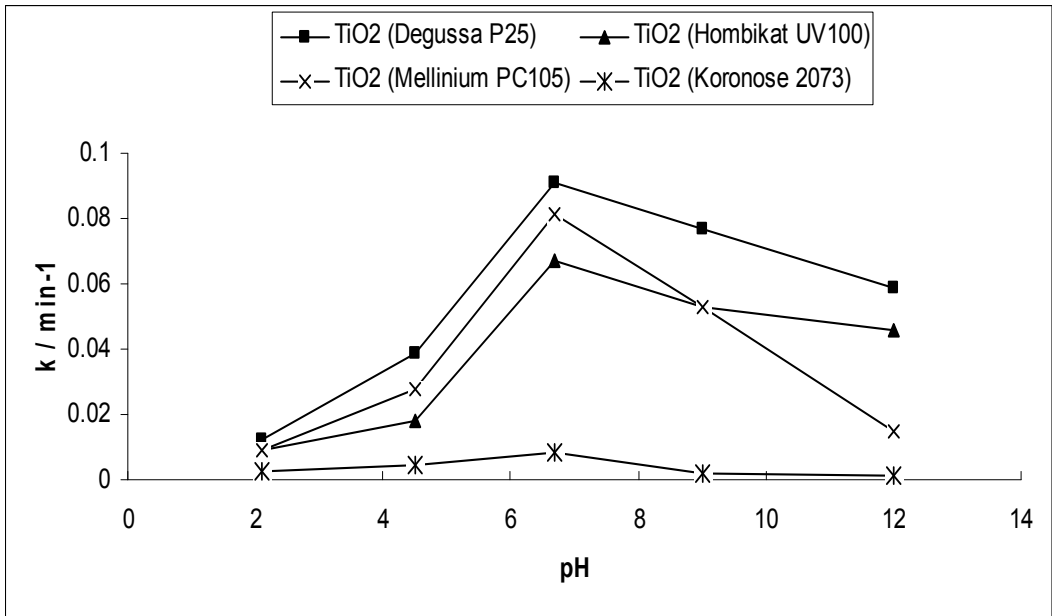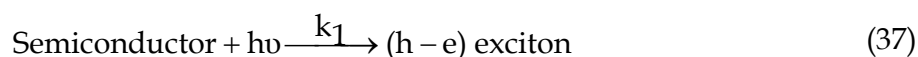


Fig. 9. Effect of pH on photocatalytic decolorization efficiency of Bismarck R brown on different types of $TiO_2$

This behavior could be explained (as mentioned before) on the basis of zero point charge (ZPC). The zero point charge is equal to 9.00 for ZnO and 6.25 for TiO$_2$ (Degussa P25). With the increase of the pH of solution, the surface of catalyst will be negatively charged by adsorbed hydroxyl ions. The presence of large quantities of adsorbed OH$^-$ ions on the surface of catalyst favor the formation of ·OH radical. However, if pH is lower than ZPC, the hydroxyl ions adsorbed on the surface will be decreased and, therefore, hydrogen ions adsorbed on the surface will increase and the surface will become positive charged. Both the acidic and basic media leave an inverse impact on the photodecolorization efficiency because of the decrease of the formation of the hydroxyl radical.

The decolorization of Bismarck brown R decreases dramatically at strong acid media (pH = 2.1) for ZnO. This could be explained due to photocorrosion of ZnO as shown in the following equations:

$$ZnO \xrightarrow{h\nu} e^-_{CB} + h^+_{VB} \tag{35}$$

$$ZnO + 2h^+_{VB} \rightarrow Zn^{2+} + \frac{1}{2}O_2 \tag{36}$$
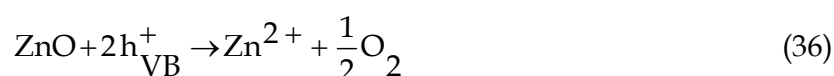
### 6.4 Effect of Light Intensity

Egerton & King, (1979) show that square root of light intensity depends on the activity of titanium dioxide for different wavelengths of light. However, this relationship cannot be applied to all range of light intensities. The primary electronic processes which occur in the absorption of photons with energy equal or greater than the band gap of semiconductor are:

$$Semiconductor + h\upsilon \xrightarrow{k_1} (h-e)\ exciton \tag{37}$$

$$(h-e) \xrightarrow{k_2} h^+ + e^- \tag{38}$$

$$h^+ + e^- \xrightarrow{k_3} Radiationless\ Recombination \tag{39}$$

For photocatalysis processes, it is necessary that the excitons dissociate and the photoholes and photoelectrons reach the catalyst surface where they are trapped by surface species:

$$h^+ + OH^-_{(s)} \xrightarrow{k_4} \dot{O}H_{(s)} \tag{40}$$

$$e^- + O_2 \xrightarrow{k_5} O^-_{2(ads)} \tag{41}$$

The concentration of excitons, photoholes and photoelectrons may be considered by applying a steady state treatment:

$$\frac{d[h-e]}{dt} = k_1 I_{(abs)} - k_2[(h-e)] = 0 \tag{42}$$

So that:

$$[(h-e)] = \frac{k_1}{k_2} I_{(abs)} \tag{43}$$

Similarly:

$$\frac{d[h]}{dt} = k_2[(h-e)] - k_3[h^+][e^-] - k_4[h^+]\left[OH_{(S)}^-\right] = 0 \tag{44}$$

