Photochemical Treatments of Textile Industries Wastewater†

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Textile industry is one of the most water and chemical intensive industries worldwide. About 200-400 L of water are needed to produce 1 kg of textile fabric in textile factories. The water used in this industry is almost entirely discharged as waste. Moreover, the lost of dye in the effluents of textile industry can reach up to 50 %. The effluents are very complex, containing salt, surfactants, ionic metals and their metal complexes, toxic organic chemicals, biocides and toxic anions. Semiconductors are used to degrade pollutants in water to less harmful inorganic material. There have been numerous studies carried out across the globe focusing on the decolourization of textile wastewater. The importance of these types of research is being increasingly in the recent and has become a subject of major public health concern and scientific interest. Titanium dioxide and zinc oxide have good photocatalytic properties nominated both catalysts to be promising substrates for photodegradation of water pollutants and show the appropriate activity in the range of solar radiation. Recent studies focused on the most important photocatalytic applications of titanium dioxide and zinc oxide. These applications include the photodegradation of various pollutants killing bacteria and killing tumor cell in cancer treatments. In recent years there is a substantial interest in decolourization of industrial wastewater, especially textile wastewater. Textile industry generates large quantities of wastewater and also regarded as very toxic due to the difficulty of its disrobement by physical, chemical and microbiological methods. The overall benefits of the decolourization of textile industrial wastewater may include very interesting subjects, saving a huge amount of water and minimizing environmental pollutions. The treated water may be recycled in the same factory or reused in other applications such as other industries or agriculture that require a less quality water. This is considered to be very excellent means for saving huge amounts of water, especially, in the countries which are suffered with water deficiency. This work[*1] will describe some of the more common features of textile industrial wastewater and the evaluation of the treated wastewater by using titanium dioxide and zinc oxide to judge the validity of this type of water for using in different fields.

Key Words: Photochemical treatment, Textile industries wastewater.

INTRODUCTION

Textile industry is one of the most water and chemical intensive industries worldwide due to the fact that 200-400 L of water are needed to produce 1 kg of textile fabric in textile factories[2,3]. 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 %[4]. 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[5]. 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[6]. 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[7,8].

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[9,10]. Recent studies have demonstrated that heterogeneous photocatalysis is the most efficient technique in the degradation of coloured chemicals[11-19]. 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.

EXPERIMENTAL

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[20,21]. However, these techniques have many disadvantages[22]. 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 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[5].

RESULTS AND DISCUSSION

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:

$$\text{Semiconductor} + h\nu \rightarrow h^+ + e^- \qquad (1)$$
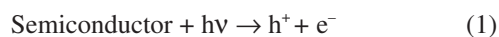
If the photoholes and photoelectrons produced by this process migrate to the surface, they may interact with adsorbed species in the elementary steps, which collectively constitute photocatalysis.
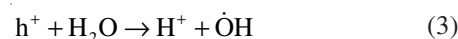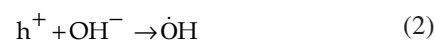
The numerous gas- and liquid-phase reactions photocatalyzed by TiO_2 and ZnO have been reviewed. There is a general agreement that adsorption is necessary since the surface species act as traps for both; photogenerated holes and electrons, which otherwise recombine.
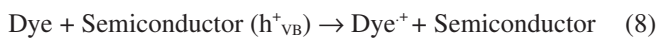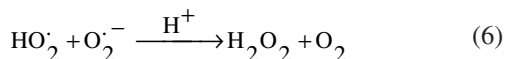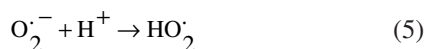
In addition to participating in conventional surface reaction steps, adsorbed dye molecules assist in the separation of photoholes and photoelectrons, which may otherwise recombine within the semiconductor particles. A major factor affecting the efficiency of photocatalysis process is electron/hole recombination.

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.
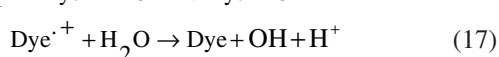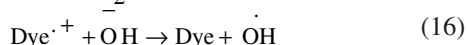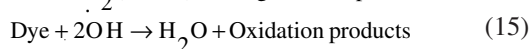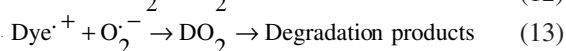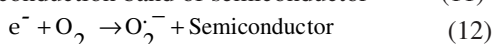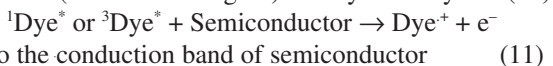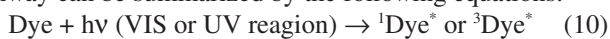
There are different types of semiconductors, whose band gaps range between 1.4 and 3.9 eV, _i.e._, it could be excited with a light of 318-886 nm wavelengths. This means that most of the known semiconductors could be excited by using visible light. However, not all these semiconductors could be used in the photocatalytic reactions. Bahnemann _et al._,[23] reported 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 explained 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.

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[24]: 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 ˙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 ($HO_2\dot{}$) with high chemical activity[25]. The processes in this pathway can be summarized by the following equations:
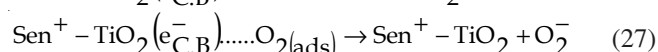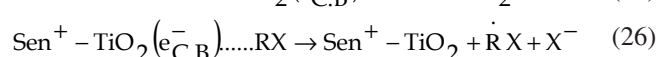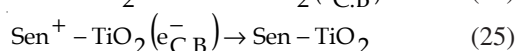
$$h^+ + OH^- \rightarrow \dot{O}H \qquad (2)$$

$$h^+ + H_2O \rightarrow H^+ + \dot{O}H \qquad (3)$$

$$e^- + O_2 \rightarrow O_2^{\dot{-}} \qquad (4)$$

$$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot} \qquad (5)$$

$$HO_2^{\cdot} + O_2^{\cdot -} \xrightarrow{H^+} H_2O_2 + O_2 \qquad (6)$$

$$H_2O_2 \rightarrow 2\,\overset{\cdot}{O}H \qquad (7)$$

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

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

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 decolourized by a photosensitization process. The photocatalytic decolourization 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[14,16,18]. The excited coloured dye (dye*) (in the singlet or triplet state) will inject an electron to the conduction band of the semiconductor[26]. The processes in this pathway can be summarized by the following equations:
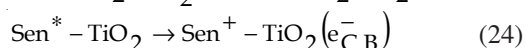
$$\text{Dye} + h\nu\ (\text{VIS or UV reagion}) \rightarrow {}^1\text{Dye}^* \text{ or } {}^3\text{Dye}^* \qquad (10)$$

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

$$e^- + O_2 \rightarrow O_2^{\cdot -} + \text{Semiconductor} \qquad (12)$$

$$\text{Dye}^{\cdot +} + O_2^{\cdot -} \rightarrow DO_2 \rightarrow \text{Degradation products} \qquad (13)$$

$$\text{Dye}^{\cdot +} + HO_2^{\cdot}\,(\text{or}\,H\overset{\cdot}{O}) \rightarrow \text{Degradation products} \qquad (14)$$

$$\text{Dye} + 2\,\overset{\cdot}{O}H \rightarrow H_2O + \text{Oxidation products} \qquad (15)$$

$$\text{Dye}^{\cdot +} + \overset{\cdot}{O}H \rightarrow \text{Dye} + \overset{\cdot}{O}H \qquad (16)$$

$$\text{Dye}^{\cdot +} + H_2O \rightarrow \text{Dye} + OH + H^+ \qquad (17)$$

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:
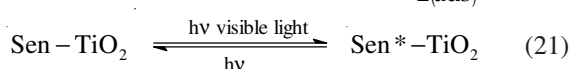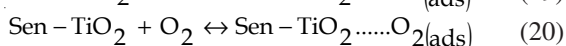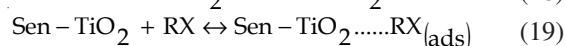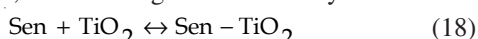
$$\text{Sen} + TiO_2 \leftrightarrow \text{Sen} - TiO_2 \qquad (18)$$

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

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

$$\text{Sen} - TiO_2 \underset{h\nu}{\overset{h\nu\ \text{visible light}}{\rightleftharpoons}} \text{Sen}^* - TiO_2 \qquad (21)$$