Since:

$$[h^+] = [e^-] \tag{45}$$

Then:

$$\frac{d[h]}{dt} = k_1 I_{(abs)} - k_3[h^+]^2 - k_4[h^+]\left[OH_{(s)}^-\right] = 0 \tag{46}$$

So that:

$$k_1 I_{(abs)} = k_3[h^+]^2 + k_4[h^+]\left[OH_{(s)}^-\right] \tag{47}$$

There are two possibilities concerning the light intensity:
a. At high light intensities, where the recombination of photoholes and photoelectrons is predominate, then:

$$k_3[h^+]^2 \gg k_4[h^+]\left[OH_{(s)}^-\right] \tag{48}$$

So equation 48 becomes:

$$k_1 I_{(abs)} = k_3[h^+]^2 \tag{49}$$

Then:

$$[h^+] = \left(\frac{k_1}{k_3}\right)^{\frac{1}{2}} I_{(abs)}^{\frac{1}{2}} \tag{50}$$

If the rate controlling step in the overall photocatalysis processes involves the surface trapping of photoholes at surface OH$^-$, then the rate will be given by equation 40.
The reaction rate is given by:

$$\text{Reaction rate} = k_4\left(\frac{k_1}{k_3}\right)^{\frac{1}{2}} I_{(abs)}^{\frac{1}{2}}\left[OH_{(s)}^-\right] \tag{51}$$

Then:

$$\text{Reaction rate } \alpha \left[ I_{(abs)} \right]^{\frac{1}{2}} \tag{52}$$

If, on the other hand, the rate controlling step involves photoelectron trapping by oxygen, then the rate controlling step will be equation 41. The reaction rate is given by:

$$\text{Reaction rate} = k_5 \left( \frac{k_1}{k_3} \right)^{\frac{1}{2}} I_{abs} \left[ O_{2(ads)} \right] \tag{53}$$

Then:

$$\text{Reaction rate } \alpha \left[ I_{(abs)} \right]^{\frac{1}{2}} \tag{54}$$

b.   At low light intensities, it is expected that recombination of photoholes and photoelectrons will be low, then:

$$k_4 \left[ h^+ \right] \left[ OH^-_{(s)} \right] \rangle\rangle \, k_3 \left[ h^+ \right]^2 \tag{55}$$

So equation 47 becomes:

$$k_1 I_{(abs)} = k_4 \left[ h^+ \right] \left[ OH^-_{(s)} \right] \tag{56}$$

Then:

$$\left[ h^+ \right] = \frac{k_1 \left[ I_{(abs)} \right]}{k_4 \left[ OH^-_{(s)} \right]} \tag{57}$$

It follows that:

$$\text{Reaction rate} = k_1 \left[ I_{(abs)} \right] \tag{58}$$

Alternatively, if photoelectron trapping is considered to be rate controlling, then:

$$\text{Reaction rate} = k_5 \frac{k_1}{k_4} \left[ \left( I_{(abs)} \right) \right] \tag{59}$$

Hence, a linear dependence would be expected at low light intensities. Square-root intensity dependence was observed with rutile I, rutile 11, anatase, uncoated anatase pigment and

platinized anatase and also independent on wavelength of incident radiation (Harvey et al., 1983 a; Hussein & Rudham, 1987). Bahnemann et al., (1991) reported that the change in kinetic constant is a function of the square root of the radiation entering at high light intensities, while this change can be linear with light intensity of incident radiation low light intensities (Peterson et al., 1991).

Ollis et al., (1991) summarize the effect of light intensity on the kinetics of the photocatalytic degradation of dye as follows:

a. At low light intensities (0–20 mW/cm$^2$), the rate of photocatalytic degradation is proportional directly with light intensity (first order).

b. At high light intensities (25 mW/cm$^2$), the rate of photocatalytic degradation is proportional directly with the square root of the light intensity (half order).

c. At high light intensities the rate of photocatalytic degradation is independent of light intensity (zero order). See Figure 10.