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

$$\text{Sen}^+ - TiO_2 + O_2^- \rightarrow \text{Sen} - TiO_2 + O_2 \qquad (23)$$

$$\text{Sen}^* - TiO_2 \rightarrow \text{Sen}^+ - TiO_2\left(e^-_{C.B}\right) \qquad (24)$$

$$\text{Sen}^+ - TiO_2\left(e^-_{C.B}\right) \rightarrow \text{Sen} - TiO_2 \qquad (25)$$

$$\text{Sen}^+ - TiO_2\left(e^-_{C.B}\right)......RX \rightarrow \text{Sen}^+ - TiO_2 + \overset{\cdot}{R}X + X^- \qquad (26)$$

$$\text{Sen}^+ - TiO_2\left(e^-_{C.B}\right)......O_{2(ads)} \rightarrow \text{Sen}^+ - TiO_2 + O_2^- \qquad (27)$$
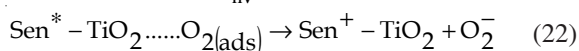
Cho et al.[27] concluded that there is no direct electron transfer between an excited sensitizer and CCl_4 molecules, in homogeneous solution and the existence of semiconductor is essential for sensitized photocatalysis. Platinum supported on titanium dioxide acts as an excellent sensitizer and could have practical advantages as a mild and convenient photocatalyst

for selective oxidation processes[28]. The addition of Rhodamine-B, as sensitizer to TiO_2 dispersion system increases the rate of photooxidation properties[29]. 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.

Advanced oxidation processes: Glaze and co-workers[30] define advanced oxidation processes for water treatments as the processes that occur near ambient temperature and pressure which involve the generation of highly reactive radicals, especially hydroxyl radicals ($\overset{\cdot}{O}H$), 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, ultraviolet 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. Hydroxyl radical as the second strongest oxidant after fluorine[31-34].

The attack of organic pollutants by hydroxyl radicals occurs via the following mechanisms[32,35,36]:

Electron transfer from organic pollutants to hydroxyl radicals:

$$\overset{\cdot}{O}H + RX \rightarrow RX^{\cdot +} + OH^- \qquad (28)$$
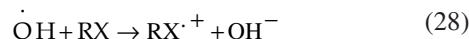
1) Hydrogen atom abstraction from the C-H, N-H or O-H bonds of organic pollutants:

$$\overset{\cdot}{O}H + RH \rightarrow R^{\cdot} + H_2O \qquad (29)$$
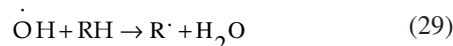
2) Addition of hydroxyl radical to one atom of a multiple atom compound:

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

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[37,38].
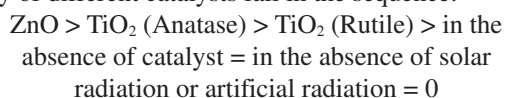
Effect of type of catalyst: Haque and Muneer[39] observed that Degussa P25 is more reactive for degradation of a textile dye derivative, bromothymol blue, in aqueous suspensions than other commercially available photocatalysts types of titanium dioxide, namely Hombikat UV100, PC500 and TTP. They explained 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[40] reported that anatase has higher photoactivity than rutile due to the difference in surface area.

Decolourization percentage of real textile industrial wastewater on rutile, anatase and zinc oxide shows that the activity of different catalysts falls in the following sequence[41]:

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

ZnO is more active than TiO_2 due to the absorption of wider spectrum light[42]. However, the amount of zinc oxide required to reach the optimum activity is two times more than that for titanium dioxide (anatase or rutile). In another study, Hussein *et al.*,[24] observed that ZnO is less active than anatase when the same weight of catalysts is used for photocatalytic degradation of textile wastewater. Akyol and co-workers[43] reported that ZnO is more active than TiO_2 for the decolourization efficiency of aqueous solution of a commercial textile dye due to the band gap energy, the charge carrier density and the crystal structure.

Decolourization efficiency of real textile industrial wastewater in the presence and absence of catalyst and/or solar radiation was also investigated[44]. The results indicate that the activity of different catalysts fall in the sequence:

$$ZnO > TiO_2 \text{ (Anatase)} > TiO_2 \text{ (Rutile)} > \text{ in the}$$
absence of catalyst = in the absence of solar
radiation or artificial radiation = 0

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

Effect of mass of catalyst: Photocatalysts dosage added to the reaction vessel is a major parameter affecting the photocatalytic degradation efficiency[45]. Photocatalytic degradation efficiency increases with an increase in catalysts mass. This behaviour 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[46]. The extrapolation of Hird's data[47] 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 behaviour may be due to the followings two reasons[48]: 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 favour 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 region. 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 decolourization decrease with increase of catalyst concentration for all types of catalysts. This behaviour 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[49,50]. Deactivation of activated photocatalyst molecules colliding ground state molecules with increasing the load of photocatalyst may be also cause reduction in photocatalyst activity[46]. Photocatalytic decolourization 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 min of irradiation[44]. The results are plotted in Fig. 1.
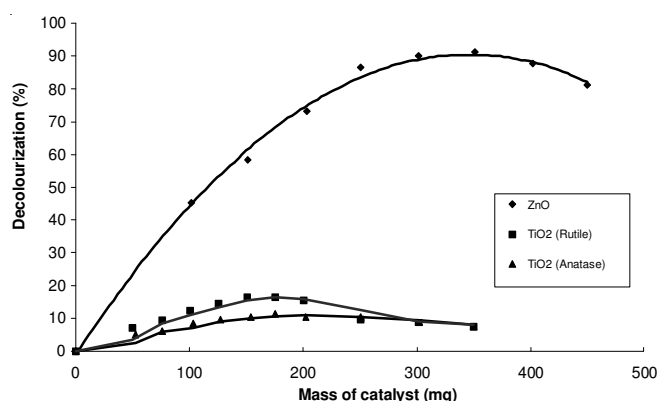

Fig. 1. Effect of mass on photocatalytic decolourization efficiency of real textile industrial wastewater

The results in all cases indicate that the decolourization 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 decolourization decreased with increasing catalyst concentration, for all types of catalysts used in this project.
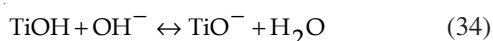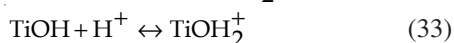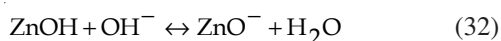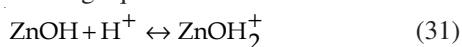
Effect of pH: Aqueous solution pH is an important variable in the evaluation of aqueous phase mediated photocatalytic decolourization reactions. pH change effects the adsorption quantity of organic pollutants and the ways of adsorption on the surface of photocatalyst (coordination). As a result, the 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 and then the adsorption of anions is favoured and as a consequence, the acidic water donates more protons than hydroxide groups.

The infrared spectroscopy study of Szczepantiewicz *et al.*[51] 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 and co-workers[52]. At pH below zero point charge 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 photodegradation[53].

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

$$ZnOH + H^+ \leftrightarrow ZnOH_2^+ \qquad (31)$$

$$ZnOH + OH^- \leftrightarrow ZnO^- + H_2O \qquad (32)$$

$$TiOH + H^+ \leftrightarrow TiOH_2^+ \qquad (33)$$

$$TiOH + OH^- \leftrightarrow TiO^- + H_2O \qquad (34)$$

Effect of pH on photocatalytic decolourization 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 298.15 K, the effect of change in solution pH on decolourization percentage has been studied in the range 2-12 (Fig. 2). The decolourization per cent has been found to be strongly dependent on pH of solution because the reaction takes place on the surface of semiconductor. The decolourization percentages of Bismarck brown R increases with the increase of pH, exhibiting maximum decolourization at pH 9.
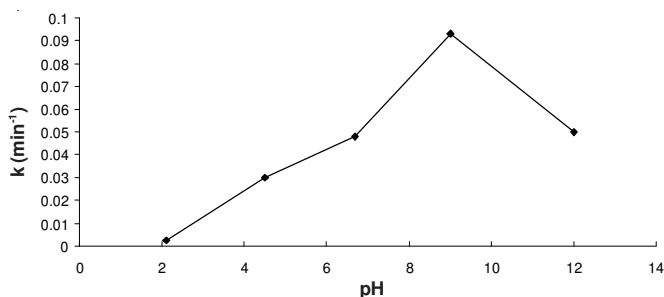
Fig. 2.   Effect of pH on photocatalytic decolourization efficiency of Bismarck R brown on ZnO