However, Hussein et al (2011) found that the rate of photocatalytic decolorization of Bismarck brown R on ZnO and different types of titanium dioxide is proportional directly with the light intensity of incident UVA radiation in the range of 0- 2.0 mW/cm$^2$ and with the square root of light intensity in the range of 2.0- 3.5 mW/cm$^2$.
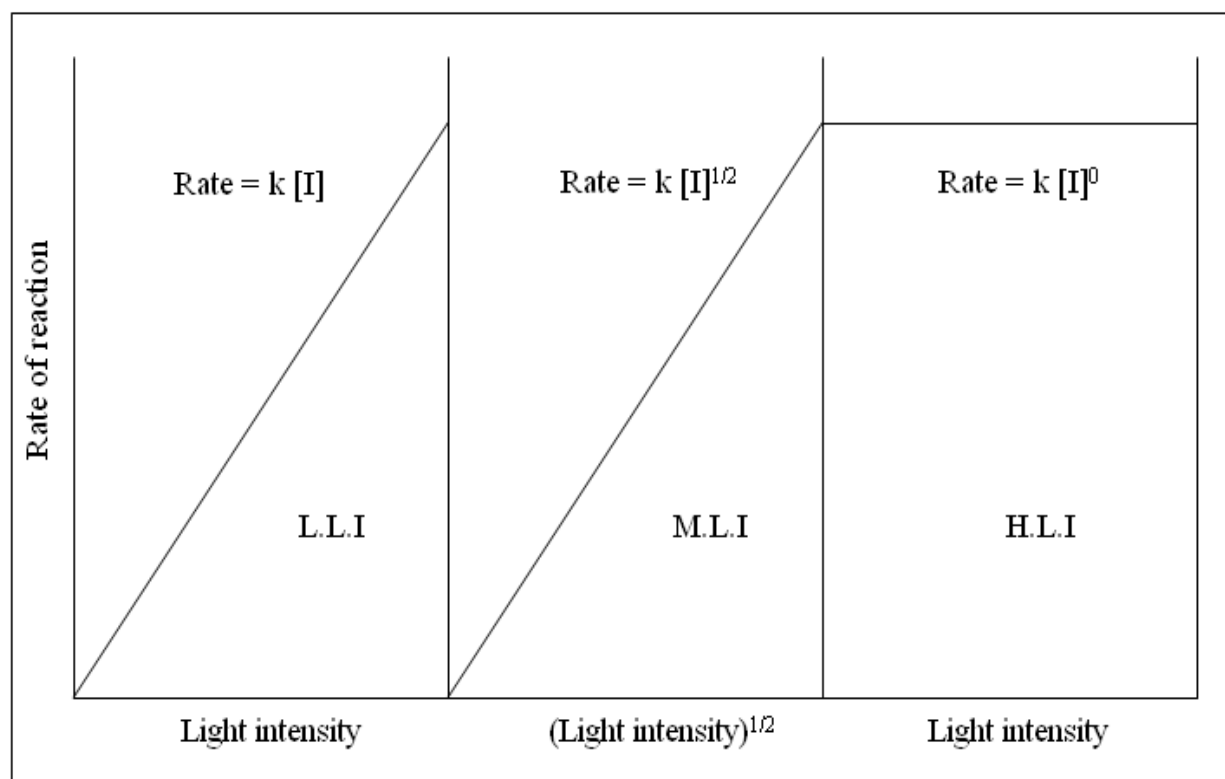


Fig. 10. Effect of light intensity on the kinetics of the photocatalytic degradation of dye

Figures 11 and 12 illustrate the impact of initial light intensity on the value of rate constant for photocatalytic decolorization of Bismarck brown R on ZnO and different types of titanium dioxide, respectively. The results indicate that the photocatalytic decolorization of Bismarck brown R increases with the increase in light intensity, attaining a maximum value at 3.52 mW.cm$^{-2}$.
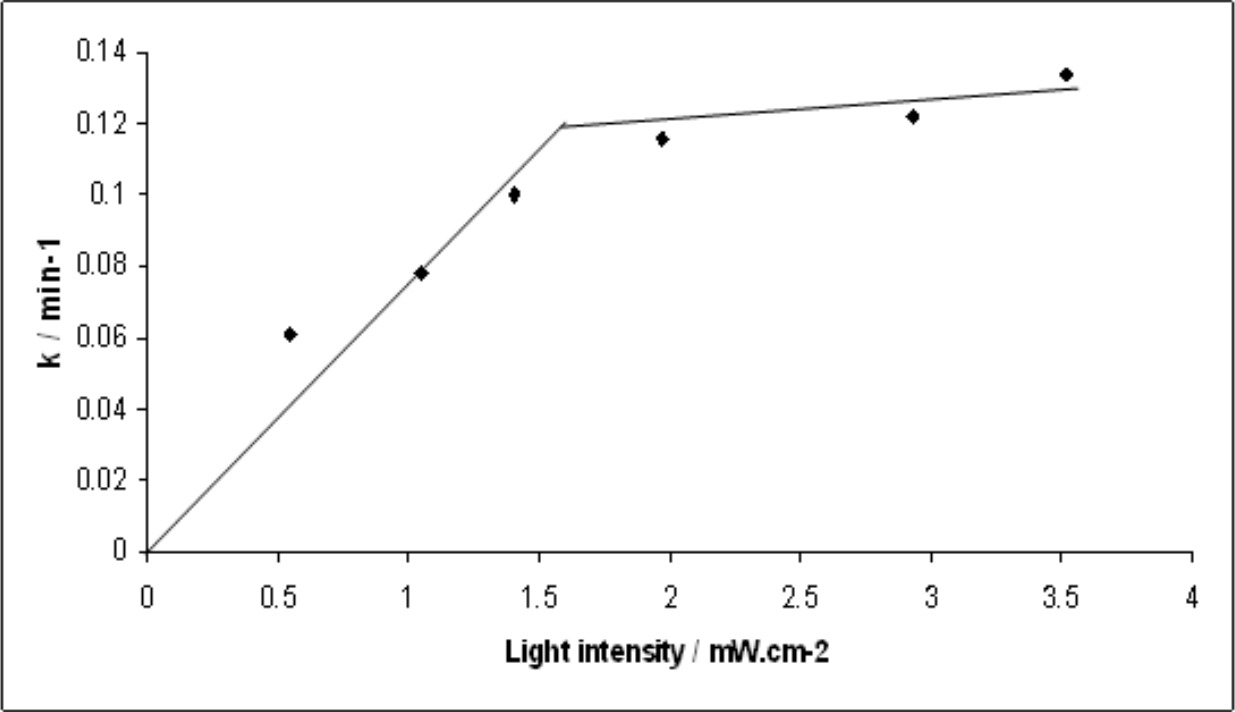
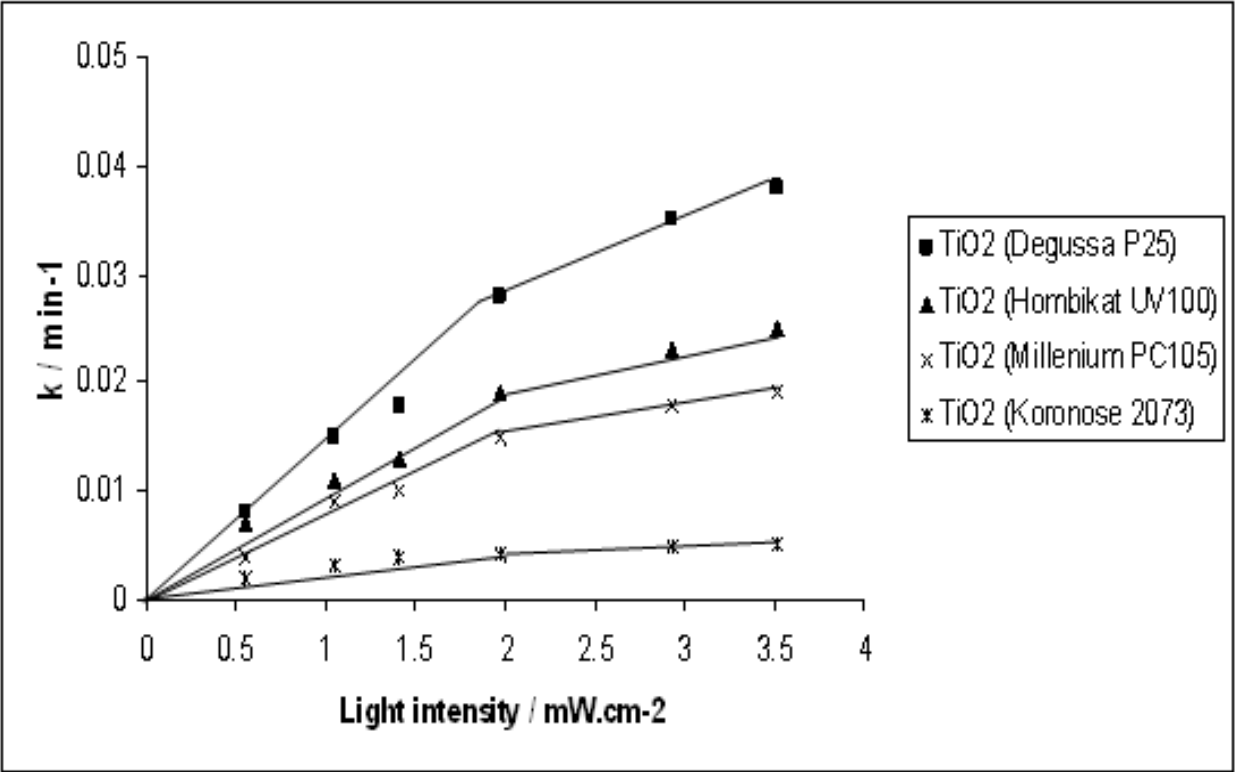Fig. 11. Effect of initial light intensity on rate constant of  photocatalytic decolorization of Bismarck brown R on ZnO



Fig. 12. Effect of initial light intensity on rate constant of photocatalytic decolorization of Bismarck brown R using different types of $TiO_2$