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 298.15 K, the effect of change in solution pH on decolourization percentage has been studied in the pH range 2-10. The results are plotted in Fig. 3, for TiO$_2$ (Degussa P25), TiO$_2$ (Hombikat UV100), TiO$_2$ (Millennium PC105) and TiO$_2$ (Koronose2073). It was observed that the decolourization percentage strongly depends on the pH of solution because the reaction takes place on the surface of semiconductor. The decolourization percentage of Bismarck brown R increases with the increase of pH, exhibiting maximum decolourization at pH that is equal to
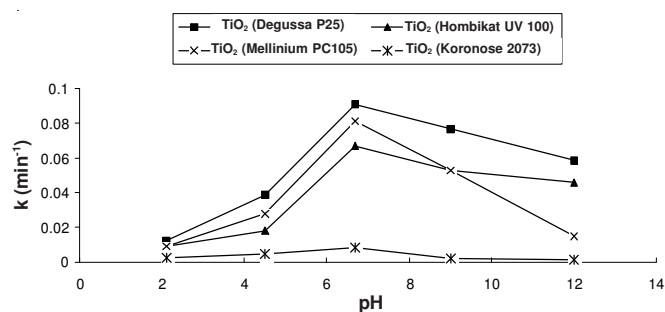
Fig. 3.   Effect of pH on photocatalytic decolourization efficiency of Bismarck R brown on different types of TiO$_2$

6.61, 6.54, 6.75, 6.63 for TiO$_2$ (Degussa P25), TiO$_2$ (Hombikat UV100), TiO$_2$ (Millennium PC105) and TiO$_2$ (Koronose 2073), respectively.

This behaviour 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 favours the formation of $^{\cdot}$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 photodecolourization efficiency because of the decrease of the formation of the hydroxyl radical.

The decolourization 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:

$$ZnO \xrightarrow{\text{hv}} e_{CB}^- + h_{VB}^+ \qquad (35)$$

$$ZnO + 2h_{VB}^+ \rightarrow Zn^{2+} + \frac{1}{2}O_2 \qquad (36)$$
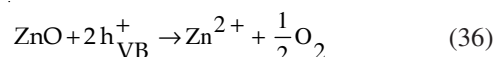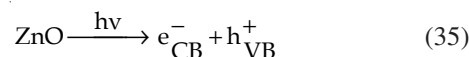
Effect of light intensity: Egerton and King[54] showed that square root of light intensity depends on the activity of titanium dioxide for different wavelengths of light. However, this relationship cannot be applied to all range of light intensities. Square-root intensity dependence was observed with rutile I, rutile-II, anatase, uncoated anatase pigment and platinized anatase and also independent on wavelength of incident radiation[55,56]. Bahnemann *et al.*,[57] 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[58].

Ollis *et al.*,[59] summarized 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).

However, Hussein *et al.*[60] found that the rate of photocatalytic decolourization 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/cm² and with the square root of light intensity in the range of 2.0-3.5 mW/cm².

The impact of initial light intensity on the value of rate constant for photocatalytic decolourization of Bismarck brown R on ZnO and different types of titanium dioxide have also investigated. The results indicate that the photocatalytic decolourization of Bismarck brown R increases with the increase in light intensity, attaining a maximum value at 3.52 mW cm⁻².

Effect of temperature: One of the advantages of photo-reaction 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[61]. Attia *et al.*,[19] have found that the activation energy of photodege-radation of real textile industrial wastewater is equal to 21 ± 1 kJ mol⁻¹ on titanium dioxide and 24 ± 1 kJ mol⁻¹ on zinc oxide. The activa-tion 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[56,62,63]. The single value of activation energy (21 ± 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[55,64]. Kim and Lee[46] 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.*,[65] observed that the effect of temperature on the photocatalytic degradation is insignificant in the range of 10-68 ºC. 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.*[66] and Chen and Ray[67] reported that raising the temperature of reaction enhances the rate of photocatalytic degradation significantly. Hussein and Abbas[44] reported that the decolourization efficiency of real textile industrial wastewater increases with increasing of temperature.

Hussein *et al.*,[60] have found that the rate of decolourization of Bismarck brown R on ZnO and different types of TiO₂ increases slightly with the increase of the temperature and the activation energy 24 ± 1 kJ mol⁻¹ for ZnO and 14 ± 1, 16 ± 1, 21 ± 1 and 22 ± 1 kJ mol⁻¹ for TiO₂ (Degussa P25), TiO₂ (Hombikat UV100), TiO₂ (Millennium PC105) and TiO₂ (Koronose 2073), respectively (Fig. 4).

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[68,69]. However, this is not general for all types of dyes[70].

Production of additional hydroxyl radicals occurs when H_2O_2 is added through the following mechanisms[45,53]:
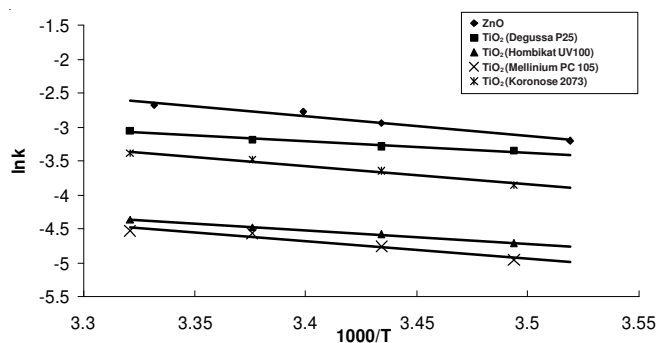

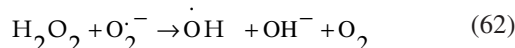Fig. 4. Arrhenius plot by different types of catalyst with Bismarck brown R
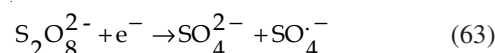
Trapping of photogenerated electrons.

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

Self-decomposition by photolysis

$$H_2O_2 + h\nu \rightarrow 2\overset{\cdot}{O}H \tag{61}$$

Reaction with superoxide radical anion O2o-

$$H_2O_2 + O_2^{\cdot -} \rightarrow \overset{\cdot}{O}H + OH^- + O_2 \tag{62}$$

The addition of persulphate leads to form sulphate radical anion by trapping the photogenerated electrons[5].

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{\cdot -} \tag{63}$$

The formed sulphate radical anion is a strong oxidant and reacts with organic molecules pollutants as follows[53]: 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.
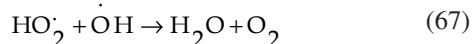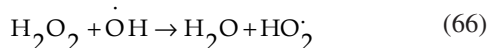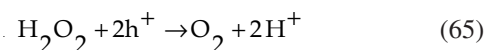
Sulphate radical anion can also react with water molecule to produce hydroxyl radical[5]:

$$SO_4^{\cdot -} + H_2O \rightarrow SO_4^{2-} + \overset{\cdot}{O}H + H^+ \tag{64}$$
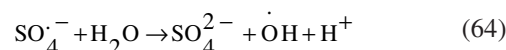
Other oxidants such as iodate and bromate can also increase the reaction rate because they are also electron scavengers, while chlorate has been proven insufficient to improve effectiveness[53]. However, these additives are too expensive to be compared to hydrogen peroxide and peroxydisulphate. Moreover, 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[5,32,71,72]:

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

$$H_2O_2 + \overset{\cdot}{O}H \rightarrow H_2O + HO_2^{\cdot} \qquad (66)$$

$$HO_2^{\cdot} + \overset{\cdot}{O}H \rightarrow H_2O + O_2 \qquad (67)$$

This behaviour 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[53]. 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.

Comparison between mineralization and photocatalytic decolourization: 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.

Mineralization of Bismarck brown R was evaluated by analyzing total organic carbon (TOC)[60]. The results indicate that photocatalytic decolourization of Bismarck R brown was faster than the decrease of TOC. The results indicate that % TOC reduction was about 73 % after 60 min of irradiation while the per cent of decolourization achieved 88 % for the same period of irradiation. These findings in good agreement with those reported before[73,74]. 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.

Conclusion

Photocatalytic degradation techniques is the most efficient and clean technology. 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. The existence of catalyst and lights are essential for photocatalytic degradation of coloured dyes. Photocatalytic degradation efficiency of textile industrial wastewater is obviously affected by illumination time, pH, initial dye concentration and photocatalyst loading. Solar photocatalytic treatment has been proved to be an efficient technique for decolourization of industrial wastewater through a photocatalytic process and the transformation is practically complete in a reasonable irradiation time. 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. 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 favours 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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