## 6.5 Effect of temperature

One of the advantages of photoreaction is that it is not affected or slightly affected by temperature change. Temperature dependent steps in photocatalytic reaction are adsorption and desorption of reactants and products on the surface of photocatalyst. None of these steps appears to be rate determining. The impact of temperature is explained as the variable with the least effect on photocatalytic degradation of aqueous solution of azo dyes (Obies, 2011). Attia et al., (2008) have found that   the activation energy of photodegeradation of real textile industrial wastewater is equal to $21 \pm 1$ kJ mol$^{-1}$ on titanium dioxide and $24 \pm 1$ kJ mol$^{-1}$ on zinc oxide. The activation energy for the photocatalytic degradation of textile industrial wastewater on titanium dioxide is similar to previous findings for photocatalytic oxidation of different types of alcohols on titanium dioxide and metalized titanium dioxide (Al-zahra et al., 2007; Hussein & Rudham, 1984, 1987). The single value of activation energy ($21 \pm 1$ kJ mol$^{-1}$) that can be related to the calculated activation energy of photooxidation of different species of titanium oxide is associated with the transport of photoelectron through the catalyst to the adsorbed oxygen on the surface (Harvey et al., 1983 a & b). Kim & Lee, (2010) explained that the very small activation energy in photocatalytic reactions is the apparent activation energy $E_a$, whereas the true activation energy $E_t$ is nil. These types of reactions are operating at room temperature.

Palmer et al., (2002) observed that the effect of temperature on the photocatalytic degradation is insignificant in the range of 10-68 º C. High temperatures may have a negative impact on the concentration of dissolved oxygen in the solution and consequently, the recombination of holes and electrons increases at the surface of photocatalyst. However, Trillas et al., (1995); Chen & Ray, (1998) reported that raising the temperature of reaction enhances the rate of photocatalytic degradation significantly. Hussein and Abbas ( 2010 b) reported that the decolorization efficiency of real textile industrial wastewater increases with increasing of temperature as shown in fig. 13.
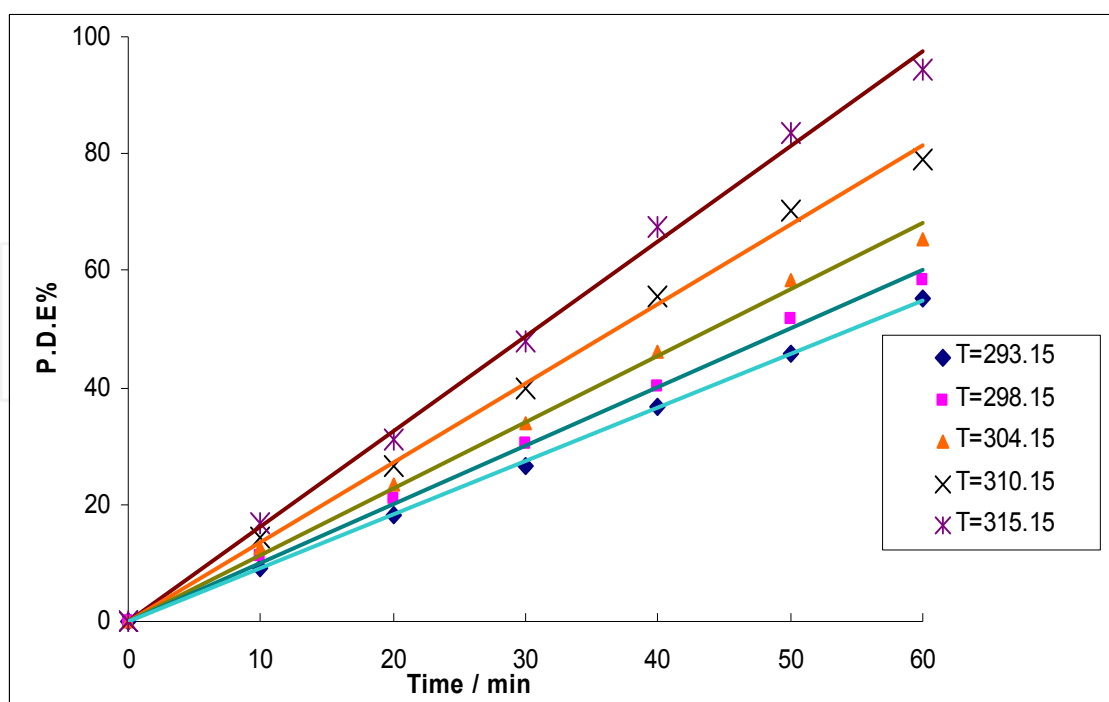


Fig. 13. Effect of temperature on P.D.E. of real textile industrial wastewater on  anatase under solar radiation

Hussein et al., (2011) have found that the rate of decolorization of Bismarck brown R on ZnO and different types of TiO$_2$ increases slightly with the increase of the temperature and the activation energy $24 \pm 1$ kJ.mol$^{-1}$ for ZnO and $14 \pm 1$, $16 \pm 1$, $21 \pm 1$ and $22 \pm 1$ kJ.mol$^{-1}$ for TiO$_2$ (Degussa P25), TiO$_2$ (Hombikat UV100), TiO$_2$ (Millennium PC105), and TiO$_2$ (Koronose 2073), respectively. Figure 13   shows the impact of temperature on photodecolorization of Bismarck brown R by using TiO$_2$ (Hombikat UV100).
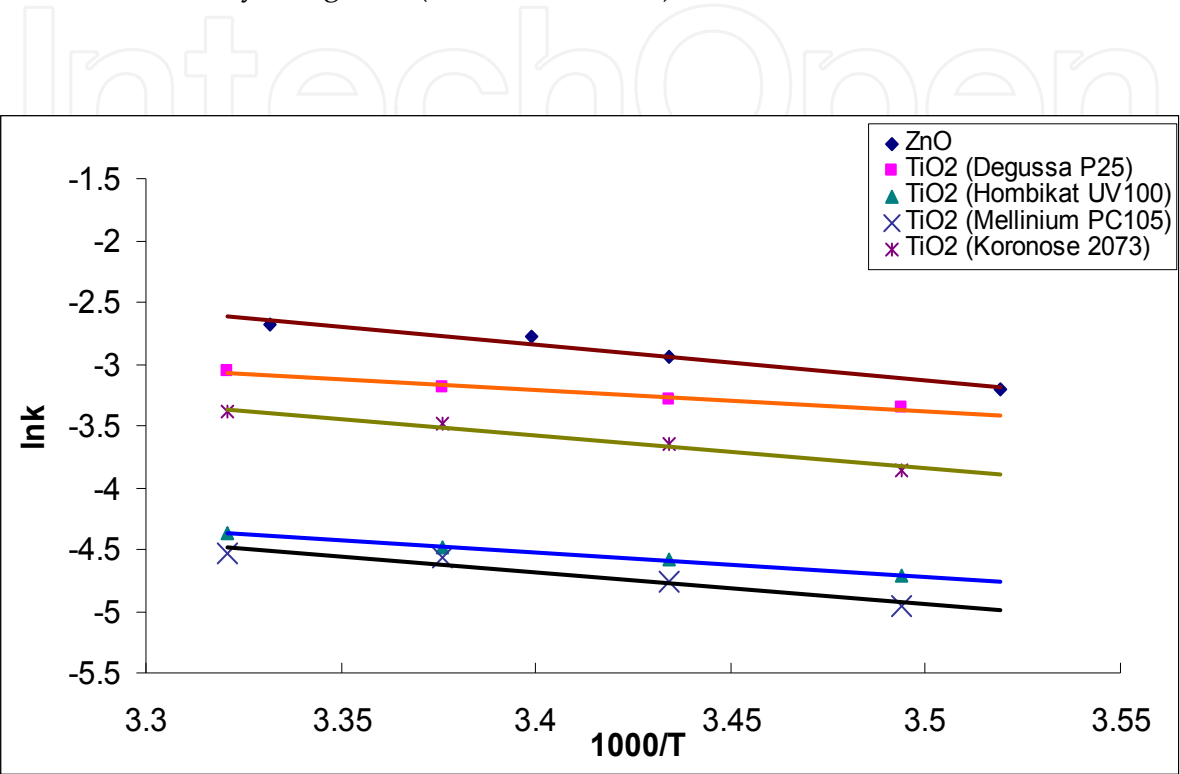


Fig. 14. Arrhenius plot by different types of catalyst with Bismarck brown R

### 6.6 Effect of addition of oxidants

It is well known that the addition of oxidants increases the rate of photocatalytic degradation of dyes by the formation of hydroxyl radicals (Salvador & Decker, 1984; Jenny & Pichat, 1991). However, this is not general for all types of dyes (Hachem et al., 2001).

Production of additional hydroxyl radicals occurs when hydrogen peroxide is added through the following mechanisms (Galvez, 2003 & Dong et al., 2010)   :

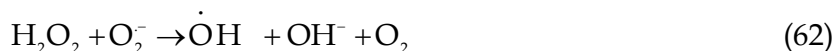1.   Trapping of photogenerated electrons.

$$H_2O_2 + 2e^- \rightarrow 2OH^- \tag{60}$$

2.   Self-decomposition by photolysis

$$H_2O_2 + h\nu \rightarrow 2\overset{\cdot}{O}H \tag{61}$$
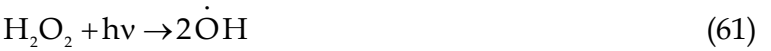
3.   Reaction with superoxide radical anion O2$^{\cdot-}$

$$H_2O_2 + O_2^- \rightarrow \dot{O}H + OH^- + O_2 \qquad (62)$$

The addition of persulphate leads to form sulphate radical anion by trapping the photogenerated electrons (Konstantinou & Albanis, 2004)

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^- \qquad (63)$$

The formed sulphate radical anion is a strong oxidant and reacts with organic molecules pollutants as follows (Galvez, 2003):
1. Abstracting a hydrogen atom from saturated carbon.
2. Adding hydrogen to unsaturated or aromatic carbon.
3. Removing one electron from carboxylate anions and from certain neutral molecules.

Sulphate radical anion can also react with water molecule to produce hydroxyl radical (Konstantinou & Albanis, 2004):

$$SO_4^- + H_2O \rightarrow SO_4^{2-} + \dot{O}H + H^+ \qquad (64)$$

Other oxidants such as iodate and bromate can also increase the reaction rate because they are also electron scavengers, while chlorate has been proven insufficient to improve effectiveness (Galvez, 2003). However, these additives are too expensive to be compared to hydrogen peroxide and peroxydisulphate. Moreover, they do not dissociate into harmless products.

The addition of oxidant to reaction mixture serves the rate of photocatalytic degradation by:
1. Generation of additional •OH and other oxidizing species.
2. Increasing the number of trapped photoelectrons.
3. Increasing the oxidation rate of intermediate compounds.
4. Replacement of oxygen role in the case of the absence of oxygen in the reaction mixture.

Table 2 shows the effect of addition of hydrogen peroxide on the rate of photocatalytic degradation of red disperse dye on ZnO. The results indicate that the apparent rate constant increases with the increase in $H_2O_2$ concentration to a certain level and a further increase in $H_2O_2$ concentration leads to decrease in the degradation rate of the red disperse dye. The presumed reason is that the addition of $H_2O_2$ to a certain level increases the production of hydroxyl radicals , but the additional amount leads to reduce the amounts of photoholes and hydroxyl radicals (Legrini et al., 1993; Malato, 1998; Daneshvar et al., 2003; Konstantinou & Albanis, 2004):

$$H_2O_2 + 2h^+ \rightarrow O_2 + 2H^+ \qquad (65)$$

$$H_2O_2 + \dot{O}H \rightarrow H_2O + HO_2 \qquad (66)$$

$$HO_2 + \dot{O}H \rightarrow H_2O + O_2 \qquad (67)$$

| Conc. of $H_2O_2$ (mmol.$L^{-1}$) | $K_{app}$ (min$^{-1}$) |
|:---:|:---:|
| 0 | 0.0893 |
| 1.5 | 0.1408 |
| 3.0 | 0.1499 |
| 4.5 | 0.1680 |
| 6.0 | 0.1404 |
| 7.5 | 0.1290 |

Table 2. Effect of addition of $H_2O_2$ on the apparent rate constant of photocatalytic decolorization of red disperse dye.

This behavior relates to the competition between the adsorption of organic pollutants and $H_2O_2$ on the surface of photocatalyst. The required amount of $H_2O_2$ reaches the highest level of enhancement for the rate of photodegradation is related to the ratio of the concentration of organic pollutants and $H_2O_2$ (Galvez, 2003). When the pollutant concentration is low compared with the concentration of $H_2O_2$, the adsorption of organic pollutants decreases due to the increase of adsorption of hydrogen peroxide and, as a result, the additional hydroxyl radicals generated by $H_2O_2$ do not react efficiently.

## 6.7 Comparison between mineralization and photocatalytic decolorization

Mineralization of dyes is a process in which dyes are converted completely into its inorganic chemical components (minerals), such as carbon dioxide, water and other species according to the structure of dye (see figs. 1&2).
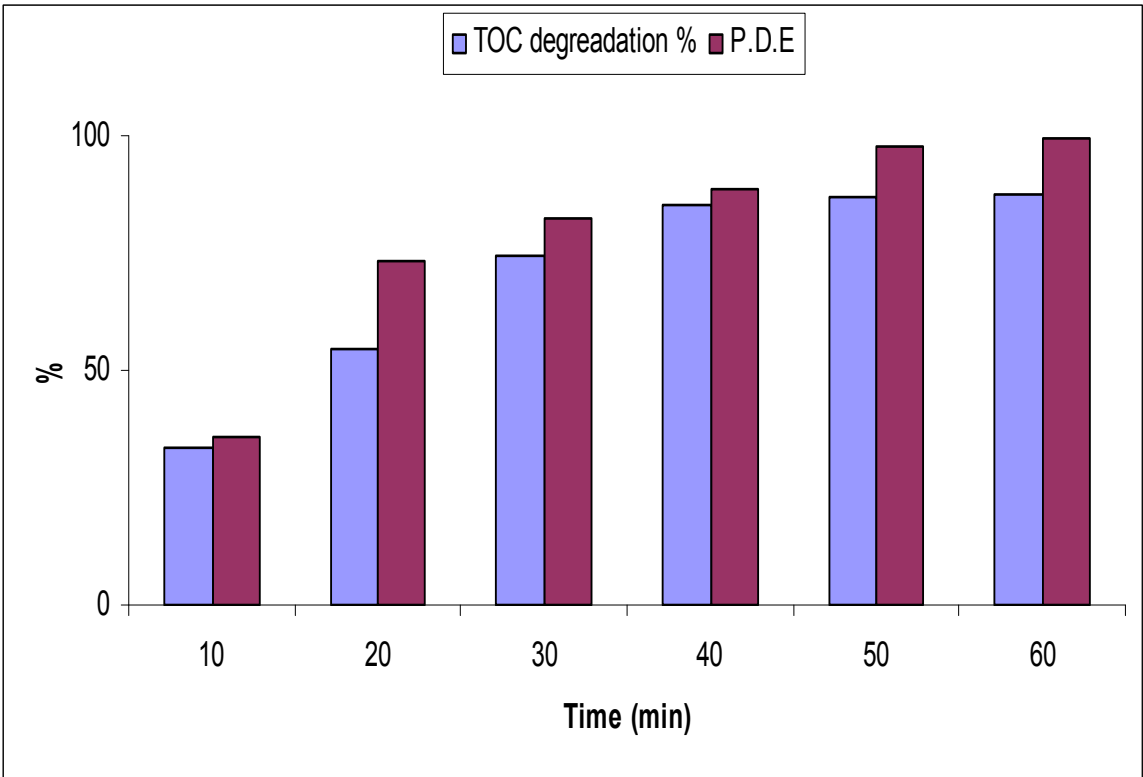


Fig. 15. Comparison between Mineralization and Photocatalytic decolorization of Bismarck brown R on ZnO

Mineralization of Bismarck brown R was evaluated by analyzing total organic carbon (TOC) (Hussein et al. 2011). The results shown in Fig.15 indicate that photocatalytic decolorization of Bismarck R brown was faster than the decrease of TOC. The results indicate that % TOC reduction was about 73% after 60 minutes of irradiation while the per cent of decolorization achieved 88% for the same period of irradiation. These findings in good agreement with those reported before (He et al. 2007 & Chen 2009). This could be explained to the formation of some by product, which resist the photocatalytic degradation. Furthermore, the formed by products need more time to destruct.

## 6.8 Effect of irradiation sources

Table 3 summarized the obtained results from the different techniques used for the treatments of textile industrial wastewater and different types of industrial dyes (Hussein, 2010). The results show that the decolorization rate of textile industrial wastewater is faster with solar light than with UV light. The results indicated that solar energy could be effectively used for photocatalytic degradation of pollutants in wastewater.

| Process | Type of treated waste or dye | Source of irradiation | Type of catalyst | Time for complete mineralization/hours | Reference |
|---|---|---|---|---|---|
| Photocatalytic | Textile industrial wastewater | Solar | ZnO | 2.7 | Alkhateeb et al., (2005) |
| Photocatalytic | Textile industrial wastewater | Solar | TiO$_2$ | 4 | Alkhateeb et al., (2005) |
| Photolysis | Murexide | Solar | - | 7.5 | Alkhateeb et al., (2007) |
| Photocatalytic | Murexide | Solar | ZnO | 3.8 | Alkhateeb et al., (2007) |
| Photocatalytic | Murexide | Solar | TiO$_2$ | 3.3 | Alkhateeb et al., (2007) |
| Photolysis | Thymol blue | Solar | - | 7 | Hussein et al., (2008) |
| Photocatalytic | Thymol blue | Solar | TiO$_2$ | 2.7 | Hussein et al., (2008) |
| Photocatalytic | Thymol blue | Solar | ZnO | 3.3 | Hussein et al., (2008) |
| Photocatalytic | Textile industrial wastewater | Mercury lamp | TiO$_2$ | 2.6 | Attia et al., (2008) |
| Photocatalytic | Textile industrial wastewater | Mercury lamp | ZnO | 3 | Attia et al., (2008) |
| Photocatalytic | Bismarck brown G | Mercury lamp | ZnO | 1 | Hussein et al., (2010a) |
| Photocatalytic | Bismarck brown R | Mercury lamp | ZnO | 0.8 | Hussein et al., (2010b) |
| Photocatalytic | Bismarck brown R | Mercury lamp | TiO$_2$ | 1.2 | Hussein et al., (2010c) |
| Photocatalytic | Textile industrial wastewater | Mercury lamp | TiO$_2$ | 3 | Hussein & Abass, (2010a) |
| Photocatalytic | Textile industrial wastewater | Mercury lamp | ZnO | 1 | Hussein & Abass, (2010a) |
| Photocatalytic | Textile industrial wastewater | Solar | TiO$_2$ | 1.8 | Hussein & Abass, (2010b) |
| Photocatalytic | Textile industrial wastewater | Solar | ZnO | 0.33 | Hussein & Abass, (2010b) |

Table 3. Effect of irradiation sources on photocatalytic decolorization of textile industrial wastewater and different dyes

## 7. Conclusions

1. Photocatalytic degradation techniques is the most efficient and clean technology.
2. Textile industries have become worldwide. Thus, this method can be considered as a promising technique for providing formidable quantities of water especially for countries facing serious suffering from water shortage.
3. The existence of catalyst and lights are essential for photocatalytic degradation of colored dyes.
4. Photocatalytic degradation efficiency (PDE) of textile industrial wastewater is obviously affected by illumination time, pH, initial dye concentration and photocatalyst loading.
5. Solar photocatalytic treatment has been proved to be an efficient technique for decolorization of industrial wastewater through a photocatalytic process and the transformation is practically complete in a reasonable irradiation time.
6. In the countries where, intense sunlight is available throughout the year, solar energy could be effectively used for photocatalytic degradation of pollutants in industrial wastewater.
7. The zero point charge is 6.4 and 9.0 for $TiO_2$ and ZnO, respectively above which the surface of photocatalyst is negatively charged by means of adsorbed hydroxyl ions; this favors the formation of hydroxyl radical, and as a result, the photocatalytic degradation of industrial wastewater increases due to inhibition of the photoholes and photoelectrons recombination.

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**Advances in Treating Textile Effluent**

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